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Stability and ionic mobility in argyrodite-related lithium solid electrolytes†

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In the search for fast lithium-ion conducting solids for the development of safe rechargeable all-solid-state batteries with high energy density, thiophosphates and related compounds have been demonstrated to be particularly promising both because of their record ionic conductivities and their typically low charge transfer resistances. In this work we explore a wide range of known and predicted thiophosphates with a particular focus on the cubic argyrodite phase with a robust three-dimensional network of ion migration pathways. Structural and hydrolysis stability are calculated employing density functional method in combination with a generally applicable method of predicting the relevant critical reaction. The activation energy for ion migration in these argyrodites is then calculated using the empirical bond valence pathway method developed in our group, while bandgaps of selected argyrodites are calculated as a basis for assessing the electrochemical window. Findings for the lithium compounds are also compared to those of previously known copper argyrodites and hypothetical sodium argyrodites. Therefrom, guidelines for experimental work are derived to yield phases with the optimum balance between chemical stability and ionic conductivity in the search for practical lithium and sodium solid electrolyte materials.

Introduction

Developing electrochemical storage devices with high energy densities is vitally important for powering our future society and the increasing demand for high energy and high-power rechargeable batteries has become the major driving force for further advances in battery technology. The available organic liquid electrolytes more and more are recognised as a bottle-neck in the effort to develop safe high-performance systems. Instead, inorganic fast-ion-conducting solids1,2 with high electrochemical stability in contact with the anode (often Li metal) and cathode material, favourable mechanical properties, cost-efficient low temperature synthesis and sufficient kinetic stability for operation over a wide temperature window increasingly appear as key components in most of the promising next generation energy storage systems including both all-solid state batteries as well as (Li-air, Li-sulphur, Li-redox flow) battery concepts wherein electrode liquids or slurries are combined with solid electrolytes to facilitate scalability. High ionic conductivity is essential to achieve a high capacity, while low electronic conductivity mitigates the electron transport through the solid electrolyte, thus preventing self-discharge of the batteries. On the other hand a certain local concentration of mobile electrons at the electrode/electrolyte interfaces mitigates charge transfer resistances (which may become a challenge for some oxide solid electrolytes). Among the solid-state Li ion conductors developed so far, the most favourable characteristics for application in electrochemical cells in terms of record ionic conductivity and lowest charge transfer resistances have been achieved by lithium thiophosphates and related compounds such as Li3P2S11,3,4 LGPS,5,6 thio-Lisicon and a recent report on a “Li3P2S11” of unknown structure.8 Therefore, it is critical to explore more in detail sulphide-based solid electrolytes to identify the most favourable compositions and structures for application as solid electrolytes in batteries. One of the ways to widen the range of known solid electrolytes with technologically interesting performance is to explore compounds containing more than one type of anions. Solid solutions of oxide- or sulphide-based solid electrolytes with alkali halides have in the past proven to be a successful strategy to enhance ionic conductivity in a wide range of Ag+, Cu+ or alkali based systems. 2,9 This straightforwardly leads to the exploration of the fast-ion conducting halide-containing lithium argyrodites that are in the focus of this work.10

The argyrodite family of compounds with the general formula A2+n-2m(Mm+X2-m)F2-nX-n, where A+ = Li+, Cu+, Ag+; M+n = Si4+, Ge4+, Sn4+, P5+, As5+; X2- = O, S, Se, Te; X+ = Cl, Br, I; 0 < x ≤ 2 are named after the mineral AgxGeS2.11 Only a few argyrodites with trivalent M+3 = Fe3+, Al3+, Ga3+ have been reported.12 A wider range of silver and copper argyrodites had been described 70 years ago13 and subsequently studied more in depth by Kuhs et al.14 and Evain et al.15 Temperature-dependent order-disorder transitions and cationic disorder in the high-temperature phase yield moderately high ionic conductivity for the high-temperature polymorphs of quaternary Cu and Ag-containing argyrodites,14,15 while the corresponding halide-free ternary argyrodites are
generally found to be semiconductors, for which changes in the fundamental absorption-edge related to the polymorphic transitions were evidenced.\textsuperscript{17} Lithium argyrodites first reported by the Deiseroth group\textsuperscript{10} are promising candidates for solid electrolytes. The most commonly studied argyrodite-type lithium ion conductor, Li$_3$PS$_4$Br, is reported to have a conductivity of $0.7\cdot10^{-3}$ S/cm.\textsuperscript{18,19} The wide electrochemical window and applicability of Lithium argyrodites in various types of rechargeable all-solid batteries have been demonstrated earlier by our group.\textsuperscript{20,21} Still, as for most fast-ion conducting lithium thiophosphates, such as Li$_3$P$_x$S$_{1-x}$ or LGPS,\textsuperscript{5,6} the structures of the known lithium argyrodites such as Li$_6$PS$_4$Br are only metastable limiting choices in their synthesis and raising questions about the long-term structural stability. More importantly, the lithium thiophosphates are typically unstable with respect to hydrolysis, so that they can only be handled in dry atmospheres, which is a serious cost factor for their technical application. Therefore this study aims at exploring the effect of possible changes in composition on the structural stability and hydrolysis stability.

Most Argyrodites adopt a cation-disordered high-temperature cubic “aristotype” phase in space group $F-43m$ with a characteristic anion arrangement in interpenetrating icosahedral cages, but argyrodites may also crystallize in an intermediate state of disorder in the lower-symmetry cubic space group $P2_13$, as well as in cation-ordered low-temperature phases in orthorhombic space group $Pmn2_1$ (e.g. for Cu$_3$(GeS)$_4$ below 330 K\textsuperscript{22}), $Pnma_1$ (e.g. for Ag$_2$SiS$_4$ below 507 K\textsuperscript{14}) and/or a monoclinic structure in space group $Cc$ (e.g. for Cu$_3$PS$_4$I\textsuperscript{23}).

For the halide-rich range of the possible argyrodite stoichiometries the argyrodite structure type is in competition to a distinct orthorhombic structure in space group $Pnma$: Ag$_6$(GeS)$_4$X$_2$ (X = Cl, Br)\textsuperscript{24,25} as well as Ag$_6$(SnS)$_4$Br$_2$\textsuperscript{26} have been found experimentally as the first members of this family of “non-metallic filled NaH$_2$ phases”, i.e. the partial structure of the non-metal atoms S and X (Cl, Br) corresponds to the arrangement of Na and Hg atoms in NaH$_2$ ($\leftrightarrow X_5$S$_4$) with Ge located in tetrahedral holes exclusively and Ag located in tetrahedral as well as octahedral holes.

Besides the required high ionic and low electronic structural conductivity, a solid electrolyte also needs to exhibit high and hydrolysis stability. Structural stability affects how easily a material can be synthesized and how stable it is against degradation during cycling. Hydrolysis stability is especially important for alkali sulphide materials, most of which will rapidly degrade in contact with humid air (or aqueous catholates). Therefore, a dry atmosphere is critically required throughout their preparation and battery assembly, increasing production costs and decreasing reliability of the batteries. When comparing compounds containing the same type of elements and hence the same potential decomposition products, the hydrolysis stability is obviously related to the structural stability of the compound.

While structural stability, hydrolysis stability, ionic conductivity and electronic conductivity can in principle be determined experimentally, synthesis of some materials could be difficult, expensive or hazardous, so that computational approaches become beneficial to estimate these properties of materials, thus providing guidance to experimentalists whether synthesizing a new material appears worthwhile. Structural stability and hydrolysis stability can be assessed from the dissociation energy of the material. While the structural stability of various phases in the quaternary system Li-P-S-O are available in the literature,\textsuperscript{27} in this work we designed a systematic way to examine structural and hydrolysis stability of any phase of known stoichiometry based on the calculated formation energies. Predicting the ionic conductivity requires identifying the ion migration pathways of the mobile ions and their activation energies. We employed the empirical bond valence-based softBV method developed in our group.\textsuperscript{28,29,30} Electronic conductivity can be estimated from the determination of the bandgap by DFT calculations.

In this work, argyrodite-type and orthorhombic NaH$_2$-related phases of $A_{3-2m}^{+}(M^{n+}Y_{2q}^{2-})Y_{x}^{2-}X_{y}$ with $A^+$ = Li$, Cu$, Ag$^+$; $M^{n+}$ = Si$^{4+}$, Ge$^{4+}$, Sn$^{4+}$; P$^{5+}$; As$^{3+}$; Y$^{2-}$ = O$^{2-}$, S$^{2-}$, Se$^{2-}$, Te$^{2-}$; X$^-$ = Cl$^-$, Br$^-$, I$^-$ are studied computationally to explore the suitability of this class of materials for practical applications in energy storage systems. Their structural stability and hydrolysis stability are determined by calculating the dissociation energies of the respective relevant critical reactions from \textit{ab initio} data, and their ionic conductivities are assessed by empirical bond valence methods.

Depending on the halide content $x$ (that may also adopt non-integer values), the cubic argyrodite phase may exhibit various degrees of site-inversion between anions $X$ and $Y^{2-}$.\textsuperscript{10,18,19,21} Moreover, the effect of anion site-inversion on stability and conductivity on the argyrodite and related phases is examined in this study. To limit the computational effort, generally only stoichiometric $A_{3-2m}^{+}(M^{n+}Y_{2q}^{2-})Y_{x}^{2-}X_{y}$ compositions with integer values of $x = 0, 1, 2$ are considered.

**Computational Methodology**

**Structural stability**

Structural stabilities are evaluated by the dissociation energy of the compound, which is the reaction energy of its \textit{critical reaction}. Taking Li$_3$PS$_4$ for instance, its critical reaction is:

$$\text{Li}_3\text{PS}_4 \leftrightarrow \frac{1}{2} S + \frac{1}{2} \text{Li}_2S + \frac{1}{2} \text{Li}_3\text{P}_2\text{S}_6$$

Accordingly, the reaction energy is computed as:
\[ \Delta E = 0.5 \times E(Li_2P_2S_4) + 0.5 \times E(Li_2S) + 0.5 \times E(S) - E(Li_3PS_4) \] (2)

Here, \( E \) is the formation energy of the compound calculated by DFT methods. In this example, the resulting value \( \Delta E = 0.205 \) eV is positive, suggesting that \( Li_3PS_4 \) is a stable compound and will not decompose.

**Formation energy of compounds**

The formation energy of a compound from its constituting elements is calculated by DFT methods as implemented in the VASP package\(^{31} \) based on a planewave basis set with using the Perdew–Burke–Ernzerhof (PBE) exchange-correlation parameterized general gradient approximation (GGA)\(^{32} \) and projector augmented-wave pseudopotentials (PAW).\(^{33,34} \) The cutoff threshold is set to 400 eV and convergence is by force < 0.03 eV/Å. Each compound has a k-mesh with a density of at least 30 k-points\(^{x8} \). Although \( +U \) techniques help in more precisely evaluating energies of many transition metal oxides\(^{35} \) such as copper, it is not applied here for two reasons: \( U \) values for most sulphides are not available in the literature; \( U \) values for oxides and sulphides are different, but in calculating hydrolysis stability, a single consistent \( U \) value would have to be used.

**Critical reaction**

With the formation energy of a compound known, the respective critical reaction remains to be determined in order to calculate the dissociation energy. The critical reaction is the reaction with the most negative reaction energy among all conceivable dissociation reactions of the compound. While experimental observation and experience is helpful in identifying such critical reactions, it appears to be more consistent for the screening approach of this work here to follow a generally applicable and exhaustive approach.

Consider a compound with formula \( A_{1b}A_{2b} \cdots A_{mbn} \), where \( A_i \) are distinct elements, \( b_i \) are the stoichiometric ratios, and \( i = 1, 2, \ldots, m \). Suppose there are \( n \) compounds in the phase diagram of \( A_1A_2 \cdots A_m \) each is denoted by \( 1_{a_1}A_{2a_2}A_{na_n} \), where \( j = 1, 2, \ldots, n \), and \( a_j \geq 0 \). Then all possible reaction equations can be summarized in the following form:

\[
A_{1b_1}A_{2b_2} \cdots A_{mb_m} \rightarrow x_1A_{1a_1}A_{2a_2} \cdots A_{na_n} + \cdots + x_nA_{1a_1}A_{2a_2} \cdots A_{na_n}
\] (3)

with \( i = 1, 2, \ldots, m \), \( m \) is the total number of elements, \( m \geq 1 \) and \( j = 1, 2, \ldots, n \), \( n \) is the total number of compounds, \( n \geq m \).

Provided that the complete list of compounds in the phase diagram is known, the search for the critical reaction can be converted into a standard linear programming problem:

Minimize \( E = E_x = E_1x_1 + E_2x_2 + \ldots + E_nx_n \), subject to the constraint \( Ax = b \) where:

- \( A = \{a_i\} \) are stoichiometric numbers of each element \( A_i \) in each of the conceivable dissociation products \( j \);
- \( b = \{b_i\} \) are stoichiometric numbers of each element in the reference compound;
- \( E = \{E_j\} \) are calculated formation energies of each compound;
- \( x = \{x_j\} \) are the coefficients of each compound to which the reference compound dissociates, \( x \) is the unknown to be solved and \( x \geq 0 \).

This minimization task has a unique solution and is here solved by a simple program written with GLPK libraries\(^{36} \) that is available from the supplementary material.

**Effects of anion site-inversion**

In the aristotype argyrodite structures of \( Li_{1-\alpha}(M^{m+}Y_q)Y \)X, each unit cell contains four free \( Y^2- \) anions that are not part of rigid \((MY_q)^{8-8m} \) groups and four \( X^- \) anions. To study the effect of anion site-inversion, the stabilities of five configurations are calculated for each composition by swapping zero to four pairs of \( Y^2/X^- \) and sulphides are different, but in calculating hydrolysis stability, sulphides are not available in the literature; \( U \) values for oxides of \( Y^2/X^- \) anions. The degree of site-inversion is defined to be \( 0 \% \) when all four free \( Y^2- \) anions are located at the regular \( Y \) sites, i.e. the \( 4d \) site\(^* \) \((\frac{1}{3}, \frac{1}{3}, \frac{1}{3}), (\frac{1}{3}, \frac{1}{3}, \frac{1}{3}), (\frac{1}{3}, \frac{1}{3}, \frac{1}{3}), (\frac{1}{3}, \frac{1}{3}, \frac{1}{3})\), and four \( X^- \)anions located at the \( 4a \) site \((0, 0, 0), (\frac{1}{2}, \frac{1}{2}, 0), (\frac{1}{2}, 0, \frac{1}{2}), (0, \frac{1}{2}, \frac{1}{2})\), which corresponds to the experimentally observed structure of \( Li_3PS_4\)I in space group \( Fm-43m \). By swapping one pair of \( Y^2/X^- \) per unit cell, the degree of site-inversion is increased to 25%. To study the effect of site-inversion more in detail, a fourfold supercell has been constructed for the model compound \( Li_3PS_4Br \), so that the model contains 16 pairs of swappable anions and the degree of site inversion can be modelled in steps of 6.25%.

**Hydrolysis stability**

Hydrolysis stability of the lithium-containing sulphides is estimated by assuming the formation of the primary products \( LiOH \) and \( H_2S \). The calculation method is essentially the same as for evaluating structural stabilities. To identify the critical reaction of hydrolysis, it is assumed that an excess number \( n \) of water molecules is available and the resulting hydrolysis products contain oxides. In the system \( Li-P-S-H-O \), the critical reaction is:

\[ Li_3PS_4 + n H_2O \leftrightarrow 4 H_2S + (n-4) H_2O + LiPO_4 \] (4a)

Eliminating the excess \( H_2O \) on both sides leads to the final critical hydrolysis reaction:

\[ Li_3PS_4 + 4 H_2O \leftrightarrow 4 H_2S + LiPO_4 \] (4b)

For many compounds hydrolys reactions may consist of more than one reaction step. To simplify the simulation, the final products of hydrolysis are here consistently limited to the most basic products, e.g. \( LiOH \) instead of the corresponding hydrated \( LiOH\cdot H_2O \).

In practice, hydrolysis reactions may be more complex. The products may e.g. be amorphous and non-stoichiometric, and the actual reaction path may depend on a number of factors such as humidity, temperature, and reaction time. Thus, the results presented in this study can only provide a rough guideline for comparing the relative (thermodynamic) hydrolysis stability of different argyrodites.

**Electronic conductivity**

To compare the electronic conductivities of the argyrodite phases, the bandgaps of the structures are calculated by DFT calculations

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\* The Wyckoff site names \( 4d \) and \( 4a \) strictly speaking apply only to the most common case of space group \( F-43m \). For the lower symmetry cubic Argyrodites both sites would be of type \( 4a \), but still symmetry-independent.
using VASP. Since the employed GGA functional has the intrinsic tendency to underestimate the bandgap, the resulting values have to be understood as lower bounds to the true bandgaps.

5 Pathway for and activation energy of ionic conductivity

All cubic phases of argyrodites exhibit a three-dimensional network of pathways connecting partially occupied sites for the migration of the monovalent $A^+$ ions and hence show ionic conductivity. In this report the activation energy for ion migration is estimated as the main influencing factor. Our empirical bond-valence based softBV forcefield is used to analyse the site energies of $Li^+$ ions $E_{BV3D}(Li)$ through the structures of lithium argyrodites. Migration pathways for $Li^+$ are then analysed as regions of low $E_{BV3D}(Li)$ in the resulting grids spanning the structure model with a resolution of typically (0.1 $\AA$), which has been demonstrated to be a simple and reliable way of identifying transport pathways in local structure models. This method provided that the local structure model captures the essential structural features. For the purpose of analyzing $E_{BV3D}(Li)$ landscapes Coulomb repulsions are considered only between mobile and immobile cations (here e.g. $Li^- – P^{5+}$), while Coulomb attraction terms are generally integrated in the Morse attraction term. Starting from an analysis of local minima and saddle points of $E_{BV3D}(Li)$, the grid analysis utilizes a modified Dewar, Healy and Stewart (DHS)-type path finding algorithm to identify low energy paths connecting the local site energy minima.

Such energy landscapes based on rigid structure models without the possibility for structural relaxation inherently overestimate the energy barriers. In order to factor in the reduction of energy barriers by relaxation effects, the initially observed barriers needs to be scaled down by an empirical factor $\approx 0.5$, which is related to the oxide ion on the anion in its first coordination shell. For details on the scaling factor see Table S1 in the supplementary material. By means of this scaling, the scaled predicted activation energies should become comparable to each other and to experimental results, while unscaled activation energies can only be compared among compounds with similar compositions.

Results and Discussion

40 Substitution of $M^{m+}$ and $X$ in $Li_{12+x} (M^{m+}S_{4}S_{2+x}X_{x})$

Structural stability

In the lithium argyrodites $Li_{12+x}(PS_{4}S_{2+x}X_{x}$, $P^{5+}$ may be substituted by $As^{5+}$, $Si^{4+}$, $Ge^{4+}$, or $Sn^{4+}$ with lithium contents adjusted to the halide content $x$ and the charge of the respective high-valent cation $M^{m+}$. When comparing the resulting compounds with respect to their structural stability, it turns out that all the $Li_{12+x} (M^{m+}S_{4}S_{2+x}X_{x})$ compounds share the same critical (decomposition) reaction expressed as eqn. (5):

$Li_{12+x} (M^{m+}S_{4}S_{2+x}X_{x}) \rightarrow Li_{8+m}M^{m+}S_{4} + (2-x) Li_{2}S + x LiX$ (5)

The results summarised in Fig. 2 show that most of the argyrodites are metastable, and thus may only be synthesized with suitable non-equilibrium low-temperature methods, as they might decompose at higher temperatures. With increasing halogen content, the structural stability of the NaHg$_2$-related

Fig. 2 Structural stability of (a) Si,Ge,Sn-argyrodites and (b) P,As-argyrodites. Higher positions in the graph indicate higher stability.
Cl, Br or I, for M = As only those with X = Br and I can be synthesized.\textsuperscript{38} In terms of choices of halogen elements, argyrodite phases containing iodide are more stable than those containing bromide and chloride.

When considering the dependence of the structural stability of the Li$_{12}$2$_{x}$S$_{6}$M$^{5+}$S$_{2}$X$_{x}$ argyrodite on the halide content $x$, the dissociation energies shown in Fig. 2 as a function of halide content $x$ exhibit a clear maximum at $x$ = 1 for M$^{5+}$ compounds (cf. solid lines in Fig. 2a), while among the M$^{5+}$ compounds only those with $X$ = I show a comparatively pronounced stability maximum. Therefrom it may be concluded that for these two groups of argyrodites a (near) stoichiometric composition with $x$ = 1 will be preferred (as also found experimentally for Li$_{7}$M$^{5+}$S$_{5}$I argyrodites).\textsuperscript{10,19,40} For the M$^{4+}$ argyrodites with the lighter halide anions Br and Cl, the dissociation energy decreases slightly as $x$ increases from 0 to 1 (for the case of M = P) or is practically constant (for M = As). In these compounds the entropy influence may preferentially lead to non-stoichiometric compounds with compositions controlled by details of the sample preparation conditions. Such a behaviour is experimentally observed for Li$_{7}$xMS$_{5}$X$_{x}$ (with M = P, X = Cl or Br and to some extent for M = As, X = Br, where only a slight deviation from stoichiometry is noted).10,21,40

Even for stoichiometric argyrodites Li$_{11}$mMS$_{5}$X (which are, as mentioned above, often close to the most preferable composition) the influence of disorder may be relevant for their structural stability. From earlier structural studies, it is known that e.g. in Li$_{17}$S$_{6}$X$_{x}$ with $X$ = Cl, Br the experimentally observed S$^{2-}$/X$^{-}$ anion distribution is disordered in the sense that there is a partial inversion between the occupancies of the nominal S$^{2-}$ and X$^{-}$ sites. Detailed neutron diffraction studies indicate a temperature dependence of this disorder.\textsuperscript{21} Here we studied whether there is a thermodynamic driving force for the site inversion. Fig. 3 surveys the effect of site-inversion on the dissociation energies of the studied argyrodites with $x$ = 1. Swapping the occupancies of the four pairs of S$^{2-}$/X$^{-}$ anions per unit cell allows varying the site occupancies in steps of 25%. From the results in Fig. 3 the effect of the S$^{2-}$/X$^{-}$ site-inversion on the structural stability seems to depend on the oxidation state $m$ of the M$^{n+}$ cation and the type of halogen atom involved. In argyrodites containing M$^{5+}$ cations, chlorides and bromides prefer around 25% site-inversion while iodides prefer the fully ordered structure (0% site-inversion). This suggests that the experimentally observed site-inversion for Li$_{7}$PS$_{5}$Cl and Li$_{7}$PS$_{5}$Br (and fully ordered nature of the anion distribution in Li$_{7}$PS$_{5}$I) is caused by an enthalpic driving force and not only a kinetic effect.

To understand more in detail the correlation between anion site-inversion and stability, configurations with random pairs of S$^{2-}$/Br$^{-}$ swapped have also been calculated for a four-fold supercell in the case of Li$_{7}$PS$_{5}$Br. Results are shown as open triangles in Fig. 3(a). Both fully ordered structures (no inversion or complete inversion) exhibit significantly more negative dissociation energy than the structures with partial S$^{2-}$/Br$^{-}$ swapping. The dissociation energy reaches its least negative value for low degrees of site inversion (6-19%) but show only a minute decrease towards higher degrees of site inversion before suddenly shooting down to the most negative value for the fully-inverted structure. The energies found for the same degrees of

Fig. 3 Variation of dissociation energies of (a) P, As-argyrodites and (b) Si, Ge, Sn-argyrodites with the degree of S$^{2-}$/X$^{-}$ anion site-inversion.

Hydrolysis stability

In contrast to the discussion of structural stability above, the critical reactions for stability against hydrolysis are no longer the same for all argyrodites but depend on the choice of the cation M$^{n+}$ according to eqns. (6) – (10):

\begin{align*}
    \text{Li}_{12}\text{PS}_{5}X_{x} + 8-2x \text{H}_{2}\text{O} & \leftrightarrow x \text{LiX} + \text{Li}_{10}\text{P}_{4} + 6-x \text{H}_{2}\text{S} + 4-x \text{LiOH} \quad (6) \\
    \text{Li}_{12}\text{AsS}_{5}X_{x} + 7-2x \text{H}_{2}\text{O} & \leftrightarrow x \text{LiX} + 0.5 \text{As}_{5}\text{S}_{3} + 3.5-x \text{H}_{2}\text{S} + 7-2x \text{LiOH} \quad (7) \\
    \text{Li}_{12}\text{SiS}_{5}X_{x} + 9-2x \text{H}_{2}\text{O} & \leftrightarrow x \text{LiX} + \text{Li}_{5}\text{SiO}_{3} + 6-x \text{H}_{2}\text{S} + 6-2x \text{LiOH} \quad (8) \\
    \text{Li}_{12}\text{GeS}_{5}X_{x} + 8-2x \text{H}_{2}\text{O} & \leftrightarrow x \text{LiX} + \text{Ge}_{5}\text{S}_{3} + 4-x \text{H}_{2}\text{S} + 8-2x \text{LiOH} \quad (9) \\
    \text{Li}_{12}\text{SnS}_{5}X_{x} + 8-2x \text{H}_{2}\text{O} & \leftrightarrow x \text{LiX} + \text{Sn}_{5}\text{S}_{3} + 4-x \text{H}_{2}\text{S} + 8-2x\text{LiOH} \quad (10)
\end{align*}
When comparing the resulting hydrolysis stability values for Li$_{12-x}$M$^{3+}$S$_6$X$_x$ argyrodites in Fig. 4 it becomes obvious that all these lithium argyrodites will decompose in contact with water, as indicated by the negative dissociation energies. Phosphorus and silicon argyrodites are highly sensitive to moisture (with the commonly studied P-compounds typically being the worst case in terms of hydrolysis stability), while germanium, tin and arsenic argyrodites are significantly less vulnerable to hydrolysis. It should however be kept in mind that the latter two also have a lower structural stability. In terms of the halide content, compounds without any halogen atoms demonstrate lower hydrolysis stability, and the vulnerability to hydrolysis only slightly decreases with the increase of the size of the halogen atom among the Li$_{12-x}$M$^{3+}$S$_6$X$_x$ argyrodites with the same halide content.

**Activation energy for Li$^+$ migration**

Fig. 5 compares the activation energies for Li$^+$ migration in the compounds containing various M$^{3+}$ cations as derived from our bond-valence based site energy mapping. For the sake of simplicity this comparison is based on the fully anion-ordered argyrodite structure models. It should also be noted that the DFT geometry optimisation will lead to some deviation of the unit cell volume from the experimentally observed room temperature values limiting the accuracy of the activation energy prediction while semiquantitative trends should be preserved. The cubic or pseudocubic argyrodites are obviously 3D conductors so that also for the *ab initio* geometry-optimised local structure models (formally in space group P1) the percolation thresholds for 1D, 2D and 3D long-range Li$^+$ ion migration differ only minutely. In contrast, the NaHg$_2$-related phases are essentially 2D ionic conductors where the migration perpendicular to the fast-ion-conducting planes requires significantly higher activation energy than within the planes.

Li$^+$ migration in argyrodites Li$_{12-x}$M$^{3+}$S$_6$ and Li$_{11-x}$M$^{3+}$S$_6$X requires lower activation energies than in halide-rich argyrodites Li$_{10-x}$M$^{3+}$S$_6$X$_2$. Moreover argyrodites containing I$^-$ tend to have higher activation energies than those containing Cl$^-$ or Br$^-$ in line with a more general rough trend that the more stable (anion ordered) compounds tend to show somewhat higher activation energies also for the Li$^+$ mobility. In addition, the lower repulsion of M$^{3+}$ and higher concentration of mobile charge carriers seems to favour on average somewhat lower activation energies in Li$_{12-x}$M$^{3+}$S$_6$X than in Li$_{12-x}$M$^{3+}$S$_6$X$_2$ compounds. Moreover, NaHg$_2$-related Li$_{12-x}$M$^{3+}$S$_6$X phases are found to have higher (and the Li$_{12-x}$M$^{3+}$S$_6$X$_2$ compounds lower) activation energies than the argyrodites of the same composition, while for the phases containing M$^{3+}$ no such systematic difference between the two structure types can be observed in terms of their activation energy for Li$^+$ migration.

The influence of the S$^2$/Br$^-$ anion site-inversion in local supercell structure models of the Li$_x$PS$_3$Br$_2$ on the predicted activation energy barrier for Li$^+$ is demonstrated in Fig. 6. Configurations of 100%, 50% and 0% site-inversion are found to have the smallest activation energies. The specific choice of local...
structures may affect this finding. Still, the observation that the difference in activation energy between the highest and lowest activation energy configurations for the same composition reaches about 0.20 eV suggests that anion disorder in argyrodites strongly influences the local and overall Lithium ion conductivity.

To assess the accuracy of the empirical approach for estimating migration barriers from structure models using the softBV forcefield, experimental activation energy data from the literature conductivity and NMR studies are compared to the calculated migration barriers.\textsuperscript{16,41,42,44,45} While local structures generated from DFT geometry-optimisation do not readily accommodate fractional occupancy and show some deviation in lattice parameters compared to experimentally determined structures, these comparisons are based on experimental structure data.\textsuperscript{10,40,46} Results are summarised in Fig. 7. It should be noted that among the calculated barrier energies values < 0.2 eV refer to barriers for local hopping and the corresponding experimental data are NMR data, while values > 0.2eV correspond to the migration barrier for percolating pathways. As seen from Fig. 7 the limiting factor for the quality of the correlation is less the quality of the computational prediction but the large spread in the experimental activation energies reported in the literature for the same compound.

Li\textsuperscript{+} ions in argyrodites are generally found to be distributed over three types of sites. Site A (48h) refers to the equilibrium site that hosts the bulk of Li\textsuperscript{+} ions in all argyrodite structures. Interstitial sites of type B (48h) are located in-between A sites, so that 3 A and 3 B sites nearly form a low energy pathway hexagon. In combination with local paths connecting directly two A sites 4 such A-B hexagons form a local pathway cage around each S\textsuperscript{2} anion in Li\textsubscript{6}P\textsubscript{5}I. The A sites in these cages are then connected via type C interstitial sites (16e) to a 3-dimensional migration pathway network. In Li\textsubscript{6}P\textsubscript{5}Se\textsubscript{2}Cl the local (A-B)\textsubscript{3} pathway hexagons are bridged by A-C-A pathways to local pathway cages around the halide ion that only for higher activation energies merge to a percolating pathway network by direct A-A bridges.

The relative site energies and activation barriers between sites are summarised in Fig. 8, in which the lowest site energy among the three types of sites is set to 0 eV. The percolation threshold (or the long-range activation energy) equals to the maximum of the three relevant migration barriers, i.e. either the barrier between two A sites or between an A site and a C site. It may also be noted that their respective barrier heights are anticorrelated. Li\textsubscript{6}P\textsubscript{5}I, for example, shows a very low activation energy between two A sites which may correspond to the experimentally observed short-range activation energy of 0.04 eV, but the much larger activation energy between A and C sites causes the relatively high activation energy of about 0.35 eV for dc conductivity.\textsuperscript{44} When the size of the halide ion is reduced by substituting I\textsuperscript{–} by Br\textsuperscript{–} the A-C barrier shrinks and the A-A barrier increases so that the activation energy for local motions slightly increases, while the activation energy for dc conductivity is considerably reduced.

To study the effect of anion disorder on the migration barriers between the different sites, we analysed the barriers in hypothetical structures derived from the experimental structure of Li\textsubscript{6}P\textsubscript{5}Br. A fully stoichiometric and anion ordered structure is compared to structures, with mixed anion site occupancy, where in steps of 0.25 increasing fractions of Br\textsuperscript{–} are assigned to the 4d sites, while the corresponding amount of S\textsuperscript{2} is redistributed to the 4a sites. The effect of the different degrees of anion disorder on the migrations barriers in Li\textsubscript{6}P\textsubscript{5}Br are summarized in Fig. 9. The increase in anion disorder has little effect on the height of the migration barrier between A and B sites, but consistently increases barrier heights between two A sites and decreases...
activation energies between A and C sites. For the case of \( \text{Li}_6\text{PS}_5\text{Br} \) the lowest activation energy for long-range ion migration (dc conductivity) results for 25% anion disorder, when the barrier heights for A-A and A-C hops are almost equal.

Selection guidelines

To select a structure with suitable properties for application as solid electrolyte, the requirement of low activation energy for lithium ion migration effectively limits the choices to the \( \text{Li}_{1+\delta}\text{M}^{3+}\text{S}_6 \text{X} \) compounds with \( \text{X} = \text{Cl} \) and \( \text{Br} \) or the halide-free \( \text{Li}_{12-\delta}\text{M}^{5+}\text{S}_6 \). Among these compounds, the structural stability of the argyrodite phases is higher than the one of the corresponding NaHg$_2$-related phases. Further examination on their dissociation energies suggests that the argyrodites with \( \text{M} = \text{P}, \text{Ge} \) and \( \text{Si} \) have higher stability, and structures with halide content (\( \text{Li}_7\text{SiS}_5 \)) are more stable than those without (\( \text{Li}_7\text{GeS}_5 \)). The halide content also somewhat mitigates the vulnerability to hydrolysis. Especially the germanium compounds show more favourable relative hydrolysis stability. In summary, except for the known \( \text{Li}_6\text{PS}_5\text{X} \) and \( \text{Li}_7\text{PS}_5 \) compounds, the most promising candidates in the search for lithium-ion conducting compounds with technically interesting properties would be \( \text{Li}_7\text{GeS}_5 \), \( \text{Li}_7\text{SiS}_5 \), \( \text{Li}_7\text{GeS}_5 \) and \( \text{Li}_7\text{SiS}_5 \) where \( \text{X} = \text{Cl} \) or \( \text{Br} \).

Substitution of \( \text{A}^+ \) and \( \text{X} \) in \( \text{A}_{7-x}\text{PS}_5\text{S}_5\text{X}_x \) argyrodites

Structural stability

Lithium ions in lithium argyrodites can be substituted by a number of monovalent cations. Here the lithium compounds are compared to the previously known copper argyrodites and possible analogous sodium argyrodites due to the lower cost and higher earth abundance of sodium compared to lithium.

Critical reactions for structural stability are given in eqs. (5), (11) and (12) for \( \text{A} = \text{Li}, \text{Na} \) or \( \text{Cu} \), respectively:

\[
\begin{align*}
\text{Na}_7\text{PS}_5\text{S}_5\text{X}_x & \leftrightarrow \text{Na}_{7-x}\text{PS}_5\text{S}_5\text{X}_x + \text{Na}_x\text{PS}_4 & (11) \\
\text{Cu}_7\text{PS}_5\text{S}_5\text{X}_x & \leftrightarrow \text{Cu}_{7-x}\text{PS}_5\text{S}_5\text{X}_x + 0.5\cdot0.25x\text{Cu} + 0.5\cdot0.25x\text{Cu}_2\text{S}_4 + \text{Cu}_x\text{PS}_4 & (12)
\end{align*}
\]

Fig. 10 compares the structural stability of compounds containing different mobile cations \( \text{A}^+ \). Sodium argyrodites are found to be less stable than lithium and copper argyrodites, consistent with the fact that most of the discovered argyrodites contain copper, silver and lithium instead of sodium. From Fig. 10, \( \text{Na}_7\text{PS}_5 \) may be the only practically accessible sodium argyrodite phase. Among the studied phases copper argyrodites are found to be the most stable, in line with the existence of natural copper-containing argyrodite \( \text{Ag}_3\text{Cu}_{4.68}\text{Ge}_6 \) in minerals.\(^{37}\) Copper argyrodites are always more stable than the NaHg$_2$-related phases of the same composition. Similar to \( \text{Li}_6\text{PS}_5\text{I} \) and in line with experimental structure determinations, \( \text{Cu}_6\text{PS}_5\text{I} \) is expected to be stoichiometric from the pronounced stability maximum around \( x=1.\)^{38,49}

Fig. 10 Structural stability of compounds containing \( \text{A}^+ = \text{Li}^+ \), \( \text{Na}^+ \) and \( \text{Cu}^+ \).

Again we explored possible effects of anion site-inversion on stability of A-argyrodites and the findings are summarized in Fig. 11. The overall shapes of the stability vs. degree of site inversion curves are similar for all three types of compounds: with the increase in size of halogen anions (and thus in the \( \text{X}^- \) size) the stability decreases. Among the studied phases copper argyrodites are found to be the most stable, in line with the existence of natural copper-containing argyrodites \( \text{Ag}_3\text{Cu}_{4.68}\text{Ge}_6 \) in minerals.\(^{37}\) Copper argyrodites are always more stable than the NaHg$_2$-related phases of the same composition. Similar to \( \text{Li}_6\text{PS}_5\text{I} \) and in line with experimental structure determinations, \( \text{Cu}_6\text{PS}_5\text{I} \) is expected to be stoichiometric from the pronounced stability maximum around \( x=1.\)^{38,49}
sulphide size difference), the most stable degree of site-inversion shifts from 25% towards 0%. Argyrodites containing I always prefer the fully ordered configuration. This suggests that the nature of the $A^+$ ion has only a minor influence on the preferable degree of site inversion.

Hydrolysis stability
Critical reactions for hydrolysis stability are given in eqs. (6), (13) and (14) for $A = Li, Na$ or $Cu$, respectively:

10 $Na_{x}A_{7}PS_{6}X + 8-2xH_{2}O \leftrightarrow xNaX + Na_{3}PO_{4} + 6-xH_{2}S + 4-2xNaOH \ (13)$

$Cu_{x}A_{7}PS_{6}X + 5/32(2-x)H_{2}O \leftrightarrow xCuX + 1/32(2-x)P_{2}O_{5} + 1/16(4+x)Cu_{3}PS_{4} + 5/16(2-x)Cu_{2}S_{4} + 5/32(2-x)H_{2} \ (14)$

Fig. 12 shows the relative stability against moist ure of compounds containing three types of mobile $A^+$ cations. Argyrodites containing copper are much more stable to moisture than the alkali argyrodites. This is because copper sulphide ($CuS_{2}$) and copper thiophosphate ($Cu_{3}PS_{4}$) are more stable than their lithium and sodium counterparts in water. The predicted decomposition reaction of copper argyrodites would thus release $H_{2}$ rather than $H_{2}S$ (as released by $Li$ and $Na$ argyrodites) and the released amount is much smaller compared to that of $H_{2}S$ in the case of the alkali. The higher hydrolysis stability of sodium argyrodites compared to lithium argyrodites is less intuitive. It may be affected by our approach of limiting ourselves to the primary reaction products $AOH$ and hydrogen-free $A$ oxides. Both of them will further react with water and the reaction energy depends largely on element $A$.

Activation energy for $A^+$ migration
From the overview of activation energies for $A^+$ motion in Fig. 13 it can be seen that sodium compounds overall demonstrate lower activation energy than lithium and copper compounds, but due to the instability of these structures the knowledge of the low activation energy may be of limited usefulness, and only $Na_{2}PS_{6}$ may be practically accessible. Copper argyrodites have similar level of activation energies compared to $Li_{4}PS_{3}Br$, and the type of halide atoms seems to affect the activation energies of copper argyrodites much less than for their alkali counterparts. The activation energies of copper argyrodites show almost linear dependence on halide content $x$, which is a characteristic shared by lithium argyrodites. Although $NaHg_{2}$-related copper compounds seem to be much more conductive than the argyrodite structures of the same composition, stability calculations (see Fig. 10) indicate that they are much harder to form than the argyrodite structures.

Selection guidelines
Judging from the low activation energy and the high concentration of mobile cations and free sites in the robust 3D network of migration pathways in lithium and copper argyrodites both will show reasonably high conductivity and (meta)stability. The alternative of sodium-ion conducting argyrodites appears less attractive as sodium argyrodites (except for $Na_{2}PS_{6}$) are unstable, and the predicted activation energy for $Na_{2}PS_{6}$ is slightly higher than for $Li_{4}PS_{3}$ (while in general the fast sodium-ion conducting solids can reach considerably lower activation energies than the best known $Li^-$-ion conductors).

Substitution of $Y^{2-}$ and $X$ in $Li_{5-x}(PY_{4})Y_{2-x}X_{x}$ argyrodites

Structural stability
Softer anions are expected promote ionic conductivity, which is why the sulphide-based solid electrolytes generally reach higher conductivities than oxide-based ones. This invites the idea that selenium and tellurium argyrodites should show even higher ionic conductivity. However, their stability may be limited and electronic conductivity due to the increase of electron density may prevent their use as solid electrolytes. For comparison, two types of experimentally known oxygen argyrodites (with low ionic conductivity) will also be investigated. Critical reactions for structural stability are determined as eqn. (5), (15)-(19):

$Li_{4}PO_{2}X \leftrightarrow LiCl + Li_{2}O + Li_{3}PO_{4} \ (15)$

$Li_{4}PSe_{6} \leftrightarrow 2Li_{2}Se + Li_{3}PSe_{4} \ (16)$

$Li_{4}PSe_{4}X \leftrightarrow 0.5Se + 1.5Li_{2}Se + LiX + 0.5Li_{4}P_{2}Se_{6} \ (17)$
Between the compounds with the two structure types are much
NaHg
reaction may change and the dissociation energy may become
of new compounds into the phase LiqPqSe diagram, the critical
most stable ternary compound calculated so far. With the addition
containing Y
the halideqcontaining compounds the stability differences
Li
oxygen argyrodites.

Can only exist in the fully ordered configuration. This is
share the same trend as sulphur argyrodites that fully ordered
inversion in Yqargyrodites. Selenium and tellurium argyrodites
ternary compounds into consideration. Two of them are
Critical reactions for determining the hydrolysis stabilities of
argyrodites containing different Yq2 anions are eqn. (6), (20)-(21):

\[
\text{Li}_6\text{PO}_5\text{X} + \text{H}_2\text{O} \leftrightarrow \text{LiX} + \text{Li}_3\text{PO}_4 + 2 \text{LiOH} \quad (20)
\]

\[
\text{Li}_6\text{PTe}_5\text{X} + 8-2x \text{H}_2\text{O} \leftrightarrow x \text{LiX} + \text{Li}_3\text{PO}_4 + 6-x \text{Se} + 6-x \text{H}_2 + 4-2x \text{LiOH} \quad (21)
\]

Fig. 16 shows the resulting hydrolysis dissociation energies of
argonides. Oxygen argyrodites have the highest calculated
hydrolysis stability, in line with the general tendency that oxides
are more stable to moisture than sulphides, selenides and
tellurides. Similar to the findings for structural stability, selenium
argyrodites and sulphur argyrodites have nearly the same level of
hydrolysis stability. The hydrolysis products are different, with
selenium argyrodites releasing H₂ while sulphur argyrodites
releasing H₂S. Though H₂Se and H₂Te exist in gaseous form, they
are not stable and would decompose into H₂ and Se/Te.

**Activation energy for Li⁺ migration**

Fig. 17 shows the activation energy for the migration of Li⁺ in the
compounds containing different Yq2 anions. Consistent with

\[
\text{Li}_{7-x}\text{PSe}_6\text{X}_x \leftrightarrow x \text{LiX} + \text{P} + 2.5 \text{Te} + 3.5-x \text{Li}_2\text{Te} \quad (19)
\]

Fig. 14 shows the dissociation energy of compounds containing
different Yq2 anions. The structural stability of lithium argyrodites
containing Yq2 increases in the order of Te < Se < S < O. The
tellurium compounds show considerably more negative
dissociation energies indicating that they may practically not be
accessible. Selenium compounds, on the other hand, have similar
dissociation energies to those of sulphur compounds. Except for
Li₃PSe₆, which has been successfully synthesized in the argyrodite
structure, the likelihood for selenium compounds containing
halogen elements to crystallize in argyrodite phase and NaHg₂
related phase are almost equal. It should be stressed that the
critical reaction of selenium argyrodites takes only three Li-P-Se
ternary compounds into consideration. Two of them are
Li₃PSe₆ and Li₃PSe₅ as reported in a study by Francisco. Another
compound Li₃PSe₅ is constructed by replacing sulphur atoms in Li₃PS₅ with selenium atoms. Li₃PSe₆ is found to be the
most stable ternary compound calculated so far. With the addition
of new compounds into the phase Li-P-Se diagram, the critical
reaction may change and the dissociation energy may become
more negative. For all the different chalcogenide compounds
studied the argyrodite phases are significantly preferred over
NaHg₂-related phases in the absence of halide anions, while for
the halide-containing compounds the stability differences
between the compounds with the two structure types are much
smaller.

Fig. 15 plots the dissociation energy versus degree of site-
inversion in Yq-argyrodites. Selenium and tellurium argyrodites
share the same trend as sulphur argyrodites that fully ordered
configurations are less stable. In contrast the oxygen argyrodites
can only exist in the fully ordered configuration. This is
consistent with the experimental structure determination of oxygen argyrodites.
experimental observation, activation energies of Li$_2$PO$_3$Cl and Li$_2$PO$_3$Br are higher than those of Li$_2$PS$_3$Cl and Li$_2$PS$_3$Br. The comparison to selenide- and telluride-based compounds is based on an estimated scaling factor of 0.5, as only two experimental activation energies 0.49 eV of Li$_2$PSe$_6$ and 0.20 eV of Li$_2$PSe$_5$Br are available for comparison. Unlike for the case of the sulphur argyrodites, among the argyrodites with $Y = $ Se, Te the Li$_2$PY$_X$X compositions with intermediate halide content have lower activation energies than the halide-free Li$_2$PY$_6$ and halide-rich Li$_2$PY$_X$X$_2$ argyrodites. In fact the activation energies predicted for Li$_2$PSe$_X$X with $X = $ Cl, Br are the lowest of all the studied argyrodite compositions. The Li$_2$PY$_X$X argyrodites with $Y = $ Se, Te also have somewhat lower activation energies than the NaHg$_2$-related phases of the same composition.

**Bandgaps and selection guidelines**

The DFT-calculated bandgaps of argyrodites Li$_2$PY$_X$Br decrease in the order O > S > Se > Te as tabulated in Table 1. In general bandgaps are predicted to decrease as the period of anion Y increases since higher electron density should promote electronic conduction. The high bandgap of the oxide argyrodite clearly qualifies it as an insulator. From the calculations Li$_2$PSe$_X$Br should be a semiconductor with a bandgap of 2.12 eV. Still it has to be kept in mind that DFT calculations using GGA functionals tend to underestimate the band gap and practically an electrochemical window $> 4$ eV has been concluded from cyclovoltammetry. Similarly, prediction of Li$_2$PTe$_X$Br to be a metal in practice might suggest that it is a narrow-band semiconductor, but definitely not suitable as a solid electrolyte. For Li$_2$PSe$_X$Br the intermediate bandgap may indicate that this may be a mixed conductor with (in view of the low activation energy for Li$^+$ migration) mainly ionic conductivity but substantial contributions of electronic conductivity preventing use of pure selenides as a solid electrolyte, but potentially of interest in compounds with e.g. S$^2$/Se$^2$ anion disorder.

<table>
<thead>
<tr>
<th>Argyrodite cubic phase</th>
<th>Calculated bandgap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$PO$_3$Br</td>
<td>5.67</td>
</tr>
<tr>
<td>Li$_2$PS$_3$Br</td>
<td>2.12</td>
</tr>
<tr>
<td>Li$_2$PSe$_3$Br</td>
<td>1.00</td>
</tr>
<tr>
<td>Li$_2$PTe$_3$Br</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Based on these calculations the stability and electrochemical window of argyrodites should increase in the order of Te << Se << S < O. While selenium argyrodites might be accessible, their limited stability will probably remain an issue for practical applications. Among the four classes of argyrodites, sulphur argyrodites still strike the best balance between stability and conductivity.

**Concluding remarks**

The search for solid electrolyte materials is often a compromise between chemical stability and ionic conductivity of a compound. Using argyrodite systems as an example, a systematic evaluation of structural stability, hydrosolubility stability, ionic conductivity and electronic conductivity is achieved combining various computational techniques. The results show that there is significant room for synthesizing argyrodite compounds with improved stability and conductivity as solid electrolyte materials for ion-conducting rechargeable batteries.

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**References**


