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Two-Dimensional Substitution: Toward a Better Understanding of the Structure-Transport Correlations in the Li-Superionic Thio-LISICONs

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ABSTRACT: A deeper understanding of the relationships among composition-structure-transport properties in inorganic solid ionic conductors is of paramount importance to develop highly conductive phases for future employment in solid-state Li-ion battery applications. To shed light on the mechanisms that regulate these relationships, in this work, we perform a "two-dimensional" substitution series in the thio-LISICON family $Li_4Ge_{1-x}Sn_xS_{4-y}Se_y$. The structural modifications brought up by the elemental substitutions were investigated via Rietveld refinements against high-resolution neutron diffraction data that allowed a precise characterization of the anionic framework and lithium substructure. The analyses show that the anionic and cationic substitutions influence the polyhedral and



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unit cell volumes in different fashions and that the size of the polyanionic groups alone is not enough to describe lattice expansion in these materials. Moreover, we show that the lithium disorder that is crucial to achieve fast ionic mobility may be correlated to the lithium polyhedral volumes. The correlation of these structural modifications with the transport properties, investigated via electrochemical impedance spectroscopy and ⁷Li nuclear magnetic resonance spin-lattice relaxation measurements, shows a nonmonotonic behavior of the ionic conductivity and activation energy against the lithium polyhedral volumes, hinting to an optimal size of the conduction pathways for the ionic diffusion. Ultimately, the results obtained in this work will help to establish new guidelines for the optimization of solid electrolytes and gain a more profound understanding of the influence of the substituents on the structure and transport properties of Li-ion conductors.

1. INTRODUCTION

For a further improvement of lithium-ion batteries, the employment of a solid material as the electrolyte may enhance the electrochemical performance and improve the device safety of the current cell architectures.¹⁻³ To guarantee an optimal cell operation, the solid electrolyte, among other requirements, must allow fast Li⁺ ionic motion among the electrodes.⁴⁻⁶ While many highly conducting phases have been recently synthesized, 7^{-11} the list of materials that exhibit high ionic conductivity at room temperature is still extremely short due to the strict structural conditions that need to be satisfied to allow fast ionic motion.¹²⁻¹⁴ High carrier concentration and a disordered lithium substructure are of paramount importance to achieve a high ionic conductivity.^{15,16} Moreover, polyhedral connectivity and different lithium coordination strongly influence the energy landscape for the ionic diffusion, where larger changes of the coordination environment lead to higher activation barriers.¹² Fast ionic jumps are possible via facesharing tetrahedra, while ionic motion through edge-sharing polyhedra is unfavorable at typical lattice volumes of sulfides and oxides.^{12,17} The anionic framework should also provide wide channels for the ionic motion, leading to the conception that larger lattice volumes are beneficial for the ionic diffusion.¹⁷⁻¹⁹ However, while this condition seems to be generally valid, a number of studies report on an optimal

channel size for the ionic conductivity.^{20–24} After exceeding an optimal value, transport properties either decrease or reach a plateau for larger volumes.²⁰⁻²⁴ In addition to these static structural parameters, larger anion polarizability is also required to lower the activation energy by means of a weaker cation-anion interaction.²⁵⁻²⁸ All these aspects are highly convoluted as, for instance, more polarizable anionic frameworks often possess larger volumes. Therefore, it is challenging to discern the precise effect that each of these features has on the transport properties.

To date, there are only few classes of solid materials that meet the above mentioned conditions, and induce structural modifications via elemental substitutions are a commonly adopted strategy to enhance the ionic conductivity of these already promising phases.^{12,14,29} However, "linear substitutions", i.e., substitutions of one single element in a given structure, do not allow for a deeper understanding of the

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properties that govern the structure-transport relations of complex crystallographic framework and compositions. Therefore, to gain a better understanding of the substituents influence on the structural modification and transport properties, we performed a systematic study of a "twodimensional" substitution series, *i.e.*, substitutions of cationic and anionic species, in the thio-LISICON family (Figure 1a).



Figure 1. (a) Graphic representation of the compositions in the solid solution between Li_4GeS_4 , Li_4SnS_4 , Li_4GeS_4 , and Li_4SnS_4 explored in this study. (b) Crystal structure of Li_4SnS_4 as an example, showing the framework composed of isolated MS_4 tetrahedra (purple) and a variety of different Li–S coordination environments (gray). Li⁺ is omitted for clarity and shown completely in Figures 5 and 6.

The thio-LISICONs are a derivative of the oxide-based LISICON materials composed of a softer and more polarizable sulfide anionic sublattice.³⁰ These materials are generally represented by the unit formula LixMS4, where the lithium content depends on the valence of the M cation. An exemplary structure is shown in Figure 1b. The anionic framework of these materials is generally composed of isolated polyanionic MCh₄ groups whose three-dimensional arrangement depends on the temperature and compositions.^{31,32} At room temperature, these moieties form a hexagonal close packed (hcp) anionic sublattice that offers a large number of octahedral and tetrahedral voids suitable for lithium occupation.³³ The different possible lithium substructures will be discussed in more detail below. Depending on the composition, the lithium ions occupy different sets of positions in a more or less disordered fashion.¹² While the origin of these differences is still unknown, the different lithium distributions have been shown to strongly impact the transport properties of these materials.^{12,32,34}

To improve the ionic transport, many aliovalent substitutions of the central element in Li_4MS_4 (M = Si, Ge, Sn)^{33–38} have been performed. Both substitutions of trivalent elements (*i.e.*, Ga, Al)^{30,39–41} and pentavalent elements (*i.e.*, P, As, Sb)^{39,42–47} for M⁴⁺ result in beneficial transport properties of Li_4MS_4 , with the ionic conductivity of the solid solutions being orders of magnitude higher than the end members. This behavior indicates that the structural changes in the compounds with mixed compositions (for both lithium excess or deficient solid solution of Li_4MS_4) strongly affect the transport properties of these materials rather than the carrier concentration *per se*.¹² Among others, the $\text{Li}_{4-x}\text{Ge}_{1-x}P_x\text{S}_4$ solid solution results in the highest ionic conductivity of these solid electrolytes (*i.e.* ~2·10⁻³ S/cm),⁴² which led to the discovery of the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ phases that show even faster Li⁺ transport.⁴⁸

While cationic substitutions have been broadly studied, anionic substitutions have not been widely explored, and only few studies, mainly focused on $\text{Li}_3\text{PS}_{4-x}\text{O}_{x^y}$ can be found in literature.^{49–52} Apart from the oxygen substitution, a selenide-based material, Li_4SnSe_4 ,⁵³ has been synthesized, possessing an ordered lithium substructure and, therefore, lower ionic

conductivity compared to the lithium-disordered Li_4SnS_4 parent phase.³⁵

The thio-LISICON family was chosen as model due to its great structural versatility that allows anionic and cationic elemental substitutions while retaining the main structural identity, namely, the polyanionic framework. Therefore, isovalent anionic and cationic substitutions were performed within $Li_4Ge_{1-x}Sn_xS_{4-y}Se_y$ to discern the influence of the different chemical nature of the substituents on the structural modifications and their impact on the ionic transport. The structural modifications, investigated by means of Rietveld refinements against high-resolution neutron diffraction data, show that the anionic and cationic substitutions have a different influence on the MCh4 and lithium polyhedral volume that in turn affect the relative lattice expansion. The substituents also strongly affect the lithium distribution whose ordered or disordered character may be correlated to the lithium polyhedral size. The correlation of these structural modifications with the transport properties, investigated by electrochemical impedance spectroscopy and variable-temperature ⁷Li nuclear magnetic resonance (NMR) spin-lattice relaxation measurements, shows a nonmonotonic behavior of the ionic conductivity and activation energy against the lithium polyhedral volumes, hinting to an optimal size of the conduction pathways. Ultimately, this work provides new insights into the composition-structure-transport relationships in solid electrolytes.

2. EXPERIMENTAL SECTION

2.1. Synthesis. All preparations and sample treatments were carried out under an Ar atmosphere. Initially, lithium selenide was prepared via gas-phase reaction to use as a precursor for the final products. Metallic lithium (Li, Alfa-Aesar, 99.9%) was placed into a graphite crucible, which was then inserted into a quartz ampule containing Se powder (Se, Alfa-Aesar, 99.999%) at the bottom. Prior to the filling, the quartz tube and carbon crucible were heated at 1073 K under dynamic vacuum to remove moisture. The reaction was performed at 673 K for 48 h (285 K/h heating rate). The obtained product was pulverized, and phase purity was confirmed by X-ray powder diffraction. Li_4MCh_4 (M = Ge, Sn; Ch = S, Se) samples were prepared via high-temperature solid-state reaction. Lithium selenide, lithium sulfide (Li2S, Alfa-Aesar, 99.9%), germanium (Ge, ChemPur, 99.995%), tin (Sn, ChemPur, 99.999%), sulfur (S, Acros Organics, 99.999%), and selenium (Se, Alfa-Aesar, 99.999%) were mixed in the appropriate stoichiometric ratio and hand-ground in an agate mortar for 15 min. The obtained mixtures were pelletized and then filled into quartz ampoules, which were sealed under vacuum. Prior to the filling, the quartz tubes were carbon coated and preheated at 1073 K under dynamic vacuum to remove all trace of water in the reaction atmosphere. The reactions were performed at 973 K for 16 h and at 873 K for 48 h for Ge and Sn containing sample, respectively. The temperature and annealing time for Ge or Sn containing samples needed to be slightly different to produce materials with sufficient purity. After annealing, the obtained products were ground and prepared for the specific characterization method.

2.2. Neutron Powder Diffraction. Neutron powder diffraction data of $\text{Li}_4\text{MS}_{4-y}\text{Se}_y$ (M = Ge, Sn; $0 < y \le 4$) and $\text{Li}_4\text{Ge}_{1-x}\text{Sn}_x\text{Se}_4$ (0 < x < 1) were collected at the Oak Ridge spallation neutron source (SNS, Oak Ridge National Laboratory) using the PAC automatic sample changer at a POWGEN diffractometer (BM11-A beamline).⁵⁴ Approximately 3 g of the sample was loaded into an 8 mm diameter cylindrical vanadium can under an inert atmosphere and sealed with a copper gasket to avoid air exposure during measurements. Using a single bank with a center wavelength of 1.5 Å, data were collected in a high-resolution mode at room temperature for approximately 3 h. This bank allowed to probe a *d*-spacing range from 0.5 up to 6 Å with



Figure 2. Increasing lattice volume stemming from the incorporation of (a) larger Se anions for S and (b) Sn for Ge cations. The unit cell expansion follows Vegard's law, confirming the successful synthesis of stable solid solutions. Considering the full substitution range, the anionic substitutions generate a more pronounced lattice expansion compared to the cationic.

a resolution $\delta d/d < 9 \cdot 10^{-3}$. The obtained diffractograms are shown in the Supporting Information, Figure S1. For the Li₄Ge_{1-x}Sn_xS₄ series, we refer the reader to ref 34.

2.3. Rietveld Analysis. Rietveld refinements were carried out using the TOPAS-Academic V6 software package.⁵⁵ The structural data obtained from neutron refinements of Li_4MS_4 (M = Ge, Sn) from Minafra et al. were used as starting model.³⁴ The peak profile shape was described by a convolution of pseudo-Voigt and GSAS back–back exponential function.⁵⁴ Fit indicators, R_{wp} and Goodnessof-fit (GoF), were used to assess the quality of the refined structural model. The following parameters were initially refined: (1) scale factor, (2) background, (3) peak shape, and (4) lattice parameters. After a good fit of the profile was achieved, the structural parameters were allowed to refine. Initially, (5) fractional atomic coordinates, (6) atomic occupancies, and (7) isotropic atomic displacement parameters were refined. Finally, lithium occupancy on other possible interstitial sites was investigated. The coordinates of these voids are tabulated in the Supporting Information, Table S1. The stability of the refinements was ensured by allowing to refine multiple correlated parameters simultaneously over several cycles. Further information about the refinement protocol and utilized constraints can be found in Supplementary Discussion 1. Finally, the crystallographic information files reported in the Supporting Information were obtained by allowing to refine all possible structural parameters at the same time, further proving the stability of the refined structure. The structural data relative to Li₄Ge_{1-x}Sn_xS₄ were taken from our previous report.³

2.4. Electrochemical Impedance Spectroscopy. Electrical conductivities were measured by ac impedance spectroscopy, using isostatically pressed pellets (325 MPa, geometric density of all samples >80%) that were subsequently coated via thermal evaporation with thin gold (200 nm) electrodes. Electrochemical impedance analysis was conducted in the temperature range of 283–333 K using a SP300 impedance analyzer (Biologic) at frequencies from 7 MHz to 50 mHz with an amplitude of 10 mV. The error associate with the results of the impedance measurements (*i.e.*, ionic conductivities and activation energies) was carried out based on standard deviations of triplicates reported in our recent report on the Li₄Ge_{1-x}Sn_xS₄ (0 < x < 1) were taken from our previous study.³⁴

2.5. Nuclear Magnetic Relaxation. All samples were fire sealed in Duran glass tubes under vacuum to protect them from any reaction with air or moisture. ⁷Li NMR spin–lattice relaxation measurements were recorded in both the laboratory and the rotating frame of reference on a Bruker Avance III spectrometer connected to a shimmed cryo magnet with a nominal magnetic field of 7T. This external magnetic field corresponds to a Larmor frequency of 116 MHz. All measurements were carried out in the temperature range of 173–333 K with a ceramic high-temperature probe (Bruker). Experiments to obtain the ⁷Li NMR spin–lattice relaxation rate in the laboratory frame $(1/T_1)$ were conducted via the well-known

saturation pulse sequence.⁵⁶ For the $\pi/2$ pulses, a power level of 200 W was chosen; pulse lengths ranged from 2.13 to 2.83 μ s depending on temperature. The area under the free induction decays was plotted versus the waiting time t_d to construct the magnetization transients $M_{\rm a}(t_{\rm d})$, which were then analyzed with stretched exponentials containing characterized by the stretching exponent γ . To record diffusion-controlled spin-lattice relaxation NMR in the rotating frame of reference, we employed the classical two-pulse spin-lock pulse sequence⁵⁶ that allows observing the decay of transversal magnetization $M_{\rho}(t_{\rm lock})$ as a function of the duration of the locking pulse. Here, a locking frequency $\omega_1/2\pi$ of 20 kHz was applied with pulse powers ranging from 5.1 to 18.5 W. In analogy to the experiments in the laboratory frame, the spin-lock rates $(1/T_{1\rho})$ were extracted from variable-temperature magnetization transients $M_{
ho}(t_{
m lock})$. Again, the corresponding transients were parameterized with stretched exponentials determined by $1/T_{1\rho}$ and the stretching exponent γ_1 . The temperature dependence of the diffusion-induced rates $1/T_{1(a)}$ was analyzed in the frame of Arrhenius plots to deduce activation energies and estimate Li⁺ motional correlation rates.

3. RESULTS

3.1. Characterization of the Polyanionic Substructure. Solid solutions within $Li_4Ge_{1-x}Sn_xS_{4-y}Se_y$ were synthesized to study the correlation between composition, structural changes, and ionic mobility in the thio-LISICON family. Highresolution neutron powder diffraction (see Figure S1) was performed for all compositions allowing a characterization of the anionic framework and lithium substructure. Rietveld refinements are reported in the Supporting Information, Figures S2-S12, showing the good agreement between the calculated and experimental diffraction profiles. In addition, the crystallographic information format (CIF) files obtained from Rietveld refinements and all the obtained diffractograms can be found in the Supporting Information. All compounds along the solid solution series are well described by the orthorhombic Pnma space group (no. 62), and only minor impurity phases (<7 wt %) can be observed for a few compositions (Table S2).

3.1.1. Unit Cell Expansion. The evolution of the unit cell size against composition, reported in Figure 2, shows a linear increase of the lattice volume upon substitution of Ge ($r_{Ge} = 0.39$ Å) by Sn ($r_{Sn} = 0.55$ Å) and S ($r_S = 1.84$ Å) by Se ($r_{Se} = 1.98$ Å) driven by the larger ionic radii.⁵⁷ Such a linear increase of the lattice volume obeys Vegard's law, therefore confirming the successful synthesis of stable solid solutions. Moreover, the good agreement between the Ge/Sn and S/Se occupancies obtained from Rietveld refinements with the nominal values



Figure 3. (a, b) Modifications of the experimental MCh₄ volumes as a function of the composition of the solid solutions. (c) The experimental M– Ch bond distance reported as a function of the theoretical values reveals that the size of the MCh₄ units is mainly driven by the radii of elements composing the tetrahedral units. (d) The experimental MCh₄ volume reported as a function of the average ionic radius of the elements composing the tetrahedral unit shows that cationic substitutions have a greater impact on the MCh₄ size compared to the anionic substitutions.

further corroborates the full incorporation of the substituents in the solid solutions (see Figure S13). It should be noted, however, that the trend of the lattice parameters against compositions does not always reflect the monotonic trend of the unit cell volume. These deviations from linearity are common in this class of materials that show a tendency of modifying the lattice parameters upon structural rearrangement (*vide infra*).^{34,39,42} The lattice parameters of all solid solutions are reported in the Supporting Information, Figures S14–S17.

Upon closer inspection of the trend of the lattice volume against composition shown in Figure 2, it can be noticed that the relative unit cell expansion stemming from anionic substitutions (~16%) is more pronounced compared to the cationic (~5%). This behavior may be caused by the larger number of anions that can be substituted compared to the single central cation. Normalizing the unit cell volume expansion by the substitution degree (*i.e.*, the maximum number of possible substituents: 4 and 1 for anionic and cationic substitution, respectively), cationic substitutions generate a slightly more pronounced expansion (~5%) compared to the anionic (~4%). To further investigate the underlying reasons behind this behavior, the local effect of the substituents on the MCh₄ and lithium polyhedral volumes needs to be examined.

3.1.2. MCh_4 Expansion. The influence of the cationic and anionic substitutions on the MCh_4 size is shown in Figure 3a,b in which the experimental volume of the MCh_4 units is reported as a function of composition of the solid solutions.

The cationic substitutions expand the MCh₄ volume more $(\sim 24\%)$ when compared to the anionic $(\sim 20\%)$ substitutions.

As the larger MCh_4 volume expansion with cationic substitution may be caused by the slightly larger difference of the ionic radii of the cations compared to the anions (*i.e.*, $\Delta_{Sn-Ge}^c = 0.16$ Å and $\Delta_{Se-S}^r = 0.14$ Å), the influence of the ionic radii of the substituents on the MCh₄ volume needs to be examined. Figure 3c shows the experimental average M–Ch distance (d_{M-Ch}^E) as function of a calculated theoretical average distance (d_{M-Ch}^c), which is based purely on the ionic radii of the constituents of the tetrahedral unit:

$$d_{\rm M-Ch}^{\rm C} = (r_{\rm Ge} n_{\rm Ge} + r_{\rm Sn} n_{\rm Sn})_{\rm M} + \left(\frac{r_{\rm S} n_{\rm S} + r_{\rm Se} n_{\rm Se}}{4}\right)_{\rm Ch}$$
(1)

where r indicates the Shannon ionic radius⁵⁷ of a specific element, and n is the number of times that elements is present in the MCh₄ unit. The trend in Figure 3c shows a linear relation between experimental and theoretical values, indicating that the M–Ch bond length is mainly driven by the different ionic radii of the elements, which is in good agreement with the hard spheres model of the bond lengths.

To further investigate the role of the different substituents on the size of the whole MCh_4 units, in Figure 3d, the volume of the MCh_4 units is reported as a function of the average ionic radius of the five elements that compose the tetrahedra, expressed as

$$R_{\text{mean}} = \left(\frac{r_{\text{S}}n_{\text{S}} + r_{\text{Se}}n_{\text{Se}} + r_{\text{Ge}}n_{\text{Ge}} + r_{\text{Sn}}n_{\text{Sn}}}{5}\right)$$
(2)



Figure 4. Occupancy weighted average lithium polyhedral volumes as a function of composition of the solid solutions. (a) The anionic substitutions generate a pronounced expansion of the lithium polyhedral volumes, while (b) the cationic substitutions have only a minor effect on their size.



Figure 5. (a) Lithium distribution on the different sites as a function of the composition. Along the solid solution series, 75% of the total lithium occupies tetrahedral positions, while the remaining 25% resides in octahedral interstices. Polyhedral representation of the (b) Li_4GeS_4 and $Li_4SnS_{e_4}$ together with (c) Li_4SnS_4 and (d) Li_4GeS_4 unit cells. While Li_4GeS_4 and Li_4SnSe_4 possess an ordered lithium substructure, Li_4SnS_4 and Li_4GeSe_4 show some degree of disorder.

As can be observed in Figure 3d, anionic and cationic substitutions describe linear trends; albeit, with different slopes. In agreement with the trend reported in Figure 3a,b, the higher relative slope of the $\text{Li}_4\text{Ge}_{1-x}\text{Sn}_x\text{Ch}_4$ solid solutions indicates that the MCh₄ volume expansion is stronger when cationic substitutions are performed. However, while useful to show that cationic and anionic substitutions affect the MCh₄ size differently, this quantity is not a real descriptor of the polyhedral volume since similar MCh₄ crystallographic volumes can be correlated with very different R_{mean} values.

Considering the whole substitution range, *i.e.*, four anions and one cation, the faster expansion of the MCh_4 units upon cationic substitution does not reflect the unit cell volume evolution (Figure 2), which is stronger for anionic substitutions. In other words, the larger expansion of the unit cell

when anionic substitutions are performed (up to four anions) cannot be explained based solely on the size difference of the MCh_4 units since these are expanded more by cationic substitution, therefore hinting to important contributions of other factors on the unit cell expansion.

3.1.3. Lithium Polyhedral Volumes. To further investigate the influence of the substituents on the structure of these materials, the lithium polyhedral volumes, calculated as an average of tetrahedral and octahedral volumes weighted by the relative lithium occupancies, are reported as a function of the composition of the solid solutions in Figure 4. While this averaging does not provide a view on the different polyhedra themselves (see Li⁺ substructure below), it provides insights into the average size of the Li⁺ coordination environments that affect the unit cell volume. The lithium polyhedral expansion is affected in a different fashion by anionic and cation substitution. The anionic substitution has a strong impact on the lithium polyhedral size, while the cationic substitutions have only a marginal effect. Within the whole substitution range, the relative expansion of the LiCh_x volume caused by the different substituents is very similar to the unit cell expansion: anionic substitutions expand both the unit cell and LiCh_x volume by ~15%, while cationic substitutions have only minor effects on the volume expansion (*i.e.*, ~5%). This behavior is a strong evidence of the interplay among the unit cell volume and Li⁺ environment.

Upon closer inspection of Figure 4, it can be noticed that the compositions along the $Li_4Ge_{1-x}Sn_xS_4$ cationic linear substitution with x = 1, and the $Li_4SnS_{1-y}Se_y$ anionic linear substitution with y = 0 and 1 result to be out of trend compared to the other samples along the solid solution. The reason for this deviation is likely due to the lithium occupancy on the Li(4) position that, while residing in a octahedral pocket, presents a coordination number closer to five (*vide infra*). However, an octahedral coordination volume for Li(4) has been considered for the sake of simplicity and consistency with other compositions, therefore resulting in slightly larger average lithium polyhedral volumes for Li_4SnS_4 and Li_4SnS_3Se .

3.2. Characterization of the Lithium Substructure. Besides the study of the structural changes of the anionic sublattice, neutron diffraction allows precise analyses of the lithium positions and occupancies in the unit cell. Thus, to probe the differences in the lithium substructure brought up by the elemental substitutions, the capacity of all possible sites in the cell to host lithium was investigated. Starting from the structural models proposed previously,^{34,35,38,53} lithium occupancy was refined for all possible available sites in the unit cell. The atomic coordinates reported in Table S1 were used as the starting point, and the resultant occupancy on the various Li⁺ positions is reported as a function of composition in Figure 5a. Further information about the refinement protocol and utilized constraints can be found in Supplementary Discussion 1. While all the studied materials crystallize in the same Pnma space group and possess identical anionic frameworks, the lithium substructure drastically changes based on the compositions and lattice volumes. For all solid solution series, 75% of the total lithium occupies tetrahedral positions and the remaining 25% reside in octahedral interstices (Figure 5a). The ratio of lithium occupancies on tetrahedral and octahedral positions remains unchanged along the substitution series. Below, we will introduce the different Li⁺ substructures found in these solid solutions.

3.2.1. Li_4GeS_4 . With regard to the lithium sublattice of Li_4GeS_4 , Li^+ ions occupy three inequivalent crystallographic positions: Li(1) and Li(2) sites resides in tetrahedral voids (Wyckoff 4*c* and 8*d*, respectively) and Li(3) in octahedral interstices (Wyckoff 8*d*). The unit cell of Li_4GeS_4 and the relative lithium occupancies are reported in Figure 5. The Li(3) sites are arranged in an edge-sharing chain along the *b*-axis representing the main pathway for ionic diffusion.^{36,37} The Li(1) tetrahedra share edges with two adjacent Li(3) octahedra bridging the ionic jumps within the linear chain along the *b*-direction.³⁴ Moreover, each Li(3) octahedra shares faces with two Li(2) sites forming Li(2)–Li(3)–Li(2) units in the *ac*-plane that support fast ionic jumps.^{34,36,37}

While fast ionic jumps are allowed within these linear units, the long-range ionic transport occurs along the *b*-direction via

the octahedral Li(3) units bridged by the Li(1) sites.³⁴ These chains are isolated and allow diffusion only in one direction. All these characteristic are highlighted in Figure 6a that shows the linear octahedral chain along the *b*-direction and local Li(2)–Li(3)–Li(2) units in the *ac*-plane.



Figure 6. (a)–(d) Local polyhedral arrangement in the *ac*-plane and along the *b*-direction of the different lithium substructures found in the solid solutions. For clarity, Li(2) is omitted in the representation along the *b*-direction, whereas Li(1) is omitted in the *ac*-plane. Different colors of the background indicate specific regions of the two-dimensional substitution series in which a certain lithium substructure was found.

3.2.2. Li₄SnS₄. Upon step-wise substitutions of Sn for Ge in $Li_4Ge_{1-r}Sn_rS_4$, the lithium substructure retains the same character of Li₄GeS₄ for $x \le 0.75$, while it drastically changes for Li₄SnS₄.³⁴ The unit cell of Li₄SnS₄ and the relative lithium occupancies are reported in Figure 5. In this structure, the lithium ions occupy four inequivalent crystallographic positions: Li(3) and Li(2), already found in Li_4GeS_4 , a tetrahedral Li(1') position (Wyckoff 4c), and an additional octahedral Li(4) site (Wyckoff 4c). Here, we use the terminology of Li(1') to denote that Li(1) repositions itself along the c-direction, which can be viewed as a flip of the tetrahedron it belongs to. Similar to Li₄GeS₄, the Li(3) octahedra form linear edge-sharing chains along the *b*-direction that support ionic diffusion. The ionic jumps between the octahedral Li(3) sites are now bridged by the Li(1') positions. In Li_4SnS_4 , Li(1') share faces with two adjacent Li(3)octahedra while in Li4GeS4 Li(1) only share edges with Li(3) (Figure 6a,b).^{35,38} Therefore, the repositioning of Li(1)into Li(1') for the thiostannate improves the connectivity of the polyhedra within the linear chains, enhancing the ionic mobility, as recently shown.³⁴ Moreover, in Li_4SnS_4 , lithium ions occupy another octahedral Li(4) position resulting in a reduced occupancy of Li(3) (Figure 5).^{35,38} The Li(4) site plays a crucial role in the ionic diffusion as it bridges the onedimensional chains formed by Li(3) and the surrounding LiS_4



Figure 7. (a) Exemplary Nyquist plots at room temperature, showing the impedance response (open circles) and the fit (gray line) with the employed equivalent circuit (insert). (b) Exemplary Arrhenius plots of the conductivity values obtained from temperature-dependent impedance spectroscopy and the respective linear fit (gray dotted line). (c) Room-temperature ionic conductivity, σ_{RT} , and (d) activation energy, E_{A} , as a function of composition in Li₄Ge_{1-x}Sn_xS_{4-y}Se_y. Uncertainties of the room-temperature ionic conductivity and the activation energies values were obtained based on the measurement of three separately synthesized samples per composition from our previous study.³⁴

tetrahedra (*i.e.*, Li(1') and Li(2)), thereby activating a threedimensional conduction behavior via Li(2)–Li(4) and Li(1')– Li(4) exchange.³⁴

Considering the effect of Li(1') and Li(4) on the lithium polyhedral connectivity shown in Figure 6b, it is evident that the lithium redistribution in Li_4SnS_4 allows a greater Li-Lipercolation together with a better polyhedral connectivity, which we have already shown to result in better transport properties compared to the Li_4GeS_4 parent phase.³⁴

3.2.3. Li_4SnSe_4 . In line with previous reports,⁵³ the lithium substructure of Li_4SnSe_4 is identical to Li_4GeS_4 . Upon anionic substitution in $Li_4SnS_{4-y}Se_y$, the lithium substructure changes progressively resulting in lithium occupancy for both Li(1) and Li(1') in Li_4SnS_3Se , while it matches the motif of Li_4SnSe_4 for $y \ge 2$ (Figures 5 and 6d).

3.2.4. Li_4GeSe_4 . The lithium substructure of Li_4GeSe_4 resembles that of Li_4GeS_4 ; however, additional lithium occupancy can be found in a new tetrahedral site (Wyckoff 8*d*), which we denote here as Li(2'). As shown in Figure 5, the lithium occupation on Li(2') sites results in reduced occupancy for Li(2) and represents an inversion of the $Li(2)S_4$ tetrahedron. The newly found Li(2') tetrahedral sites share a face with Li(2) forming a Li(2)/Li(2') double

tetrahedron. This local coordination is shown in Figure 6c. The lithium nuclear density is displaced from the centroid of each single Li(2) or Li(2') tetrahedron, and it is relocated toward the center of the shared triangular face. While a trigonal coordination for lithium ions in the typical volume range of sulfidic materials is unfavorable, the lattice volume expansion caused by the elemental substitutions may make such sites available for lithium occupation. These Li(2)/Li(2') double tetrahedra share edges with other Li(2)/Li(2') double tetrahedra, forming chains along the c-axis. Given that, the partially occupied sites define the set of pathways available for possible lithium diffusion, it is likely that the edge-sharing double tetrahedra along the c-axis support ionic diffusion. Interestingly, a further increase or decrease of the lattice volume results in reduced lithium occupancy on Li(2') for $Li_4GeS_{4-v}Se_v$ and $Li_4Ge_{1-x}Sn_xSe_4$ (Figure 5a).

Upon a closer inspection of the lithium distribution against composition reported in Figure 5a, it can be noticed that, lithium disorder that is usually highly beneficial for the ionic transport, is affected by different anion/cation combinations rather than the presence of particular chemical elements in the structure.⁵⁸ The origin of this behavior can likely be traced back to the different size of the MCh₄ or LiCh_x units that may



Figure 8. Arrhenius plot of the ⁷Li NMR spin–lattice relaxation rates in the laboratory frame $1/T_1$ (squares) and rotating-frame $1/T_{1\rho}$ (circles) of (a) Li₄SnSe₄, (b) Li₄SnSe₄, (c) Li₄GeS₄, and (d) Li₄GeSe₄. Solid lines, parameterizing the behavior of the relaxation rates, represent fits with BPP-type Lorentzian shaped spectral density functions.⁶² Dashed lines are drawn to guide the eye. Activation energies given in bold letters refer to those obtained from BPP fits. They represent the slopes of the respective peaks in the high-T limits. Activation energies of partly linear regions of $1/T_1$ and of the low-T flanks of the $1/T_{1\rho}$ rate peaks are also included. The temperatures T_{max} at which the $1/T_{1\rho}$ relaxation rate peaks reach their maximum are reported also. Upper graphs show the temperature behavior of the corresponding stretching exponents $\gamma_{(\rho)}$; lines represent guides to the eye.

generate optimal volumes and charge disorder favorable for disordered lithium distribution.^{26,58}

3.3. Characterization of Ionic Transport via Impedance Spectroscopy. The ionic transport properties of the Li₄Ge_{1-x}Sn_xS_{4-y}Se_y series were analyzed by temperaturedependent impedance spectroscopy. The impedance responses within the explored temperature range are similar throughout the solid solution series and consist of a well-resolved semicircle followed by a spike in the lower frequency region (Figure 7a). The obtained data were fitted with an equivalent circuit consisting of one parallel constant phase element (CPE)/resistor in series with a CPE (insert in Figure 7a). The capacitance of the CPE used to fit the semicircle is in the range of 10^{-11} F/cm², and all impedance spectra exhibit α -values of \sim 0.9, all of which indicate a predominant bulk contribution to the impedance response.⁵⁹ All samples in the $Li_4Ge_{1-r}Sn_rS_{4-v}Se_v$ series show Arrhenius behavior within the temperature range of 283-333 K (Figure 7b). The roomtemperature ionic conductivity values for the solid solution series and the activation energy for ionic diffusion, as determined from a linear fit of the Arrhenius plots, are reported in Figure 7c,d. While consistent with our previous studies,³⁴ the herein observed ionic conductivities for Li₄SnS₄ and Li₄SnSe₄ are significantly lower compared with the values

reported by Kaib *et al.* $(7 \cdot 10^{-5} \text{ and } 2 \cdot 10^{-5} \text{ S/cm} \text{ relative to } \text{Li}_4 \text{SnS}_4 \text{ and } \text{Li}_4 \text{SnSe}_4$, respectively).^{35,53} These differences are likely stemming from the different synthesis protocols that may influence crystallinity and purity of the materials, together with the different setup employed for the electrical characterization, applied pressure during the measurement and relative density of the pellets.⁶⁰

The room-temperature ionic conductivity and activation energy are significantly affected by the isovalent substitutions in $\text{Li}_4\text{Ge}_{1-x}\text{Sn}_x\text{S}_{4-y}\text{Se}_y$. These drastic changes indicate that the transport properties of this class of materials can be tailored by the modification of the lithium substructure and anionic framework without any change of the carrier concentration. However, a clear explanation of these trends is not possible only considering the different compositions of the solid solutions; therefore, other descriptors must be employed to better comprehend the evolution of the transport properties of these materials (*vide infra*).

3.4. Characterization of lonic Transport via Nuclear Magnetic Resonance. ⁷Li NMR spin–lattice relaxation experiments were performed in both the laboratory and rotating frame of reference to obtain information on the Li⁺ jump rates and activation energies of the underlying motional processes of the two-dimensional substitution series endmembers, namely, Li₄GeS₄, Li₄SnS₄, Li₄GeSe₄, and Li₄SnSe₄. These compositions were selected for the NMR experiments due to their different lithium substructure and unit cell volume, therefore allowing a comprehensive study of the lithium configurations and polyhedral volumes effects on the lithium motion. Moreover, since ⁷Li NMR spin—lattice relaxation rates measured in the laboratory frame of reference, $1/T_1$, are sensitive to spin fluctuations with rates on the MHz range ($\omega_0/2\pi = 116$ MHz) and spin-lock NMR rates, $1/T_{1\rho}$, to motional correlation rates in the kHz range ($\omega_1/2\pi = 20$ kHz), we were able to cover a large dynamic range of hopping processes on different time scales. Here, via variable-temperature $1/T_{1\rho}$ spin-lock ⁷Li NMR, we recorded the complete diffusion-induced rate peak.⁶¹

The corresponding Arrhenius plots of the spin-lattice relaxation rates, $1/T_1(1/T)$ and $1/T_{1\rho}(1/T)$, for each sample are shown in Figure 8. In the upper graphs, the change of the stretching exponents $\gamma_{(\rho)}$ are displayed for comparison with the behavior of $1/T_{1(\rho)}$. Note that maxima of the relaxation rate are correlated with minima of the stretching exponent. Below, we describe the different lithium dynamics and, adopting the formalism described in Supplementary Discussion 2, provide an overview on the Li⁺ attempt frequencies and activation energies for ionic motion of the samples examined (Table S3). These values provide a good description of the overall lithium dynamics but cannot be correlated to specific ionic jump processes due to the strong convolution of these processes.

3.4.1. Li_4GeS_4 . The ⁷Li NMR spin–lattice relaxation rates 1/ $T_{1(\rho)}$ of the thiogermanate are shown in Figure 8a. While the laboratory-frame rate only exhibits a weak temperature dependence with a shallow and broadened peak at 330 K, the spin-lock relaxation rate passes through two rate peaks 1/ $T_{1\rho}(1/T)$ appearing at 320 and 360 K, respectively. This feature is unique of Li₄GeS₄, and it is not observed for any of the other examined compositions (vide infra). The overall response was parameterized with a sum of two Lorentzian shaped relaxation rate peaks according to the model introduced by Bloembergen, Purcell, and Pound (BPP)⁶² (solid line). The dashed lines in Figure 8a indicate the individual diffusion-induced rate peaks. The peak located at T_{max} = 320 K reveals an activation energy of 0.58 eV and an attempt frequency of $5 \cdot 10^{13}$ s⁻¹, while the second peak at T_{max} = 360 K has to be described with a lower activation energy of 0.53 eV and an attempt frequency of only $4 \cdot 10^{12}$ s⁻¹. The appearance of the two $1/T_{1o}(1/T)$ relaxation rate peaks of Li₄GeS₄ indicates that Li⁺ diffusivity in this material is stepwise activated and different motion processes dominate at different temperatures.

3.4.2. Li_4SnS_4 . Similar to Li_4GeS_4 , but more pronounced, in the thiostannate Li_4SnS_4 , a $1/T_1$ peak appears slightly above 333 K (Figure 8b). In this temperature region, the magnetization transients show biexponential behavior characterized by two rates $1/T_{1,fast}$ and $1/T_{1,slow}$, pointing to two different spin reservoirs. The rate peak $1/T_{1,fast}(1/T)$ points to a relatively low activation energy of only 0.38 eV, which is in line with the measurements reported by Kaib *et al.*³⁵ This feature, most likely stemming from the disordered lithium substructure, reflects a rapid, localized forward-backward spin fluctuations with characteristic rates on the MHz time scale.

Contrarily to Li₄GeS₄, the spin-lock rate peak of Li₄SnS₄ reveals only a single BPP-type peak located at $T_{\rm max} = 333$ K,⁶² characterized by an activation energy of 0.54 eV and an attempt frequency of $3 \cdot 10^{13}$ s⁻¹. Worth noting, the $1/T_{\rm 1,fast}(1/$

T) peak does not affect spin-lock relaxation as a corresponding peak $1/T_{1\rho}$ at sufficiently low temperatures is missing. Obviously, the two methods are sensitive to quite different spin fluctuations in Li₄SnS₄. We assume that if several Li ion jump processes run in parallel not all of them will contribute to the distinct, time-scale-dependent NMR responses in equal shares. The process characterized by 0.38 eV is, however, considered as a key feature to explain the enhanced transport properties observed for Li₄SnS₄ as it is more pronounced than in the other compounds studied.³⁵

3.4.3. Li_4SnSe_4 . ⁷Li NMR laboratory-frame spin-lattice relaxation in Li₄SnSe₄ reveals only a shallow temperature dependence up to 333 K (Figure 8c) that is controlled by localized or correlated forward-backward Li⁺ jump processes, which also influence the $1/T_1$ rates of the other compounds at sufficiently low T.^{63,64} In contrast to the other examined compositions, for Li₄SnSe₄, the rate $1/T_1$ does not show any peak-like feature. Spin-lock NMR, however, exhibits a rate peak at $T_{max} = 328$ K that, again, can be described with a symmetric Lorentzian-shaped BPP function;⁶² the fit yields a relatively high activation energy of 0.69 eV and an attempt frequency of 7.10¹⁵ s⁻¹.

3.4.4. Li_4GeSe_4 . The laboratory-frame rate $1/T_1$ of Li_4GeSe_4 (Figure 8d) passes through a shallow maximum located at 290 K, likely stemming from the disordered lithium substructure as for Li_4SnS_4 . Compared to Li_4SnS_4 , this peak is located at much lower temperatures indicating faster diffusion processes on the Angstrom length scale. The spin-lock relaxation rate shows an almost symmetric peak at temperature $T_{max} = 320$ K slightly lower than that of Li_4SnS_4 . The high-*T* flank of the peak is to be characterized by a relatively high BPP⁶² activation energy of 0.62 eV and an attempt frequency of 10^{15} s⁻¹. The low-*T* flank can be characterized by an activation energy very similar to Li_4GeS_4 , indicating that probably for a limited window at lower temperatures; the Li⁺ local motion is similar for these two materials.

4. DISCUSSION

Solid solutions within $\text{Li}_4\text{Ge}_{1-x}\text{Sn}_x\text{S}_{4-y}\text{Se}_y$ were synthesized to study the correlation between composition, structural changes, and ionic mobility in the thio-LISICON family. Based on the above seen changes in the structure and transport properties, a number of conclusions can be drawn:

4.1. Anionic Sublattice and Lattice Expansion. The evolution of the MCh₄ and lithium polyhedral volume, against composition of the solid solutions, shows that the anionic and cationic substitutions have different effects on the polyhedral expansion. The correlation among MCh₄ and lithium polyhedral volumes is shown in Figure 9a. While the MCh₄ is reported on the x-axis and the lithium polyhedra on the yaxis, this plot is not meant to suggest that the lithium polyhedral volume is a function of the MCh₄ size but only to highlight the correlation among these structural factors. The trend in Figure 9a shows that cationic substitutions generate a more pronounced expansion of the MCh₄ units, while anionic substitutions have a greater impact on the lithium polyhedral size. The larger expansion of the MCh₄ units upon cationic substitution can be explained considering the slightly larger difference of the ionic radii of the cations compared to the anions (*i.e.*, $\Delta_{Sn - Ge}^r = 0.16$ Å and $\Delta_{Se - S}^r = 0.14$ Å). This evidence indicates that the expansion of the MCh₄ is mainly driven by the ionic radii of the elements composing such units (Figure 3c). With regard to the lithium polyhedral expansion,



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Figure 9. (a) Correlation among MCh_4 and lithium polyhedral volumes. Influence of the (b) MCh_4 units and (c) lithium polyhedra on the unit cell expansion. Anionic and cationic substitutions have different effects on the polyhedral expansion. Therefore, anionic substitutions cause major expansions of the unit cell volume by enlarging the lithium polyhedral volumes, while cationic substitutions enlarge the MCh_4 volumes with smaller lattice expansion and barely affecting the lithium polyhedral pathways.

it is clear that anionic substitutions have a much greater impact on the volume than the cationic since the cationic species do not actively take part in the LiCh_x polyhedra.

The different effects that cationic and anionic substitutions have on the local volumes of the MCh_4 and $LiCh_x$ polyhedra strongly influence the unit cell expansion. Figure 9b shows that, while cationic substitutions expand the MCh_4 units more, the relative unit cell expansion stemming from anionic substitutions is more pronounced compared to the cationic. Therefore, the larger expansion of the unit cell when anionic substitutions are performed cannot be explained based solely on the size difference of the MCh_4 units. For example, while possessing smaller MCh₄ volume, the unit cell size of Li_4GeSe_4 is substantially larger than Li_4SnS_4 (see Figure 9b). Therefore, the size of the MCh₄ units cannot be the only driving factor of the unit cell expansion. These trends may be caused by the fact that the anions participate in the coordination of Ge/Sn and Li ions, thereby increasing both the polyanionic and Li coordination volumes, while the cationic substitution, to first approximation, only affects the MCh₄ size, having therefore a less strong impact on the unit cell volume.

The larger volume expansion of the unit cell upon anionic substitutions correlates well with the lithium polyhedral expansion and is shown in Figure 9c. The relative expansion of the LiCh_x volume caused by the different substituents is indeed very similar to the unit cell expansion: within the whole range of substitutions, the anionic substitutions expand both unit cell and LiCh_x volume by ~15%, while cationic substitutions have only minor effects on the volume expansion (*i.e.*, ~5%).

Therefore, anionic substitutions cause major expansions of the unit cell volume by enlarging the lithium polyhedral volumes, while cationic substitutions enlarge the MCh_4 volumes with smaller lattice expansion and barely affecting the lithium polyhedral pathways.

All these correlations highlight the complex interplay of many structural factors that influence the lattice size. Here, by performing a two-dimensional substitution, we are able to demonstrate that the MCh_4 size is not enough to explain the lattice expansion. The $LiCh_x$ expansion instead seems to play a major role in determining the unit cell volume. This evidence indicates the importance of two-dimensional substitution studies to understand the general role of the substituents on the structural modifications.

4.2. Volume Effect on the Lithium Distribution and Transport Properties. As shown in Figure 5a, the combination of different elements that compose the crystal structure has a strong influence on the lithium distribution and disorder. As pointed out by a variety of theoretical studies, a disordered lithium substructure is of crucial importance to achieve a high ionic conductivity in the solid state.^{15,16} However, the conditions to obtain these lithium-disordered configurations are still unknown. Optimal sizes of the lithium polyhedral volumes generated by particular anion/cation combination may cause a disorder in the lithium substructure and have an impact on the transport properties. Therefore, to further investigate the influence of the lithium polyhedral size on the transport properties, in Figure 10a,b, the ionic conductivities and activation energies carried out from electrochemical impedance measurements are reported as a function of the average lithium polyhedral volume for all the composition along the $Li_4Ge_{1-x}Sn_xS_{4-y}Se_y$ solid solution series. The ionic conductivity and activation energy describe a parabolic-like trend with the lithium polyhedral size, therefore hinting at an optimal volume for the ionic conduction.

The trends obtained from the electrical measurements are in large agreement with the dynamic process sensed by ⁷Li NMR spin–lattice relaxation measurements (Figure 10c). In this case, the activation energies extracted from the modified BPP-fits of the spin-lock NMR relaxation rates increase with the lithium polyhedral volume. The higher E_A , the larger the attempt frequency determining the diffusion-induced NMR rate peaks. Even if spin-lock NMR senses only a specific dynamic process, our results support the idea that this process is linked to optimal lithium polyhedral volumes at intermediate



Figure 10. (a) Lithium ionic conductivity and (b) activation energy carried out from impedance spectroscopy alongside the (c) activation energies and attempt frequencies derived from the BPP-fits of the diffusion-induced ⁷Li NMR spin-lock rates as a function of the average lithium polyhedral volumes LiCh_x. Dashed lines in panel (c) are to guide the eye; they exclude the high-*T* peak of Li₄GeS₄ appearing at $T_{max} = 360$ K. The results of the electrical measurements, being in line with the NMR data, reveal an optimal channel size for lithium diffusion.

values. The lithium polyhedral volumes of Li_4SnS_4 are close to this value, which is also reflected in the low activation energy.

While at small volumes the ionic transport is hindered due to the large energy penalty that needs to be paid when the Li⁺ ion passes through an extremely small bottleneck,¹⁷ the exact reasons behind the decline of the ionic motion for larger volumes are still unknown. This behavior may be attributed to the fact that the mobile lithium would not migrate through the center of the structural openings but rather grazing the "walls" of the conduction pathways. This would result in larger changes of lithium coordination during diffusion that could in turn cause a higher energy penalty associated with the diffusion (Figure 11).



Figure 11. Illustrative representation of the lithium diffusion across a structural bottleneck and the expected energy landscape as function of the conduction pathways size. Mobile lithium ions and elements composing the structural framework are shown as gray and orange spheres, respectively.

5. CONCLUSIONS

In this work, a systematic study of the "two-dimensional" substitution series $Li_4Ge_{1-r}Sn_rS_{4-v}Se_v$ has been performed to discern the influence of the different substituents on the structural modifications and transport properties. Employing Rietveld refinements against high-resolution neutron diffraction data, we show that anionic and cationic substitutions have a different impact on the polyhedral and unit cell volume expansion. Considering the whole substitution range, we found that the unit cell volume expands more upon anionic substitution compared to the cationic. The expansion of the unit cell is very similar to the relative expansion of the $LiCh_x$ volume: $\sim 15\%$ via anionic substitutions and only $\sim 5\%$ for the cationic. This evidence is in contrast with the local evolution of the MCh₄ volumes that expand more upon cationic substitutions compared to the anionic (~ 24 and 20%, respectively). Therefore, performing a two-dimensional substitution series, we were able to demonstrate that the MCh₄ size is not enough to explain the lattice expansion and that the lithium polyhedra play a very important role in regulating the lattice volume.

Moreover, we showed that the lithium polyhedral volume has a great impact on the lithium distribution and ionic diffusion of these materials. Employing electrochemical impedance spectroscopy, we found a nonmonotonic behavior of the transport properties as a function of the lithium polyhedral volumes that, after an initial increase, reach a maximum and decrease for further volume expansions. This finding of an optimal lithium polyhedral volume is strongly supported by the spin-fluctuations sensed by ⁷Li spin-lattice relaxation NMR. While the correlation between lithium polyhedral volumes and transport properties was clearly demonstrated, it is still possible that the convolution of other factors, such as the different polarizability and charge distributions of the elements that form the anionic framework, may still play a role. Ultimately this work provides a better understanding of the composition-structure-transport relationships in solid electrolytes, highlighting the importance of performing two-dimensional substitution series.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.0c04150.

Experimental neutron powder diffractograms and relative Rietveld refinements for all explored compositions, alongside with the crystallographic information files and the list of the minor secondary phases obtained by Rietveld refinements; the starting point for the refinement of all possible voids suitable for lithium occupation; the Ge/Sn and S/Se ratios and the extracted lattice parameters for all explored compositions; and tabulated the activation energies and attempt frequencies obtained by ⁷Li $1/T_{1\rho}$ spin–lattice relaxation NMR carried out in the rotating frame of reference together with the temperature at which the respective peak occurs (PDF)

Crystallographic files of compounds (CIF)

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Notes

The authors declare no competing financial interest.

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