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Inducing high ionic conductivity in the lithium superionic argyrodites $\text{Li}_{6+x}\text{P}_{1-x}\text{Ge}_x\text{S}_5\text{I}$ for all-solid-state batteries

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Abstract

Solid-state batteries with inorganic solid electrolytes are currently being discussed as a more reliable and safer future alternative to the current lithium-ion battery technology. To compete with state-of-the-art lithium-ion batteries, solid electrolytes with higher ionic conductivities are needed, especially if thick electrode configurations are to be used. In the search for optimized ionic conductors, the lithium argyrodites have attracted a lot of interest. Here, we systematically explore the influence of aliovalent substitution in $\text{Li}_{6+x}\text{P}_{1-x}\text{Ge}_x\text{S}_5\text{I}$ using a combination of X-ray and neutron diffraction, as well as impedance spectroscopy and nuclear magnetic resonance. With increasing Ge content, an anion site disorder is induced and the activation barrier for ionic motion drops significantly, leading to the fastest lithium argyrodite so far with $5.4 \pm 0.8 \text{ mS cm}^{-1}$ in a cold-pressed state and $18.4 \pm 2.7 \text{ mS cm}^{-1}$ upon sintering. These high ionic conductivities allow for successful implementation within a thick-electrode solid-state battery that shows negligible capacity fade over 150 cycles. The observed changes in the activation barrier and changing site disorder provide an additional approach toward designing better performing solid electrolytes.

1. Introduction

Solid-state batteries provide a possibility for energy storage with higher energy densities and improved safety by using a solid electrolyte and lithium metal anode, as compared to using liquid electrolytes.¹⁻⁷ There have been many recent advances in the field concerning a better understanding of the interfacial reactions,⁸⁻¹⁰ the employment of coatings,^{11,12} the minimized use of carbon additives,¹³⁻¹⁵ as well as strain design and particle size optimization in the electrodes,¹⁶⁻¹⁸ the challenge for thick electrode configurations¹⁹ still remains: the use of solid electrolytes in thick electrode configurations is currently limited by the low ionic conductivity of solid electrolytes.^{2,19} Electrolytes with high ionic conductivities are needed to achieve higher energy densities.

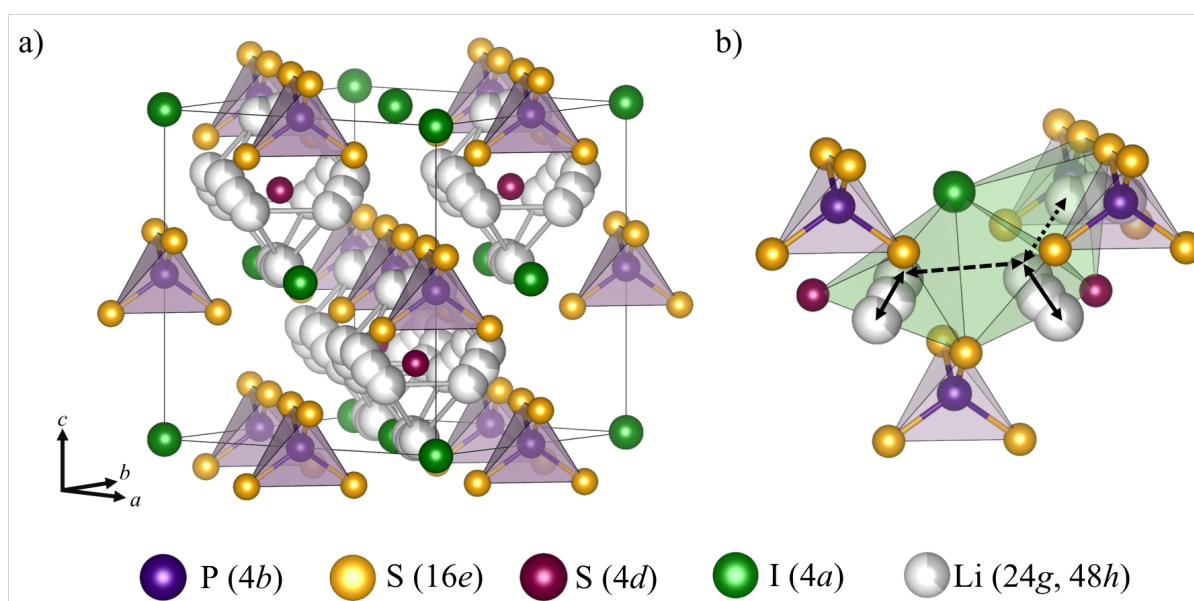


Figure 1: a) Crystal structure of $\text{Li}_6\text{PS}_4\text{X}$ ($\text{X} = \text{I}$), in which the I form a face-centered cubic lattice, with PS_4 tetrahedra in the octahedral voids and a free S^{2-} on half of the tetrahedral vacant sites (4d). The Li^+ forms pseudo-octahedral cages around the S^{2-} site with two crystallographically distinct positions, 24g and 48h. b) For lithium transport effected by discrete jumps between sites, the rate-determining step is the inter-cage 48h – 48h jump, as shown by the LiS_4I polyhedra. This requires lithium to move past a window the 4a iodine site and the sulfur of the PS_4 tetrahedra.

Recently, among all of the well-performing lithium thiophosphates, such as the $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ glass phases and $\text{Li}_{10}\text{MP}_2\text{S}_{12}$ ($M = \text{Ge}, \text{Sn}$),²⁰⁻²⁹ the class of argyrodites $\text{Li}_6\text{PS}_4\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) has attracted considerable interest.³⁰⁻³⁴ The crystal structure of $\text{Li}_6\text{PS}_4\text{X}$ is shown in Figure 1. In a fully ordered arrangement, the halide anions X^- form a face-centered cubic lattice (Wyckoff 4a) with PS_4^{3-} tetrahedra on the octahedral sites (P on Wyckoff 4b) and the free S^{2-} in half of the tetrahedral

sites (Wyckoff $4d$). Diffusion in solid electrolytes is usually analyzed in terms of jumps between individual sites.³⁵ Crystallographic studies in the argyrodites have identified two distinct Li positions, namely the $48h$ and $24g$ Wyckoff positions, which form Li⁺ cages around the free S²⁻ on Wyckoff $4d$. Within a site-jump model of lithium diffusion there are three inequivalent jumps: $48h - 24g - 48h$ (doublet jump), $48h - 48h$ within the cage (intra-cage jump) and $48h - 48h$ between the cages (inter-cage jump).^{30,33} For X = Cl, Br the S²⁻ and X⁻ positions exhibit significant fraction of anion site-disorder.^{32-34,36} If iodine is the halide in the structure, no site-disorder occurs due to the large size mismatch between S²⁻ and I,³⁰ opening up the question as to whether the site-disorder can be influenced further. Kraft *et al.* have recently shown that the absence of the disorder in the iodine containing argyrodites is associated with high activation barriers for ion migration and a low ionic conductivity of $1.3 \cdot 10^{-6}$ S cm⁻¹.³⁰ While substitutions have been performed mostly on the anion sites in the argyrodites, a recent study shows the possibility of aliovalent doping in Li_{6+x}P_{1-x}Si₃S₃Br,³¹ producing an increase in the ionic conductivity. It should be noted however that, the incorporation of Ge⁴⁺ in Li₆PS₃Br was not possible due to the larger ionic radius of Ge⁴⁺ in the smaller lattice volume in Li₆PS₃Br.

Inspired by the possibility of incorporating Ge into a composition possessing a larger unit cell, we have investigated the effect of Ge⁴⁺ substitution in Li_{6+x}P_{1-x}Ge₃S₃I on the structure-transport relationships. Using a combination of Rietveld refinements against neutron and X-ray diffraction data, we identify the underlying structural changes associated with the Li- and anion-substructures including changes to the site-disorder. Impedance spectroscopy and lithium nuclear magnetic resonance were used to monitor the changing ionic transport. With increasing Ge-fraction, the diffusion pathways for Li⁺ expand and site disorder between the S²⁻ and I positions appears. The increasing disorder is correlated to a sharp decrease in the activation barrier and an increase in the conductivity over orders of magnitude leading to the highest lithium argyrodites reported so far with $\sigma = 5.4 \pm 0.8$ mS cm⁻¹, when cold-pressed, and $\sigma = 18.4 \pm 2.7$ mS cm⁻¹ upon sintering. We further show that this fast-ionic conductor can be used to build solid-state batteries with thick anode and cathode layers, exhibiting stable capacities for at least 150 cycles, even at higher C-rates. This work demonstrates that inducing disorder in materials using elemental substitutions is a promising approach to alter the potential energy landscape tailoring the ionic conductivity of solid electrolytes for better performing all-solid-state batteries.

2. Experimental Methods

Synthesis. All preparations and sample treatments for $\text{Li}_{6-x}\text{P}_{1-x}\text{Ge}_x\text{S}_5\text{I}$ were carried out under argon atmosphere. Lithium sulfide (Li_2S , Sigma Aldrich, 99.98 %), phosphorus pentasulfide (P_2S_5 , Sigma Aldrich, 99 %), germanium sulfide (GeS , Alpha Aesar, 99.99 %), sulfur (S, ACROS Organics, 99.999%) and LiI (Alpha Aesar, 99.995 %) were mixed in the appropriate stoichiometric ratio. Before the synthesis, all precursors were thoroughly dried and sulfur sublimated. All mixtures were hand ground in an agate mortar, pressed into pellets and then filled into quartz ampoules (10 mm inner diameter and 10 - 12 cm in length), which were sealed under vacuum. All ampoules were carbon-coated and pre-heated at 800 °C under dynamic vacuum to avoid all traces of water in the reaction atmosphere. The reactions were performed at 550 °C for two weeks in order to ensure a complete reaction. The obtained mixture was subsequently ground and isostatically pressed into pellets (10 mm diameter) for the impedance measurements or kept as powder for the diffraction studies.

Neutron powder diffraction. High-resolution neutron powder diffraction data collection on the argyrodite samples $\text{Li}_{6-x}\text{P}_{1-x}\text{Ge}_x\text{S}_5\text{I}$ with $x = 0, 0.15, 0.25, 0.3, 0.6$ was performed in a Debye-Scherrer geometry at the Heinz Maier-Leibnitz Zentrum (research reactor FRM II, Garching b. München, Germany) on the high-resolution diffractometer SPODI.³⁷ Data collection was performed using one wavelength, i.e. monochromatic neutrons ($\lambda = 1.54817(2) \text{ \AA}$), that were obtained from the thermal neutron beam at a 155° take-off angle using the 551 and 331 reflections of a vertically focused composite Ge monochromator of 200 mm height. The vertical position-sensitive multidetector (300 mm vertical sensitivity range at 1.117 m sample-to-detector distance) consisting of 80 ^3He tubes and covering an angular range of 160° 2θ was used for data collection. The samples (approx. 2 cm³ in volume) were filled into a thin-wall (0.15 mm) vanadium can of 12 mm in diameter under argon atmosphere and then metal-sealed using indium wire. The vanadium container was then mounted on a capillary spinner enabling sample rotation and thus, minimizing effects of preferred crystallite orientations. Two-dimensional powder diffraction data of the continuously rotated sample were collected and corrected for geometrical aberrations and detector nonlinearities.³⁸

X-ray powder diffraction. X-ray diffraction measurements of $\text{Li}_{6-x}\text{P}_{1-x}\text{Ge}_x\text{S}_5\text{I}$ were carried out on a PANalytical Empyrean powder diffractometer in Bragg-Brentano θ - θ geometry with $\text{Cu K}\alpha$ radiation. Measurements were carried out in the 2θ range between 10° and 90° with a step size of 0.026°. The counting time per step was 300 s. All powders were placed on (911)-oriented Silicon zero background holders and sealed using a 7.5 μm thick Kapton® polyimide film.

Rietveld analysis. Rietveld refinements were carried out using the TOPAS-Academic V6 software package.³⁹ Similar to recent work on $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$,²⁵ 2θ range of $10\text{--}26.5^\circ$ was excluded from the refinements of X-ray diffractions in order to mitigate the interfering diffraction intensity from the polyimide film background. The resultant structural data obtained with excluding the lower 2θ range is in good agreement with the one from the neutron diffraction data over the whole measured 2θ range. The peak profile shape was described by a pseudo-Voigt function using the modified Thomson-Cox-Hastings setting.⁴⁰ Fit indicators: R_{wp} , R_{exp} , and the goodness-of-fit S were used to assess the quality of the refined structural models.⁴¹ The following parameters were initially refined: (1) scale factor, (2) 30 coefficients for a Chebyshev background, (3) peak shape, (4) lattice parameters including sample displacement, (5) fractional atomic coordinates, (6) isotropic atomic displacement parameters. Finally (7), atomic occupancies of the anions were then allowed to refine simultaneously with all other parameters, to quantify the anion site disorder.

Electrochemical impedance spectroscopy. Electrical conductivities were measured by AC impedance spectroscopy, using pellets with vapor deposited gold layers. Electrochemical impedance spectroscopy (EIS) was conducted in the temperature range of $-20\text{ }^\circ\text{C}$ to $60\text{ }^\circ\text{C}$ using a VMP300 impedance analyzer (Bio-Logic Science Instruments) at frequencies from 7 MHz to 100 mHz with an amplitude of 10 mV. All fits were performed using the RelaxIS software package (rhd instruments, Version 3).

Nuclear magnetic resonance. Variable-temperature T_1 and quadrupolar echo experiments have been performed on a Bruker NMR spectrometer operating at a lithium (^7Li) frequency of 77.8 MHz. All experiments were performed in the static mode. Quadrupolar echo experiments were acquired to estimate temperature-induced line narrowing, which reports on the dynamics in kHz frequency range. The pulse sequence consisted of two 90° -pulses separated by $30\ \mu\text{s}$ echo delay; after the second $30\ \mu\text{s}$ echo delay acquisition started. 64 scans have been collected to obtain a spectrum at each temperature and a recycle delay of 5 s was found to be sufficient to obtain full restoration of the initial spin state before each repetition. Full-width half-height (FWHH) has been used as a measure of motional-averaging of the “rigid” linewidth. For T_1 -relaxation time measurements a saturation-recovery pulse sequence has been used. Relaxation delays have been varied from 1 ms up to 10 s and 16 transitions have been accumulated to gain each point of the relaxation build-up curve. After acquisition, a single exponential function has been fitted to the experimental relaxation data to get a characteristic relaxation time T_1 .

Cell assembly. All-solid-state battery cells using the $\text{Li}_{0.6}\text{P}_{0.4}\text{Ge}_{0.6}\text{S}_4$ electrolyte in combination with an $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NCM-622) cathode and a $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) anode (both provided by

BASF SE) were assembled inside of a hot-press setup under argon atmosphere. The diameter of the cell was 12 mm. Details on the setup are provided in a previous publication.⁴² Prior to use, the active materials were dried in a vacuum Büchi oven at 250 °C overnight. The cathode composite was prepared in an agate mortar consisting of NCM-622 and SE in a mass ratio of 70:30. A total of 55 mg of the cathode composite was used, corresponding to an areal loading of 6.80 mAh cm² and a thickness of approximately 160 μm. A mass of 150 mg of solid electrolyte served as a separator (thickness ~ 450 μm). The anode composite consisted of LTO and SE in a mass ratio of 50:50. A mass of 91 mg of the anode composite was employed (capacity = 7.04 mAh cm²), resulting in an anode thickness of 340 μm. The layered powders were compressed at 30 kN (~ 2650 bar) and heated to 60 °C. The conditions were maintained during electrochemical experiments.

The battery cycling and electrochemical impedance spectroscopy (EIS) on the complete cell were carried out using an SP-150 potentiostat/galvanostat (Bio-Logic Science Instruments). The galvanostatic cycling was performed at a C-rate of 0.25 C (1.71 mA cm²), C-rate of 0.5 C (3.42 mA cm²) and C-rate of 1 C (6.84 mA cm²) in a voltage range of 1.10 - 2.75 V vs. Li₄Ti₅O₁₂/Li₄Ti₅O₁₂, corresponding to approximately 2.65 - 4.30 V vs. Li⁺/Li. The current density was calculated based on a theoretical capacity of 200 mAh g⁻¹ of the cathode active material. After electrochemical relaxation of 30 min, EIS measurements were conducted with an amplitude of 20 mV in a frequency range of 1 MHz to 0.1 Hz.

Scanning electron microscopy and energy dispersive X-ray analysis. Cross-sectional images of the battery stack after disassembly were obtained on a Merlin high-resolution scanning electron microscope (Carl Zeiss AG, Germany). The samples were transferred from a glove box in the analysis chamber under argon atmosphere using a transfer vessel (Leica EM VC500). EDX analysis was conducted using an XMAX EXTREME EDX detector (Oxford Instruments, United Kingdom). Measurements were carried out by application of an acceleration voltage of 5 kV and a probing current of 1000 pA.

3. Results

Structural characterization. The Li^+ superionic argyrodites $\text{Li}_{0.6x}\text{P}_{1-x}\text{Ge}_x\text{S}_5\text{I}$ have been synthesized with increasing $\text{Ge}^{4+}/\text{P}^{5+}$ ratios in order to study the structural changes and assess the effect of the increasing lithium content on the ionic conductivity. For the structural characterization, X-ray diffraction was performed on all samples. Moreover, due to the low X-ray form factor of Li^+ , selected samples of ($x = 0, 0.15, 0.25, 0.3$ and 0.6) were also investigated using neutron diffraction to better probe the changing Li^+ substructure. These sample compositions were selected based on the occurring changes in the ionic transport (*vide infra*).

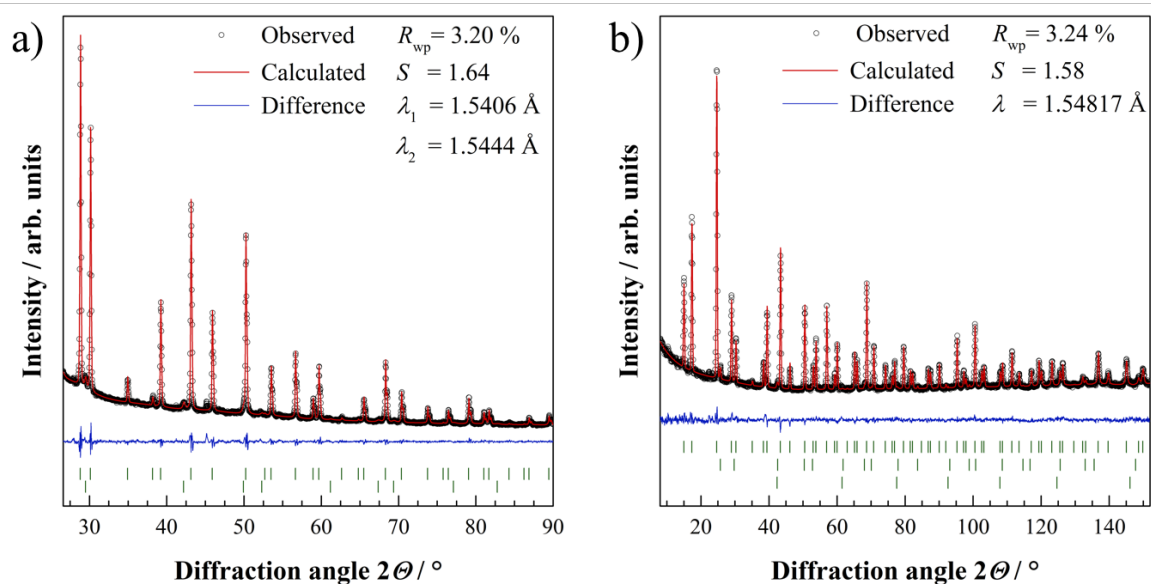


Figure 2: Representative X-ray (a) and neutron (b) diffraction pattern of $\text{Li}_{0.6}\text{P}_{0.4}\text{Ge}_{0.6}\text{S}_5\text{I}$ and the corresponding Rietveld refinements. Small fractions of impurity phases can be found that correspond to ~ 1.6 wt.% LiI in the X-ray diffraction data and ~ 3.4 wt.% LiI in the neutron diffraction data, along with reflections of the V sample holder. R_{wp} and S are weighted profile R -factor and goodness of fit, respectively.

Figure 2 shows a representative Rietveld refinement of an X-ray and a neutron diffraction pattern for the compound with the nominal composition $\text{Li}_{0.6}\text{P}_{0.4}\text{Ge}_{0.6}\text{S}_5\text{I}$. All samples exhibit minor impurity phase fractions of LiI and/or Li_4GeS_4 in the diffraction data for the series of solid solutions (see Table S1 - S16 in Supporting Information). The minor impurities are unlikely to affect the ionic transport^{30,31} and the obtained structural data of all solid solutions, obtained via Rietveld refinement against laboratory X-ray and neutron diffraction patterns, can also be found tabulated in the Supporting Information. Recently, we have shown that the Si^{4+} substitution was possible in $\text{Li}_{0.6x}\text{P}_{1-x}\text{Si}_x\text{S}_5\text{Br}$ up to 30 at.%, whereas the incorporation of Ge^{4+} was unsuccessful.³¹

Here in $\text{Li}_{6-x}\text{P}_{1-x}\text{Ge}_x\text{S}_5\text{I}$, the refined lattice parameters show an increasing unit cell volume up to 80 at.% Ge corresponding to the formation of a solid solution (Figure 3a). However, the samples of $x = 0.8, 0.9$ and 1.0 exhibit high fractions of the impurity phase Li_4GeS_4 (see Supporting Information Figure S1), indicating that a solubility limit has been reached. A Rietveld refinement of the occupancies of Ge on Wyckoff $4b$ shows an increasing occupancy of Ge up to 70 at.% (Figure 3b). At higher nominal Ge contents, x_n , the Ge occupancy remains constant and only the amount of the impurity phase Li_4GeS_4 increases. The refinement of the Ge occupancy in the $x = 0.9$ sample is not possible due to the large amount of overlapping impurity reflections. The minor discrepancy between the solubility limits of the lattice volume ($x = 0.8$) and the Ge occupancy ($x = 0.7$) is likely due to the larger uncertainty on the refined occupancy coming from overlapping reflections of the main phase with the Li_4GeS_4 impurity phase. While there seems to be a degree of uncertainty on the exact solubility limit, full solid solutions of $\text{Li}_{6-x}\text{P}_{1-x}\text{Ge}_x\text{S}_5\text{I}$ can be synthesized up to a composition of at least $\text{Li}_{6.7}\text{P}_{0.3}\text{Ge}_{0.7}\text{S}_5\text{I}$. Despite the solubility limit, the samples with $x = 0.8$ are included in the following structural and transport data, whenever applicable, to allow for a discussion beyond the solubility limit in this material. In addition, in order to allow for a better discussion of the data, all subsequent data are shown against the refined Ge fraction x_r , as obtained from the neutron and X-ray diffraction data, respectively.

With increasing Ge^{4+} occupancy on the $(\text{P}/\text{Ge})\text{S}_4^{2-}$ tetrahedra, the volumes of the tetrahedra increase due to the larger ionic radius of Ge^{4+} vs P^{5+} , *i.e.* 0.39 pm vs. 0.19 pm,⁴³ in the tetrahedral coordination (Figure 3c). Another structural characteristic within the argyrodite structure is the possible site-disorder between the free S^{2-} anion located on Wyckoff $4d$ and the halide anion I⁻ on Wyckoff $4a$. While Cl⁻ and Br⁻ containing argyrodites show a high degree of anion site-disorder, in which the disorder decreases with increasing anionic size mismatch, no disorder had been found for $\text{Li}_6\text{PS}_5\text{I}$ due to the large difference in ionic radii between I⁻ and S^{2-} .³⁰ Figure 3d shows the I/ S^{2-} site-disorder, as obtained from the Rietveld refinements against X-ray and neutron diffraction data. At a Ge fraction of ~ 20 at.% there is a clear onset of I/ S^{2-} site-disorder, reaching $\sim 7\%$ around the solubility limit. Whether the changing disorder occurs due to a larger unit cell after Ge^{4+} substitution, which allows for better mixing of the mismatched anions, or due to the increasing Li^+ density in the structure, remains unclear. Within the series of solid solutions $\text{Li}_6\text{PS}_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), a decreasing site-disorder due to the incorporation of I⁻ is correlated to an increase in the activation barrier for the migrating Li^+ cations³⁰, as measured by impedance spectroscopy, and similar effects on the ionic transport may be expected here.

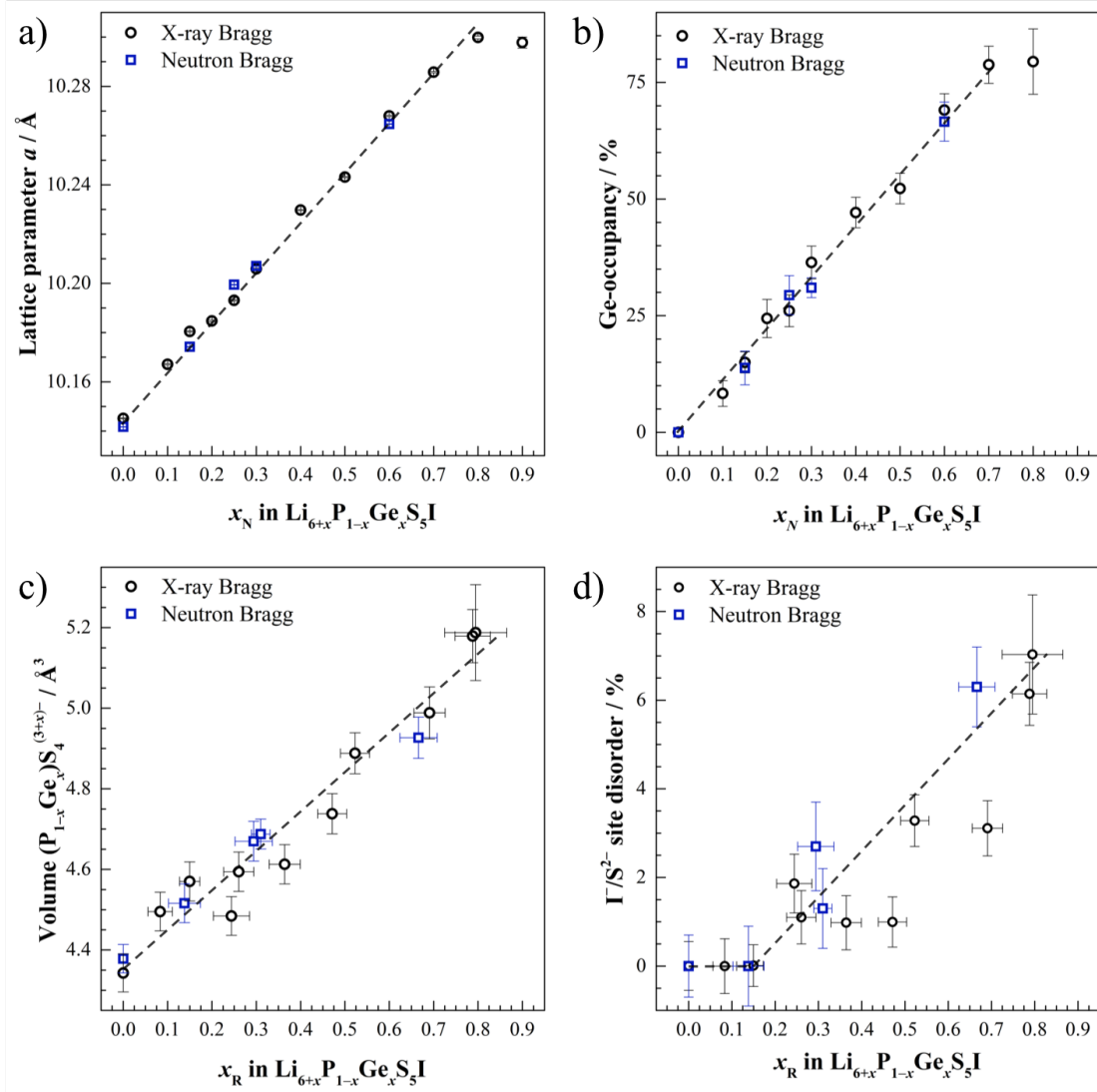


Figure 3: a) Lattice parameters of the solid solutions $\text{Li}_{6+x}\text{P}_{1-x}\text{Ge}_x\text{S}_5\text{I}$ vs. nominal Ge content x_N . With increasing Ge^{4+} content, the unit cell increases until a solubility limit is reached that corresponds to the maximum solubility of $\sim 70\%$ Ge^{4+} on the P^{5+} position as shown in b). c) Increasing $(\text{P}/\text{Ge})\text{S}_4$ tetrahedral volume during the substitution of the larger Ge^{4+} for P^{5+} against the refined Ge occupancy x_R . d) While the undoped I-argyrodite is known to exhibit no site-disorder,³⁰ the substitution with Ge leads to a growing S^{2-}/I -disorder starting around 20 at.% of Ge^{4+} .

In addition to the structural changes of the $(\text{Ge}/\text{P})\text{S}_4$ tetrahedra and I/S^{2-} site-disorder, the neutron diffraction data allows the analysis of the changes in the Li^+ substructure (Figure 4). With increasing Ge^{4+} occupancy, the Li^+ occupancy of the 24g site increases (Figure 4a) and essentially all additional Li^+ occupies this site, similar to the behavior observed for the incorporation of Si^{4+} in $\text{Li}_6\text{PS}_5\text{Br}$.³¹ The increasing Li occupancy on the 24g site leads to the larger Coulombic repulsion, which results in the longer doublet distance $48h - 24g - 48h$, whereas

a minor decrease of the distance between the Li cages (i.e. the inter-cage distance) can be found. Furthermore, with increasing Li^+ and Ge^{4+} content in the structure the tetrahedral volume of $\text{Li}(48h)\text{S}_3\text{I}$ polyhedra and the area of the $\text{Li}(24g)\text{S}_3$ triangular plane increase. As the $\text{Li}(48h)\text{S}_3\text{I}$ polyhedra represent the bottleneck for the rate-determining inter-cage jump, the wider diffusion pathways for Li^+ in the structure may affect the mobility of the moving cation.

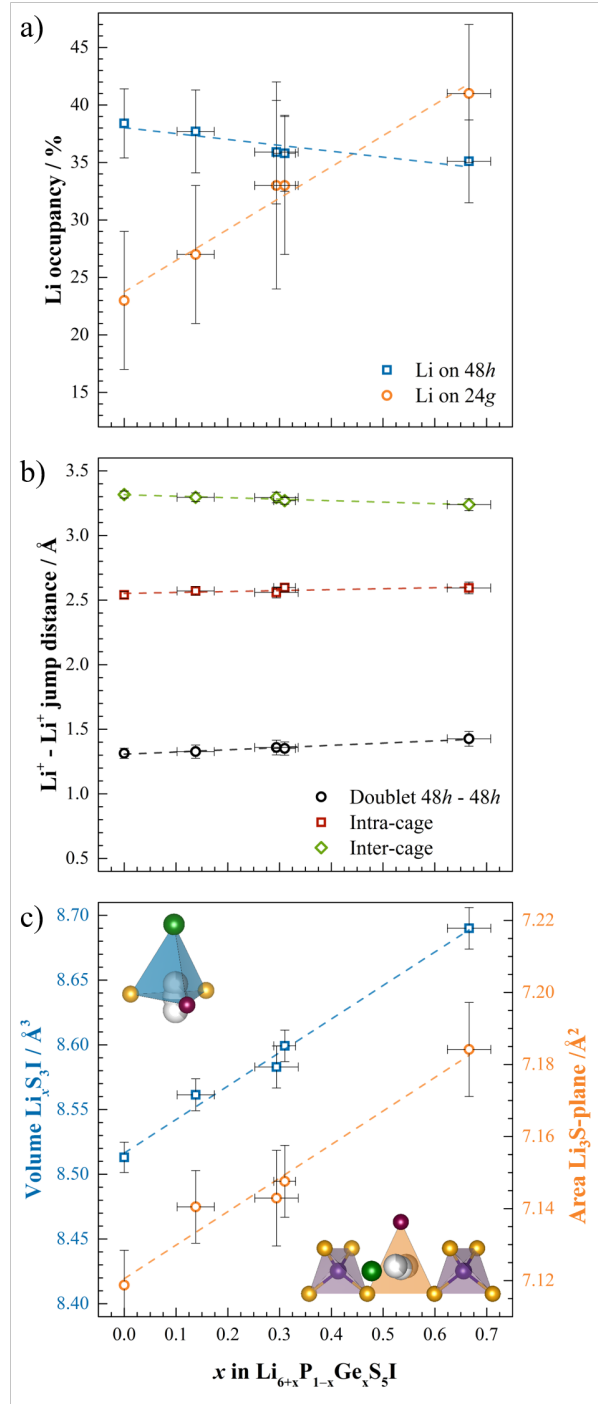


Figure 4: Changes to the Li-substructure in $\text{Li}_{6+x}\text{P}_{1-x}\text{Ge}_x\text{S}_5\text{I}$, as obtained from the neutron diffraction data as a function of the refined Ge content x_r . With increasing Ge^{4+} occupancy, additional Li^+ is incorporated into the structure to maintain charge neutrality. a) Percentage of

sites occupied by Li^+ with the additional Li^+ being placed on the Wyckoff 24g position. b) The increasing Li^+ content produces an increase in the distance between the 48h - 24g - 48 positions (doublet distance), which can be attributed to increased Coulombic repulsion, and a decreasing jump distance between the Li^+ cages (inter-cage jump). c) With increasing unit cell size and size of the adjacent $(\text{P}/\text{Ge})\text{S}_4$ tetrahedra, the $\text{Li}(48\text{h})\text{S}_4$ polyhedra and $\text{Li}(24\text{g})\text{S}_3$ triangle areas are increasing, corresponding to wider diffusion pathways for Li^+ .

Ionic transport. Temperature-dependent impedance spectroscopy and nuclear magnetic resonance measurements were performed to assess changes to the ionic conductivity. Arrhenius plots of all samples of $\text{Li}_{0.6x}\text{P}_{1-x}\text{Ge}_x\text{S}_5\text{I}$ and their corresponding impedance responses with the respective fits are shown in Figure 5. The impedance data were fit with an equivalent circuit consisting of one parallel constant phase element (CPE)/resistor in series with a CPE, representing the blocking electrodes. In the samples with a high Ge-fraction, the CPE/resistor has shifted to frequencies that are too high to measure with the impedance analyzer and only the tail of the blocking electrodes was used for the fit. The resolvable impedance spectra exhibit α -values of ~ 0.9 , representing the ideality of the CPE,⁴⁴ and geometric capacitances around 16 to 47 pF cm^{-2} . The extracted values of the impedance analyses are tabulated in the Supporting Information (Table S 1 – S 16). Bulk and grain boundary contributions cannot be de-convoluted, however, the obtained ideality of the semi-circle and capacitances correspond well with bulk transport,⁴⁵ as typically observed for these Li^+ conducting argyrodites.^{30,31}

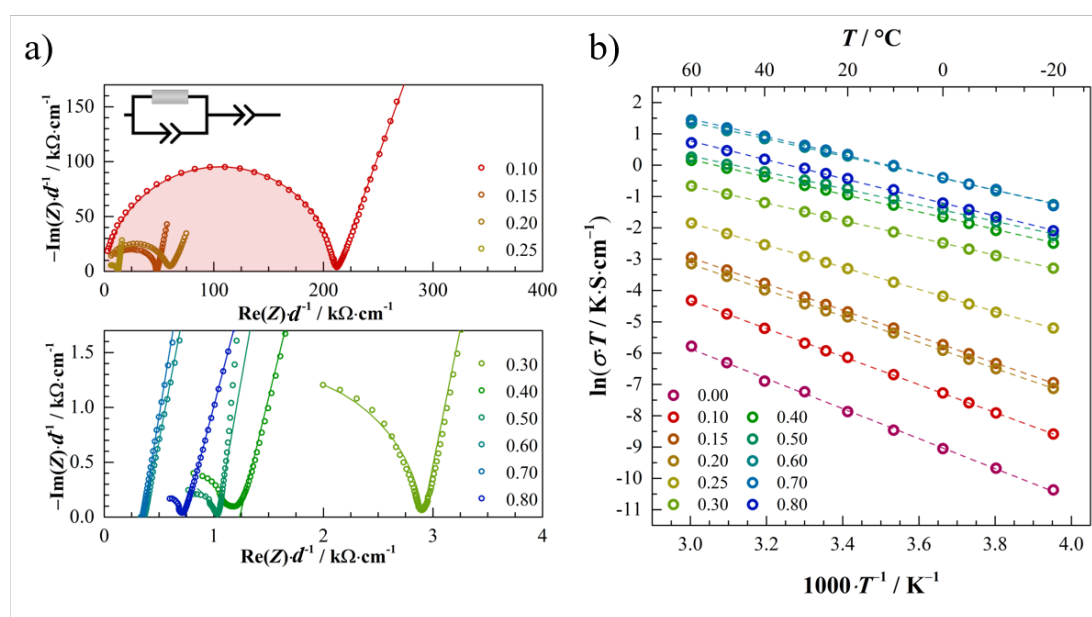


Figure 5: a) Nyquist plots for all degrees of substitution along the series of solid solutions at 298 K, as well as the employed equivalent circuit. The resistance has been normalized to the

respective pellet thickness d for visual comparison. b) Arrhenius plots of the conductivity values for $\text{Li}_{6+x}\text{P}_{1-x}\text{Ge}_x\text{S}_5\text{I}$ ($0 \leq x \leq 0.8$).

Figure 6 shows the ionic conductivities of $\text{Li}_{6+x}\text{P}_{1-x}\text{Ge}_x\text{S}_5\text{I}$, as measured by impedance spectroscopy, as well as the extracted activation barrier for Li^+ migration. With increasing fraction of Ge^{4+} and Li^+ , the conductivity increases over three-orders of magnitude and reaches a maximum conductivity of $\sigma = 5.4 \pm 0.8 \text{ mS cm}^{-1}$ for $\text{Li}_{6.6}\text{P}_{0.4}\text{Ge}_{0.6}\text{S}_5\text{I}$. As the observed increase in the conductivity cannot be directly explained by the minor increase in charge carrier density, the activation energy must be having a tremendous influence. With increasing x , the activation barrier remains constant at first and then significantly drops, showing an inflection around $x_R = 0.25$ that is responsible for the high ionic conductivity in the Ge-substituted $\text{Li}_{6+x}\text{P}_{1-x}\text{Ge}_x\text{S}_5\text{I}$. Sintering of the cold pressed pellets at 823 K for ten minutes increases the conductivity further to $\sigma = 18.4 \pm 2.7 \text{ mS cm}^{-1}$, likely due to better grain contact. The variance in the conductivity is calculated from multiple measurements conducted with different measurement setups to corroborate these high conductivity values (see Supporting Information Figure S2).

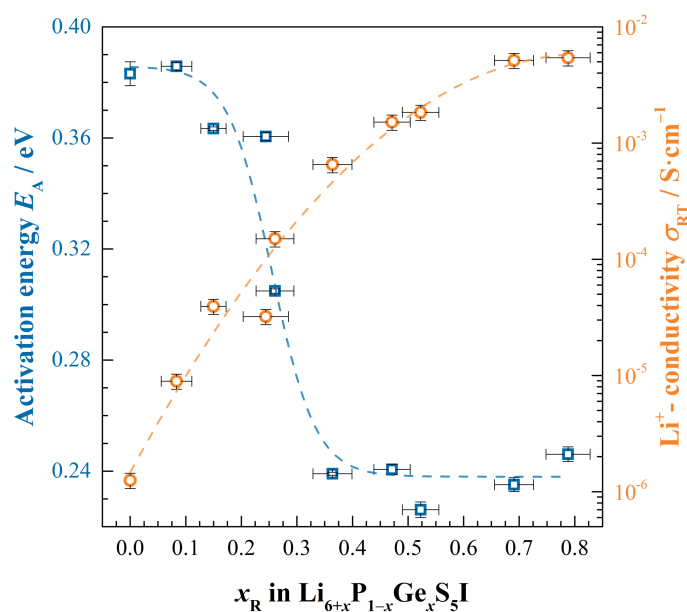


Figure 6: Activation barrier and ionic conductivity of $\text{Li}_{6+x}\text{P}_{1-x}\text{Ge}_x\text{S}_5\text{I}$ as a function of the refined Ge content, as obtained from impedance spectroscopy. With increasing Ge^{4+} and Li^+ concentration, the ionic conductivity increases over three orders of magnitude, reaching a conductivity of $\sigma = 5.4 \text{ mS cm}^{-1}$. An inflection point starting $\sim 20\%$ Ge can be seen that leads to a strong decrease of the activation barrier.

In addition to the impedance data, selected sample compositions were investigated using ^7Li nuclear magnetic resonance spectroscopy. Figure 7a shows changes of the signal linewidth as

a function of temperature for three measured samples with the compositions of $x = 0.0$, 0.25 and 0.6 in $\text{Li}_{6-x}\text{P}_{1-x}\text{Ge}_3\text{S}_4\text{I}$, chosen for their different activation barriers (*vide infra*). Only $\text{Li}_6\text{PS}_4\text{I}$ demonstrates significant dependence of the signal width, whereas the full-width of half height FWHH for all other samples appears to be rather small, even at the lowest available temperatures. Line narrowing starts when the mobility of nuclei in frequency units matches the line width in the rigid limit (a plateau at very low temperatures). Thus, one can estimate the activation energy and the speed of the local ionic motion. As a low temperature plateau is only observed in the $\text{Li}_6\text{PS}_4\text{I}$ sample, the Hendrickson-Bray approach⁴⁶ can be used to obtain motional parameters in this composition. For the undoped $\text{Li}_6\text{PS}_4\text{I}$ this procedure gives an estimation of the activation energy of 0.49 eV (Figure 7b). The frequency of the corresponding motion can be extrapolated to room temperature and is found to be $1 \cdot 10^6 \text{ s}^{-1}$. In contrast, samples with $x = 0.25$ and $x = 0.6$ undergo much faster motional processes, which cannot be characterised with the current method. Therefore, T_1 relaxation time studies (for more information see the section of Nuclear magnetic resonance in Supporting Information) are employed to expand the sensitivity window of the dynamical NMR to nanoseconds. The samples with $x = 0$ and $x = 0.6$ can be accurately fitted with a single symmetric curve around the maximum indicating equal E_a values at high and low temperatures. However, the sample with $x = 0.25$ reveals different slopes for both flanks, which can be attributed to the co-existence of two types of motion. The first one is activated at lower temperatures and has an activation energy of $E_a^{\text{LT}} = 0.11 \text{ eV}$, and another one appears at higher temperatures and is characterized by $E_a^{\text{HT}} = 0.21 \text{ eV}$. All T_1 -defined dynamical parameters and analysis procedures are listed in the Supporting Information (Table S18).

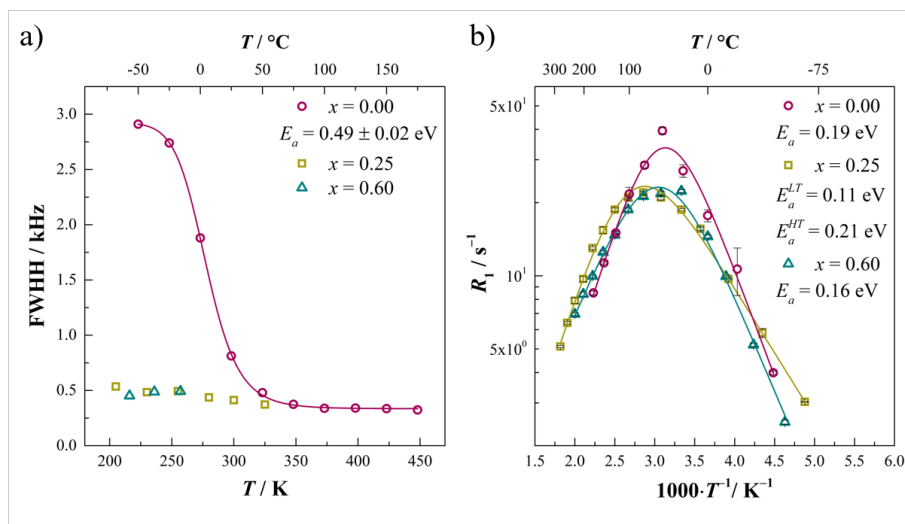


Figure 7: a) Temperature-induced line narrowing of highlighted samples from NMR quadrupolar-echo experiments. b) Relaxation rates R_i as a function of inverse temperature and the activation barriers as the result of the fitting procedure (solid lines).

Assuming that Li^+ transport consists of hops between well-defined crystallographic sites, there are three different jump-processes possible in $\text{Li}_x\text{PS}_3\text{X}$ argyrodites, *i.e.* the doublet $48h$ jumps, the intra-cage and the inter-cage movements. Moreover, while all jumps are necessary for the long-range transport of Li^+ ions,³³ inter-cage jumps have been proposed to be the rate-determining step. Combining this knowledge with the results of our dynamical NMR studies, one can describe the motional picture in the Ge-doped samples. The undoped $\text{Li}_x\text{PS}_3\text{I}$ undergoes two different motional changes in the μs - ns time scale. We suppose that the faster (visible in T_1 relaxation) corresponds to the $48h - 24g - 48h$ (doublet jumps) or $48h - 48h$ (intra-cage jumps) and does not lead to long-range transfer of the Li^+ ions. In contrast, the slower mobility, which becomes apparent in motional narrowing experiments is characterized by a much higher activation energy and will be the limiting step in the observable bulk transport, *i.e.* the inter-cage jump. The Einstein-Smoluchowski and Nernst-Einstein equations can be used to estimate the conductivity of the sample.^{47,48} First, the diffusion coefficient (D) is defined from the frequency of motion (K_{exchange}) and the distance between Li sites $d_{\text{Li-Li}}$ as obtained from the Rietveld refinement of neutron diffraction data:

$$D = \frac{d_{\text{Li-Li}}^2}{6} \cdot K_{\text{exchange}} \cdot \quad \text{Eq. (1)}$$

Assuming ion-jumps are uncorrelated,^{49,50} the conductivity is calculated via:

$$\sigma = \frac{DNq^2}{k_{\text{B}}T} \cdot \quad \text{Eq. (2)}$$

where N is the charge carrier density approximated by the number of Li^+ ions per unit cell, q is the charge of the charge carriers, and T is the temperature. Based on these equations, a conductivity of $2.6 \cdot 10^{-3} \text{ S cm}^{-1}$ at room temperature can be estimated for $\text{Li}_x\text{PS}_3\text{I}$, close to the ionic conductivity obtained via impedance spectroscopy.

Although NMR on the sample $\text{Li}_{0.25}\text{P}_{0.75}\text{Ge}_{0.25}\text{S}_5\text{I}$ also reveals two separate processes, which are likewise described by different activation energies, both modes are visible only in T_1 -relaxation measurements suggesting much faster rates than those existing in the undoped sample. We propose that the mode with an activation energy of 0.11 eV corresponds to small fluctuations between $48h$ and $24g$ sites or the intra-cage jump process, and the second process can be ascribed to inter-cage jumps. The sample with a Ge-content of 0.6 undergoes a single motional

process in the current timescale window with rather low activation energy, in good agreement with the data from impedance spectroscopy. We suppose that this corresponds to inter-cage jumps, whereas all smaller scale movements stay outside of the sensitivity window of the method. Using the Eq. 1 and 2, a conductivity of 3.9 mS cm^{-1} can be estimated for $x = 0.25$ and 7.5 mS cm^{-1} for $x = 0.6$ in $\text{Li}_{6-3x}\text{P}_{1-x}\text{Ge}_3\text{S}_5\text{I}$. Overall, the estimated Li-ion conductivities obtained here are in good agreement with the conductivities measured via impedance spectroscopy, suggesting the reduction in the activation energy of the rate-limiting inter-cage jumps is key to the high conductivity. The slight discrepancy to the conductivity obtained by impedance spectroscopy can likely be attributed to the changing correlation factors with changing Li-carrier density.^{49,51}

Structure-transport correlation. The collected data on the aliovalent substitution of $\text{Li}_{6-3x}\text{P}_{1-x}\text{Ge}_3\text{S}_5\text{I}$ show that simple substitutions can have a tremendous influence on the ionic transport in the argyrodite structure and that a high conductivity in the solid electrolytes can be obtained. Impedance spectroscopy and nuclear magnetic resonance data show a decrease in the activation barrier for ionic motion with the inflection point around $x_r = 0.25$. In addition, the structural data obtained by Rietveld refinements against neutron and X-ray diffraction data show an increasing width of the diffusion pathway and an increase in the I/S²⁻ site-disorder. In Figure 8a, the changing activation barriers are shown together with the changing of I/S²⁻ site-disorder on Wyckoff 4a. There is a clear correlation between the onset of the site-disorder and the drop in the activation barrier. As recently theoretically suggested³³ and experimentally corroborated³⁰, disorder between the free sulfur site (Wyckoff 4d) and the halide site (Wyckoff 4a) leads to lower activation barriers. In $\text{Li}_6\text{PS}_5\text{Br}_{1-x}\text{I}_x$, Kraft *et al.*³⁰ were able to show that a subsequent replacement of Br⁻ with I⁻ leads to fewer halide anions on the free sulfur site and vice versa, resulting in an increasing activation barrier for ionic motion. In this work, the occurrence of disorder leads to a sharp decrease of the activation barrier.

Despite the clear correlation between the disorder and the decreasing activation barrier, it remains puzzling that such a small degree of disorder can affect the transport so significantly. Both Wyckoff positions for I and S²⁻ form interpenetrating face-centered cubic lattices, in which the bond-percolation threshold in one face-centered cube is expected at 12 % disorder.⁵² However, Figure 8b shows that the Li⁺ ions surround the S²⁻ site, forming four clusters that are directly linked to the I site. Each cluster faces the I site with three possible 48h positions of Li⁺ and from each cluster six jumps are possible to clusters adjacent to the same I position. Each S²⁻ on a the I site (Wyckoff 4a) then opens up three low-energy inter-cage pathways (see Figure

8c) and percolation would then be expected at 4 % for a random distribution. In other words, the high multiplicity of the Li⁺ site seemingly makes percolation possible, even at low degrees of disorder. This change in the local environment of Li⁺ and a schematic of the changing potential energy landscape is schematically shown in Figure 8c.

The here-observed correlation between the site-disorder and the activation barrier shows that structural changes can have a tremendous influence on the ionic transport in argyrodites. In this example of Li₆PS₄X, tailoring the disorder in such materials clearly helps to optimize solid electrolytes toward higher ionic conductivities.

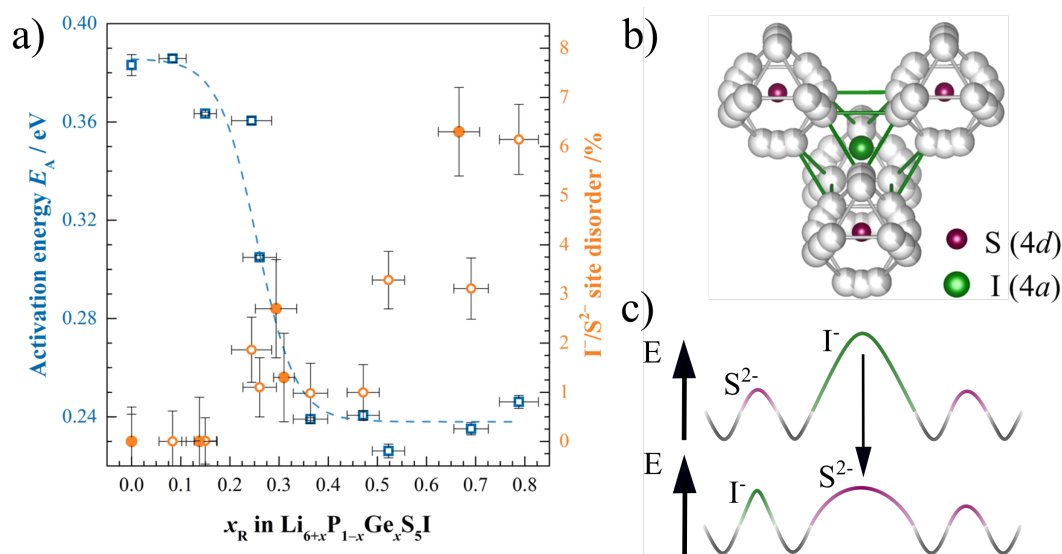


Figure 8: a) Activation barriers and refined S^{2-}/I disorder of $Li_{6+x}P_{1-x}Ge_xS_5I$ as a function of x_R . At the onset of the occurring S^{2-}/I disorder the activation barriers drop sharply, leading to a high ionic conductivity. b) Local environment of four Li⁺ clusters around the S^{2-}/I site Wyckoff 4a and c) schematic of how the potential energy landscape of the migrating ion changes once site-disorder occurs. Around the S^{2-}/I position, six total jumps (three spatially distinct, i.e. starting from a different Li⁺) can occur to the neighboring three Li⁺ clusters.

Solid State Battery. Successful implementation of solid-state batteries requires maximizing the energy densities, making thick electrode configurations necessary.¹⁹ While the conductivity of the sintered $Li_{6.6}P_{0.4}Ge_{0.6}S_5I$ is the highest Li⁺ - conductivity reported in the argyrodites so far, solid-state batteries employing thiophosphates commonly use cold-pressed electrolytes, so this high conductivity value for the sintered sample will not be utilized in a practical all-solid-state battery setup. Therefore, using the cold-pressed fast conducting $Li_{6.6}P_{0.4}Ge_{0.6}S_5I$, solid-state cells were constructed with thick cathode and anode composites. The cathode has an approximate thickness of 160 μm and the anode, having a higher SE fraction, is estimated to be 340 μm thick

(Figure 9d). The separator thickness is approximately 450 μm . At a charging rate of 0.25 C and a temperature of 60 °C, the thick electrode cell offers an initial charging capacity of 120.8 mAh g⁻¹. The initial discharge capacity is 88.8 mAh g⁻¹, which stabilizes to 99.3 mAh g⁻¹ in the subsequent cycles, indicating a beneficial interphase formation (Figure 9a and b).⁸⁻¹⁰ Without the addition of carbon additives or protective interfacial modifications,¹⁴ the cell shows stable cycling with little to no capacity fade over 50 cycles, maintaining a very high Coulombic efficiency. The stability of the capacity is even obtained when increasing the C-rate to 0.5 C and even further to 1 C, upon cycling for 50 additional cycles at each rate. Despite this thick electrode configuration, the total resistance of the cell is below 13 $\Omega\text{ cm}^2$ at 60 °C (see Supporting Information Figure S3). The herein presented cell demonstrates the feasibility of high and stable performances when employing a superionic thiophosphate solid electrolyte with non-detrimental interphase formation.

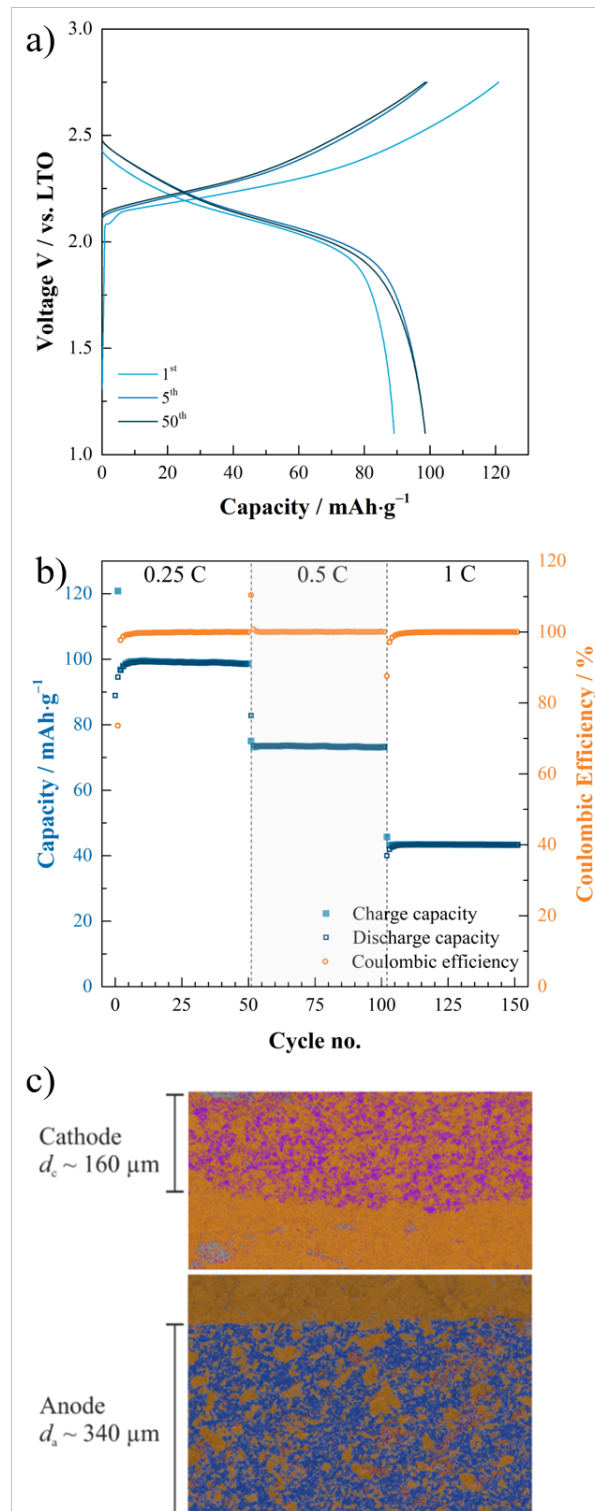


Figure 9: a) Representative charge and discharge curves of the thick electrode cell for the first, 5th and 50th cycles. b) Charge and discharge capacities (blue rectangles) over 150 cycles and corresponding Coulombic efficiency (orange circles). After a formation period within the first 5 cycles, the cell offers a stable capacity and cycling efficiency. c) EDX mapping of the cathode (top) and anode (bottom) cross-sections for the all-solid-state battery. The solid electrolyte is represented by the sulfur signal (orange). The NCM-622 cathode is represented by the Ni signal (purple) and the LTO anode by the O signal (blue), respectively.

5. Conclusion

In this work, aliovalent substitution in $\text{Li}_{6-x}\text{P}_{1-x}\text{Ge}_x\text{S}_3\text{I}$ was performed and the changes to the structure and transport were investigated. Using a combination of X-ray and neutron diffraction, nuclear magnetic resonance and impedance spectroscopy, the lattice variations, Ge solubility and, more specifically, the Li^+ occupancies and I/S²⁻ site-disorder were monitored. With increasing Ge content, a significant change in the activation barrier was observed, which coincides with an increase of the I/S²⁻ site-disorder. The structural changes and increasing lattice volume lead to an opening of the bottle necks and nuclear magnetic resonance indicates more facile inter-cage jumps. The interpenetration of face-centered cubic lattices in the argyrodite structure means that only a low degree of disorder is needed to reach the percolation threshold. The drop in the activation barrier due to these structural changes leads to a high ionic conductivity of $5.4 \pm 0.8 \text{ mS cm}^{-1}$ in $\text{Li}_{6.0}\text{P}_{0.3}\text{Ge}_{0.6}\text{S}_3\text{I}$ and sintering of the pellets can further increase the ionic conductivity to $18.4 \pm 2.7 \text{ mS cm}^{-1}$. With these high-performance solid electrolytes, solid-state batteries with thick electrode configurations were successfully cycled, showing no apparent capacity fade over 150 cycles.

This work shows that structural changes and site-disorder can be used to induce severe changes in the potential energy landscape. These structural changes strongly affect the activation barrier for the mobile ions, which helps to further optimize electrolytes toward obtaining high ionic conductivities and allows their practical use in thick-electrode cells for solid-state battery applications.

Supporting Information

All refined diffraction data are tabulated here. Stacked plots of the diffraction data are shown as well as the tabulated results from nuclear magnetic resonance and impedance spectroscopy. Information on the fitting of the nuclear magnetic resonance T_1 relaxation rate can be found here. The measurements of the sintered materials in multiple measurement setups and geometries can further be found here as well as the impedance data of the solid-state battery cells.

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Notes

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