# Mechanical Effects on the Phase Stability of Ceramic-Sulfide Solid-Electrolytes 

## Citation

Fitzhugh, William. 2020. Mechanical Effects on the Phase Stability of Ceramic-Sulfide SolidElectrolytes. Doctoral dissertation, Harvard University, Graduate School of Arts \& Sciences.

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# Mechanical Effects on the Phase Stability of Ceramic-Sulfide Solid-Electrolytes 

A dissertation presented<br>by<br>William Aylett Fitzhugh

to

The School of Engineering and Applied Sciences
in partial fulfillment of the requirements
for the degree of

Doctor of Philosophy
in the subject of

Applied Physics

Harvard University

Cambridge, Massachusetts

September 2019
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# Mechanical Effects on the Phase Stability of Ceramic-Sulfide Solid-Electrolytes 


#### Abstract

This dissertation presents the theoretical, computational and experimental results of studies on the voltage widening of ceramic-sulfide solid-electrolytes. In particular, we demonstrate the use of mechanically-induced metastability as a method to expand the operating voltage windows of all-solid-state lithium ion batteries based on $L i_{10} G e P_{2} S_{12}$ and/or $L i_{10} \mathrm{SiP}_{2} S_{12}$. In short, mechanical constriction is seen to improve the bulk and interfacial stability by introducing energy barriers that oppose structural decay. The impact of mechanical constriction on both the bulk stability of these ceramic-sulfides as well as the interfaces with common electrode materials are considered.


A theory of mechanically induced metastability is first formulated and introduced with experimental and computational evidence for the case of core-shell $\operatorname{Li}_{10} \mathrm{SiP}_{2} S_{12}$. Here we show that the electrochemical stability window of sulfide electrolytes can be improved by controlling synthesis parameters and the consequent core-shell microstructural compositions. This results in a stability window of $0.7-3.1 \mathrm{~V}$ and quasi-stability window of up to 5 V for Li-Si-P-S sulfide electrolytes with high Si composition in the shell, a window much larger than the intrinsic 1.7-2.1V. Theoretical and computational work explains this improved voltage window in terms of volume constriction, which resists the expansion of the solid electrolyte that accompanies decomposition. It is shown that in the limiting case of a core-shell morphology that imposes a constant volume constraint
on the electrolyte, the stability window can be further expanded.

Next, a framework is introduced to generalize the above theory for the case of arbitrary decay morphologies. Two limiting cases, hydrostatic decay and spherically nucleated decay, are explored to better understand the impact of decay morphology on the stability window. $L i_{10} G e P_{2} S_{12}$ is experimentally seen to decay in a nucleated form, which is predicted to generate higher local stress and hence a larger energy barrier for decomposition. This allows the use of thinner stabilizing shell structures than would be required if the material was to decay homogeneously.

In addition to a limited intrinsic electrochemical window of roughly $1.7-2.1 \mathrm{~V}$, the ceramic-sulfides are known to [electro-]chemically react when in contact with typical commercial electrode materials such as $\mathrm{LiCoO}_{2}$. Thus coating materials that form physical separation layers between the electrolyte and the electrode materials are required. High-throughput calculations are performed to search over 67,000 material phases to find the best coating materials for use in $\mathrm{Li}_{10} \mathrm{SiP}_{2} S_{12}$ based batteries. Over 2,000 materials are found to be suitable for the case of cathode voltage ranges and over 1,000 materials are found to be suitable for the case of anode voltage ranges. New computational methods are developed to enable this rapid high-throughput searching. Six phases ranging in predicted stability from stable to highly unstable are experimentally evaluated to confirm computational predictions.

Finally, evidence is presented that battery cell level mechanical constriction can provide even greater capability than core-shell morphologies for voltage widening. We show that ceramic-sulfides in cell level constriction mechanisms can achieve kinetically stable operation up to nearly 10 V . This is in stark contrast with current commercial
liquid electrolytes which begin to decay at approximately 4.5 V . This behavior is attributed to rate-limited kinetic processes that occur in pressurized electrolytes.

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## Acknowledgments

It is a great pleasure to thank all of the many people who have made this dissertation possible. First, I owe a tremendous debt of gratitude to my advisor, Prof. Xin Li. I could not have asked for a better advisor and mentor. The countless hours that he has invested in me have, without question, made me a better scientist, student, teacher, and collaborator. Xin routinely demonstrated an unbelievable ability to be supportive and understanding, as well as provide ample guidance and scientific vision to keep my work progressing.

This work would not have been possible without the amazing collaborative nature of the Li lab. As a theorist, my experimental collaborators have been essential to my professional development. I'd like to especially thank Fan Wu and Luhan Ye, both of whom played a major role in virtually every aspect of this work. Their experimental insight not only lead to validation of my work, but their guidance helped shape its direction.

Sooran Kim and Xi Chen were both instrumental in developing various computational aspects of this work. Sooran taught me almost everything I know about ab-initio computation. Sooran and Xi were always available for brainstorming and troubleshooting some DFT error or numerical code. Thank you both for the patience you had with my constantly wanting your input, and even more thanks for always giving it.

Thanks to Eva Gil Gonzalez, Jiaxin Ning, Haoqing Su, Wenye Deng, Yibo Su and Pengfei Qi. These experiments only worked due to your considerable effort synthesizing

## Acknowledgments

and coating materials and testing too many solid-state batteries to count. To Yichao Wang, In Kim, Li Hai, James Feng and Jingyu Lu, thank you for many countless conversations and pieces of advice on every possible topic with regards to battery science.

To everyone at SEAS, thank you for providing such a great academic environment. I learned as much from questions posed over lunches, summer seminars and while getting coffee as I ever could in any class. Special thanks to Professors Spaepen and Aziz and all of the members of their labs for such thoughtful discussions. Also, thank you to all of the members of the SEAS staff for keeping everything moving so smoothly behind the scenes.

Thank you to all of the many friends I've made during my time at Harvard. Zach Gault, Eric Fell and Baptiste Lemaire definitely kept me sane there towards the end. Sarah Conyngham and Vinay Subbiah are two of the most supportive people I've ever met. To Bryan Kaye, Jesse Crossno and Dan Wintz, you guys are great - I wish I had come to Harvard sooner so that we could have overlapped more. I also want to thank David Bergkamp, Melissa Griffith, Chris Johnson, Jesse Nobbe and Andrew Smolie for all of their remote support and for being a source of catharsis during trips back home.

Above all, thank you to my family, to whom this text is dedicated. To my parents, who have loved, supported and encouraged me more in the past 29 years than I deserve. Anything I achieve in life, I owe to you. To my siblings, Caroline, Anna and Bullitt, you have been the best role models I could have hoped for. You've all built wonderful extensions to our family, who have in turn had a profound impact on me. Finally, to Katie Lamb. You've inspired me and loved me throughout this work, despite the years of stress and long times apart. This work would never have happened without the sacrifices

## Acknowledgments

you've made.

Dedicated to my family.

## Chapter 1

## Overview \& Context

This dissertation describes methods for improving the operating voltage windows of solid-state batteries constructed using ceramic-sulfide solid-electrolytes. Following how the work was originally published, my theoretical and computational work is presented herein alongside supporting experimental evidence that was obtained by my experimental collaborators. In short, we show that mechanical constriction can be used to introduce energy barriers that oppose structural decay. These energy barriers lead to expanded operating windows in what is termed mechanically-induced metastability. While the intrinsic electrochemical stability of ceramic-sulfides is on the order of $1.7-2.1 \mathrm{~V}$ versus lithium metal, we demonstrate through both ab-initio computational methods and electrochemical experiments that the mechanically-induced metastability window can be much wider. Depending on the nature of the constraining mechanism, oxidation onsets well above 4.5 V versus lithium metal have been achieved. This result is significant as commercial liquid electrolytes are typically limited to 4.5 V . Given that ceramic-sulfides have already surpassed liquid electrolytes in terms of conductivity, this expansion of the

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operational window is an important step towards commercial adoption.

Chapter 2 provides an introduction to the field of ceramic-sulfide solid-electrolytes as a basis for solid-state lithium batteries. Of particular focus are the inconsistencies reported in the literature regarding the operating voltage windows for the electrolytes $L i_{10} G e P_{2} S_{12}$ (LGPS) and $L i_{10} S i P_{2} S_{12}$ (LSPS). While many works have confirmed the thermodynamic stability windows of these materials to be on the order of $1.7-2.1 \mathrm{~V}$, many other studies have presented batteries that have been operationally stable well beyond this range (up to $4-5 \mathrm{~V}$ ). These contradicting reports suggest that there remains an unaccounted-for degree of freedom in sulfide battery design that can have significant impact on the stability of the batteries. We suggest that these inconsistencies may be due, in part, to battery material and cell designs with varying degrees of mechanical constriction. To this point, we highlight the development of two common solid-state battery designs which can have significant mechanical effects, but which are rarely discussed in terms of stability. The first is the pressurized battery cell. The pressurized battery cell was adopted to minimize voids and improve interfacial contact for the purpose of achieving high conductivity. The second is a glassy matrix which embeds the crystalline sulfide electrolyte. Again, these glassy embedding matrices were originally adopted under pursuit of higher conductivity and are rarely discussed in-terms of stability. In the follow chapters we demonstrate that both of these approaches to conductivity can greatly impact stability. With previous works only evaluating the impact of these mechanical effects on conductivity, it is not surprising that such inconsistent stability measurements have been reported.

Chapter 3 consists of our work, Advanced Sulfide Solid Electrolyte by Core-Shell Structural Design, in which we first introduce the concept of mechanically-induced

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metastability as a means by which the stability window can be expanded. We show that when LSPS is synthesized in a core-shell morphology with a glassy shell and LSPS core, the stability window varies significantly with the composition of the shell. When the shell is a sulfide-rich glass, the stability is poor. In contrast, when the shell is a silicon-rich glass, the stability improves considerably. Electrochemical measurements show that the silicon-rich system can be readily cycled as high as 5 V . We hypothesize that the silicon-rich glass is a higher modulus than that of the sulfur-rich and, hence, provides a greater degree of mechanical constraint. We derive our first thermodynamic model for this mechanically-induced metastability to quantify these effects. A new perturbative computational method is developed that allows us to combine this metastability model with ab-initio calculations to predict the level to which the stability window can be expanded. Remarkable agreement between the resulting theoretical window and the observed experimental window is found. The key insight gained from Chapter 3 is that, in mechanically constrained systems, pristine LSPS and decomposed LSPS exist at different pressures. This differentiates mechanically-induced metastability from high-pressure stability. Mechanical constraints range from isobaric (weak or no constraint) to isovolumetric (strong or ideal constraint). In the latter case, any decomposition of the LSPS forces the neighborhood to become compressed. That is to say that the reactants of the decomposition, the pristine LSPS, exists at zero-stress whereas the decomposed products exist at an elevated stress.

This physical picture is futher expanded in Chapter 4, originally Strain Stabilized Ceramic-Sulfides. In this chapter, we derive a generalized thermodynamic framework that allows us to explore the importance of the decay morphology on the potential for mechanically-induced metastability. We show that the model of Chapter 3 is a mean

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field solution to this more generalized model. In particular, we focus on understanding how the constraint requirements (i.e. the thickness and rigidity of the constraining shell) differ between the cases where the electrolyte decays in a uniform versus a localized inclusion manner. It is predicted that a thin-shell (thickness much less than the core radius) will only stabilize the core if the nature of the core is to decay in localized inclusions. In contrast, if the sulfide core is likely to decay homogenously, a thick-shell is needed (as was used in Chapter 3). A thin-shell LGPS is synthesized with a 20 nm thick shell (200-300nm core) and shown to have a significantly expanded window. Moreover, post-decomposition microscopy reveals that the LGPS does, in-fact, decay via inclusions as was predicted by our theoretical framework.

Chapter 4 also introduces an alternative computational approach to the perturbation method introduced in Chapter 3. The relative advantages and disadvantages of each method are compared. The underlying computational challenge is that, unlike isobaric calculations, constrained systems are not convex. This stems from the fact that the pressure is dependent on the decomposition products, which are not known prior to the calculation of the ground state. The perturbation approach addresses this issue by using the ground state configuration of the unconstrained material as a reference state. This sacrifices some accuracy in order to maintain compatibility with convex hull optimization, which is a computationally efficient approach. On the other hand, the newly introduced Lagrange-based method fully solves the system, including changes in ground state, but can be computationally more burdensome. Chapter 4 compares the results of both methods for the case of LGPS. It is seen that while the ground-states do change, introducing the possibility of error in the perturbation method, the resulting errors are typically small in this case. Thus the perturbation method is largely the preferred

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approach when computational resources are limited, such as during high-throughput calculations. Appendix A also compares these methods from a more pragmatic view point and suggests how each of these methods can be effectively implemented at large-scale.

In Chapter 5, originally A High-Throughput Search for Functionally Stable Interfaces in Sulfide Solid-State Lithium Ion Conductors, we consider the impact of mechanically-induced metastability on interface reactions between ceramic-sulfides and common electrode materials. LSPS and LGPS are known to form reactive interfaces with most electrode materials. As a result, sulfide based batteries typically utilize coating materials to inhibit contact between the LGPS/LSPS and the active material(s). Here, we develop new computational processes for screening high-volume material data to search for the best coating materials for mechanically constrained systems. We use these algorithms to search over 67,000 phases resulting in 2,000 promising coating candidates for cathodes and over 1,000 candidates for anodes. The key development of this chapter is the ability to separate the interfacial and bulk contributions of the interfacial reaction. We then apply mechanically-induced metastability computation methods (Chapters $3 \& 4)$ to the bulk component in order to determine if the system will become stabilized when mechanically constrained. Appendix B discusses how these methods can be readily performed at large-scale and best practices for implementation.

Chapter 6 overviews our on-going work to better develop mechanically-induced metastability for practical operation beyond the lab. In particular, the use of cell level mechanical constraints (e.g. pressurized battery cells) in place of core-shell morphologies and better understanding of how the decomposition of interfaces with electrode materials develop with cycling. Current liquid-electrolytes used in the battery industry are limited to approximately 4.5 V before failing. Our current work shows that

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operational stability can be obtained in excess of 6 V . These high-voltage results are hypothesized to be due to a combination of mechanically-induced metastability combined with mechanically-induced kinetic limitations. That is, in addition to the mechanically constrained energy barriers that oppose decomposition, once the decomposition does occur, highly localized pressure will form. In turn, these pockets of highly localized stress decrease ion mobility that kinetically opposes further decay. This process forms a negative feedback loop for material decay in which partial decomposition of LGPS/LSPS becomes self-limiting. If this can be implemented in a practical manner, it would be a transformative development for the field as it would enable the use of new high-voltage redox chemistries in the electrode materials.

The appendices detail computational methodologies developed to handle the high-throughput nature of this work. Plain language pseudo-code is included to describe these approaches in a way that can be readily generalized to other electrolytes. These include perturbation and Langrange-based calculation of electrochemical metastability (Appendix A), high-throughput screening of interfacial stability via pseudo-binary (Appendix B), and interphase electrochemical stability for interface reaction propagation (Appendix C).

## Chapter 2

# Introduction to Sulfide 

## Solid-Electrolytes

## Authorship

This thesis chapter covers material that originally appeared in the literature as "The Effects of Mechanical Constriction on the Operation of Sulfide based Solid-State Batteries" by William Fitzhugh, Luhan Ye, and Xin Li and published as Journal of Materials Chemistry A: Emerging Investigators 7, 23604-23627 (2019).

### 2.1 Solid-State Batteries

Solid-state batteries offer paradigm shifting performance over conventional liquidelectrolyte counterparts.[1-7] By implementing solid-electrolytes, solid-state batteries

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can enable the adoption of higher-energy density electrode materials[8-11] while simultaneously providing improved temperature robustness[12-14]. Moreover, solid-state batteries eliminate the most dangerous component in current batteries, the flammable liquid-electrolyte. On the negative electrode side, solid-electrolytes can potentially enable the adoption of lithium metal by providing a physical barrier that prevents lithium dendrite formation. [15, 16] Such lithium metal anodes represent the theoretical optimum for negative electrodes with a capacity of $3860 \mathrm{mAh} g^{-1}$ and a voltage of 0 V . This, in contrast with graphite's $372 \mathrm{mAh} g^{-1}$ and 0.2 V [17, 18], would represent a significant improvement in the anode material. With regards to the positive electrode, solidelectrolytes have demonstrated compatibility with a multitude of high-energy density cathodes including both $1,000 \mathrm{mAh}^{-1}$ high-capacity[11] as well as 5 V high-voltage[9] materials. Solid-electrolytes also maintain superior performance at low temperatures, where viscosity increases can plague liquid-electrolytes, a key performance metric for many applications including electric-vehicles for low-temperature markets.

In evaluating the potential of solid-electrolytes, two of the most important criteria are the lithium ion conductivity and the electrochemical stability window. The stability window constitutes the range of voltages versus lithium metal in which the solid-electrolyte will not electrochemically decompose. Considering the two most studied families of solid-electrolytes, the oxides and the sulfides, there remains an inherent trade-off between these metrics. Oxides have a wider stability window than sulfides, but suffer from ionic conductivities well below the current organic liquids ( $0.1-1$ vs $\left.10 \mathrm{mS} \mathrm{cm}{ }^{-1}\right)$.[19-23] On the other hand, sulfide solid-electrolytes have reached ionic conductivities up to $25 \mathrm{mS} \mathrm{cm}^{-1}$, exceeding most liquids, but suffer from poor electrochemical stability.[24-27] With intrinsic stability windows of approximately 1.7-2.1

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V versus lithium metal, sulfide solid-electrolytes are, theoretically, incompatible with most electrode materials.[28, 29] In addition, compatibility of the electrolytes with mass production procedures, including brittleness and air stability[30] of the electrolytes as well as the applicability of the low-cost cold press procedure, also remain critical factors for solid-state battery development.

Historically, sulfide solid-electrolytes have progressed from glass to glass-ceramic to ceramic, with each progression resulting in a corresponding increase in ionic conductivity. Glass sulfides, which maintain the advantage of not having grain boundary resistances, were among the first solid-electrolytes to be discovered. Ionic conductivities in these materials typically range from $0.01-1 \mathrm{mS} \mathrm{cm}^{-1} .[31,32]$ The $L i_{2} S-P_{2} S_{5}-L i I$ glass system, for example, achieved an impressive $1.7 \mathrm{mS} \mathrm{cm}^{-1}$.[33] The partial crystallization of glass sulfides to form glass-ceramics, or ceramic-sulfides embedded in a glass framework, can significantly boost the ionic conductivity. In some cases, this partial crystallization can increase ionic conductivity by as much as two orders magnitude. Glass-ceramics frequently exhibit conductivities on the order of $1 \mathrm{mS} \mathrm{cm}{ }^{-1} .[34-36]$. Ceramic $L i_{10} G e P_{2} S_{12}$ (LGPS) was amongst the first solid-electrolytes to meet or exceed conventional liquid electrolytes with a conductivity of $12 \mathrm{mS} \mathrm{cm}^{-1}$ in 2011.[37] Five years later, it was surpassed by $\operatorname{Li}_{10} \mathrm{SiP}_{2} S_{12}$ (LSPS) which reached an astonishingly high $25 \mathrm{mS} \mathrm{cm}^{-1} .[14]$

Despite a huge amount of interest in the ceramic-sulfide solid-electrolytes due to these exceptional conductivities, there has remained contradictory reports with regards to the electrochemical stability. Solid-state batteries based on ceramic-sulfides have been demonstrated with good cyclability up to around 4 V as well as at large current rates (18C or approximately 3 minutes for full charge/discharge).[14] These results

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imply that the ceramic-sulfides are either stable up to around 4 V or, at the very least, kinetically stable. Some other experimental results have suggested that ceramic-sulfides are not, in-fact, stable in this voltage range. Oxidation of ceramic-sulfides above 2.5 V has been reported by cyclic-voltammetry measurements.[24] Ab-initio computation agrees with the latter experiments, predicting that LSPS and LGPS are only stable at room-temperature in the narrow voltage range of approximately $1.7-2.1 \mathrm{~V} .[25,26]$ Moreover, computation predicts that at 4 V , the reaction energy of LSPS/LGPS oxidation is on the order of -1 eV atom $^{-1}$. To further complicate these contradictory reports, the ceramic-sulfides have also demonstrated a propensity to react with common electrode materials.[28, 29] Despite having been cycled to 4 V with $\mathrm{LiCoO}_{2}$ (LCO) for over 1,000 cycles, computational studies have suggested that ceramic-sulfides will react with LCO with a reaction energy on the order of $-300 \mathrm{meV}_{\mathrm{atom}}{ }^{-1}$, indicating the importance of the cathode coating material $\mathrm{LiNbO}_{3}$ for interfacial stability.

### 2.2 History of the Sulfides

Since inception, the sulfide field has been principally focused on developing solidelectrolytes with a comparable ionic conductivity to that of commercial liquid counterparts. Recently, with materials such as LGPS/LSPS achieving these conductivity goals, the amount of attention given to electrochemical stability has increased dramatically. Below is a brief overview detailing how experimental conditions relevant to mechanical constriction (e.g. pressurized cells and glass embedding matrices) originated from the pursuit of high conductivity and ultimately became common place within the field. In accordance with these historical norms, mechanically relevant developments are

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introduced here in terms of the field's pursuit of conductivity.

### 2.2.1 Glass Sulfides

Glass sulfides first reached prominence in the 1980's as one of the earliest high performance solid-electrolytes.[3, 38-40] The basic structure of glass sulfide systems consists of $L i_{2} S$ plus glass-formers such as $G e S_{2}[40]$, SiS $S_{2}[30,41]$, or $P_{2} S_{5}[42,43]$. While the conductivity of glass sulfides is typically one to three orders of magnitude below that of the industrial standards set by liquid electrolytes, they are amongst the highest conductivity glasses. Figure 2.1a depicts the relative scale of conductivity for sulfide glasses versus the next most promising family, the oxide glasses.[43] Compared to crystalline solid-electrolytes of the time, these glass phases enjoy the benefits of isotropic conduction, decreased grain boundary resistances[44], and high conductivity at a variety of compositions. An additional advantage of the glass sulfides over other solid-electrolytes is the compatibility with multiple synthesis techniques, potentially easing the barriers to commercial adoption. Some of the most prevalent synthesis methods for glass sulfide electrolytes have been quenching, twin-roller quenching, and mechanochemical milling.[31, 40, 45, 46]

The glass sulfides experience characteristic ionic conductivities on the order of $10^{-3}-1 \mathrm{mS} \mathrm{cm}{ }^{-1}$ and stability windows that can exceed 4V. Successful pursuits to reach the higher range of conductivities have included the doping of a small amount of oxide[47-49] or halide salts[45, 50] as well as the adoption of pressurization to improve contact and reduce the presence of voids[51]. Figure 2.1b, for example, shows the impact of oxide doping in the system $(100-z)\left(0.6 \cdot L i_{2} S+0.4 \cdot S i S_{2}\right)+z L i_{4} S i O_{4}$.


Figure 2.1: (a) Conductivity at $25^{\circ} C\left(\sigma_{25}\right)$ versus composition for glass (G) and glassceramic (GC) sulfide solid-electrolytes. Image from ref[43]. (b) Temperature dependence $\left(1000 K T^{-1}\right)$ of conductivities for $(100-z)\left(0.6 \cdot L i_{2} S+0.4 \cdot S i S_{2}\right)+z L i_{4} S i O_{4}$. Image from $\operatorname{ref}[47]$.

A small ( $5 \mathrm{~mol} \%$ ) doping is seen to approximately double the ionic conductivity of the glass. Pressing $80 \mathrm{LiS}_{2}+20 P_{2} S_{5}$ glass pellets at pressures up to 360 MPa was shown to decrease the presence of voids and increase the conductivity by nearly an order of magnitude.[51] The adoption of battery cells which remain pressurized during electrochemical cycling (illustrated in Figure 2.2) have become common place.[3, 42, 52] In a study on silicon anodes by Piper et al.[53], this pressurization of the cell was considered as an independent variable and the impact on battery operation beyond just conductivity has been reported. In many other works, particularly those focused on increasing the conductivity, however, the pressurized cells have simply been listed as an experimental detail rather than a systematic point of study.


Figure 2.2: Typical solid-state battery cell design for applying and maintaining pressure. Image from ref[53].

### 2.2.2 Glass-Ceramic Sulfides

An alternative approach to improve the conductivity of the glass sulfides has been the partial crystallization to form the so-called glass-ceramic sulfides.[34] These phases consist of crystalline materials embedded in a matrix of glass sulfides. Generally, partial crystallization is seen to reduce bulk conductivity as most crystalline phases are poor ionic conductors. However, in specific cases, the crystallized phase can be highly conductive, leading to bulk conductivities that surpass the values of the mother glass. For example, this phenomenon is depicted in Figures 2.3a and 2.3b for the composition $70 \mathrm{Li}_{2} S+30 P_{2} S_{5}(\mathrm{~mol} \%)$.[34] In this case, the base glass was synthesized via mechanochemical milling of crystallized $L i_{2} S$ and $P_{2} S_{5}$. The glass had a room temperature ionic conductivity of $5.4 \cdot 10^{-2} \mathrm{mS} \mathrm{cm}^{-1}$. Crystallization was performed by heating to $240^{\circ} \mathrm{C}$ for 2 hours, resulting in a glass-ceramic with a drastically improved room temperature ionic conductivity of $3.2 \mathrm{mS} \mathrm{cm}^{-1}$. In contrast, the same precursors were used for solid-state synthesis and resulted in an ionic conductivity of


Figure 2.3: (a) Temperature dependency of the conductivity $\left(\log _{10}\left(\sigma / S \mathrm{~cm}^{-1}\right)\right.$ ) of $70 L i_{2} S+30 P_{2} S_{5}$ samples prepared by mechanical milling or solid-state reaction. LIPON, a typical oxide solid electrolyte, is also shown. (b) XRD patterns of a) the $70 L i_{2} S+30 P_{2} S_{5}$ glass, b) the glass-ceramic, and c) the sample obtained by the solid-state reaction. Both images from ref[34].
$2.6 \cdot 10^{-5} \mathrm{mS} \mathrm{cm}^{-1}$. As shown in the XRD of Figure 2.3b, the crystallization step and solid-state synthesis resulted in completely different crystal phases. The solid-state reaction produced the low conductivity phases of $L i_{4} P_{2} S_{6}$ and $L i_{3} P S_{4}$. Recrystallization, however, resulted in an unknown crystalline phase with high conductivity (later determined [54] to be $L i_{7} P_{3} S_{11}$ ).[55]

Later work showed that this high conductivity $\operatorname{Li}_{7} P_{3} S_{11}$ (LPS) phase could also be crystallized directly from the melt via quenching, suggesting that it is the thermodynamically favored phase at high temperatures.[56] This is in contrast to the low temperature phases of $L i_{4} P_{2} S_{6}$ and $L i_{3} P S_{4}$, which have low conductivity. Thus, it was concluded that while LPS is not a thermodynamically stable phase at room temperature,

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it can become metastable at room temperature when embedded in certain glass matrices. However, little has been studied about the mechanism by which this metastability arises.

### 2.2.3 Thio-LISICON

Amongst the first crystalline lithium solid-electrolytes families to be discovered was the oxide lithium superionic conductor (LISICON) family.[57] The LISICON family is based on the framework $L i_{(16-2 x)} D_{x}\left(T O_{4}\right)_{4}$ where D and T represent divalent and tetravalent cations, respectively. The LISICON member $L i_{14} \mathrm{Zn}\left(\mathrm{GeO}_{4}\right)_{4}$ was recorded as achieving a remarkable $100 \mathrm{mS} \mathrm{cm}{ }^{-1}$ conductivity at elevated temperatures.[57] The sulfide equivalent, thio-LISICON, family was introduced based on the similarly structured $L i_{4} G e S_{4}$ framework.[58, 59] The introduction of lithium vacancies via phosphorus substitutions $\left(V_{L i}^{(1-)} \leftrightarrow P_{G e}^{(1+)}\right)$ resulted in crystalline phases with conductivities as high as $2.2 \mathrm{mS} \mathrm{cm}^{-1}$ at room temperature.[58] Varying the vacancy concentration from $x=0$ to 1 in $L i_{(4-x)} G e_{(1-x)} P_{x} S_{4}$, resulted in a seemingly continuous shift in the XRD signature as shown in Figure 2.4a from that of $L i_{4} G e S_{4}$ to $L i_{3} P S_{4}$. Analysis of the lattice parameters (Figure 2.4b), however, indicated that the cation ordering could be separated into three distinct ranges. Thio-LISICON I are those for which $x<0.6$, whereas thio-LISICON II and III have $0.6<x<0.8$ and $x>0.8$, respectively.

The ionic conductivities of $L i_{(4-x)} G e_{(1-x)} P_{x} S_{4}$ are seen to increase monotonically with $x$ through regions I and II (Figure 2.4c) before sharply decreasing in region III. The maximum observed conductivity reached was $2.2 \mathrm{mS} \mathrm{cm}^{-1}$, which occurred in region II at $x=0.75$. The other region II compositions $(x=0.65,0.7)$ were the only others to exceed the $1 \mathrm{mS} \mathrm{cm}{ }^{-1}$ threshold. CV was performed using a $L i / L i_{3.25} G e_{0.25} P_{0.75} S_{4} / A u$

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cell to evaluate the electrochemical stability window. With the exception of lithium deposition and dissolution $\left(L i^{+}+e^{-} \Longleftrightarrow L i(m)\right)$, negligible current was seen in the window of $-0.5-5 \mathrm{~V}$ (Figure 2.4 d ).

### 2.2.4 LGPS/LSPS

$L i_{10} G e P_{2} S_{12}$ (LGPS) was first demonstrated by Kamaya et al.[37] to have a remarkably high room temperature conductivity of $12 \mathrm{mS} \mathrm{cm}{ }^{-1}$, making it the first room temperature solid-electrolyte to reach typical liquid electrolyte conductivities. Five years later, the silicon analog, $L i_{10} S i P_{2} S_{12}$ (LSPS), provided an even greater conductivity of $25 \mathrm{mS} \mathrm{cm}^{-1}$.[14] LGPS/LSPS are tetragonal crystals with highly conductive channels running alongside the $c$-axis. Additional channels in the $a b$-plane allow three-dimensional migration. The structure of LGPS consists of a framework of $P S_{4}$ and $L i S_{4}$ tetrahedra, $L i S_{6}$ octahedra as well as disordered[60] $\left(G e_{0.5} P_{0.5}\right) S_{4}$ tetrahedra. As depicted in Figure 2.5, the $c$-axis of LGPS consists of one-dimensional chains of edge-sharing $\left(G e_{0.5} P_{0.5}\right) S_{4}$ tetrahedra and $L i S_{6}$ octahedra. Those chains are in turn connected by $P S_{4}$ tetrahedrons. LGPS differs from the thio-LISICONs in structure by the ordering of $(G e / P) S_{4}$ tetrahedra.[61]

Understanding the mechanism by which LGPS and LSPS derive this remarkable conductivity has been the subject of intense computational and experimental work. He at al[62] showed that LGPS experiences low lithium migration barriers when multiple lithium ions move in concert, rather than in single ion steps. Additionally, both experiment and computation have shown that the lithium ion conduction is largely, but not exclusively, along the $c$-axis channels.[25, 63] The importance of the $a b$-plane

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diffusion pathway is believed to be that it enables transitions from one one-dimensional channel to another. In the event of a defect or a blocked channel, these pathways would allow alternative diffusion routes to circumvent the blockage.[61, 63] The presence of such $c$-axis channel blocking events are extremely likely in the thermodynamic limit, hence the need for a three-dimensional mechanism is paramount. Recent work has confirmed this anisotropic mechanism in single crystal LGPS.[64] In short, LGPS/LSPS combine the high conductivity of one-dimensional diffusion pathways with the robustness of three-dimensional pathways.

### 2.3 Inconsistent Stability Reports

The initial reports on the stability of LGPS by Kamaya et al.[37] were surprisingly good. Not only could LGPS be synthesized (implying chemical stability), but it also survived cycling in a battery cell with an indium metal anode and $\mathrm{LiNbO}_{3}$-coated LCO cathode. Such cycling clearly demonstrated that LGPS was sufficiently electrochemically stable for battery operation. Similarly, LSPS was used to construct solid-state full cells with lithium titanate (LTO) anodes and LCO cathodes with good cyclability, indicating electrochemical stability.[14] Additionally, these full cells could sustain charge-discharge currents of 18C (charge/discharge in circa 3 minutes). In this regard, LGPS/LSPS seemed to have joined the growing number of sulfide solid-electrolytes with operational electrochemical stability windows that reach above 4 V versus lithium metal.[58, 65-67] However, other reports indicated that this was not the case and that battery cycling with LGPS/LSPS would quickly decay.[24, 52] First principle calculations have supported the latter viewpoint, showing that the stability window for LGPS/LSPS is limited to roughly

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$1.7-2.1 \mathrm{~V}$ versus lithium metal.[24-26, 29]

Figure 2.6 illustrates these complicated reports of electrochemical stability for LGPS and LSPS. Figure 2.6a shows the initially reported CV for LGPS by Kamaya et al. No decomposition peaks were reported from below 0 V to 5 V , except for the lithium dissolution/deposition peaks. The battery was constructed as Li/LGPS/Au in the CV test, where no carbon was mixed with LGPS. Conversely, Han et al.[24] drew the differing conclusion that LGPS reduces in the range 0-2.0V (Figure 2.6b) and oxidizes in the range $1-3.5 \mathrm{~V}$ (Figure 2.6c) when combined with carbon in the LGPS cathode. Adjusting for the weight of LGPS in the cathode ( 7.5 mg LGPS +2.5 mg graphite), the oxidation current is on the order of $0.001 \mathrm{Ag}^{-1}$. While this decomposition current was quite small, the CV supported the computationally determined voltage range of 1.71-2.14V. Figures 2.6d,e,f[68] show how core-shell LSPS can change decomposition current by orders of magnitude depending on the nature of the surrounding shell of the core-shell particle. These measurements were made with carbon added and in the absence of external pressure. The measured current rates ranged from a small $0.01 \mathrm{Ag}^{-1}$ at the 3.1 V onset of decomposition and around $0.1 \mathrm{Ag}^{-1}$ up to 5 V in some samples, to a large $100 \mathrm{Ag}^{-1}$ catastrophic decomposition beyond 3.5 V in other samples, depending on the shell composition. This order of magnitude change was attributed to the differing mechanical stabilization provided by each shell as will be discussed in-depth in Chapter 3. The decomposition currents of $0.01-0.1 \mathrm{Ag}^{-1}$ observed between $3-4 \mathrm{~V}$ for strong core-shell particles had no obvious detrimental effect to solid-state battery performance, and the voltage window was reported to be $0.7-3.1 \mathrm{~V}$ with quasi-stable performance up to $5 \mathrm{~V} .[68]$ LSPS with a voltage window up to 4.1 V paired with LCO was also reported in an earlier solid state battery test,[14] however, without any discussion of microstructural

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morphology or mechanical constriction effects.

These reports are compared in Table 2.1 to survey the disparate findings for LGPS and LSPS. Voltage windows listed in Table 2.1 are distinguished by computation, CV, and battery cycling. For computational windows, the values given are the voltages at which the hull energy exceeds thermal energy. CV windows are where significant redox currents begin, whereas battery cycling windows are the voltage ranges in which the batteries were cycled. For reference, CV results for a characteristically stable glass sulfide ( $0.7 \mathrm{Li}_{2} \mathrm{~S}+0.3 P_{2} S_{5}$ ) up to 5 V , an exceptionally stable glass sulfide (95 (0.6 $\left.\left.\mathrm{Li}_{2} \mathrm{~S}+0.4 \mathrm{SiS}_{2}\right)+5 \mathrm{Li}_{4} \mathrm{SiO}_{2}\right)$ up to 10 V , and a characteristic glass-ceramic sulfide up to 4.3 V are also included. Computational predictions of the electrochemical stability of glass sulfides are generally absent given the complexity in the atomic structures.

Doping of LGPS, both isovalent (e.g. LSPS) and aliovalent, for improved conductivity and/or stability has been the focus of major research attention. The simplest doping scheme is the deviation of LGPS away from $L i_{10} G e P_{2} S_{12}$. For example, Du et al.[60] computationally investigated the stability of $L i_{x} G e P_{2} S_{12}$ and concluded that LGPS will lithiate [delithiate] at voltage below [above] approximately 1V [3V]. This nonzero capacity suggests that lithiation/delithiation might improve the electrochemical window. However, the energy gain of this effect is only on the order of $100 \mathrm{meV}^{\text {atom }}{ }^{-1}$, which would not be able to account for all of the voltage widening reported previously. XRD of LGPS at composition $L i_{(10+\delta)} G e_{(1+\delta)} P_{(2-\delta)} S_{12}$ showed smooth shifting of the XRD peaks as $\delta$ increased from 0 to 0.35 .[69] This implies that the material is, in-fact, a solid solution with respect to $(G e / P) S_{4}$ tetrahedra, as a stoichiometrically fixed phase would require the adoption of impurity phase(s) as the precursor ratio shifts.

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Ong et al.[26] performed a systematic first-principles study on $L i_{(10 \pm 1)} M P_{2} X_{12}$ where $M=G e, S i, S n, A l, P$ and $X=O, S, S e$. The chemical and electrochemical stability were studied using convex hull analysis[70] and the conductivity was evaluated using ab-initio molecular dynamics. This work concluded that sulfur could not feasibly be replaced with oxygen or selenium. Oxygen substituted structures were found to have large chemical instabilities ( $>90 \mathrm{meV}^{\text {atom }}{ }^{-1}$ ) and poor lithium ion conductivity (circa $0.03 \mathrm{mS} \mathrm{cm}^{-1}$ ). Selenium substitution was predicted to increase conductivity $\left(24 \mathrm{mS} \mathrm{cm}^{-1}\right)$ but came at the cost of weaker electrochemical stability.

In short, there exists substantial variance in the reported feasible operating window for ceramic-sulfide based solid-state batteries. The possible operating windows range from as narrow as $1.7-2.1 \mathrm{~V}$ to as wide as $0-5 \mathrm{~V}$ and possibly even wider. These results suggest that there exists an independent variable of battery design that can control this operating range, offering the wide stability needed for pragmatic battery development. Based on computational studies regarding doping, it seems unlikely that compositional differences between the aforementioned studies could potentially account for this variability in results. Moreover, the results of recent computational and experimental studies suggest that unreported on mechanical differences in the experimental design may be able to account for these disparate findings.

| Electrolyte <br> Type | Operating <br> Window <br> Type | Reported Window | Method | Ref |
| :---: | :---: | :---: | :---: | :---: |
| LSPS | Wide | 2.5-4.1 V | B | [14] |
|  | Narrow | None | C | [26] |
|  | Both | Not Constrained: 1.7-2.1 V <br> Constrained: $0.7-3.1 \mathrm{~V}$ | B+C | $[68]$ <br> Ch3 |
| LGPS | Wide | 0-5 V | CV | [37] |
|  | Narrow | $1.71-2.14 \mathrm{~V}$ | $\mathrm{CV}+\mathrm{C}$ | [24] |
|  | Both | Not Constrained: 1.7-2.1 V <br> Constrained: 1.25-4.0 V | $B+C$ | [71] <br> Ch4 |
| Glass | Wide | 0-5 V | CV | [72] |
| Glass | Wide | 0-10 V | CV | [73] |
| Glass- <br> Ceramic | Wide | 2.6-4.3 V | B | [43] |

Table 2.1:: Electrochemical windows of sulfide electrolyte systems as reported by experiment (CV or battery) or computational prediction. Method is listed as: CV-CV, B-Battery, C-Computation. Reported battery windows are not exclusive (i.e. 2.5-4V for a battery window does not mean that a voltage outside that range is unstable). Computation and CV results are exclusive as they represent the onset of electrochemical reduction or oxidation.


Figure 2.4: (a) XRD patterns of $L i_{(4-x)} G e_{(1-x)} P_{x} S_{4}$. (b) Compositional dependence of the lattice parameters ( $a, b, c$ ) and angle $\beta$ of $L i_{(4-x)} G e_{(1-x)} P_{x} S_{4}$ determined by XRD analysis. (c) Compositional dependence of ionic conductivity $\left(\log _{10}(\sigma)\right)$ at $25^{\circ} \mathrm{C}$. (d) CV of a $L i / L i_{3.25} G e_{0.25} P_{0.75} S_{4} / A u$ cell. The type of cell design used, pressurized or otherwise, was not reported. All images from ref[58].


Figure 2.5: The structure of LGPS. (a) The ion conduction framework. (b) Onedimensional chains formed by $\operatorname{LiS}_{6}$ octahedra and $\left(G e_{0.5} P_{0.5}\right) S_{4}$ tetrahedra, which are connected by a common edge. (c) Conduction pathways of lithium ions. Zigzag conduction pathways along the c axis are indicated. Lithium ions in the $L i S_{4}$ tetrahedron (16h and 8 f sites) participate in ionic conduction. All images from ref[37].


Figure 2.6: Various CV results for ceramic sulfides. (a) A 0-5V CV sweep of LGPS shows no noticeable decomposition at any voltage. Image from ref[37]. (b) Reduction experienced by LGPS in the $0-2.0 \mathrm{~V}$ range. Image from ref[24]. (c) Oxidation experience by LGPS in the $1-3.5 \mathrm{~V}$ range. Image from ref[24]. (d-f) Order of magnitude change in decomposition current experienced by core-shell LSPS as a function of synthesis temperature, which controlled the shell compositions. Temperature ranges from $400-500^{\circ} \mathrm{C}$. Image from ref[68].

## Chapter 3

## Advanced Sulfide Solid Electrolyte by Core-Shell Structural Design

## Authorship

This thesis chapter covers material that originally appeared in the literature as "Avanced Sulfide Solid Electrolyte by Core-Shell Structural Design" by Fan Wu, William Fitzhugh, Luhan Ye, Jiaxin Ning and Xin Li and published as Nature Communications, (9), 4037 (2018).

## Abstract

Solid electrolyte is critical to next-generation solid-state lithium-ion batteries with high energy density and improved safety. Sulfide solid electrolytes show some unique

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properties, such as the high ionic conductivity and low mechanical stiffness. Here we show that the electrochemical stability window of sulfide electrolytes can be improved by controlling synthesis parameters and the consequent core-shell microstructural compositions. This results in a stability window of $0.7-3.1 \mathrm{~V}$ and quasi-stability window of up to 5 V for Li-Si-P-S sulfide electrolytes with high Si composition in the shell, a window much larger than the previously predicted one of 1.7-2.1 V. Theoretical and computational work explains this improved voltage window in terms of volume constriction, which resists the decomposition accompanying expansion of the solid electrolyte. It is shown that in the limiting case of a core-shell morphology that imposes a constant volume constraint on the electrolyte, the stability window can be further opened up. Advanced strategies to design the next-generation sulfide solid electrolytes are also discussed based on our understanding.

### 3.1 Introduction

The fast development of portable electronic devices and electric vehicles demands lithiumion batteries with high power, energy density, and safety.[74] Solid-state batteries, using solid electrolytes such as polymers, oxides, or sulfides, are hence promising for nextgeneration lithium-ion batteries.[14, 21-24] The application requires solid electrolytes with good chemical compatibility, high Li-ion conductivity and a wide electrochemical stability window. High lithium-ion conductivity has been achieved in various solid electrolytes, including sulfide glasses, sulfide glass-ceramics, and crystalline sulfides. Sulfide glass solid electrolytes[32] were reported to have a lithium-ion conductivity of $0.1-1 \mathrm{mS} \mathrm{cm}^{-1}$. Sulfide glass-ceramics were produced by precipitation of crystalline

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phases from the precursor sulfide glasses to reduce the grain-boundary resistance. For example, the $L i_{2} S+P_{2} S_{5}$ glass-ceramic system with $L i_{7} P S_{6}[35], L i_{7} P_{3} S_{11}[36]$, and $L i_{3.25} P_{0.95} S_{4}[34]$ precipitates showed improved conductivities of over $1 \mathrm{mS} \mathrm{cm}^{-1}$. Crystalline sulfide solid electrolytes of $L i_{3.25} G e_{0.25} P_{0.75} S_{4}, L i_{10} G e P_{2} S_{12}$ (LGPS)[58] and $L i_{9.54} S i_{1.74} P_{1.44} S_{11.7} C l_{0.3}$ (LSPS)[14] were reported with high conductivity.

Despite the superior lithium-ion conductivity of LGPS and LSPS, various groups $[24,25,75]$ reported the narrower stability windows of around $1.7-2.1 \mathrm{~V}$, while others reported wider voltage windows[14, 37]. We suggest that changes in the micro-structure of the electrolyte materials or in the volume constriction condition of the battery cells may result in different voltage stability windows. Although the structure of the crystalline LGPS or LSPS has been studied by diffraction techniques, change in the synthesis details from various groups may decorate the same crystalline phase with different microstructures of amorphous or glassy phases. This is very possible considering that sulfide systems with mixed glass-ceramic phases can exist from synthesis $[35,36]$ and there lacks a systematic check and understanding about the effect of such amorphous/glassy phases on the materials properties in the previous reports. An understanding of how these possible changes in microstructure can control the electrochemical properties of crystalline sulfide electrolytes, especially the voltage stability and interface compatibility, is hence critical. The goal of our paper is to demonstrate that the control and modification of the microstructures in LGPS and LSPS can adjust and improve their voltage stabilities. More importantly, we aim to reveal the underlying mechanism between the microstructure and the performance of sulfide solid electrolytes, which can serve as the guidelines for the future materials and battery cell designs.

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Here, we show experimentally that the voltage stability of our core-shell LSPS sulfide solid electrolytes can be largely improved by modifying the composition of the amorphous shell that encloses the crystalline LSPS core. The shell compositions are controlled by adjusting the synthesis parameters. The shells with high silicon compositions increase the voltage stability window of the compounds, while low silicon compositions in the shells decrease the voltage stability. Using density functional theory (DFT) simulations, we further demonstrate that the major underlying mechanism of this phenomenon is that in the sulfide solid electrolytes with appropriate core-shell microstructures to provide the volume constriction on the materials level, the work necessary to accommodate the large local strains during decomposition exceeds the energy release of decomposition and, hence, the decomposition is not thermodynamically favorable, leading to enlarged voltage stability windows. The results herein also provide a design strategy from a predictive formalism to further stabilize sulfide solid electrolytes by microstructure modifications, and more generally by volume constriction or pressurization that can be realized on both

### 3.2 Results

### 3.2.1 Theoretical Rationale

Our computational results reveal that the sulfide electrolytes tend to expand during decay, leading to a positive reaction dilation, which is defined by Equation 3.1 in terms of the volume of the decay products $\left(V_{d}\right)$ and of the initial solid electrolyte $\left(V_{S E}\right)$. This dilation is the trace of the strain tensor representing the mechanical transformation from the solid electrolyte to the decomposed products. In some cases, the reaction dilation for

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LSPS is predicted to reach levels as high as $56 \%$.

$$
\begin{equation*}
\epsilon_{R X N}=V_{S E}^{-1}\left(V_{d}-V_{S E}\right)>0 \tag{3.1}
\end{equation*}
$$

In the case of a rigid shell, because the decomposed products are larger than the pristine material and the shell forbids total particle expansion, any partial decomposition must compress the remaining pristine material enough as to make room for the decomposed products. If the decomposition energy (energy above the hull) is less than the work needed to adequately compress the surroundings, then this reaction is energetically forbidden. The effective compressibility of the shell defined by Equation 3.2 represents a metric for the performance of the shell in terms of volume constriction. The limit of $\beta_{\text {shell }} \rightarrow 0$ represents a rigid shell allowing zero volume expansion, whereas $\beta_{\text {shell }} \rightarrow \infty$ recovers the no shell condition.

$$
\begin{equation*}
\beta_{\text {shell }}=V_{\text {core }}^{-1} \frac{\partial V_{\text {core }}}{\partial p} \tag{3.2}
\end{equation*}
$$

Note that $\beta_{\text {shell }}$ is therefore not the shell's material compressibility, but an effective compressibility of the core-shell structure. It is a function of not only the material properties but also the geometry of the shell, including the curvature and thickness. We show that a low effective compressibility provided by the core-shell structure will suppress solid electrolyte decomposition with large enough reaction dilation, a mechanism that can effectively widen the voltage stability window. An amorphous shell with high Si composition falls into this category based on the high Youngs modulus of amorphous Si reported previously.[76, 77]

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Figure 3.1: Color under visible light and XRD patterns of the LSPS powders. The LSPS powder changes color along with the annealing temperature from 400 to $500^{\circ} \mathrm{C}$. All the XRD patterns can be indexed by the same space group, $P 4_{2} / n m c$ (137).

At the onset of decay, where the fraction of the decomposed material is approximately linear with pressure (SI equation 11), Equations 3.1 and 3.2 imply that there is a direct mapping from the fraction of decomposed product to the internal pressure of the core-shell system as well as the volume. Therefore, for the core-shell morphology with low compressibility, expansion of the particle into any neighboring region or void requires significant strain energy. Thermodynamically comparing the energies of the decomposed, expanded, void-filling state with that of the pristine solid electrolyte state, it is the latter that is more energetically favorable. The core-shell structure is thus stable at zero pressure, with no tendency to expand.

### 3.2.2 Characterization of Core-Shell Microstructure

Cl-doped LSPS powders $\left(L i_{9.54} S i_{1.74} P_{1.44} S_{11.7} C l_{0.3}\right.$, or LSPS $)$ were synthesized at seven different annealing temperatures ranging from 400 to $500^{\circ} \mathrm{C}$. The as-synthesized LSPS materials were confirmed to have the same LGPS-type crystal structure[37] (space group $P 4_{2} / n m c, 137$ ) by X-ray diffraction (XRD) (Figure 3.1). Comparable full-width at half-maximum of the Bragg peaks suggest close particle sizes among the LSPS powder samples, which is consistent with the scanning electron microscopy (SEM) images (Figure 3.2a) showing similar morphology and particle sizes.

Both SEM and transmission electron microscopy (TEM) (Figures 3.2a,b) images of LSPS annealed at $450,460,480$, and $500^{\circ} \mathrm{C}$ (hereafter LSPS 450, 460, 480, and 500) show the particles with the core-shell structure. Nano-particles embedded inside the amorphous shells (Supplementary Figure 3.S1) are shown to be single-crystalline by high-resolution TEM (HRTEM) images (Supplementary Figure 3.S2). To measure the composition of different regions (i.e. core, shell and particle in the shell), scanning TEM (STEM) energy-dispersive X-ray spectroscopy (EDS) analyses were performed on multiple areas inside different particles for each material (Supplementary Figure 3.S3). The analyzed atomic compositions of LSPS 450, 460, 480, and 500 obtained from STEM EDS are summarized in Figure 3.2c and Supplementary Figure 3.S4, showing that all regions of these particles are comprised of $\mathrm{Si}, \mathrm{P}, \mathrm{S}$, and Cl (note that lithium cannot be detected by EDS technique). There are relatively small variations in the elemental compositions of the core regions among the four samples, compared with the obvious compositional difference in the shells. As the annealing temperature increases from 450 to $500^{\circ} \mathrm{C}$, the atomic concentration of silicon in the shell generally decreases from $40 \%$


Figure 3.2: Microstructural study on the morphology and composition of LSPS powders annealed at $450,460,480$, and $500^{\circ} \mathrm{C}$. (a) SEM and (b) TEM images show their typical core-shell structures. (c) STEM EDS analyses of these samples show a continuously decreasing Si concentration and increasing $S$ concentration in the shell of these samples versus the increasing annealing temperature.


Figure 3.3: Cyclic voltammetry (CV) test and analyses of the LSPS samples annealed at various temperatures. (a) Low-voltage (0.1-2.0 V) and (b, c) high-voltage (1.0-5.0 V) stabilities of LSPS materials. (d) Initial decomposition onset voltage and (e) integral spectrum intensity of three representative LSPS materials (LSPS 400, 470, 500) in the categories of minor, medium, and severe decompositions. (f) Summary diagram to show the core-shell-structured LSPS materials with similar voltage stability window of 0.7-3.1 V. The decomposition of minor-decomposition materials (LSPS 450-470) above 3.1 V is largely suppressed, giving a quasi-stability window up to 5 V .

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Figure 3.4: Battery performance of $L i_{4} T i_{5} O_{12}+$ LSPS $+\mathrm{C} / \mathrm{LSPS} /$ glass fiber/Li cells incorporating different LSPS materials annealed at different temperatures. (a) First and 20th-cycle charge/discharge curves for batteries incorporating medium-and minordecomposition materials (LSPS 400,450-470). (b) First-cycle charge/discharge curves for batteries incorporating severe-decomposition materials (LSPS 480-500). (c) 20th-cycle charge/ discharge curves for batteries incorporating (LSPS 400, 450-470). (d) Cycle performance of the batteries incorporating LSPS 400, 450, 460, and 470 within the first 20 cycles.

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to less than $10 \%$, while that of sulfur increases from $40 \%$ to $80 \%$.

### 3.2.3 Electrochemical Stability and Battery Performance

Cyclic voltammetry (CV) was used to experimentally evaluate the electrochemical stability of LSPS materials in low-voltage ( $0.1-2.0 \mathrm{~V}$ ) and high-voltage (1.0-5.0 V) ranges. Figure 3.3a shows that in the low-voltage range, all seven LSPS materials show a peak at 0.7 V with similar current densities, indicating the reactions or decompositions at almost the same voltage with similar intensity. However, the high-voltage-range CV tests (Figure 3.3b) show obvious difference among the seven LSPS materials. The current densities of LSPS 480, 490, and 500 increase dramatically beyond 3.1 V , indicating severe decompositions of these materials at high voltages, while the LSPS 450, 460, and 470 materials show little current densities at high voltages. Figure 3.3c magnifies Figure 3.3b by around 500 times, demonstrating the high-voltage decompositions beyond 3.1 V of LSPS 450, 460, and 470 samples are at least two orders of magnitudes smaller than other samples. The onset voltage of the decomposition peak is defined by the cross section of the two tangent lines drawn from the horizontal baseline and the current density curves near the onset for each LSPS material (Figure 3.3d and Supplementary Figure 3.S5). They all show the onset voltages near 3.1 V , with a maximum value for LSPS 490 at 3.20 V and a minimum value for LSPS 460 at 2.87 V . Therefore, the voltage stability windows of these LSPS materials with core-shell structure are all from 0.7 to around 3.1 V as summarized in Figure 3.3f, much larger than the $1.7-2.1 \mathrm{~V}$ window reported previously.[24-26, 75]

As depicted in Figures 3.3b,c, despite the similar stability voltage windows for the

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seven LSPS materials, their decompositions above 3.1 V are completely different. To quantify the difference, the seven current density - voltage curves were integrated from 2.5 to 5 V to obtain the integrated current (Figures 3.3e, f, Supplementary Figure 3.S6 and Supplementary Table 3.S1), according to which the seven LSPS materials can be classified into three categories: minor-, medium-, and severe-decomposition. LSPS 480, 490 , and 500 are severely decomposed samples with the integrated currents in the range of $70-188 \mathrm{VAg}^{-1}$. In comparison, the materials (LSPS 450, 460, and 470) with minor decompositions show the integrated currents that are several hundred times smaller, ranging from 0.25 to $0.41 \mathrm{VAg}^{-1}$. This indicates that the decomposition of LSPS 450, 460 , and 470 above 3.1 V is successfully suppressed, leading to a quasi-stable voltage window up to 5 V . LSPS 400 is the only sample in the medium-decomposition category with an integrated current of $4.8 \mathrm{VAg}^{-1}$.

The different stabilities of LSPS are also reflected in the battery cycling test between 1 and 5 V incorporating the seven different LSPS materials (see Methods). Figure 3.4a shows the first-cycle voltage curves of LSPS 400, 450, 460, and 470 batteries with all of them being able to charge up to 5 V . The LSPS 450, 460, 470 batteries can cycle between 1 and 5 V smoothly, consistent with their high-voltage stabilities up to 5 V . While an obvious voltage bump appears at 4 V on the first charge profile of LSPS 400 battery, most probably due to the medium- degree decomposition of LSPS 400 at high voltages. In contrast, due to the severe decomposition of LSPS 480, 490, and 500, the corresponding batteries cannot be charged above 4 V and failed eventually within the first cycle. Only the batteries incorporating minor/medium-decomposition materials (LSPS 400, 450, 460, and 470) can cycle smoothly between 1 and 5 V for multiple cycles. Figure 3.4c shows the voltage profiles of the 20th cycle for these batteries, in which the 1.5 V charge

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plateau remains flat for LSPS 450, 460, 470 batteries, while that of LSPS 400 battery deforms significantly. The cycle performance of these batteries (Figure 3.4d) also shows that the specific capacity of LSPS 400 battery decays faster than that of LSPS 450, 460, 470 batteries, consistent with their voltage stabilities analyzed earlier. The derivative of capacity versus voltage (dQ/dV) plots for the seven batteries (Supplementary Figure 3.S7a) show peaks at 1.5 V in all cases, corresponding to the phase transition of LTO, and peaks at $3.5-4 \mathrm{~V}$ only for batteries incorporating medium- or severe- decomposition materials, corresponding well to the CV results (Figure 3.3 b ). dQ/dV of these batteries cycled between 0.1 and 2 V (Supplementary Figure $3 . \mathrm{S} 7 \mathrm{~b}$ ) further confirms the 0.7 V decomposition peak for all the seven LSPS materials, again consistent with the CV results (Figure 3.3a). Note that the LSPS samples with high-voltage stabilities coincide with the high lithium-ion conductivities measured by impedance spectroscopy. LSPS 400,460 , and 480 were selected as the representative materials of each category for the ionic conductivity measurement. Results (Supplementary Figure 3.S8) show that LSPS 460 has the highest ionic conductivity of $3.1 \mathrm{mS} \mathrm{cm}{ }^{-1}$, while LSPS 400 and 480 show relatively lower ionic conductivity of 2.28 and $2.39 \mathrm{mS} \mathrm{cm}^{-1}$, respectively. Note that even higher ionic conductivity may be obtained by applying higher pressure[78] during the impedance measurement, which was not applied during our test (see Methods).

It is worth noting that for the above-mentioned CV and charge/discharge tests, the half-cell batteries contain a glass fiber separator to avoid the influence from the interfacial interaction between the LSPS and lithium metal. Small amount of liquid electrolyte is thus added to the glass fiber to allow the lithium-ion conduction. However, to rule out any effect of the liquid electrolyte that may permeate into the cathode layer, all-solid-state battery without any glass fiber separator layer was fabricated and tested.

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Special treatment was performed on Li foil to form a protective layer (see Methods) so that the interfacial reaction between LSPS solid electrolyte and Li can be avoided. Results show that all-solid-state battery using a mixture of LTO + LSPS $460+$ carbon black (C) powers as cathode (Figure 3.5a) can be charged to 4 V smoothly, while the all-solid-state battery using LTO + LSPS $500+\mathrm{C}$ cathode failed at 3.6 V (Figure 3.5b) due to a much more severe decomposition of LSPS 500. These all-solid-state battery results correspond very well to the trend obtained by semi-solid-state battery configuration (Figure 3.4), confirming again that LSPS solid electrolytes synthesized with different conditions do have different electrochemical stabilities.

Making use of the same solid-state battery configuration, solid-state CV test was performed to rule out the possible effect of liquid electrolyte on the electrochemical stability test results of LSPS. Figures $3.5 \mathrm{c}, \mathrm{d}$ shows the CV scan results in the voltage range of 1-5 V for all-solid-state batteries using LTO $+\operatorname{LSPS} 460+\mathrm{C}$ and LTO + LSPS $500+$ C cathode, respectively. The CV peaks of LTO around 1.5 V exist for both batteries. However, no decomposition can be observed for LSPS 460, while the decomposition of LSPS 500 starting at 3.5 V is very strong and obvious. These results match well with the CV results obtained by semi-solid cell, confirming the different electrochemical stabilities of various LSPS solid electrolytes. More importantly, the semi-solid-state battery configuration is proved to be a valuable configuration in terms of evaluating material properties, such as the voltage stability of solid electrolytes. Supplementary Figures 3.S9-12 show the relation between the CV measured decomposition and the accumulation of oxidized LSPS accumulation on the glass fiber separator after testing. LSPS 460 is seen to have negligible product accumulation after either 1-5V (Supplementary Figure 3.S9) or 1-10V (Supplementary Figure 3.s10) voltage

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Figure 3.5: Battery performance and CV test results of all-solid-state batteries using: (a,c) LTO + LSPS $460+$ carbon black (C) as cathode, LGPS as solid electrolytes and LPS-coated lithium foil as anode. (b,d) The same tests for LSPS 500. Current rate for battery test is 0.1 C . Sweeping rate for CV test is $0.1 \mathrm{mV} \mathrm{s}^{-1}$.
sweeps. In contrast, the LSPS 500 shows significant particle build up after being swept from 1-5V (Supplementary Figure 3.S9).

### 3.2.4 Theoretical Simulation Results

The ability of a core-shell structure to stabilize the sulfide solid electrolytes via mechanical constriction was predicted due to the large reaction dilations defined in Equation 3.1. For example, at 0 V vs. lithium metal, LSPS decays or decomposes to

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$L i_{3} P, L i_{21} S i_{5}, L i_{2} S$ with a reaction dilation of $56.2 \%$. Conversely, at 3.5 V vs. lithium metal, LSPS decays to $P_{2} S_{5}, S i S_{2}, S$ with a reaction dilation of $21.5 \%$. Similar reaction dilations are found for LGPS as well as doped derivatives of both LGPS and LSPS. If conditions are created such that the work necessary to accommodate this strain is greater than the decay energy, then the decay cannot proceed and the stability window will be expanded.

One route, in theory, to increase such work and prevent the decay is to apply a constant pressure. If the solid electrolyte is pressurized, then any volume expansion must exert certain mechanical work. Such a constant pressure ensemble can be directly calculated via DFT simulations. The relevant free energy, at zero temperature, for a lithium open system at constant pressure is:

$$
\begin{equation*}
\phi\left(p, \mu_{L i}\right)=H(p)-\mu_{L i} N_{L i} \tag{3.3}
\end{equation*}
$$

where $H$ is the enthalpy of the structure (calculated via DFT), $p$ is the pressure, $\mu_{L i}$ is the lithium chemical potential and $N_{L i}$ is the number of lithium atoms in the cell. Results (Supplementary Figures 3.S13-14) clearly show that applying large pressures can improve the stability window of sulfide solid electrolytes considerably.

Alternatively to this direct-pressure approach, consider the limit of a perfectly rigid shell enclosing a particle of solid electrolyte. The constraint of the shell on the core in this extreme is that of constant volume. If a portion of the particle decays, and hence expands, an internal pressure within the core must be created that compresses the neighboring solid electrolyte (SE) sufficiently as to make the room for the volume expansion associated with the reaction dilation. For the decay of a particle with a

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perfectly rigid shell, the decomposition energy is given in terms of the fraction of pristine SE $\left(x_{S E}\right)$ and decomposed $\mathrm{SE}\left(x_{d}\right)$ by the following equation:

$$
\begin{equation*}
\Delta \phi_{V}\left(\mu_{L i}\right)=x_{S E} \phi_{S E}\left(p, \mu_{L i}\right)+x_{d} \phi_{d}\left(p, \mu_{L i}\right)-\phi_{S E}\left(0, \mu_{L i}\right) \tag{3.4}
\end{equation*}
$$

Solving Equation 3.4 for a given lithium chemical potential is complicated by the fact that the pressure is dependent on the decomposed fraction $\left(p\left(x_{d}\right)\right)$ and is not an experimentally controlled variable. At the onset of decay (e.g. $\lim x_{d} \rightarrow 0$ ), the volumes of both the pristine and decomposed phases are approximated to first order by the Taylor expansion $V_{(d, S E)}(p) \approx V_{(d, S E)}^{0}-V_{(d, S E)}^{0} \beta_{(d, S E)} p$ where $V_{(d, S E)}^{0}$ is the volume of the respective phase at zero pressure and $\beta_{(d, S E)}=-V_{(d, S E)}^{-1} \partial_{p} V_{(d, S E)}$ is the material's compressibility. If the system is isovolumetric, then the volume at a given pressure $\left(x_{d} V_{d}(p)+x_{S E} V_{S E}(p)\right)$ must be equal to the initial volume of the core $\left(V_{\text {core }}=V_{S E}^{0}\right)$. Combining these allows an expression of pressure as a function of decomposed fraction as shown in Equation 3.5.

$$
\begin{gather*}
x_{d} V_{d}(p)+x_{S E} V_{S E}(p)=V_{S E}^{0} \\
x_{d} V_{d}^{0}\left(1-\beta_{d} p\right)+x_{S E} V_{S E}^{0}\left(1-\beta_{S E} p\right)=V_{S E}^{0} \\
p=\frac{x_{d}\left(V_{d}^{0}-V_{S E}^{0}\right)}{x_{d} V_{d}^{0} \beta_{d}+x_{S E} V_{S E}^{0} \beta_{S E}} \\
\rightarrow p \approx \frac{x_{d} \epsilon_{R X N}}{\beta_{S E}} \tag{3.5}
\end{gather*}
$$

Where the final equality applied the limit $x_{d} \rightarrow 0$. When combined with Equation

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3.4 , this leads to an expression of the volume constrained decay energy, $\Delta \phi_{V}$, in terms of the constant pressure decay, $\Delta \phi\left(p, \mu_{L i}\right)$, at the onset of decay (Equation 3.6). Ultimately, this allows evaluation of the volume restricted decay energy, which cannot be calculated directly from DFT.

$$
\begin{equation*}
\Delta \phi_{V}\left(\mu_{L i}\right) \approx \frac{p \beta_{S E}}{\epsilon_{R X N}} \Delta \phi\left(p, \mu_{L i}\right)+\phi_{S E}\left(p, \mu_{L i}\right)-\phi_{S E}\left(0, \mu_{L i}\right) \tag{3.6}
\end{equation*}
$$

For this decay to be energetically favorable (e.g. for Equation 3.6 to be negative), the constant pressure decay energy must exceed the work done to compress the remaining solid electrolyte.

$$
\begin{equation*}
\left|\Delta \phi\left(p, \mu_{L i}\right)\right|>\frac{\epsilon_{R X N}}{p \beta_{S E}}\left(\phi_{S E}\left(p, \mu_{L i}\right)-\phi_{S E}\left(0, \mu_{L i}\right)\right) \tag{3.7}
\end{equation*}
$$

The conclusion of this inequality is that in order for solid electrolyte to decompose inside of a perfectly rigid shell, the decomposition energy must be sufficiently high as to be able to compress the remaining solid electrolyte enough to accommodate the larger volume of the decomposed products.

To further generalize this conclusion derived for a perfectly rigid shell to an elastic shell, the decomposition inequality is modified to be:

$$
\begin{equation*}
\left|\Delta \phi\left(p, \mu_{L i}\right)\right|>\frac{\epsilon_{R X N}}{p\left(\beta_{S E}+\beta_{\text {shell }}\right)}\left(\phi_{S E}\left(p, \mu_{L i}\right)-\phi_{S E}\left(0, \mu_{L i}\right)\right) \tag{3.8}
\end{equation*}
$$

Where $\beta_{\text {shell }}$ is the effective compressibility of the shell as defined in Equation 3.2 and the core volume is now allowed to vary with pressure as $V_{\text {core }}(p) \approx V_{S E}^{0}+V_{S E}^{0} \beta_{\text {shell }} p$. The decay conditions for both isobaric (no shell) and isovolumetric (ideal shell) can

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be recovered by taking the shell compressibility ( $\beta_{\text {shell }}$ ) to infinity or zero, respectively. Finally, Equations 3.7 and 3.8 can be reduced in the limit of $p=0 \rightarrow \delta p$ (i.e. at the onset of decay). Defining the effective bulk modulus $K_{\text {eff }}=\left(\beta_{S E}+\beta_{\text {shell }}\right)^{-1}$ and noting that $V=\partial_{p} \phi\left(p, \mu_{L i}\right)$, the inequality of Equations 3.7, 3.8 becomes a familiar stress-strain type relation:

$$
\begin{equation*}
\frac{\left|\Delta \phi\left(p, \mu_{L i}\right)\right|}{V}>K_{e f f} \epsilon_{R X N} \tag{3.9}
\end{equation*}
$$

Our DFT simulations, in conjunction with grand canonical post-processing and further analysis based on the above formalism (see Methods), show that while LSPS decay remains largely unchanged with doping and initial composition in a zero- pressure isobaric environment, which shows a narrow voltage stability window similar to LGPS at zero pressure (Figure 6a), the application of a shell with certain rigidity in our case can greatly improve the stability window (Figure 6b). Additionally, Equation 3.1 may in fact underestimate the reaction dilation as the decay converts a single-crystal solid electrolyte into a polycrystalline mixture. In the latter case, perfect packing is unlikely. If the decay products would have a packing efficiency of $\eta$, then the reaction dilation would be given by Equation 3.10. Figure 6c illustrates the significant potential impact of such a packing efficiency to further open up the voltage stability window, suggesting the additional importance of different decay processes within the rigid shell picture.

$$
\begin{equation*}
\epsilon_{R X N}=\frac{V_{d} \eta^{-1}-V_{S E}}{V_{S E}} \tag{3.10}
\end{equation*}
$$

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Figure 3.6: Computational simulation results showing the effects of doping and shell compressibility on stability windows of LSPS-based solid electrolytes. (a) Zeropressure decomposition energy for $L i_{10} S i P_{2} S_{12}$ (LSPS), $L i_{10} S i_{1.5} P_{1.5} S_{11.5} C l_{0.5}$ (LSPSC), and $L i_{10} S i_{1.5} P_{1.5} S_{12}$ (LS+PS). (b) Stability windows for LSPS, LSPSC, and LS + PS as a function of shell effective compressibility. The zero limit of $\beta_{\text {shell }}$ (left extreme of x-axis) corresponds to a perfectly rigid shell (isovolumetric decay). $\beta_{\text {shell }} \gg \beta_{\text {core }}$ (right extreme of x -axis) corresponds to no shell (isobaric decay). (c) Stability window for LSPS at different decay packing fractions. Stability was only considered within the range of $0-5 \mathrm{~V}$ vs. lithium.

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### 3.3 Discussion

Experiment and computation have been shown here to agree that while solid electrolytes are plagued by narrow stability windows, microstructured materials, namely core-shell structures in this particular case, show significantly improved performance. These results suggest a new direction for solid-state Li battery development and that for such core-shell microstructures, three overarching conditions are needed to significantly increase the stability of solid electrolytes.

1. The effective compressibility of the shell must be low. The ideal shell structure would be completely rigid $\left(\beta_{\text {shell }}=0\right)$, which forces any decomposition to exert work on the neighboring solid electrolytes, leading to an increased threshold for the decomposition energy.
2. The compressibility of the pristine sulfide must be low. By making the pristine solid electrolyte more rigid, it requires more work to be locally compressed.
3. reaction dilations should be maximized. $\epsilon_{R X N}$ indicates how much of the neighboring solid electrolytes must be compressed for decomposition to occur, multiplying the effects of condition 2.

Conditions 2 and 3 are intrinsic to the solid electrolytes, whereas condition 1 is dependent on the microstructure and composition of the shell. Supplementary Figure 3.S15 shows biaxial modulus data for all Li-Si-P-S materials available within the Materials Project database[79]. The biaxial moduli were obtained via the KVRH approximation. The overall trends show that, within this family of compounds, materials

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tend to increase in modulus with increasing Si content. Conversely, these materials tend to become lower in modulus (higher in compressibility) as either the S or P content is increased.

These results suggest that excess Si would be beneficial to the stability of sulfide solid electrolyte. Given that Si and P sit in the same site, this excess Si would have to come at the expense of P . In fact, this is in line with the best known performing $L i_{10} S i P_{2} S_{12}$ derivative, $L i_{9.54} S i_{1.74} P_{1.44} S_{11.7} C l_{0.3}$, which was successfully cycled over 500 times.[14] Note that the Si:P ratio is over twice that of typical LSPS.

It is also interesting to note that if we simply consider the monovalent defects $\left(V_{L i}^{1-}, S i_{P}^{1-}, P_{S} i^{1+}, C l_{S}^{1+}\right)$, the general doping structure is $L i_{10-x} S i_{1-x+y} P_{2+x-y} S_{12-y} C l_{y}$. For the doping structure to have $\left[V_{L i}\right]=0.46,\left[C l_{S}\right]=0.3$, and for everything to remain in its ideal valence state, the $\mathrm{Si}, \mathrm{P}$, and S concentration would be fixed at $L i_{9.54} S i_{0.84} P_{2.16} S_{11.7} C l_{0.3}$. This composition likely has an increased rigidity compared to $L i_{10} \mathrm{SiP}_{2} S_{12}$ given the excess Si . Forcing even more Si (such as the compound we synthesized) could lead to an amorphous shell phase with Si rich, consistent with our STEM-EDS measurement.

Given the high modulus of amorphous Si (biaxial modulus $140 \mathrm{GPa}[76,77]$ ), it is likely that such Si distribution in the core-shell LSPS would lead to both a core of decreased compressibility and a relatively rigid shell. A spherical core-shell model with the morphology and composition consistent with our TEM observation corresponds to a $\beta_{\text {shell }}$ value of around $3 \cdot 10^{-2} G P a^{-1}$, giving an estimated voltage stability window of 0.7-3.1 V based on Figure 3.6b. The estimation here used a shell modulus of around 75 GPa, which is obtained based on an unusually high Si composition of around 40 at\% as

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characterized by our STEM-EDX (Figure 3.2) and using the modulus vs. Si composition relationship in Supplementary Figure 3.S15. In comparison the Si composition in the core of our crystalline LSPS is only less than $10 \mathrm{at} \%$. It should also be noted that even if the shell modulus is comparable to the core ( $20-30 \mathrm{GPa}$ ), the stability window of a core-shell-structured solid electrolyte is still significantly larger than that without shell at an estimated $\beta_{\text {shell }}$ value of around $10^{-1} G P a^{-1}$ based on Figure 3.6b.

The decreased compressibility of the core and a rigid shell here in our core-shell LSPS thus would satisfy both conditions 1 and 2 for improved stability windows of sulfide solid electrolyte. Lastly, given that Si has a larger atomic radius than P , it would not be surprising that Si-rich LSPS would have an increased reaction dilation. To confirm the latter, we compared the zero pressure isobaric decompositions for $\mathrm{Li}_{10} \mathrm{SiP}_{2} \mathrm{~S}_{12}$ and $L i_{10} S i_{1.5} P_{1.5} S_{12}$. The result was that in both the low $(<1 V)$ and high $(>4 V)$ chemical potential ranges, the Si-rich material had a 2.3-3.6\% higher reaction dilation than the non-Si-rich material.

Our simulation of the LGPS system show that its voltage stability can also be improved by the same mechanism, suggesting the universality of the theory for the sulfide solid electrolytes. Note that it is also possible that the passivation layer mentioned in the previous literatures $[25,80]$ actually serves as a similar core-shell microstructure generated by the reaction on the surface of solid electrolyte. However, we want to emphasize that our mechanism of solid electrolyte stabilization is beyond the conventional passivation layer argument. In order to be useful in a lithium conductive system, any passivation layer must itself be lithium conductive. Given that the lithium stability window of bulk solid electrolyte is determined by the lithium chemical potential, the adoption of a lithium potential conserving passivation layer may have minimal impact on the chemical

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tendency towards decay. A quantitative description of how a passivation layer could directly lead to improved stability remains undemonstrated. However, if the passivation layer is made to be rigid, even if only comparable to the core ( $20-30 \mathrm{GPa}$ ), recovering the core-shell structure discussed herein, then the passivation layer could both be lithium conductive and inhibit lithium reactions via mechanical, rather than chemical, stabilization.

It is worth noting that in a constant pressure system, the strain energy is simply proportional to the volume expansion. However, in a quasi-constant volume system as represented by our core-shell structure before any actual decomposition, an infinitesimal change in decomposition fraction $\left(\delta x_{d}\right)$ requires an infinitesimal increase in strain energy ( $\delta U_{\text {strain }}$ ), given by both an increase in pressure and volume. Within the voltage stability window predicted by Figure 3.6, the relation of $\delta U_{\text {strain }} \geq|\delta \Delta G|$ is always satisfied, giving no actual decomposition, internal pressure nor particle swelling at 0 GPa external pressure.

In closing we wish to highlight that what we have shown here is that the pressurization accompanying decomposition within a core-shell morphology can require an amount of work that cannot be provided by chemical decomposition within the expanded voltage stability range. It is also entirely possible that there are additional energetic factors that result from this mechanism, which could explain our high voltage stability vs. lithium. For example, lithium conductivity and lithium configurational entropy are directly related[81]. Given that the lattice parameter constriction is known to drastically reduce conductivity[26], it is possible that pressurization due to decomposition leads to lithium ordering in the non-decomposed fraction of the particle. This lithium ordering would of course oppose the reaction with a magnitude given by the change in

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lithium configurational entropy. Similar to how the work associated with pressurization inhibits any decomposition in which the work is greater than the chemical reaction energy, the addition of entropic effects would inhibit any decomposition when the decay energy is not sufficient to overcome both the work and the entropy decreases. This is also possibly extended to other terms that are dependent on pressure (i.e., defects, surface interactions, kinetics).

Practically, we expect a macroscopic sulfide solid electrolyte material to contain particles with a distribution of $\beta_{\text {shell }}$. It should be noted that the shell serves as a pressure vessel for the sulfide solid electrolyte core. As such, the effective compressibility of shell is a complicated function of the shell mechanical properties, thickness, curvature, core volume, etc. In general, however, shell structures with high moduli, such as amorphous silicon, are preferred for enhanced voltage stabilities. Considering the different lithium-ion conductivities in the microstructures, if the shell conductivity is lower than the core, a thin rigid shell is thus preferred, in addition to the criteria for the core of low compressibility and high reaction dilation, for the design of next-generation sulfide solid electrolytes. As a final note, we wish to highlight that while this work has focused on microstructure volume constraints, other methods could be used to take advantage of this theoretical understanding. For example, many works have shown that sulfide electrolytes show strong performance when used in battery cells that are designed for the application of pressure. [82, 83]

### 3.4 Methods

Synthesis. The starting materials used for the synthesis of $L i_{9.54} S i_{1.74} P_{1.44} S_{11.7} C l_{0.3}$ solid electrolyte were $L i_{2} S$ ( $99.9 \%$ purity, Alfa Aesar), $P_{2} S_{5}$ ( $99 \%$ purity, Sigma Aldrich), $\mathrm{SiS}_{2}$ ( $99 \%$ purity, American Elements), and LiCl ( $99 \%$ purity, Alfa Aesar). All of the reagents were weighed in the appropriate molar ratio and then placed into a $\mathrm{ZrO}_{2}$ ball-mill jar containing $\mathrm{ZrO}_{2}$ milling balls. All of the procedures were conducted under an argon atmosphere inside a glove box. The mixture was then mechanically milled using a planetary ball milling facility for 40 h . Following the ball milling procedure, the mixture was sealed into glass tubes and then heated at 400, 450, 460, 470, 480, 490, and $500^{\circ} \mathrm{C}$, respectively, for 8 h , followed by a slow cooling procedure back to room temperature.

Electrochemistry Characterization. The cyclic voltammograms (CV) of $\mathrm{Li} /$ glass fiber/LSPS $+\mathrm{C} / \mathrm{Au}$ cells were measured between 0.1 and 2 V for low-voltage range and 1-5 V for high-voltage range at a scan rate of $0.1 \mathrm{mV} \mathrm{s}^{-1}$ on a Solartron electrochemical potentiostat (1470E), using lithium as reference electrode. The obtained current densities of CV tests for different LSPS were obtained by normalizing to 1 g of LSPS with the same area. For battery performance test, the composite cathode was prepared by mixing $\mathrm{Li}_{4} \mathrm{Ti}_{5} \mathrm{O}_{12}$ (LTO), LSPS, Polytetrafluoroethylene (PTFE) and carbon black with a weight ratio of $60: 30: 5: 5$. This mixture was then rolled into a thin film. LSPS thin film was prepared by mixing LSPS and PTFE with a weight ratio of $95: 5$. The Swagelok battery cell of cathode film/LSPS film/glass fiber/Li was then assembled in an argon-filled glove box. The piece of glass fiber separator was inserted between LSPS film and Li metal foil to avoid interfacial reaction between

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them in order to best reflect the intrinsic stability difference among various core-shell LSPS materials. One drop of $1 \mathrm{M} \mathrm{LiPF} F_{6}$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) solution (1:1) was carefully applied onto the glass fiber to allow the lithium-ion conduction through the separator. The galvanostatic battery cycling test was performed on an ArbinBT2000 work station at room temperature. The specific capacity was calculated based on the amount of LTO ( $60 \mathrm{wt} \%$ ) in the cathode film. For impedance measurement, C-LSPS/LSPS/C-LSPS cell was fabricated by sandwiching and cold pressing (applied force 0.6 ton, sample cross area $=0.316 \mathrm{~cm}^{2}$ ) an electrolyte powder layer with two carbon black-electrolyte powder layers. $50 \mathrm{wt} \%$ carbon black was mixed with electrolyte to form the conductive layer, with the purpose of decreasing the interface resistance. The measurement was performed in a Solartron electrochemical potentiostat (1470E +1455 FRA). The frequency range of the measurement was from 100 Hz to 1 MHz and the amplitude was 10 mV . For all-solid-state batteries, lithium anode was coated with a protection layer in the following steps: Firstly, a solution was prepared by mixing $L i_{2} S_{6}(0.5 \mathrm{M})$ and $P_{2} S_{5}(1 \mathrm{M})$ in the mixture solvent of DME and DOL (1:1, v/v) in the glove box for 1 h . Then lithium foil ( $5 / 16$ inch in diameter) was soaked into the prepared solution for 2 h . The soaked lithium foils were assembled into $\mathrm{Li} / \mathrm{Li}$ symmetric battery for five cycles of charge-discharge, with 1 M LiTFSI, 0.025 M $L i_{2} S_{6}$, and $0.05 \mathrm{M} P_{2} S_{5}$ in DME and DOL $(1: 1, \mathrm{v} / \mathrm{v})$. Finally, the lithium foils after the above process were taken out of the symmetric battery for use as the anode (hereafter LPS-Li). The cathode of the all-solid-state cell is a mixture of LTO + LSPS + carbon black powder (75:20:5), and solid electrolyte is pure LGPS powder. 0.5 mg of cathode mixture powder and 80 mg of solid electrolyte powder were pressed together to form a disc-shape pellet, which is pressed onto a freshly prepared LPS-Li in a Swagelock Cell to

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form an all-solid-state battery. The same battery configuration was used for solid-state CV test with $0.1 \mathrm{mV} \mathrm{s}^{-1}$ sweeping rate.
(Micro)structural analysis. XRD data were obtained using a Rigaku Miniflex 6 G with a Cu target X-ray source (wavelength $=1.54056 \AA$ ). The various LSPS powders were placed onto standard XRD sample holders and sealed with Kapton film and vacuum grease under an argon atmosphere in a glove box. Structural parameters were refined in the Topas software by using Rietveld refinement technique. TEM samples were prepared by dropping the as-synthesized powder directly to the TEM copper grid, sealed inside the airtight bottles in the glove box and opened immediately before loading into the TEM column with an air exposure less than 30 s . The Gatan vacuum transfer TEM sample holder was used to double check, which confirms the same results. JOEL 2010F was used for TEM and STEM EDS characterization on multiple particles for each LSPS sample, and the average composition values of the obtained data were statistically analyzed.

Density functional theory calculations. In order to allow comparability with the Material Project crystal database, all DFT calculations were performed using the Material Project criteria.[79] All calculations were performed in VASP using the recommended Projector Augmented Wave (PAW) pseudopotentials. An energy cutoff of 520 eV with k-point mesh of 1000 per atom was used. Compressibility values were found by discretely evaluating the average compressibility of the material between 0 and 1 GPa. Enthalpies were calculated at various pressures by applying external stresses to the stress tensor during relaxation and self-consistent field calculations.

Pre/post-process calculations. The Python Materials Genomics (pymatgen) library was used for pre/post-processing of high-throughput calculations.[84] In

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particular, the phase diagram modules were used to calculate the convex hull for each elemental system. All possible oxidation (lithium extraction) and reduction (lithium insertion) reactions were accounted for by modifying the free energy as governed by Equation 3.3.[70] For isobaric calculations (Supplementary Figures 3.S13 and 14), H(p) is calculated at every pressure for both LGPS and decomposition products. Then the convex hull is determined using Equation 3.3. In isovolumetric calculations, we are interested in the onset of decay, which is equivalent to there being zero radial pressure $\left(\lim x_{d} \rightarrow 0: p=0\right)$. Pymatgen was used in conjunction with the Materials Project API[85] for accessing the Materials Project crystal databases Materials Explorer[86]. Biaxial moduli were calculated from the Poissons ratio and $K_{V R H}$ approximation of the bulk modulus.

## Chapter 4

## Strain Stabilized Ceramic-Sulfides

## Authorship

This thesis chapter covers material that originally appeared in the literature as "Strain-Stabilized Ceramic-Sulfide Electrolytes" by William Fitzhugh, Fan Wu, Luhan Ye, Haoqing Su and Xin Li and published as Small, 1901470 (2019).


#### Abstract

Ceramic-sulfide solid-electrolytes are a promising material system for enabling solid-state batteries. However, one challenge that remains is the discrepancy in the reported electrochemical stability. Recent work has suggested that these conflicting reports may be due to the sensitivity of ceramic-sulfides to mechanically-induced stability. Small changes in ceramic-sulfide microstructure, for example, have been shown to cause


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substantial differences in the electrochemical stability. In this work, we construct a rigorous theoretical framework to enable a strict simulation of such mechanically induced stability for a generalized constraint mechanism. We show that the susceptibility for voltage-widening in ceramic-sulfides can be significantly influenced by the choice of different decay morphology models. This results in a less intrusive microstructure requirement or, equivalently, wider voltage stability for a given microstructure in practice. We show that this improved stability stems from the tendency of sulfides to decay via inclusions rather than homogeneously. We experimentally confirm this predicted decay morphology and demonstrate $L i_{10} G e P_{2} S_{12}$ stabilized by a thin amorphous shell, which prior models predict to be too thin for stabilization. We also discuss the generality of this framework and its application to stabilization methods beyond microstructure, such as on the battery cell level. Lastly, the theoretical framework is shown to also explain the observations of lithium dendrites forming within the bulk of ceramic-sulfide layers.

### 4.1 Introduction

Solid-electrolytes, and the resulting solid-state batteries, are one of the most pursued directions in the battery field.[1, 2, 87] The strong interest in solid-state batteries stems principally from the significantly improved safety, higher energy densities enabled by new electrode materials, and better low-temperature performance as compared to conventional liquid-based batteries. Non-flammable solid-electrolytes are expected to improve the safety over flammable commercial liquid-electrolytes. Moreover, solidelectrolytes are compatible with several high-energy-density electrode materials that cannot be implemented in liquid-electrolyte-based configurations.[8-11] Solid-electrolytes

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also maintain better low-temperature ionic conductivity than liquid-electrolytes.[12-14] These advantages make solid-state batteries the most promising technology for the next generation electric-vehicle market.

Among the families of solid-electrolytes, sulfides retain the highest ionic conductivity.[14, 24, 27, 29, 88] Sulfide glass solid-electrolytes[31, 32] and glass-ceramic solid-electrolytes[34-36] have demonstrated ionic conductivities on the order of $0.1-1 \mathrm{mS} \mathrm{cm}^{-1}$ and above $1 \mathrm{mS} \mathrm{cm}{ }^{-1}$, respectively. The ceramic-sulfide electrolytes, most notably $L i_{10} G e P_{2} S_{12}$ (LGPS) and $\mathrm{Li}_{10} \mathrm{SiP}_{2} S_{12}$ (LSPS), are particularly promising as they maintain exceptionally high ionic conductivities. LGPS was one of the first solid-electrolytes to reach ionic conductivities comparable with liquid-electrolytes[37] at $12 \mathrm{mS} \mathrm{cm}{ }^{-1}$, only to then be displaced by LSPS[14] which achieved the highest reported ionic conductivity of $25 \mathrm{mS} \mathrm{cm}^{-1}$. However, despite these superior ionic conductivities, the ceramic-sulfide family has been plagued by reports of narrow electrochemical stability windows $[25,29]$ and interfacial reactions with common electrode materials[8, 28, 29].

Moreover, the reported electrochemical stability windows of ceramic-sulfides suffer from substantial inconsistencies. Several works, both computational and experimental, have shown that the ceramic-sulfides are only stable in the narrow voltage window on the order of $1.7-2.1 \mathrm{~V}$ vs lithium [24, 25, 29], which we agree is the correct general thermodynamic prediction. Many others, however, have experimentally found that the upper voltage limit can reach in excess of 4-6 V vs lithium.[14, 37, 89, 90] A consolidated understanding of these findings is needed in order to establish any design principles for practical ceramic-sulfide batteries.

In this work, we develop a generalized thermodynamic theory that unifies these

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disparate findings and, hence, provides the unique design principle through mechanoelectrochemical effect for ceramic-sulfide based solid-state batteries. Expanding upon our previous work[68], in which core-shell morphologies were used to widen the voltage window of LSPS, we derive a generalized strain stabilization model that indicates at which voltages strain-induced stabilization can lead to metastability of the ceramic-sulfide phases. A mean-field solution to our generalized strain model recovers our previous model and is shown to be a lower limit on the strain induced stability. The second solution we explore, a nucleated or inclusion decay, is shown to provide a greater capability for stabilization. Note that our current and previous understanding forms a general theoretical framework for the design of ceramic electrolyte with widened voltage stability, which is not limited to any particular design strategy, such as the core-shell morphology of LGPS particle demonstrated in experiment in this work. Other design strategies, on material or battery cell level, guided by the mechano-electrochemical effect induced metastability can also in principle stabilize the solid-state battery system.

Four points of experimental validation of our theoretical framework are provided. First, we use electron microscopy to visualize LGPS after partial decay, confirming that the post-decay morphology is in fact the predicted inclusion morphology. We then show that LGPS can be stabilized by the application of a thin-shell (thickness approximately 0.1 times the core radius) as compared to the thick-shell of ref[68] (thickness approximately equal to core radius). The ability of the thin-shell to stabilize at a level comparable to the prior thick-shell, as predicted by the inclusion model, indicates that a perfect thin shell can effectively work for stabilization and, hence, a thick shell is not necessary. Solid-state batteries with both an $L i_{4} T i_{5} O_{12}$ (LTO) cathode versus a lithium metal anode and with an $\mathrm{LiCoO}_{2}(\mathrm{LCO})$ cathode versus a LTO anode

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are demonstrated to have strong cyclability using constrained LGPS. Lastly, we show that our model correctly predicts that upon oxidation, ceramic-sulfides will form lithium metal dendrites locally, rather than deposit lithium ions to the anode.[91, 92]

### 4.2 Theory

The Physical Picture. The mechanism by which strain can expand the LGPS stability window is depicted in Figure 4.1. Consider the decomposition of LGPS to some arbitrary set of decomposed products, denoted $D(L G P S \rightarrow D)$, at standard temperature and pressure. The Gibbs energy of the system as a function of the fraction of LGPS that has decomposed $\left(x_{D}\right)$ is given by the dashed orange line in Figure 1 and analytically in Equation 4.1.

$$
\begin{equation*}
G^{0}\left(x_{D}\right)=\left(1-x_{D}\right) G_{L G P S}+x_{D} G_{D} \tag{4.1}
\end{equation*}
$$

The lowest Gibbs energy state is $x_{D}=1$ (all decomposed) and the initial state is $x_{D}=0$ (pristine LGPS). Accordingly, the reaction energy is $\Delta G^{0}=G^{0}(1)-G^{0}(0)=$ $G_{D}-G_{L G P S}$. This system is inherently unstable. That is, $\partial_{x_{D}} G^{0}$ is negative for all values of $x_{D}$. Hence, for any initial value of $x_{D}$, the system will move to decrease $G^{0}$ by increasing $x_{D}$, ultimately ending at the final state $x_{D}=1$.

Next, consider the application of a mechanical system that constrains the LGPS particle. Given that LGPS tends to expand during decay[68], any mechanical constraint will require the decomposition to induce a strain in the surrounding neighborhood. Such a constraining system could be either materials-level (i.e. a core-shell microstructure) or

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systems-level (i.e. a pressurized battery cell) or a combination of the two. Ultimately, this mechanical system can only induce a finite strain before failing. The maximum energy the system can withstand is denoted $G_{\text {fracture }}$.

Prior to the actual failing of the constraining mechanism, any decomposition of the LGPS must lead to an increase in strain energy. The solid line in Figure 4.1 plots the constrained Gibbs energy ( $\mathrm{G}^{\prime}$ ) in terms of the unconstrained Gibbs $\left(G^{0}\right)$ and the constraint induced strain term $\left(G_{\text {strain }}\right)$. The gray highlighted curve indicates the decomposition pathway of the LGPS.

1. The particle begins as pristine LGPS $\left(x_{D}=0\right)$ with an unfractured constraint mechanism.
2. As the particle begins to decompose $\left(x_{D}: 0 \rightarrow \delta x_{D}\right)$, the constraint mechanism requires an increase in $G_{s t r a i n}$. The strain term is assumed to be a function of $x_{D}$ that goes to zero as $x_{D}$ goes to zero.
3. Once the Gibbs energy of the constrained system $\left(G^{\prime}\left(x_{D}\right)\right)$ exceeds the Gibbs energy of the fractured system $\left(G^{0}\left(x_{D}\right)+G_{\text {fracture }}\right)$, the constraining mechanism will fail. This occurs at the fracture point $x_{D}=x_{f}$
4. Once $x_{D}>x_{f}$, the system will proceed to completely decompose as $\partial_{x_{D}}\left(G^{0}+\right.$ $\left.G_{\text {fracture }}\right)<0$

It is worth emphasizing that if the constraint induced strain term $\left(G_{\text {strain }}\right)$ is sufficiently steep, the slope of the total Gibbs at $x_{D}<x_{f}$ will be positive (as depicted in Figure 4.1). In this case, the LGPS will be metastable about the pristine state ( $x_{D}=0$ ). In this work, we focus on the quantification of constraining systems such that $\partial_{x_{D}} G^{\prime}>0$

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at $x_{D} \approx 0$, allowing metastable ceramic sulfide electrolytes to exist in a widened voltage range. Note that this picture is universal, which can be realized by various strategies in applications, as long as such local energy minimum is effectively created.

The Gibbs Differential. As discussed in our previous work[68], the presence of $G_{\text {strain }}$ as a function of $x_{D}$ stems from the nature of LGPS to expand upon decomposition. Depending on the set of decomposed products, as determined by the applied voltage, this volume expansion can well exceed $20 \%$. As such, the process of LGPS decomposition is one that can include significant stress-free strain - that is, strain that is the result of decomposition and not an applied stress. Anticipating the consideration of inclusions, we adopt the notation used by Eshelby[93].

The stress and strain tensors are separated into the compression and distortion terms via the use of deviatoric tensors as defined in Equation 4.2. Using Einstein summation notation, the pressure is generalized in terms of the stress matrix $p \equiv-1 / 3 \operatorname{tr}(\sigma)=-\sigma_{i i} / 3$ and volume dilation is introduced in terms of the reference [undeformed] state $\left(V^{0}\right)$ as $\epsilon \equiv\left(V-V^{0}\right) / V^{0}$.

$$
\begin{align*}
\sigma_{i j}^{d} & \equiv \sigma_{i j}+p \delta_{i j}  \tag{4.2}\\
\epsilon_{i j}^{d} & \equiv \epsilon_{i j}-\epsilon / 3 \delta_{i j}
\end{align*}
$$

Using these definitions, the differential work can be separated into one term that only includes compression and one term that only includes deformation.

$$
\begin{equation*}
\delta W=V^{0} \sigma_{i j} \delta \epsilon_{i j}=V^{0} \sigma_{i j}^{d} \delta \epsilon_{i j}^{d}-p \delta V \tag{4.3}
\end{equation*}
$$

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Thus, for a homogenous volume of the material, the energy can be expressed by Equation 4.4. For non-homogenous materials, Equation 4.4 is integrated over all homogenous subsystems.

$$
\begin{equation*}
\delta E=T \delta S+\mu_{\alpha} \delta N_{\alpha}+\sigma_{i j}^{d} \delta\left(V^{0} \epsilon_{i j}^{d}\right)-p \delta V \tag{4.4}
\end{equation*}
$$

Transforming to the Gibbs energy (Equation 4.5) yields the differential Gibbs form (Equation 4.6)

$$
\begin{equation*}
G=E-T S+p V-V^{0} \sigma_{i j}^{d} \epsilon_{i j}^{d}=\mu_{\alpha} N_{\alpha} \tag{4.5}
\end{equation*}
$$

$$
\begin{equation*}
\delta G=-S \delta T+\mu_{\alpha} \delta N_{\alpha}+V \delta p-V^{0} \epsilon_{i j}^{d} \delta \sigma_{i j}^{d} \tag{4.6}
\end{equation*}
$$

At constant temperature, Equation 4.7 gives the differential form of $G^{\prime}\left(x_{D}\right)$ in terms of the chemical $\left(\delta G^{0}=\mu_{\alpha} \delta N_{\alpha}\right)$ and the strain components $\left(\delta G_{s t r a i n}=V \delta p-V^{0} \epsilon_{i j}^{d} \delta \sigma_{i j}^{d}\right)$.

$$
\begin{gather*}
\partial_{x_{D}} G^{\prime}=\mu_{\alpha} \partial_{x_{D}} N_{\alpha}+V \partial_{x_{D}} p-V^{0} \epsilon_{i j}^{d} \partial_{x_{D}} \sigma_{i j}^{d}=\partial_{x_{D}} G^{0}+\partial_{x_{D}} G_{\text {strain }} \\
\partial_{x_{D}} G^{0}=G_{D}-G_{L G P S} \rightarrow \partial_{x_{D}} G^{\prime}=G_{D}-G_{L G P S}+\partial_{x_{D}} G_{\text {strain }} \tag{4.7}
\end{gather*}
$$

Accordingly, the case for metastability about the pristine LGPS case $\left(\partial_{x_{D}} G^{\prime}\left(x_{D}=\right.\right.$ $0)>0)$ is satisfied at any voltage where the strain term is sufficiently steep $\partial_{x_{D}} G_{\text {strain }}\left(x_{D}=0\right)>G_{L G P S}-G_{D}$.

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In the following discussion we consider two limiting cases for $G_{s t r a i n}$ as a function of $x_{D}$. The first case is that of an LGPS particle that decomposes homogenously and is a mean field approximation. The fraction of decomposed LGPS is assumed to be uniform throughout the particle $\left(x_{D}(\vec{r})=x_{D}\right.$ for all $\left.\vec{r}\right)$. The second limiting case is that of spherically symmetric inclusions, where LGPS is completely decomposed within a spherical region of radius $R_{i}\left(x_{D}(\vec{r})=1: r \leq R_{i}\right)$ and pristine outside this region $\left(x_{D}(\vec{r})=0: r>R_{i}\right)$. As is shown below, the homogenous case yields a lower value for $\partial_{x_{D}} G_{\text {strain }}$, whereas the inclusion model shows how this value could, in practice, be much higher. In both cases, we will use the simplified model that both the LGPS and the decay products are isotropic with moduli values given by the polycrystalline averages.

### 4.2.1 Hydrostatic Limit/Mean Field Theory

The local stress $\sigma(\vec{r})$ experienced by a subsection of an LGPS particle is directly a function of the decomposition profile $x_{D}(\vec{r})$ as well as the mechanical properties of the particle and, if applied, the mechanically constraining system. In the homogenous approximation, the local stress is taken to be hydrostatic throughout the particle $\left(\sigma_{i j}(\vec{r})=-p \delta_{i j}\right)$. In the mean field approximation, the same is said for the decomposed fraction $\left(x_{D}(\vec{r})=x_{D}\right)$. Assuming that changes in the stress experienced within the bulk of the solid-electrolyte $(\delta \sigma(\vec{r}))$ are the result of changes in the local decomposition profile $\left(\delta x_{D}\left(\vec{r}^{\prime}\right)\right.$ where $|\vec{r}-\vec{r}| \leq R_{\text {local }}$ for some local length scale $\left.R_{\text {local }}\right)$, the mean field approximation implies a homogeneous stress. That is, if the decomposition profile is identical everywhere within the bulk, then the stress due to that decomposition profile should also be identical everywhere within the bulk. Thus, these two approximations are

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equivalent in the bulk of the solid-electrolyte.

We restrict our focus to the limit as $x_{D} \rightarrow 0$ to evaluate the metastability of LGPS about the pristine state. If $\partial_{x_{D}} G^{\prime}\left(x_{D}=0\right)>0$, then the particle is known to be at least metastable with total stability being determined by the magnitude of $G_{\text {fracture }}$. The relationship between the pressure and decomposed fraction was shown in previous work[68] to be, in the hydrostatic limit, $p\left(x_{D}\right)=x_{D} K_{\text {eff }} \epsilon_{R X N}$, where $K_{\text {eff }}$ is the effective bulk modulus of the system, accounting for both the compressibility of the material and the applied mechanical constraint, and $\epsilon_{R X N}$ is the reaction dilation describing the tendency of LGPS to expand upon decomposition. The reaction dilation is given by the volumes of the decomposed products $\left(V_{D}\right)$ and the pristine LGPS $\left(V_{L G P S}\right)$ as $\epsilon_{R X N}=\left(V_{D}-V_{L G P S}\right) V_{L G P S}^{-1}$. The differential strain Gibbs is solved assuming a homogenous hydrostatic pressure as shown in Equation 4.8.

$$
\begin{gather*}
\partial_{x_{D}} G_{\text {strain }}=V \partial_{x_{D}} p  \tag{4.8}\\
\partial_{x_{D}} G_{\text {strain }}=V \epsilon_{R X N} K_{e f f} \tag{4.9}
\end{gather*}
$$

Combining Equation 4.7 and Equation 4.9 with the metastability condition, it is found that hydrostatic LGPS will be stabilized whenever Equation 4.10 is satisfied.

$$
\begin{equation*}
\epsilon_{R X N} K_{e f f}>\left(G_{L G P S}-G_{D}\right) / V \tag{4.10}
\end{equation*}
$$

Equation 4.10 is solved in Figure 4.2 for the case of a core-shell constriction mechanism with a core composed of LGPS and a shell of an arbitrary rigid material. In

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Figure 4.2a, Equation 4.10 is evaluated for all of the decomposition reactions that are predicted for LGPS in the unconstrained case. The value of the effective bulk modulus is given by $K_{\text {eff }}^{-1}=K_{L G P S}^{-1}+K_{\text {sys }}^{-1}$, where $K_{L G P S}$ is the actual bulk modulus of LGPS and $K_{\text {sys }}$ is the inverse of the constraints effective compressibility $\left(K_{\text {sys }}=\beta_{\text {shell }}^{-1}\right)$.[68] When the system is under isovolumetric conditions, $\beta_{\text {shell }}=0$ and $K_{e f f}=K_{L G P S}$. On the other hand, if the system is isobaric, $\beta_{\text {shell }}=\infty$ and $K_{\text {eff }}=0$. As shown in Figure 4.2a, the isovolumetric condition leads to significant voltage widening.

Figure 4.2b expands upon these results, showing the derivative $\partial_{x_{D}} G^{\prime}$ (Appendix A). In contrast with the method depicted in Figure 4.2a, which focuses on those decomposition reactions known to be problematic in the absence of constraint, Figure 4.2 b finds the set of decomposition products that minimize $\partial_{x_{D}} G^{\prime}$ (i.e. thermodynamic worst case). The effective bulk modulus is swept from 0 GPa (no constraint) to 20 GPa . When LGPS is metastable, the set of decomposed products that minimize $\partial_{x_{D}} G^{\prime}$ is that of no decay (i.e. $L G P S \rightarrow L G P S$ ), in which case $\partial_{x_{D}} G^{\prime}$ is identically 0 . Hence, in practice, the computationally determined value for $\partial_{x_{D}} G^{\prime}$ will never be strictly positive. Instead it will be either negative when the material is unstable or zero when the material is [meta]stable.

### 4.2.2 Spherical Inclusion Limit

The maximally localized decomposition mechanism is that of a spherical inclusion as illustrated in Figure 4.3a. In this model, an LGPS particle of outer radius $R_{o}$ undergoes a decomposition at its center. The decomposed region corresponds to the material that was initially within a radius of $R_{i}$. The new reference state is of higher volume

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than the pristine state as the material has decomposed to a larger volume given by $4 / 3 \pi R_{D}^{3}=4 / 3 \pi R_{i}^{3}\left(1+\epsilon_{R X N}\right)$. The decomposed fraction is no-longer a constant in the particle as it was in the hydrostatic case. Instead, $x_{D}(\vec{r})=1$ for all material that was initially (prior to decomposition) within the region $r<R_{i}$ and $x_{D}(\vec{r})=0$ for all material initially outside this region, $r>R_{i}$. The total decomposed fraction is denoted $\bar{x}_{D}$ and is given by the average value of $x_{D}(\vec{r})$ over all $\vec{r}$.

To fit the decomposed reference state of radius $R_{D}$ into the void of radius $R_{i}$, both the decomposed sphere and the remaining LGPS must become strained as shown in Figures 4.3a.iii and 4.3a.iv. Thus, solving for the stress in terms of the decomposed fraction $x_{D}$ becomes the problem of a thick-walled spherical pressure vessel compressing a solid sphere. The pressure-vessel has reference states of inner and outer radii given by $R_{i}$ and $R_{o}$, and the spherical particle has an undeformed radius of $R_{D}=\left(1+\epsilon_{R X N}\right)^{1 / 3} R_{i}$.

In terms of the displacement vector of the decomposed and pristine materials, $\vec{u}^{D}(\vec{r})$ and $\vec{u}^{P}(\vec{r})$, and the radial stress components, $\sigma_{r r}^{D}(\vec{r})$ and $\sigma_{r r}^{P}(\vec{r})$, the boundary conditions are:

1. Continuity between the decomposed and pristine products: $R_{D}+u^{D}\left(R^{D}\right)=$ $R_{i}+u^{P}\left(R_{i}\right)$. Where vector notation has been dropped to reflect the radial symmetry of the system.
2. Continuity between the radial components of stress for those materials at the interface between the decomposed and pristine products, which is defined as the compressive pressure: $-p^{0} \equiv \sigma_{r r}^{D}\left(R_{D}\right)=\sigma_{r r}^{P}\left(R_{i}\right)$.

For a spherically symmetric stress in an isotropic material, the displacement vector

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is known to be of the form $u(r)=A r+B r^{-2}$ (again, vector notation has been removed to reflect symmetry). The stress induced in an isotropic compressed sphere under condition 2 has an effective pressure $p=p^{0}$ and a zero deviatoric component ( $\sigma^{d}=0$ ). For a thick-walled spherical pressure vessel of isotropic material under condition 2 , and the additional constraint that because $R_{i} \ll R_{o}$ in the $\bar{x}_{D} \rightarrow 0$ limit, the outer surface does not move $\left(u^{P}\left(R_{o}\right)=0\right)$, the compressive pressure is found to be $p=\bar{x}_{D} p^{0}(1+\nu) / 2(1-2 \nu)$ where $\nu$ is the Poissons ratio of the material. For a typical value, $\nu \approx 0.2$, the compressive pressure is $p \approx \bar{x}_{D} p^{0}$.

An increase in the amount of the total decomposed fraction $\left(\bar{x}_{D} \rightarrow \bar{x}_{D}+\delta \bar{x}_{D}\right)$ corresponds to a decomposition of the material initially between $R_{i}$ and $R_{i}+\delta R_{i}$. In the nearly pristine limit $\left(\bar{x}_{D} \approx 0\right)$, the material at this location experiences a change of pressure from $\left.\bar{x}_{D} p^{0}(1+\nu)\right) / 2(1-2 \nu) \approx 0$ to $p^{0}$ as $x_{D}\left(R_{i}\right)$ changes from 0 to 1 . Thus, the pressure derivative is $\partial_{x_{D}} p=p^{0}$ and the metastability condition becomes:

$$
\begin{equation*}
p^{0} \geq\left(G_{D}-G_{L G P S}\right) / V \tag{4.11}
\end{equation*}
$$

Note that the metastability conditions described in Equations 4.10 and 4.11 and the condition of $\partial_{x_{D}} G^{\prime}\left(x_{D}=0\right)>0$, used to generate Figure 4.2, are a general theoretical understanding, which is not limited to any particular realization strategy. However, we will use a core-shell morphology on the electrolyte materials level to demonstrate this idea in the following discussions.

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### 4.2.3 Model Comparison

Solving Equation 4.11 requires an expression for $p^{0}$ as a function of reaction dilation $\left(\epsilon_{R X N}\right)$. For the inclusion decay illustrated in Figure 4.3a, the mechanics leading to $p^{0}$ are equivalent to that of the core-shell structure solved in the hydrostatic case. That is, the inclusion decay consists of a core of decomposed products embedded in a constricting shell of pristine LGPS. In the limit $\bar{x}_{D} \rightarrow 0$, the nucleated site is much smaller than the embedding LGPS, hence the mechanics is that of a shell thickness that trends towards infinity. Figure 4.3 b plots the pressure resulting from such an inclusion decay as well as two hydrostatic core-shell models. The hydrostatic core-shell models are either thin-shell, where the shell thickness $(t)$ is approximately $10 \%$ of the core radius $(r)$, or thick-shell, where the shell thickness is equal to the core radius. As expected, the inclusion decay, with an approximately infinite shell thickness, is seen to have a higher pressure than either of the hydrostatic alternatives.

In short, inclusion decay is, in the $\bar{x}_{D} \rightarrow 0$ limit, equivalent to the case of a hydrostatic core-shell with a shell thickness $(t)$ much larger than the core. Since $R_{o}=R_{i}+t$, this is termed the infinitely thick shell as $R_{i} / R_{o}$ tends to zero. Thus, the inclusion decay is seen to be most susceptible to mechanically induced stability. As will be discussed in following sections, this allows for the use of a much less intrusive microstructure than would be required if the system were to decay hydrostatically.

As discussed is section 4.2.2, for spherically symmetric inclusions, the deviatoric stresses are approximately zero. In practice, however, the materials of interest will not be so perfectly spherical. Nonetheless, for inclusions that are far from the surface of the solid-electrolyte particles, the system is mechanically approximate to a spherical pressure

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vessel with infinitely thick walls. Thus, the impact of non-spherical solid-electrolyte particles on inclusion formation should only be experienced near the surface of the particles. Moreover, for core-shell particles, the inclusions cannot form near the surface of the shell. The impact of non-spherical inclusions (versus non-spherical electrolyte particles) has not yet been studied and represents a potential future topic of study.

### 4.2.4 Passivation Layer Theory and Local Lithium Formation

Electrolytes, either liquid or solid, are likely to react with electrodes when the electrode potential is outside the electrolyte stability window.[74] To address this, it is suggested that electrolytes be chosen such that they form a passivating solid-electrolyte-interface (SEI) that is at least kinetically stable at the electrode potential. Previous works have suggested that such stabilizing passivation layers can be formed for sulfide solid-electrolytes by using an electronically insulating coating layer. In this section, we show that an electronically insulating layer does in fact improve the stability of ceramic-sulfide, conditional that the LGPS already be mechanically constrained. This is due to the electronically insulating layer maximizing the number of retained lithium ions and, hence, maximizing the reaction dilation. This retention of lithium ions predicts that upon oxidation, ceramic-sulfides will form lithium metal dendrites locally, rather than deposit lithium ions to the anode. Such understanding can explain why dendrites form even more readily in solid-state batteries than in conventional liquid-electrolyte cells $[92,94]$ suggesting the importance of the design taking into account the mechano-electronic-electrochemical interactions.

As a reference, Figure 4.4a gives the thermodynamic equilibrium state for the


Figure 4.1: Illustration of the impact of strain on LGPS decomposition, where $x_{D}$ is the fraction of LGPS that has decomposed. The dashed-orange line represents the Gibbs energy $\left(G^{0}\left(x_{D}\right)\right)$ of a binary combination of pristine LGPS and an arbitrary set of decay products $(D)$ when negligible pressure is applied. The solid-green line $\left(G^{\prime}\right)$ shows the Gibbs when a mechanical constraint is applied to the LGPS. Since LGPS tends to expand upon decomposition, the strain Gibbs $\left(G_{\text {strain }}\right)$ increases when such a mechanical constraint is applied. At some fracture point, denoted $x_{f}$, the Gibbs energy of the system exceeds the energy needed to fracture the mechanical constraints (the dashed-blue line). The highlighted gray path is the suggested ground state for a mechanically constrained LGPS system. The region $x_{D}<x_{f}$ is metastable if $\partial_{x_{D}} G^{\prime}>0$


Figure 4.2: Stability calculations for LGPS and LGPSO. (a) Stability window of those reactions that occur in the unconstrained case, perturbed by the application of constraints.
(b) The minimum slope about pristine LGPS for any decomposition products. A value of 0 implies metastability at the given voltage. Increasing $K_{\text {eff }}$ is seen to widen the range of voltages such that material is metastable.


Figure 4.3: (a) Illustration of the nucleated or inclusion decay mechanism. A pristine LGPS particle of radius $R_{o}$ undergoes a decay within a region of radius $R_{i}$ at its center. The decomposed regions radius in the absence of stress is now $R_{D}$, which must be squeezed into the void of $R_{i}$. The final result is a nucleated particle (iv) where the strain is non-zero. (b) The pressure generated for a given reaction dilation in either the hydrostatic (thin and thick-shell) or the inclusion model. The inclusion model shows the highest pressure generation, and hence the most voltage widening.

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Figure 4.4: Voltage $(\phi)$, lithium chemical potential ( $\mu_{L i^{+}}$) and Fermi level $\left(E_{f}\right)$ distributions in various battery configurations. (a) Conventional battery design. (b) Conventional battery with hybrid solid-electrolyte/active material cathode. $\chi_{I}$ gives the interface voltage that forms due to the different lithium ion chemical potentials. (c) Illustration of how insulating layers could lead to variable lithium metal chemical potentials within the cell when both the Li ions and electrons are conserved. (d) Illustration of how the voltage from part (c) would relax given the effective electronic conduction. The charge separation of lithium/lithium-holes induces a voltage $V_{s}$ that changes the electrostatic potential in the SE from the unrelaxed value $\phi_{S E}$ (dark blue line) to some relaxed value $\phi_{S E} \rightarrow \phi_{S E}-V_{s}$ (light blue dashed line). (e) The result of part (d) once the voltage exceeds the intrinsic stability window of the solid-electrolyte. Local lithium is seen to form within the insulated region with an interface voltage $\left(\chi_{I}\right)$ equal to the applied voltage.

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most basic battery half-cell model. A cathode is separated from lithium metal by an electrically insulating and ionically conducting material $(\sigma=0, \kappa \neq 0$ where $\sigma, \kappa$ are the electronic and ionic conductivities, respectively) and a voltage $\phi$ is applied to the cathode relative to the lithium metal. The voltage of the lithium metal is defined to be the zero point. In terms of the number of electrons $(n)$, the number of lithium ions $(N)$, the Fermi level $\left(E_{f}\right)$ and the lithium ion chemical potential $\left(\mu_{L i^{+}}\right)$, the differential Gibbs energy can be written as Equation 12 (superscripts a, c differentiate the anode from the cathode).

$$
\begin{equation*}
\delta G=\mu_{L i^{+}}^{a} \delta N^{a}+\left(\mu_{L i^{+}}^{c}+e \phi\right) \delta N^{c}+E_{f}^{a} \delta n^{a}+\left(E_{f}^{c}-e \phi\right) \delta n^{c} \tag{4.12}
\end{equation*}
$$

Applying conservation $\delta N^{a}=-\delta N^{c}, \delta n^{a}=-\delta n^{c}$ gives the well-known equilibrium conditions:

$$
\begin{align*}
\delta G= & \left(\mu_{L i^{+}}^{c}+e \phi-\mu_{L i^{+}}^{a}\right) \delta N^{c}+\left(E_{f}^{c}-e \phi-E_{f}^{a}\right) \delta n^{c}  \tag{4.13}\\
& \rightarrow \mu_{L i^{+}}^{c}-\mu_{L i^{+}}^{a}=-e \phi=-\left(E_{f}^{c}-E_{f}^{a}\right)
\end{align*}
$$

Or, in other words, the electrochemical potential $(\eta=\mu+z e \phi)$ of both the electrons and the lithium ions must be constant everywhere within the cell. As a result, the lithium metal potential ( $\mu_{L i}=\eta_{L i^{+}}+\eta_{e^{-}}$) also remains constant throughout the cell. The band diagrams found in Figure 4.4a illustrate how the chemical potential of each species, as well as the voltage, varies throughout the cell while the electrochemical potential remains constant.

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Figure 4.4 b depicts the expected equilibrium state in the case of a solid-electrolyte cathode, where the cathode material is embedded in a matrix of solid-electrolyte. For cathode materials that typically delithiate at voltages of approximately 4 V , compared to LGPS at 2.1 V , the lower (i.e. more-negative) Li ion chemical potential of the cathode material relative to the electrolyte causes charge separation that results in an interface voltage $\chi_{I}$. Analogous to the procedure following Equation 4.12, it can be shown that the equilibrium points now include the anode (a), cathode (c) and the solid-electrolyte (SE):

$$
\begin{gather*}
\mu_{L i^{+}}^{S E}+e \phi=\mu_{L i^{+}}^{a}, \quad \mu_{L i^{+}}^{c}+e\left(\phi+\chi_{I}\right)=\mu_{L i^{+}}^{a}  \tag{4.14}\\
E_{f}^{S E}-e \phi=E_{f}^{a}, \quad E_{f}^{c}-e\left(\phi+\chi_{I}\right)=E_{f}^{a}
\end{gather*}
$$

Like Equation 4.13, Equation 4.14 leads to the condition that the lithium metal potential remains constant throughout the cell.

When a solid-electrolyte particle is coated by an electronically insulating passivation layer, Figure 4.4c depicts the electrochemical state prior to any lithium ion migration out of the insulated electrolyte particle. Since the external circuitry does not directly contact the solid-electrolyte and there is no electron conducting pathway, the number of electrons within the solid-electrolyte is fixed. Hence the Fermi energy cannot equilibrate via electron flow. This effect in principle could be utilized to allow a deviation of the lithium metal potential within the solid-electrolyte relative to the electrodes, leading to a wider operational voltage window. The band diagrams of Figure 4.4c illustrate how the electron electrochemical potential can experience a local maximum (or minimum) in the solid-electrolyte due to a lack of electron conduction. This local maximum (or

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minimum) is carried over to the lithium metal potential.

However, small amounts of lithium ion capacity always exist in the sulfide solidelectrolyte even with a passivated coating layer. Therefore, effective electron conduction can occur due to the lithium holes that are created when a lithium ion migrates out of the insulated region, leaving behind the corresponding electron. The term lithium holes is used here to refer to the lithium vacancies that migrate as the lithium ions conduct - in effect creating a negative charge carrier for conduction. The differential Gibbs energy of this system is represented by adding a solid-electrolyte term to Equation 4.12 (denoted by superscript SE).

$$
\begin{align*}
\delta G= & \mu_{L i+}^{a} \delta N^{a}+\left(\mu_{L i^{+}}^{c}+e \phi^{c}\right) \delta N^{c}+\left(\mu_{L i^{+}}^{c}+e \phi^{S E}\right) \delta N^{S E}  \tag{4.15}\\
& +E_{f}^{a} \delta n^{a}+\left(E_{f}^{c}-e \phi^{c}\right) \delta n^{c}+\left(E_{f}^{S E}-e \phi^{S E}\right) \delta n^{S E}
\end{align*}
$$

The excess electron and lithium constraints are now:

1. $\delta n^{S E}=-\delta N^{S E}$ : For each lithium ion removed from the SE, the SE gains one excess electron in the form of a lithium hole.
2. $\delta n^{a}=-\delta n^{c}+\delta N^{S E}$ : Gaining a lithium ion, but not the corresponding electron, at the anode reduces the number of excess electrons at the anode.
3. $\delta N^{a}=-\delta N^{c}-\delta N^{S E}$ : Conservation of total lithium.

Constraints 1 and 2 represent the tethering of the electron and lithium density in the case of an insulated particle. Unlike the system governed by Equation 4.12, the Fermi level of the solid-electrolyte is not fixed by an external voltage. The result is that

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by lowering the number of atoms within the solid-electrolyte from extracting lithium ions, and hence increasing the number of electrons per atom within the insulated region, the number of excess electrons increases. In effect, this is equivalent to the conduction of electrons by way of lithium-holes. Solving Equation 4.15 for the equilibrium points given the above constraints lead to those of Equation 14 between the anode/cathode as well as the following relation between the anode and solid-electrolyte.

$$
\begin{equation*}
\mu_{L i^{+}}^{S E}+e \phi^{S E}=\mu_{L i^{+}}^{a}, \quad E_{f}^{c}-e \phi^{S E}=E_{f}^{a} \tag{4.16}
\end{equation*}
$$

Equation 4.16 implies that lithium ion/hole migration is sufficient to equilibrate the electron electrochemical potential between the solid-electrolyte and the anode. The system illustrated in Figure 4.4c thus does not satisfy these equilibrium conditions and will hence relax to an equilibrium state. Such an equilibrium state is depicted in Figure 4.4d, where lithium ions have migrated from the solid-electrolyte to the anode. The charge separation of the migrated lithium ions from the corresponding electrons causes a charge separation voltage. In other words, if prior to lithium migration the voltage in the sold-electrolyte was $\phi^{S E}=\phi^{0}$, then after the lithium migration the voltage within the solid-electrolyte is $\phi^{S E}=\phi^{0}-V_{S}$ where $V_{S}$ is the voltage due to the charge separation. This charge separation voltage acts as a degree of freedom and will vary until Equation 4.16 is satisfied. In this case, because the charge separation has made the electron electrochemical potential constant throughout the cell, so too is the lithium metal potential.

The ultimate result of this voltage relaxation within the electronically insulated region is depicted in Figure 4.4e. Given the effective electron transport via lithium hole

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conduction, negatively charged lithium metal can form locally within the electrolyte particle once the applied voltage exceeds the intrinsic stability of the solid-electrolyte. The negative charge is due to the lithium ions that have left the insulated region to equilibrize the lithium metal potential. As such, the local (i.e. within the insulated region) lithium metal is expected to have an interface voltage $\chi_{I}$ with the remaining solid-electrolyte. The voltage must be equal to the voltage between the anode lithium and the solid-electrolyte $\chi_{I}=\phi^{S E}$. In short, from a thermodynamic perspective, applying a voltage $\phi^{S E}$ to an electronically insulated solid-electrolyte particle relative to a lithium metal anode is equivalent to applying a charged lithium metal directly in contact with the solid-electrolyte.

However, the electronically insulating coating can still improve stability by coexisting with a mechanical constraint. By allowing lithium metal to form locally within the particle, rather than in the anode, the reaction dilation is maximized. That is, if the lithium ions go to the anode, they do not act to swell the particle from within. Hence it is important to note the function of the electronically insulating shell under our new picture:

1. Such an insulator cannot create a deviation of the lithium metal potential within the solid-electrolyte relative to the electrodes, nor lead directly to a wider operational voltage window. This is because lithium ions still relax until the lithium metal chemical potential is equal everywhere (Figure 4.4e)
2. Unlike conventional battery models, this picture recognizes that in battery systems the components are not necessarily charge neutral. In this case, the separation of lithium ions from the corresponding electrons leads to the thermodynamic

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possibility of forming charged lithium metal locally.
3. The reaction dilation is maximized by the formation of local lithium metal and ergo the insulating shell improves the ability of an arbitrary mechanical constraint to stabilize the system.

### 4.3 Experiment and Discussion

### 4.3.1 Structure and Composition

The impact of mechanical constriction on the stability of LGPS was studied by comparing decay metrics between LGPS and the same LGPS with an added core-shell morphology that provides a constriction mechanism. To minimize chemical changes, the constricting core-shell morphology was created using the post-synthesis ultrasonication. This core-shell LGPS (ultra-LGPS hereafter) was achieved by high-frequency ultrasonication that results in the conversion of the outer layer of LGPS to an amorphous material. Bright-field transmission electron microscopy (TEM) images of the LGPS particles before (Figure 4.5a) and after (Figure 4.5b) sonication show the distinct layer of an amorphous shell. Statistically-analyzed Energy Dispersive X-ray Spectroscopy (EDS) (Figures 4.5c and d) shows that this amorphous shell is sulfur deficient whereas the bulk regions of LGPS and ultra-LGPS maintain similar elemental distributions. EDS line-scans on significant number of different (ultra-) LGPS particles (Supplementary Figures 4.S1-3) confirm that surface layers with, on average, sulfur-deficient composition exist for ultra-LGPS particles within a wide size range, whereas no such phenomenon is observed for LGPS particles. Note that this is true for LGPS sonication in both solvents

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tested, dimethyl carbonate (DMC) and diethyl carbonate (DEC) (Supplementary Figures 4.S2-4). Simply soaking LGPS in DMC without sonication had no obvious effect (Supplementary Figure 4.S5). This method of post-synthesis core-shell formation minimizes structural changes to the bulk of the LGPS, allowing us to evaluate the effects of the volume constriction on stability without compositional changes in the bulk. The amorphous nature of the shell, combined with the high conductivity of the total material, suggests that the shell is a glassy sulfide.[41, 42, 45] For intrinsic LGPS, the stoichiometrically expected glassy system would be $5 L i S_{2}+G e S_{2}+P_{2} S_{5}$. Based on the EDS, the shell composition should be of the form $(5-\delta) L i S_{2}+G e S_{2}+P_{2} S_{5}$, with a shell modulus equal to or larger than the one without sulfur deficiency, since Ge amorphous phase, just like Si , exhibits large modulus. Considering the bulk modulus of crystalline LGPS is on the order of 20-30 GPa, the amorphous shell serves as an effective mechanical constriction for the ultra-LGPS running beyond 4V based on our prediction in Figure 4.2.

### 4.3.2 Electrochemical Stability

The electrochemical stabilities of non-constricted LGPS and constricted ultra-LGPS were demonstrated by charge-discharge curves and cycling performance of batteries cycled at 0.5 C in the voltage range of $1.0-2.2 \mathrm{~V}$. For LGPS battery (LTO+LGPS+C/Glass fiber separator/Li) (Figure 4.6a), a flat voltage plateau at 1.55 V appeared for 70 cycles, which can be ascribable to the redox of titanium. However, the plateau length decreases from cycle 1 to cycle 70 by almost $85.7 \%$, indicating a large decay of the cathode. On the other hand, ultra-LGPS (LTO+ultra-LGPS+C/Glass fiber separator/Li) battery (Figure


Figure 4.5: Comparison between microstructures and chemical composition of LGPS and ultra-LGPS particles. ( $\mathbf{a}, \mathbf{b}$ ) Typical TEM bright-field images of LGPS and ultra-LGPS particles respectively, showing a distinct surface layer for ultra-LGPS particle. (c, d) Statistically analyzed STEM EDS linescans performed on various LGPS and ultra-LGPS particles with different sizes, showing a uniform distribution of sulfur concentration from the surface to the bulk for LGPS particles, but a decreased sulfur concentration in the surface layer for ultra-LGPS.


Figure 4.6: (a,b) 1st - 70th charge-discharge profiles of LGPS-Li ion battery (LTO+LGPS+C/Glass fiber separator/Li) and ultra-LGPS-Li ion battery (LTO+ultraLGPS+C/Glass fiber separator/Li) cycled at 0.5 C current rate in the voltage range of 1.0-2.2 V. (c,d) Cyclic capacity curves and Columbic Efficiency of LGPS-Li ion battery and ultra-LGPS-Li ion battery. (e) 1st charge and discharge performance of all-solid-state battery: LTO+LGPS+C/LGPS/ $\mathrm{LiH}_{2} \mathrm{PO}_{4}$-coated lithium foil. The battery failed at 1st charge and cannot be charged above 3.6 V . (f) 1st, 2nd and 5th charge and discharge curves of all-solid-state battery: LTO+ultra-LGPS+C/ultra-LGPS/ $\mathrm{LiH}_{2} \mathrm{PO}_{4}{ }^{-}$ coated lithium foil. The battery can be charged to 4 V and cycle smoothly.

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4.6b) shows the same flat voltage plateau remaining almost unchanged after 70 cycles. This increase in the cathode stability is further confirmed by the cyclic capacity curves (Figures 4.6c and 4.6d). For LGPS, the specific charge and discharge capacities decrease from $159 \mathrm{mAh} / \mathrm{g}$ to $27 \mathrm{mAh} / \mathrm{g}$, and $170 \mathrm{mAh} / \mathrm{g}$ to $28 \mathrm{mAh} / \mathrm{g}$, respectively, after 70 cycle. However, ultra-LGPS demonstrates a much better cyclic stability than its LGPS counterpart. After 70 cycles the discharge capacity is still as high as $160 \mathrm{mAh} / \mathrm{g}$, with only roughly $5 \%$ of capacity loss. It is worth mentioning that the stability advantages of ultra-LGPS over LGPS can be supported by cycling performance of various battery configurations. For example, if another (ultra-)LGPS solid-electrolyte layer is inserted between cathode and glass fiber separator, the cycling performance of ultra-LGPS batteries are still obviously better than that of LGPS batteries (Supplementary Figure 4.S6,7).

To rule out the potential influence of liquid electrolyte, all-solid-state batteries in the configuration of LTO+(ultra-)LGPS+C+PTFE/(ultra-)LGPS/Li were constructed to further prove the stability difference between LGPS and ultra-LGPS. Special treatment was performed on Li foil to form a protective layer (see Methods) so that the interfacial reaction between (ultra-)LGPS solid-electrolyte and Li can be avoided. Results show that all-solid-state battery using a mixture of LTO + LGPS $+\mathrm{C}+\mathrm{PTFE}$ as cathode (Figure 4.6e) failed at 3.5 V and cannot be charged above it, due to severe decomposition of LGPS at high voltage. In contrast, the ultra-LGPS counterpart can be charged to 4 V smoothly (Figure 4.6f), indicating the largely-improved stability of constricted ultra-LGPS up to at least 4 V . In addition, the ultra-LGPS solid-state battery can be cycled well between 1-4V (Figure 4.6f), proving again its better stability than non-constricted LGPS.

In each of these results, ultra-LGPS particles with core-shell morphologies have

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Figure 4.7: 1st - 140th charge-discharge profiles of ultra-LGPS-Li ion full cell battery using LTO anode and LCO cathode (LTO+ultra-LGPS/ultra-LGPS/ LCO+ultra-LGPS). Charged/discharged at 0.3C.
outperformed the stability of LGPS counterparts, consistent with our above theoretical analysis. The experimental electrochemical stability data herein agrees well with this theory. Sulfur deficient amorphous shells, as seen in the case of ultra-LGPS, are expected to lower the effective compressibility of the system and hence increase the volume constraint. Solid-state battery cycling performance demonstrates that ultra-LGPS has, in practice, improved stability over LGPS in the cases of both LGPS oxidation and reduction. A solid state full-cell battery (Figure 4.7) using LTO+LGPS+C+PTFE as anode and $\mathrm{LiCoO}_{2}+$ LGPS $+\mathrm{C}+$ PTFE as cathode shows strong cyclability after 140 cycles. The full-cell was cycled at charge/discharge rate of 0.3 C . The ultra-LGPS was found to have a bulk conductivity of $4 \mathrm{mS} \mathrm{cm}{ }^{-1}$ by the impedance measurement.

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### 4.3.3 Decomposition Mechanism

To better understand the mechanism by which LGPS decomposes, TEM analyses were performed to study the microstructure of LTO/[ultra-]LGPS interfaces after cycling of an all-solid-state battery. A focused ion beam (FIB) sample (Figure 4.8a), in which the composite cathode (LTO+LGPS+C) and solid-electrolyte layer (LGPS) are included, was prepared after 1 charge-discharge cycle versus a lithium metal anode. A platinum layer was deposited onto the cathode layer during FIB sample preparation for protection from ion beam milling. A transit layer with multiple small dark particles exists at the cathode/solid-electrolyte interface (hereafter LTO/LGPS primary interface), as manifested in the TEM bright-field (BF) images (Figure 4.8b, Supplementary Figure 4.S8) and STEM dark-field (DF) images (Figure 4.8d, Supplementary Figure 4.S8). The particles within the transit layer of STEM DF images show bright contrast, indicating the accumulation of heavy elements. To understand the chemical composition of this transit layer, STEM EELS (electron energy loss spectroscopy) line-scans were performed. The EELS spectra show that Li K, Ge $M_{4,5}$ (Supplementary Figure 4.S9), Ge $M_{2,3}$ and P $L_{2,3}$ (Figure 4.8e) peaks exist throughout the transit layer, but sulfur peaks ( $\mathrm{S} L_{2,3}, \mathrm{~S}$ $L_{1}$ ) only show up inside the brighter regions, and are absent in the darker regions (EELS spectra 12-14 in Figure 4.8e). This result indicates that the decomposition results in multiple phases of products. Those phases which constitute the bright regions within the transit layer are sulfur-rich, which is not only supported by the Z-contrast and EELS line-scan (Figure 4.8e, Supplementary Figures 4.S9-10), but also corroborated by previous studies reporting that the decomposition products of LGPS include sulfur-rich phases such as $S, L i_{2} S, P_{2} S_{5}$ and $G e S_{2}$. These results also set the length scale for decomposed phases in LGPS at the order of 20 nm .

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Since the composite cathode layer is composed of LTO, LGPS and C, there will be minor LTO/LGPS interfaces (hereafter LTO/LGPS secondary interface) that are ubiquitous within the cathode layer. Figure 4.8 f demonstrates the typical STEM DF image of LTO/LGPS secondary interfaces, in which bright regions show up again. The density of such bright particles is much higher, possibly due to higher carbon concentration within cathode layer and the consequently facilitated LGPS decomposition. The corresponding STEM EELS line-scan spectra (Figure 4.8 g ) show that strong S $L_{2,3}$ peaks exist at the interface region, corroborating again that the bright particles are sulfur-rich. Therefore, sulfur-rich particles exist at both primary and secondary LTO/LGPS interfaces in LGPS half-cells after 1 charge-discharge cycle.

As comparison, Figure 4.9 shows the microstructural and compositional (S)TEM studies for ultra-LGPS half-cells. The primary LTO/ultra-LGPS interface after 1 charge-discharge cycle was characterized by TEM BF image (Figure 4.9a). A smooth interface was observed between the ultra-LGPS solid-electrolyte layer and the composite cathode layer. The primary LTO/ultra-LGPS interface is clean and uniform, showing no transit layer or dark particles (Figure 4.9b). The secondary LTO/ultra-LGPS interfaces were also investigated for comparison by STEM DF image, EDS line-scan and EDS mapping (Figures 4.9c-e). Results show that the atomic percentage of sulfur continuously decreases, as the STEM EDS line-scan goes from inner ultra-LGPS particle across the secondary LTO/ultra-LGPS interface, and finally into LTO + C composite region (Figure 4.9 d and Supplementary Figure 4.S11). In other words, the sulfur-deficient-shell feature of ultra-LGPS particles is maintained after cycling, and no sulfur-rich transit layer is formed at the LTO/ultra-LGPS secondary interface. STEM EDS quantitative analyses (Figure 9f) show that the atomic percentage of sulfur inside ultra-LGPS particle is as


Figure 4.8: Microstructural and compositional (S)TEM studies of LTO/LGPS interfaces after cycling in LGPS solid-state battery. (a) FIB sample prepared from LGPS solid-state battery after 1 charge-discharge cycle, in which the cathode layer (LTO+LGPS+C) and SE layer (LGPS) are included. (b) TEM BF images of LTO/LGPS primary interface, showing a transit layer with multiple dark particles. (c) HRTEM image of LTO particle and its corresponding FFT pattern. (d) STEM DF image of LTO/LGPS primary interface shows bright regions within the transit layer, indicating the accumulation of heavy elements. (e) STEM EELS linescans performed across the primary interface, indicating that the bright regions within the transit layer are sulfur-rich. (f) STEM DF image of LTO/LGPS secondary interface, in which a high density of bright particles with similar morphology exist. (g) STEM EELS linescans performed across the secondary interface, indicating that the bright particles are sulfur-rich.

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high as $38 \%$, while that of secondary LTO/ultra-LGPS interface is as low as $8 \%$.

These results suggest that the inclusion limit discussed in our theory part is a more faithful representation of the true decay process than the hydrostatic limit. The sulfur rich particles formed in LGPS have a length scale on the order of $R_{i} \approx 20 \mathrm{~nm}$. In ultra-LGPS, the shell thickness is also roughly $l \approx 20 \mathrm{~nm}$. Hence if we consider the formation of such a sulfur rich particle near the core-shell boundary in ultra-LGPS, the minimum distance from the center of the sulfur rich particle to the exterior of the shell is $R_{o}=R_{i}+l \approx 40 \mathrm{~nm}$. In this case $R_{o}^{3} \approx 8 R_{i}^{3}$ which satisfies the condition $R_{i}^{3} \ll R_{o}^{3}$ needed to apply the inclusion model. In summary, experimental results show that LGPS decays via a mechanism with inclusion of sulfur rich particles on the surface. A shell layer with a thickness close to nuclei size inhibits such decay in ultra-LGPS. These results suggest that the pristine core-shell state is at least metastable with respect to the decay towards the state with inclusion decay just below the core-shell interface.

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Figure 4.9: Figure next page. Microstructural and compositional (S)TEM studies of LTO/ultra-LGPS interfaces after cycling in ultra-LGPS all-solid-state Li ion battery. (a) TEM BF image of LTO/ultra-LGPS primary interface, showing a smooth and clean interface. (b) STEM EELS line-scan spectra corresponding to the red line in panel (a). (c) STEM DF image of LTO/ultra-LGPS secondary interface. (d) STEM EDS line scans show a continuously decreasing atomic percentage of sulfur from inner ultra-LGPS particle to secondary LTO/ultra-LGPS interface, and finally into LTO + C composite region. (e) STEM EDS mapping shows that the large particle in panel (c) is LGPS particle. (f) STEM EDS quantitative analyses show that the atomic percentage of sulfur inside ultra-LGPS particle is as high as $38 \%$, while that of secondary LTO/ultra-LGPS interface is as low as $8 \%$. Small

Figure 4.9: Continued


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### 4.4 Conclusion

We have developed a generalized strain model to show how mechanical constriction, given the nature of LGPS to expand upon decay, can lead to metastability in a significantly expanded voltage range. The precise level to which constriction expands the voltage window depends on the morphology of the decay. We performed a theoretical analysis of two limits of the decay morphology, i.e. the minimally and maximally localized cases. The minimally localized case consisted of a mean field theory where every part of the particle decays simultaneously, whereas the maximally localized case consisted of an inclusion decay. It was demonstrated that, while the maximally localized case was best, both cases had the potential for greatly expanding the stability window. We also developed a theory for the role of an electrically insulating passivation layer in such a stain-stabilized system. This model suggests that such passivation layers improve the voltage stability by keeping lithium ions localized within the mechanically constrained particle, maximizing the reaction dilation.

Experimental evidence for the stability of LGPS before and after the formation of a constricting shell supports this theory. After the formation of shell via ultrasonication, core-shell structured LGPS demonstrated remarkably improved performance in solidstate battery performance. The post-synthesis approach of shell formation prevents the LGPS core composition from deviation, which might otherwise affect stability. The core-shell is believed to be an instance of mechanically constrained LGPS, as during any decomposition, the LGPS core will seek to expand whereas the shell will largely remain fixed. In other words, the shell provides a quasi-isovolumetric constraint on the core dependent on the biaxial modulus of the shell and the particle geometry.

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Analysis of the decay morphology found in LGPS particles but not in ultra-LGPS particle suggests that the inclusion decay limit more accurately reflects the true thermodynamics. It was found that, in LGPS, inclusion sulfur-rich decay centers were embedded in the surface of the LGPS particles after cycling. In contrast, these inclusion decay centers were not found in the cycled ultra-LGPS. The ultra-LGPS maintained a shell thickness comparable to the decay cites in LGPS (approximately 20 nm ), which was predicted to be sufficient for the high level of stabilization afforded by the inclusion decay model. These results, combined with the improved stability of ultra-LGPS, indicate that not only is strain-stabilization occurring, but that the magnitude at which it is occurring is dominated by maximally localized decay mechanism. This is a promising result as such inclusion decay has been shown to provide a larger value of $\partial_{x_{D}} G_{\text {strain }}$, opening up the door to solid-state batteries that operate at much higher voltages and thus with higher energy densities.

### 4.5 Methods

Sample preparation. LGPS powder was purchased from MSE Supplies company. Ultra-LGPS was synthesized by soaking LGPS powder into organic electrolytes, such as dimethyl carbonate (DMC) and diethyl carbonate (DEC), and then sonicated for 70 h .

Electrochemistry. For all-solid-state batteries, lithium anode was coated with a protection layer in the steps described in previous work[28]. The cathode of the all-solid-state cell is a mixture of LTO+(ultra-)LGPS+carbon black+PTFE(68:19:10:3), and solid-electrolyte is pure (ultra-)LGPS powder. The cathode thin film and solidelectrolyte powder were pressed together to form a disc-shape pellet, which is pressed

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onto a freshly prepared Li-P-S amorphous layer coated Li in a Swagelock Cell to form an all-solid-state battery. Swagelok-type cells were assembled inside an argon-filled glove box. The charge/discharge behavior was tested using an ArbinBT2000 workstation (Arbin Instruments, TX, USA) at room temperature. For the semi-solid-batteries, a piece of glass fiber is used as separator to prevent the interfacial reaction between Li metal and LGPS solid-electrolyte. For LCO-LTO full all-solid-state battery, LCO+ultra-LGPS+carbon black (70:25:5) + PTFE (extra 3\%) were mixed and rolled into a thin film as the cathode. LTO+ultra-LGPS+carbon black (30:60:10) + PTFE (extra 3\%) were made as the anode using the same method. Three films of LCO cathode, LGPS separator and LTO anode were pressed together and tested under 78 MPa in a homemade pressurized cell. Here, LCO was coated with $5 \mathrm{wt} \% \mathrm{LiNbO}_{3}$ using a sol-gel method.[90] The capacity is calculated based on the mass of LTO.

Characterization. For FIB sample preparation, the cold-pressed thin film of composite cathode and (ultra-)LGPS after 1 charge-discharge cycle in (ultra)LGPS all-solid-state battery was taken out inside an argon-filled glove box. It was then mounted onto a SEM stub and sealed into a plastic bag inside the same glove box. FIB sample preparation was conducted on an FEI Helios 660 dual-beam system. The prepared FIB sample was then immediately transferred into JOEL 2010F for TEM and STEM EDS/EELS characterization.

Density functional theory (DFT) calculations. All calculations were performed in VASP using the recommended Projector Augmented Wave (PAW) pseudopotentials. An energy cutoff of 520 eV with k-point mesh of 1000/atom was used. Compressibility values were found by discretely evaluating the average compressibility of the material between 0 GPa and 1 GPa . Enthalpies were calculated at various pressures by

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applying external stresses to the stress tensor during relaxation and self-consistent field calculations. Crystal structures spanning Li-Ge-P-S phase space were obtained from the Materials Project.[79]

Thermodynamic calculations. Unconstrained $\left(K_{e f f}=0\right)$ decomposition reactions were calculated using DFT energies following previous methods.[70] Figure 2a was calculated by comparing the reaction dilations and hull energies of the unconstrained decomposition reactions at $K_{e f f}>0$. Figure 2 b was calculated by minimizing $\partial_{x_{D}} G^{\prime}$ with respect to all possible decomposition products (Appendix A).

## Chapter 5

## A High-Throughput Search for

Functionally Stable Interfaces in
Sulfide Solid-State Lithium Ion

## Conductors

## Authorship

This thesis chapter covers work that originally appeared in the literature as "A
High-Throughput Search for Functionally Stable Interfaces in Sulfide Solid-State Lithium Ion Conductors" by William Fitzhugh, Fan Wu, Luhan Ye, Wenye Deng, Pengfei Qi, and Xin Li and published as Advanced Energy Materials, 1900817 (2019).

## Chapter 5: High-Throughput Coating Search


#### Abstract

Interfacial reactions between ceramic-sulfide solid-electrolytes and common electrode materials have remained a major impediment to the development of solid-state lithium ion batteries. In practice, this means that ceramic-sulfide batteries require a suitable coating material to isolate the electrolyte from the electrode materials. In this work, the interfacial stability of $\operatorname{Li}_{10} \operatorname{SiP}_{2} S_{12}$ with over 67,000 materials is computationally evaluated. Over 2,000 materials that are predicted to form stable interfaces in the cathode voltage range and over 1,000 materials for the anode range are reported on and cataloged. Further, $\mathrm{LiCoO}_{2}$ is chosen as an example cathode material to identify coating compounds that are stable with both LSPS and a common cathode. The correlation between elemental composition and multiple instability metrics (e.g. chemical/electrochemical) is analyzed, revealing key trends in, amongst others, the role of anion selection. A new binary-search algorithm is introduced for evaluating the pseudo-phase with improved speed and accuracy. Computational challenges posed by high-throughput interfacial phase-diagram calculations are highlighted as well as pragmatic computational methods to make such calculations routinely feasible. In addition to the over 3,000 materials cataloged, representative materials from the anionic classes of oxides, fluorides, and sulfides were chosen to experimentally demonstrate chemical stability when in contact with $L i_{10} S i P_{2} S_{12}$.


## Chapter 5: High-Throughput Coating Search

### 5.1 Introduction

Solid-state lithium ion batteries represent one of the most promising directions in the field of next-generation energy storage. [1, 2, 87] Most notably, ceramic solid-electrolytes, which are intrinsically non-flammable, eliminate many of the safety issues that accompany highly-flammable organic liquid-electrolytes. Moreover, unlike liquid-electrolytes, solid-electrolytes do not experience viscosity increases that inhibit operation at low temperatures,[12-14] a key operating condition for the rapidly developing electric-vehicle market. In some cases, solid-electrolytes can even maintain a higher ionic conductivity than that of liquid-electrolytes.[13, 14] Solid-electrolytes also offer the potential to construct batteries using higher energy density electrode materials than what is permissible with liquid-electrolytes.[8, 10] For example, lithium metal represents the theoretical limit for the negative electrode material possible for Li ion batteries, due to the maximized contrast with the low Li chemical potential positive electrodes. However, the practical use of lithium metal and other high capacity materials is inhibited by the issue of lithium dendrites. Ceramic solid electrolytes offer the possibility to physically inhibit the formation of such dendrites.[10, 11]

Like liquid counterparts, the key performance metrics for solid-electrolytes are stability and ionic conductivity. For lithium systems, two very promising families of solid-electrolytes are garnet-type oxides[19-23] and ceramic-sulfides[37, 58, 95]. These families are represented, respectively, by the high-performance electrolytes $L i-L a-Z r-O$ (LLZO) oxides and $L i-X-P-S(L X P S$ where $X=S i, G e$, etc. $)$ sulfides. Oxides tend to maintain good stability in a wide range of voltages[24] but often show lower ionic conductivity $\left(<1 \mathrm{mS} \mathrm{cm}^{-1}\right)$. Conversely, the sulfides can reach

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excellent ionic conductivities up to $25 \mathrm{mS} \mathrm{cm}^{-1}[14]$ but tend to decompose under battery operating conditions[24-26].

Prior studies have revealed that the most common lithium ion electrode materials, such as $\mathrm{LiCoO}_{2}$ (LCO) and $\mathrm{LiFePO}_{4}$ (LFPO), form unstable interfaces with most solid electrolytes, particularly the high performance ceramic-sulfides.[28, 29, 96] Successful implementation of ceramic-sulfides in solid-state batteries will hence require suitable coating materials that can mitigate these interfacial instabilities. These coating materials will need both intrinsic electrochemical stability and interface electrochemical stability with the ceramic-sulfide, in the full voltage range of operation. In addition, if different solid-electrolytes are to be used in different cell components for maximum material-level stability, then the coating materials must also change to maintain chemically stable interfaces.

In short, the choice of a coating material is complex and depends on both the type of solid-electrolyte and the intended use of operation voltage (anode film, separator, cathode film, etc.). Pseudo-binary computational methods[5, 28, 29] can approximately solve for the stability of a given interface at these operating conditions, but are computationally expensive and have not yet been deployed in very-large scale. A major algorithmic component of determining phase-diagrams is the calculation of the convex-hull[70, 97], which is known to scale in computational complexity as $O\left(n^{d / 2}\right)[98,99]$, where $n$ is the number of materials considered and $d$ is the dimensionality of the phase-diagram (binary, ternary, etc.). This scaling factor indicates that interfacial stability calculations can quickly increase the computation cost. For example, calculating the phase stability of LCO requires only the ternary phase diagram $\mathrm{Li}-\mathrm{Co}-\mathrm{O}$, whereas the $\mathrm{LCO}+$ $L i_{10} S i P_{2} S_{12}$ (LSPS) interface requires a 6 -dimensional phase diagram Li-Co-O-Si-P-S.

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This increase in dimensionality will over square the cost as $d$ doubles and $n$ increases monotonically with $d$. The result is that while computational resources may be able to brute force calculate high-throughput material stability, care is needed in interfacial calculations to avoid unattainable computational needs.

In this work, we report high-throughput analysis of the interfacial stability between LSPS, which has shown the highest lithium conductivity of around $25 \mathrm{mS} \mathrm{cm}^{-1}$, and over 67,000 materials from the Materials Project (MP)[79]. We use pre-processing methods to first determine what is the minimal [i.e. optimal] number of convex-hulls needed to evaluate all 67,000 materials and then we introduce a new binary-search method to speed up the pseudo-binary evaluation while retaining high accuracy. We consider both the chemical and electrochemical stability of the interface and partition the coating candidate materials into those that are stable at anode and cathode voltage ranges, respectively. Coating material candidates that are both intrinsically stable at the material level and form stable interfaces with LSPS within the prescribed voltage range are termed functionally stable. This high-throughput data is used to highlight major trends in the correlation of elemental composition with LSPS-interfacial stability. We show that anionic composition can be a strong indicator of stability metrics. Ultimately, we provide a catalog (Appendix D) of all of those materials determined to be functionally stable.

It is worth noting that in order to obtain the maximum amount of data for statistical analysis, we do not implement a restrictive sequential filtering method. Such a filtering method (i.e. only calculating the interfacial stability of materials that have already passed a material-level threshold) can reduce the computational burden, but eliminates many of the datapoints that are useful for gaining scientific understanding through

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statistical analysis. In this work, every one of the over 67,000 materials undergo 24 stability calculations. Both the material and the material-LSPS interface are evaluated for chemical stability plus electrochemical stability at 11 voltages ranging from $0-5 \mathrm{~V}$ vs lithium metal in 0.5 V increments. This results in the first large-scale understanding of the electrochemical reactions experienced by LSPS when operating in standard battery voltage ranges.

In order to maximize the applicability of our functional stability catalog, we in general have not considered the equally important interface between the coating material and the active material. This has been done because searching for materials that are functionally stable for one active material (e.g. LCO) may not also be functionally stable for another active material (e.g. LFPO or NMC). By cataloging these materials that are functionally stable with LSPS, we aim to reduce the future complexity of choosing a coating material from the 2-dimensional case of simultaneously finding a coating compatible with both LSPS and the active material to a much faster 1-dimensional case of searching from the provided catalog of LSPS stable materials for a material compatible with the given active material. However, a special 2-dimensional case of coating materials that are also chemically stable with LCO are marked in the supplemental catalog (Appendix D), which forms a subset of the predicted compounds in the 1-dimensional case. To establish standards, we focus on finding anode coating materials, which are functionally stable in a window of 0-1.5 volts versus lithium metal, and cathode coating materials, which are functionally stable in a window of $2-4$ volts versus lithium metal. These voltage ranges are based on cycling ranges commonly found in today's lithium ion batteries. Within the anode range, we are particularly interested in finding materials that are stable at 0 volts versus lithium metal, as it could enable the use of lithium as

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an anode material.

Due to remaining computational limitations, this work focuses only on those materials that require an LSPS interfacial hull-dimensionality of less than or equal to 8 . In other words, materials were only considered if the elements present in that material consisted of Li, Si, P, S plus up to four additional elements. A total of 69,640 crystal structures were evaluated for material-level voltage windows. Of those, 67,062 materials satisfied the less than 8-dimensional requirement and were accordingly evaluated for functional stability with LSPS. In total, over 1,000 entries were found to be functionally stable in the anode range and over 2,000 were functionally stable in the cathode range for LSPS. These material phases are cataloged in Appendix D. To demonstrate the validity of these predictions, a few selected materials from the provided list are used to confirm interfacial stability with LSPS.

### 5.2 Results and Discussion

### 5.2.1 Data Acquisition and Computational Efficiency

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Figure 5.1: Figure next page. (A) Flowchart describing computational evaluation of materials for LSPS coating. (B) The number of hulls required to evaluate the stability of the 67 k materials considered if the evaluation schema is material iteration (red) or elemental set iteration (blue). (C) An illustration of the pseudo-binary approach to interfacial stability between LSPS and an arbitrary material A. The x-axis variable $(x)$ represents the fraction of A consumed in an arbitrary reaction and, hence, fixes the composition. $G_{\text {hull }}(x)$ is the energy of the decay products. $\Delta G_{R X N}(x)$ is the change in energy of a reaction that consumes $x A$ and $(1-x) L S P S . \Delta G_{R X N}^{0}(x), \Delta G_{R X N}^{\prime}(x)$ are the fractions of $\Delta G_{R X N}$ that are due to intrinsic materials-level instabilities and interfacialinstabilities, respectively. The most kinetically driven reaction (maximum $\Delta G_{R X N}$ ) occurs when $x=x_{m} . D_{A}$ and $D_{L S P S}$ are the decomposed coating material and LSPS in the absence of an interface (e.g. at $x=0,1$ ). (D) Correlation of elemental fraction with the added chemical interfacial instability $\left(\Delta G_{R X N}^{\prime}\left(x_{m}\right)\right)$. Negative (red) values are those atomic species such that increasing the concentration decreases $\Delta G_{R X N}^{\prime}$ and improves interfacial stability. Conversely, positive (blue) values are those atomic species that tend to increase $\Delta G_{R X N}^{\prime}$ and worsen interfacial stability. Elements that are only present in less than 50 crystal structures are grayed out due to lack of high-volume data.

Figure 5.1: Continued


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Figure 5.1A describes the computational methodology used to screen input DFT phase energy data for LSPS interfacial stability. In order to minimize the computational costs needed to evaluate the interface between each of these 67,062 potential coating materials and LSPS, two strategies were adopted. First, prior to the construction of the convex hulls, the materials were pre-processed and binned into groups that represent the minimum number of required convex hulls. Each unique set of elements requires a different hull, but elemental subsets can be simultaneously solved. For example, the calculation of interfacial stability between LSPS and iron-sulfate $\left(\mathrm{Fe}_{2}\left(\mathrm{SO}_{4}\right)_{3}\right)$ requires solving for the convex hull of the 6 -dimensional element set $\mathrm{Li}, \mathrm{Si}, \mathrm{P}, \mathrm{S}, \mathrm{Fe}, \mathrm{O}$. This hull is the same hull that must be calculated for the interface between LSPS and LFPO, which includes, as a subset, the 5 -dimensional hull needed for the evaluation of iron-sulfide (FeS). To capitalize on this, rather than iterate through each of the 67,062 materials and calculate the hull needed for that material, the minimum number of elemental sets that spans the entirety of the materials were determined (Figure 5.1B). Then for each elemental set, only one hull is needed to evaluate all of materials that can be constructed using those elements. This approach reduces the total number of hulls needed from 67,062 (one per material) to 11,935 (one per elemental set). As seen in Figure 5.1B, few hulls with a dimensionality below 7 were needed. Those compounds that would otherwise require a low dimensional hull are solved as a subset of a larger element set. Additionally, the number of required 7 and 8 dimensional hulls are largely reduced due to multiple phases of the same compositional space requiring the same hull. It should be noted that the impact of such a minimization strategy is more pronounced in interfacial calculations than in single-phase material calculations for two reasons. The first, as discussed above, is that interfacial reactions are inherently higher dimensional than single-phase

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calculations due to the additional elements and, hence, the poor convex hull scaling is more prominent. The second is that because every material is checked with LSPS, there is more overlap between the required convex hulls. This is exemplified above for the case LFPO and iron-sulfide. While the interfacial phase diagram of LSPS-LFPO contains the iron-sulfide interface as a subset, the material phase diagram of LFPO does not contain the material iron-sulfide phase diagram as a subset. Hence, this pre-processing step is both more important in high dimensional interfacial calculations and more effective as compared to single-phase material calculations.

The second strategy used to minimize computational cost was a binary search algorithm for determining the pseudo-binary (a.k.a. pseudo-phase) once a hull was calculated. The pseudo-binary approach $[28,29]$ is illustrated in Figure 5.1C. Since decomposition at an interface between two materials can consume an arbitrary amount of each material, the fraction of one of the two materials ( $x$ in Equation 5.1) consumed can vary from 0-1.

$$
\begin{equation*}
(1-x) L S P S+x A \rightarrow \sum_{i} d_{i} D_{i} \tag{5.1}
\end{equation*}
$$

The pseudo-binary is a computational approach that determines for which value of $x$ the decomposition described by Equation 5.1 is the most kinetically driven (e.g. when is the decomposition energy the most severe). The right-hand-side (RHS) of Equation 5.1 represents the fraction $\left(\left\{d_{i}\right\}\right)$ of each of the thermodynamically favored decay products and defines the convex hull for a given $x$ in terms of the products' Gibbs energies $\left(G_{\text {hull }}(x)=\sum_{i} d_{i}(x) G_{i}\right)$. The total decomposition reaction or hull energy accompanying Equation 5.1 is:

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$$
\begin{equation*}
\Delta G_{R X N}(x)=G_{\text {hull }}(x)-(1-x) G_{L S P S}-x G_{A} \tag{5.2}
\end{equation*}
$$

The most kinetically driven reaction between LSPS and the coating material is the one that maximizes the magnitude (i.e. most negative) of equation 2 , which defines the parameter $x_{m}$.

$$
\begin{equation*}
\left|\Delta G_{R X N}\left(x_{m}\right)\right| \equiv \max \left|\Delta G_{R X N}(x)\right| \tag{5.3}
\end{equation*}
$$

This maximum decomposition energy is the result of two factors, as illustrated in Figure 5.1C. The first, denoted $\Delta G_{R X N}^{0}(x)$, is the portion of the decomposition or hull energy that is due to the intrinsic material-level instability of the two materials separately. That is, it represents the energy that would be released following the spontaneous decay of LSPS and A when isolated from one another. In terms of the decomposed products of LSPS $\left(D_{L S P S}\right)$ and the coating material $\left(D_{A}\right), \Delta G_{R X N}^{0}(x)$ is the decomposition or hull energy corresponding to the reaction $(1-x) L S P S+x A \rightarrow(1-x) D_{L S P S}+x D_{A}$. By subtracting this materials-level instability from the total hull energy, the fraction of the decomposition or hull energy that is due solely to the interface $\left(\Delta G_{R X N}^{\prime}(x)\right)$ can be isolated as defined in Equation 5.4.

$$
\begin{equation*}
\Delta G_{R X N}^{\prime}(x)=\Delta G_{R X N}-\Delta G_{R X N}^{0}(x) \tag{5.4}
\end{equation*}
$$

Physically, $\Delta G_{R X N}^{0}(x)$ represents the instability of the materials when separated and $\Delta G_{R X N}^{\prime}(x)$ represents the increase in instability caused by the interface once the materials are brought into contact.

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The binary search algorithm for determining $x_{m}$ is illustrated in Supplementary Figures 5.S1A,B along with a linear search method for contrast. A linear method solves for $\Delta G_{R X N}(x)$ at interval values of x between 0 and 1 and returns the x-value which maximizes Equation 5.3. In contrast, the binary search method evaluates both $\Delta G_{R X N}(x)$ and $\partial_{x} \Delta G_{R X N}(x)$ at an initial x-value guess and uses the derivative to make the next guess (see Methods). As depicted in Supplementary Figure 5.S1A, the binary search spends considerably less time evaluating the hull far from $x_{m}$ as compared to the linear method. The result (Supplementary Figure 5.S1B) is that the binary search method can reach the same accuracy for $x_{m}$ as the linear method in far fewer evaluations. In this case, where prescribed accuracy is $x_{m}$ to within $0.01 \%$, a linear method would require 10,000 evaluations (error $\approx 1 / N$ ) whereas the binary search requires only 14 evaluations (error $\approx 2^{-N}$ ). Alternative simplex based methods have been used that minimize $G_{\text {hull }}(x)$ rather than maximize Equation 5.3. While in many cases these two optimization problems occur with the same $x_{m}$, there is not enough evidence, however, that this is true in general in high-throughput evaluations.

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Figure 5.2: Figure next page. (A) Hull energy vs voltage relative to lithium metal for LSPS. Blue [red] shading highlights where the decomposition is oxidative [reductive]. Green shading represents the region where LSPS decays to without consuming or producing lithium (e.g. lithium neutral). The oxidation [reduction] region is characterized by a hull energy that increases [decreases] with increasing voltage. (B) and (C) Hull energies at the boundary voltages for the anode and cathode ranges, respectively, in terms of anionic species (e.g. oxygen containing compounds vs sulfur containing compounds, etc.). Data points above [below] the neutral decay line are net oxidative [reductive] in the anode/cathode ranges. Those compounds on the neutral decay line are decaying without reacting with the lithium ion reservoir. (D) Average hull energy for material-level electrochemical decompositions versus voltage.

Figure 5.2: Continued


### 5.2.2 Functional Stability

Functional stability at a given voltage $V$ was determined for each of the over 67,000 materials by requiring that both (i) the material's intrinsic electrochemical instability $\left(\Delta G_{R X N}(x=1, V)\right)$ and (ii) the instability added by the interface $\left(\Delta G_{R X N}^{\prime}\left(x_{m}, V\right)\right)$ were less than 50 meV atom $^{-1}$. Under these conditions, the only remaining instability in the system is that of the LSPS intrinsic material-level instability, which can be stabilized via strain induced methods[68], kinetic metastability, etc. Evaluation of the entire reaction energy $\Delta G_{R X N}\left(x_{m}, V\right)$ will always return an unstable interface prediction above $V>2.1$ as LSPS is intrinsically unstable at these voltages (Figure 5.2A). Hence, this approach of subtracting away the intrinsic LSPS instability is essential for determining what interfaces will be stable in systems where LSPS has been stabilized via these various approaches (stress, kinetic, etc.).

Of the candidate materials, over 1,000 were found to be functionally stable in the anode range ( $0-1.5 \mathrm{~V}$ vs. lithium metal) and over 2,000 were found to be functionally stable in cathode range (2-4 V vs. lithium metal). Additionally, over 100 materials in both the anode and cathode ranges were determined to violate condition (i) but only decompose by lithiation/delithiation to a single product. The practical use of such materials as an LSPS coating material depends on the reversibility of this lithiation/delithiation process, as such these materials are referred to as potentially functionally stable. All functionally stable and potentially functionally stable materials are cataloged in the supplementary information.

The correlation between each element's atomic fraction and the interfacial stability is depicted in Figure 5.1D and Supplementary Figure 5.S2. Figure 5.1D depicts

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the correlation of each element with $\Delta G_{R X N}^{\prime}\left(x_{m}, V\right)$ for chemical reactions whereas Supplementary Figures 5.S2A,B,C depict the correlations with $\Delta G_{R X N}^{\prime}\left(x_{m}, V\right)$ for electrochemical reactions at 0,2 and 4 V versus lithium metal, respectively. A negative correlation between elemental composition and $\Delta G_{R X N}^{\prime}\left(x_{m}, V\right)$ implies that increasing the content of that element improves the interfacial stability. Figure 5.1D indicates that chemical stability is best for those compounds that contain large anions such as sulfur, selenium and iodine. In general, Supplementary Figures 5.S2A,C indicate that there is reduced correlation between elemental species and $\Delta G_{R X N}^{\prime}\left(x_{m}, V\right)$ at low and high voltages, respectively. This suggests that at these voltage extremes, the interfacial decomposition is dominated by intrinsic materials-level reduction/oxidation ( $\Delta G_{R X N}^{0}$ ) rather than interfacial effects $\left(\Delta G_{R X N}^{\prime}\right)$. At 2 V vs. lithium (Supplementary Figure 5.S2B) positive correlation (higher instability) is seen for most elements with the notable exception of the chalcogen and halogen anion groups, which are negatively correlated.

### 5.2.3 Anionic Species Impact on Material-Level Stability

Given the high correlation contrast for anionic species with respect to interfacial stability, analysis of the dataset in terms of anionic composition was performed. To eliminate overlap between the datapoints, the only compounds that were considered were those that are either monoanionic with only one of $\{\mathrm{N}, \mathrm{P}, \mathrm{O}, \mathrm{S}, \mathrm{Se}, \mathrm{F}, \mathrm{I}\}$ or oxy-anionic with oxygen plus one of $\{\mathrm{N}, \mathrm{S}, \mathrm{P}\}$. 45,580 entries met one of these criteria is outlined in Table 5.1. The percentage of each anionic class that was found to be electrochemically stable at the material-level is also provided.

Figure 5.2A illustrates the impact of applied voltage on the hull energy of a material,

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| Anion(s) | F | I | N | O | $\mathrm{O}+\mathrm{N}$ | $\mathrm{O}+\mathrm{P}$ | $\mathrm{O}+\mathrm{S}$ | P | S | Se |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Number <br> of Entries | 2,902 | 911 | 1,808 | 24,241 | 1,171 | 7,469 | 1,220 | 982 | 3,150 | 1,726 |
| Anode <br> Stable | $0.6 \%$ | $1.1 \%$ | $0.3 \%$ | $0.01 \%$ | $4.1 \%$ | $0.5 \%$ | $0.3 \%$ | $9.3 \%$ | $4.0 \%$ | $5.7 \%$ |
| Cathode <br> Stable | $17.3 \%$ | $13.4 \%$ | $12.5 \%$ | $5.7 \%$ | $83.9 \%$ | $64.8 \%$ | $13.3 \%$ | $35.7 \%$ | $73.9 \%$ | $55.8 \%$ |

Table 5.1:: Sizes of monoanionic and oxy-anionic datasets and the percentage of each that is electrochemically stable in the anode range ( $0-1.5 \mathrm{~V}$ ) and the cathode range (2-4V). For example, F represents all compounds that contain F in the chemical formula, while $\mathrm{O}+\mathrm{N}$ represents all compounds that contain both O and N in the chemical formula
in this case LSPS. When the slope of the hull energy with respect to voltage is negative, the corresponding decomposition is a reduction, whereas it is an oxidation if the slope is positive. In the middle there is a region where the hull slope is zero, implying there is no reaction with the lithium ion reservoir (i.e. the reaction is neutral with respect to lithium). Considering this, Figures 5.2B,C plot the characteristic redox behavior of each anionic class in the anode and cathode ranges, respectively (plotted again, independently, in Supplementary Figures 5.S3 and 5.S4 for clarity). The neutral decay line at $45^{\circ}$ represents those compounds that have the same hull energy at both voltage extremes and hence aren't reacting with the lithium ions. Data-points above [below] this line are increasing [decreasing] in hull energy with respect to voltage and are hence are characteristically oxidative [reductive] in the plotted voltage range.

Figure 5.2B indicates that, in agreement with expectations, most compounds are

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reduced in the anode voltage range of $0-1.5 \mathrm{~V}$ vs. lithium metal. Nitrogen containing compounds are seen to disproportionately occupy the y-axis, indicating a higher level of stability when in direct contact with lithium metal. This is in line with prior computation work that indicates binary and ternary nitrides are more stable against lithium metal than sulfides or oxides[83]. Within the cathode voltage range (Figure 5.2C), however, much more variance in anionic classes is seen. The oxy-anionic and fluorine containing compounds remain principally reductive whereas the phosphorus, sulfide, and selenium containing compounds are characteristically oxidative. Oxygen containing compounds are found on both side of the neutral decay line, implying that oxides are likely to lithiate/delithiate in this $2-4 \mathrm{~V}$ range.

The average hull energy of each anionic class is given in 0.5 V steps from $0-5 \mathrm{~V}$ in Figure 5.2D. Nitrogen containing compounds are confirmed to be the most stable at 0V with iodine and phosphorus compounds maintaining comparable stability. phosphorus and iodine surpass nitrogen in average stability for voltages above 0.5 V and 1.0 V , respectively. At high voltages $(>4 V)$, it is seen that fluorine and iodine containing compounds are stable whereas nitrogen containing compounds are the least stable. Note that Figure 5.2D and Supplementary Figure 5.S2B highlight the importance of maintaining both materials-level and interface-level electrochemical stability separately. For example, fluorides show high reactivity at 2V (Figure 5.2D) with the lithium reservoir but are negatively correlated with interfacial electrochemical decomposition at 2V (Supplementary Figure 5.S2B). This implies that at 2V, a fluoride coating material would likely reduce with the lithium reservoir but leave the LSPS in-tact.


Figure 5.3: Comparison of average LSPS interfacial stability of compounds sorted by anionic species. (A) The average total maximum kinetic driving energy $\left(\Delta G_{R X N}\left(x_{m}\right)\right)$ and the contribution due to the interface $\left(\Delta G_{R X N}^{\prime}\left(x_{m}\right)\right)$ for chemical reactions between LSPS and each of the considered anionic classes. (B) The total electrochemical instability ( $\left.\Delta G_{R X N}\left(x_{m}\right)\right)$ of each anionic class at a given voltage. (C) The average contribution of the interface $\left(\Delta G_{R X N}^{\prime}\left(x_{m}\right)\right)$ to the electrochemical instability of each anionic class at a given voltage

### 5.2.4 Anionic Species Impact on Interface-Level Stability

The average values of total decomposition energy $\left(\Delta G_{R X N}\left(x_{m}\right)\right)$ and the fraction that is a result of the interface instability $\left(\Delta G_{R X N}^{\prime}\left(x_{m}\right)\right)$ are depicted in Figure 5.3 for each anionic class. Figure 5.3A shows the average instability due to chemical reactions between the anionic classes and LSPS. Sulfur and selenium containing compounds form, on average, the most chemically inert interfaces with LSPS. Conversely, fluorine and oxygen containing compounds are the most reactive. As a general trend, those compound classes that are more unstable in total terms (higher $\Delta G_{R X N}\left(x_{m}\right)$ ) also maintain a higher interfacial contribution $\left(\Delta G_{R X N}^{\prime}\left(x_{m}\right)\right)$ relative to the intrinsic material contribution $\left(\Delta G_{R X N}^{0}\left(x_{m}\right)\right)$. This implies that the difference of each class's intrinsic chemical stability plays a less significant role than its reactivity with LSPS in determining the chemical stability of the interface.

Figure 5.3B shows the average total electrochemical decomposition energy for the interfaces in 0.5 V steps from $0-5 \mathrm{~V}$. In general, each anionic class follows a path that appears to be dominated by the materials-level electrochemical stability of LSPS (Figure 5.2A). This is particularly true in the low voltage $(<1 V)$ and high voltage $(>4 V)$ regimes, where electrochemical effects will be the most pronounced. The biggest deviations of the interfacial stability from LSPS's intrinsic stability occur in the region of $1-3 \mathrm{~V}$. Those compounds with the lowest chemical decomposition energies (compounds containing S, Se, I, P) deviate the least from LSPS within this middle' voltage range, while those with large decomposition energies (compounds containing $\mathrm{N}, \mathrm{F}, \mathrm{O}, \mathrm{O}+$ ) deviate more significantly. This trend suggests that the low and high voltage ranges are dominated by materials-level electrochemical reduction and oxidation,

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respectively, while the middle range is dominated by interface-level chemical reactions. For example, at 0 V the interface between $\mathrm{Al}_{2} \mathrm{O}_{3}$ and LSPS is expected to decay to $\left\{L i_{9} A l_{4}, L i_{2} O, L i_{3} P, L i_{2} S, L i_{21} S i_{5}\right\}$ which is the same set of decay products that would result from each material independently decomposing at 0V. Hence the existence of the interface has no energetic effect.

The average interface-level contribution for electrochemical decomposition is shown in Figure 5.3C. All anionic classes trend to $\Delta G_{R X N}^{\prime}\left(x_{m}\right)=0$ at 0 V , implying that the materials tend to become fully reduced to lithium binaries at 0 V , in which case interfacial effects are negligible compared to material-level instabilities. Significant interfacial instabilities arise in the middle voltage range and then lower again at high voltages. Again, this implies that interface-level chemical effects are dominant in the middle voltage range whereas material-level reduction [oxidation] dominate at low [high] voltages. At high voltage, the interfacial contribution to the instability approaches the reaction energy between the maximally oxidized material and LSPS. As a result, for any voltage above 4 V , the interface will add an instability of energy equal to this chemical reaction. This agrees with the high-voltage asymptotic behavior, whereas the low-voltage behavior always trends towards $0 \mathrm{eV} \mathrm{atom}^{-1}$. For example, for any voltage above 4V, LFPO will decompose to $\left\{\mathrm{Li}_{\mathrm{V}}, \mathrm{FePO}_{4}\right\}$ whereas LSPS will decompose to $\left\{L i, P_{2} S_{5}, S i S_{2}, S\right\}$. The introduction of the interface allows these oxidized products to chemically react and form $\mathrm{FeS}_{2}$ and $\mathrm{SiO}_{2}$.

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Figure 5.4: Functionally stable results for compounds sorted by anionic species. (A) and (B) The total number (line) and percentage (bar) of each anionic class that was determined to be functionally stable. The bottom bar (red) represented the percentage of materials that are functionally stable and the top bar (blue) represents the percentage of materials that are potentially functionally stable depending on the reversibility of lithiation/delithiation.

### 5.2.5 Anionic Species Impact on Functional Stability

The total number of each anionic class that were determined to be functionally stable or potentially functionally stable are given in Figure 5.4A (anode range) and 5.4B (cathode range), where they are both intrinsically stable at the material level and form stable interfaces with LSPS within the prescribed voltage range. For the anode range, nitrogen, phosphorus, and iodine containing compounds have the highest percentage of stable compounds (2-4\%), whereas all other classes are below $1 \%$. The cathode range showed much higher percentages with sulfur containing compounds reaching $35 \%$. Iodine and

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selenium were both above $10 \%$. Table 5.2 provides a list of representative materials from each of the six highest performing anionic classes recommended for future study.

| Anion(s) | F | I | O | P | S | Se |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Cathode | $\mathrm{AlF}_{3}$ | AgI | $\mathrm{LiAl}_{5} \mathrm{O}_{8}$ | CoP | $\mathrm{CoNi}_{2} \mathrm{~S}_{4}$ | $\mathrm{MoSe}{ }_{2}$ |
| Coating | $\mathrm{CaF}_{2}$ | $\mathrm{PbI}_{2}$ | $\mathrm{MgSiO}_{3}$ | $\mathrm{Ni}_{2} \mathrm{P}$ | $\mathrm{Si}_{2} \mathrm{Cu}_{5} \mathrm{~S}_{7}$ | $\mathrm{ZrSe}{ }_{2}$ |
| Examples | $\mathrm{LiAlCaF}_{6}$ | $\mathrm{SnI}_{2}$ | $\mathrm{SiO}_{2}$ |  | ZnS | $\mathrm{Cu}_{2} \mathrm{GeS}_{3}$ |

Table 5.2:: Representative materials found to be functionally stable in the cathode voltage range. The six anionic classes that have the largest success rate (Figure 5.4B) are represented.

It should be noted that there are many cathode range coating materials that do not contain lithium, as the absence of lithium precludes delithiation/oxidation at high voltages vs lithium metal. Accordingly, if a non-lithium containing material is chemically stable against LSPS, it is likely to be a viable cathode coating. This effect explains why sulfur containing compounds have a high cathode stability presence (35\%) yet display a tendency to oxidize more than, for example, oxides at high voltage (Supplementary Figures $5 . S 4 \mathrm{~A}, \mathrm{~B}$ ). Those sulfur-based compounds with lithium are predisposed to electrochemical decomposition at high voltage, but those without lithium are not.

### 5.2.6 Experimental Comparison

The chemical compatibility between various coating materials and LSPS were tested experimentally by hand-milling the mixture powder of LSPS and coating materials with/without high-temperature annealing, followed by X-ray diffraction (XRD)

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measurements at room temperature. Any chemical reaction between the powder will cause compositional and structural changes in the original phases, which can be detected by the change of peak positions and intensities in XRD patterns. It is worth noting that even if interfacial reactions are predicted to happen based on thermodynamic calculations, a certain amount of energy may be needed to overcome the kinetic energy barrier for these reactions to happen.[8] Therefore, the mixed powders were annealed at high temperatures $\left(300^{\circ} \mathrm{C}, 400^{\circ} \mathrm{C}, 500^{\circ} \mathrm{C}\right)$ to determine the onset temperature of interfacial reactions as well as the reaction products, and to further assess the role of kinetics by comparing these results with the DFT computed thermodynamic reaction products.

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Figure 5.5: Figure next page. (A-C) Comparison of XRD patterns to demonstrate increasingly severe structural decay of LCO, $\mathrm{SnO}_{2}$, and LTO at the solid-electrolyte material interface (with no applied voltage). In (A) $\mathbf{\Delta}, \boldsymbol{*}, \boldsymbol{\square}, \boldsymbol{\nabla}$, $\boldsymbol{*}^{\text {stand for }}$ LCO, LSPS, $\mathrm{SiO}_{2}, \mathrm{Li}_{3} \mathrm{PO}_{4}$, Cubic $\mathrm{Co}_{4} S_{3}$, Monoclinic $\mathrm{Co}_{4} S_{3}$ respectively. In (B) $\boldsymbol{A}$, $\boldsymbol{*}$, , ■, * stand for $\mathrm{SnO}_{2}$, LSPS, $\mathrm{SiO}_{2}, \mathrm{P}_{2} S_{5}$, and $L i_{2} S$ respectively. In (C) $\mathbf{A}$, *, 0.6 stand for LTO, LSPS and $L i_{1.95} T i_{2.05} S_{4}$ respectively. (D-F) Comparison of XRD patterns for materials predicted to be chemically stable vs LSPS. One representative is provided from each class of oxides, fluorides, and sulfides. In (D) $\mathbf{\Delta}$, *stand for $\mathrm{SiO}_{2}$ and LSPS respectively. In (E) ■, * stand for $M g F_{2}$ and LSPS respectively. In (F) * * stand for $Z n S$ and LSPS respectively. The shaded regions in (A-C) highlight where significant phase change happened after heating to $500^{\circ} \mathrm{C}$. The interfacial chemical compatibility decreases from (A) to (F), corresponding well with the predicted energy over hulls (negative of reaction energies) of 200,97 , and $75 \mathrm{meV} /$ atom for LCO, $\mathrm{SnO}_{2}$, and LTO, respectively, and $\leq k_{B} T /$ atom for $\mathrm{SiO}_{2}, \mathrm{MnF}_{3}, \mathrm{ZnS}$. (G,H) CV results for $\mathrm{Li}_{2} \mathrm{~S}$ and $\mathrm{SnO}_{2}$. The blue, red, and green shaded regions predict if the curve in that region will be dominantly oxidation, reduction, neutral.

Figure 5.5: Continued

(G)

(H)


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Figures 5.5A-C depict representative materials that are not predicted to be chemically stable vs LSPS whereas Figures 5.5D-F depict representative materials that are predicted to be chemically stable vs LSPS. The latter cases (Figure 5.5D-F), predicted to be stable, show negligible changes in XRD structure after heating, whereas the former (Figures $5.5 \mathrm{~A}-\mathrm{C}$ ), predicted to be unstable, show the disappearance of several XRD peaks. The XRD patterns for each individual phase at room temperature and $500^{\circ} \mathrm{C}$ are used as reference (Supplementary Figure 5.S5). By comparing these XRD patterns, it is obvious that at room temperature, no coating materials reacts with LSPS, since the XRD patterns only show peaks of the original phases. However, after being annealed at $500^{\circ} \mathrm{C}$ for 6 h , different materials show completely different reaction capabilities with LSPS. LCO is observed to react severely with LSPS, because the peak intensities and positions of the XRD pattern for the mixed powders changed completely in the whole 2-theta range of 10-80 degrees (Figure 5.5A). The original LCO and LSPS peaks either disappeared or decreased, while extra peaks belonging to new reaction products appeared (such as $\mathrm{SiO}_{2}, \mathrm{Li}_{3} \mathrm{PO}_{4}$, cubic $\mathrm{Co}_{4} S_{3}$ and monoclinic $\mathrm{Co}_{4} S_{3}$ ), indicating that LCO is not compatible with LSPS. As a sharp contrast, peak intensities and positions of the XRD patterns for $\mathrm{SiO}_{2}+$ LSPS mixture never change, showing only original peaks both before and after $500^{\circ} \mathrm{C}$ annealing. This is the direct evidence to show that no interfacial reaction happens when $\mathrm{SiO}_{2}, \mathrm{MgF}_{2}$, or ZnS is in contact with LSPS, despite large external thermal energy provided. $\mathrm{SnO}_{2}$ and LTO also show incompatibility with LSPS, as new peaks belonging to reaction products appeared in the XRD patterns for their $500^{\circ} \mathrm{C}$-annealed sample, however, the peaks of reaction products are much weaker than the case of LCO+LSPS. The 2-theta ranges, where peak positions and intensities change for four materials, are highlighted by color regions in Figures 5.5A-C, as an indication of

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the incompatibility of different materials with LSPS. It can be observed from panel that such incompatibility order is $\mathrm{LCO}>\mathrm{SnO}_{2}>\mathrm{LTO}>\mathrm{SiO}_{2}, \mathrm{MgF}_{2}, \mathrm{ZnS}$, which agrees with our theoretical prediction based on thermodynamic calculations. Respectively, LCO, $\mathrm{SnO}_{2}$, and LTO have predicted interfacial chemical reaction energies of -200 , -97 , and $-75 \mathrm{meV} /$ atom, corresponding well to the decreasing amount of XRD change from Figure 5.5A-C. $\mathrm{SiO}_{2}, \mathrm{MgF}_{2}, \mathrm{ZnS}$ are all predicted to have interfacial chemical reaction energies lower in magnitude (i.e. more positive) than $-50 \mathrm{meV} / \mathrm{atom}$. The onset temperature for interfacial reactions of various materials with LSPS are shown in Supplementary Figure 5.S6.

The electrochemical stability of typical coating materials is characterized by Cyclic Voltammetry (CV) technique, in which the decomposition of the testing material can be manifested by current peaks at certain voltages relevant to Lithium. Two typical coating materials were used as a demonstration to show good correspondence between our theoretical prediction and experimental observation. The CV test of $L i_{2} S$ (Figure 5.5 G ) shows a relevantly flat region between $0-1.5 \mathrm{~V}$, while a large oxidation peak dominates the region of $2-4 \mathrm{~V}$. In contrast, the CV test of $\mathrm{SiO}_{2}$ (Figure 5.5 H ) demonstrates net reduction in the region of $0-1.5 \mathrm{~V}$, and a neutral region with little decomposition between 2 and 4 V . These results are again direct evidence to corroborate our theoretical predictions based on thermodynamic calculations.

### 5.2.7 Application to Particular Active Materials

Ultimately, developing a functional solid-state battery requires careful consideration of not only the LSPS-coating interface but also the coating-electrode interface. Two

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alternative approaches are to either coat the LSPS and the electrodes with independent materials (i.e. two separating coating materials) or to find a single coating material that is simultaneously stable with both the LSPS and the electrode. The later method has the benefit of being the simplest to experimentally implement and can be quickly calculated for an arbitrary electrode using the material catalog provided in Appendix D. For a given cathode material, LCO, for example, all the materials that form a stable interface with both LCO and LSPS form a subset of the materials provided in the coating catalog. Hence, only those materials need be checked for compatibility with LCO, rather than the full $67,000+$ database. To consider the full range of LCO lithiation, each of the materials found to be stable in the cathode range against LSPS were checked for stability against $\mathrm{LiCoO}_{2}$ and $\mathrm{Li}_{0.5} \mathrm{CoO}_{2}$. Amongst those materials found to form stable interfaces with both LSPS and LCO are the well known $\mathrm{SiO}_{2}, \mathrm{Al}_{2} \mathrm{O}_{3}$ as well as less known materials such as $\mathrm{AgI}, \mathrm{CaF}_{2}, \mathrm{Li}_{3} \mathrm{AlF}_{6}, \mathrm{LiAl}_{5} \mathrm{O}_{8}, \mathrm{MgSiO}_{2}$. All coating materials that are stable with both LCO and LSPS are also marked in our list in the coating catalog. This process can be repeated for the many other types of cathodes, including NMC, LFPO, phosphates, oxyfluorides, etc., to determine the best coating material for each cathode when combined with LSPS.

### 5.3 Methods

Data Acquisition. The input phase energy data used in this work was the result of prior Density Functional Theory calculations that were performed as part of the Materials Project (MP)[79, 100] and was interfaced with using the Materials Application Programming Interface (API).[85] The Python Materials Genomics (pymatgen) library

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was used to calculate convex hulls following the methods of refs[29, 70, 101]. Of the initial 69,640 structures that were evaluated, 2,578 structures were not considered due to requiring hulls of dimension equal to or greater than 9 .

Elemental Set Iterations. To minimize the computational cost of analyzing all 67,062 structures, the smallest number of elemental sets that spanned all the materials were determined. To do this, the set of elements in each structure were combined with the elements of LSPS, resulting in a list of element sets with each set's length equal to the dimensionality of the required hull for that material. This list was ordered based on decreasing length of the set (e.g. ordered in decreasing dimensionality of the required hull). This set was then iterated through and any set that equals to or is a subset of a previous set was removed. The result was the minimum number of elemental sets in which every material could be described.

Chemical decomposition hulls were calculated using the energies and compositions from the MP. Changes in the volume and entropy were neglected $(\Delta G \approx \Delta E)[25,70]$. Similarly, electrochemical decomposition hulls were founded by using the lithium grand canonical free energy and subtracting a term $\mu_{L i} N_{L i}$ from the energies $\left(\Delta \phi \approx \Delta E-\mu_{L i} \Delta N_{L i}\right)$, where $\mu_{L i}$ is the chemical potential of interest and $N_{L i}$ is the number of lithium ions in the structure. After a hull was calculated, it was used to evaluate every material that exists within the span of its elemental set.

The Pseudo-binary. The pseudo-binary, as described in section 5.2, seeks to find the ratio of LSPS to coating material such that the decomposition energy is the most severe and, hence, is the most kinetically driven. This problem is simplified by using a vector notation to represent a given composition by mapping atomic occupation to a

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vector element. For example, $\mathrm{LiCoO}_{2} \rightarrow$ (112) in the basis of (Li Co O), meaning that there are 1 lithium, 1 cobalt, and 2 oxygen in the unit formula. Using this notation, the decomposition in equation 1 can be written in vector form.

$$
(1-x)\left[\begin{array}{c}
\mid  \tag{5.5}\\
L S P S \\
\mid
\end{array}\right]+x\left[\begin{array}{l}
\mid \\
A \\
\mid
\end{array}\right]=\sum_{i} d_{i}\left[\begin{array}{c}
\mid \\
D_{i} \\
\mid
\end{array}\right]
$$

Using $\bar{u}$ to represent a vector and $\overline{\bar{U}}$ to represent a matrix, Equation 5.5 becomes:

$$
\begin{equation*}
(1-x) \overline{L S P S}+x \bar{A}=\overline{\bar{D}} \bar{d} \tag{5.6}
\end{equation*}
$$

The relative composition derivatives for each decay product can be found by inverting $\overline{\bar{D}}$ in Equation 5.6.

$$
\begin{equation*}
\partial_{x} \bar{d}=\overline{\bar{D}}^{-1}(\bar{A}-\overline{L S P S}) \tag{5.7}
\end{equation*}
$$

Equation 5.7 allows for the calculation of the derivative of the hull energy with respect to the fraction parameter $x$.

$$
\partial_{x} G_{\text {hull }}=G_{A}-G_{L S P S}+\left[G_{\left.D_{1} \ldots G_{D_{n}}\right]}\left[\begin{array}{c}
\partial_{x} d_{1}  \tag{5.8}\\
\ldots \\
\partial_{x} d_{n}
\end{array}\right]\right.
$$

By using Equation 5.7, and the fact that the hull is a convex function of $x$, a binary search can be performed to find the maximum value of $G_{\text {hull }}$ and the value at which

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it occurs $x_{m}$. This process consists of first defining a two-element vector that defines the range in which $x_{m}$ is known to exist $x_{\text {range }}=(0,1)$ and an initial guess $x_{0}=0.5$. Evaluating the convex hull at the initial guess yields the decomposition products $D_{i}$ and the corresponding energies $G_{D_{i}}$. Equations 5.7 and 5.8 can then be used to find the slope of the hull energy. If the hull energy slope is negative, $x_{\text {range }} \rightarrow\left(x_{0}, 1\right)$, whereas if it is positive $x_{\text {range }} \rightarrow\left(0, x_{0}\right)$. This process is repeated until the upper and lower limits differ by a factor less than the prescribed threshold of $0.01 \%$, which will always be achieved in 14 steps ( $2^{-14} \approx 0.006 \%$ ).

Equations 5.5-8 are defined for chemical stability. In the case of electrochemical (lithium open) stability, the free energy is replaced with $\phi_{i}=G_{i}-\mu N_{i}$ where is the chemical potential and $N_{i}$ is the number of lithium in structure $i$. Additionally, lithium composition is not included in the composition vectors of Equation 5.6 to allow for the number of lithium atoms to change.

X-ray Diffraction. The compatibility of the candidate materials and solid electrolyte was investigated at room temperature (RT) by XRD. The XRD sample was prepared by hand-milling the candidate materials ( $\mathrm{LCO}, \mathrm{SnO}_{2}, \mathrm{SiO}_{2}$, LTO) with LSPS powder (weight ratio=55:30) in an Ar-filled glovebox. To test the onset temperature of reactions for candidate materials and LSPS solid electrolyte, the powder mixtures were well spread on a hotplate to heat to different nominal temperatures (300,400 and 500 degree Celsius) and then characterized by XRD.

XRD tests were performed on Rigaku Miniflex 600 diffractometer, equipped with Cu K radiation in the 2-theta range of $10-80^{\circ}$. All XRD sample holders were sealed with Kapton film in Ar-filled glovebox to avoid air exposure during the test.

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Cyclic Voltammetry. Candidate coating materials ( $\mathrm{Li}_{2} \mathrm{~S}$ and $\mathrm{SiO}_{2}$ ), carbon black, and poly(tetra- fluoroethylene) (PTFE) were mixed together in a weight ratio of 90:5:5 and hand-milled in an Ar-filled glovebox. The powder mixtures were sequentially hand-rolled into a thin film, out of which circular disks (5/16-inch in diameter, 1-2 mg loading) were punched out to form the working electrode for Cyclic Voltammetry (CV) test. These electrodes were assembled into Swagelok cells with Li metal as the counter electrode, two glass fiber separators and commercial electrolyte (1M LiPF $F_{6}$ in 1:1 (volumetric ratio) ethylene carbonate/dimethyl carbonate (EC/DMC) solvent).

CV tests were conducted by Solartron 1455A with a voltage sweeping rate of $0.1 \mathrm{mV} / \mathrm{s}$ in the range of $0-5 \mathrm{~V}$ at room temperature, to investigate the electrochemical stability window of the candidate coating materials ( $\mathrm{Li}_{2} \mathrm{~S}$ and $\mathrm{SiO}_{2}$ ).

### 5.4 Conclusion

Our high-throughput pseudo-binary analysis of Material Project DFT data has revealed that interfaces with LSPS decay via dominantly chemical means within the range of 1.5 to 3.5 V and electrochemical reduction [oxidation] at lower [higher] voltages. The fraction of decomposition energy attributed to interfacial effects disappears as the voltage approaches 0 V . This result suggests that all material classes tend to decay to maximally lithiated Li binary and elemental compounds at low voltage, in which case the presence of the interface has no impact.

In terms of anionic content, we see that appropriately matching operating conditions to the coating material is paramount. Sulfur and selenium containing compounds, for

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example, demonstrate a very high chance to be functionally stable (over $25 \%$ among all sulfides and selenides) in the $2-4 \mathrm{~V}$ cathode range. However, less than $1 \%$ of these same materials form a functionally stable coating material in the $0-1.5 \mathrm{~V}$ anode range, where iodine, phosphorus and nitrogen have the highest performance. Oxygen containing compounds have a high number of phases that are functionally stable in both voltage regions, but the percentage is low due to the even higher number of oxygen containing datapoints. Our results demonstrate the power of our new computational platform for chemical, electrochemical and functional stability analysis of materials database with big data, while our specific example on LSPS sulfide solid electrolyte predicts numerous valuable coating materials for both cathode and anode sides. Our work thus will speed up the design of next generation solid state batteries with superior interface stabilities.

## Chapter 6

## Mechanical Constraint Enables

## High-Voltage Battery System Using

## Solid-State Electrolyte

## Authorship

This thesis chapter is based on yet-to-be-published work by Luhan Ye, William Fitzhugh, Eva Gil Gonzalez, Yibo Su and Xin Li.


#### Abstract

The potential energy density of battery systems is limited in large part by the electrochemical window of the electrolyte. The lead-acid battery, for example, can only


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be utilized in a small voltage range $(1.5 \mathrm{~V})$ due to the limitation imposed by the aqueous electrolyte. Lithium-ion batteries can utilize higher voltage materials than lead-acid because of the wider stability window of the organic electrolyte. Indeed, lithium ion batteries show operating potential up to 4.5 V , which can significantly increase the energy and power densities. However, most organic electrolytes used in lithium ion battery suffer from decomposition beyond this range. The operating voltage of 4.5 V is again a limitation in pursuing higher energy density storage systems. In this work, we show how mechanical constraint can widen the stability of ceramic solid electrolyte, pushing up the electrochemical window of the solid electrolyte to levels beyond organic liquid electrolytes. A CV test shows that properly designed solid-state electrolytes can operate up to 10 V . An all-solid-state lithium metal battery with 6 V-class cathode $L i C o_{0.5} \mathrm{Mn}_{1.5} \mathrm{O}_{2}$ is demonstrated, offering one of the highest working voltage batteries to date. We anticipate that this work can be a catalyst for the study of energy storage systems focused on very-high voltage ( $>6 \mathrm{~V}$ ) electrochemistry.

### 6.1 Introduction

The specific energy of a battery system is given by its specific capacity multiplied with the average working voltage. Extensive studies have been conducted to obtained cells $>5.0$ V. Unfortunately, the narrow electrochemical window of the conventional nonaqueous electrolytes (<5.0 V) limits the development of such systems.[100] Traditional organic liquid electrolytes suffer from severe electrochemical instability at voltage higher than 4.5 V.[102] As a result, the energy storage horizon is limited by cathode materials with plateaus of around 4 V , and the development of batteries with higher energy density is

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slow and largely limited. The ever-increasing demand for batteries with higher energy densities urgently requires new electrolyte systems with higher voltage stability windows.

Ceramic-sulfide solid-state electrolytes have spurred great interest due to their high ionic conductivity.[103] Amongst them, ceramic-sulfide solid electrolytes were reported with conductivities of $12-25 \mathrm{mS} / \mathrm{cm}$, which is similar to or even higher than traditional liquid electrolytes. Additionally, the ceramic-sulfides have the added benefits of overcoming serious safety issues related to the flammability of the organic components of liquid electrolytes.[14, 37] Unfortunately, the intrinsic voltage window of ceramic-sulfide solid electrolytes is narrow (1.7-2.1 V).[24] Despite this, previous works have reported that $L i_{10} G e P_{2} S_{12}$ (LGPS) or $L i_{9.54} S i_{1.74} P_{1.44} S_{11.7} C l_{0.3}$ (LSPS-Cl) based batteries can be stable up to 5 V . These seemingly contradictory results remain one of the most pressing issues facing the solid-electrolyte field. Attempts to explain this have focused on contact or good cathode coating[37] and electronic insulating layers[29]. None of these theories fully explain the disparate results. In our previous work, we have shown that the stability window of ceramic-sulfides can be controlled, and substantially widened, using mechanical constraint.[68, 71, 104]

Here, we show how the external application of pressure can be used to stabilize LGPS at the cell-level, rather than at the microstructural level. Under proper isovolumetric conditions, the stability window of the constrained LGPS is found to be as wide as 9.8 V. Additionally, we construct solid-state full cells using this method with some of the most promising and popular cathodes materials. We pair $L i_{4} T i_{5} O_{12}$ (LTO) anodes with $\mathrm{LiCo}_{0.5} \mathrm{Mn}_{1.5} \mathrm{O}_{2}$ (LCMO), $\mathrm{LiNi}_{0.5} \mathrm{Mn}_{1.5} \mathrm{O}_{2}$ (LNMO) and $\mathrm{LiCoO}_{2}$ (LCO) cathodes to demonstrate the high-voltage stability of constrained LGPS. To further probe the electrochemical window of LGPS, we report the first all-solid-state battery based on


Figure 6.1: CV test of uniaxially pressed LGPS powder into pellets at 1 ton ( 78 MPa , black), 3 tons ( 234 MPa , red), 6 tons ( 468 MPa , blue) and a constant volume (pressed at 468 MPa and fastened, pink) during the test. 10 percent carbon is added in the cathode. The voltage range is set from open circuit to 9.8 V .
lithium metal and LCMO, which can be charged to $6-9 \mathrm{~V}$ and cycled up to 5.5 V . This work provides a new scientific understanding of how mechanical constraints can lead to mechanically induced metastability and, moreover, how mechanical constraints can control decomposition kinetics to reach unparalleled voltages.

### 6.2 Electrochemical Results

To illustrate how mechanical constraints influence the stability of LGPS, cyclic voltammetry (CV) tests of LGPS+C/LGPS/Li cells were performed. Four battery cells were tested. The first three were isobaric where the system was pressed with 1,3 , or 6 tons of force ( $78 \mathrm{MPa}, 233 \mathrm{MPa}$ and 467 MPa , respectively). The density of the LGPS

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pellets after being pressed at these pressures were $62 \%, 69 \%$ and $81 \%$ of the single crystal density, respectively. The fourth cell was initially pressed at 6 tons and then was cycled in an isovolumetric cell design.

As shown in Figure 6.1, there exists a threshold voltage after which each cell begins to severely decompose. These thresholds are 4.5 V for 1 ton, 5 V for 3 tons and 5.8 V for 6 tons. The isovolumetric cell was tested up to 9.8 V and never showed severe decomposition. In the low-voltage region (shown in Figure 6.1 inset), two minor decomposition peaks can be seen at 3 V and 3.6 V . The application of pressure reduces the maximum current for each of these peaks. The isovolumetric cell completely eliminates these peaks. Previous works have suggests that pressurization of ceramic-sulfides is required to minimize interfacial resistances. While this is certainly true to an extent at lower pressures, such conductivity enhancements are far from sufficient to account for this behavior. These results provide direct evidence that the electrochemical window of ceramic-sulfides can be significantly widened by the proper application of mechanical constraints. This lays a significant foundation to utilize ceramic-sulfides as the electrolyte material in next generation high-voltage-cathode energy storage.

Figure 6.2 shows the galvanostatic cycling of all-solid-state batteries with LCO, LNMO and LCMO cathodes, constrained LGPS separators and LTO anodes. The battery tests were performed under quasi-isovolumetric conditions, where the cells were initially pressed with 6 tons. It should be noted that LCO is the most common and widely used cathode material, included in commercial Li-ion batteries, with a plateau at approximately 4 V against $\mathrm{Li}^{+} / \mathrm{Li}$, whereas LNMO is considered one of the most promising high voltage cathode materials with a flat operating voltage at 4.7 V versus $L i^{+} / \mathrm{Li}$. The charge and discharge curves of LCO and LNMO are depicted in Figures

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Figure 6.2: Galvanostatic charge and discharge voltage curves for all-solid-state batteries using: (a) LCO, (c) LNMO and (e) LCMO as cathode material versus LTO. The cyclability of the batteries is represented in (b), (d) and (f) for LCO, LNMO and LCMO, respectively. Here, LCO and LNMO are charged and discharged at 0.3C, whereas LCMO is charged at 0.3 C and discharged at 0.1 C . All batteries are tested at room temperature, and active materials are coated with $\mathrm{LiNbO}_{3}$, as shown in Supplementary Figure 1.
6.2 a and 6.2 c , respectively. The batteries show a flat working plateau centered at 2 $\mathrm{V}\left(3.5 \mathrm{~V}\right.$ vs $\left.\mathrm{Li} i^{+} / \mathrm{Li}\right)$ for LCO and $2.9 \mathrm{~V}\left(4.4 \mathrm{~V}\right.$ vs. $\left.L i^{+} / L i\right)$ for LNMO in the first discharge cycle. Moreover, both batteries exhibit excellent cyclability performance, with a capacity fading of just $9 \%$ in the first 360 cycles for LCO and $18 \%$ in the first 100 cycles for LNMO. This is an indication that there is limited decomposition or interfacial reaction of the cathode materials with LGPS. These results agree with the CV tests reported in Figure 6.1, where it was shown that mechanical constraint can inhibit the decomposition of LGPS and widen its operational voltage range to much higher values than those previously reported.[71]

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To further probe the stability of LGPS, LCMO was chosen as a cathode due to the fact that it presents an even higher operating working plateau than LNMO (Figure 6.2e). In both charge and discharge profiles, two plateaus can be observed centered at approximately 2.2 V and $3.2 \mathrm{~V}\left(3.7 \mathrm{~V}\right.$ and 4.7 V versus $\left.\mathrm{Li}^{+} / L i\right)$ in the discharge curve of the first cycle, which are associated with the redox of $\mathrm{Mn}^{3+} / \mathrm{Mn}^{4+}$ and $\mathrm{Co}^{3+} / \mathrm{Co}^{4+}$, respectively. As shown in Figure 6.2f, upon cycling some capacity fading is observed, which may be attributed to the side reactions between LCMO and LGPS at high voltage state and corresponds to a $33 \%$ loss by the 50th cycle. In contrast to previously reported results, which claim that the stability window of LGPS is limited to a low voltage range, this demonstrates that LGPS can potentially be used as the electrolyte material in high-voltage-cathode all-solid-state batteries, showing a relatively good cycling performance even when the charging plateau is as high as 3.8 V ( 5.3 V versus $\left.L i^{+} / L i\right)$.

Figure 6.3 provides contrast between isovolumetric LGPS and organic liquid electrolyte when operated at high-voltage. Figure 6.3a shows that the LGPS LCMO cathode can be charged up to 9 V , which simulates the compatibility with future high-voltage chemistries. Discharging capacities of $99,120,146,111 \mathrm{mAh} / \mathrm{g}$ are obtained by charging LCMO at $6,7,8,9 \mathrm{~V}$, respectively. It indicates that the extra capacity is delithiated from LCMO's higher voltage states. Despite the observed side reactions, the battery can still be cycled after charging to the high voltage ( 9 V ) state. At highly delithiated states, cathode materials usually show poor electrochemical stability and the reaction between cathode materials and electrolyte is also more severe.[105] As shown in Figure 6.3b, organic liquid electrolyte shows significant decomposition plateaus before reaching 5 V and fails completely during the 3 rd cycle. The same graphite-LCMO


Figure 6.3: (a) Galvanostatic charge and discharge profiles for all-solid-state batteries using LCO and LCMO as cathode and graphite coated lithium metal as anode, with cutoff voltage from 2.6-4.5 $\mathrm{V}(\mathrm{LCO})$ and 2.6-(6-9) V (LCMO). Cycling performance of LCMO lithium metal battery using (b) $1 \mathrm{M} L i P F_{6}$ in EC/DMC and (c) constrained LGPS as electrolyte, with cut-off voltage from $2.5-5.5 \mathrm{~V}$. All batteries were tested at $55^{\circ} \mathrm{C}$.
configuration with isovolumetric LGPS is presented in Figure 6.3c and demonstrates a much more stable cycling performance.

### 6.3 Theory and Discussion

In our previous work[68, 71], we discussed in depth how the application of mechanical constraints can induce metastability. In short, given an unconstrained reaction in which LGPS decomposes with a Gibbs energy change of $\Delta G_{c h e m}<0$, the reaction can be inhibited by the application of a mechanical constraint with effective bulk modulus
$\left(K_{e f f}\right)$ if:

$$
\begin{equation*}
\Delta G_{\text {chem }}+V K_{\text {eff }} \epsilon_{R X N}>0 \tag{6.1}
\end{equation*}
$$

Where $\epsilon_{R X N}$ is the stress-free reaction dilation - in other words $\epsilon_{R X N}$ is the volume change of LGPS following decomposition in the absence of any applied stress. The effective bulk modulus ( $K_{e f f}$ ) of Equation 6.1 is the bulk modulus of the ceramic-sulfide added in parallel with the mechanical constraint as given in Equation 6.2.[8]

$$
\begin{equation*}
K_{\text {eff }}^{-1}=K_{\text {material }}^{-1}+K_{\text {constraint }}^{-1} \tag{6.2}
\end{equation*}
$$

Considering these effects, the intrinsic stability window of LGPS can be mechanically expanded up to approximately 4V.[71] However, the results of Figure 6.1 clearly suggest that under proper mechanical constraint, the operating window could be much larger than 4 V . This is to say that even when the material is not metastable, it can remain kinetically stable if the decay time scales are much larger than the time scales of operation. For example, if the electrolyte only decays one part per million per charge cycle, then it is sufficiently stable for practical battery designs that only need last thousands of cycles.

One proposed mechanism for this mechanically-induced kinetic stability is depicted in Figure 6.4. Within a given particle of LGPS that is undergoing decomposition, the particle can be partitioned into three regions. The first two are the decomposed and pristine regions, which are indicated in Figure 6.4 (top) by the mole fraction of decomposed LGPS ( $x_{D}=1$ for purely decomposed, $x_{D}=0$ for pristine). The third

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region is the interface, where the mole fraction transitions from 0 to 1 . The propagation direction of the decomposition front is controlled by thermodynamic relation of Equation 6.1. If Equation 6.1 is satisfied, the front will propagate inwards, preferring the pristine LGPS. Accordingly, the LGPS will not decompose. When Equation 6.1 is violated, the front will propagate into the LGPS and ultimately consume the particle.

However, even when Equation 6.1 is violated, the speed with which the front propagates into the pristine LGPS is still controlled by the mechanical constraint. This is illustrated in Figure 6.4 (bottom). As the decomposition front propagates, there must exist ionic currents tangential to the front's curvature. This requires the presence of an overpotential to accommodate the finite conductivity of the front for each elemental species. The ohmic portion of the overpotential is given by the sum of Equation 6.3, where $\rho_{i}(p)$ is the resistivity of the front for each element at the pressure $p$ that is present at the front, $l_{i}$ is the characteristic length scale of the decomposed morphology, and $j_{i}$ is the ionic current density.

$$
\begin{equation*}
\eta=\sum_{i} \rho_{i}(p) l_{i} j_{i} \tag{6.3}
\end{equation*}
$$

Given that $\rho_{i}(p)$ can quickly grow with constriction, it is to be expected that this overpotential becomes significant at high pressures. This effect can be seen by comparing the expected constriction with prior molecular dynamics results of constricted LGPS unit cells.[26] The pressure on the decomposition front is given by $p=K_{\text {eff }} \epsilon_{R X N}$ and the elastic volume strain of the material at that pressure is $p=K_{\text {material }} \epsilon_{V}$. Since the strain of a single lattice vector is approximately $\epsilon=1 / 3 \epsilon_{V}$, the strain of the ab plane of LGPS near the front is expected to be on the order of $\epsilon_{a b} \approx \epsilon_{R X N} K_{\text {eff }} / 3 K_{\text {material }}$. For


1. Pristine LGPS ( $x_{D}=0$ )
2. Decomposed LGPS $\left(x_{D}=1\right)$
3. Decomposition Front

$$
\begin{gathered}
\boldsymbol{L G P S} \rightarrow\left(\mathbf{1}-\boldsymbol{x}_{\boldsymbol{D}}\right) \boldsymbol{L G P S}+\boldsymbol{x}_{\boldsymbol{D}} \boldsymbol{D} \rightarrow \boldsymbol{D} \\
D=x_{\alpha} \alpha+x_{\beta} \beta+x_{\gamma} \gamma+\cdots
\end{gathered}
$$



Figure 6.4: (top) Illustration of decomposition front propagation. Decomposed phases are marked with $\alpha \ldots \gamma$. Such propagation is seen to require tangential ionic conduction. (bottom) Energy landscape for reaction coordinates. The final result is a shift in Gibbs energy by $\Delta G$, which is positive or negative based on Equation 6.2. Even when $\Delta G$ is negative (reaction is thermodynamically favorable), the presence of a sufficient overpotential due to tangential currents can significantly reduce the front's propagation rate.

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well constrained systems $K_{\text {eff }} \approx K_{\text {material }}$, thus a high voltage reaction dilation of $30 \%$ can easily result in a $\epsilon_{a b}$ value above the $4 \%$ simulated by Ong et al.[26] Given that the activation energy for Li migration in LGPS increases from 230 meV to $590 \mathrm{meV}[26]$ upon constriction by $4 \%$, the rate at which lithium reordering can occur decreases by a factor of:

$$
\begin{equation*}
\frac{\exp \left(-560 \mathrm{meV} / k_{B} T\right)}{\exp \left(-230 \mathrm{meV} / k_{B} T\right)} \approx 10^{-6} \tag{6.4}
\end{equation*}
$$

This many order of magnitude reduction in the possible reordering rate could explain why, for any voltage below 10 V , the isovolumetric cell showed virtually no decomposition current.

### 6.4 Conclusion

We have shown here that the external application of cell-level constraints can significantly impact the operational stability window of LGPS based solid-state batteries. In the case of quasi-isovolumetric constraints, the batteries have not experienced catastrophic decay at voltages up to nearly 10 V . Utilizing this high operational stability, we have demonstrated solid-state batteries with high-voltage cutoffs that are beyond the capability of liquid electrolytes. The mechanism by which this is achieved is suggested to be mechanically-induced metastability up to circa 4 V and mechanically-induced kinetic stability beyond 4 V . The kinetic stability is hypothesized to arise from strong local pressures that increase ionic resistivity. That is, once the decomposition does occur, highly localized pressure will form. In turn, these pockets of highly localized

## Chapter 6: High-Voltage Solid-State Batteries

stress decrease ion mobility that kinetically opposes further decay. This process forms a negative feedback loop for material decay in which partial decomposition of LGPS/LSPS becomes self-limiting. If this can be implemented in a practical manner, it would be a transformative development for the field as it would enable the use of new high-voltage redox chemistries in the electrode materials. More experimental works are being carried out to characterize the microscopic details of this proposed self-limiting kinetic effect, and to complete the picture of mechanical constriction for ultra-high-voltage stabilities. Additionally, future work on pairing these high-voltage cathodes with lithium metal anodes, delivering the best full cell voltage, is being considered. To date, such attempts have been complicated by the use of thick lithium metal foils which, due to the softness of the lithium metal, do not survive pressurization.

## Appendix A

## Mechanically-Induced Metastability

## Calculations

## A. 1 Perturbation Method

Figure A. 1 shows the basic organization for a program to determine if a given mechanical constraint, specified by an effective bulk modulus ( $K_{\text {eff }}$ ), is sufficient to induce metastability.

Phase Structures and DFT Engergies. The first requirement in determining any thermodynamic stability metric is acquiring sufficient phase data for the phase diagram of interest. For LSPS and LGPS, this means the energy of phases spanning the quaternary phase space Li-Si-P-S and Li-Ge-P-S, respectively. The most straight forward way to achieve this is using the PyMatGen - Materials Project API.

If data is required for phases beyond what is available in the Materials Project, large

Appendix $A$


Figure A.1: Data flow chart for perturbation based calculation of mechanically-induced metastability
volumes of crystal structures can be downloaded from crystal databases such as ICSD. Once these crystal structures are downloaded, the DFT energy can be calculated for each. The PyMatGen VASP module and ASE are both excellent resources for handling such high throughput DFT calculations.

Unconstrained Phase Diagram. Once the DFT energies have been found via either in-house calculations or download from an external database, the phase diagram can be calculated. For chemical stabilities, use the Phase Diagram module. For electrochemical stabilities, use the Grand Phase Diagram module.

Unconstrained Thermodynamic Dominant Reaction. Once the phase diagram is found, the thermodynamically favored products and the given reaction energy can be calculated.

Reaction Energy and Reaction Dilation. With the unconstrained reaction energy and products determined, Equation 3.9 can be evaluated. For each phase present in the products reported, the phase's volume can be found via the initial entry's crystal

Appendix A


Figure A.2: Data flow chart for Lagrange multiplier based calculation of mechanicallyinduced metastability
structure entry or by querying the MP API.

## A. 2 Lagrange Method

The Lagrange method is most noticeably differentiated from the perturbation method by the presence of a stress function. The stress is still given by the reaction dilation, but the volume of the decomposed products is now not known a-priori. If each of the known phases is denoted by a subscript $i$, the ground state free energy $\left(\phi_{G S}\right)$ is given by minimizing Equation 7.1 with respect to the mole fractions of each possible phase (given by the set $\left.\left\{x_{i}\right\}\right)$.

$$
\begin{equation*}
\phi\left(\left\{x_{i}\right\}\right)=\sum_{i} x_{i}\left(U_{i}^{D F T}+p\left(\left\{x_{i}\right\}\right) V_{i}\right) \tag{A.1}
\end{equation*}
$$

If LSPS is stable/metastable (i.e. $\phi_{G S}=\phi_{L S P S}$ ), then the set of mole fractions that minimize equation 7.1 will be $x_{L S P S}=1$ and $x_{j}=0$ for all $j \neq L S P S$. Additionally, the reaction dilation/pressure in this case will be zero.

Appendix A

Stress Function. The stress function $\left(p\left(\left\{x_{i}\right\}\right)\right.$ in Equation 7.1) must be explicitly presented for Lagrange optimization. This code from the LiLabPy ElectroChem module represents one implementation.

Lagrange Minimization. The Lagrange minimization consists of minimizing Equation 7.1 subject to the constraint that the closed atoms (e.g. non-Lithium atoms) are conserved. The first step is to define a function that gives Equation 7.1 for an arbitrary set $\left\{x_{i}\right\}$.

Once the free energy function is defined, the Lagrange minimization can be performed. The SciPy Optimization module is use below to minimize FreeEnergy() subject to the constraint that the total closed composition does not change.

Reaction Energy, Stress, and Products. Finally, with the set of mole fractions that minimize Equation 7.1 (i.e. the decomposition products), the reaction energy is given by $\phi_{G S}-\phi_{L S P S}$. The decomposed volume is given by $\sum_{i} x_{i} V_{I}$ and the resulting pressure is calculated for the prescribed $K_{\text {eff }}$.

## Appendix B

## Interfacial Stability Calculations via

## Pseudo-Binary Techniques

Phase Energies (DFT). Obtaining phase data for pseudo-binary interfacial calculations is similar to the methods outlined in section 7.1. The principle difference is that now there are two phases which require addition data points. For example, the LSPS +LCO interface will require phase data spanning the senary phase diagram Li-Si-P-S-Co-O. This can be significantly more data than the unioned quaternary Li-Si-P-S and ternary Li-Co-O phase space.

Dimensional Filtering. Convex-hull calculations scale with computational cost as $O\left(N^{n / 2}\right)$ where $N$ is the number of data points (number of phases) and $n$ is the dimensional of the hull (number of elements). These costs can quickly become inhibiting for high-throughput calculations as the dimensionality rises. Thus, a sometimes necessary step is to eliminate phases which exceed dimensional constraints. For example, Figure B. 1 eliminates any phase from a high through-put candidate pool that would require the

Appendix B


Figure B.1: Data flow chart for pseudo-binary based calculation of mechanically-induced metastability for interfacial reactions.
calculation of a convex-hull of dimension 9 or higher. In practice, this threshold of only calculating 8 dimensional hulls and below has been a successful balance.

Materials-Level Stability. Material-level stability must be performed for each of the two interfacing materials (e.g. LSPS and LCO). This must be done using an unconstrained and/or perturbation method (Appendix A), not a constrained Lagrange method, for each stability of interest. The structure in Figure B. 1 calculates stabilities for 12 ensembles - chemical stability plus electrochemical stability at 11 difference voltages ranging from $0-5 \mathrm{~V}$. Each of these ensemble calculations is independent from one another and can be paralleled to reduce computational burden.

Interface-Level Stability. The interface level stability is determined by finding the material stability of a pseudo-phase that is a linear combination of the two phases in question (Chapter 5). LiLabPy implements a binary search algorithm to quickly find the thermodynamic worst case ratio for the two materials. Alternatively, linear extrapolation can manually check every linear combination to find the worst case or

## Appendix B

off-set simplex methods can be used. Like materials-level stability calculations, these can also be paralleled as they are independent from each other.

## Appendix C

## Interphase Cycling Evolution

## Calculations

In contrast with Chapter 5 and Appendix B, which computationally determine if an interface can be mechanically stabilized, interphase cycling evolution determine if the product of an interfacial reaction (termed an "interphase") is stable during cycling. This is most akin to the solid-electrolyte-interphase (SEI) of conventional batteries. The goal is not necessary to avoid the formation of an interphase, but instead to make sure that it does not grow continuously with cycling. Figure C. 1 is a flowchart for screening a large amount (>50,000) coating candidates to see which form mechanically-metastable interphases after chemical reaction.

The physical picture is that when a coating is applied to LSPS/LGPS prior to cell construction, there is immediately a chemical reaction that forms an interphase at the surface of the electrolyte. In order to inhibit growth of the interphase during cycling, this interphase must be mechanically-metastable in the cell prior to cycling. Figure

Appendix $C$


Figure C.1: Data flow chart for pseudo-binary based calculation of mechanically-induced metastability for interfacial reactions.
C. 1 represents a program that calculates the interphase of each coating candidate with LSPS, then determines how much, if any, mechanical constriction is needed to stabilize the interphase at 4 V . The phase energies and dimensional filtering steps are identical to Appendix B.

Intrinsic Screening. After dimensional screening is performed, candidate coating materials are further refined by eliminating any conductors or intrinsically unstable materials. Electronically conductive coatings with short the separating layer of the lithium ion battery. Intrinsically unstable materials will be difficult to synthesis and/or cost prohibitive.

Interphase Calculations. Using the pseudo-binary methods of Appendix B, the chemical reaction products between the electrolyte and coating material are determined.

Appendix $C$

A higher-dimensional analog to the pseudo-bianry (Chapter 5) is used to define a pseudo-phase representation of the interphase. The energy, composition, and volume of the pseudo-phase are all linear combinations of the constituent phases based on the atomic fractions produced by the original pseudo-binary calculations.

Electrochemical Decomposition of Interphase. Using the perturbation method of Appendix A, the interphase can be tested for stability at a voltage of interest (4V in Figure C.1). Rather than determining if the inequality of Equation 3.9 is satisfied for a given value of $K_{e f f}$, this step determines the critical value ( $K_{c r i t}$ ) for which Equation 3.9 becomes an equality. This critical value quantifies the ability of the interphase to be mechanically stabilized. If the actual effective modulus exceeds $K_{c r i t}$, the interphase should not grow. Thus a low value of $K_{\text {crit }}$ is preferred.

## Appendix D

# High-Throughput LSPS Coating <br> <br> Catalog 

 <br> <br> Catalog}

## D. 1 LSPS Coating Material Catalog

## Notation

All listed materials have [potentially] functional stability at 0 V (anodes) or 4 V (cathodes). Materials with "*" also have chemical stability vs LSPS even without an intrinsic LSPS electrochemical stabilization mechanism. Materials with "\&" have chemical stability vs $\mathrm{Li}_{0.5} \mathrm{CoO}_{2}$ and $\mathrm{LiCoO}_{2}$ (cathode coatings only).

## D.1.1 Functionally Stable Anode Coatings for LSPS

| Ac1.00: mp-10018 | Ac0.33Cl0.33O0.33: mp-30273 | Ac0.40O0.60: mp-11107 |
| :---: | :--- | :--- |
| Ac0.33Br0.33O0.33: mp-30274 | Ac0.33H0.67: mp-24147 | Ac0.33O0.33F0.33: mp-36526 |

## Appendix D

| Al0.50Co0.50: mp-284 | Al0.50Os0.50: mp-875 | B0.50W0.50: mp-7832 |
| :---: | :---: | :---: |
| Al0.50Co0.25Ir0.25: mp-867319 | Al0.60Os0.40: mp-16521 | B0.50W0.50: mp-1008487 |
| Al0.50Co0.25Os0.25: mp-984352 | Al0.67Os0.33: mp-7188 | Ba1.00: mp-10679 |
| Al0.50Co0.25Ru0.25: mp-862695 | Al0.33Re0.67: mp-10909 | Ba1.00: mp-122 |
| Al0.25Cr0.25Fe0.50: mp-16495 | Al0.50Rh0.50: mp-364 | Ba0.33Br0.67*: mp-27456 |
| Al0.25Cr0.25Ru0.50: mp-862781 | Al0.67Ru0.33: mp-10910 | Ba0.33Br0.33Cl0.33*: mp-1012551 |
| Al0.50Fe0.50: mp-2658 | Al0.50Ru0.50: mp-542569 | Ba0.33Br0.33F0.33*: mp-23070 |
| Al0.25Fe0.75: mp-2018 | Al0.50Ru0.25Ir0.25: mp-865989 | Ba0.36Br0.55O0.09: mp-555218 |
| Al0.20Fe0.40B0.40: mp-3805 | Al0.50Ru0.25Rh0.25: mp-867326 | Ba0.22Ca0.11I0.67*: mp-756725 |
| Al0.25Fe0.25Co0.50: mp-10884 | Al0.25Si0.25Ru0.50: mp-862778 | Ba0.33Cl0.67*: mp-23199 |
| Al0.50Fe0.25Co0.25: mp-862691 | Al0.33Tc0.67: mp-1018166 | Ba0.33Cl0.67*: mp-568662 |
| Al0.50Fe0.25Ni0.25: mp-867330 | Al0.25V0.25Co0.50: mp-4955 | Ba0.33Cl0.33F0.33*: mp-23432 |
| Al0.25Fe0.50Si0.25: mp-867878 | Al0.25V0.25Fe0.50: mp-5778 | Ba0.36Cl0.55O0.09: mp-23063 |
| Al0.25Fe0.50W0.25: mp-862288 | Al0.25V0.25Os0.50: mp-862700 | Ba0.33H0.33Br0.33: mp-24424 |
| Al0.50Ir0.50: mp-1885 | Al0.25V0.25Ru0.50: mp-866001 | Ba0.33H0.33Cl0.33: mp-23861 |
| Al0.50Ir0.25Os0.25: mp-866284 | Al0.25Zn0.25Rh0.50: mp-866033 | Ba0.33H0.33I0.33: mp-23862 |
| Al0.50Ir0.25Rh0.25: mp-862694 | Ar1.00*: mp-568145 | Ba0.33H0.5010.17: mp-1018651 |
| Al0.50N0.50*: mp-661 | Ar1.00*: mp-23155 | Ba0.33I0.67*: mp-23260 |
| Al0.50N0.50*: mp-1700 | B0.67Mo0.33: mp-2331 | Ba0.33I0.67*: mp-568536 |
| Al0.50Ni0.50: mp-1487 | B0.50Mo0.50: mp-1890 | Ba0.33I0.33F0.33*: mp-22951 |
| Al0.25Ni0.75: mp-2593 | B0.50Mo0.50: mp-999198 | Ba0.40I0.40O0.20: mp-551835 |
| Al0.38Ni0.62: mp-16514 | B0.50Os0.50: mp-997617 | Ba0.36I0.55O0.09: mp-29909 |
| Al0.60Ni0.40: mp-1057 | B0.33W0.67: mp-1113 | Ba0.50P0.25Cl0.25: mp-27869 |
| Al0.50Ni0.25Ru0.25: mp-867775 | B0.67W0.33: mp-569803 | Ba0.50S0.50: mp-1500 |

## Appendix D

| Ba0.50Se0.50*: mp-1253 | Be0.67Cu0.33: mp-2031 | C1.00*: mp-997182 |
| :---: | :---: | :---: |
| Ba0.22Sr0.11I0.67*: mp-760418 | Be0.50Cu0.25Ir0.25: mp-867273 | C1.00*: mp-568806 |
| Ba0.11Sr0.22I0.67*: mp-772876 | Be0.50Cu0.25Rh0.25: mp-865308 | C1.00*: mp-606949 |
| Ba0.22Sr0.11I0.67*: mp-772878 | Be0.50Cu0.25Ru0.25: mp-865147 | C1.00*: mp-169 |
| Ba0.22Sr0.11I0.67*: mp-756624 | Be0.75Fe0.25: mp-983590 | C1.00*: mp-48 |
| Ba0.22Sr0.1110.67*: mp-756202 | Be0.25Fe0.50Si0.25: mp-862669 | C1.00*: mp-990424 |
| Ba0.11Sr0.22I0.67*: mp-754212 | Be0.75Ir0.25: mp-862714 | C1.00*: mp-1040425 |
| Ba0.22Sr0.11I0.67*: mp-752397 | Be0.50Ni0.50: mp-1033 | Ca0.43As0.14Br0.43: mp-27294 |
| Ba0.22Sr0.1110.67*: mp-772875 | Be0.75Ni0.25: mp-865168 | Ca0.43As0.14Cl0.43: mp-28069 |
| Ba0.22Sr0.11I0.67*: mp-752671 | Be0.50Ni0.25Ir0.25: mp-865229 | Ca0.50As0.25I0.25: mp-28554 |
| Ba0.25Sr0.08I0.67*: mp-756235 | Be0.50Ni0.25Rh0.25: mp-864895 | Ca0.50Br0.25N0.25: mp-23009 |
| Ba0.17Sr0.17I0.67*: mp-754852 | Be0.50O0.50*: mp-1778 | Ca0.50Cd0.50: mp-1073 |
| Ba0.11Sr0.22I0.67*: mp-754224 | Be0.50O0.50*: mp-7599 | Ca0.36Cl0.55O0.09: mp-23326 |
| Ba0.50Te0.50*: mp-1000 | Be0.50O0.50*: mp-2542 | Ca0.17Cu0.83: mp-1882 |
| Be1.00: mp-87 | Be0.83Pd0.17: mp-650 | Ca0.33F0.67*: mp-2741 |
| Be0.25Al0.25Ir0.50: mp-865966 | Be0.50Rh0.50: mp-11276 | Ca0.67Ge0.33: mp-1009755 |
| Be0.25Al0.25Rh0.50: mp-862287 | Be0.75Ru0.25: mp-865562 | Ca0.33H0.33Br0.33: mp-24422 |
| Be0.67C0.33: mp-1569 | Be0.25Si0.25Os0.50: mp-867107 | Ca0.33H0.50Br0.17: mp-1018656 |
| Be0.50Co0.50: mp-2773 | Be0.25Si0.25Ru0.50: mp-867835 | Ca0.33H0.33Cl0.33: mp-23859 |
| Be0.50Co0.25Ir0.25: mp-867274 | Be0.75Tc0.25: mp-977552 | Ca0.33H0.33I0.33: mp-24204 |
| Be0.50Co0.25Ni0.25: mp-867271 | Be0.25V0.25Os0.50: mp-867275 | Ca0.50Hg0.50: mp-11286 |
| Be0.50Co0.25Pt0.25: mp-867270 | C1.00*: mp-568286 | Ca0.33I0.67*: mp-30031 |
| Be0.25Co0.50Si0.25: mp-865901 | C1.00*: mp-937760 | Ca0.50N0.25Cl0.25: mp-22936 |
| Be0.50Cu0.50: mp-2323 | C1.00*: mp-990448 | Ca0.25Nd0.25Hg0.50: mp-865955 |

## Appendix $D$

| Ca0.50O0.50: mp-2605 | Ce0.25Ni0.25C0.50: mp-19741 | Cr0.75Si0.25: mp-729 |
| :---: | :---: | :---: |
| Ca0.43P0.14Cl0.43: mp-29342 | Ce0.50O0.50: mp-10688 | Cr0.25Si0.25Ru0.50: mp-865791 |
| Ca0.50P0.25I0.25: mp-23040 | Ce0.50P0.50: mp-2154 | Cs1.00: mp-1 |
| Ca0.50Pd0.50: mp-213 | Ce0.14Re0.57Si0.29: mp-27861 | Cs1.00: mp-11832 |
| Ca0.25Pr0.25Hg0.50: mp-867217 | Ce0.50S0.50: mp-1096 | Cs0.12Ba0.25Br0.62*: mp-541722 |
| Ca0.50S0.50*: mp-1672 | Ce0.33Si0.33Cu0.33: mp-22740 | Cs0.50Br0.50*: mp-571222 |
| Ca0.50Se0.50*: mp-1415 | Ce0.20Si0.40Cu0.40: mp-5452 | Cs0.11C0.89: mp-28861 |
| Ca0.20Si0.40Ni0.40: mp-5292 | Ce0.20Si0.40Ir0.40: mp-4433 | Cs0.29Ca0.14Br0.57*: mp-1025267 |
| Ca0.50Te0.50: mp-1519 | Ce0.17Si0.33Mo0.33C0.17: mp- | Cs0.20Ca0.20Br0.60*: mp-30056 |
| Ce1.00: mp-28 | 1018666 | Cs0.29Ca0.14Cl0.57*: mp-1025185 |
| Ce0.17Al0.50Pd0.33: mp-4785 | Ce0.20Si0.40Ni0.40: mp-4537 | Cs0.20Ca0.20I0.60*: mp-998428 |
| Ce0.50As0.50: mp-2748 | Ce0.20Si0.40Os0.40: mp-4767 | Cs0.20Ca0.20I0.60*: mp-998333 |
| Ce0.14B0.86: mp-21343 | Ce0.20Si0.40Rh0.40: mp-4090 | Cs0.50Cl0.50*: mp-573697 |
| Ce0.20Co0.40Si0.40: mp-3437 | Ce0.20Si0.40Ru0.40: mp-3566 | Cs0.20Eu0.20Br0.60*: mp-638685 |
| Ce0.11Cr0.22B0.67: mp-2873 | Ce0.50Zn0.50: mp-986 | Cs0.5010.50*: mp-614603 |
| Ce0.17Cr0.33Si0.33C0.17: mp-6258 | Co1.00: mp-54 | Cs0.20Li0.30Br0.50*: mp-571409 |
| Ce0.17Cu0.83: mp-761 | Co1.00: mp-102 | Cs0.25Li0.25Br0.50*: mp-23057 |
| Ce0.33Cu0.33Ge0.33: mp-20766 | Co0.20B0.40W0.40: mp-7573 | Cs0.17Li0.33Br0.50*: mp-606680 |
| Ce0.20Fe0.40Si0.40: mp-3035 | Cr1.00: mp-90 | Cs0.12Li0.38Cl0.50*: mp-571666 |
| Ce0.33Ga0.67: mp-2209 | Cr0.50B0.50: mp-260 | Cs0.33Li0.17Cl0.50*: mp-571390 |
| Ce0.50Ge0.12S0.38: mp-675328 | Cr0.67B0.33: mp-15809 | Cs0.17Li0.33Cl0.50*: mp-569117 |
| Ce0.20Mn0.40Si0.40: mp-2965 | Cr0.25Ni0.75: mp-1007923 | Cs0.25Li0.25Cl0.50*: mp-23364 |
| Ce0.50N0.50: mp-2493 | Cr0.25Ni0.75: mp-1007974 | Cs0.30Li0.20Cl0.50*: mp-570756 |
| Ce0.17Ni0.33B0.33C0.17: mp-10860 | Cr0.33Ni0.67: mp-784631 | Cs0.38Li0.12I0.50*: mp-569238 |

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| Cs0.20Li0.3010.50*: mp-608311 | Dy0.25Ni0.25C0.50: mp-4587 | Er0.33H0.67: mp-24192 |
| :---: | :---: | :---: |
| Cs0.33Na0.33Te0.33*: mp-5339 | Dy0.50P0.50: mp-2014 | Er0.50Ir0.50: mp-2713 |
| Cs0.20Sr0.20Br0.60*: mp-998297 | Dy0.50Pd0.50: mp-2226 | Er0.20Mn0.40Si0.40: mp-4729 |
| Cs0.20Sr0.20Br0.60*: mp-998433 | Dy0.50Rh0.50: mp-232 | Er0.50N0.50: mp-19830 |
| Cs0.20Sr0.20Cl0.60*: mp-998561 | Dy0.50S0.50: mp-2470 | Er0.25Ni0.25C0.50: mp-11723 |
| Cs0.20Sr0.20I0.60*: mp-998417 | Dy0.40S0.2000.40: mp-12669 | Er0.50P0.50: mp-1144 |
| Cs0.67Te0.33*: mp-573763 | Dy0.33Si0.33Cu0.33: mp-5365 | Er0.50Pd0.50: mp-851 |
| Dy0.50Ag0.50: mp-2167 | Dy0.20Si0.40Ir0.40: mp-4065 | Er0.50Rh0.50: mp-2381 |
| Dy0.50Al0.50: mp-11843 | Dy0.20Si0.40Ni0.40: mp-4692 | Er0.40S0.20O0.40: mp-12671 |
| Dy0.50As0.50: mp-2627 | Dy0.20Si0.40Os0.40: mp-12088 | Er0.33Si0.33Cu0.33: mp-8122 |
| Dy0.50Au0.50: mp-1007918 | Dy0.20Si0.40Rh0.40: mp-2893 | Er0.20Si0.40Ir0.40: mp-3907 |
| Dy0.33B0.67: mp-2057 | Dy0.20Si0.40Ru0.40: mp-4177 | Er0.20Si0.40Ni0.40: mp-4881 |
| Dy0.25Co0.25C0.50: mp-3847 | Dy0.50Zn0.50: mp-2303 | Er0.20Si0.40Os0.40: mp-3958 |
| Dy0.20Co0.40Si0.40: mp-5976 | Er0.50Ag0.50: mp-2621 | Er0.20Si0.40Rh0.40: mp-5386 |
| Dy0.17Cu0.83: mp-30578 | Er0.50As0.50: mp-1688 | Er0.20Si0.40Ru0.40: mp-5022 |
| Dy0.50Cu0.50: mp-2334 | Er0.50Au0.50: mp-2442 | Er0.50Zn0.50: mp-1660 |
| Dy0.33Cu0.33Ge0.33: mp-20010 | Er0.50Au0.50: mp-11243 | Eu0.14B0.86: mp-20874 |
| Dy0.25Fe0.25C0.50: mp-1018065 | Er0.33B0.67: mp-1774 | Eu0.33C0.67: mp-1018177 |
| Dy0.20Fe0.40Si0.40: mp-4939 | Er0.25Co0.25C0.50: mp-13501 | Eu0.29C0.14N0.29Cl0.29: mp-582618 |
| Dy0.50Ge0.50: mp-20122 | Er0.20Co0.40Si0.40: mp-3239 | Eu0.50Cd0.50: mp-580236 |
| Dy0.33H0.67: mp-24151 | Er0.17Cu0.83: mp-30579 | Eu0.20Co0.40Si0.40: mp-672294 |
| Dy0.20Mn0.40Si0.40: mp-4985 | Er0.50Cu0.50: mp-1955 | Eu0.25Cs0.12I0.62*: mp-29613 |
| Dy0.50N0.50: mp-1410 | Er0.25Fe0.25C0.50: mp-1018064 | Eu0.17Cu0.83: mp-2066 |
| Dy0.17Ni0.33B0.33C0.17: mp-6223 | Er0.20Fe0.40Si0.40: mp-5688 | Eu0.20Fe0.40Si0.40: mp-582357 |

## Appendix D

| Eu0.33H0.50Br0.17: mp-1018691 | Fe0.50Co0.50: mp-2090 | Gd0.50Rh0.50: mp-1742 |
| :---: | :---: | :---: |
| Eu0.33H0.50Cl0.17: mp-1018693 | Fe0.50Ni0.50: mp-2213 | Gd0.50S0.50: mp-510402 |
| Eu0.22H0.67Ru0.11: mp-634945 | Fe0.25Ni0.75: mp-1007855 | Gd0.40S0.2000.40: mp-4805 |
| Eu0.50Hg0.50: mp-11375 | Fe0.25Ni0.75: mp-1418 | Gd0.40Se0.20O0.40: mp-13973 |
| Eu0.40I0.40O0.20: mp-558258 | Fe0.75Si0.25: mp-2199 | Gd0.33Si0.33Cu0.33: mp-607182 |
| Eu0.20Li0.20H0.60: mp-541365 | Fe0.25Si0.25Ru0.50: mp-3464 | Gd0.20Si0.40Cu0.40: mp-20677 |
| Eu0.50N0.50: mp-20340 | Fe0.25Si0.25Tc0.50: mp-862790 | Gd0.20Si0.40Ir0.40: mp-20700 |
| Eu0.17Ni0.33B0.33C0.17: mp-21064 | Gd0.50Ag0.50: mp-542779 | Gd0.20Si0.40Ni0.40: mp-20956 |
| Eu0.50O0.50: mp-21394 | Gd0.50Al0.50: mp-12753 | Gd0.20Si0.40Os0.40: mp-21408 |
| Eu0.50P0.25Br0.25: mp-613052 | Gd0.50As0.50: mp-510374 | Gd0.20Si0.40Rh0.40: mp-21240 |
| Eu0.50P0.25I0.25: mp-569689 | Gd0.50Au0.50: mp-635426 | Gd0.20Si0.40Ru0.40: mp-569302 |
| Eu0.25Rb0.12I0.62*: mp-29612 | Gd0.33C0.67: mp-12765 | Gd0.40Te0.20O0.40: mp-16035 |
| Eu0.50S0.50*: mp-20587 | Gd0.50Cd0.50: mp-1031 | Gd0.50Zn0.50: mp-2497 |
| Eu0.50Se0.50*: mp-21009 | Gd0.25Co0.25C0.50: mp-1018146 | He1.00*: mp-754382 |
| Eu0.50Si0.50: mp-21279 | Gd0.20Co0.40Si0.40: mp-542985 | He1.00*: mp-23156 |
| Eu0.20Si0.40Ir0.40: mp-21849 | Gd0.17Cu0.83: mp-636253 | He1.00*: mp-614456 |
| Eu0.20Si0.40Ni0.40: mp-4768 | Gd0.50Cu0.50: mp-614455 | He1.00*: mp-23158 |
| Eu0.20Si0.40Rh0.40: mp-21383 | Gd0.17Cu0.67Pd0.17: mp-1025013 | Hf0.25Al0.25Cu0.50: mp-10887 |
| Eu0.20Si0.40Ru0.40: mp-581736 | Gd0.25Fe0.25C0.50: mp-1018176 | Hf0.25Al0.25Ni0.50: mp-5748 |
| Eu0.50Te0.50*: mp-542583 | Gd0.20Fe0.40Si0.40: mp-542986 | Hf0.25Al0.25Rh0.50: mp-864671 |
| Eu0.50Zn0.50: mp-1261 | Gd0.33H0.67: mp-24092 | Hf0.25Al0.25Ru0.50: mp-864909 |
| Fe1.00: mp-13 | Gd0.50N0.50: mp-940 | Hf0.33B0.67: mp-1994 |
| Fe0.50B0.50: mp-1007881 | Gd0.17Ni0.33B0.33C0.17: mp-20728 | Hf0.33Be0.67: mp-2553 |
| Fe0.29B0.57Mo0.14: mp-15722 | Gd0.50P0.50: mp-510401 | Hf0.33Be0.33Si0.33: mp-12571 |

## Appendix D

| Hf0.50C0.50: mp-21075 | Ho0.33H0.67: mp-24152 | K0.20Ca0.20Cl0.60*: mp-998421 |
| :---: | :---: | :---: |
| Hf0.50Co0.50: mp-2027 | Ho0.50Ir0.50: mp-11476 | K0.50Cl0.50*: mp-23193 |
| Hf0.20Co0.40Si0.40: mp-571367 | Ho0.25Lu0.25Au0.50: mp-973285 | K0.50I0.50*: mp-22898 |
| Hf0.50N0.50: mp-2828 | Ho0.20Mn0.40Si0.40: mp-5796 | K0.33Li0.33Te0.33*: mp-4495 |
| Hf0.17Nb0.17B0.67: mp-38818 | Ho0.50N0.50: mp-883 | Kr1.00*: mp-612118 |
| Hf0.50Os0.50: mp-11452 | Ho0.17Ni0.33B0.33C0.17: mp-6646 | Kr1.00*: mp-567365 |
| Hf0.50Pt0.50: mp-1007691 | Ho0.25Ni0.25C0.50: mp-5154 | Kr1.00*: mp-975590 |
| Hf0.50Rh0.50: mp-11457 | Ho0.50P0.50: mp-744 | Kr1.00*: mp-974400 |
| Hf0.50Ru0.50: mp-2802 | Ho0.50Pd0.50: mp-832 | Kr1.00*: mp-976347 |
| Hf0.25Si0.25Ru0.50: mp-866062 | Ho0.50Rh0.50: mp-2163 | La1.00: mp-156 |
| Hf0.50Tc0.50: mp-11460 | Ho0.40S0.20O0.40: mp-12670 | La0.17Al0.50Pd0.33: mp-30815 |
| Ho1.00: mp-10765 | Ho0.33Si0.33Cu0.33: mp-4476 | La0.50As0.50: mp-708 |
| Ho0.50Ag0.50: mp-2778 | Ho0.20Si0.40Ir0.40: mp-567513 | La0.14B0.86: mp-2680 |
| Ho0.50As0.50: mp-295 | Ho0.20Si0.40Ni0.40: mp-2924 | La0.33Br0.33O0.33: mp-23023 |
| Ho0.50Au0.50: mp-1007666 | Ho0.20Si0.40Os0.40: mp-5219 | La0.33C0.67: mp-2367 |
| Ho0.33B0.67: mp-2267 | Ho0.20Si0.40Rh0.40: mp-3895 | La0.50Cd0.50: mp-776 |
| Ho0.25Co0.25C0.50: mp-9241 | Ho0.20Si0.40Ru0.40: mp-5720 | La0.33Cl0.33O0.33: mp-23025 |
| Но0.20Co0.40Si0.40: mp-5835 | Ho0.50Zn0.50: mp-2249 | La0.20Co0.40Si0.40: mp-5526 |
| Ho0.50Cu0.50: mp-1971 | K1.00: mp-972981 | La0.33Cu0.67: mp-2051 |
| Ho0.17Cu0.83: mp-30585 | K1.00: mp-58 | La0.17Cu0.83: mp-2613 |
| Ho0.17Cu0.83: mp-580364 | K1.00: mp-10157 | La0.20Fe0.40Si0.40: mp-4088 |
| Ho0.17Cu0.67Pd0.17: mp-1025134 | K0.50Br0.50*: mp-23251 | La0.33Ga0.67: mp-19839 |
| Ho0.25Fe0.25C0.50: mp-1018052 | K0.11C0.89: mp-28930 | La0.40Ge0.2010.40: mp-570597 |
| Ho0.20Fe0.40Si0.40: mp-3191 | K0.20Ca0.20Br0.60*: mp-998599 | La0.33H0.67: mp-24153 |

## Appendix $D$

| La0.33I0.33O0.33: mp-30993 | Li0.50Cl0.50*: mp-22905 | Lu0.50Pd0.50: mp-2205 |
| :---: | :---: | :---: |
| La0.20Mn0.40Si0.40: mp-5069 | Li0.50F0.50*: mp-1138 | Lu0.50Rh0.50: mp-377 |
| La0.50N0.50: mp-256 | Li0.33Hf0.17O0.50: mp-755352 | Lu0.50Ru0.50: mp-11495 |
| La0.25Ni0.25C0.50: mp-1018048 | Li0.50I0.50*: mp-570935 | Lu0.40S0.20O0.40*: mp-12673 |
| La0.40O0.60: mp-1968 | Li0.25Lu0.25O0.50: mp-754605 | Lu0.50Si0.50: mp-1001612 |
| La0.33O0.33F0.33: mp-7100 | Li0.67O0.33: mp-1960 | Lu0.33Si0.33Cu0.33: mp-8125 |
| La0.33O0.33F0.33: mp-8111 | Li0.67S0.33*: mp-1153 | Lu0.20Si0.40Ni0.40: mp-12100 |
| La0.50P0.50: mp-2384 | Li0.67Se0.33*: mp-2286 | Lu0.20Si0.40Os0.40: mp-12101 |
| La0.40P0.20I0.40: mp-571647 | Li0.67Te0.33*: mp-2530 | Lu0.20Si0.40Rh0.40: mp-3108 |
| La0.50S0.50: mp-2350 | Lu0.50Ag0.25Au0.25: mp-865445 | Lu0.20Si0.40Ru0.40: mp-10453 |
| La0.40S0.20O0.40: mp-4511 | Lu0.50As0.50: mp-2017 | Lu0.50Zn0.50: mp-11496 |
| La0.50Se0.50: mp-1161 | Lu0.50Au0.50: mp-11249 | Mg0.25Al0.25Rh0.50: mp-865155 |
| La0.40Se0.20O0.40: mp-7233 | Lu0.33B0.67: mp-11219 | Mg0.20Be0.40N0.40: mp-11917 |
| La0.20Si0.40Cu0.40: mp-3995 | Lu0.40C0.20Cl0.40: mp-573376 | Mg0.33Cu0.67: mp-1038 |
| La0.20Si0.40Ir0.40: mp-3585 | Lu0.25Co0.25C0.50: mp-1001614 | Mg0.20Ni0.60C0.20: mp-10700 |
| La0.20Si0.40Ni0.40: mp-5898 | Lu0.17Cu0.83: mp-580136 | Mg0.50Rh0.50: mp-1172 |
| La0.20Si0.40Os0.40: mp-567203 | Lu0.25Fe0.25C0.50: mp-1001606 | Mg0.25Sc0.25Pd0.50: mp-977566 |
| La0.20Si0.40Rh0.40: mp-5936 | Lu0.20Fe0.40Si0.40: mp-571098 | Mg0.33Si0.17Ni0.50: mp-15779 |
| La0.20Si0.40Ru0.40: mp-5105 | Lu0.33H0.67: mp-24288 | Mn0.50Al0.50: mp-771 |
| La0.50Te0.50: mp-1560 | Lu0.50Ir0.50: mp-1529 | Mn0.25Al0.25Co0.50: mp-3623 |
| La0.40Te0.2000.40: mp-4547 | Lu0.25Mg0.25Pd0.50: mp-865253 | Mn0.50Al0.25Cr0.25: mp-864988 |
| La0.50Zn0.50: mp-2615 | Lu0.50N0.50: mp-1102 | Mn0.25Al0.25Fe0.50: mp-31185 |
| Li0.50Br0.50*: mp-976280 | Lu0.25Ni0.25C0.50: mp-1001603 | Mn0.25Al0.25Ni0.50: mp-4922 |
| Li0.40C0.20N0.40: mp-9610 | Lu0.50P0.50: mp-10192 | Mn0.25Al0.25Os0.50: mp-864951 |

## Appendix $D$

| Mn0.50Al0.25Re0.25: mp-864989 | Mn0.50V0.25Si0.25: mp-865026 | Nb0.33Ni0.33B0.33: mp-9985 |
| :---: | :---: | :---: |
| Mn0.25Al0.25Rh0.50: mp-10894 | Mo1.00: mp-129 | Nb0.50Ru0.50: mp-432 |
| Mn0.50Al0.25V0.25: mp-10895 | Mo0.50C0.50: mp-2305 | Nb0.50Ru0.50: mp-11516 |
| Mn0.50Al0.25W0.25: mp-864990 | Na1.00: mp-982370 | Nb0.38Si0.31Cu0.31: mp-13967 |
| Mn0.67B0.33: mp-20318 | Na1.00: mp-974920 | Nb0.33Si0.33Ir0.33: mp-21248 |
| Mn0.50B0.50: mp-8365 | Na1.00: mp-974558 | Nb0.33Si0.33Rh0.33: mp-10470 |
| Mn0.20B0.40W0.40: mp-19789 | Na1.00: mp-973198 | Nb0.25Si0.25Tc0.50: mp-864672 |
| Mn0.25Be0.75: mp-973292 | Na1.00: mp-127 | Nd1.00: mp-159 |
| Mn0.25Be0.50Co0.25: mp-978261 | Na0.50Br0.50*: mp-22916 | Nd0.17Al0.50Pd0.33: mp-12734 |
| Mn0.25Be0.50Ir0.25: mp-864943 | Na0.02C0.98*: mp-571003 | Nd0.50As0.50: mp-2602 |
| Mn0.25Be0.50Rh0.25: mp-864945 | Na0.50Cl0.50*: mp-22862 | Nd0.50Au0.50: mp-999338 |
| Mn0.50Co0.50: mp-1009133 | Na0.50I0.50*: mp-23268 | Nd0.14B0.86: mp-1929 |
| Mn0.25Co0.50Si0.25: mp-4492 | Nb1.00: mp-75 | Nd0.33C0.67: mp-2297 |
| Mn0.50Co0.25Si0.25: mp-13082 | Nb0.25Al0.75: mp-1842 | Nd0.20Co0.40Si0.40: mp-4228 |
| Mn0.25Fe0.50Si0.25: mp-5529 | Nb0.25Al0.25Fe0.50: mp-865280 | Nd0.17Cu0.83: mp-1140 |
| Mn0.25Ga0.25Co0.50: mp-21171 | Nb0.25Al0.25Ni0.50: mp-4813 | Nd0.20Fe0.40Si0.40: mp-3489 |
| Mn0.33Nb0.33Si0.33: mp-7829 | Nb0.25Al0.25Os0.50: mp-865278 | Nd0.33Ga0.67: mp-2524 |
| Mn0.25Ni0.75: mp-11501 | Nb0.25Al0.25Ru0.50: mp-11537 | Nd0.33H0.67: mp-24096 |
| Mn0.50Rh0.50: mp-417 | Nb0.43B0.57: mp-10255 | Nd0.33I0.33O0.33: mp-755336 |
| Mn0.75Si0.25: mp-20211 | Nb0.33B0.67: mp-450 | Nd0.20Mn0.40Si0.40: mp-3018 |
| Mn0.25Si0.25Ru0.50: mp-864966 | Nb0.50B0.50: mp-2580 | Nd0.50N0.50: mp-2599 |
| Mn0.50Si0.25Ru0.25: mp-999576 | Nb0.67C0.33: mp-2318 | Nd0.17Ni0.33B0.33C0.17: mp-6102 |
| Mn0.25Si0.25Tc0.50: mp-864970 | Nb0.25Ga0.25Ru0.50: mp-977401 | Nd0.25Ni0.25C0.50: mp-5383 |
| Mn0.50V0.50: mp-316 | Nb0.25Ni0.75: mp-11513 | Nd0.50P0.50: mp-2823 |

## Appendix $D$

| Nd0.50S0.50: mp-1748 | Pa0.50C0.50: mp-567580 | Pr0.40Se0.20O0.40: mp-4764 |
| :---: | :---: | :---: |
| Nd0.40S0.20O0.40: mp-3211 | Pa0.50N0.50: mp-1009545 | Pr0.20Si0.40Cu0.40: mp-4014 |
| Nd0.40Se0.20O0.40: mp-13971 | Pm0.25Al0.25Cu0.50: mp-862838 | Pr0.33Si0.33Cu0.33: mp-8119 |
| Nd0.33Si0.33Cu0.33: mp-8120 | Pm0.25Ca0.25Hg0.50: mp-862883 | Pr0.20Si0.40Ni0.40: mp-4439 |
| Nd0.20Si0.40Cu0.40: mp-2877 | Pm0.50N0.50: mp-1018160 | Pr0.25Si0.50Ni0.25: mp-5493 |
| Nd0.20Si0.40Ir0.40: mp-567130 | Pr1.00: mp-97 | Pr0.20Si0.40Os0.40: mp-5852 |
| Nd0.20Si0.40Ni0.40: mp-4007 | Pr0.50As0.50: mp-10622 | Pr0.20Si0.40Rh0.40: mp-4815 |
| Nd0.20Si0.40Os0.40: mp-571586 | Pr0.14B0.86: mp-12762 | Pr0.20Si0.40Ru0.40: mp-4904 |
| Nd0.20Si0.40Rh0.40: mp-3651 | Pr0.33C0.67: mp-1995 | Pr0.40Te0.2000.40: mp-16032 |
| Nd0.20Si0.40Ru0.40: mp-4013 | Pr0.20Co0.40Si0.40: mp-5112 | Pr0.50Zn0.50: mp-460 |
| Nd0.40Te0.2000.40: mp-5459 | Pr0.17Cu0.83: mp-2462 | Pu0.25Co0.25C0.50: mp-999290 |
| Nd0.50Zn0.50: mp-1053 | Pr0.20Fe0.40Si0.40: mp-5627 | Pu0.20Co0.40Si0.40: mp-22383 |
| Ne1.00*: mp-111 | Pr0.33Ga0.67: mp-668 | Pu0.50N0.50: mp-1719 |
| Ni1.00: mp-10257 | Pr0.33H0.67: mp-24095 | Pu0.25Ni0.25C0.50: mp-975570 |
| Ni1.00: mp-23 | Pr0.33I0.33O0.33: mp-29254 | Pu0.20Si0.40Ni0.40: mp-20171 |
| Ni0.67B0.33: mp-2536 | Pr0.20Mn0.40Si0.40: mp-5423 | Pu0.20Si0.40Ru0.40: mp-22559 |
| Ni0.20B0.40Mo0.40: mp-9999 | Pr0.50N0.50: mp-343 | Rb1.00: mp-975519 |
| Ni0.67Mo0.33: mp-784630 | Pr0.17Ni0.33B0.33C0.17: mp-6140 | Rb1.00: mp-70 |
| Ni0.80W0.20: mp-30811 | Pr0.25Ni0.25C0.50: mp-9312 | Rb1.00: mp-975204 |
| Np0.33B0.67: mp-1083 | Pr0.40O0.60: mp-2063 | Rb1.00: mp-975129 |
| Np0.50N0.50: mp-2596 | Pr0.50P0.50: mp-601 | Rb1.00: mp-639755 |
| Os1.00: mp-49 | Pr0.14Re0.57Si0.29: mp-1025309 | Rb0.50Br0.50*: mp-22867 |
| Pa1.00: mp-10740 | Pr0.50S0.50: mp-2495 | Rb0.11C0.89: mp-568643 |
| Pa1.00: mp-62 | Pr0.40S0.20O0.40: mp-3236 | Rb0.20Ca0.20Br0.60*: mp-998536 |

## Appendix D

| Rb0.20Ca0.20Cl0.60*: mp-998324 | Sc0.50Ir0.50: mp-1129 | Sm0.20Mn0.40Si0.40: mp-13473 |
| :---: | :---: | :---: |
| Rb0.20Ca0.20Cl0.60*: mp-998197 | Sc0.50N0.50: mp-2857 | Sm0.50N0.50: mp-749 |
| Rb0.20Ca0.20I0.60*: mp-998592 | Sc0.50Ni0.50: mp-11521 | Sm0.17Ni0.33B0.33C0.17: mp-9220 |
| Rb0.50Cl0.50*: mp-23295 | Sc0.50Pd0.50: mp-2781 | Sm0.25Ni0.25C0.50: mp-999144 |
| Rb0.50I0.50*: mp-22903 | Sc0.50Pt0.50: mp-892 | Sm0.50P0.50: mp-710 |
| Rb0.25Li0.25Br0.50*: mp-28237 | Sc0.50Rh0.50: mp-1780 | Sm0.50Rh0.50: mp-436 |
| Rb0.25Li0.25Cl0.50*: mp-28243 | Sc0.50Ru0.50: mp-30867 | Sm0.50S0.50: mp-1269 |
| Rb0.20Sr0.20Cl0.60*: mp-998755 | Sc0.50Si0.50: mp-9969 | Sm0.40S0.20O0.40: mp-5598 |
| Re1.00: mp-975065 | Sc0.50Zn0.50: mp-11566 | Sm0.40Se0.20O0.40: mp-13972 |
| Re1.00: mp-8 | Si0.50Ru0.50*: mp-381 | Sm0.33Si0.33Cu0.33: mp-8121 |
| Re0.75B0.25: mp-15671 | Si0.50Ru0.50*: mp-189 | Sm0.20Si0.40Ir0.40: mp-12097 |
| Re0.33B0.67*: mp-1773 | Sm1.00: mp-21377 | Sm0.20Si0.40Ni0.40: mp-3939 |
| Re0.67C0.33: mp-974437 | Sm0.17Al0.50Pd0.33: mp-11539 | Sm0.20Si0.40Os0.40: mp-567408 |
| Ru1.00: mp-33 | Sm0.50As0.50: mp-1738 | Sm0.20Si0.40Rh0.40: mp-3882 |
| Sc0.50Al0.50: mp-331 | Sm0.50As0.25Se0.25: mp-38593 | Sm0.20Si0.40Ru0.40: mp-4072 |
| Sc0.25Al0.25Cu0.50: mp-16497 | Sm0.50Au0.50: mp-999193 | Sm0.40Te0.20O0.40: mp-16033 |
| Sc0.25Al0.25Ni0.50: mp-10898 | Sm0.33C0.67: mp-12764 | Sm0.50Zn0.50: mp-2165 |
| Sc0.25Al0.25Rh0.50: mp-867922 | Sm0.25Co0.25C0.50: mp-999190 | Sr1.00: mp-95 |
| Sc0.33B0.67: mp-2252 | Sm0.20Co0.40Si0.40: mp-15968 | Sr1.00: mp-76 |
| Sc0.50Co0.50: mp-2212 | Sm0.17Cu0.83: mp-227 | Sr0.14B0.86: mp-242 |
| Sc0.20Co0.40Si0.40: mp-4131 | Sm0.25Fe0.25C0.50: mp-999178 | Sr0.12Be0.38O0.50: mp-27791 |
| Sc0.50Cu0.50: mp-1169 | Sm0.20Fe0.40Si0.40: mp-567859 | Sr0.33Br0.67*: mp-567744 |
| Sc0.33Cu0.67: mp-1018149 | Sm0.33Ga0.67: mp-477 | Sr0.33Br0.67*: mp-32711 |
| Sc0.33H0.67: mp-24237 | Sm0.33H0.67: mp-24658 | Sr0.33Br0.53Cl0.13*: mp-28021 |

## Appendix $D$

| Sr0.33Br0.33F0.33*: mp-23024 | Sr0.33I0.33F0.33*: mp-23046 | Ta0.25Mn0.50Al0.25: mp-867120 |
| :---: | :---: | :---: |
| Sr0.50Br0.25N0.25: mp-23056 | Sr0.5010.25N0.25: mp-569677 | Ta0.50Mo0.25Os0.25: mp-864770 |
| Sr0.36Br0.55O0.09: mp-556049 | Sr0.40I0.40O0.20: mp-551203 | Ta0.67N0.33: mp-10196 |
| Sr0.25C0.25N0.50: mp-12317 | Sr0.36I0.55O0.09: mp-29910 | Ta0.33Ni0.67: mp-1157 |
| Sr0.29C0.14N0.29Cl0.29: mp-567655 | Sr0.50N0.25Cl0.25: mp-23033 | Ta0.25Ni0.75: mp-570491 |
| Sr0.50Cd0.50: mp-30496 | Sr0.5000.50: mp-2472 | Ta0.50Os0.25W0.25: mp-864650 |
| Sr0.33Cl0.67*: mp-23209 | Sr0.50S0.50*: mp-1087 | Ta0.50Re0.25Mo0.25: mp-977353 |
| Sr0.33Cl0.33F0.33*: mp-22957 | Sr0.50Se0.50*: mp-2758 | Ta0.50Ru0.50: mp-1601 |
| Sr0.36Cl0.55O0.09: mp-23321 | Sr0.50Te0.50*: mp-1958 | Ta0.67Si0.33: mp-2783 |
| Sr0.17Cu0.83: mp-2726 | Ta1.00: mp-50 | Ta0.33Si0.33Rh0.33: mp-20436 |
| Sr0.33F0.67*: mp-981 | Ta0.25Al0.25Co0.50: mp-3340 | Ta0.50Tc0.50: mp-11572 |
| Sr0.33H0.33Br0.33: mp-24423 | Ta0.25Al0.25Fe0.50: mp-867249 | Ta0.50Tc0.25W0.25: mp-972209 |
| Sr0.33H0.33Cl0.33: mp-23860 | Ta0.25Al0.25Ni0.50: mp-5921 | Ta0.25Ti0.25Os0.50: mp-867123 |
| Sr0.33H0.33I0.33: mp-24205 | Ta0.25Al0.25Os0.50: mp-862445 | Ta0.25Ti0.25Re0.50: mp-867846 |
| Sr0.33H0.5010.17: mp-1019269 | Ta0.25Al0.25Ru0.50: mp-862446 | Ta0.25W0.75: mp-979289 |
| Sr0.25H0.62Rh0.12: mp-35152 | Ta0.45B0.55: mp-28629 | Ta0.25Zn0.25Os0.50: mp-979291 |
| Sr0.22H0.67Ru0.11: mp-24292 | Ta0.33B0.67: mp-1108 | Tb1.00: mp-7163 |
| Sr0.25Hf0.25N0.50: mp-9383 | Ta0.50B0.50: mp-1097 | Tb0.50Ag0.50: mp-2268 |
| Sr0.20Hf0.20O0.60: mp-550908 | Ta0.43B0.57: mp-10142 | Tb0.50Al0.50: mp-1009839 |
| Sr0.20Hf0.20O0.60: mp-3721 | Ta0.67C0.33: mp-7088 | Tb0.25Al0.25Cu0.50: mp-971985 |
| Sr0.20Hf0.2000.60: mp-13109 | Ta0.50C0.50: mp-1086 | Tb0.50As0.50: mp-2640 |
| Sr0.50Hg0.50: mp-542 | Ta0.50Cr0.25Os0.25: mp-867774 | Tb0.50Au0.50: mp-999141 |
| Sr0.33I0.67*: mp-568284 | Ta0.25Ga0.25Os0.50: mp-867788 | Tb0.33B0.67: mp-965 |
| Sr0.33I0.67*: mp-23181 | Ta0.25Ga0.25Ru0.50: mp-867781 | Tb0.25Co0.25C0.50: mp-5106 |

## Appendix D

| Tb0.20Co0.40Si0.40: mp-3292 | Tc0.33B0.67*: mp-1019317 | Ti0.25Al0.25Cu0.50: mp-4771 |
| :---: | :---: | :---: |
| Tb0.50Cu0.50: mp-1837 | Th1.00: mp-37 | Ti0.25Al0.25Fe0.50: mp-31187 |
| Tb0.17Cu0.83: mp-11363 | Th0.33Al0.67: mp-669 | Ti0.25Al0.25Fe0.25Co0.25: mp-998980 |
| Tb0.33Cu0.33Ge0.33: mp-9387 | Th0.50C0.50: mp-1164 | Ti0.25Al0.25Ni0.50: mp-7187 |
| Tb0.25Fe0.25C0.50: mp-999122 | Th0.25Co0.25C0.50: mp-999088 | Ti0.25Al0.25Os0.50: mp-865442 |
| Tb0.20Fe0.40Si0.40: mp-5399 | Th0.20Co0.40Si0.40: mp-7072 | Ti0.25Al0.25Rh0.50: mp-866153 |
| Tb0.33H0.67: mp-24724 | Th0.33Cu0.67: mp-1377 | Ti0.25Al0.25Ru0.50: mp-866155 |
| Tb0.20Mn0.40Si0.40: mp-5677 | Th0.20Fe0.40Si0.40: mp-7600 | Ti0.43B0.57: mp-1025170 |
| Tb0.50N0.50: mp-2117 | Th0.33Ga0.67: mp-11419 | Ti0.33B0.67: mp-1145 |
| Tb0.17Ni0.33B0.33C0.17: mp-6092 | Th0.20Mn0.40Si0.40: mp-4458 | Ti0.50Be0.50: mp-11279 |
| Tb0.25Ni0.25C0.50: mp-3061 | Th0.50N0.50: mp-834 | Ti0.25Be0.50Ir0.25: mp-866139 |
| Tb0.50P0.50: mp-645 | Th0.33Ni0.67: mp-220 | Ti0.25Be0.25Rh0.50: mp-866143 |
| Tb0.50Rh0.50: mp-11561 | Th0.17Ni0.33B0.33C0.17: mp-1025034 | Ti0.50C0.50: mp-631 |
| Tb0.50S0.50: mp-1610 | Th0.33O0.67: mp-643 | Ti0.50Co0.50: mp-823 |
| Tb0.40S0.20O0.40*: mp-12668 | Th0.50P0.50: mp-931 | Ti0.25Co0.50Si0.25: mp-3657 |
| Tb0.40Se0.2000.40: mp-755340 | Th0.20Si0.40Cu0.40: mp-5948 | Ti0.33Co0.33Si0.33: mp-15657 |
| Tb0.33Si0.33Cu0.33: mp-5514 | Th0.20Si0.40Ni0.40: mp-5682 | Ti0.67Cu0.33: mp-742 |
| Tb0.20Si0.40Ir0.40: mp-5752 | Th0.20Si0.40Os0.40: mp-3166 | Ti0.50Cu0.50: mp-2078 |
| Tb0.20Si0.40Ni0.40: mp-4466 | Th0.20Si0.40Rh0.40: mp-4413 | Ti0.50Fe0.50: mp-305 |
| Tb0.20Si0.40-so.40: mp-5429 | Th0.20Si0.40Ru0.40: mp-5165 | Ti0.25Fe0.50Si0.25: mp-866141 |
| Tb0.20Si0.40Rh0.40: mp-3097 | Th0.20Si0.40Tc0.40: mp-8375 | Ti0.25Ga0.25Co0.50: mp-20145 |
| Tb0.20Si0.40Ru0.40: mp-3678 | Ti1.00: mp-46 | Ti0.25Ga0.25Fe0.25Co0.25: mp-998964 |
| Tb0.50Zn0.50: mp-836 | Ti0.50Al0.50: mp-1953 | Ti0.50Ga0.25N0.25: mp-1025550 |
| Tc1.00: mp-113 | Ti0.25Al0.25Co0.50: mp-5407 | Ti0.25Ga0.25Ru0.50: mp-865448 |

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| Ti0.25Mn0.50Si0.25: mp-865652 | Tm0.20Co0.40Si0.40: mp-3262 | U0.33C0.67: mp-2486 |
| :---: | :---: | :---: |
| Ti0.50N0.50*: mvc-13876 | Tm0.17Cu0.83: mp-30600 | U0.20Fe0.40Si0.40: mp-20924 |
| Ti0.50N0.50*: mp-492 | Tm0.50Cu0.50: mp-985 | U0.50N0.50: mp-1865 |
| Ti0.67N0.33: mp-8282 | Tm0.20Fe0.40Si0.40: mp-2938 | U0.20Re0.20B0.60: mp-28607 |
| Ti0.67N0.33: mp-7790 | Tm0.50Ge0.50: mp-998911 | U0.20Si0.40Os0.40: mp-5786 |
| Ti0.50Os0.50: mp-291 | Tm0.33H0.67: mp-24727 | U0.20Si0.40Ru0.40: mp-3388 |
| Ti0.67Pd0.33: mp-13164 | Tm0.50Ir0.50: mp-11483 | V1.00: mp-146 |
| Ti0.50Re0.50: mp-2179 | Tm0.50N0.50: mp-1975 | V0.43B0.57*: mp-569270 |
| Ti0.25Re0.50W0.25: mp-865664 | Tm0.25Ni0.25C0.50: mp-4037 | V0.50B0.50: mp-9973 |
| Ti0.67Rh0.33: mp-1018124 | Tm0.50P0.50: mp-7171 | V0.33B0.67*: mp-1491 |
| Ti0.50Ru0.50: mp-592 | Tm0.50Pd0.50: mp-348 | V0.60B0.40: mp-2091 |
| Ti0.33Si0.33Ni0.33: mp-510409 | Tm0.50Rh0.50: mp-11564 | V0.40B0.60*: mp-9208 |
| Ti0.33Si0.33Rh0.33: mp-672645 | Tm0.40S0.2000.40*: mp-3556 | V0.67C0.33: mp-1008632 |
| Ti0.25Si0.25Ru0.50: mp-865681 | Tm0.33Si0.33Cu0.33: mp-8123 | V0.20Co0.20B0.60*: mp-10057 |
| Ti0.25Si0.25Tc0.50: mp-865669 | Tm0.20Si0.40Ni0.40: mp-4469 | V0.33Co0.33Si0.33: mp-21371 |
| Ti0.50Tc0.50: mp-11573 | Tm0.20Si0.40Os0.40: mp-570217 | V0.50Cr0.25Os0.25: mp-865485 |
| Ti0.25Zn0.25Cu0.50: mp-865930 | Tm0.20Si0.40Rh0.40: mp-8528 | V0.50Cr0.25Re0.25: mp-865484 |
| Ti0.25Zn0.25Rh0.50: mp-861961 | Tm0.20Si0.40Ru0.40: mp-568371 | V0.50Fe0.50: mp-1335 |
| Tm0.50Ag0.50: mp-2796 | Tm0.50Zn0.50: mp-2316 | V0.25Fe0.50Si0.25: mp-4595 |
| Tm0.50As0.50: mp-1101 | U1.00: mp-44 | V0.25Ga0.25Fe0.50: mp-21883 |
| Tm0.50Au0.50: mp-1017507 | U0.33B0.67: mp-1514 | V0.25Ga0.25Ru0.50: mp-865586 |
| Tm0.50Au0.50: mp-447 | U0.33B0.33C0.33: mp-5816 | V0.25Ni0.75: mp-171 |
| Tm0.33B0.67: mp-800 | U0.33B0.33N0.33: mp-5311 | V0.33Ni0.67: mp-11531 |
| Tm0.25Co0.25C0.50: mp-13502 | U0.50C0.50: mp-2489 | V0.50Os0.50: mp-12778 |

## Appendix $D$

| V0.50Re0.25W0.25: mp-971754 | Y0.20Mn0.40Si0.40: mp-3854 | Yb0.33Cl0.67*: mp-23220 |
| :---: | :---: | :---: |
| V0.50Ru0.50: mp-1395 | Y0.50N0.50: mp-2114 | Yb0.33Cl0.33F0.33*: mp-557483 |
| V0.25Si0.25Ru0.50: mp-865507 | Y0.17Ni0.33B0.33C0.17: mp-6576 | Yb0.36Cl0.55O0.09: mp-554831 |
| V0.25Si0.25Tc0.50: mp-865472 | Y0.50P0.50: mp-994 | Yb0.20Co0.40Si0.40: mp-5326 |
| V0.50Tc0.50: mp-2540 | Y0.50Rh0.50: mp-191 | Yb0.20Cs0.20Br0.60*: mp-568005 |
| W1.00: mp-91 | Y0.50S0.50: mp-1534 | Yb0.17Cu0.83: mp-1607 |
| W0.50C0.50: mp-1894 | Y0.40S0.20O0.40: mp-12894 | Yb0.33F0.67*: mp-865934 |
| Xe1.00*: mp-979286 | Y0.33Si0.33Cu0.33: mp-8126 | Yb0.20Fe0.40Si0.40: mp-2866 |
| Xe1.00*: mp-972256 | Y0.20Si0.40Ir0.40: mp-4653 | Yb0.50Hg0.50: mp-2545 |
| Xe1.00*: mp-611517 | Y0.20Si0.40Ni0.40: mp-5176 | Yb0.33I0.67*: mp-570418 |
| Xe1.00*: mp-570510 | Y0.20Si0.40Os0.40: mp-567749 | Yb0.25Li0.12Cl0.62*: mp-23421 |
| Xe1.00*: mp-979285 | Y0.20Si0.40Rh0.40: mp-3441 | Yb0.17Mg0.17Cu0.67: mp-1025021 |
| Y0.50Ag0.50: mp-2474 | Y0.20Si0.40Ru0.40: mp-568673 | Yb0.50O0.50: mp-1216 |
| Y0.50A10.50: mp-11229 | Y0.50Si0.12S0.38: mp-677445 | Yb0.50Pd0.50: mp-2547 |
| Y0.50As0.50: mp-933 | Y0.50Zn0.50: mp-2516 | Yb0.50Pd0.25Au0.25: mp-864800 |
| Y0.33B0.67: mp-1542 | Yb1.00: mp-71 | Yb0.25Pm0.25Au0.50: mp-865894 |
| Y0.50Cd0.50: mp-915 | Yb1.00: mp-162 | Yb0.20Rb0.20Br0.60*: mp-571418 |
| Y0.25Co0.25C0.50: mp-4248 | Yb0.50Ag0.50: mp-2266 | Yb0.09Rb0.36I0.55*: mp-23347 |
| Y0.20Co0.40Si0.40: mp-5129 | Yb0.14B0.86: mp-419 | Yb0.20Rb0.20I0.60*: mp-568796 |
| Y0.50Cu0.50: mp-712 | Yb0.33Br0.67*: mp-22882 | Yb0.50Rh0.50: mp-567089 |
| Y0.17Cu0.83: mp-2797 | Yb0.33Br0.67*: mp-571232 | Yb0.50S0.50*: mp-1820 |
| Y0.20Fe0.40Si0.40: mp-5288 | Yb0.36Br0.55O0.09: mp-850213 | Yb0.50Se0.50*: mp-286 |
| Y0.33H0.67: mp-24650 | Yb0.50Cd0.50: mp-1857 | Yb0.20Si0.40Ni0.40: mp-5916 |
| Y0.50Ir0.50: mp-30746 | Yb0.33Cl0.67*: mp-865716 | Yb0.20Si0.40Os0.40: mp-567093 |

## Appendix $D$

| Yb0.20Si0.40Rh0.40: mp-10626 | Zr0.50C0.50: mp-2795 | Zr0.50Ru0.50: mp-214 |
| :---: | :---: | :---: |
| Yb0.20Si0.40Ru0.40: mp-3415 | Zr0.50Co0.50: mp-2283 | Zr0.50Si0.50: mp-11322 |
| Yb0.50Te0.50: mp-1779 | Zr0.33Co0.33P0.33: mp-8418 | Zr0.50Si0.50: mp-893 |
| Yb0.50Tl0.50: mp-11576 | Zr0.20Co0.40Si0.40: mp-569344 | Zr0.33Si0.22Cu0.44: mp-7930 |
| Yb0.50Zn0.50: mp-1703 | Zr0.17Cu0.83: mp-30603 | Zr0.33Si0.33Pt0.33: mp-972187 |
| Zn0.25Cu0.50Ni0.25: mp-30593 | Zr0.50Cu0.50: mp-2210 | Zr0.33Ti0.33As0.33: mp-30147 |
| Zn0.25Cu0.25Ni0.50: mp-971738 | Zr0.33Cu0.44Ge0.22: mp-15985 | Zr0.33V0.33P0.33: mp-22302 |
| Zn0.25Ni0.75: mp-971804 | Zr0.20Fe0.40Si0.40: mp-569247 | Zr0.33V0.33Si0.33: mp-5541 |
| Zn0.50Ni0.50: mp-429 | Zr0.33H0.67: mp-24286 | Zr0.50Zn0.50: mp-570276 |
| Zr0.25Al0.25Cu0.50: mp-3736 | Zr0.33H0.67: mp-24155 | Zr0.25Zn0.25Cu0.50: mp-11366 |
| Zr0.25Al0.25Ni0.50: mp-3944 | Zr0.33Mn0.33P0.33: mp-20147 | Zr0.17Zn0.17Ni0.67: mp-11533 |
| Zr0.25Al0.25Rh0.50: mp-977435 | Zr0.50N0.50: mp-1352 | Zr0.25Zn0.25Rh0.50: mp-977582 |
| Zr0.33B0.67: mp-1472 | Zr0.50Os0.50: mp-11541 |  |
| Zr0.33Be0.33Si0.33: mp-10200 | Zr0.50Pt0.50: mp-11554 |  |

## D.1.2 Potentially Functionally Stable Anode Coatings for LSPS

| Ba0.30Li0.70: mp-569841 | Li0.50Al0.50: mp-1067 | Li0.50A10.25Rh0.25: mp-30820 |
| :--- | :--- | :--- |
| Li0.50Ag0.50: mp-2426 | Li0.25Al0.75: mp-975906 | Li0.73As0.27: mp-676620 |
| Li0.25Ag0.75: mp-862716 | Li0.25Al0.75: mp-10890 | Li0.30As0.70: mp-680395 |
| Li0.75Ag0.25: mp-865875 | Li0.25Al0.50Os0.25: mp-982667 | Li0.50As0.50: mp-7943 |
| Li0.75Ag0.25: mp-976408 | Li0.33Al0.33Pt0.33: mp-1025063: | Li0.25Au0.75*: mp-11248 |
| Li0.75Ag0.25: mp-977126 | Li0.50Al0.25Pt0.25: mp-30818 | Li0.75Au0.25: mp-11247 |
| Li0.50Ag0.50: mp-1018026 |  |  |

## Appendix D

| Li0.25Au0.75*: mp-975909 | Li0.75Ga0.25: mp-976025 | Li0.25In0.75: mp-867161 |
| :---: | :---: | :---: |
| Li0.79Au0.21: mp-567395 | Li0.50Ga0.50: mp-1307 | Li0.25In0.75: mp-973748 |
| Li0.50B0.50: mp-1001835 | Li0.50Ga0.25Ir0.25: mp-31441 | Li0.75In0.25: mp-976055 |
| Li0.75Bi0.25: mp-23222 | Li0.50Ga0.25Pt0.25: mp-3726 | Li0.67In0.33: mp-31324 |
| Li0.50Bi0.50: mp-22902 | Li0.50Ga0.25Rh0.25: mp-2988 | Li0.81In0.19: mp-510430 |
| Li0.50Br0.50*: mp-23259 | Li0.75Ge0.25: mp-867342 | Li0.50In0.50: mp-22460 |
| Li0.08C0.92: mp-1021323 | Li0.79Ge0.21: mp-1777 | Li0.50In0.25Rh0.25: mp-31442 |
| Li0.50C0.50: mp-1378 | Li0.50Ge0.50: mp-9918 | Li0.50Ir0.50: mp-279 |
| Li0.14C0.86: mp-1001581 | Li0.50Ge0.50: mp-8490 | Li0.50La0.17As0.33: mp-1018766 |
| Li0.75C0.25: mp-976060 | Li0.65Ge0.35: mp-29631 | Li0.50La0.17P0.33: mp-8407 |
| Li0.50Ca0.25Pb0.25: mp-865892 | Li0.78Ge0.22: mp-29630 | Li0.25Lu0.25O0.50: mp-754537 |
| Li0.50Ca0.25Sn0.25: mp-865964 | Li0.69Ge0.31: mp-27932 | Li0.25Mg0.50Pd0.25: mp-977380 |
| Li0.75Cd0.25: mp-867343 | Li0.25Ge0.25Rh0.50: mp-13322 | Li0.25Mg0.50Pt0.25: mp-864614 |
| Li0.25Cd0.75: mp-973940 | Li0.50H0.50: mp-23703 | Li0.75N0.25: mp-2251 |
| Li0.75Cd0.25: mp-975904 | Li0.50Hf0.50: mp-973948 | Li0.25P0.75*: mp-1025406 |
| Li0.25Co0.50Si0.25: mp-867293 | Li0.75Hg0.25: mp-1646 | Li0.75P0.25: mp-736 |
| Li0.25Cu0.75: mp-862658 | Li0.25Hg0.75: mp-973824 | Li0.50P0.50: mp-9588 |
| Li0.25Cu0.75: mp-974058 | Li0.75Hg0.25: mp-976047 | Li0.12P0.88*: mp-27687 |
| Li0.75Cu0.25: mp-975882 | Li0.25Hg0.75: mp-976599 | Li0.17P0.83: mp-32760 |
| Li0.50Eu0.25Sn0.25: mp-867474 | Li0.50Hg0.50: mp-2012 | Li0.17P0.83: mp-2412 |
| Li0.50F0.50*: mp-1009009 | Li0.50I0.50*: mp-568273 | Li0.30P0.70: mp-28336 |
| Li0.60Ga0.40: mp-9568 | Li0.5010.50*: mp-22899 | Li0.81Pb0.19: mp-574275 |
| Li0.25Ga0.75: mp-867205 | Li0.60In0.40: mp-21293 | Li0.50Pb0.50: mp-2314 |
| Li0.75Ga0.25: mp-976023 | Li0.75In0.25: mp-867226 | Li0.75Pb0.25: mp-30760 |

## Appendix D

| Li0.77Pb0.23: mp-504760 | Li0.20S0.80*: mp-995393 | Li0.78Sn0.22: mp-30767 |
| :---: | :---: | :---: |
| Li0.78Pb0.22: mp-30761 | Li0.67Sb0.33: mp-9563 | Li0.70Sn0.30: mp-30768 |
| Li0.81Pb0.19: mp-573651 | Li0.75Sb0.25: mp-7955 | Li0.50Sn0.50: mp-569073 |
| Li0.73Pb0.27: mp-27587 | Li0.75Sb0.25: mp-2074 | Li0.81Sn0.19: mp-573471 |
| Li0.25Pd0.75: mp-861936 | Li0.73Sb0.27: mp-676024 | Li0.50Sn0.50: mp-13444 |
| Li0.50Pd0.50: mp-2744 | Li0.78Si0.22: mp-27930 | Li0.25Te0.75*: mp-27466 |
| Li0.75Pd0.25: mp-976281 | Li0.67Si0.33: mp-27705 | Li0.71Tl0.29: mp-12283 |
| Li0.75Pd0.25: mp-11489 | Li0.25Si0.75: mp-975321 | Li0.25Tl0.75: mp-973191 |
| Li0.50Pd0.50: mp-2743 | Li0.63Si0.37: mp-1314 | Li0.50T10.50: mp-934 |
| Li0.67Pd0.33: mp-728 | Li0.50Si0.50: mp-795 | Li0.75Tl0.25: mp-7396 |
| Li0.75Pt0.25: mp-867227 | Li0.79Si0.21: mp-569849 | Li0.25Tm0.25O0.50: mp-777047 |
| Li0.50Pt0.50: mp-11807 | Li0.50Si0.50: mp-570363 | Li0.25U0.25N0.50: mp-31066 |
| Li0.67Pt0.33: mp-2170 | Li0.81Si0.19: mp-542598 | Li0.25Zn0.75: mp-865907 |
| Li0.75Pt0.25: mp-976322 | Li0.76Si0.24: mp-672287 | Sr0.33Li0.33P0.33: mp-10614 |
| Li0.75Re0.25: mp-983152 | Li0.81Si0.19: mp-29720 | Sr0.33Li0.33P0.33: mp-13276 |
| Li0.50Rh0.50: mp-600561 | Li0.25Si0.25Ni0.50: mp-10181 | Sr0.25Li0.50Pb0.25: mp-867174 |
| Li0.50S0.50*: mp-32641 | Li0.25Si0.25Rh0.50: mp-867902 | Sr0.25Li0.50Sn0.25: mp-867171 |
| Li0.67S0.33*: mp-557142 | Li0.71Sn0.29: mp-30766 | Yb0.25Li0.50Pb0.25: mp-866180 |
| Li0.67S0.33*: mp-1125 | Li0.29Sn0.71: mp-7924 | Yb0.25Li0.50Sn0.25: mp-866192 |
| Li0.67S0.33*: mp-32899 | Li0.72Sn0.28: mp-30769 |  |

## D.1.3 Functionally Stable Cathode Coatings for LSPS

Ac0.40S0.60*: mp-32800

## Appendix $D$

| Ag1.00*\&: mp-989737 | Ag0.25Ge0.12Pb0.12S0.50*: mp- | Ag0.31P0.15S0.54*: mp-27482 |
| :---: | :---: | :---: |
| Ag1.00*\&: mp-10597 | 861942 | Ag0.33P0.17S0.50*: mp-558469 |
| Ag1.00*\&: mp-8566 | Ag0.53Ge0.07S0.40*: mp-9770 | Ag0.50P0.07Se0.43*: mp-8594 |
| Ag1.00*\&: mp-124 | Ag0.33Ge0.17S0.50*: mp-9900 | Ag0.33P0.17Se0.50*: mp-13956 |
| Ag0.17As0.17Pb0.17S0.50*: mp-22665 | Ag0.53Ge0.07Se0.40*: mp-18474 | Ag0.38P0.12Se0.50*: mp-30908 |
| Ag0.33As0.33S0.33*: mp-984714 | Ag0.53Ge0.07Te0.40*: mp-685969 | Ag0.67S0.33*: mp-32884 |
| Ag0.38As0.12S0.50*: mp-9538 | Ag0.09H0.36W0.09S0.36N0.09*: | Ag0.67S0.33*: mp-32669 |
| Ag0.25As0.25S0.50*: mp-13740 | mp-643431 | Ag0.67S0.33*: mp-556225 |
| Ag0.50As0.07S0.43*: mp-15077 | Ag0.11Hg0.37As0.21I0.32*: mp-23592 | Ag0.67S0.33*: mp-31053 |
| Ag0.43As0.14S0.43*: mp-4431 | Ag0.17Hg0.17As0.17S0.50*: mp-6215 | Ag0.67S0.33*: mp-36216 |
| Ag0.25As0.25S0.50*: mp-542609 | Ag0.29Hg0.07Ge0.14S0.50*: mp- | Ag0.67S0.33*: mp-610517 |
| Ag0.43As0.14S0.43*: mp-555843 | 542199 | Ag0.17Sb0.17Pb0.17S0.50*: mp- |
| Ag0.33As0.33Se0.33*: mp-985442 | Ag0.29Hg0.14I0.57*: mp-570256 | 560848 |
| Ag0.43As0.14Se0.43*: mp-5145 | Ag0.29Hg0.14I0.57*: mp-23485 | Ag0.25Sb0.25S0.50*: mp-3922 |
| Ag0.25Au0.75*\&: mp-985287 | Ag0.25Hg0.25S0.25I0.25*: mp-558446 | Ag0.50Sb0.10S0.40*: mp-4004 |
| Ag0.25Au0.75*\&: mp-867303 | Ag0.25Hg0.25S0.25I0.25*: mp-23140 | Ag0.43Sb0.14S0.43*: mp-4515 |
| Ag0.50Au0.17S0.33*: mp-27554 | Ag0.33Hg0.17S0.17I0.33*: mp-556866 | Ag0.25Sb0.25Se0.50*: mp-33683 |
| Ag0.50Au0.17S0.33*: mp-34460 | Ag0.50I0.50*\&: mp-684580 | Ag0.25Sb0.25Te0.50*: mp-12360 |
| Ag0.10Bi0.10P0.20S0.60*: mp-556434 | Ag0.50I0.50*\&: mp-22925 | Ag0.67Se0.33*: mp-568936 |
| Ag0.10Bi0.10P0.20Se0.60*: mp-569126 | Ag0.50I0.50*\&: mp-567809 | Ag0.67Se0.33*: mp-568971 |
| Ag0.25Bi0.25S0.50*: mp-29678 | Ag0.5010.50*\&: mp-22894 | Ag0.67Se0.33*: mp-754954 |
| Ag0.11Bi0.33S0.56*: mp-23474 | Ag0.33P0.14S0.52*: mp-683910 | Ag0.20Se0.60I0.20*: mp-569052 |
| Ag0.25Bi0.25Se0.50*: mp-27916 | Ag0.38P0.12S0.50*: mp-12459 | Ag0.25Sn0.12Hg0.12Se0.50*: mp- |
| Ag0.25Bi0.25Te0.50*: mp-29656 | Ag0.33P0.17S0.50*: mp-561822 | 10963 |

## Appendix $D$

| Ag0.53Sn0.07S0.40*: mp-15645 | Al0.25F0.75*: mp-468 | Al0.40S0.60*: mp-684638 |
| :---: | :---: | :---: |
| Ag0.53Sn0.07Se0.40*: mp-17984 | Al0.25F0.75*: mp-1323 | Al0.40S0.60*: mp-2654 |
| Ag0.67Te0.33*: mp-1592 | Al0.25F0.75*: mp-555026 | Al0.24Si0.10B0.03O0.62*\&: mp- |
| Ag0.25Te0.75*: mp-28246 | Al0.04H0.62N0.21-10.12*: mp-699469 | 1019381 |
| Ag0.50Te0.50*: mp-568761 | Al0.08H0.50N0.17Cl0.25*: mp-740718 | Al0.08Si0.12H0.32N0.08O0.40*: |
| Ag0.17Te0.67Au0.17*: mp-3291 | Al0.10H0.40N0.10F0.40*: mp-696815 | mp-706243 |
| Ag0.20Te0.60I0.20*: mp-570431 | Al0.36H0.07O0.57* \& : mp-626161 | Al0.25Si0.12O0.62* \& : mp-4753 |
| Ag0.33Te0.17S0.50*: mp-29163 | Al0.29Hg0.14S0.57*: mp-7906 | Al0.25Si0.12O0.62* \&: mp-4934 |
| Al0.25Ag0.25S0.50*: mp-5782 | Al0.29Hg0.14Se0.57*: mp-3038 | Al0.25Si0.12O0.62*\&: mp-5065 |
| Al0.25Ag0.25Se0.50*: mp-14091 | Al0.13Hg0.33Se0.53*: mp-685952 | Al0.18Si0.18O0.64*\&: mp-755043 |
| Al0.33B0.07O0.60*\&: mp-3281 | Al0.20In0.20S0.60*: mp-504482 | Al0.22Si0.11O0.44F0.22*\&: mp-6280 |
| Al0.16B0.24O0.60*\&: mp-31408 | Al0.50N0.50*: mp-661 | Al0.32Tl0.14S0.55*: mp-28759 |
| Al0.21B0.17O0.52F0.10*\&: mp-6738 | Al0.50N0.50*: mp-1700 | Al0.25Tl0.25S0.50*: mp-985477 |
| Al0.29Bi0.14S0.57*: mvc-16098 | Al0.4000.60*\&: mp-7048 | Al0.35Tl0.08S0.57*: mp-28790 |
| Al0.29Bi0.14S0.57*: mp-557737 | Al0.40O0.60*\&: mp-1143 | Al0.25Tl0.25Se0.50*: mp-867359 |
| Al0.29Cd0.14S0.57*: mp-9993 | Al0.4000.60*\&: mp-2254 | Al0.25Tl0.25Se0.50*: mp-9579 |
| Al0.29Cd0.14S0.57*: mp-5928 | Al0.08P0.12H0.35C0.12O0.35*: | Al0.29Zn0.14S0.57*: mp-4842 |
| Al0.29Cd0.14Se0.57*: mp-3159 | mp-556858 | Ar1.00*\&: mp-568145 |
| Al0.25Cu0.25S0.50*: mvc-16090 | Al0.08P0.08H0.36N0.04O0.44*: | Ar1.00*\&: mp-23155 |
| Al0.36Cu0.07S0.57*: mvc-16094 | mp-23819 | As1.00*: mp-158 |
| Al0.36Cu0.07S0.57*: mp-35267 | Al0.17P0.17O0.67*\&: mp-558088 | As1.00*: mp-11 |
| Al0.25Cu0.25S0.50*: mp-4979 | Al0.17P0.17O0.67* \& : mp-667310 | As0.67Ir0.33*: mp-15649 |
| Al0.25F0.75*: mp-559871 | Al0.17P0.17O0.67* \& : mp-683883 | As0.75Ir0.25*: mp-540912 |
| Al0.25F0.75*: mp-8039 | Al0.17P0.17S0.67*: mp-27462 | As0.67Os0.33*: mp-2455 |

## Appendix D

| As0.14Pb0.32S0.54*: mp-27594 | B0.25H0.25O0.50*\&: mp-721851 | Ba0.14Bi0.14B0.14S0.57*: mp-861618 |
| :---: | :---: | :---: |
| As0.22Pb0.22S0.56*: mp-608653 | B0.50N0.50*: mp-7991 | Ba0.13Bi0.26Pb0.04Se0.57*: mp- |
| As0.67Pd0.33*: mp-20465 | B0.50N0.50*: mp-629015 | 669415 |
| As0.33Pd0.33S0.33*: mp-10848 | B0.50N0.50*: mp-13150 | Ba0.14Bi0.29S0.57*: mp-28057 |
| As0.33Pd0.33Se0.33*: mp-10849 | B0.50N0.50*: mp-984 | Ba0.33Br0.67*\&: mp-27456 |
| As0.67Pt0.33*: mp-2513 | B0.50N0.50*: mp-604884 | Ba0.33Br0.33Cl0.33*\&: mp-1012551 |
| As0.75Rh0.25*: mp-8182 | B0.4000.60*: mp-306 | Ba0.22Ca0.11I0.67*: mp-756725 |
| As0.67Rh0.33*: mp-15954 | B0.22Pb0.22S0.56*: mp-662553 | Ba0.14Cd0.14Ge0.14S0.57*: mp-13831 |
| As0.67Ru0.33*: mp-766 | B0.33S0.67*: mp-540668 | Ba0.14Cd0.14Sn0.14S0.57*: mp-12306 |
| As0.50S0.50*: mp-542810 | B0.40S0.60*: mp-572670 | Ba0.33Cl0.67*\&: mp-23199 |
| As0.47S0.53*: mp-31070 | Ba0.12Ag0.25Ge0.12S0.50*: mp-7394 | Ba0.33Cl0.67*\&: mp-568662 |
| As0.57S0.43*: mp-557321 | Ba0.12Ag0.25Ge0.12Se0.50*: mp- | Ba0.12Cu0.25Ge0.12S0.50*: mp-17947 |
| As0.57S0.43*: mp-27543 | 569790 | Ba0.06Cu0.35Ge0.12S0.47*: mp- |
| As0.50S0.50*: mp-542846 | Ba0.07Ag0.57S0.36*: mp-29682 | 556714 |
| As0.50S0.50*: mp-556328 | Ba0.12Ag0.25Sn0.12S0.50*: mp- | Ba 0.12 Cu 0.25 Ge 0.12 Se 0.50 *: mp- |
| As0.40S0.60*: mp-641 | 555166 | 17252 |
| As0.44S0.56*: mp-502 | Ba0.12Ag0.25Sn0.12Se0.50*: mp- | Ba0.12Cu0.25Sn0.12S0.50*: mp-17954 |
| As0.40Se0.60*: mp-909 | 569114 | Ba0.12Cu0.25Sn0.12Se0.50*: mp- |
| As0.50Se0.50*: mp-542570 | Ba0.08Al0.33S0.58*: mp-8258 | 12364 |
| Au1.00*\&: mp-81 | Ba0.14Al0.29S0.57*: mp-14246 | Ba0.12Dy0.08P0.16S0.64*: mp-560798 |
| Au1.00*\&: mp-1008634 | Ba0.22As0.22S0.56*: mp-28134 | Ba0.17Er0.17Cu0.17S0.50*: mp-14969 |
| Au0.67S0.33*: mp-947 | Ba0.05B0.36O0.59*\&: mp-27794 | Ba0.12Er0.08P0.16S0.64*: mp-560534 |
| Au0.50Se0.50*: mp-2793 | Ba0.14B0.29S0.57*: mp-30126 | Ba0.14Ga0.29Se0.57*: mp-7841 |
| Au0.50Se0.50*: mp-570325 | Ba0.14B0.14Sb0.14S0.57*: mp-866301 | Ba0.12Gd0.08P0.16S0.64*: mp-684036 |

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| Ba0.29Ge0.14Se0.57*: mp-11902 | Ba0.20P0.20Se0.60*: mp-11008 | Ba0.26Ta0.14S0.60*: mp-676889 |
| :---: | :---: | :---: |
| Ba0.20Hf0.20S0.60*: mp-998352 | Ba0.14Pd0.29S0.57*: mp-28967 | Ba0.23Ta0.15S0.62*: mp-29354 |
| Ba0.23Hf0.18S0.59*: mp-557032 | Ba0.14Sb0.29S0.57*: mp-28129 | Ba0.20Te0.20S0.60*: mp-27499 |
| Ba0.20Hf0.20S0.60*: mp-998419 | Ba0.14Sb0.29Se0.57*: mp-4727 | Ba0.20Ti0.20S0.60*: mp-7073 |
| Ba0.22Hf0.19S0.59*: mp-554688 | Ba0.33Si0.11S0.56*: mp-27805 | Ba0.29Ti0.14S0.57*: mp-17908 |
| Ba0.25Hg0.25S0.50*: mp-28007 | Ba0.29Si0.14S0.57*: mp-5838 | Ba0.22Ti0.19S0.56O0.04*: mp-555781 |
| Ba0.12Ho0.08P0.16S0.64*: mp-559171 | Ba0.14Sn0.14Hg0.14S0.57*: mp- | $\mathrm{Ba} 0.09 \mathrm{Tm} 0.18 \mathrm{~F} 0.73 * \&: \mathrm{mp}-7693$ |
| Ba0.33I0.67*: mp-23260 | 555954 | Ba0.20V0.20S0.60: mp-555857 |
| Ba0.33I0.67*: mp-568536 | Ba0.29Sn0.14S0.57*: mp-541832 | Ba0.20V0.20S0.60: mp-3451 |
| Ba0.22In0.11Bi0.11S0.56*: mp-864638 | Ba0.25Sn0.17S0.58*: mp-556291 | Ba0.20V0.20S0.60: mp-4227 |
| Ba0.14In0.29S0.57*: mp-21943 | Ba0.29Sn0.14S0.57*: mp-540689 | Ba0.14Y0.29S0.57*: mp-29036 |
| Ba0.14In0.29Se0.57*: mp-21766 | Ba0.25Sn0.12Se0.62*: mp-31307 | Ba0.20Zr0.20S0.60*: mp-540771 |
| Ba0.14La0.07Ag0.36S0.43*: mp- | Ba0.22Sr0.1110.67*: mp-760418 | Be0.14Al0.29O0.57*\&: mp-3081 |
| 553874 | Ba0.11Sr0.22I0.67*: mp-772876 | Be0.06Al0.35O0.59*\&: mp-560974 |
| Ba0.10La0.10Bi0.20S0.60*: mp-555699 | Ba0.22Sr0.11I0.67*: mp-772878 | Be0.11Al0.11Si0.11H0.11O0.56* : |
| Ba0.04Li0.04B0.35O0.58*\&: mp-17672 | Ba0.22Sr0.11I0.67*: mp-756624 | mp-759686 |
| Ba0.04Li0.04B0.35O0.58*\&: mp- | Ba0.22Sr0.11I0.67*: mp-756202 | Be0.10Al0.07Si0.21O0.62*\&: mp-6030 |
| 558890 | Ba0.11Sr0.22I0.67*: mp-754212 | Be0.25B0.12H0.12O0.50*\&: mp-23883 |
| Ba0.14Lu0.29S0.57*: mp-984052 | Ba0.22Sr0.11I0.67*: mp-752397 | Be0.29B0.14O0.43F0.14*\&: mp- |
| $\mathrm{Ba} 0.04 \mathrm{Na} 0.04 \mathrm{~B} 0.35 \mathrm{O} 0.58 * \&: \mathrm{mp}-$ | Ba0.22Sr0.11I0.67*: mp-772875 | 554023 |
| 17864 | Ba0.22Sr0.1110.67*: mp-752671 | Be0.33F0.67*: mp-561543 |
| Ba0.23P0.15S0.62*: mp-561443 | Ba0.25Sr0.08I0.67*: mp-756235 | Be0.33F0.67*: mp-559400 |
| Ba0.20P0.20S0.60*: mp-11006 | Ba0.17Sr0.17I0.67*: mp-754852 | Be0.33F0.67*: mp-558118 |
| Ba0.23P0.15S0.62*: mp-554255 | Ba0.11Sr0.22I0.67*: mp-754224 | Be0.33F0.67*: mp-15951 |

## Appendix D

| Be0.07H0.53N0.13F0.27*: mp-24614 | Bi0.40Se0.60*: mp-541837 | Ca0.06B0.35O0.59*\&: mp-558358 |
| :---: | :---: | :---: |
| Be0.07H0.53N0.13F0.27*: mp-604245 | Bi0.33Se0.33I0.33*: mp-23020 | Ca0.33Cl0.33F0.33*\&: mp-27546 |
| Be0.11H0.44N0.11F0.33*: mp-696961 | Bi0.47Te0.53*: mp-580062 | Ca0.20Er0.10F0.70*\&: mp-532089 |
| Be0.07H0.53N0.13F0.27*: mp-720982 | Bi0.40Te0.60*: mp-34202 | Ca0.33F0.67* \& : mp-2741 |
| Be0.50O0.50*\&: mp-1778 | Bi0.33Te0.33Br0.33*: mp-33723 | Ca0.14Gd0.29S0.57*: mp-36358 |
| Be0.50O0.50*\&: mp-7599 | Bi0.33Te0.33I0.33*: mp-22965 | Ca0.29Ge0.14S0.57*: mp-540773 |
| Be0.50O0.50*\&: mp-2542 | Bi0.33Te0.58Pb0.08*: mp-23005 | Ca0.33I0.67*: mp-30031 |
| Be0.50S0.50*: mp-422 | Bi0.29Te0.57Pb0.14*: mp-676250 | Ca0.14La0.29S0.57*: mp-35421 |
| Be0.24Si0.12H0.12O0.53*\&: mp- | Bi0.40Te0.37S0.23*: mp-557619 | Ca0.14Lu0.29S0.57*: mp-505362 |
| 707304 | Bi0.40Te0.40S0.20*: mp-27910 | Ca0.05Mg0.13Si0.21O0.56F0.05*\&: |
| Be0.25Si0.25N0.50*: mp-15704 | Bi0.40Te0.40Se0.20*: mp-29666 | mp-557662 |
| Be0.25Si0.25N0.50*: mp-7913 | C1.00*: mp-568286 | Ca0.08Mn0.31S0.62*: mvc-93 |
| Be0.29Si0.14O0.57* \& : mp-3347 | C1.00*: mp-937760 | Ca0.14Nd0.29S0.57*: mp-35876 |
| Bi0.25I0.75*: mp-22849 | C1.00*: mp-990448 | Ca0.20P0.20S0.60*: mp-9789 |
| Bi0.25I0.75*: mp-569157 | C1.00*: mp-997182 | Ca0.20P0.20Se0.60*: mp-11007 |
| Bi0.17P0.17S0.67*: mp-27133 | C1.00*: mp-568806 | Ca0.17Pb0.17I0.67*: mp-753670 |
| Bi0.22Pb0.22S0.56*: mp-680181 | C1.00*: mp-606949 | Ca0.17Pb0.17I0.67*: mp-754540 |
| Bi0.18Pb0.27S0.55*: mp-629690 | C1.00*: mp-169 | Ca0.17Pb0.17I0.67*: mp-756451 |
| Bi0.29Pb0.14S0.57*: mp-641924 | C1.00*: mp-48 | Ca0.14Pr0.29S0.57*: mp-34185 |
| Bi0.29Pb0.14Se0.57*: mp-675543 | C1.00*: mp-990424 | Ca0.50S0.50*: mp-1672 |
| Bi0.22Pb0.22Se0.56*: mp-570930 | C1.00*: mp-1040425 | Ca0.22Sb0.22S0.56*: mvc-16380 |
| Bi0.40S0.60*: mp-22856 | Ca0.14Al0.29S0.57*: mp-14422 | Ca0.22Sb0.22S0.56*: mp-29284 |
| Bi0.33S0.33I0.33*: mp-23514 | Ca0.12B0.29Br0.06O0.53* \& : mp- | Ca0.50Se0.50*: mp-1415 |
| Bi0.40Se0.60*: mp-23164 | 554056 | Ca0.14Sm0.29S0.57*: mp-36100 |

## Appendix $D$

| Ca0.29Sn0.14S0.57*: mp-866503 | Cd0.14In0.29Se0.57*: mp-568661 | Ce0.25Mn0.08Al0.08S0.58*: mp- |
| :---: | :---: | :---: |
| Ca0.29Sn0.14S0.57*: mp-866818 | Cd0.50S0.50*: mp-672 | 866500 |
| Ca0.04Ti0.32S0.64*: mvc-16026 | Cd0.50S0.50*: mp-2469 | Ce0.17P0.17S0.67*: mp-561261 |
| Ca0.08Ti0.31S0.62*: mvc-11744 | Cd0.05Sb0.32S0.42I0.21*: mp-560411 | Ce0.17Pa0.17O0.67* \& : mp-686050 |
| Ca0.08Ti0.31S0.62*: mvc-16037 | Cd0.50Se0.50*: mp-2691 | Ce0.40S0.60*: mp-32629 |
| Ca0.14Y0.29S0.57*: mp-18642 | Cd0.50Se0.50*: mp-1070 | Ce0.34S0.66*: mp-645688 |
| Cd0.12Ag0.25Ge0.12S0.50*: mp- | Cd0.12Si0.12Cu0.25S0.50*: mp-6449 | Ce0.33S0.67*: mp-13567 |
| 554105 | Cd0.36Si0.09S0.55*: mp-18179 | Ce0.33S0.67*: mp-1018663 |
| Cd0.07Ag0.29Ge0.14S0.50*: mp- | Cd0.36Si0.09Se0.55*: mp-17791 | Ce0.40S0.60*: mp-20973 |
| 542200 | Ce0.25Ag0.08Ge0.08S0.58*: mp- | Ce0.33S0.67*: mp-20594 |
| Cd0.14Ag0.2910.57*: mp-1025377 | 866604 | Ce0.33S0.33F0.33*: mp-4973 |
| Cd0.12Cu0.25Ge0.12S0.50*: mp-13982 | Ce0.20Cr0.20S0.60*: mp-21871 | Ce0.20Sc0.20S0.60*: mp-20953 |
| Cd0.12Cu0.25Ge0.12Se0.50*: mp- | Ce0.25Cu0.08Ge0.08S0.58*: mp- | Ce0.33Se0.67* : mp-1320 |
| 10967 | 558303 | Ce0.33Se0.67* : mp-1021484 |
| Cd0.12Cu0.25Sn0.12Se0.50*: mp- | Ce0.25Cu0.08Ge0.08Se0.58*: mp- | Ce0.33Se0.67* ${ }^{\text {* }}$ mp-1018665 |
| 16565 | 570564 | Ce0.34Se0.66*: mp-652044 |
| Cd0.25Ga0.12Ag0.12S0.50*: mp-6356 | Ce0.25Cu0.25S0.50*: mp-5766 | Ce0.25Si0.08Ag0.08S0.58*: mp-866605 |
| Cd0.14Ga0.29Se0.57*: mp-3772 | Ce0.25Cu0.08Sn0.08S0.58*: mp- | Ce0.25Si0.08Cu0.08S0.58*: mp-558375 |
| Cd0.36Ge0.09S0.55*: mp-5151 | 510567 | Ce0.25Si0.12S0.62*: mp-558269 |
| Cd0.36Ge0.09Se0.55*: mp-18163 | Ce0.20Dy0.20S0.60*: mp-20775 | Ce0.21Si0.14S0.57Br0.07*: mp-669378 |
| Cd0.09Hg0.36As0.18I0.36*: mp-570838 | Ce0.25Hf0.12S0.62*: mp-985298 | Ce0.21Si0.14S0.57Cl0.07*: mp-542133 |
| Cd0.14In0.29S0.57*: mp-559200 | Ce0.11Lu0.30S0.59*: mp-680039 | Ce0.21Si0.14S0.57I0.07*: mp-555409 |
| Cd0.14In0.29Se0.57*: mp-568032 | Ce0.25Mg0.08Al0.08S0.58*: mp- | Ce0.08Tl0.17P0.17S0.58*: mp-638100 |
| Cd0.14In0.29Se0.57*: mp-22304 | 866517 | Ce0.20Tm0.20S0.60*: mp-541836 |

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| Ce0.20Tm0.20S0.60*: mp-683985 | Co0.33Sb0.33S0.33*: mp-4962 | Cs0.33Ag0.17I0.50*: mp-540881 |
| :---: | :---: | :---: |
| Ce0.25U0.12S0.62*: mp-985558 | Co0.43Se0.57: mp-11800 | Cs0.17Ag0.33I0.50*: mp-23496 |
| Ce0.10Y0.30S0.60*: mp-1006324 | Co0.33Se0.67*: mp-22309 | Cs0.17Ag0.17P0.17Se0.50*: mp-865980 |
| Co0.25As0.75*: mp-452 | Co0.33Se0.67*: mp-20862 | Cs0.17Ag0.50S0.33*: mp-561902 |
| Co0.33As0.67*: mp-1018672 | Co0.33Te0.67*: mp-9945 | Cs0.08Ag0.08Sb0.31S0.54*: mp-554408 |
| Co0.25As0.75*: mp-672216 | Co0.33Te0.67*: mp-1009641 | Cs0.25Ag0.12Sb0.12S0.50*: mp-510710 |
| Co0.33As0.33S0.33*: mp-553946 | Cr0.25Ag0.25S0.50*: mp-4182 | Cs0.17Ag0.17Se0.67*: mp-18105 |
| Co0.33As0.33S0.33*: mp-16363 | Cr0.25Ag0.25Se0.50*: mp-3532 | Cs0.11Ag0.56Se0.33*: mp-10480 |
| Co0.33As0.33S0.33*: mp-4627 | Cr0.25Au0.25S0.50*: mp-7113 | Cs0.17Ag0.50Se0.33*: mp-16234 |
| Co0.33As0.33Se0.33*: mp-505511 | Cr0.29Cd0.14S0.57*: mp-4338 | Cs0.11Ag0.56Te0.33*: mp-9206 |
| $\mathrm{Co0.29Cu0.14S0.57*:} \mathrm{mp-3925}$ | Cr0.29Cu0.14S0.57*: mp-22803 | Cs0.17Al0.17F0.67*\&: mp-572702 |
| Co0.29Ni0.14S0.57*: mp-22658 | Cr0.29Cu0.14Se0.57*: mp-3880 | Cs0.17Al0.17F0.67*\&: mp-14866 |
| Co0.14Ni0.29S0.57*: mp-674355 | Cr0.05H0.6310.08N0.24*: mp-720712 | Cs0.17Al0.17F0.67*\&: mp-554899 |
| Co0.29Ni0.14Se0.57*: mp-1025190 | Cr0.29Hg0.14S0.57*: mp-15973 | Cs0.14Al0.14Si0.14O0.57* \& : mp- |
| Co0.14Ni0.29Se0.57*: mp-1025318 | Cr0.29Hg0.14Se0.57*: mp-5602 | 561457 |
| Co0.25P0.75*: mp-1944 | Cr0.23In0.17S0.60*: mp-676500 | Cs0.10Al0.10Si0.2000.60*\&: mp- |
| Co0.50P0.50*: mp-22270 | Cr0.20Sb0.20S0.60*: mp-9130 | 562920 |
| Co0.33P0.67*: mp-14285 | Cr0.20Sb0.20Se0.60*: mp-15236 | Cs0.09As0.35S0.57*: mp-650280 |
| Co0.33P0.33Pd0.33*: mp-1018673 | Cr0.33Se0.67*: mvc-11653 | Cs0.17As0.33Se0.50*: mp-645172 |
| Co0.33P0.33Se0.33*: mp-10368 | Cr0.33Se0.67*: mp-1009581 | Cs0.25As0.25Se0.50*: mp-581864 |
| Co0.33S0.67*: mp-2070 | Cs0.25Ag0.12As0.12S0.50*: mp- | Cs0.25As0.25Se0.50*: mp-28563 |
| Co0.43S0.57*: mp-943 | 561622 | Cs0.17Au0.50S0.33*: mp-9384 |
| Co0.33S0.67*: mp-850049 | Cs0.14Ag0.29As0.14S0.43*: mp- | Cs0.29Au0.29Se0.43*: mp-29194 |
| Co0.53S0.47*: mp-1513 | 866615 | Cs0.33Au0.33Se0.33*: mp-574599 |

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| Cs0.17Au0.50Se0.33*: mp-9386 | Cs0.20Cd0.20Au0.20S0.40*: mp- | 582708 |
| :---: | :---: | :---: |
| Cs0.20Au0.20Se0.60*: mp-567913 | 560558 | Cs0.14Ge0.14Bi0.14S0.57*: mp-553970 |
| Cs0.07B0.36O0.57*\&: mp-1019710 | Cs0.29Cd0.14I0.57*: mp-568134 | Cs0.22Ge0.22S0.56*: mp-572598 |
| Cs0.07B0.36O0.57*\&: mp-510535 | Cs0.33Cd0.11I0.56*: mp-669317 | Cs0.29Hg0.14I0.57*: mp-28421 |
| Cs0.07B0.36O0.57*\&: mp-581194 | Cs0.17Ce0.17Cu0.17S0.50*: mp- | Cs0.29Hg0.14I0.57*: mp-567594 |
| Cs0.04B0.38O0.58*\&: mp-680683 | 510569 | Cs0.33Hg0.11I0.56*: mp-651121 |
| Cs0.43B0.14S0.43*: mp-30222 | Cs0.25Ce0.25S0.50*: mp-7015 | Cs0.15Hg0.23I0.62*: mp-540574 |
| Cs0.12Ba0.25Br0.62*\&: mp-541722 | Cs0.14Ce0.14Si0.14Se0.57*: mp- | Cs0.13Hg0.40S0.47*: mp-17905 |
| Cs0.06Be0.24B0.18O0.53*\&: mp- | 573969 | Cs0.25Ho0.25S0.50*: mp-505158 |
| 1019718 | Cs0.50Cl0.50*\&: mp-573697 | Cs0.17Ho0.17Zn0.17Se0.50*: mp- |
| Cs0.20Be0.20F0.60*\&: mp-12262 | Cs0.12Cu0.12Bi0.25S0.50*: mp-558907 | 505712 |
| Cs0.12Be0.25F0.62*: mp-27192 | Cs0.17Cu0.17S0.67*: mp-18003 | Cs0.50I0.50*: mp-614603 |
| Cs0.21Bi0.14I0.64*: mp-624214 | Cs0.17Cu0.50S0.33*: mp-7786 | Cs0.17In0.1710.67*: mp-607987 |
| Cs0.21Bi0.14I0.64*: mp-669458 | Cs0.17Cu0.17Se0.67*: mp-17095 | Cs0.07In0.36S0.57*: mp-22007 |
| Cs0.11Bi0.33S0.56*: mp-29531 | Cs0.21Cu0.07Te0.07S0.64*: mp-560345 | Cs0.25In0.25S0.50*: mp-559459 |
| Cs0.14Bi0.32Se0.55*: mp-650619 | Cs0.25Dy0.12Cl0.62*: mp-540695 | Cs0.20K0.10Sc0.10Cl0.60*: mp-571124 |
| Cs0.09Bi0.35Se0.57*: mp-680317 | Cs0.25Dy0.25S0.50*: mp-984555 | Cs0.03K0.16Zn0.12Sn0.16S0.53*: |
| Cs0.11Bi0.33Se0.56*: mp-567928 | Cs0.25Dy0.25S0.50*: mp-9086 | mp-641018 |
| Cs0.50Br0.50*\&: mp-571222 | Cs0.14Er0.14Si0.14S0.57*: mp-16972 | Cs0.30La0.10Cl0.60*\&: mp-582080 |
| Cs0.29Ca0.14Br0.57*\&: mp-1025267 | Cs0.20Ga0.20S0.60*: mp-562726 | Cs0.17La0.17Hg0.17Se0.50*: mp-11124 |
| Cs0.20Ca0.20Br0.60*\&: mp-30056 | Cs0.25Ga0.25S0.50*: mp-5038 | Cs0.25La0.25S0.50*: mp-561586 |
| Cs0.29Ca0.14Cl0.57*\&: mp-1025185 | Cs0.20Ga0.20Se0.60*: mp-510283 | Cs0.11Li0.06Al0.17F0.67*\&: mp-13634 |
| Cs0.20Ca0.20I0.60*: mp-998428 | Cs0.14Gd0.14Si0.14S0.57*: mp-630711 | Cs0.06Li0.06B0.33O0.56*\&: mp- |
| Cs0.20Ca0.20I0.60*: mp-998333 | Cs0.30Ge0.10As0.10Se0.50*: mp- | 1019715 |

## Appendix $D$

| Cs0.06Li0.06B0.33O0.56* \& : mp-5990 | Cs0.20Na0.10Y0.10Br0.60*: mp- | Cs0.36Pb0.09Br0.55*\&: mp-23436 |
| :---: | :---: | :---: |
| Cs0.20Li0.10Lu0.10Cl0.60*: mp- | 571467 | Cs0.20Pb0.20Br0.60*\&: mp-567681 |
| 570379 | Cs0.20Na0.10Y0.10Cl0.60*: mp-23120 | Cs0.20Pb0.20Br0.60*\&: mp-600089 |
| Cs0.20Li0.10Y0.10Cl0.60*: mp-567652 | Cs0.25Nb0.12Ag0.12S0.50*: mp- | Cs0.20Pb0.20Br0.60*\&: mp-567629 |
| Cs0.25Lu0.25S0.50*: mp-561619 | 623028 | Cs0.20Pb0.20I0.60*: mp-540839 |
| Cs0.02Mg0.07Al0.15Si0.15O0.61*\&: | Cs0.25Nb0.12Ag0.12Se0.50*: mp- | Cs0.22Pd0.33S0.44*: mp-510268 |
| mp-695133 | 14637 | Cs0.22Pd0.33Se0.44*: mp-11694 |
| Cs0.01Mg0.07Al0.14Si0.17O0.62*\&: | Cs0.18Nb0.12As0.06Se0.65*: mp- | Cs0.18Pd0.09Se0.73*: mp-31285 |
| mp-695172 | 683903 | Cs0.17Pr0.17Hg0.17Se0.50*: mp-7211 |
| Cs0.20Mg0.20Br0.60*: mp-29750 | Cs0.25Nb0.12Cu0.12Se0.50*: mp- | Cs0.25Pr0.25S0.50*: mp-9037 |
| Cs0.25Mg0.17Cl0.58*: mp-568137 | 15223 | Cs0.25Pr0.25S0.50*: mp-9080 |
| Cs0.20Mg0.20Cl0.60*: mp-23004 | Cs0.07Nb0.14P0.07S0.71*: mp-641699 | Cs0.22Pt0.33S0.44*: mp-13992 |
| Cs0.29Mg0.14Cl0.57*: mp-568909 | Cs0.19Nb0.12S0.69*: mp-669313 | Cs0.17Pt0.33Se0.50*: mp-573316 |
| Cs0.10Mg0.05Si0.25O0.60*\&: mp- | Cs0.30Nd0.10Cl0.60* \& : mp-582081 | Cs0.09Pu0.09P0.18S0.64*: mp-680370 |
| 1019610 | Cs0.21Nd0.07P0.14S0.57*: mp-572442 | Cs0.17Re0.26S0.57*: mp-652494 |
| Cs0.18Mn0.09P0.18Se0.55*: mp- | Cs0.22Ni0.33S0.44*: mp-28486 | Cs0.22Re0.22S0.56*: mp-653954 |
| 867332 | Cs0.17Np0.17Cu0.17S0.50*: mp- | Cs0.50S0.50*: mp-29266 |
| Cs0.29Mo0.14S0.57*: mp-560635 | 862802 | Cs0.21Sb0.14I0.64*: mp-23029 |
| Cs0.11Na0.06Al0.17F0.67*\&: mp- | Cs0.14P0.14Pb0.14S0.57*: mp-562569 | Cs0.21Sb0.14I0.64*: mp-541014 |
| 12309 | Cs0.27P0.13Pd0.07Se0.53*: mp-866688 | Cs0.10Sb0.34S0.56*: mp-642535 |
| Cs0.20Na0.10Er0.10Cl0.60*: mp- | Cs0.20P0.20S0.60*: mp-504838 | Cs0.25Sb0.25S0.50*: mp-561639 |
| 580589 | Cs0.38P0.12Se0.50*: mp-583193 | Cs0.15Sb0.31S0.54*: mp-27146 |
| Cs0.20Na0.10Ho0.10Cl0.60*: mp- | Cs0.27P0.13Se0.60*: mp-569193 | Cs0.12Sb0.12S0.75*: mp-28701 |
| 542951 | Cs0.25P0.12Se0.62*: mp-569060 | Cs0.14Sb0.29S0.57*: mp-8890 |

## Appendix $D$

| Cs0.14Sb0.29Se0.57*: mp-3312 | Cs0.20Sn0.20Se0.60*: mp-613162 | Cs0.11Ti0.11Cu0.33Se0.44*: mp- |
| :---: | :---: | :---: |
| Cs0.38Sb0.12Se0.50*: mp-17811 | Cs0.20Sr0.20Br0.60*\&: mp-998297 | 570706 |
| Cs0.25Sb0.25Se0.50*: mp-2969 | Cs0.20Sr0.20Br0.60*\&: mp-998433 | Cs0.08Ti0.08P0.17S0.67*: mp-645687 |
| Cs0.29Se0.71*: mp-541055 | Cs0.20Sr0.20Cl0.60*\&: mp-998561 | Cs0.33Ti0.17S0.50*: mp-3247 |
| Cs0.40Se0.60*: mp-7449 | Cs0.20Sr0.20I0.60*: mp-998417 | Cs0.19Ti0.14S0.67*: mp-542011 |
| Cs0.10Si0.20B0.10O0.60*\&: mp- | Cs0.25Ta0.12Ag0.12S0.50*: mp-15218 | Cs0.15Ti0.15S0.69*: mp-680170 |
| 1019719 | Cs0.12Ta0.12Ge0.12S0.62*: mp-865606 | Cs0.25Tm0.25S0.50*: mp-9089 |
| Cs0.14Si0.14Bi0.14S0.57*: mp-558426 | Cs0.11Ta0.11P0.11S0.67*: mp-553976 | Cs0.17Tm0.17Zn0.17Se0.50*: mp- |
| Cs0.22Si0.22Se0.56*: mp-542550 | Cs0.11Ta0.11P0.11S0.67*: mp-555592 | 505713 |
| Cs0.44Si0.11Se0.44*: mp-29834 | Cs0.19Ta0.12S0.69*: mp-556091 | Cs0.17U0.17Ag0.17S0.50*: mp-13346 |
| Cs0.29Si0.14Se0.57*: mp-637251 | Cs0.38Ta0.12S0.50*: mp-17054 | Cs0.17U0.17Ag0.17Se0.50*: mp- |
| Cs0.21Sm0.07P0.14S0.57*: mp-572833 | Cs0.17Tc0.26S0.57*: mp-579058 | 510662 |
| Cs0.14Sm0.14Si0.14S0.57*: mp-561635 | Cs0.40Te0.60*: mp-505634 | Cs0.17U0.17Cu0.17S0.50*: mp-13348 |
| Cs0.14Sn0.07As0.14Se0.64*: mp- | Cs0.13Te0.87*: mp-505464 | Cs0.17U0.17Cu0.17Se0.50*: mp-7151 |
| 568403 | Cs0.12Te0.88*: mp-620471 | Cs0.25V0.12Ag0.12S0.50*: mp-8684 |
| Cs0.22Sn0.11Au0.22S0.44*: mp- | Cs0.33Te0.33Au0.33*: mp-573755 | Cs0.09V0.09P0.18S0.64*: mp-12324 |
| 561641 | Cs0.20Te0.20Se0.60*: mp-9462 | Cs0.29W0.14S0.57*: mp-17361 |
| Cs0.13Sn0.13Hg0.20S0.53*: mp-561185 | Cs0.22Th0.11Cl0.67*: mp-27501 | Cs0.17Y0.17Zn0.17Se0.50*: mp-574620 |
| Cs0.20Sn0.20I0.60*: mp-614013 | Cs0.13Th0.07P0.20S0.60*: mp-640389 | Cs0.22Zn0.33S0.44*: mp-505633 |
| Cs0.20Sn0.20I0.60*: mp-568570 | Cs0.14Th0.07P0.18Se0.61*: mp- | Cs0.17Zr0.17Cu0.17Se0.50*: mp-7152 |
| Cs0.20Sn0.20I0.60*: mp-616378 | 680198 | Cs0.19Zr0.14S0.67*: mp-680246 |
| Cs0.20Sn0.20I0.60*: mp-27381 | Cs0.22Ti0.11Ag0.22S0.44*: mp-10488 | Cs0.19Zr0.14Se0.67*: mp-768674 |
| Cs0.20Sn0.20S0.60*: mp-561710 | Cs0.13Ti0.15Ag0.03Se0.69*: mp-16000 | Cu0.14Ag0.02Bi0.29Pb0.02S0.52*: |
| Cs0.12Sn0.06S0.82*: mp-505141 | Cs0.22Ti0.11Cu0.22Se0.44*: mp-10489 | mp-651706 |

## Appendix D

| Cu0.33Ag0.33S0.33*: mp-8911 | Cu0.25Bi0.25S0.50*: mp-22982 | Cu0.50S0.50*: mp-555599 |
| :---: | :---: | :---: |
| Cu0.33Ag0.33S0.33*: mp-5014 | Cu0.21Bi0.26S0.53*: mp-27124 | Cu0.17Sb0.17Pb0.17S0.50*: mp- |
| Cu0.17As0.17Pb0.17S0.50*: mp- | Cu0.24Bi0.24S0.53*: mp-559551 | 649774 |
| 628643 | Cu0.33Ge0.17S0.50*: mp-15252 | Cu0.40Sb0.14S0.46*: mp-686109 |
| Cu0.38As0.12S0.50*: mp-20545 | Cu0.44Ge0.11S0.44*: mp-565590 | Cu0.38Sb0.12S0.50*: mp-22171 |
| Cu0.32As0.21S0.47*: mp-28717 | Cu0.33Ge0.17Se0.50*: mp-4728 | Cu0.43Sb0.14S0.43*: mp-17691 |
| Cu0.38As0.12S0.50*: mp-3345 | Cu0.33Ge0.17Se0.50*: mp-677105 | Cu0.25Sb0.25S0.50*: mp-4468 |
| Cu0.41As0.14S0.45*: mp-504753 | Cu0.38Ge0.06W0.06S0.50*: mp- | Cu0.43Sb0.14S0.43*: mp-554272 |
| Cu0.33As0.33S0.33*: mp-5305 | 557225 | Cu0.38Sb0.12S0.50*: mp-5702 |
| Cu0.38As0.12Se0.50*: mp-675626 | Cu0.24Hg0.12As0.16S0.48*: mp-6287 | Cu0.41Sb0.14S0.45*: mp-647164 |
| Cu0.33As0.33Se0.33*: mp-574367 | Cu0.25Hg0.12Ge0.12S0.50*: mp-10952 | Cu0.38Sb0.12Se0.50*: mp-9814 |
| Cu0.25Au0.75*: mp-2103 | Cu0.25Hg0.12Ge0.12S0.50*: mp- | Cu0.25Sb0.25Se0.50*: mp-20331 |
| Cu0.17Au0.17Se0.67*: mp-30151 | 557574 | Cu0.49Se0.51*: mp-684923 |
| Cu0.25B0.25S0.50*: mp-12954 | Cu0.25Hg0.12Ge0.12Se0.50*: mp- | Cu0.60Se0.40*: mp-20683 |
| Cu0.10Bi0.10P0.20Se0.60*: mp-569715 | 12855 | Cu0.33Se0.67*: mp-2280 |
| Cu0.10Bi0.10P0.20Se0.60*: mp-683998 | Cu0.25Hg0.25S0.25I0.25*: mp-542426 | Cu0.50Se0.50*: mp-488 |
| Cu0.07Bi0.30Pb0.07S0.56*: mp-680461 | Cu0.14Ir0.29S0.57*: mp-15065 | Cu0.50Se0.50*: mp-571486 |
| Cu0.06Bi0.31Pb0.06S0.56*: mp-642316 | Cu0.38P0.12S0.50*: mp-3934 | Cu0.53Se0.47*: mp-673255 |
| Cu0.12Bi0.24Pb0.12S0.53*: mp-652196 | Cu0.38P0.12Se0.50*: mp-5756 | Cu0.33Se0.67*: mp-2000 |
| Cu0.11Bi0.25Pb0.11S0.54*: mp-680135 | Cu0.14Pt0.29S0.57*: mp-28888 | Cu 0.25 Sn 0.12 Hg 0.12 S 0.50 *: mp- |
| Cu0.09Bi0.27Pb0.09S0.55*: mp-542302 | Cu0.14Rh0.29S0.57*: mp-15613 | 1025467 |
| Cu0.17Bi0.17Pb0.17S0.50*: mp-624191 | Cu0.14Rh0.29Se0.57*: mp-15614 | Cu 0.25 Sn 0.12 Hg 0.12 Se 0.50 * $\mathrm{mp}-$ |
| Cu0.06Bi0.23Pb0.17S0.54*: mp-669445 | Cu0.50S0.50*: mp-760381 | 16566 |
| Cu0.17Bi0.17Pt0.17S0.50*: mp-865018 | Cu0.50S0.50*: mp-504 | Cu0.15Sn0.26S0.59*: mp-530411 |

## Appendix $D$

| Cu0.33Sn0.17S0.50*: mp-10519 | Er0.33Se0.33F0.33*: mp-27123 | Fe0.33As0.67: mp-2008 |
| :---: | :---: | :---: |
| Cu0.44Sn0.11S0.44*: mp-504536 | Er0.25Si0.08Cu0.08S0.58*: mp-558980 | Fe0.33As0.33S0.33*: mp-561511 |
| Cu0.15Sn0.26S0.59*: mp-675137 | Er0.25Tl0.25S0.50*: mp-4123 | Fe0.14Ni0.29S0.57*: mp-673824 |
| Cu0.33Sn0.17Se0.50*: mp-11658 | Er0.25Tl0.25Se0.50*: mp-570117 | Fe0.33S0.67*: mp-226 |
| Cu0.29W0.14S0.57*: mp-557373 | Eu0.17Dy0.17Cu0.17S0.50*: mp- | Fe0.33S0.67*: mp-1522 |
| Cu0.29W0.14S0.57*: mp-8976 | 542765 | Fe0.33Se0.67*: mp-760 |
| Cu0.29W0.14Se0.57*: mp-1025340 | Eu0.14Gd0.29S0.57*: mp-675143 | Ga0.25Ag0.25S0.50*: mp-556916 |
| Dy0.29Cd0.14S0.57*: mp-16267 | Eu0.20K0.10Cu0.10S0.60*: mp-680171 | Ga0.25Ag0.25S0.50*: mp-5342 |
| Dy0.10Cr0.30S0.60*: mp-530588 | Eu0.07K0.27P0.13S0.53*: mp-669560 | Ga0.25Ag0.25Se0.50*: mp-5518 |
| Dy0.10Cr0.30S0.60*: mp-532220 | Eu0.14K0.14P0.14Se0.57*: mp-10382 | Ga0.06Ag0.56Se0.38*: mp-27163 |
| Dy0.25Cu0.08Ge0.08S0.58*: mp- | Eu0.25Na0.25S0.50*: mp-1007910 | Ga0.25Cu0.25S0.50*: mp-5238 |
| 558740 | Eu0.14Nd0.29S0.57*: mp-37693 | Ga0.25Cu0.25Se0.50*: mp-4840 |
| Dy0.25Cu0.08Sn0.08S0.58*: mp- | Eu0.20P0.20S0.60*: mp-20217 | Ga0.29Hg0.14Se0.57*: mp-4730 |
| 561499 | Eu0.20P0.20Se0.60*: mp-20742 | Gd0.25Cu0.08Ge0.08S0.58*: mp- |
| Dy0.17P0.17S0.67*: mp-5241 | Eu0.12Pd0.38S0.50*: mp-20961 | 573114 |
| Dy0.40S0.60*: mp-32826 | Eu0.14Pr0.29S0.57*: mp-34309 | Gd0.25Cu0.08Ge0.08Se0.58*: mp- |
| Dy0.35Se0.65*: mp-32633 | Eu0.50S0.50*: mp-20587 | 568189 |
| Dy0.25Si0.08Cu0.08S0.58*: mp-557998 | Eu0.19Sb0.25S0.56*: mp-684111 | Gd0.25Cu0.25S0.50*: mp-510471 |
| Dy0.21Si0.16S0.63*: mp-10771 | Eu0.29Si0.14S0.57*: mp-22504 | Gd0.25Cu0.25Se0.50*: mp-510528 |
| Dy0.25Tl0.25S0.50*: mp-31166 | Eu0.29Sn0.14S0.57*: mp-632490 | Gd0.25Cu0.08Sn0.08S0.58*: mp- |
| Dy0.25Tl0.25Se0.50*: mp-568062 | Eu0.25Sn0.17S0.58*: mp-504621 | 556782 |
| Er0.10Ag0.10P0.20Se0.60*: mp-13384 | Eu0.14Tl0.14P0.14S0.57*: mp-657233 | Gd0.25Cu0.08Sn0.08Se0.58*: mp- |
| Er0.29Cd0.14S0.57*: mp-3041 | Eu0.17Tm0.17Cu0.17S0.50*: mp- | 568811 |
| Er0.25F0.75*\&: mp-9371 | 12728 | Gd0.10Lu0.30S0.60*: mp-22563 |

## Appendix $D$

| Gd0.17Pa0.17O0.67*\&: mp-37014 | Ge0.33S0.67*: mp-542613 | H0.67S0.33*: mp-721582 |
| :---: | :---: | :---: |
| Gd0.40S0.60*: mp-669509 | Ge0.33S0.67*: mp-553973 | H0.53S0.33N0.13*: mp-28143 |
| Gd0.40S0.60*: mp-608146 | Ge0.33S0.67*: mp-7582 | H0.53W0.07S0.27N0.13*: mp-697283 |
| Gd0.34S0.66*: mp-646008 | Ge0.08Sb0.33Te0.58*: mp-29641 | He1.00*\&: mp-754382 |
| Gd0.40S0.60*: mp-684712 | Ge0.50Se0.50*: mp-10759 | He1.00*\&: mp-23156 |
| Gd0.33S0.33F0.33*: mp-3799 | Ge0.33Se0.67*: mp-540625 | He1.00* \& : mp-614456 |
| Gd0.33S0.3310.33*: mp-556135 | Ge0.33Se0.67*: mp-10074 | He1.00*\&: mp-23158 |
| Gd0.40S0.56O0.04*: mp-556437 | Ge0.31Se0.69*: mp-680333 | Hf0.33O0.67* : mp-776532 |
| Gd0.33Se0.67*: mp-1018707 | Ge0.08Te0.58As0.33*: mp-8645 | Hf0.33O0.67*\&: mp-352 |
| Gd0.25Si0.08Cu0.08Se0.58*: mp- | H0.67Br0.17N0.17*: mp-23675 | Hf0.33O0.67* ${ }^{\text {P }}$ : mp-1858 |
| 641576 | H0.67Br0.17N0.17*: mp-36248 | Hf0.33O0.67* : mp-775757 |
| Gd0.25Sn0.12S0.62*: mp-561122 | H0.80C0.20*: mp-1021328 | Hf0.20Pb0.20S0.60*: mp-22147 |
| Gd0.25T10.25S0.50*: mp-557655 | H0.55C0.09N0.27Cl0.09*: mp-707023 | Hf0.33S0.67*: mp-985829 |
| Gd0.25Tl0.25Se0.50*: mp-569393 | H0.41C0.18N0.35Cl0.06*: mp-761870 | Hf0.25S0.75*: mp-9922 |
| Ge0.08Bi0.33Te0.58*: mp-29644 | H0.50C0.12S0.12N0.25*: mp-23930 | Hf0.33S0.33O0.33*: mp-7787 |
| Ge0.14Pb0.29S0.57*: mp-531296 | H0.50C0.12S0.12N0.25*: mp-721896 | Hf0.17Si0.17O0.67* \& : mp-4609 |
| Ge0.14Pb0.29S0.57*: mp-560370 | H0.50C0.12S0.12N0.25*: mp-735023 | Hf0.20Sn0.20S0.60*: mp-8725 |
| $\mathrm{Ge} 0.20 \mathrm{~Pb} 0.20 \mathrm{S0.60}$ *: mp-624190 | H0.67I0.17N0.17*: mp-34381 | Hf0.17Te0.17Se0.67*: mp-989651 |
| Ge0.33Pd0.67*: mp-423 | H0.67I0.17N0.17*: mp-643062 | Hf0.17Tl0.17Cu0.17S0.50*: mp-9396 |
| Ge0.20Pd0.20S0.60*: mp-541785 | H0.70I0.10N0.20*: mp-721084 | Hf0.17Tl0.17Cu0.17Se0.50*: mp-9397 |
| Ge0.33Pt0.33Se0.33*: mp-20817 | H0.67N0.17Cl0.17*: mp-34337 | Hf0.20Tl0.13Cu0.13Se0.53*: mp- |
| Ge0.38Rh0.25Se0.38*: mp-976401 | H0.67N0.17F0.17*: mp-23794 | 570700 |
| Ge0.33S0.67*: mp-572892 | H0.67S0.33*: mp-696805 | Hg1.00*: mp-864900 |
| Ge0.33S0.67*: mp-622213 | H0.67S0.33*: mp-33024 | Hg1.00*: mp-1017981 |

## Appendix $D$

| Hg1.00*: mp-569289 | Hg0.50S0.50*: mp-973676 | In0.18Ag0.18Ge0.09Se0.55*: mp- |
| :---: | :---: | :---: |
| Hg1.00*: mp-10861 | Hg0.43S0.29I0.29*: mp-29956 | 505607 |
| Hg1.00*: mp-975272 | Hg0.38Sb0.12As0.12S0.38*: mp- | In0.10Ag0.10P0.20Se0.60*: mp-20902 |
| Hg1.00*: mp-982872 | 554950 | In0.25Ag0.25S0.50*: mp-21459 |
| Hg1.00*: mp-753304 | Hg0.44Sb0.22I0.33*: mp-29043 | In0.36Ag0.07S0.57*: mp-36751 |
| Hg1.00*: mp-121 | Hg0.08Sb0.31S0.62*: mp-542596 | In0.25Ag0.25S0.50*: mp-19833 |
| Hg1.00*: mp-569360 | Hg0.50Se0.50*: mp-820 | In0.25Ag0.25Se0.50*: mp-20554 |
| Hg0.40As0.10I0.50*: mp-567798 | Hg0.43Se0.29I0.29*: mp-29955 | In0.36Ag0.07Se0.57*: mp-571103 |
| Hg0.44As0.22I0.33*: mp-28590 | Hg0.43Se0.29I0.29*: mp-571404 | In0.25Ag0.25Te0.50*: mp-22386 |
| Hg0.09As0.36S0.36I0.18*: mp-554735 | Hg0.50Te0.50*: mp-2730 | In0.14As0.14Pd0.71*: mp-1025293 |
| Hg0.33As0.11Se0.44I0.11*: mp-570084 | Hg0.43Te0.29I0.29*: mp-28579 | In0.09Bi0.17Pb0.17S0.57*: mp-650840 |
| Hg0.45Au0.55*: mp-1812 | Ho0.10B0.30O0.60* \& : mp-680713 | In0.25Bi0.15S0.60*: mp-504646 |
| Hg0.14Bi0.29S0.57*: mp-554921 | Ho0.29Cd0.14S0.57*: mp-6942 | In0.27Bi0.13S0.60*: mp-27195 |
| Hg0.29Ge0.14Se0.57*: mp-3167 | Ho0.25Cu0.08Ge0.08S0.58*: mp- | In0.36Cu0.07S0.57*: mp-674514 |
| Hg0.50I0.50*: mp-22859 | 555509 | In0.25Cu0.25S0.50*: mp-22736 |
| Hg0.33I0.67*: mp-583213 | Ho0.25F0.75*\&: mp-561877 | In0.25Cu0.25Se0.50*: mp-22811 |
| Hg0.33I0.67*: mp-568742 | Ho0.33S0.33F0.33*: mp-10931 | In0.20Ga0.10Bi0.10S0.60*: mp-556231 |
| Hg0.33I0.67*: mp-567471 | Ho0.35Se0.65*: mp-32833 | $\mathrm{In} 0.29 \mathrm{Hg} 0.14 \mathrm{~S} 0.57^{*}: \mathrm{mp}-22356$ |
| Hg0.33I0.67*: mp-23192 | Ho0.25Si0.08Cu0.08S0.58*: mp-17486 | In0.29Hg0.14Se0.57*: mp-20731 |
| $\mathrm{Hg} 0.14 \mathrm{P} 0.14 \mathrm{Pd} 0.71^{*}: \mathrm{mp}-1025302$ | Ho0.10Sn0.15Pb0.15S0.60*: mp- | In0.29Hg0.14Te0.57*: mp-19765 |
| Hg0.29Pb0.14S0.29I0.29*: mp-557605 | 559287 | In0.14P0.14Pd0.71*: mp-1025161 |
| Hg0.50S0.50*: mp-634 | Ho0.25Tl0.25S0.50*: mp-1007665 | In0.17P0.17S0.67*: mp-20790 |
| Hg0.50S0.50*: mp-1123 | Ho0.25Tl0.25Se0.50*: mp-569178 | In0.27Pb0.16S0.57*: mp-622755 |
| Hg0.50S0.50*: mp-9252 | In0.18Ag0.18Ge0.09S0.55*: mp-560386 | In0.30Pb0.13S0.57*: mp-21934 |

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| In0.29Pb0.14S0.57*: mp-619279 | K0.25Ag0.12Sb0.12S0.50*: mp-553923 | K0.25Au0.25Se0.50*: mp-29138 |
| :---: | :---: | :---: |
| In0.27Pb0.16S0.57*: mp-662823 | K0.12Ag0.25Sb0.12S0.50*: mp-9490 | K0.33Au0.33Se0.33*: mp-9881 |
| In0.40S0.60*: mp-22216 | K0.17Ag0.50Se0.33*: mp-9782 | K0.14Au0.14Se0.71*: mp-3257 |
| In0.20Sb0.20S0.60*: mp-21365 | K0.22Ag0.44Se0.33*: mp-573891 | K0.18Au0.06Se0.76*: mp-28606 |
| In0.12Sb0.25S0.50Br0.12*: mp-559864 | K0.10Ag0.29Sn0.14S0.48*: mp-559880 | K0.15B0.30Br0.05O0.50* \& : mp-23612 |
| In0.12Sb0.25Se0.50Br0.12*: mp- | K0.20Ag0.07Sn0.20Se0.53*: mp- | K0.09B0.35O0.56* \& : mp-554996 |
| 570321 | 571594 | K0.11B0.33O0.56* \& : mp-559636 |
| In0.40Se0.60*: mp-612740 | K0.22Ag0.22Sn0.11Se0.44*: mp- | K0.07B0.36O0.57* \& : mp-12183 |
| In0.33Se0.33I0.33*: mp-505357 | 570887 | K0.25B0.25S0.50*: mp-15012 |
| In0.18Si0.09Ag0.18S0.55*: mp-558407 | K0.11Al0.04B0.30O0.56* \& mp- | K0.18B0.18S0.64*: mp-4351 |
| In0.18Si0.09Ag0.18Se0.55*: mp-640614 | 561447 | K0.04Ba0.04Al0.12Si0.19O0.62* ${ }^{*}$ : |
| In0.31Sn0.08S0.62*: mp-675124 | K0.03Al0.38O0.59*\&: mp-760755 | mp-677121 |
| Ir0.33S0.67*: mp-2833 | K0.04Al0.38O0.58*\&: mp-1019803 | K0.14Ba0.14Nb0.14S0.57*: mp-16780 |
| Ir0.33Se0.67*: mp-1361 | K0.10Al0.10Si0.20O0.60* \& mp- | K0.14Ba0.14P0.14S0.57*: mp-17088 |
| Ir0.27Se0.73*: mp-9888 | 554433 | K0.14Ba0.14P0.14Se0.57*: mp-18156 |
| K0.09Ag0.27As0.18S0.45*: mp-561304 | K0.08Al0.08Si0.23O0.62* \& mp- | K0.27Ba0.07V0.13S0.53*: mp-558121 |
| K0.26Ag0.11As0.16Se0.47*: mp- | 697670 | K0.08Be0.15B0.23O0.54* : mp- |
| 570836 | K0.12Al0.12Si0.18O0.59* \& mp- | 1019808 |
| K0.17Ag0.08As0.25Se0.50*: mp- | 1019744 | K0.08Be0.15B0.23O0.54* : mp- |
| 541915 | K0.25As0.12Au0.12S0.50*: mp-9511 | 1019809 |
| K0.22Ag0.22Ge0.11S0.44*: mp-558500 | K0.25As0.25Se0.50*: mp-14659 | K0.08Be0.08Si0.24O0.60*\&: mp- |
| K0.33Ag0.17I0.50*: mp-569943 | K0.14Au0.14S0.71*: mp-3592 | 561549 |
| K0.12Ag0.25P0.12S0.50*: mp-12532 | K0.27Au0.40S0.33*: mp-29341 | K0.14Bi0.05As0.27Se0.55*: mp-865961 |
| K0.17Ag0.50S0.33*: mp-18577 | K0.33Au0.33S0.33*: mp-7077 | K0.09Bi0.09P0.18S0.64*: mp-23572 |

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| K0.30Bi0.03P0.13S0.53*: mp-554554 | K0.13Cu0.07P0.20S0.60*: mp-559644 | K0.12Gd0.25Cu0.12S0.50*: mp-15553 |
| :---: | :---: | :---: |
| K0.10Bi0.10P0.20S0.60*: mp-557437 | K0.17Cu0.17P0.17Se0.50*: mp-568611 | K0.12Gd0.12P0.15S0.62*: mp-604889 |
| K0.21Bi0.07P0.14S0.57*: mp-554216 | K0.11Cu0.11P0.22Se0.56*: mp-622199 | K0.25Gd0.25S0.50*: mp-15784 |
| K0.10Bi0.10P0.20Se0.60* : mp-568802 | K0.12Cu0.12Pd0.12Se0.62*: mp-11114 | K0.17Ge0.17Au0.17S0.50*: mp-554859 |
| K0.10Bi0.10P0.20Se0.60*: mp-569435 | K0.12Cu0.50Se0.38*: mp-10092 | K0.14Ge0.14Bi0.14S0.57*: mp-866646 |
| K0.09Bi0.35Se0.57* : mp-28800 | K0.20Cu0.40Se0.40*: mp-567657 | K0.18Ge0.18Pb0.09S0.55*: mp-561132 |
| K0.50Br0.50* \& : mp-23251 | K0.21Dy0.07As0.14S0.57*: mp-866661 | K0.22Ge0.22S0.56*: mp-541878 |
| K0.20Ca0.20Br0.60* \& : mp-998599 | K0.11Dy0.21Cu0.21S0.47* : mp-680676 | K0.33Ge0.17Se0.50*: mp-9692 |
| K0.20Ca0.20Cl0.60* \& : mp-998421 | K0.25Dy0.25S0.50*: mp-15785 | K0.29Ge0.14Se0.57*: mp-29022 |
| K0.18Cd0.09Au0.36S0.36*: mp-557832 | K0.30Er0.10Cl0.60*: mp-30197 | K0.22Ge0.22Se0.56*: mp-29388 |
| K0.10Ce0.20Cu0.10Se0.60*: mp- | K0.07Er0.21F0.71*\&: mp-683945 | K0.22Ge0.22Se0.56*: mp-569826 |
| 669330 | K0.07Er0.21F0.71*\&: mp-18451 | K0.33H0.33S0.33*: mp-38011 |
| K0.14Ce0.14Ge0.14Se0.57*: mp-21176 | K0.10Er0.20F0.70* \& : mp-27925 | K0.33H0.33S0.33*: mp-634676 |
| K0.21Ce0.07P0.14S0.57* : mp-21557 | K0.10Er0.20F0.70* \& : mp-558238 | K0.17Hf0.17Cu0.17S0.50*: mp-9855 |
| K0.25Ce0.25S0.50*: mp-7329 | K0.09Er0.09P0.18S0.64*: mp-554741 | K0.13Hg0.20Ge0.13S0.53*: mp-17792 |
| K0.14Ce0.14Si0.14S0.57*: mp-11170 | K0.25Er0.25S0.50*: mp-4326 | K0.13Hg0.20Ge0.13S0.53*: mp-11131 |
| K0.14Ce0.14Si0.14S0.57*: mp-22809 | K0.14Eu0.14As0.14S0.57*: mp-867419 | K0.13Hg0.20Ge0.13Se0.53*: mp-17307 |
| K0.50Cl0.50* \& : mp-23193 | K0.17Eu0.17As0.17S0.50*: mp-646548 | K0.18Hg0.09P0.18Se0.55*: mp-568855 |
| K0.15Cr0.10P0.15S0.60*: mp-559251 | K0.22Eu0.11Ge0.11Se0.56*: mp- | K0.17Hg0.17Sb0.17S0.50*: mp-6678 |
| K0.09Cr0.09P0.18S0.64*: mp-7147 | 628810 | K0.11Ho0.11Be0.11F0.67* \& : mp- |
| K0.10Cu0.40As0.10S0.40*: mp-557728 | K0.14Eu0.14P0.14S0.57*: mp-628735 | 558826 |
| K0.14Cu0.29As0.14S0.43*: mp-554421 | K0.14Eu0.14P0.14Se0.57*: mp-628715 | K0.12Ho0.25Cu0.12S0.50*: mp-11606 |
| K0.12Cu0.12Bi0.25S0.50*: mp-558063 | K0.17Ga0.25Cu0.08Se0.50*: mp-10973 | K0.11Ho0.21Cu0.21S0.47*: mp-680679 |
| K0.23Cu0.08P0.15S0.54*: mp-558415 | K0.25Ga0.25S0.50*: mp-17650 | K0.10Ho0.20F0.70*\&: mp-31030 |

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| K0.25Ho0.25S0.50*: mp-15786 | K0.25Lu0.25S0.50*: mp-1007636 | 542545 |
| :---: | :---: | :---: |
| K0.50I0.50*: mp-22898 | K0.02Mg0.07Al0.15Si0.15O0.61*\&: | K0.25Nb0.12Cu0.12S0.50*: mp-9763 |
| K0.17In0.25Ag0.08Se0.50*: mp-21705 | mp-686653 | K0.19Nb0.12Cu0.19S0.50*: mp-581419 |
| K0.17In0.25Ag0.08Se0.50*: mp-680403 | $\mathrm{K} 0.11 \mathrm{Mg} 0.11 \mathrm{Be} 0.16 \mathrm{~F} 0.63^{*}$ \& : mp- | K0.12Nb0.12Cu0.25Se0.50*: mp-6599 |
| K0.17In0.25Cu0.08Se0.50*: mp-21713 | 13613 | K0.17Nb0.11Cu0.06Se0.67* : mp-6168 |
| K0.09In0.09P0.18S0.64*: mp-22583 | K0.18Mg0.09P0.18Se0.55*: mp-11643 | K0.25Nb0.12Cu0.12Se0.50*: mp-9003 |
| K0.17In0.08P0.17S0.58*: mp-862780 | K0.18Mn0.09P0.18S0.55*: mp-542638 | K0.07Nb0.14P0.07S0.71*: mp-542972 |
| K0.15In0.08P0.15Se0.62*: mp-581517 | K0.18Mn0.09P0.18Se0.55*: mp-867228 | K0.24Nb0.12S0.65*: mp-15148 |
| K0.07In0.36S0.57*: mp-22199 | K0.18Mn0.09Sn0.18Se0.55*: mp- | K0.38Nb0.12S0.50*: mp-18383 |
| K0.25In0.25S0.50*: mp-505412 | 669410 | K0.17Nb0.11S0.71*: mp-560348 |
| K0.06In0.36Se0.58*: mp-21836 | K0.15Mo0.15Se0.70*: mp-651347 | K0.20Nb0.10S0.70*: mp-574909 |
| K0.25In0.25Se0.50*: mp-505700 | K0.09Mo0.13Se0.78*: mp-542749 | K0.19Nb0.12S0.69*: mp-680410 |
| K0.06In0.36Se0.58*: mp-675614 | K0.07Na0.04B0.33O0.56* \& : mp- | K0.19Nb0.12Se0.69*: mp-28428 |
| K0.14In0.14Sn0.14Se0.57*: mp-568379 | 558293 | K0.21Nd0.07As0.14S0.57*: mp-559059 |
| K0.14La0.14Ge0.14Se0.57* : mp-21097 | $\mathrm{K} 0.02 \mathrm{Na} 0.04 \mathrm{Si0} 0.25 \mathrm{~B} 0.06 \mathrm{O} 0.62 *$ : | K0.12Nd0.25Cu0.12S0.50*: mp-11603 |
| K0.10La0.10P0.20S0.60*: mp-560649 | mp-15541 | K0.14Nd0.14Ge0.14S0.57*: mp-861866 |
| K0.17La0.08P0.17S0.58*: mp-542081 | K0.20Na0.07Sn0.20Se0.53*: mp- | K0.17Nd0.08P0.17S0.58*: mp-16690 |
| K0.21La0.07P0.14S0.57*: mp-16209 | 628185 | K0.12Nd0.12P0.15S0.62*: mp-555172 |
| K0.21La0.07P0.14Se0.57*: mp-542079 | K0.13Na0.03Ti0.15Se0.69*: mp-569806 | K0.21Nd0.07P0.14S0.57*: mp-542974 |
| K0.10La0.10P0.20Se0.60*: mp-571662 | K0.19Nb0.12Ag0.19S0.50*: mp-581115 | K0.25Nd0.25S0.50*: mp-1006885 |
| K0.17La0.08P0.17Se0.58*: mp-542078 | K0.25Nb0.12Ag0.12S0.50*: mp-15214 | K0.14Ni0.14P0.14S0.57*: mp-662530 |
| K0.14La0.14Si0.14S0.57*: mp-861938 | K0.12Nb0.12Ag0.25Se0.50*: mp- | K0.17Np0.17Ag0.17S0.50*: mp-865937 |
| K0.14La0.14Si0.14S0.57*: mp-12924 | 567177 | K0.17Np0.17Cu0.17S0.50*: mp-867312 |
| K0.14Li0.14Be0.14F0.57* \& : mp-6253 | K0.18Nb0.12As0.06Se0.65*: mp- | K0.25P0.12Au0.12S0.50*: mp-9509 |

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| K0.06P0.12Au0.31S0.50*: mp-561218 | mp-694852 | 567322 |
| :---: | :---: | :---: |
| K0.17P0.17Au0.17Se0.50*: mp-862850 | K0.29S0.71*: mp-17146 | K0.25Sm0.25Se0.50*: mp-1006891 |
| K0.21P0.14Au0.07Se0.57*: mp-866660 | K0.10Sb0.10P0.20S0.60*: mp-556609 | K0.12Sn0.12As0.12S0.62*: mp-554119 |
| K0.14P0.14Pb0.14S0.57*: mp-638150 | K0.10Sb0.10P0.20Se0.60*: mp-7123 | K0.18Sn0.09As0.18S0.55*: mp-10776 |
| K0.27P0.13Pd0.07S0.53*: mp-867268 | K0.38Sb0.12S0.50*: mp-9781 | K0.22Sn0.11Au0.22S0.44*: mp-557121 |
| K0.14P0.14Pd0.14S0.57*: mp-866637 | K0.25Sb0.25S0.50*: mp-11703 | K0.13Sn0.13Hg0.20S0.53*: mp-18115 |
| K0.16P0.26Ru0.05Se0.53*: mp-568011 | K0.38Sb0.12S0.50*: mp-9911 | K0.25Sn0.12Hg0.12Se0.50*: mp- |
| K0.20P0.20S0.60*: mp-8267 | K0.15Sb0.31S0.54*: mp-27749 | 568968 |
| K0.38P0.12S0.50*: mp-17989 | K0.07Sb0.36S0.57*: mp-15559 | K0.12Sn0.25I0.62*: mp-23534 |
| K0.15P0.05Se0.80*: mp-29947 | K0.25Sb0.25Se0.50*: mp-542642 | K0.22Sn0.22S0.56*: mp-8965 |
| K0.20P0.20Se0.60*: mp-571452 | K0.14Sb0.29Se0.57*: mp-9797 | K0.17Sn0.17S0.67*: mp-541379 |
| K0.33P0.17Se0.50*: mp-31314 | K0.38Sb0.12Se0.50*: mp-8704 | K0.22Sn0.22Se0.56*: mp-8966 |
| K0.38P0.12Se0.50*: mp-31313 | K0.25Sb0.25Se0.50*: mp-9576 | K0.33Sn0.17Se0.50*: mp-9693 |
| K0.12P0.12Se0.75*: mp-18625 | K0.29Se0.71*: mp-18609 | K0.40Sn0.13Se0.47*: mp-29386 |
| K0.20P0.20Se0.60*: mp-569702 | K0.14Si0.14Bi0.14S0.57* ${ }^{*}$ mp-866651 | K0.27Sn0.20Se0.53*: mp-4971 |
| K0.20Pa0.10F0.70* \& : mp-542445 | K0.21Sm0.07As0.14S0.57*: mp-560964 | K0.14Sn0.29Se0.57*: mp-28769 |
| K0.22Pd0.33S0.44*: mp-9910 | K0.13Sm0.13As0.13Se0.60*: mp- | K0.25Ta0.12Ag0.12S0.50*: mp-15216 |
| K0.22Pd0.04Se0.74*: mp-570241 | 571473 | K0.19Ta0.12Ag0.19S0.50*: mp-573202 |
| K0.15Pd0.08Se0.77*: mp-505138 | K0.12Sm0.25Cu0.12S0.50*: mp-11604 | K0.12Ta0.12Ag0.25Se0.50*: mp- |
| K0.14Pr0.14Ge0.14Se0.57*: mp-12012 | K0.14Sm0.14Ge0.14Se0.57*: mp-11634 | 571288 |
| K0.25Pr0.25S0.50*: mp-15782 | K0.17Sm0.08P0.17S0.58*: mp-555587 | K0.19Ta0.12Ag0.19Se0.50*: mp- |
| K0.14Pr0.14Si0.14Se0.57* ${ }^{\text {\% }}$ mp-13538 | K0.09Sm0.09P0.18S0.64*: mp-554581 | 582161 |
| K0.17Pt0.33S0.50*: mp-30533 | K0.25Sm0.25S0.50*: mp-15783 | K0.18Ta0.12As0.06Se0.65*: mp- |
| K0.16Rb0.03Zn0.12Sn0.16S0.53*: | K0.07Sm0.14Sb0.21Se0.57*: mp- | 683905 |

## Appendix $D$

| K0.25Ta0.12Cu0.12Se0.50*: mp-8972 | K0.33Ti0.17S0.50*: mp-28766 | K0.29Zr0.14S0.57*: mp-560331 |
| :---: | :---: | :---: |
| K0.12Ta0.12Cu0.25Se0.50*: mp-6013 | K0.19Ti0.14S0.67*: mp-541735 | K0.18Zr0.13Se0.69*: mp-674338 |
| K0.11Ta0.11P0.11S0.67*: mp-683955 | K0.17U0.17Cu0.17S0.50*: mp-13349 | Kr1.00* \& : mp-612118 |
| K0.19Ta0.12S0.69*: mp-680400 | K0.18U0.09Cu0.27S0.45*: mp-557249 | Kr1.00*\&: mp-567365 |
| K0.24Ta0.12S0.65*: mp-4361 | K0.17U0.06Cu0.34S0.43*: mp-559811 | Kr1.00*\&: mp-975590 |
| K0.38Ta0.12S0.50*: mp-18148 | K0.17U0.17Cu0.17Se0.50*: mp-582421 | Kr1.00*\&: mp-974400 |
| K0.14Ta0.14S0.71*: mp-31308 | K0.13U0.07P0.20Se0.60*: mp-574428 | Kr1.00*\&: mp-976347 |
| K0.19Ta0.12S0.69*: mp-558967 | K0.11U0.22Se0.67*: mp-12414 | La0.25Ag0.08Ge0.08S0.58*: mp- |
| K0.24Ta0.12S0.65*: mp-18664 | K0.25V0.12Ag0.12S0.50*: mp-8900 | 617632 |
| K0.18Tc0.27Se0.55*: mp-541354 | K0.25V0.12Ag0.12Se0.50*: mp-14634 | La0.25Ag0.08Sn0.08S0.58*: mp-542888 |
| K0.33Te0.17S0.50*: mp-29692 | K0.25V0.12Cu0.12S0.50*: mp-15147 | La0.27Bi0.13S0.60*: mp-28727 |
| K0.33Te0.17Se0.50*: mp-28419 | K0.12V0.12Cu0.25S0.50*: mp-6376 | La0.25Cu0.08Ge0.08S0.58*: mp- |
| K0.20Th0.13Cu0.20S0.47*: mp-638086 | K0.12V0.12Cu0.25Se0.50*: mp-10091 | 582767 |
| K0.17Th0.17Cu0.17S0.50*: mp-12365 | K0.25V0.12Cu0.12Se0.50*: mp-15220 | La0.25Cu0.08Ge0.08Se0.58*: mp- |
| K0.22Th0.11Cu0.22S0.44*: mp-555425 | K0.25V0.06P0.12S0.56*: mp-556552 | 510011 |
| K0.17Th0.05P0.17S0.61*: mp-680237 | K0.38V0.12S0.50*: mp-3529 | La0.29Cu0.14S0.57*: mp-31273 |
| K0.24Th0.05P0.14S0.57*: mp-628680 | K0.04V0.37S0.59*: mp-27889 | La0.25Cu0.08Sn0.08S0.58*: mp- |
| K0.13Th0.07P0.20Se0.60*: mp-541946 | K0.12Y0.25Cu0.12S0.50*: mp-11602 | 510566 |
| K0.13Th0.07P0.20Se0.60*: mp-568203 | K0.10Y0.10P0.20Se0.60*: mp-571057 | La0.29Eu0.14S0.57*: mp-677272 |
| K0.10Th0.10Sb0.20Se0.60*: mp- | K0.25Y0.25S0.50*: mp-1006888 | La0.25Ge0.12S0.62*: mp-622086 |
| 568904 | K0.14Y0.14Si0.14S0.57*: mp-867328 | La0.30In0.10S0.60*: mp-540877 |
| K0.11Th0.22Se0.67*: mp-9522 | K0.11Y0.21Sn0.11S0.58*: mp-560785 | La0.18In0.23S0.59*: mp-21571 |
| K0.12Ti0.12P0.12S0.62*: mp-560977 | K0.17Zr0.17Cu0.17S0.50*: mp-9317 | La0.25Mn0.08Al0.08S0.58*: mp- |
| K0.12Ti0.12P0.12Se0.62*: mp-571544 | K0.17Zr0.17Cu0.17Se0.50*: mp-9318 | 866692 |

## Appendix $D$

| La0.17P0.17S0.67*: mp-560571 | Li0.30Al0.10F0.60*\&: mp-556020 | Lu0.29Cd0.14S0.57*: mp-8269 |
| :---: | :---: | :---: |
| La0.29Pb0.14S0.57*: mp-36538 | Li0.07Al0.36O0.57*\&: mp-530399 | Lu0.17Cu0.17Pb0.17Se0.50*: mp- |
| La0.12Pd0.38S0.50*: mp-2889 | Li0.06Al0.06Si0.25O0.62*\&: mp-6442 | 865492 |
| La0.40S0.60*: mp-32906 | Li0.06B0.29H0.12O0.53* \& : mp-740714 | Lu0.25Cu0.25S0.50*: mp-1001780 |
| La0.40S0.60*: mp-7475 | Li0.11B0.33O0.56* \& : mp-3660 | Lu0.25Cu0.25S0.50*: mp-12457 |
| La0.33S0.67*: mp-1508 | Li0.14B0.32O0.55* \&: mp-16828 | Lu0.29Mg0.14S0.57*: mp-14304 |
| La0.34S0.66*: mp-558229 | Li0.09B0.34O0.56* \& : mp-1020014 | Lu0.29Mn0.14S0.57*: mp-14305 |
| La0.33S0.33F0.33*: mp-5394 | Li0.06B0.35O0.53F0.06*\&: mp-558105 | Lu0.17P0.17O0.67* \& : mp-2940 |
| La0.40S0.58O0.02*: mp-773116 | Li0.29Be0.14F0.57* : mp-4622 | Lu0.17P0.17S0.67*: mp-30287 |
| La0.34Se0.66*: mp-8866 | Li0.17Be0.13P0.13Br0.04O0.52*\&: | Lu0.40S0.60*: mp-2826 |
| La0.33Se0.67*: mp-1019091 | mp-554560 | Lu0.40S0.20O0.40*: mp-12673 |
| La0.33Se0.67*: mp-570668 | Li0.17Be0.13P0.13Cl0.04O0.52*\&: | Lu0.18Si0.18O0.64*\&: mp-7193 |
| La0.25Si0.08Ag0.08S0.58*: mp-17719 | mp-560894 | Lu0.18Si0.18O0.64*\&: mp-18385 |
| La0.25Si0.08Cu0.08S0.58*: mp-504650 | Li0.11Ca0.11Al0.11F0.67*\&: mp-6134 | Lu0.25Tl0.25S0.50*: mp-1001604 |
| La0.25Si0.12S0.62*: mp-558724 | Li0.17Lu0.17F0.67*\&: mp-561430 | Lu0.25Tl0.25Se0.50*: mp-1001611 |
| La0.21Si0.14S0.57Br0.07*: mp-560523 | Li0.06Mg0.17P0.17O0.61*\&: mp- | Lu0.29Zn0.14S0.57*: mp-18332 |
| La0.21Si0.14S0.57Cl0.07*: mp-556246 | 1020109 | Mg0.14Al0.14B0.14O0.57*\&: mp-8376 |
| La0.21Si0.14S0.57I0.07*: mp-23090 | Li0.17Y0.17F0.67*\&: mp-3700 | Mg0.14Al0.29O0.57*\&: mp-531840 |
| La0.25Sn0.12S0.62*: mp-12170 | Li0.17Y0.17F0.67* \& : mp-556472 | Mg0.14Al0.29O0.57**: mp-3536 |
| La0.14Tl0.14Ge0.14Se0.57*: mp- | Li0.17Y0.17F0.67*\&: mp-3941 | Mg0.07Al0.34O0.59*\&: mp-39003 |
| 684022 | Lu0.25Ag0.25S0.50*: mp-676410 | Mg0.14Al0.29O0.57*\&: mp-34144 |
| La0.36T10.07S0.57*: mp-35714 | Lu0.20B0.20O0.60*\&: mp-7560 | Mg0.14Al0.29O0.57*\&: mp-530722 |
| La0.20Tm0.20S0.60*: mp-556841 | Lu0.15B0.25O0.60*\&: mp-554282 | Mg0.14Al0.29O0.57*\&: mp-531530 |
| Li0.30Al0.10F0.60*\&: mp-15254 | Lu0.10B0.30O0.60*\&: mp-680724 | Mg0.04Al0.37O0.59*\&: mp-757911 |

## Appendix $D$

| Mg0.14Al0.29S0.57*: mp-3872 | Mg0.11In0.31S0.58*: mp-685878 | Mg0.04Ti0.32S0.64*: mp-36982 |
| :---: | :---: | :---: |
| Mg0.07Al0.14Si0.17O0.62*\&: mp-6174 | Mg0.14In0.29S0.57*: mp-20493 | Mn0.12Cu0.25Ge0.12S0.50*: mp-20474 |
| Mg0.07Al0.14Si0.17O0.62*\&: mp- | Mg0.08Mn0.31S0.62*: mvc-13559 | Mn0.12Cu0.25Sn0.12S0.50*: mp-19722 |
| 684265 | Mg0.20P0.20S0.60*: mp-675651 | Mn0.12Cu0.25Sn0.12Se0.50*: mp- |
| $\mathrm{Mg} 0.12 \mathrm{~B} 0.29 \mathrm{Cl0.04O} 0.54^{*}$ \&: mp- | Mg0.20P0.20Se0.60*: mp-30943 | 22400 |
| 23617 | Mg0.50S0.50*: mp-1315 | Mn0.14In0.29S0.57*: mp-22168 |
| Mg0.12B0.29Cl0.04O0.54* \& : mp- | Mg0.50S0.50*: mp-13032 | Mn0.08Nb0.31S0.62*: mp-3669 |
| 23087 | Mg0.14Si0.19H0.10O0.57* \& : mp- | Mn0.33S0.67*: mvc-14047 |
| Mg0.22B0.22O0.56*\&: mp-5547 | 696497 | Mn0.33S0.67*: mvc-34 |
| Mg0.08B0.33O0.58*\&: mp-14234 | Mg0.20Si0.20O0.60* \& : mp-557803 | Mn0.04Sb0.24Pb0.16S0.56*: mp- |
| Mg0.22B0.22O0.56* \& : mp-18256 | Mg0.20Si0.20O0.60*\&: mp-4321 | 683891 |
| Mg0.22B0.22O0.56* \& : mp-560772 | Mg0.20Si0.20O0.60* \& : mp-5834 | Mn0.14Sb0.29S0.57*: mp-10412 |
| Mg0.29B0.14O0.43F0.14* : mp-7995 | Mg0.20Si0.20O0.60*\&: mp-5026 | Mn0.12Si0.12Cu0.25S0.50*: mp-12023 |
| Mg0.30B0.10O0.30F0.30* \& mp- | Mg0.20Si0.20O0.60*\&: mp-1020125 | Mo0.33S0.67*: mp-1025874 |
| 554542 | Mg0.20Si0.20O0.60*\&: mp-1020124 | Mo0.33S0.67*: mp-1023924 |
| $\mathrm{Mg} 0.11 \mathrm{Be} 0.04 \mathrm{Al} 0.29 \mathrm{O} 0.57 *$ * | Mg0.20Si0.20O0.60*\&: mp-1020361 | Mo0.33S0.67*: mp-1023939 |
| mp-554018 | Mg0.20Si0.20O0.60*\&: mp-1020123 | Mo0.33S0.67*: mp-2815 |
| $\mathrm{Mg} 0.11 \mathrm{Be} 0.04 \mathrm{Al} 0.29 \mathrm{O} 0.57 *$ *: | Mg0.20Si0.20O0.60*\&: mp-1020118 | Mo0.33S0.67*: mp-1018809 |
| mp-17313 | Mg0.20Si0.20O0.60*\&: mp-3470 | Mo0.33S0.67*: mp-1434 |
| Mg0.14Cr0.29S0.57*: mvc-91 | Mg0.20Si0.20O0.60*\&: mp-1020115 | Mo0.33S0.67*: mp-1027525 |
| Mg0.33F0.67* \& : mp-1249 | Mg0.20Si0.20O0.60*\&: mp-1020117 | Mo0.33Se0.67*: mp-1025799 |
| Mg0.29Ge0.14S0.57*: mp-17441 | Mg0.30Si0.10O0.40F0.20*\&: mp- | Mo0.33Se0.67*: mp-1023934 |
| Mg0.09H0.55Br0.18N0.18*: mp-697170 | 558458 | Mo0.33Se0.67*: mp-1023940 |
| Mg0.09H0.55N0.18Cl0.18*: mp-697168 | Mg0.08Ti0.31S0.62*: mvc-11283 | Mo0.33Se0.67*: mp-7581 |

## Appendix D

| Mo0.33Se0.67*: mp-1018807 | Mo0.17W0.17S0.67*: mp-1027335 | Mo0.25W0.08Se0.33S0.33*: mp- |
| :---: | :---: | :---: |
| Mo0.33Se0.67*: mp-1634 | Mo0.25W0.08S0.67*: mp-1027569 | 1026927 |
| Mo0.33Se0.67*: mp-1027692 | Mo0.17W0.17S0.67*: mp-1027647 | Mo0.17W0.17Se0.17S0.50*: mp- |
| Mo0.33Se0.44S0.22*: mp-1025906 | Mo0.25W0.08S0.67*: mp-1027645 | 1026975 |
| Mo0.33Se0.44S0.22*: mp-1025819 | Mo0.08W0.25S0.67*: mp-1029246 | Mo0.25W0.08Se0.17S0.50*: mp- |
| Mo0.33Se0.33S0.33*: mp-1018806 | Mo0.17W0.17S0.67*: mp-1030119 | 1026946 |
| Mo0.33Se0.33S0.33*: mp-1023953 | Mo0.11W0.22Se0.22S0.44*: mp- | Mo0.17W0.17Se0.17S0.50*: mp- |
| Mo0.33Se0.22S0.44*: mp-1025925 | 1025824 | 1027292 |
| Mo0.33Se0.22S0.44*: mp-1025988 | Mo0.22W0.11Se0.44S0.22*: mp- | Mo0.25W0.08Se0.33S0.33*: mp- |
| Mo0.33Se0.50S0.17*: mp-1026980 | 1025879 | 1027267 |
| Mo0.33Se0.33S0.33*: mp-1026916 | Mo0.22W0.11Se0.44S0.22*: mp- | Mo0.17W0.17Se0.17S0.50*: mp- |
| Mo0.33Se0.33S0.33*: mp-1027580 | 1025748 | 1027274 |
| Mo0.33Se0.50S0.17*: mp-1027483 | Mo0.11W0.22Se0.22S0.44*: mp- | Mo0.25W0.08Se0.17S0.50*: mp- |
| Mo0.33Se0.33S0.33*: mp-1027492 | 1025663 | 1027294 |
| Mo0.33Se0.33S0.33*: mp-1027687 | Mo0.17W0.17Se0.33S0.33*: mp- | Mo0.17W0.17Se0.17S0.50*: mp- |
| Mo0.33Se0.17S0.50*: mp-1027608 | 1023955 | 1027391 |
| Mo0.33Se0.17S0.50*: mp-1027890 | Mo0.22W0.11Se0.22S0.44*: mp- | Mo0.25W0.08Se0.17S0.50*: mp- |
| Mo0.22W0.11S0.67*: mp-1025911 | 1026023 | 1027472 |
| Mo0.11W0.22S0.67*: mp-1025689 | Mo0.22W0.11Se0.22S0.44*: mp- | Mo0.25W0.08Se0.33S0.33*: mp- |
| Mo0.17W0.17S0.67*: mp-1023954 | 1025941 | 1027524 |
| Mo0.11W0.22S0.67*: mp-1026034 | Mo0.22W0.11Se0.22S0.44*: mp- | Mo0.25W0.08Se0.17S0.50*: mp- |
| Mo0.22W0.11S0.67*: mp-1025922 | 1025948 | 1027537 |
| Mo0.17W0.17S0.67*: mp-1027269 | Mo0.25W0.08Se0.33S0.33*: mp- | Mo0.25W0.08Se0.33S0.33*: mp- |
| Mo0.08W0.25S0.67*: mp-1027273 | 1027051 | 1027551 |

## Appendix $D$

| Mo0.25W0.08Se0.17S0.50*: mp- | Mo0.08W0.25Se0.33S0.33*: mp- | Na0.03Al0.38O0.59*\&: mp-3405 |
| :---: | :---: | :---: |
| 1027795 | 1029026 | Na0.03Al0.38O0.59*\&: mp-676014 |
| Mo0.25W0.08Se0.17S0.50*: mp- | Mo0.08W0.25Se0.33S0.33*: mp- | Na0.03Al0.38O0.59*\&: mp-759230 |
| 1027646 | 1029031 | Na0.43Al0.14S0.43*: mp-560538 |
| Mo0.25W0.08Se0.50S0.17*: mp- | Mo0.17W0.17Se0.33S0.33*: mp- | Na0.25Al0.25Se0.50*: mp-17060 |
| 1027729 | 1029077 | Na0.25Al0.25Se0.50*: mp-10166 |
| Mo0.17W0.17Se0.33S0.33*: mp- | Mo0.17W0.17Se0.17S0.50*: mp- |  |
| 1027671 | 1030146 | mp-23147 |
| Mo0.17W0.17Se0.50S0.17*: mp- | Mo0.17W0.17Se0.50S0.17*: mp- | $\mathrm{Na} 0.10 \mathrm{Al0.07Si0} 22 \mathrm{Cl0.02O} 0.59^{*}$ \&: |
| 1027672 | 1030513 | mp-676431 |
| Mo0.25W0.08Se0.33S0.33*: mp- | Mo0.17W0.17Se0.50S0.17*: mp- | $\mathrm{Na} 0.17 \mathrm{Al0.13Si0.13Cl0.04O} 0.52 *$ : |
| 1027714 | 1030519 | mp-23145 |
| Mo0.25W0.08Se0.50S0.17*: mp- | Mo0.17W0.17Se0.50S0.17*: mp- |  |
| 1027802 | 1030522 | mp-23655 |
| Mo0.17W0.17Se0.50S0.17*: mp- | Mo0.08W0.25Se0.33S0.33*: mp- | Na0.08Al0.08Si0.23O0.62*\&: mp- |
| 1028541 | 1030536 | 721988 |
| Mo0.08W0.25Se0.33S0.33*: mp- | Mo0.08W0.25Se0.17S0.50*: mp- | Na0.10Al0.10Si0.20O0.60*\&: mp- |
| 1028930 | 1030520 | 1020661 |
| Mo0.08W0.25Se0.33S0.33*: mp- | Mo0.08W0.25Se0.33S0.33*: mp- | Na0.25As0.25S0.50*: mp-5942 |
| 1028947 | 1030566 | Na0.25As0.25Se0.50*: mp-27374 |
| Mo0.17W0.17Se0.50S0.17*: mp- | Mo0.17W0.17Se0.17S0.50*: mp- | Na0.25As0.25Se0.50*: mp-984519 |
| 1028998 | 1030745 | Na0.39Au0.28S0.33*: mp-28856 |
| Mo0.08W0.25Se0.17S0.50*: mp- | Na0.17Ag0.50S0.33*: mp-16992 | Na0.25Au0.25Se0.50*: mp-29139 |
| 1029037 | Na0.03Al0.38O0.59*\&: mp-867577 | Na0.28Au0.06Se0.67*: mp-29198 |

## Appendix D

| Na0.15B0.31O0.54* \& mp-1020142 | 569618 | Na0.36Ge0.18Se0.45*: mp-568762 |
| :---: | :---: | :---: |
| Na0.09B0.35O0.57* \& : mp-542300 | Na0.07Ce0.36S0.57*: mp-37496 | Na0.33Ge0.17Se0.50*: mp-28278 |
| Na0.11B0.33O0.56* \& : mp-556226 | Na0.25Ce0.25S0.50*: mp-36536 | Na0.22Ge0.22Se0.56*: mp-17964 |
| Na0.11B0.33O0.56* \& : mp-557406 | Na0.25Ce0.25Se0.50*: mp-999491 | Na0.36Ge0.18Se0.45*: mp-28355 |
| Na0.09B0.35O0.57* \& : mp-764966 | $\mathrm{Na0.50Cl0.50*} \mathrm{\&:} \mathrm{mp-22862}$ | Na0.40Ge0.13Se0.47*: mp-18100 |
| Na0.13B0.26P0.04O0.57* \& mp- | Na0.15Cr0.10P0.15S0.60*: mp-559281 | Na0.33H0.33S0.33*: mp-36582 |
| 556801 | Na0.25Cr0.25S0.50*: mp-5693 | Na0.11Hf0.22Cu0.11Se0.56*: mp- |
| Na0.18B0.29S0.53*: mp-29000 | Na0.25Cr0.25S0.50*: mp-637292 | 571189 |
| Na0.43B0.14S0.43*: mp-29976 | Na0.11Cu0.44S0.44*: mp-29069 | Na0.17Hf0.17Cu0.17Se0.50*: mp- |
| Na0.25B0.25S0.50*: mp-15011 | Na0.29Cu0.14Sb0.14S0.43*: mp- | 505448 |
| Na0.22B0.22S0.56*: mp-29411 | 555871 | Na0.22Hg0.33S0.44*: mp-505121 |
| Na0.18B0.29S0.06O0.47*: mp-560266 | Na0.33Cu0.11Sn0.11Se0.44*: mp- | Na0.40Hg0.20S0.40*: mp-28858 |
| Na0.09Be0.09B0.27O0.55* \& mp- | 623030 | Na0.25Ho0.25S0.50*: mp-5694 |
| 1020624 | Na0.25Dy0.25S0.50*: mp-999490 | Na0.25Ho0.25Se0.50*: mp-999474 |
| Na0.10Be0.19B0.19O0.52* \& : mp- | Na0.25Dy0.25Se0.50*: mp-999488 | Na0.50I0.50*: mp-23268 |
| 1020144 | Na0.10Er0.10P0.20S0.60*: mp-12384 | Na0.25In0.25S0.50*: mp-20289 |
| Na0.25Bi0.25S0.50*: mp-675531 | Na0.25Er0.25S0.50*: mp-3613 | Na0.25In0.25Se0.50*: mp-22473 |
| Na0.25Bi0.25Se0.50*: mp-35015 | Na0.25Er0.25Se0.50*: mp-8584 | Na0.25La0.25S0.50*: mp-675230 |
| Na 0.50 Br 0.50 * : mp-22916 | Na0.11Ga0.33Se0.56*: mp-570622 | Na0.25La0.25Se0.50*: mp-999472 |
| $\mathrm{Na} 0.11 \mathrm{Ca} 0.11 \mathrm{Al} 0.11 \mathrm{~F} 0.67 *$ \& $\mathrm{mp}-$ | Na0.25Gd0.25S0.50*: mp-8260 | Na0.15Li0.15Al0.10F0.60* \& : mp-6711 |
| 558169 | Na0.25Gd0.25Se0.50*: mp-999489 | Na0.20Li0.10Al0.10F0.60*\&: mp-6604 |
| Na0.25Cd0.12Sn0.12S0.50*: mp- | Na0.22Ge0.22S0.56*: mp-18568 | Na0.25Lu0.25S0.50*: mp-9035 |
| 561075 | Na0.33Ge0.17S0.50*: mp-4068 | Na0.18Mg0.09Al0.09F0.64* ${ }^{*}$ |
| Na0.10Ce0.10P0.20Se0.60*: mp- | Na0.22Ge0.22Se0.56*: mp-18619 | mp-19931 |

## Appendix D

| Na0.18Mg0.09Al0.09F0.64* ${ }^{*}$ : | Na0.22Si0.22S0.56*: mp-18104 | Na0.22Zr0.11Cu0.22S0.44*: mp- |
| :---: | :---: | :---: |
| mp-6319 | Na0.22Si0.22Se0.56*: mp-18562 | 556536 |
| Na0.23Nb0.06Cu0.11S0.60*: mp- | Na0.10Sm0.10P0.20S0.60*: mp-561232 | Na0.17Zr0.17Cu0.17Se0.50*: mp- |
| 554071 | Na0.25Sm0.25S0.50*: mp-999455 | 505172 |
| Na0.12Nb0.12Cu0.25S0.50*: mp-6181 | Na0.25Sm0.25Se0.50*: mp-999450 | Na0.32Zr0.18S0.50*: mp-686139 |
| Na0.07Nb0.14P0.07S0.71*: mp-557436 | Na0.27Sn0.20S0.53*: mp-29626 | Na0.33Zr0.17Se0.50*: mp-7219 |
| Na0.25Nd0.25S0.50*: mp-676360 | Na0.44Sn0.11S0.44*: mp-29628 | Nb0.21Co0.11Pd0.05Se0.63*: mp- |
| Na0.25Nd0.25S0.50*: mp-999470 | Na0.44Sn0.11Se0.44*: mp-28768 | 624253 |
| Na0.25Nd0.25Se0.50*: mp-999471 | Na0.33Sn0.17Se0.50*: mp-568543 | Nb0.14Cr0.14Se0.71*: mp-28019 |
| Na0.21P0.14Pb0.10S0.55*: mp-560831 | Na0.33Sn0.17Se0.50*: mp-571470 | Nb0.12Cu0.38S0.50*: mp-5621 |
| Na0.14P0.14Pd0.14S0.57*: mp-559446 | Na0.22Sn0.22Se0.56*: mp-16167 | Nb0.12Cu0.38Se0.50*: mp-4043 |
| Na0.38P0.12S0.50*: mp-985584 | $\mathrm{Na0.33Te0.17Se0.50*:} \mathrm{mp-573581}$ | Nb0.30Pb0.10S0.60*: mp-21852 |
| Na0.38P0.12S0.50*: mp-28782 | Na0.17Ti0.17Cu0.17S0.50*: mp- | Nb0.15Pd0.23Se0.62*: mp-504898 |
| Na0.38P0.12S0.38O0.12*: mp-11738 | 505171 | Nb0.18Se0.82*: mp-541106 |
| Na0.33P0.17Se0.50*: mp-567228 | Na0.09Ti0.30S0.61*: mp-675056 | Nb0.25Se0.75*: mp-525 |
| Na0.25Pa0.08F0.67*\&: mp-27478 | Na0.17Ti0.17Se0.67*: mp-28566 | Nb0.19Se0.75I0.06*: mp-23410 |
| Na .25 Pr 0.25 S 0.50 *: mp-675199 | Na0.15Ti0.15Se0.69*: mp-680191 | Nb0.19Se0.75I0.06*: mp-567252 |
| Na0.25Pr0.25Se0.50*: mp-999461 | Na0.25Tm0.25S0.50*: mp-9076 | Nb0.19Se0.75I0.06*: mp-569026 |
| Na0.25Sb0.25S0.50*: mp-5414 | Na0.33U0.17S0.50*: mp-15886 | Nb0.30Sn0.10S0.60*: mp-557640 |
| Na0.25Sb0.25S0.50*: mp-557179 | Na0.38V0.12S0.50*: mp-29143 | Nb0.30Sn0.10S0.60*: mp-9407 |
| Na0.25Sb0.25Se0.50*: mp-33333 | Na0.14V0.29S0.57*: mp-676586 | Nb0.11Tl0.17Cu0.06Se0.67*: mp- |
| Na0.25Sc0.25S0.50*: mp-999460 | Na0.25Y0.25S0.50*: mp-10226 | 570757 |
| Na0.08Si0.23B0.08O0.62*\&: mp- | Na0.25Y0.25Se0.50*: mp-999448 | Nb0.12Tl0.24S0.65*: mp-17803 |
| 696416 | Na0.17Zr0.17Cu0.17S0.50*: mp-9107 | Nb0.12Tl0.38Se0.50*: mp-1025396 |

## Appendix $D$

| Nb0.12Tl0.24Se0.65*: mp-638104 | Nd0.33Se0.67*: mp-570707 | Ni0.53S0.47*: mp-976920 |
| :---: | :---: | :---: |
| Nd0.36Ag0.07S0.57*: mp-37449 | Nd0.33Se0.67*: mp-1018817 | Ni0.50S0.50*: mp-1547 |
| Nd0.25Al0.08Ni0.08S0.58*: mp-975614 | Nd0.33Se0.33F0.33*: mp-12620 | Ni0.43S0.57*: mp-1050 |
| Nd0.25Cu0.08Ge0.08S0.58*: mp- | Nd0.25Si0.08Ag0.08S0.58*: mp-864666 | Ni0.33Sb0.33S0.33*: mp-3679 |
| 554150 | Nd0.25Si0.08Cu0.08S0.58*: mp-556975 | Ni0.40Sb0.20Te0.40*: mp-3250 |
| Nd0.25Cu0.08Ge0.08Se0.58*: mp- | Nd0.22Si0.15S0.63*: mp-555407 | Ni0.43Se0.57*: mp-573 |
| 568954 | Nd0.21Si0.14S0.57Br0.07*: mp-559237 | Ni0.33Se0.67*: mp-20901 |
| Nd0.25Cu0.25S0.50*: mp-10495 | Nd0.27Si0.09S0.55Cl0.09*: mp-559779 | Ni0.50Se0.50*: mp-15651 |
| Nd0.25Cu0.08Sn0.08S0.58*: mp- | Nd0.21Si0.14S0.57I0.07*: mp-561126 | Ni0.35Te0.65*: mp-684997 |
| 560300 | Nd0.25Sn0.12S0.62*: mp-555750 | Ni0.33Te0.67* : mp-2578 |
| Nd0.21Ge0.16S0.63*: mp-560086 | Nd0.25Tl0.25S0.50*: mp-3664 | Np0.38S0.62*: mp-982385 |
| Nd0.18In0.23S0.59*: mp-21582 | Nd0.25Tl0.25Se0.50*: mp-568588 | Np0.33S0.33O0.33*: mp-8137 |
| Nd0.25Mn0.08Al0.08S0.58*: mp- | Ne1.00*\&: mp-111 | Os0.33S0.67*: mp-20905 |
| 864652 | Ni0.33As0.67*: mp-21873 | Os0.33Se0.67*: mp-2480 |
| Nd0.17P0.17S0.67*: mp-3694 | Ni0.33As0.67*: mp-505510 | P0.67Ir0.33*: mp-10155 |
| Nd0.12Pd0.38S0.50*: mp-15227 | Ni0.33As0.67*: mp-19814 | P0.75Ir0.25*: mp-13853 |
| Nd0.40S0.60*: mp-438 | Ni0.33As0.33S0.33*: mp-3830 | P0.67Os0.33*: mp-2319 |
| Nd0.40S0.60*: mp-32586 | Ni0.33As0.33Se0.33*: mp-10846 | P0.15Pb0.23S0.62*: mp-28140 |
| Nd0.33S0.67*: mp-13568 | Ni0.56P0.44*: mp-1920 | P0.20Pb0.20S0.60*: mp-20199 |
| Nd0.34S0.66*: mp-560786 | Ni0.71P0.29*: mp-2790 | P0.20Pb0.20Se0.60*: mp-20316 |
| Nd0.33S0.33F0.33*: mp-5760 | Ni0.67P0.33*: mp-21167 | P0.25Pd0.75*: mp-19879 |
| Nd0.40S0.56O0.04*: mp-560608 | Ni0.50P0.50*: mp-27844 | P0.15Pd0.23S0.62*: mp-3006 |
| Nd0.34Se0.66*: mp-673692 | Ni0.33P0.33Rh0.33*: mp-1018823 | P0.33Pd0.33S0.33*: mp-7280 |
| Nd0.34Se0.66*: mp-14650 | Ni0.29Rh0.14S0.57*: mp-675691 | P0.33Pd0.33Se0.33*: mp-3123 |

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| P0.67Pt0.33*: mp-730 | Pb0.33I0.67*: mp-567178 | Pr0.21Ge0.16S0.63*: mp-542269 |
| :---: | :---: | :---: |
| P0.43Rh0.57*: mp-621581 | Pb0.33I0.67*: mp-22893 | Pr0.25Mn0.08Al0.08S0.58*: mp- |
| P0.33Rh0.67*: mp-2732 | Pb0.33I0.67*: mp-567199 | 867323 |
| P0.75Rh0.25*: mp-1357 | Pb0.50S0.50*: mp-21276 | Pr0.17P0.17S0.67*: mp-3954 |
| P0.67Rh0.33*: mp-15953 | Pb0.38S0.15I0.46*: mp-23066 | Pr0.05Pb0.44Se0.51*: mp-676516 |
| P0.67Ru0.33*: mp-1413 | Pb0.50Se0.50*: mp-2201 | Pr0.40S0.60*: mp-32692 |
| P0.75Ru0.25*: mp-28400 | Pd0.25Au0.75* \& : mp-973839 | Pr0.33S0.67*: mp-17329 |
| P0.57Se0.43*: mp-569094 | Pd0.25Au0.75* \& : mp-973834 | Pr0.40S0.60*: mp-15179 |
| Pa0.20Br0.60O0.20*: mp-540540 | Pd0.50S0.50*: mp-20250 | Pr0.33S0.67*: mp-555096 |
| Pa 0.33 O 0.67 * : mp-2364 | Pd0.33S0.67*: mp-13682 | Pr0.34S0.66*: mp-561375 |
| Pa0.40S0.60*: mp-862869 | Pd0.50Se0.50*: mp-571383 | Pr0.33S0.33F0.33*: mp-3992 |
| Pa0.25S0.75*: mp-862857 | Pd0.50Se0.50*: mp-21165 | Pr0.32Sb0.08S0.60*: mp-554935 |
| Pa0.25Se0.75*: mp-862867 | Pd0.53Se0.47*: mp-21765 | Pr0.34Se0.66*: mp-14613 |
| Pb0.33I0.67*: mp-567246 | Pd0.33Se0.67*: mp-2418 | Pr0.33Se0.67*: mp-570205 |
| Pb0.33I0.67*: mp-580202 | Pm0.40S0.60*: mp-867180 | Pr0.33Se0.67*: mp-1018940 |
| Pb0.33I0.67*: mp-574189 | Pr0.25Ag0.08Ge0.08S0.58*: mp- | Pr0.25Si0.08Ag0.08S0.58*: mp-867322 |
| Pb0.33I0.67*: mp-640058 | 862792 | Pr0.25Si0.08Ag0.08Se0.58*: mp-17389 |
| Pb0.33I0.67*: mp-22883 | Pr0.36Ag0.07S0.57*: mp-34486 | Pr0.25Si0.08Cu0.08S0.58*: mp-555893 |
| Pb0.33I0.67*: mp-567542 | Pr0.20B0.20S0.60*: mp-862754 | Pr0.22Si0.15S0.63*: mp-559955 |
| Pb0.33I0.67*: mp-672671 | Pr0.25Cu0.08Ge0.08S0.58*: mp- | Pr0.21Si0.14S0.57Br0.07*: mp-560468 |
| Pb0.33I0.67*: mp-569595 | 556962 | Pr0.21Si0.14S0.57Cl0.07*: mp-556179 |
| Pb0.33I0.67*: mp-540789 | Pr0.25Cu0.08Ge0.08Se0.58*: mp- | Pr0.21Si0.14S0.57I0.07*: mp-558259 |
| Pb0.33I0.67*: mp-680205 | 571347 | Pr0.25Sn0.12S0.62*: mp-554244 |
| Pb0.33I0.67*: mp-567503 | Pr0.25Cu0.08Sn0.08S0.58*: mp-560014 | Pr0.25Tl0.25Se0.50*: mp-999289 |

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| Pt0.33S0.67*: mp-762 | Rb0.15As0.05Se0.80*: mp-29501 | 558536 |
| :---: | :---: | :---: |
| Pt0.50S0.50*: mp-558811 | Rb0.33Au0.33S0.33*: mp-9010 | Rb0.18Cd0.09P0.18Se0.55*: mp- |
| Pt0.50S0.50*: mp-288 | Rb0.33Au0.33Se0.33*: mp-9731 | 541897 |
| Pt0.33Se0.67*: mp-1115 | Rb0.17Au0.50Se0.33*: mp-9385 | Rb0.21Ce0.07P0.14Se0.57*: mp- |
| Pu0.17Pa0.17O0.67* \& mp-675479 | Rb0.09B0.35O0.56* \& : mp-553925 | 669351 |
| Pu0.40S0.60*: mp-862796 | Rb0.07B0.36O0.57* \& : mp-561814 | Rb0.50Cl0.50*\&: mp-23295 |
| Pu0.33S0.67*: mp-639690 | Rb0.25B0.25S0.50*: mp-15013 | Rb0.12Cu0.12Pd0.12Se0.62*: mp- |
| Pu0.40S0.60*: mp-33239 | Rb0.20B0.20S0.60*: mp-9047 | 11115 |
| Pu0.33Se0.67*: mp-1018954 | Rb0.14Ba0.14Ta0.14S0.57*: mp- | Rb0.17Cu0.17Se0.67*: mp-18365 |
| Rb0.08Ag0.17As0.25Se0.50*: mp- | 867884 | Rb0.25Dy0.25S0.50*: mp-7046 |
| 570593 | Rb0.06Be0.24B0.18O0.53* \& : mp- | Rb0.09Er0.18Cu0.27S0.45*: mp-17344 |
| Rb0.17Ag0.08As0.25Se0.50*: mp- | 556393 | Rb0.07Er0.21F0.71*\&: mp-555932 |
| 541916 | Rb0.08Be0.15B0.23O0.54*\&: mp- | Rb0.12Er0.12P0.15S0.62*: mp-583084 |
| Rb0.22Ag0.22Ge0.11S0.44*: mp- | 1020621 | Rb0.17Eu0.17As0.17S0.50*: mp- |
| 555852 | Rb0.21Bi0.14I0.64*: mp-29895 | 646129 |
| Rb0.33Ag0.17I0.50*: mp-23399 | Rb0.25Bi0.25S0.50*: mp-30041 | Rb0.25Ga0.25S0.50*: mp-561407 |
| Rb0.11Ag0.56S0.33*: mp-28703 | Rb0.09Bi0.35Se0.57*: mp-30145 | Rb0.12Gd0.25Cu0.12S0.50*: mp-12322 |
| Rb0.12Ag0.25Sb0.12S0.50*: mp-17756 | Rb0.50Br0.50*\&: mp-22867 | Rb0.11Gd0.21Cu0.21S0.47*: mp- |
| Rb0.11Ag0.56Se0.33*: mp-29685 | Rb0.20Ca0.20Br0.60*\&: mp-998536 | 669578 |
| Rb0.17Ag0.17Se0.67*: mp-18585 | Rb0.20Ca0.20Br0.60*\&: mp-998198 | Rb0.12Gd0.25Cu0.12Se0.50*: mp- |
| Rb0.17Ag0.50Se0.33*: mp-10477 | Rb0.20Ca0.20Cl0.60*\&: mp-998324 | 574448 |
| Rb0.20Ag0.07Sn0.20Se0.53*: mp- | Rb0.20Ca0.20Cl0.60*\&: mp-998197 | Rb0.25Gd0.25S0.50*: mp-7045 |
| 571164 | Rb0.20Ca0.20I0.60*: mp-998592 | Rb0.25Gd0.25Se0.50*: mp-10781 |
| Rb0.17Ag0.50Te0.33*: mp-10481 | Rb0.20Cd0.20Au0.20S0.40*: mp- | Rb0.14Ge0.14Bi0.14S0.57*: mp- |

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| 559227 | Rb0.20Na0.10Tm0.10Cl0.60*: | Rb0.20Pb0.20I0.60*: mp-23517 |
| :---: | :---: | :---: |
| Rb0.25Ge0.08P0.08Se0.58*: mp- | mp-567498 | Rb0.22Pd0.33S0.44*: mp-11695 |
| 861898 | Rb0.25Nb0.12Ag0.12S0.50*: mp-14636 | Rb0.11Pd0.05Se0.84* : mp-31292 |
| Rb0.22Ge0.22S0.56*: mp-541879 | Rb0.25Nb0.12Ag0.12Se0.50*: mp-9764 | Rb0.22Pd0.33Se0.44*: mp-14340 |
| Rb0.33Ge0.17S0.50*: mp-11639 | Rb0.18Nb0.12As0.06Se0.65*: mp- | Rb0.12Pr0.12P0.15S0.62*: mp-555448 |
| Rb0.33Ge0.17Se0.50*: mp-9794 | 683902 | Rb0.25Sb0.12Au0.12S0.50*: mp- |
| Rb0.22Ge0.22Se0.56*: mp-541880 | Rb0.25Nb0.12Cu0.12S0.50*: mp-15221 | 556894 |
| Rb0.22Hg0.11P0.11Se0.56*: mp- | Rb0.25Nb0.12Cu0.12Se0.50*: mp- | Rb0.09Sb0.18Au0.27S0.45*: mp- |
| 569349 | 15222 | 558739 |
| Rb0.17Hg0.17Sb0.17Se0.50*: mp-6300 | Rb0.12Nb0.12P0.12S0.65*: mp-554147 | Rb0.38Sb0.12S0.50*: mp-17154 |
| Rb0.09Ho0.18Cu0.27S0.45*: mp-17929 | Rb0.07Nb0.14P0.07S0.71*: mp-6708 | Rb0.15Sb0.31S0.54*: mp-561051 |
| Rb0.50I0.50*: mp-22903 | Rb0.19Nb0.12S0.69*: mp-541745 | Rb0.15Sb0.31S0.54*: mp-4818 |
| Rb0.17In0.17I0.67*: mp-28198 | Rb0.12Nd0.25Cu0.12S0.50*: mp-10834 | Rb0.25Sb0.25S0.50*: mp-10621 |
| Rb0.11In0.33S0.56*: mp-542654 | Rb0.25Nd0.25S0.50*: mp-9363 | Rb0.11Sb0.33Se0.56*: mp-4721 |
| Rb0.25In0.25S0.50*: mp-601861 | Rb0.17Np0.17Cu0.17S0.50*: mp- | Rb0.14Sb0.29Se0.57*: mp-9798 |
| Rb0.07In0.36S0.57*: mp-20938 | 867188 | Rb0.14Si0.14Bi0.14S0.57*: mp-560051 |
| Rb0.25In0.25Se0.50*: mp-31309 | Rb0.14P0.14Pb0.14S0.57*: mp-638009 | Rb0.33Si0.17S0.50*: mp-12016 |
| Rb0.14La0.14Si0.14S0.57*: mp-18658 | Rb0.27P0.13Pb0.07Se0.53*: mp- | Rb0.09Sm0.18Ag0.27Se0.45*: mp- |
| Rb0.07Lu0.21F0.71*\&: mp-558186 | 867964 | 18710 |
| Rb0.25Lu0.25S0.50*: mp-9370 | Rb0.20P0.20S0.60*: mp-556953 | Rb0.12Sm0.25Cu0.12S0.50*: mp-10835 |
| Rb0.29Mg0.14Cl0.57*: mp-1025227 | Rb0.27P0.13Se0.60*: mp-569862 | Rb0.14Sm0.14Ge0.14Se0.57*: mp- |
| Rb0.18Mn0.09P0.18S0.55*: mp-559643 | Rb0.12P0.12Se0.75*: mp-17945 | 567873 |
| Rb0.07Na0.03Al0.20F0.70*\&: mp- | Rb0.20P0.20Se0.60*: mp-571464 | Rb0.21Sm0.07P0.14S0.57*: mp-17894 |
| 560570 | Rb0.36Pb0.09Br0.55*\&: mp-28564 | Rb0.13Sn0.13Hg0.20S0.53*: mp- |

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| 561434 | Rb0.17Ta0.11S0.71*: mp-680284 | Rb0.38V0.12S0.50*: mp-505721 |
| :---: | :---: | :---: |
| Rb0.20Sn0.20I0.60*: mp-29405 | Rb0.24Th0.05P0.14S0.57*: mp-572864 | Rb0.30Y0.10Cl0.60*: mp-574571 |
| Rb0.21Sn0.04P0.12Se0.62*: mp- | Rb0.19Th0.06P0.17Se0.58*: mp- | Rb0.25Y0.25S0.50*: mp-999265 |
| 571228 | 585963 | Rb0.11Zr0.07P0.18S0.64*: mp-561527 |
| Rb0.17Sn0.06P0.17Se0.61*: mp- | Rb0.13Th0.07P0.20Se0.60*: mp- | Rb0.19Zr0.14Se0.67*: mp-542013 |
| 570167 | 541947 | Re0.33S0.67*: mp-572758 |
| Rb0.17Sn0.17S0.67*: mp-557059 | Rb0.11Th0.22Se0.67*: mp-9523 | Re0.33Se0.67*: mp-541582 |
| Rb0.33Sn0.17Se0.50*: mp-9145 | Rb0.13Ti0.15Ag0.03Se0.69*: mp-16001 | Re0.29Te0.33Se0.38*: mp-667286 |
| Rb0.22Sn0.22Se0.56*: mp-9322 | Rb0.22Ti0.11Cu0.22S0.44*: mp-7129 | Rh0.40S0.60*: mp-974381 |
| Rb0.20Sr0.20Cl0.60*\&: mp-998755 | Rb0.12Ti0.12P0.12S0.62*: mp-758985 | Rh0.43S0.57*: mp-29841 |
| Rb0.25Ta0.12Ag0.12S0.50*: mp-15217 | Rb0.11Ti0.05P0.16Se0.68*: mp-567491 | Rh0.33S0.67*: mp-22555 |
| Rb0.17Ta0.11Ag0.06Se0.67*: mp- | Rb0.19Ti0.14S0.67*: mp-542067 | Rh0.40S0.60*: mp-17173 |
| 569378 | Rb0.25Tm0.25S0.50*: mp-9368 | Rh0.27Se0.73*: mp-32861 |
| Rb0.25Ta0.12Cu0.12S0.50*: mp-11923 | Rb0.17U0.17Ag0.17S0.50*: mp-13350 | Rh0.27Se0.73*: mp-1407 |
| Rb0.12Ta0.12Cu0.25Se0.50*: mp- | Rb0.17U0.17Ag0.17Se0.50*: mp-13351 | Rh0.33Se0.67*: mp-983 |
| 11925 | Rb0.17U0.17Au0.17Se0.50*: mp- | Rh0.31Se0.69*: mp-684800 |
| Rb0.25Ta0.12Cu0.12Se0.50*: mp- | 867830 | Ru0.33S0.67*: mp-2030 |
| 11924 | Rb0.17U0.17Cu0.17S0.50*: mp-13352 | Ru0.33Se0.67*: mp-1922 |
| Rb0.12Ta0.12Ge0.12S0.62*: mp- | Rb0.08U0.17Sb0.08S0.67*: mp-559405 | S1.00*: mp-96 |
| 867823 | Rb0.25V0.12Ag0.12S0.50*: mp-8901 | S1.00*: mp-557869 |
| Rb0.11Ta0.11P0.11S0.67*: mp-680498 | Rb0.25V0.12Ag0.12Se0.50*: mp-14635 | S1.00*: mp-77 |
| Rb0.24Ta0.12S0.65*: mp-14577 | Rb0.25V0.12Cu0.12S0.50*: mp-15219 | Sb0.33Ir0.33S0.33*: mp-8630 |
| Rb0.38Ta0.12S0.50*: mp-17220 | Rb0.12V0.12Cu0.25S0.50*: mp-15998 | Sb0.33Ir0.33S0.33*: mp-9270 |
| Rb0.19Ta0.12S0.69*: mp-541975 | Rb0.09V0.09P0.18S0.64*: mp-9102 | Sb0.17P0.17S0.67*: mp-572597 |

## Appendix $D$

| Sb0.20Pb0.25S0.55*: mp-638022 | Sb0.33Te0.33I0.33*: mp-28051 | Si0.33O0.67* \& : mp-556218 |
| :---: | :---: | :---: |
| Sb0.31Pb0.12S0.58*: mp-22737 | Sb0.29Te0.57Pb0.14*: mp-31507 | Si0.33O0.67* \&: mp-556591 |
| Sb0.26Pb0.17S0.57*: mp-27907 | Sb0.33Te0.33Pd0.33*: mp-10850 | Si0.33O0.67* : mp-557837 |
| Sb0.22Pb0.22S0.56*: mp-504814 | Sb0.40Te0.40Se0.20*: mp-3525 | Si0.33O0.67* : mp-549166 |
| Sb0.21Pb0.21S0.59*: mp-630376 | Sb0.40Te0.20Se0.40*: mp-8612 | Si0.33O0.67*\&: mp-639695 |
| Sb0.24Pb0.21S0.56*: mp-641987 | Sc0.10Ag0.10P0.20Se0.60*: mp-13383 | Si0.33O0.67**: mp-7648 |
| Sb0.21Pb0.24S0.55*: mp-649982 | Sc0.04U0.31S0.65*: mp-619571 | Si0.33O0.67* \& : mp-553945 |
| Sb0.26Pd0.74*: mp-30066 | Se1.00*: mp-542461 | Si0.33O0.67*\&: mp-8059 |
| Sb0.33Pd0.67*: mp-542106 | Se1.00*: mp-542605 | Si0.33O0.67* \& : mp-559550 |
| Sb0.50Pd0.50*: mp-1769 | Se1.00*: mp-14 | Si0.33O0.67*\&: mp-7087 |
| Sb0.29Pd0.71*: mp-569451 | Se1.00*: mp-570481 | Si0.33O0.67* : mp-561181 |
| Sb0.27Pd0.73*: mp-680057 | Si0.07Ag0.53S0.40*: mp-7614 | Si0.33O0.67* \& : mp-640556 |
| Sb0.67Pd0.33*: mp-1356 | Si0.14Cu0.29Ni0.07S0.50*: mp-557274 | Si0.33O0.67* \& : mp-560708 |
| Sb0.33Pd0.33Se0.33*: mp-4368 | Si0.12Cu0.25Pb0.12S0.50*: mp-555818 | Si0.33O0.67* : $\mathrm{mp}-554573$ |
| Sb0.67Pt0.33*: mp-562 | Si0.17Cu0.33S0.50*: mp-9248 | Si0.33O0.67* \& : mp-680204 |
| Sb0.67Rh0.33*: mp-2682 | Si0.17Cu0.33S0.50*: mp-15895 | Si0.33O0.67* \& : mp-555483 |
| Sb0.75Rh0.25*: mp-2395 | Si0.14Cu0.36S0.50*: mp-510418 | Si0.33O0.67*\&: mp-17909 |
| Sb0.50Rh0.50*: mp-20619 | Si0.04H0.65S0.12N0.19*: mp-557080 | Si0.33O0.67*\&: mp-733790 |
| Sb0.40S0.60*: mp-2809 | Si0.09Hg0.36S0.55*: mp-17948 | Si0.33O0.67*\&: mp-600071 |
| Sb0.33S0.33I0.33*: mp-973217 | Si0.09Hg0.36Se0.55*: mp-18230 | Si0.33O0.67* : mp-556882 |
| Sb0.33S0.3310.33*: mp-23041 | Si0.43N0.57*: mp-2245 | Si0.33O0.67*\&: mp-558115 |
| Sb0.40Se0.60*: mp-2160 | Si0.43N0.57*: mp-988 | Si0.33O0.67* \& : mp-560336 |
| Sb0.33Se0.33I0.33*: mp-22996 | Si0.40N0.40O0.20*: mp-4497 | Si0.33O0.67* \& : mp-557465 |
| Sb0.40Te0.60*: mp-1201 | Si0.33O0.67*\&: mp-554243 | Si0.33O0.67* \& : mp-600053 |

## Appendix $D$

| Si0.33O0.67*\&: mp-557933 | Si0.33O0.67*\&: mp-600024 | Si0.33O0.67* \& : mp-600023 |
| :---: | :---: | :---: |
| Si0.33O0.67*\&: mp-18280 | Si0.33O0.67*\&: mp-600022 | Si0.33O0.67*\&: mp-558947 |
| Si0.33O0.67*\&: mp-557264 | Si0.33O0.67*\&: mp-600001 | Si0.33O0.67* : mp-555891 |
| Si0.33O0.67*\&: mp-600052 | Si0.33O0.67*\&: mp-561090 | Si0.33O0.67* \& : mp-639558 |
| Si0.33O0.67*\&: mp-562490 | Si0.33O0.67*\&: mp-639480 | Si0.33O0.67* \& : mp-558025 |
| Si0.33O0.67*\&: mp-560809 | Si0.33O0.67* \& : mp-556961 | Si0.33O0.67* : mp-600033 |
| Si0.33O0.67*\&: mp-555211 | Si0.33O0.67*\&: mp-639741 | Si0.33O0.67*\&: mp-10851 |
| Si0.33O0.67*\&: mp-600057 | Si0.33O0.67*\&: mp-972808 | Si0.33O0.67* \& : mp-600059 |
| Si0.33O0.67*\&: mp-600055 | Si0.33O0.67*\&: mp-7029 | Si0.33O0.67* : mp-600054 |
| Si0.33O0.67*\&: mp-554267 | Si0.33O0.67*\&: mp-557211 | Si0.33O0.67*\&: mp-6930 |
| Si0.33O0.67*\&: mp-560998 | Si0.3300.67*\&: mp-651707 | Si0.33O0.67* \& : mp-559962 |
| Si0.33O0.67*\&: mp-615993 | Si0.33O0.67* \& : mp-559091 | Si0.33O0.67*\&: mp-600111 |
| Si0.33O0.67*\&: mp-985590 | Si0.33O0.67* \& : mp-600032 | Si0.33O0.67*\&: mp-600045 |
| Si0.33O0.67*\&: mp-600015 | Si0.33O0.67*\&: mp-600031 | Si0.33O0.67* \& : mp-600041 |
| Si0.33O0.67*\&: mp-554258 | Si0.33O0.67*\&: mp-557004 | Si0.33O0.67* : mp-560155 |
| Si0.33O0.67*\&: mp-639512 | Si0.33O0.67* \& : mp-600016 | Si0.33O0.67*\&: mp-669426 |
| Si0.33O0.67*\&: mp-6922 | Si0.33O0.67*\&: mp-600014 | Si0.33O0.67* : mp-15078 |
| Si0.33O0.67*\&: mp-555700 | Si0.33O0.67*\&: mp-600018 | Si0.33O0.67*\&: mp-600070 |
| Si0.33O0.67*\&: mp-985570 | Si0.33O0.67* \& : mp-557894 | Si0.33O0.67* : mp-557118 |
| Si0.33O0.67*\&: mp-560826 | Si0.33O0.67*\&: mp-6945 | Si0.33O0.67* \&: mp-600072 |
| Si0.33O0.67*\&: mp-546794 | Si0.33O0.67*\&: mp-8352 | Si0.33O0.67*\&: mp-600078 |
| Si0.33O0.67*\&: mp-557881 | Si0.33O0.67*\&: mp-600029 | Si0.33O0.67* : mp-667377 |
| Si0.33O0.67*\&: mp-600027 | Si0.33O0.67*\&: mp-600028 | Si0.33O0.67* \& : mp-554089 |
| Si0.33O0.67*\&: mp-644923 | Si0.33O0.67*\&: mp-558326 | Si0.33O0.67* \& : mp-639705 |

## Appendix $D$

| Si0.33O0.67*\&: mp-639511 | Si0.33O0.67**: mp-556654 | Si0.33O0.67* \& : mp-558891 |
| :---: | :---: | :---: |
| Si0.33O0.67*\&: mp-667371 | Si0.33O0.67*\&: mp-646895 | Si0.33O0.67*\&: mp-560920 |
| Si0.33O0.67*\&: mp-667376 | Si0.33O0.67*\&: mp-554151 | Si0.33O0.67*\&: mp-559347 |
| Si0.33O0.67*\&: mp-560527 | Si0.33O0.67*\&: mp-667373 | Si0.33O0.67* : mp-554543 |
| Si0.33O0.67*\&: mp-600061 | Si0.33O0.67*\&: mp-554755 | Si0.33O0.67* \& : mp-639734 |
| Si0.33O0.67* \&: mp-17279 | Si0.33O0.67*\&: mp-560064 | Si0.33O0.67* \& : mp-555556 |
| Si0.33O0.67*\&: mp-600065 | Si0.33O0.67*\&: mp-600037 | Si0.33O0.67*\&: mp-8602 |
| Si0.33O0.67*\&: mp-639506 | Si0.33O0.67*\&: mp-556262 | Si0.33O0.67* \& : mp-667383 |
| Si0.33O0.67*\&: mp-600060 | Si0.33O0.67*\&: mp-542814 | Si0.33O0.67* \& : mp-559313 |
| Si0.33O0.67*\&: mp-558351 | Si0.33O0.67*\&: mp-662706 | Si0.33O0.67*\&: mp-561351 |
| Si0.33O0.67*\&: mp-600063 | Si0.33O0.67*\&: mp-639478 | Si0.33O0.67* : mp-559872 |
| Si0.33O0.67*\&: mp-667368 | Si0.33O0.67*\&: mp-556469 | Si0.33O0.67* \& : mp-600002 |
| Si0.33O0.67*\&: mp-639724 | Si0.33O0.67*\&: mp-32895 | Si0.33O0.67* \& : mp-600005 |
| Si0.33O0.67*\&: mp-554682 | Si0.33O0.67*\&: mp-600080 | Si0.33O0.67*\&: mp-600004 |
| Si0.33O0.67*\&: mp-555521 | Si0.33O0.67*\&: mp-600083 | Si0.33O0.67* \& : mp-600000 |
| Si0.33O0.67*\&: mp-555235 | Si0.33O0.67*\&: mp-600084 | Si0.33O0.67* \& : mp-532105 |
| Si0.33O0.67*\&: mp-559360 | Si0.33O0.67*\&: mp-600085 | Si0.33O0.67* : mp-600003 |
| Si0.33O0.67*\&: mp-600091 | Si0.33O0.67*\&: mp-653763 | Si0.33O0.67* \& : mp-600007 |
| Si0.33O0.67*\&: mp-600098 | Si0.33O0.67*\&: mp-7000 | Si0.33O0.67* \& : mp-530546 |
| Si0.33O0.67*\&: mp-556454 | Si0.33O0.67*\&: mp-555251 | Si0.33O0.67* : mp-639733 |
| Si0.33O0.67* \&: mp-16964 | Si0.33O0.67* \& : mp-12787 | Si0.14Pb0.29S0.57*: mp-504564 |
| Si0.33O0.67*\&: mp-600051 | Si0.33O0.67*\&: mp-560941 | Si0.14Pb0.29Se0.57*: mp-27532 |
| Si0.33O0.67*\&: mp-554946 | Si0.33O0.67*\&: mp-639463 | Si0.33S0.67*: mp-1602 |
| Si0.33O0.67*\&: mp-600038 | Si0.33O0.67*\&: mp-600109 | Sm0.36Ag0.07S0.57*: mp-37923 |

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| Sm0.20B0.20S0.60*: mp-972448 | Sm0.22Si0.15S0.63*: mp-557561 | Sn0.40S0.60*: mp-1509 |
| :---: | :---: | :---: |
| Sm0.20Cr0.20S0.60*: mp-15932 | Sm0.21Si0.14S0.57Br0.07*: mp-555527 | Sn0.33S0.67*: mp-9984 |
| Sm0.25Cu0.08Ge0.08S0.58*: mp- | Sm0.27Si0.09S0.55Cl0.09*: mp-556910 | Sn0.36S0.0910.55*: mp-540644 |
| 555978 | Sm0.21Si0.14S0.57I0.07*: mp-560356 | Sn0.40S0.20I0.40*: mp-23386 |
| Sm0.25Cu0.25S0.50*: mp-5081 | Sm0.25Sn0.12S0.62*: mp-7355 | Sn0.22Sb0.22S0.56*: mp-17835 |
| Sm0.25Cu0.08Si0.08S0.58*: mp-554097 | Sm0.25Tl0.25S0.50*: mp-999138 | Sn0.14Sb0.29Te0.57*: mp-27947 |
| Sm0.25Cu0.08Sn0.08S0.58*: mp- | Sm0.25Tl0.25Se0.50*: mp-999137 | Sn0.33Se0.67*: mp-665 |
| 558042 | Sm0.25U0.12S0.62*: mp-555276 | Sn0.50Se0.50*: mp-691 |
| Sm0.21Eu0.21S0.57*: mp-675396 | Sn0.17Au0.83*: mp-30418 | Sn0.50Se0.50*: mp-2693 |
| Sm0.29Eu0.14S0.57*: mp-675037 | Sn0.14Bi0.29Te0.57*: mp-677596 | Sn0.50Se0.50*: mp-2168 |
| Sm0.25F0.75*\&: mp-7384 | Sn0.14Bi0.29Te0.57*: mp-38605 | Sn0.50Te0.50*: mp-1883 |
| Sm0.30In0.10S0.60*: mp-21604 | Sn0.20Ge0.20S0.60*: mp-5045 | Sr0.02Al0.39O0.60*\&: mp-531590 |
| Sm0.25Mn0.08Al0.08S0.58*: mp- | Sn0.06Hg0.39As0.22I0.33*: mp-571478 | Sr0.14Al0.29S0.57*: mp-14424 |
| 867965 | Sn0.14Hg0.29Se0.57*: mp-10955 | Sr0.12B0.29Cl0.06O0.53* : mp- |
| Sm0.17P0.17S0.67*: mp-3897 | Sn0.33I0.67*: mp-27194 | 557330 |
| Sm0.40S0.60*: mp-1403 | Sn0.33I0.67*: mp-978846 | Sr0.05B0.36O0.59*\&: mp-684018 |
| Sm0.40S0.60*: mp-32645 | Sn0.14P0.14Pd0.71*: mp-1025296 | Sr0.14B0.29S0.57*: mp-11012 |
| Sm0.34S0.66*: mp-10534 | Sn0.20P0.20S0.60*: mp-13923 | Sr0.27B0.18S0.55*: mp-30239 |
| Sm0.33S0.33F0.33*: mp-3931 | Sn0.20P0.20S0.60*: mp-4252 | Sr0.14B0.29S0.57*: mp-8947 |
| Sm0.33S0.33I0.33*: mp-541073 | Sn0.25Pd0.75*: mp-718 | Sr0.20Bi0.20Se0.60*: mp-28476 |
| Sm0.40S0.56O0.04*: mp-560711 | Sn0.33Pd0.67*: mp-1851 | Sr0.17Bi0.26Se0.57*: mp-28397 |
| Sm0.33Se0.67*: mp-1019253 | Sn0.33S0.67*: mp-1170 | Sr0.33Br0.67* \& mp-567744 |
| Sm0.34Se0.66*: mp-29832 | Sn0.50S0.50*: mp-2231 | Sr0.33Br0.67* \& : mp-32711 |
| Sm0.25Si0.08Ag0.08S0.58*: mp-867929 | Sn0.50S0.50*: mp-559676 | Sr0.33Br0.53Cl0.13* \& : mp-28021 |

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| Sr0.33Br0.33F0.33*\&: mp-23024 | Sr0.17Lu0.17Cu0.17S0.50*: mp-13189 | Sr0.20Zr0.20S0.60*: mp-558760 |
| :---: | :---: | :---: |
| Sr0.22Ca0.11I0.67*: mp-771645 | Sr0.17Mg0.17F0.67* \& : mp-561022 | Ta0.20Ag0.20S0.60*: mp-5821 |
| Sr0.22Ca0.11I0.67*: mp-756798 | Sr0.14Nd0.29S0.57*: mp-37108 | Ta0.07Ag0.50S0.43*: mp-620369 |
| Sr0.22Ca0.11I0.67*: mp-756238 | Sr0.20P0.20S0.60*: mp-9788 | Ta0.20Ag0.20S0.60*: mp-561242 |
| Sr0.22Ca0.11I0.67*: mp-756131 | Sr0.20P0.20Se0.60*: mp-7198 | Ta0.21Co0.11Pd0.05Se0.63*: mp- |
| Sr0.33Cl0.67* \& mp-23209 | Sr0.14Pr0.29S0.57*: mp-38240 | 505133 |
| Sr0.33Cl0.33F0.33* \& mp-22957 | Sr0.50S0.50*: mp-1087 | Ta0.12Cu0.38S0.50*: mp-10748 |
| Sr0.12Cu0.25Ge0.12S0.50*: mp-18685 | Sr0.19Sb0.25S0.56*: mp-29295 | Ta0.20Cu0.20S0.60*: mp-3102 |
| Sr0.12Cu0.25Ge0.12Se0.50*: mp-16179 | Sr0.21Sb0.21S0.59*: mp-16061 | Ta0.12Cu0.38Se0.50*: mp-4081 |
| Sr0.12Cu0.25Sn0.12S0.50*: mp-16988 | Sr0.20Sb0.20Se0.40F0.20*: mp-556194 | Ta0.31Mn0.08S0.62*: mp-3581 |
| Sr0.12Cu0.25Sn0.12S0.50*: mp-17322 | Sr0.50Se0.50*: mp-2758 | Ta0.15Ni0.23S0.62*: mp-562537 |
| Sr0.14Dy0.29S0.57*: mp-980666 | Sr0.08Si0.15B0.15O0.62* : mp-6032 | Ta0.25Ni0.12S0.62*: mp-28308 |
| Sr0.14Ga0.29S0.57*: mp-14425 | Sr0.14Sm0.29S0.57*: mp-34508 | Ta0.20Ni0.10Se0.70*: mp-541183 |
| Sr0.22Ga0.22S0.56*: mp-14680 | Sr0.29Sn0.14S0.57*: mp-30294 | Ta0.15Ni0.23Se0.62*: mp-541509 |
| Sr0.14Gd0.29S0.57*: mp-37183 | Sr0.25Sn0.12S0.38F0.25*: mp-17676 | Ta0.30Pb0.10S0.60*: mp-20784 |
| Sr0.29Ge0.14S0.57*: mp-4578 | Sr0.25Sn0.12Se0.62*: mp-568525 | Ta0.22Pd0.11S0.67*: mp-8435 |
| Sr0.33I0.67*: mp-568284 | Sr0.27Sn0.13Se0.60*: mp-570983 | Ta0.15Pd0.23Se0.62*: mp-18010 |
| Sr0.33I0.67*: mp-23181 | Sr0.25Sn0.12Se0.38F0.25*: mp-17057 | Ta0.22Pd0.11Se0.67*: mp-8436 |
| Sr0.33I0.33F0.33*: mp-23046 | Sr0.25Ta0.14S0.61*: mp-531358 | Ta0.15Pt0.23S0.62*: mp-560046 |
| Sr0.14In0.29S0.57*: mp-21781 | Sr0.25Ta0.14S0.61*: mp-532315 | Ta0.25S0.75*: mp-30527 |
| Sr0.14In0.29Se0.57*: mp-21733 | Sr0.22Ti0.19S0.58*: mp-676818 | Ta0.25Se0.75*: mp-29652 |
| Sr0.14La0.29S0.57*: mp-34141 | Sr0.14Tl0.14P0.14S0.57*: mp-17090 | Ta0.18Se0.73I0.09*: mp-30531 |
| Sr0.11Li0.11Al0.11F0.67* : mp-6591 | Sr0.14Y0.29S0.57*: mp-29035 | Ta0.30Sn0.10S0.60*: mp-9132 |
| Sr0.04Li0.04B0.35O0.58* \& : mp-18495 | Sr0.20Zr0.20S0.60*: mp-5193 | Ta0.12Tl0.25Ag0.12S0.50*: mp-558241 |

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| Ta0.12Tl0.19Cu0.19S0.50*: mp-554994 | Tb0.25Cu0.08Sn0.08S0.58*: mp- | Tb0.25Tl0.25Se0.50*: mp-569507 |
| :---: | :---: | :---: |
| Ta0.12Tl0.12Cu0.25S0.50*: mp-9815 | 554781 | Tc0.33S0.67*: mp-9481 |
| Ta0.12Tl0.38S0.50*: mp-7562 | Tb0.25F0.75*\&: mp-11347 | Te1.00*: mp-567313 |
| Ta0.12Tl0.24S0.65*: mp-18344 | Tb0.15In0.25S0.60*: mp-20606 | Te1.00*: mp-19 |
| Ta0.20Tl0.20S0.60*: mp-10795 | Tb0.25K0.12Cu0.12S0.50*: mp-11605 | Te0.60As0.40*: mp-484 |
| Ta0.12Tl0.38Se0.50*: mp-10644 | Tb0.21K0.07F0.71*\&: mp-17838 | Te0.60As0.40*: mp-9897 |
| Ta0.12Tl0.24Se0.65*: mp-542140 | Tb0.14K0.14Ge0.14S0.57*: mp-12011 | Te0.67Au0.33*: mp-20123 |
| Tb0.10B0.30O0.60*\&: mp-559434 | Tb0.25K0.25S0.50*: mp-999129 | Te0.67Au0.33*: mp-571547 |
| Tb0.10B0.30O0.60*\&: mp-683867 | Tb0.25Na0.25S0.50*: mp-999126 | Te0.67Au0.33*: mp-1662 |
| Tb0.08Ba0.12P0.16S0.64*: mp-554264 | Tb0.25Na0.25Se0.50*: mp-999127 | Te0.67Au0.33*: mp-567525 |
| Tb0.29Ca0.14S0.57*: mp-38327 | Tb0.17P0.17O0.67* \& : mp-4340 | Te0.67Ir0.33*: mp-1551 |
| Tb0.18Cs0.09Ag0.27Se0.45*: mp- | Tb0.17P0.17S0.67*: mp-4672 | Te0.73Ir0.27*: mp-32682 |
| 542164 | Tb0.25Rb0.25S0.50*: mp-9365 | Te0.67Ir0.33*: mp-569322 |
| Tb0.10Cs0.20K0.10Cl0.60*: mp- | Tb0.25Rb0.25Se0.50*: mp-10782 | Te0.67Ir0.33*: mp-569388 |
| 580631 | Tb0.40S0.60*: mp-673644 | Te0.50Pb0.50*: mp-19717 |
| Tb0.10Cs0.20Na0.10Cl0.60*: mp- | Tb0.40S0.60*: mp-9323 | Te0.50Pd0.50*: mp-564 |
| 568670 | Tb0.33S0.33F0.33*: mp-10930 | Te0.67Pd0.33*: mp-782 |
| Tb0.25Cs0.25S0.50*: mp-972199 | Tb0.33Se0.67*: mp-1025077 | Te0.67Pt0.33*: mp-399 |
| Tb0.25Cs0.25S0.50*: mp-9085 | Tb0.25Si0.08Cu0.08S0.58*: mp-560501 | Te0.60Pt0.40*: mp-541180 |
| Tb0.17Cs0.17Zn0.17Se0.50*: mp- | Tb0.21Si0.16S0.63*: mp-16402 | Te0.73Rh0.27*: mp-7273 |
| 573710 | Tb0.21Si0.14S0.57I0.07*: mp-560853 | Te0.67Rh0.33*: mp-754 |
| Tb0.25Cu0.08Ge0.08S0.58*: mp- | Tb0.25Si0.12S0.19O0.44*: mp-16590 | Te0.67Rh0.33*: mp-228 |
| 557517 | Tb0.25Sn0.12S0.62*: mp-555069 | Th0.11P0.22S0.67*: mp-14249 |
| Tb0.25Cu0.25S0.50*: mp-5737 | Tb0.25Tl0.25S0.50*: mp-999119 | Th0.33S0.67*: mp-1146 |

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| Th0.29S0.71*: mp-1666 | Tl0.10Ag0.10As0.20Pb0.10S0.50*: | Tl0.25Bi0.25S0.50*: mp-554310 |
| :---: | :---: | :---: |
| Th0.33S0.33O0.33*: mp-8136 | mp-697231 | Tl0.36Bi0.18S0.45*: mp-23408 |
| Th0.29Se0.71*: mp-2392 | Tl0.10Ag0.10As0.20Pb0.10S0.50*: | Tl0.25Bi0.25Se0.50*: mp-29662 |
| Ti0.07Ag0.53S0.40*: mp-557833 | mp-677611 | Tl0.25Bi0.25Te0.50*: mp-27438 |
| Ti0.32Ag0.05S0.63*: mp-675920 | Tl0.33Ag0.33Se0.33*: mp-29238 | Tl0.50Br0.50*\&: mp-568560 |
| Ti0.33Cu0.02S0.65*: mp-767157 | Tl0.33Ag0.33Te0.33*: mp-5874 | Tl0.50Br0.50*\&: mp-568949 |
| Ti0.30Cu0.10S0.60*: mp-686094 | Tl0.09As0.27Pb0.09S0.55*: mp-647900 | Tl0.36Cd0.09I0.55*: mp-570339 |
| Ti0.11Cu0.44S0.44*: mp-29091 | Tl0.43As0.14S0.43*: mp-9791 | Tl0.17Cu0.17P0.17Se0.50*: mp-569129 |
| Ti0.29Cu0.14S0.57*: mp-3951 | Tl0.07As0.36S0.57*: mp-28442 | Tl0.20Cu0.40S0.40*: mp-8676 |
| Ti0.29Cu0.14S0.57*: mp-559918 | Tl0.25As0.25S0.50*: mp-4988 | Tl0.12Cu0.50Se0.38*: mp-1025447 |
| Ti0.29Ni0.14S0.57*: mp-1025263 | Tl0.43As0.14Se0.43*: mp-7684 | Tl0.25Cu0.25Se0.50*: mp-14090 |
| Ti0.30Ni0.10S0.60*: mp-13993 | T10.22Au0.44S0.33*: mp-29898 | Tl0.20Cu0.40Se0.40*: mp-5000 |
| Ti0.30Ni0.10S0.60*: mp-13994 | T10.25B0.25S0.50*: mp-8946 | Tl0.25Ga0.25Se0.50*: mp-680555 |
| Ti0.33S0.67*: mvc-11238 | Tl0.19B0.19S0.62*: mp-17823 | Tl0.25Ga0.25Se0.50*: mp-17254 |
| Ti0.33S0.67*: mvc-10843 | Tl0.43B0.14S0.43*: mp-29337 | Tl0.25Ga0.25Se0.50*: mp-9580 |
| Ti0.33S0.67*: mp-558110 | Tl0.20B0.20S0.60*: mp-28809 | Tl0.25Ge0.12Pb0.12S0.50*: mp-653561 |
| Ti0.33S0.67*: mp-9027 | Tl0.30Bi0.10I0.60*: mp-571219 | Tl0.22Ge0.22S0.56*: mp-12307 |
| Ti0.25S0.75*: mp-9920 | T10.27Bi0.12I0.62*: mp-684055 | Tl0.33Ge0.17S0.50*: mp-7277 |
| Ti0.33S0.67*: mp-2156 | Tl0.21Bi0.14I0.64*: mp-569203 | Tl0.33Ge0.17Se0.50*: mp-14242 |
| Ti0.35S0.65*: mp-684731 | Tl0.09Bi0.09P0.18S0.64*: mp-556665 | Tl0.22Ge0.22Se0.56*: mp-540818 |
| Ti0.33Se0.67*: mp-2194 | Tl0.17Bi0.08P0.17S0.58*: mp-559093 | Tl0.17Hg0.17As0.17S0.50*: mp-555199 |
| Ti0.15Tl0.13Ag0.03Se0.69*: mp- | Tl0.10Bi0.10P0.20S0.60*: mp-556592 | Tl0.09Hg0.09As0.27S0.55*: mp-6096 |
| 570021 | Tl0.10Bi0.10P0.20Se0.60*: mp-567864 | Tl0.11Hg0.08Sb0.05As0.22S0.54*: |
| Ti0.12Tl0.12P0.12S0.62*: mp-558747 | Tl0.10Bi0.10P0.20Se0.60*: mp-567917 | mp-553948 |

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| Tl0.50I0.50*: mp-22858 | Tl0.17Pt0.33Se0.50*: mp-541487 | Tl0.07V0.36S0.57*: mp-29227 |
| :---: | :---: | :---: |
| Tl0.50I0.50*: mp-571102 | Tl0.55S0.09Br0.36*: mp-28518 | Tl0.38V0.12S0.50*: mp-5513 |
| Tl0.10In0.10P0.20Se0.60*: mp-19985 | Tl0.55S0.0910.36*: mp-27938 | Tl0.38V0.12Se0.50*: mp-1025549 |
| Tl0.25In0.25S0.50*: mp-20042 | Tl0.07Sb0.17As0.16Pb0.03S0.57*: | Tm0.10Ag0.10P0.20Se0.60*: mp-13385 |
| Tl0.25In0.25S0.50*: mp-865274 | mp-581586 | Tm0.05Al0.15B0.2000.60*\&: mp- |
| Tl0.25In0.25S0.50*: mp-22566 | Tl0.07Sb0.21As0.14S0.57*: mp-558174 | 13516 |
| Tl0.25In0.25Se0.50*: mp-22232 | Tl0.11Sb0.33S0.56*: mp-27515 | Tm0.10B0.3000.60*\&: mp-680717 |
| Tl0.30In0.20Se0.50*: mp-686102 | Tl0.25Sb0.25S0.50*: mp-28230 | Tm0.15B0.25O0.60*\&: mp-558534 |
| Tl0.20In0.30Se0.50*: mp-685385 | Tl0.07Sb0.36S0.57*: mp-3267 | Tm0.29Cd0.14S0.57*: mp-4324 |
| Tl0.14In0.14Si0.14S0.57*: mp-556744 | Tl0.25Sb0.25S0.50*: mp-676540 | Tm0.25Cu0.25S0.50*: mp-12455 |
| Tl0.25P0.12Au0.12S0.50*: mp-9510 | Tl0.25Sb0.25Se0.50*: mp-567318 | Tm0.17P0.17O0.67*\&: mp-5884 |
| Tl0.17P0.17Au0.17Se0.50*: mp-569287 | Tl0.25Sb0.25Te0.50*: mp-4573 | Tm0.40S0.60*: mp-18529 |
| Tl0.14P0.14Pb0.14S0.57*: mp-510646 | Tl0.55Se0.09I0.36*: mp-28517 | Tm0.40S0.60*: mp-14787 |
| Tl0.38P0.12S0.50*: mp-16848 | Tl0.33Si0.17S0.50*: mp-8190 | Tm0.40S0.60*: mp-2309 |
| Tl0.33P0.17S0.50*: mp-28217 | Tl0.44Si0.11S0.44*: mp-8479 | Tm0.40S0.20O0.40*: mp-3556 |
| Tl0.33P0.17Se0.50*: mp-28394 | Tl0.44Si0.11Se0.44*: mp-28334 | Tm0.40S0.4000.20*: mp-8763 |
| Tl0.38P0.12Se0.50*: mp-4160 | Tl0.33Si0.17Se0.50*: mp-14241 | Tm0.29Zn0.14S0.57*: mp-17043 |
| Tl0.38P0.12Se0.50*: mp-614491 | Tl0.18Sn0.09As0.18S0.55*: mp-6023 | U0.31Cr0.04S0.65*: mp-540544 |
| Tl0.33Pb0.11I0.56*: mp-23380 | Tl0.14Sn0.14P0.14S0.57*: mp-6057 | U0.29Cu0.10S0.62*: mp-28356 |
| Tl0.20Pb0.20I0.60*: mp-27552 | Tl0.19Sn0.24S0.57*: mp-29303 | U0.25Cu0.17S0.58*: mp-619067 |
| Tl0.36Pb0.09I0.55*: mp-29212 | Tl0.22Sn0.22S0.56*: mp-7499 | U0.31Fe0.04S0.65*: mp-559388 |
| Tl0.17Pd0.33Se0.50*: mp-7038 | Tl0.33Sn0.17S0.50*: mp-542623 | U0.11Pd0.38S0.51*: mp-531882 |
| Tl0.17Pt0.33S0.50*: mp-9272 | Tl0.33Te0.17S0.50*: mp-17172 | U0.29Pd0.14S0.57*: mp-5335 |
| Tl0.15Pt0.38S0.46*: mp-28805 | Tl0.07V0.21Cr0.14S0.57*: mp-554140 | U0.26Rh0.09Se0.66*: mp-37167 |

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| U0.33S0.67*: mp-685066 | V0.33S0.67*: mp-1013526 | Y0.25Cu0.08Ge0.08S0.58*: mp-556781 |
| :---: | :---: | :---: |
| U0.25S0.75*: mp-12406 | V0.33S0.67*: mp-557523 | Y0.17Cu0.17Pb0.17S0.50*: mp-865203 |
| U0.33S0.67*: mp-639 | V0.38S0.62*: mp-690772 | Y0.17Cu0.17Pb0.17S0.50*: mp-542802 |
| U0.33S0.67*: mp-2849 | V0.18Se0.82*: mp-28256 | Y0.25Cu0.08Sn0.08S0.58*: mp-17747 |
| U0.25Se0.75*: mp-9429 | V0.33Se0.67*: mp-694 | Y0.25Hf0.12S0.62*: mp-16919 |
| U0.33Se0.33S0.33*: mp-19924 | W0.33S0.67*: mp-1025571 | Y0.29Mg0.14S0.57*: mp-1001024 |
| V0.10Ag0.10P0.20Se0.60*: mp-6543 | W0.33S0.67*: mp-1023925 | Y0.17P0.17S0.67*: mp-31266 |
| V0.25Au0.25S0.50*: mp-11193 | W0.33S0.67*: mp-1023937 | Y0.33S0.33F0.33*: mp-10086 |
| V0.12Cu0.38S0.50*: mp-3762 | W0.33S0.67*: mp-9813 | Y0.25Si0.08Cu0.08S0.58*: mp-561173 |
| V0.12Cu0.38Se0.50*: mp-21855 | W0.33S0.67*: mp-224 | Yb0.08B0.33O0.58*\&: mp-752484 |
| V0.03Cu0.39Sn0.03As0.06S0.48*: | W0.33S0.67*: mp-1028441 | Yb0.33Cl0.67* ${ }^{\text {\% }}$ : mp-865716 |
| mp-720486 | W0.33Se0.22S0.44*: mp-1025577 | Yb0.33Cl0.67* ${ }^{\text {\% }}$ : mp-23220 |
| V0.31Ga0.08S0.62*: mp-4474 | W0.33Se0.22S0.44*: mp-1025584 | Yb0.33Cl0.33F0.33*\&: mp-557483 |
| V0.31Ge0.08S0.62*: mp-8688 | W0.33Se0.17S0.50*: mp-1028487 | Yb0.20Cs0.20Br0.60*: mp-568005 |
| V0.31Ge0.08Se0.62*: mp-8689 | W0.33Se0.17S0.50*: mp-1028558 | Yb0.20Cs0.20F0.60*\&: mp-8398 |
| V0.30Ni0.10S0.60*: mp-676058 | Xe1.00*\&: mp-979286 | Yb0.14Dy0.29S0.57*: mp-676154 |
| V0.31Ni0.08S0.62*: mp-696867 | Xe1.00*\&: mp-972256 | Yb0.14Er0.29S0.57*: mp-865865 |
| V0.29Ni0.14S0.57*: mp-4909 | Xe1.00*\&: mp-611517 | Yb0.33F0.67* \& : mp-865934 |
| V0.33S0.67*: mvc-11241 | Xe1.00* \&: mp-570510 | Yb0.14Gd0.29S0.57*: mp-675856 |
| V0.33S0.67*: mp-849060 | Xe1.00*\&: mp-979285 | Yb0.14K0.14Si0.14S0.57*: mp-12376 |
| V0.33S0.67*: mp-1013525 | Y0.07Ag0.21P0.14S0.57*: mp-561467 | Yb0.14La0.29S0.57*: mp-675767 |
| V0.43S0.57*: mp-799 | Y0.05Be0.11B0.26O0.58*\&: mp- | Yb0.11Li0.11Al0.11F0.67* : mp- |
| V0.33S0.67*: mp-9561 | 1020740 | 10103 |
| V0.43S0.57*: mp-1081 | Y0.29Cd0.14S0.57*: mp-35785 | Yb0.10Na0.10P0.20S0.60*: mp-10838 |

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| Yb0.14Nd0.29S0.57*: mp-675244 | 1025500 | Zn0.50S0.50*: mp-556716 |
| :---: | :---: | :---: |
| Yb0.14Pr0.29S0.57*: mp-675668 | Zn0.12Cu0.25Sn0.12Se0.50*: mvc- | Zn0.50S0.50*: mp-554004 |
| Yb0.20Rb0.20Br0.60*: mp-571418 | 16089 | Zn0.50S0.50*: mp-556152 |
| Yb0.09Rb0.36I0.55*: mp-23347 | Zn0.07Cu0.27Sn0.13Se0.53*: mvc- | Zn0.50S0.50*: mp-556155 |
| Yb0.50S0.50*: mp-1820 | 14983 | Zn0.50S0.50*: mp-581412 |
| Yb0.50Se0.50*: mp-286 | Zn0.12Cu0.25Sn0.12Se0.50*: mp-16564 | Zn0.50S0.50*: mp-556000 |
| Yb0.14Sm0.29S0.57*: mp-675677 | Zn0.14Ga0.29Se0.57*: mp-15776 | Zn0.50S0.50*: mp-556105 |
| Yb0.14Tb0.29S0.57*: mp-673682 | Zn0.29Ge0.14S0.57*: mp-675748 | Zn0.50S0.50*: mp-581405 |
| Yb0.14Y0.29S0.57*: mp-675293 | Zn0.29Ge0.14Se0.57*: mp-35539 | Zn0.50S0.50*: mp-581602 |
| Zn0.38Cd0.12S0.50*: mp-981379 | Zn0.14In0.29S0.57*: mp-22052 | Zn0.50S0.50*: mp-581601 |
| Zn0.25Cd0.25S0.50*: mp-971712 | Zn0.14In0.29S0.57*: mp-674328 | Zn0.50S0.50*: mp-557418 |
| Zn0.25Cd0.25Se0.50*: mp-1017534 | Zn0.14In0.29Se0.57*: mp-34169 | Zn0.50S0.50*: mp-554630 |
| Zn0.14Cr0.29S0.57*: mvc-11256 | Zn0.14In0.29Se0.57*: mp-22607 | Zn0.50S0.50*: mp-554253 |
| Zn0.14Cr0.29S0.57*: mp-4194 | Zn0.50S0.50*: mp-556448 | Zn0.50S0.50*: mp-581258 |
| Zn0.14Cr0.29Se0.57*: mvc-11651 | Zn0.50S0.50*: mp-555583 | Zn0.50S0.50*: mp-554999 |
| Zn0.14Cr0.29Se0.57*: mp-4697 | Zn0.50S0.50*: mp-581476 | Zn0.50S0.50*: mp-556784 |
| Zn0.12Cu0.25Ge0.12S0.50*: mvc- | Zn0.50S0.50*: mp-557054 | Zn0.50S0.50*: mp-554713 |
| 16091 | Zn0.50S0.50*: mp-556280 | Zn0.50S0.50*: mp-582680 |
| Zn0.12Cu0.25Ge0.12S0.50*: mp-6408 | Zn0.50S0.50*: mp-557026 | Zn0.50S0.50*: mp-555773 |
| Zn0.12Cu0.25Ge0.12Se0.50*: mvc- | Zn0.50S0.50*: mp-556732 | Zn0.50S0.50*: mp-557062 |
| 16079 | Zn0.50S0.50*: mp-555628 | Zn0.50S0.50*: mp-555381 |
| Zn 0.12 Cu 0.25 Ge 0.12 Se 0.50 *: mp- | Zn0.50S0.50*: mp-556815 | Zn0.50S0.50*: mp-555782 |
| 10824 | Zn0.50S0.50*: mp-556207 | Zn0.50S0.50*: mp-554608 |
| Zn0.12Cu0.25Sn0.12S0.50*: mp- | Zn0.50S0.50*: mp-556363 | Zn0.50S0.50*: mp-555666 |

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| Zn0.50S0.50*: mp-554961 | Zn0.50S0.50*: mp-557009 | Zn0.50S0.50*: mp-561286 |
| :---: | :---: | :---: |
| Zn0.50S0.50*: mp-556543 | Zn0.50S0.50*: mp-581425 | Zn0.50S0.50*: mp-554405 |
| Zn0.50S0.50*: mp-554829 | Zn0.50S0.50*: mp-555594 | Zn0.50S0.50*: mp-543011 |
| Zn0.50S0.50*: mp-555858 | Zn0.50S0.50*: mp-553916 | Zn0.50S0.50*: mp-556989 |
| Zn0.50S0.50*: mp-560725 | Zn0.50S0.50*: mp-555664 | Zn0.50S0.50*: mp-9946 |
| Zn0.50S0.50*: mp-561258 | Zn0.50S0.50*: mp-680085 | Zn0.50S0.50*: mp-647075 |
| Zn0.50S0.50*: mp-555543 | Zn0.50S0.50*: mp-557308 | Zn0.50S0.50*: mp-556392 |
| Zn0.50S0.50*: mp-557346 | Zn0.50S0.50*: mp-556775 | Zn0.50S0.50*: mp-554820 |
| Zn0.50S0.50*: mp-555311 | Zn0.50S0.50*: mp-556161 | Zn0.50Se0.50*: mp-380 |
| Zn0.50S0.50*: mp-555280 | Zn0.50S0.50*: mp-680087 | Zn0.50Se0.50*: mp-1190 |
| Zn0.50S0.50*: mp-554115 | Zn0.50S0.50*: mp-13456 | Zn0.12Si0.12Cu0.25S0.50*: mp-977414 |
| Zn0.50S0.50*: mp-554503 | Zn0.50S0.50*: mp-554889 | Zr0.29Cu0.14S0.57*: mp-14025 |
| Zn0.50S0.50*: mp-555151 | Zn0.50S0.50*: mp-560588 | Zr0.20Pb0.20S0.60*: mp-20244 |
| Zn0.50S0.50*: mp-561118 | Zn0.50S0.50*: mp-555410 | Zr0.33S0.67*: mp-1186 |
| Zn0.50S0.50*: mp-555763 | Zn0.50S0.50*: mp-557175 | Zr0.25S0.75*: mp-9921 |
| Zn0.50S0.50*: mp-555779 | Zn0.50S0.50*: mp-555079 | Zr0.33Se0.67*: mp-2076 |
| Zn0.50S0.50*: mp-555214 | Zn0.50S0.50*: mp-554681 | Zr0.25Se0.75*: mp-1683 |
| Zn0.50S0.50*: mp-10281 | Zn0.50S0.50*: mp-556395 | Zr0.20Sn0.20S0.60*: mp-17324 |
| Zn0.50S0.50*: mp-10695 | Zn0.50S0.50*: mp-556468 | Zr0.17Ti0.17Se0.67*: mp-570062 |
| Zn0.50S0.50*: mp-18377 | Zn0.50S0.50*: mp-556005 | Zr0.17Tl0.17Cu0.17S0.50*: mp-7049 |
| Zn0.50S0.50*: mp-556950 | Zn0.50S0.50*: mp-556576 | Zr0.17Tl0.17Cu0.17Se0.50*: mp-7050 |
| Zn0.50S0.50*: mp-553880 | Zn0.50S0.50*: mp-554986 |  |
| Zn0.50S0.50*: mp-557151 | Zn0.50S0.50*: mp-561196 |  |

## Appendix $D$

## D.1.4 Potentially Functionally Stable Cathode Coatings for LSPS

| Ba0.30Li0.70: mp-569841 | Li0.75Cu0.25: mp-975882 | Li0.40Fe0.20S0.40*: mp-775931 |
| :---: | :---: | :---: |
| K0.20Li0.10Al0.10F0.60* \& : mp- | Li0.33Cu0.33S0.33*: mp-774736 | Li0.25Gd0.25Se0.50*: mp-37680 |
| 722903 | Li0.33Cu0.33S0.33*: mp-867689 | Li0.25Gd0.25Se0.50*: mp-15792 |
| Li0.50Ag0.50: mp-2426 | Li0.33Cu0.33S0.33*: mp-766480 | Li0.79Ge0.21: mp-1777 |
| Li0.75Ag0.25: mp-865875 | Li0.33Cu0.33S0.33*: mp-774712 | Li0.50Ge0.50: mp-9918 |
| Li0.75Ag0.25: mp-976408 | Li0.33Cu0.33S0.33*: mp-753508 | Li0.50Ge0.50: mp-8490 |
| Li0.75Ag0.25: mp-977126 | Li0.33Cu0.33S0.33*: mp-753826 | Li0.65Ge0.35: mp-29631 |
| Li0.50Ag0.50: mp-1018026 | Li0.33Cu0.33S0.33*: mp-766467 | Li0.78Ge0.22: mp-29630 |
| Li0.50As0.50: mp-7943 | Li0.33Cu0.33S0.33*: mp-753371 | Li0.69Ge0.31: mp-27932 |
| Li0.75As0.25: mp-757 | Li0.33Cu0.33S0.33*: mp-753605 | Li0.50Ge0.25Pd0.25: mp-30080 |
| Li0.75Au0.25: mp-11247 | Li0.14Fe0.29S0.57*: mp-1040470 | Li0.75Hg0.25: mp-1646 |
| Li0.79Au0.21: mp-567395 | Li0.40Fe0.20S0.40*: mp-754407 | Li0.75Hg0.25: mp-976047 |
| Li0.08C0.92: mp-1021323 | Li0.33Fe0.22S0.44*: mp-753818 | Li0.50Hg0.50: mp-2012 |
| Li0.50C0.50: mp-1378 | Li0.40Fe0.20S0.40*: mp-753943 | Li0.50I0.50*: mp-568273 |
| Li0.14C0.86: mp-1001581 | Li0.25Fe0.25S0.50*: mp-754660 | Li0.50I0.50*: mp-570935 |
| Li0.75C0.25: mp-976060 | Li0.40Fe0.20S0.40*: mp-755796 | Li0.5010.50*: mp-22899 |
| Li0.14Co0.29S0.57*: mvc-16740 | Li0.25Fe0.25S0.50*: mp-756094 | Li0.81In0.19: mp-510430 |
| Li0.25Co0.25S0.50*: mp-752928 | Li0.40Fe0.20S0.40*: mp-756348 | Li0.37Mn0.32As0.32: mp-531949 |
| Li0.25Co0.25S0.50*: mp-753946 | Li0.40Fe0.20S0.40*: mp-756187 | Li0.33Mn0.33P0.33: mp-504691 |
| Li0.25Co0.25S0.50*: mp-757100 | Li0.33Fe0.22S0.44*: mp-768335 | Li0.14Mn0.29S0.57*: mvc-16742 |
| Li0.20Co0.27S0.53*: mp-767412 | Li0.33Fe0.22S0.44*: mp-768360 | Li0.14Mn0.29S0.57*: mvc-16773 |

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| Li0.14Mn0.29S0.57*: mvc-16758 | Li0.20S0.80*: mp-995393 | Li0.10Ti0.30S0.60*: mp-19755 |
| :---: | :---: | :---: |
| Li0.25Mo0.25S0.50: mp-30248 | Li0.75Sb0.25: mp-7955 | Li0.25Ti0.25S0.50*: mp-1001784 |
| Li0.75N0.25: mp-2341 | Li0.75Sb0.25: mp-2074 | Li0.10Ti0.30Se0.60*: mp-8132 |
| Li0.75N0.25: mp-2251 | Li0.73Sb0.27: mp-676024 | Li0.33U0.17S0.50*: mp-15885 |
| Li0.25Nb0.25S0.50*: mp-7936 | Li0.50Sb0.25Pd0.25: mp-10180 | Li0.14V0.29S0.57*: mvc-16776 |
| Li0.19Nb0.27S0.54*: mp-767171 | Li0.67Se0.33*: mp-2286 | Li0.14V0.29S0.57*: mvc-16735 |
| Li0.18Nb0.27S0.55*: mp-767218 | Li0.78Si0.22: mp-27930 | Li0.38V0.12S0.50*: mp-768440 |
| Li0.08Ni0.46Ge0.46: mp-15949 | Li0.63Si0.37: mp-1314 | Li0.38V0.12S0.50*: mp-768423 |
| Li0.25P0.75*: mp-1025406 | Li0.79Si0.21: mp-569849 | Li0.44V0.11S0.44*: mp-768414 |
| Li0.75P0.25: mp-736 | Li0.81Si0.19: mp-542598 | Li0.38V0.12S0.50*: mp-768476 |
| Li0.50P0.50: mp-9588 | Li0.76Si0.24: mp-672287 | Li0.38V0.12S0.50*: mp-760375 |
| Li0.17P0.83: mp-2412 | Li0.81Si0.19: mp-29720 | Li0.38V0.12S0.50*: mp-755642 |
| Li0.81Pb0.19: mp-574275 | Li0.81Sn0.19: mp-573471 | Li0.25V0.25S0.50*: mp-7543 |
| Li0.77Pb0.23: mp-504760 | Li0.50Sn0.25Pt0.25: mp-866202 | Li0.25V0.25S0.50*: mp-754542 |
| Li0.81Pb0.19: mp-573651 | Li0.25Sn0.25S0.50*: mp-27683 | Li0.18V0.27S0.55*: mp-756195 |
| Li0.25Pr0.25S0.50*: mp-675419 | Li0.25Sn0.25S0.50*: mp-1001783 | Li0.14Zr0.29O0.57: mp-770731 |
| Li0.75Re0.25: mp-983152 | Li0.18Ta0.27S0.55*: mp-755664 | Sr0.11Li0.11Al0.11F0.67* \& mp- |
| Li0.50S0.50*: mp-32641 | Li0.67Te0.33*: mp-2530 | 555591 |
| Li0.67S0.33*: mp-1153 | Li0.25Te0.75*: mp-27466 | Tb0.25Li0.25Se0.50*: mp-15793 |
| Li0.67S0.33*: mp-557142 | Li0.14Ti0.29S0.57*: mvc-16738 | Tb0.25Li0.25Se0.50*: mp-38695 |
| Li0.67S0.33*: mp-1125 | Li0.25Ti0.25S0.50*: mp-755414 |  |
| Li0.67S0.33*: mp-32899 | Li0.25Ti0.25S0.50*: mp-9615 |  |

## Appendix E

Supplementary Information:
Advanced Sulfide Solid Electrolyte
by Core-Shell Structural Design

Table 3.S1 Summary of the decomposition voltages and severities of LSPS samples annealed at various temperatures derived from CV curves.

| Sample | Low-Voltage |  |  |  |
| :--- | :--- | :--- | :--- | :--- |
| Peak (V) | High-Voltage <br> Decomposition <br> Onset | Integrated Current <br> Density (VA/g) | Decomposition <br> Degree |  |
| 400 | 0.66 | 3.15 | 4.77612 | Medium |
| 450 | 0.66 | 3.16 | 0.24920 | Minor |
| 460 | 0.68 | 2.87 | 0.37556 | Minor |
| 470 | 0.71 | 3.09 | 0.41444 | Minor |
| 480 | 0.69 | 3.04 | 69.63326 | Severe |
| 490 | 0.67 | 3.20 | 105.19533 | Severe |
| 500 | 0.68 | 3.06 | 187.98299 | Severe |

Appendix E


Figure 3.S1 TEM diffraction pattern of an example shell for core-shell LSPS 460. Results show a clear amorphous diffraction pattern.


Figure 3.S2 Typical HRTEM images of particles inside the amorphous shell of LSPS 450. Results indicate that these particles are single-crystals embedded in the amorphous shell. Scale bars in the left and right figures represent 5 and 2 nm , respectively.


Figure 3.S3 Illustration of the core-shell structure and example EDS signal source regions for an LSPS particle. For this example particle, 3 different areas of the shell, 4 different particles inside the shell and the whole core area were chosen for EDS signal acquisition. This procedure was repeated for multiple particles for each LSPS sample. The average values of the obtained data were statistically analyzed and summarized in Figure 3.2c in the main text.


Figure 3.S4 STEM EDS analyses of LSPS 400, 450, 480 and 500. Atomic concentration is reported for $\mathrm{Si}, \mathrm{P}, \mathrm{S}$ and Cl in each region. Li is excluded as it cannot be detected by EDS due to its small atomic weight.


Figure 3.S5 The onset voltages of decomposition for the 7 LSPS samples annealed at different temperatures. Onset voltage is obtained by projecting the tangent of the CV curve just above decomposition onset on to the x -axis.


Figure 3.S6 The integrated decomposition current density for each of the 7 LSPS samples.


Figure 3.S7 Derivative of capacity versus voltage plots for 7 batteries cycled between high and low voltage ranges. (a) $1-5 \mathrm{~V}$, (b) $0.1-2 \mathrm{~V}$.


Figure 3.S8 Impedance profiles and ionic conductivities of LSPS solid electrolytes annealed at different temperatures. (a) Impedance profiles of carbon + LSPS/ LSPS/carbon + LSPS cells with electrolytes at different annealing temperatures tested under a low pressure of 1 MPa . The total thicknesses of the cells are $800-900 \mu \mathrm{~m}$. The carbon + LSPS layers are kept thin ( $2 \%$ of total thickness) to minimize any impact of the carbon. (b) Ionic conductivities of LSPS with different annealing temperatures extrapolated from panel a.


Figure 3.S9 Images of glass fiber separators before and after CV tests for LSPS 460 and LSPS 500. (a) Original separator. (b) Separator after CV test of minor-decomposition material (LSPS 460) between 1V and 5V. (c) Separator after CV test of severe-decomposition material (LSPS 500) between 1V and 5V. (d,e) The corresponding CV test results. Severedecomposition as determined by CV is seen to correspond to significant decomposed particle accumulation on the glass fiber.


Figure 3.S10 CV test result of LSPS 500 and separator photo after CV test. (a) CV test result for severe-decomposition material (LSPS 500) between 1 V and 3.5 V to avoid the high voltage decomposition. (b) Picture of separator in the battery for severedecomposition material (LSPS 500) after CV test between 1 V and 3.5 V .


Figure 3.S11 CV test result of LSPS 460 and separator photo after CV test. (a) CV test result for minor-decomposition material (LSPS 460) between 1V and 10V. (b) Picture of separator in the battery for minor-decomposition material (LSPS 460) after CV test between 1 V and 10 V .


Figure 3.S12 SEM image and energy dispersive spectrum of the black region on the separator in Supplementary Figure 3.S9c. Scale bar in the left figure stands for $200 \mu \mathrm{~m}$.

Appendix E


Figure 3.S13 Decay energies and electrochemical stability windows for LGPS at varying levels of applied pressure. The set of compounds above each partition indicate which decay pathway is dominant for LGPS in that electrochemical potential region and the y axis plots with how much energy that decay will proceed. The yellow shaded region indicates at which chemical potentials LGPS is stable at room temperature. (a) At no applied pressure, the voltage window is 1.75 to 2.2 V (b) 1 GPa of applied pressure increases the voltage window slightly to 1.7 to 2.28 V . (c) By 10 GPa the upper threshold has exceeded 2.5 V and the lower is at 1.75 V (d) Finally, at 20 GPa of applied pressure, the LGPS is stable from 0.495 V to in excess of 2.5 V .

## Stability Voltage vs Pressure



Figure 3.S14 The stability voltage window of LGPS as a function of various pressures from $0-20 \mathrm{GPa}$.


Figure 3.S15 Biaxial modulus (GPa) v.s. mole fraction of different elements. Si (top), S (middle), and P (bottom). Data points come from the Materials Project.

## Appendix F

## Supplementary Information: Strain

## Stabilized Ceramic-Sulfides



Figure 4.S1 STEM EDS linescans across individual LGPS particles with different particle sizes ranging from 100 nm to $3 \mu \mathrm{~m}$. The sulfur concentration from surface to the bulk is seen to have no regular pattern.


Figure 4.S2 STEM EDS linescans across individual LGPS particles sonicated in dimethyl carbonate (DMC) for 70 h with different particle sizes ranging from 60 nm to $4 \mu \mathrm{~m}$. The sulfur concentration is significantly reduced at surface region compared to that in the bulk.

## Appendix F



Figure 4.S3 STEM EDS linescans across individual LGPS particles sonicated in diethyl carbonate (DEC) for 70 h with different particle sizes ranging from 120 nm to $4 \mu \mathrm{~m}$. The sulfur concentration is significantly reduced at surface region compared to that in the bulk.


Figure 4.S4 Quantitative STEM EDS analysis of LGPS particles before and after ultrasonic preparation show that surface/bulk ratio of $S$ is obviously lower after sonication in organic electrolytes (DEC and DMC).


Figure 4.S5 STEM EDS linescans across individual LGPS particles soaked in DMC for 70 h without sonication with different particle sizes ranging from 160 nm to $3 \mu \mathrm{~m}$. The sulfur concentration from surface to the bulk is seen to have no regular pattern.


Figure 4.S6 Cycling performance of LGPS (LTO+LGPS+C as cathode, LGPS and glass fiber layers as electrolyte, and Li as anode) V.S. ultra-LGPS (LTO+ultra-LGPS+C as cathode, ultra-LGPS and glass fiber layers as electrolyte, and Li as anode) at 0.02 C .


Figure 4.S7 Cycling performance of LGPS (LTO+LGPS+C as cathode, LGPS and glass fiber layers as electrolyte, and Li as anode) V.S. ultra-LGPS (LTO+ultra-LGPS+C as cathode, ultra-LGPS and glass fiber layers as electrolyte, and Li as anode) at 0.1C.


Figure 4.S8 TEM bright-field images and STEM dark-field image of primary LTO/LGPS interface (interface between cathode and LGPS solid electrolyte layer) of LGPS battery (LTO+LGPS+C as cathode, LGPS as solid electrolyte, and Li as anode). An obvious transit layer is seen between the cathode and solid electrolyte layer


Figure 4.S9 STEM dark-field image of and EELS linescan on primary LTO/LGPS interface (interface between cathode and LGPS solid electrolyte layer) of LGPS battery (LTO+LGPS+C as cathode, LGPS as solid electrolyte, and Li as anode), showing that Li K and Ge $M_{4,5}$ peaks exist for regions both inside and outside bright particles within the transit layer.


Figure 4.S10 STEM dark-field image of and EELS linescan on primary LTO/LGPS interface (interface between cathode and LGPS solid electrolyte layer) of LGPS battery (LTO + LGPS +C as cathode, LGPS as solid electrolyte, and Li as anode), showing that S $L_{1}$ peak intensity is stronger on those S -rich bright-contrast regions within the transit layer.


Figure 4.S11 Additional STEM EDS linescans showing a much lower S concentration at the secondary LTO/ultra-LGPS interface than inner ultra-LGPS particle region.

Appendix G

Supplementary Information: A
High-Throughput Search for
Functionally Stable Interfaces in
Sulfide Solid-State Lithium Ion
Conductors


Figure 5.S1 (A) The pseudo-binary construction for $(1-x) \cdot L S P S+x \cdot L C O$ where $x$ is evaluated both linearly and using a binary search. The binary search is shown to quickly converge to $x=x_{m}$. (B) Complexity scaling of the linear and binary evaluation methods for determining $x_{m}$.

## Appendix $G$



Figure 5.S2 (A-C) Correlation of elemental species fraction with the added electrochemical interfacial instability $\left(\Delta G_{R X N}^{\prime}\left(x_{m}\right)\right)$ at 0,2 and 4 V , respectively. Negative (red) values are those species such that increasing concentration decreases $\Delta G_{R X N}^{\prime}$ and improves interfacial stability. Conversely, positive (blue) values are those species that tend to increase $\Delta G_{R X N}^{\prime}$ and worsen interfacial stability. Elements that are only present in less than 50 crystal structures are grayed out due to lack of high-volume data.

## Appendix $G$



Figure 5.S3 Anode stability plots by anionic class. (A) oxygen-only, (B) sulfur-only, (C) selenium-only, (D) fluorine-only, (E) phosphorus-only, (F) nitrogen-only, (G) iodine-only, (H) oxygen plus phosphorus, (I) oxygen plus nitrogen, (J) oxygen plus sulfur.

## Appendix $G$



Figure 5.S4 Cathode stability plots by anionic class. (A) oxygen-only, (B) sulfur-only, (C) selenium-only, (D) fluorine-only, (E) phosphorus-only, (F) nitrogen-only, (G) iodineonly, (H) oxygen plus phosphorus, (I) oxygen plus nitrogen, (J) oxygen plus sulfur.


Figure 5.S5 Comparison of XRD patterns for each individual phase (i.e. $\mathrm{LiCoO}_{2}$, LSPS , $L i_{4} \mathrm{Ti}_{5} \mathrm{O}_{12}, \mathrm{SnO} \mathrm{O}_{2}$ and $\mathrm{SiO}_{2}$ ) at room temperature and $500^{\circ} \mathrm{C}$. No significant change between room temperature and $500^{\circ} \mathrm{C}$ can be observed for each phase.


Figure 5.S6 Comparison of XRD patterns for mixture powders (i.e. $\mathrm{LiCoO}_{2}+\mathrm{LSPS}$, $\mathrm{SnO}_{2}+\mathrm{LSPS}, \mathrm{Li}_{4} \mathrm{Ti}_{5} \mathrm{O}_{12}+\mathrm{LSPS}$ and $\mathrm{SiO}_{2}+\mathrm{LSPS}$ ) at various temperatures (room temperature, $300^{\circ} \mathrm{C}, 400^{\circ} \mathrm{C}$ and $\left.500^{\circ} \mathrm{C}\right)$. The onset reaction temperature is observed to be $500^{\circ} \mathrm{C}, 400^{\circ} \mathrm{C}$ and $500^{\circ} \mathrm{C}$ for $\mathrm{LiCoO}_{2}+\mathrm{LSPS}, S n O_{2}+$ LSPS and $\mathrm{Li}_{4} \mathrm{Ti}_{5} \mathrm{O}_{12}+$ LSPS, respectively. No reaction is observed to happen for $\mathrm{SiO}_{2}+$ LSPS up to $500^{\circ} \mathrm{C}$.

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