Cation Disorder and Large Tetragonal Supercell Ordering in the Li-Rich Argyrodite Li$_7$Zn$_{0.5}$SiS$_6$

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ABSTRACT: A tetragonal argyrodite with >7 mobile cations, Li$_7$Zn$_{0.5}$SiS$_6$, is experimentally realized for the first time through solid state synthesis and exploration of the Li–Zn–Si–S phase diagram. The crystal structure of Li$_7$Zn$_{0.5}$SiS$_6$ was solved ab initio from high-resolution X-ray and neutron powder diffraction data and supported by solid-state NMR. Li$_7$Zn$_{0.5}$SiS$_6$ adopts a tetragonal $I4$ structure at room temperature with ordered Li and Zn positions and undergoes a transition above 411.1 K to a higher symmetry disordered $F43m$ structure more typical of Li-containing argyrodites. Simultaneous occupation of four types of Li site (T5, T5a, T2, T4) at high temperature and typical of Li-containing argyrodites. Simultaneous occupation of four types of Li site (T5, T5a, T2, T4) at high temperature and five types of Li site (T5, T2, T4, T1, and a new trigonal planar T2a position) at room temperature is observed. This combination of sites forms interconnected Li pathways driven by the incorporation of Zn$^{2+}$ into the Li sublattice and enables a range of possible jump processes. Zn$^{2+}$ occupies the 48h T5 site in the high-temperature $F43m$ structure, and a unique ordering pattern emerges in which only a subset of these T5 sites are occupied at room temperature in $I4$ Li$_7$Zn$_{0.5}$SiS$_6$. The ion conductivity, examined via AC impedance spectroscopy and VT-NMR, is 1.0(2) × 10$^{-2}$ S cm$^{-1}$ at room temperature and 4.3(4) × 10$^{-4}$ S cm$^{-1}$ at 503 K. The transition between the ordered $I4$ and disordered $F43m$ structures is associated with a dramatic decrease in activation energy to 0.34(1) eV above 411 K. The incorporation of a small amount of Zn$^{2+}$ exercises dramatic control of Li order in Li$_7$Zn$_{0.5}$SiS$_6$ yielding a previously unseen distribution of Li sites, expanding our understanding of structure—property relationships in argyrodite materials.

1. INTRODUCTION

The argyrodite family of materials, related to the mineral Ag$_6$GeSe$_6$ exhibit considerable compositional flexibility and have been extensively studied for various applications including fast ion conduction (e.g., Ag$_6$GeSe$_6$ and Cu$_x$PS$_3$Cl)$_{1,1}$ thermoelectrics (e.g., Cu$_x$Ge$_{3-x}$S$_x$ and Ag$_x$SnSe$_y$)$_{3,4}$ and nonlinear optical (Cd$_{12.2}$PS$_{35.1}$I$_{0.3}$) materials. The degree of structural disorder, which can be controlled through cationic or anionic substitution, determines the properties of argyrodite materials, so reliable characterization of such crystal structures is critical to expanding our knowledge of these systems. The crystal structures of argyrodites such as Li$_6$PS$_5$X (X = Cl, Br) have tetrahedral close packed topologies related to that of the Laves phases (e.g., MgCu$_2$) with high symmetry aristotype argyrodite polymorphs adopting cubic $F43m$ symmetry. Recently, we demonstrated that the argyrodite structure can also be considered equivalent to that of antiperovskite through anion and vacancy ordering within a cubic stacking of two close-packed layers that enabled the discovery of a hexagonal argyrodite Li$_6$SiO$_4$Cl$_2$. The argyrodite Li$_6$MS$_4$XX' structure can be described for sulfides as a cubic close-packed arrange-
with Li atoms removed. MS₄ polyaniions have a cubic close-packed arrangement while X anions occupy octahedral voids and \( X' \) anions occupy half of the tetrahedral voids between the MS₄ tetrahedra. (b) Five types of vacant tetrahedral voids can be occupied by Li\(^+\) and their Wyckoff positions.\(^{5,7}\) T5a is a trigonal planar position that occupies the shared face between two T5 tetrahedra. Reproduced from Acc. Chem. Res. 2021, 54, 2717–2728 (ref 5). Copyright 2021 American Chemical Society.

2. EXPERIMENTAL SECTION

2.1. Exploratory Synthesis in the Li\(_{2}\)Zn\(_0.5\)SiS\(_6\) Phase Field.

All reagents and samples were handled under inert helium atmosphere (O\(_2\) < 1 ppm). Solid state reactions were carried out by flame sealing reagent mixtures (typically, 300 mg for each reaction) inside carbon-coated evacuated quartz ampules (<10\(^{-5}\) mbar). Stoichiometric mixtures of lithium sulfide (Li, Sigma-Aldrich, 99.98%), zinc sulfide (ZnS, Sigma-Aldrich, 99.99%), silicon powder (Si, Alfa Aesar, 325 mesh, 99.5%), and elemental sulfur (S, Sigma-Aldrich, 99.99%) were used as provided and thoroughly ground for 15 min using an agate pestle and mortar. For initial exploratory reactions in the Li\(_{2}\)Zn\(_0.5\)SiS\(_6\) phase field, these reaction mixtures were heated to 673 K at a heating rate of 5 K min\(^{-1}\), then heated to 973 K at a slower rate of 0.5 K min\(^{-1}\), and held at 973 K for 24 h before being cooled to ambient temperature at a rate of 5 K min\(^{-1}\). Resulting powders were ground.
before being fired again to 973 K for 24 h using a heating and cooling rate of 5 K min~1.

2.2. Synthesis of \( \text{Li}_7\text{Zn}_0.5\text{Si}_6 \). Powders of Li\(_x\)Zn\(_{1-x}\)Si\(_6\) were obtained using stoichiometric mixtures of the above starting materials sealed in carbon-coated evacuated quartz ampules, which were fired to 973 K for 24 h using a heating and cooling rate of 5 K min~1 twice with the powders ground in between the two firings. This reaction procedure yielded phase pure samples of Li\(_x\)Zn\(_{1-x}\)Si\(_6\) as assessed by laboratory powder X-ray diffraction (PXRD) data.

2.3. Powder Diffraction. Routine PXRD analysis of phase purity and lattice parameters was performed on a Bruker D8 Advance diffractometer with a monochromatic Cu X-ray source (\( K_{\alpha 1} \), \( \lambda = 1.54056 \) Å) or Mo X-ray source (\( K_{\alpha 1} \), \( \lambda = 0.70932 \) Å) in Debye–Scherrer geometry. Powder samples were sealed inside borosilicate glass capillaries. Structure determination and Rietveld refinements were carried out on synchrotron X-ray diffraction (SRXD) data collected at the 111 beamline (Diamond Light Source, U.K.) with an incident wavelength of 0.824878 (10) Å. High-resolution data were collected at room temperature using the multianalyzer crystal (MAC) detectors. Samples were sealed inside Ø = 0.3 mm borosilicate capillaries. Variable temperature SRXD measurements from ambient temperature to 448 K in 25 K steps were carried out on beamline 111 using an Oxford Cryostream Plus with the Mythen position sensitive detector (PSD). Data were collected on heating using a heating and cooling rate of 10 K min~1.

Time-of-flight neutron powder diffraction (NPD) data were collected at ambient temperature (300 K) and at 448 K using the low temperature furnace on the Polaris instrument at ISIS, the U.K. Spallation neutron source. Powders were loaded into thin-walled vanadium metal cans of 6 mm diameter under an inert helium atmosphere and sealed using a copper gasket. Data were collected on a \(^7\)Li enriched sample to minimize the impact of absorption using a \(^29\)Si precursor, which was synthesized from \(^{29}\)SiO\(_4\) (Sigma-Aldrich, 99%) that was heated to 923 K under flowing \( \text{CS}_2 \) vapor for 6 h.

2.4. Elemental Analysis. Elemental analysis of Li\(_x\)Zn\(_{1-x}\)Si\(_6\) was carried out by Mikroanalytisches Labor Pascher (Remagen-Bandorf, Germany). The powder was dissolved, and elements were detected by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Thermo Fisher Scientific iCap 6500 instrument.

2.5. Differential Scanning Calorimetry (DSC). Heat flux profiles were measured from 17 mg of powdered sample in a 100 µL Ni/Cr crucible sealed under a helium atmosphere (\( \text{O}_2 < 1 \) ppm) using a Netzsch DSC 404 F1 differential scanning calorimeter. Data were recorded on heating from 303 to 773 K and then cooling to 303 K using a heating and cooling rate of 1 K min~1 under a constant 50 mL min~1 flow of helium. The temperature of the observed transition is the average of the values obtained from both the heating and cooling data sets, which were extracted through peak fitting.

2.6. Raman Spectroscopy. Raman spectra were collected on samples sealed under a helium atmosphere in borosilicate glass capillaries (\( \text{O}_2 < 1 \) ppm) using an inVia Reflex Qntor Confocal Raman Microscope from Renishaw with a laser excitation wavelength of 523 nm.

2.7. Alternating Current (AC) Impedance Spectroscopy and Direct Current (DC) Polarization. A pellet of Li\(_x\)Zn\(_{1-x}\)Si\(_6\) was prepared by uniaxially pressing ~30 mg of materials with a 5 mm cylindrical steel die at a pressure of 125 MPa and subsequent sintering at 923 K for 14 h using heating and cooling rates of 5 K min~1. Using this method, a density of 81% was achieved. The pellet faces were sputtered with gold, which were used as ion-blocking electrodes. Temperature dependent AC-impedance measurements were carried out by heating the sample from 303 to 503 K in an Ar-filled glovebox (\( \text{O}_2 < 1 \) ppm, \( \text{H}_2\text{O} < 1 \) ppm) at a rate of 3 K min~1. Measurements were recorded in 20 K steps following a 10 min equilibration period at each target temperature. Impedance data were recorded using a Keysight Impedance Analyzer E4990A. A sinusoidal amplitude of 50 mV was employed in the frequency range of 100 MHz to 100 mHz. Impedance data were fitted with an equivalent circuit using the program ZView2. The same pellet used for AC impedance measurements was used for DC polarization measurements. DC polarization data were collected at ambient conditions on an AuLi\(_x\)Zn\(_{1-x}\)Si\(_6\)Au symmetric cell using potentiostatic polarization measurements between 0.05 and 1.0 V for 2 h and monitoring the current variation with time using an Autolab 8451S instrument.

2.8. Nuclear Magnetic Resonance (NMR). \(^7\)Li and \(^29\)Si magic angle spinning (MAS) NMR experiments were recorded at room temperature on a 9.4 T Bruker DSX spectrometer equipped with a 4 mm HHX MAS probe (in double resonance mode) with the X channel tuned to \(^7\)Li at \( \omega_{1}/2\pi (\text{Li}) = 59 \) MHz and \(^29\)Si at \( \omega_{1}/2\pi (\text{Si}) = 79.5 \) MHz. 90° pulses of duration 3 ms at a radiofrequency (rf) amplitude of \( \omega_{1}/2\pi = 83 \) kHz were used. The MAS frequency \( \omega_{1}/2\pi \) was set to 10 kHz. All spectra were obtained under quantitative recycle delays of more than 5 times longer than the respective longitudinal relaxation times \( T_1 \) measured through the saturation recovery pulse sequence, and the data were fitted with a stretch exponential function in the form of \( 1 - \exp[-(\tau/T_1^\alpha)] \) (with \( \alpha \) values of 0.9 for the \(^7\)Li and \(^29\)Si data sets).

Static \(^7\)Li variable temperature (VT) NMR experiments on a sample sealed in a glass ampule were recorded on a 9.4 T Bruker Avance III HD spectrometer equipped with a 4 mm HHX MAS probe (in double resonance mode) with the X channel tuned to \(^7\)Li at \( \omega_{1}/2\pi (\text{Li}) = 156 \) MHz. All \(^7\)Li NMR spectra were recorded with a 90° pulse at rf field amplitude of \( \omega_{1}/2\pi = 83 \) kHz and under quantitative recycle delays of more than 5 times longer than the \( T_1^\alpha \) time measured through the saturation recovery pulse sequence with data also fitted to the same stretch exponential function as above (with \( \alpha \) ranging from 0.8 to 0.95). The stretch exponential was used in order to account for any distribution of correlation times and temperature gradients across the sample.

The temperature calibration of the probe was carried out using the \(^{207}\)Pb NMR chemical shift thermometer Pb(NO\(_3\))\(_2\). The temperature standard error associated with this method arises from the temperature gradients across the sample, which ranged from 2 to 8 K.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Isolation of New Li\(_7\)Zn\(_{0.5}\)Si\(_6\). The Li\(_{8-x}\)-Zn-Si\(_3\) phase field was explored using solid state methods with reagent mixtures sealed inside the carbon-coated evacuated quartz ampules (<10~4 mbar). Syntheses were carried out within a range of reaction temperatures (873–973 K) with all starting materials and resulting powders handled under an inert helium atmosphere (\( \text{O}_2 < 1 \) ppm). First, a selection of compositions within the phase field were synthesized, and the resulting phases were carefully matched to known materials through analysis of PXRD data (Figure 2a, red points). The majority of the synthesized compositions contained mixtures of binary sulfides and Li\(_7\)ZnSi\(_3\), which is the only quaternary that has been previously characterized within the Li\(_{8-x}\)-Zn-Si\(_3\) phase field. Second, to explore the Li-rich composition space of the phase field at greater granularity, compositions within solid solutions between the end member materials Li\(_4\)Si\(_3\), Li\(_7\)ZnSi\(_3\), Li\(_{2-x}\)Zn\(_x\)Si\(_3\), and a proposed Li\(_7\)ZnS\(_4\) were examined (Figure 2b).

No evidence was observed for the formation of new phases in the solid solution Li\(_{8-x}\)-Zn-Si\(_3\) with end members Li\(_4\)Si\(_3\) and Li\(_7\)ZnSi\(_3\), being the only observed phases (Figures 2b (purple line) and S1). Reactions along the Li\(_{8-x}\)-Zn\(_{1-x}\)Si\(_3\) tie line yielded mixtures of Li\(_x\)Zn\(_{1-x}\)Si\(_3\), Li\(_7\)Si\(_3\), Li\(_{2-x}\)Zn\(_x\)Si\(_3\), and ZnS (Figures 2b (green line) and S2). A first firing at 973 K for 24 h at the composition \( x = 0.2 \) along the Li\(_{8}\)Zn\(_{1}\)Si\(_{3}\) tie line (Figure 2b blue line) produced a set of reflections in the PXRD pattern that could not be assigned to any known phase with the \( x = 0.4 \) composition also yielding these peaks but with lower intensity (Figure S3). A second additional firing at 973 K for 24 h was critical to increase the amount of this phase at other compositions with the reflections of the new phase observed strongly in Li\(_{8-x}\)Zn\(_{0.2-x}\)Si\(_3\) (\( x = 0.267 \)) after the additional firing. The synthesis temperature was found to be critical to
produce this new phase with the formation observed only in the reactions carried out at 973 K (Figure S4). Below this temperature, a mixture of Li$_4$S and Li$_4$SiS$_4$ is obtained instead. A phase pure powder sample was obtained at the composition $x = 0.33$ (Li$_{4+2}$Zn$_{0.5}$SiS$_6$). The optimal reaction conditions for the formation of Li$_{4+2}$Zn$_{0.5}$SiS$_6$ are firing at 973 K for 24 h twice using heating and cooling rates of 5 K min$^{-1}$ with the powder ground using a pestle and mortar between the two firings.

The nominal composition of $x = 0.33$ in Li$_{4+2}$Zn$_{0.5}$SiS$_6$ can be written as Li$_{7}$Zn$_{0.5}$SiS$_6$, indicating that the new phase is related to argyrodite, a well-known family of superionic conductors. The bulk composition of Li$_{7}$Zn$_{0.5}$SiS$_6$ was determined through the analysis of synchrotron X-ray diffraction (SXRD) and neutron powder diffraction data (NPD) described in detail in the following sections. All of the reflections observed for new Li$_{7}$Zn$_{0.5}$SiS$_6$ can be indexed to a tetragonal unit cell at room temperature with lattice parameters $a = b = 21$ Å and $c = 10$ Å with systematic absences that are consistent with the $I$-4 $mm$ diffraction symbol (Figure S5). High-resolution SXRD data were collected on Li$_{7}$Zn$_{0.5}$SiS$_6$ powder in the temperature range of 298–448 K in 25 K steps. Above 423 K, the convergence of some peaks and disappearance of many small peaks associated with the tetragonal lattice indicate a phase transition to a higher-symmetry structure takes place (Figures S5 (inset) and S6). This transition, observed by powder diffraction, is consistent with differential scanning calorimetry (DSC) data, which show a single endothermic and exothermic thermal event at 411.1(5) K observed on heating and cooling, respectively, highlighting that the transition is reversible (Figure 2c). The peaks in the powder pattern of Li$_{7}$Zn$_{0.5}$SiS$_6$ measured at $>423$ K can be indexed to a cubic unit cell with $a = 10.04444(3)$ Å and space group symmetry $Fm3m$ (Figure S5), which is similar to those observed for argyrodite materials. It is not possible to stabilize the high-temperature $Fm3m$ structure of Li$_{7}$Zn$_{0.5}$SiS$_6$ to room temperature through quenching. This yields tetragonal ($I$) Li$_{7}$Zn$_{0.5}$SiS$_6$ and Li$_4$SiS$_4$ as a secondary phase (Figure S7).

### 3.2. Structure Determination. 3.2.1. Determination of Li$_{7}$Zn$_{0.5}$SiS$_6$ High-Temperature Structure.

The high-temperature $Fm3m$ structure of Li$_{7}$Zn$_{0.5}$SiS$_6$ was obtained from the combined refinement of SXRD and NPD data, fitted using TOPAS Academic. The structure of Li$_{4}$PS$_5$Br (space group $Fm3m$ with approximate lattice parameter of $a = 10.04$ Å) was used as the starting point with P substituted for Si on the 4th Wyckoff site and Br substituted for S on the anion positions. The lattice parameter, background, and peak shapes were refined using the Le Bail method and then fixed throughout until the final refinement. Two Li sites (48h T5 and 24g T5a) were present in the starting model. Compared against the nominal composition of Li$_{7}$Zn$_{0.5}$SiS$_6$, this structure is missing 1.5 cations (1 Li$^+$ and 0.5 Zn$^{2+}$). Three additional tetrahedral Li sites were suggested from a Fourier difference map generated using NPD data from Bath 3 of Polaris with the initial model and profile parameters from the Le Bail fit. The Li site occupancies were initially set such that the total Li content within the model was equal to 7.5 from five sites (four tetrahedra and one trigonal planar). The four tetrahedral sites were duplicated for Zn and set to an initial occupancy of zero. The site distribution of Li/Zn within the structural model was then refined using the automatic simulated annealing algorithm in TOPAS, refining for 100 000 cycles. During the simulated annealing, only the occupancies of the Li/Zn sites were allowed to vary, and the refinement was subject to a global composition restraint set by the nominal composition (Li$_{7}$Zn$_{0.5}$SiS$_6$). The simulated annealing resulted in Zn located on the 48h (T5) site only with Li occupying the 48h (T5), 24g (T5a), 48h (T2), and 16e (T4) sites. The fifth candidate tetrahedral site was refined to an occupancy of zero, so it was removed from the refinement. These results from simulated annealing were then used as the basis for a Rietveld refinement in which all structural parameters and profile parameters were refined. During this final refinement, the results of which are
shown in Figures 3a−c and S9a−c and given in Table 1, the global composition restraint was still used, and soft restraints were applied to the Si−S and Li−S distances of 2.1(1) and 2.5(1) Å, respectively. These values were based on the averages if both distances were freely refined, while corresponding to sensible Si−S and Li−S distances as found in other argyrodites.13 The final refinement resulted in the unit cell parameter a = 10.04444(3) Å and composition of Li7.00(12)Zn0.497(6)SiS6, which is in good agreement with the composition of Li 7.07(2) Zn0.472(2) Si1.068(6) S6.00(6) determined analytically from ICP-AES analysis (Table S1). Though many Cu and Ag argyrodites exist with high mobile cation content (e.g., Cu8GeS6 and Ag8SnSe6),3,4 comparatively few Li argyrodites with such a high occupancy of the mobile cation sites exist.

### 3.2.2. Determination of Li7Zn0.5SiS6 Room-Temperature Structure

In principle, it should be possible to solve the room-temperature ordering of Li7Zn0.5SiS6 by creating the corresponding supercell of the high-temperature structure using ISODISTORT23,24 and then performing a Rietveld refinement. However, this generates a supercell containing 77 unique Li/Zn sites, 3 Si sites, and 15 S sites (a total of 95 sites). Consequently, solving the room-temperature structure via this route was impractical, as preliminary refinement attempts immediately indicate that the majority of the potential Li/Zn sites are not occupied at room temperature; therefore, the determination of which sites were occupied by Li and Zn starting from all possible sites would be less efficient compared to resolving through the method described below.

To solve the room-temperature structure of Li7Zn0.5SiS6, the unit cell was first indexed using the autoindexing function in GSAS-II with the SXRD data,25 which resulted in the unit cell indexed as tetragonal with approximate lattice parameters a ≈ b = 21 Å and c ≈ 10 Å and systematic absences which are consistent with the I−−−diffraction symbol. This approximate unit cell was then used as the basis for a Le Bail refinement in Jana2006.26 For the Le Bail fit, the space group was set to P1 and the background, peak profile, the six unit cell parameters, and zero error were then refined. The ”make space group test” function within Jana2006 was used to suggest
possible space groups with a tolerance of 0.02 Å on the \(a\), \(b\), and \(c\) unit cell parameters and 0.2° on the unit cell angles and was combined with the HKL table from the Le Bail fit to suggest possible space groups, which typically returns the highest symmetry space group from the best fitting diffraction symbol. The best achieved fit was to the space group \(I\bar{4}\), consistent with \(I\bar{4}\). The initial structure was solved using SUPERFLIP\(^{27,28}\) as implemented in Jana2006. The best solutions from this method can often be achieved by starting with the lowest symmetry space group allowed by the \(I\bar{4}\)diffraction symbol. As such, the structure solution was started in space group \(I\bar{4}\), and SUPERFLIP with its own symmetry determination is able to suggest higher symmetry solutions, where appropriate, although none that yielded a solution with an improved fitting parameter were found.

The solution from SUPERFLIP using the results from a Le Bail fit in \(I\bar{4}\) symmetry against SXRD data yielded a structure containing \(15\times S, 3\times Si, \) and \(12\times mixed Li/Zn sites and retained the \(I\bar{4}\) symmetry. This model was refined using the Rietveld method in Jana2006 against the SXRD data, allowing the occupancies of the mixed Li/Zn sites to be refined while restricting each total site occupancy to one, resulting in a structural model with an approximate composition of \(Li_{4.55}Zn_{0.5}SiS_6\). This indicated a significant amount of Li that was unaccounted for in the structure. In this model, no further sites could be located using Fourier difference mapping against the SXRD data, and due to the large difference between the model and nominal composition of \(Li_{4.55}Zn_{0.5}SiS_6\) it was concluded that the additional Li was likely distributed across several partially occupied sites.

To locate further Li sites within the structure, the structure derived above was refined in TOPAS academic to create an equivalent starting point and NPD data were now included in the refinement. Computing Fourier difference maps against the NPD data from Bank 3 of Polaris did not locate any additional Li sites. We repeated the following process until no new sites could be located: an additional Li/Zn site was included in the structure with randomly generated (within TOPAS) fractional coordinates with the total occupancy of the site restricted to one; this updated model is then refined using the Rietveld method for at least 10 000 refinement cycles, and each time the refinement converged, the coordinates of the new site were re-randomized (the rest of the structure and profile parameters continue to be refined as normal). Then, the solution with the lowest \(R_{wp}\) fit parameter is carried forward. This process resulted in the location of an additional four Li sites, bringing the approximate composition to \(Li_{7}Zn_{0.5}SiS_6\) in line with the nominal composition.

At this stage, the restriction of all Li/Zn sites having a total occupancy of one led to a number of nonphysical M–M

![Figure 4](https://doi.org/10.1021/acs.chemmater.2c00320)
distances ($M = Li$ and $Zn$) of approximately 1.6 Å between sites within the model. This was resolved by restricting the total occupancies of these neighboring positions (sites with short $M−M$ distances) to a maximum of one. The original restriction that maintained $Li/Zn$ site occupancies to equate to one was changed such that the occupancy contribution on any given $Li/Zn$ site could not fall below zero. With these restrictions in place, simulated annealing was used in TOPAS for at least 100 000 refinement cycles using its automatic temperature regime, allowing only the occupancies of the $Li/Zn$ sites to be refined.

After each simulated annealing run, further $Li$ sites were trialed in the structure as outlined previously. With the addition of each new $Li/Zn$ site, the constraints on the occupancy of the neighboring $Li/Zn$ sites were updated and the simulated annealing stage repeated. This process introduced an additional five $Li/Zn$ sites into the structure at which point the composition of the model was stable and no new sites could be located (i.e., no new $Li/Zn$ sites could be introduced that had total refined occupancies greater than one estimated standard deviation above zero). The refined composition of the model at this stage was $Li_{6.85(10)}Zn_{0.470(6)}SiS_6$.

To achieve the final refinement model, distance restraints were used for the $Si−S$ and $Li/Zn−S$ bonds. $Si−S$ distances were constrained softly to $2.1(±0.1)$ Å, while for $Li/Zn−S$ bonds, the distance was constrained to $2.5(±0.1)$ Å. These values were based on the averages if distances were freely refined, while simultaneously corresponding to sensible $Si−S$ and $Li−S$ distances as found in other argyrodites. Additionally, a soft global composition restraint, set to the nominal composition of $Li_7Zn_{0.5}SiS_6$, was used in the model. The final refined model has the composition $Li_{7.00(8)}Zn_{0.480(5)}SiS_6$ in excellent agreement with the composition determined through ICP analysis ($Li_{7.07(2)}Zn_{0.472(2)}Si_{1.068(6)}S_{6.00(6)}$) with lattice parameters $a = b = 21.15065(2)$ Å and $c = 10.05640(15)$ Å and a global $R_{wp}$ of 5.6% and $χ^2$ of 14.8 for 245 parameters. For reference, the equivalent Le Bail fit of the data used in the final refinement has a $R_{wp}$ of 5.1% and $χ^2$ of 12. Attempts to identify additional symmetry elements in the final model using FINDSYM were unsuccessful, confirming the $I4$ space group. The results from the final structure solution are shown in Figures 3d–f and S9d–f and given in Table S2. The room-temperature structure of $Li_7Zn_{0.5}SiS_6$ contains 40 unique atomic sites, 22 $Li$ sites, of
which 6 contain Zn, 3× S1 sites, and 15× S2 sites, and are discussed in detail below.

3.3. Structure Description. 3.3.1. Description of High-Temperature Li7Zn0.5SiS6 Structure. Li7Zn0.5SiS6 adopts the typical cubic F43m argyrodite structure at high temperatures (>423 K), comparable to that of Li6PS5X (X = Cl and Br) from the analysis of high-resolution neutron Mini data,33 and the simultaneous occupation of hLi+ (0.099(7)) is found in the high-temperature structure, which is the 48h (T5) site with an occupancy of 0.0414(5) Zn, giving an overall cation occupancy of 0.992(2) across the TS and T5a sites (Figure 4b,c). The remaining Li+ occupies the 16e (T4) and 48h (T2) positions with occupancies of 0.243(6) and 0.048(5), respectively (Figure 4b,c). These additional (T4 and T2) positions are sites that are less frequently occupied than the T5 and T5a sites in most Li-containing argyrodites; however, they have been observed in several other systems such as Li6.15 Al0.15 Si1.35 S5.734 O0.266,32 and Li4P2S3X (X = Cl and Br) from the analysis of high-resolution neutron diffraction data,33 and the simultaneous occupation of T5, T5a, T2, and T4 sites was very recently reported in Li6.6P0.4Ge0.6S5I.34 The 48h (T5) tetrahedra share two corners with the SiS4 tetrahedral environment in the average high-temperature structure of F43m Li7Zn0.5SiS6 and are shown in (c) and (d), respectively.

Figure 6. (a) Unit cell of room-temperature F4 Li7Zn0.5SiS6 and (b–d) representation of the Li sublattice within the three types of Friauf polyhedra. The Friauf polyhedra are formed from four SiS4 tetrahedra (blue) around a central S2− anion on the 2d and two 8g Wyckoff positions (corresponding to the 4c site in the high-temperature F43m structure). The orange, purple, and blue lines in (a) show the Friauf polyhedra within the unit cell. In total, there are 22 distinct Li positions in F4 Li7Zn0.5SiS6 and all are shown in (b–d). Tetrahedra for different types of Li sites are shown: gray, T5 and T5a; green, T2; light blue, T4; purple, T1; orange, new trigonal planar T2a position. The T1 and new trigonal planar T2a positions (which occupy the shared face between two T2 neighboring tetrahedra) are not occupied in high-temperature F43m Li7Zn0.5SiS6 and are shown in (c) and (d), respectively.

Li+ cations are dynamically disordered across four distinct crystallographic sites in the high-temperature structure of Li7Zn0.5SiS6 and can be represented by viewing Friauf polyhedra formed from the four SiS4tetrahedra that are centered around the 4c S2− position (Figure 4). The 48h (T5) and 24g (T5a) positions are occupied with 0.405(8) and 0.099(7) Li, respectively, accounting for most of the Li. Despite having a comparable ionic radius to Li+ (tetrahedral rLi+= 0.59 Å and rZn2+ = 0.6 Å),30 Zn+ occupies only one site in the high-temperature structure, which is the 48h (T5) site with an occupancy of 0.0414(5) Zn, giving an overall cation occupancy of 0.992(2) across the TS and T5a sites (Figure 4b,c). The remaining Li+ occupies the 16e (T4) and 48h (T2) positions with occupancies of 0.243(6) and 0.048(5), respectively (Figure 4b,c). These additional (T4 and T2) positions are sites that are less frequently occupied than the T5 and T5a sites in most Li-containing argyrodites; however, they have been observed in several other systems such as Li6.15 Al0.15 Si1.35 S5.734 O0.266,32 and Li4P2S3X (X = Cl and Br) from the analysis of high-resolution neutron diffraction data,33 and the simultaneous occupation of T5, T5a, T2, and T4 sites was very recently reported in Li6.6P0.4Ge0.6S5I.34 The 48h (T5) tetrahedra share two corners with the SiS4 tetrahedra and share edges with the 48h (T5) tetrahedra. As such, all four faces of the 48h (T5) tetrahedral environment in the average high-temperature structure of Li7Zn0.5SiS6 are shared with other tetrahedral environments.
(one 48T S5, two 48T T2, one 16T T4), yielding a significantly delocalized distribution of Li+ such as those observed recently in Li4.15Al0.15Si1.35S5.734O0.266 and Li6.6P0.4Ge0.6S5.31, where the 48T T2 site is located within the Li cages, which are formed by the T'S and T5a Li+ positions centered around the 4d S4<sup>+</sup> X' site, whereas the T4 site is located between these cages; both the T2 and T4 sites are known to play an important role in the formation of ionic diffusion pathways throughout the argyrodite structure, which will be discussed in Section 3.4.

3.3.2. Description of Room-Temperature Li7Zn0.5SiS6 Structure. Below 411 K, Li7Zn0.5SiS6 orders in a tetragonal structure with unit cell parameters of a = b = 21.15065(2) Å and c = 10.05640(15) Å with I4/m symmetry, which is related to the high-temperature F43m unit cell through the relationship a<sub>i</sub> = \( \frac{4a}{3} \), where a and a<sub>i</sub> are the unit cell parameters of the tetragonal and cubic structures, respectively. There are no previous reports of a tetragonal argyrodite, which arises here from the combination of Li+ and a small amount Zn<sup>2+</sup> (6.7% of the total number of cations) on the mobile cation sites. The anion sublattice (S<sup>2-</sup> and SiS<sub>4</sub><sup>+</sup>) of the Li7Zn0.5SiS6 room-temperature I<sub>4</sub> symmetry is occupied by Zn. The large number of T5 sites occupied by Zn in the room-temperature I<sub>4</sub> structure of Li7Zn0.5SiS6; therefore, any of the T5 sites in Li7Zn0.5SiS6 can be occupied by Zn. However, only a subset of the T5 sites in the room-temperature I<sub>4</sub> structure are occupied by Zn. Six of the 14 T5 sites (48T position in high-temperature F43m structure) are occupied by both Li<sup>+</sup> and Zn<sup>2+</sup>, the smallest and largest Zn occupancies being 0.031(5) and 0.473(4), respectively. These six T5 sites are the only positions that are occupied by Zn in the room-temperature I<sub>4</sub> structure of Li7Zn0.5SiS6. Almost all of the T5 sites have occupancies higher than 0.85; five T5 sites are fully occupied by Li, and a further seven have occupancies higher than 0.86(4). The two remaining T5 sites (1×0.162(S)Zn/0.59(6)Li and 1×0.031(S)Zn/0.21(6)Li) occupy face-sharing tetrahedra, giving a combined occupancy of 0.99(9) across both sites, analogous to the disordered environments in the high-temperature F43m structure (Figure 6c). The large number of T5 sites occupied in Li7Zn0.5SiS6 is consistent with other ordered Li-rich argyrodites, such as Li7PCh6 (Ch = S, Se), in which Li predominantly occupies tetrahedral T5 sites (six T5 sites and one T5a site).7

None of the trigonal planar 24g (T5a) positions occupied in the high-temperature F43m structure are occupied at room temperature, reflecting the preference for a higher (tetrahedral) coordination environment for Li+ in Li7Zn0.5SiS6. This is distinct from the low temperature (Cc) structures of Li4AsS<sub>4</sub>I and Li4PS<sub>4</sub>I and the F43m structure of Li4PO<sub>4</sub>Br, all of which contain trigonal planar T5a positions fully occupied by Li.7,10 This is not exclusive to anion-ordered argyrodites, as fully occupied planar T5a environments are also observed in Li7PCh<sub>6</sub> (Ch = S, Se).7

Two of the four T2 sites in Li7Zn0.5SiS6 are fully occupied with Li at room temperature and share edges with their neighboring Li sites. The remaining two T2 sites have low occupancies (<0.09) and share faces with occupied neighboring T5 sites. The two T4 sites are both fully occupied with Li at room temperature (Figure 6c.d). The occupancy of a single T1 site at room temperature in Li7Zn0.5SiS6 (Figure 6c) is surprising as this position is not usually occupied in other argyrodites. Through consideration of the tetrahedral holes available for occupancy by Li in the argyrodite structure, this site is the least favorable as it shares a common face with the SiS<sub>4</sub><sup>+</sup> tetrahedra, which would result in significant repulsion from the nearby Si<sup>2+</sup>cation located only 2.1(2) Å away. This is likely the reason the T1 site in Li7Zn0.5SiS6 is occupied with only 0.12(3) Li, and the position is not occupied in the high-temperature F43m structure. Finally, there is one Li site that adopts trigonal planar geometry in Li7Zn0.5SiS6 at room temperature (4e Wyckoff position), different from the commonly occupied T5a site, is not observed in other argyrodites, and like the T1 position is not occupied in the high-temperature structure. This is the trigonal face that is shared between two neighboring T2 tetrahedra, and as such, this new site is denoted as T2a. This position shares edges with one SiS<sub>4</sub><sup>+</sup> tetrahedra and two T5 Li tetrahedra, yielding a short Li−
Li of 1.82(7) Å (Figure 6d). The combined occupancy of these positions sums to unity.

$^6$Li MAS NMR was utilized to obtain insights into the local structure and ordering of Li$_7$Zn$_{0.5}$Si$_6$S$_6$ at room temperature. The $^6$Li MAS NMR spectrum recorded at room temperature (Figure S12b) displays a single narrow resonance at 1.65 ppm, which agrees well with all (but one) of the lithium atoms occupying tetrahedral sites. The low occupancy of the remaining single lithium in the T2a trigonal planar position among the 21 other Li sites likely limits the clear observation of this local environment in the $^6$Li spectrum. It is also quite likely that the $^6$Li MAS NMR spectrum is motionally averaged over all crystallographic sites due to fast Li ion hopping (see $^7$Li NMR data below) and prevents spectral resolution of the two different Li local environments.

The addition of a relatively small amount of Zn$^{2+}$ (Li/Zn ratio is 14:1 in Li$_7$Zn$_{0.5}$Si$_6$S$_6$) results in the ordering observed below 411 K in the tetragonal $I$4$_1$ Li$_7$Zn$_{0.5}$Si$_6$S$_6$ structure. Argyrodites that contain more than one metal on the mobile cation sites (i.e., sharing the site with Li$^{+}$) are rare but are not unheard of. Both Al$^{3+}$ and Si$^{4+}$ occupy 48h and 16c positions alongside Li$^{+}$ in Li$_6$(Al$_{15}$Si$_{13}$S$_{41}$O$_{6.6}$ and Li$_6$(Al$_{15}$Si$_{13}$S$_{734}$O$_{2600}$) while Li$_3$(Ge$_{3}$Zn$_{8}$P$_{10}$O$_{33}$) has Ge$^{4+}$ present on both the 48h (shared with Li$^{+}$) and 4b (shared with P$^{5+}$) positions. These three materials retain the $Fm$3m symmetry typical of argyrodites, and the additional cations (Al$^{3+}$, Si$^{4+}$, and Ge$^{4+}$) present on the Li sites in these materials do not exhibit ordering of any kind. This is distinct from Li$_7$Zn$_{0.5}$Si$_6$S$_6$ in which a unique ordering pattern occurs in the Zn distribution that stabilizes the room-temperature $I$4$_1$ structure, explaining why only 6 of the 14 available T5 positions are occupied by Zn in the room-temperature $I$4$_1$ structure. The distribution of Zn at room temperature in the $I$4$_1$ structure is separated into groups on the basis of Zn site occupancy. At the center of each group are four corner-connected tetrahedral sites with the highest Zn occupancy of 0.473(4) (the remainder is 0.51(5) Li) as shown in Figure 7a. Additional Zn occupied positions are located around these clusters, and Zn site occupancies decrease with an increase in distance from the group center (Figure 7a–c). These groups of Zn-rich sites are ordered to maximize the distance (15.78 Å) between neighboring groups (Figure 7a). This is distinct from the high-temperature $Fm$3m structure in which Zn is distributed throughout the structure on the disordered 48h T5 positions (Figure 7d). Though beyond the scope of the current study, this unique ordering of Zn positions in $I$4$_1$ Li$_7$Zn$_{0.5}$Si$_6$S$_6$ could be further investigated through electron microscopy, pair distribution analysis, and large-box reverse Monte Carlo modeling.

### 3.4. Ionic Transport in Li$_7$Zn$_{0.5}$Si$_6$S$_6$

The total ionic conductivity of Li$_7$Zn$_{0.5}$Si$_6$S$_6$ was investigated using AC impedance spectroscopy, and local lithium mobility was assessed through $^7$Li solid-state NMR. AC impedance measurements were carried out on a sintered pellet of Li$_7$Zn$_{0.5}$Si$_6$S$_6$ of 81% theoretical density ($\sim$30 mg of powder pressed into a 5 mm diameter pellet at a pressure of 125 MPa). A typical data set measured at 303 K under an inert Ar atmosphere is shown in Figure 8a. The impedance complex plane plots, $Z''$, consist of a higher-frequency arc and low frequency spike with the latter being associated with the capacitance of the sample–electrode interface that blocks the Li ions. The higher-frequency arc is attributed to the total conductivity ($\sigma$) of Li$_7$Zn$_{0.5}$Si$_6$S$_6$ with an associated capacitance of 0.1 pF cm$^{-2}$, corresponding to a permittivity of $\approx$1, consistent with the bulk response of the sample (Figure S13). To a first approximation, this arc can be modeled with an equivalent circuit consisting of a resistor in parallel with a constant phase element (CPE) (Figure 8a (inset)). Li$_7$Zn$_{0.5}$Si$_6$S$_6$ presents a total conductivity of 1.0(2) $\times$ 10$^{-7}$ S cm$^{-1}$ at 303 K and 4.3(4) $\times$ 10$^{-4}$ S cm$^{-1}$ at 503 K. Values of total resistance were obtained in the temperature range from 303 to 503 K from the low-frequency intercept on the Z$'$ axis of the impedance arc and are shown in an Arrhenius plot in Figure 8b. Two separate regimes are observed, separated by a change in slope between 403 and 423 K, which coincides with the structural transition from tetragonal ($I$4$_1$) to cubic ($Fm$3m) symmetry observed via DSC and VT-PXRD measurements. Tetragonal Li$_7$Zn$_{0.5}$Si$_6$S$_6$ has an activation energy of 0.66(1) eV, while cubic Li$_7$Zn$_{0.5}$Si$_6$S$_6$ exhibits an activation energy of 0.34(1) eV above 423 K. Figure S14b–d shows the current–time curves of the AuLi$_7$Zn$_{0.5}$Si$_6$S$_6$Au cell under DC polarization measured at −0.05, 0.1, and 0.7 V at which steady state current is achieved. The steady current is attributed to electronic leakage as two ion-blocking electrodes were used. Such a method provides an estimation of the upper limit of the electronic conductivity.

The electronic conductivity ($\sigma_e$) determined from the $I$–$E$ curve is 5.14(4) $\times$ 10$^{-10}$ S cm$^{-1}$ at 303 K, which accounts for 0.51% of the overall conductivity, extracted through $\sigma_\ell = Id/EA$ where $I$ is the current, $d$ is the pellet thickness, $E$ is the polarization voltage, and $A$ is the electrode area.

Insights into the local Li ion mobility in tetragonal Li$_7$Zn$_{0.5}$Si$_6$S$_6$ were obtained through VT $^7$Li solid-state NMR. Static $^7$Li NMR spectra over the 140–410 K temperature range were recorded (Figure 8c) to observe the temperature dependence of the $^7$Li line width. At temperatures below...
eV is obtained for tetragonal Li7Zn0.5SiS6. This value is lower than that obtained through AC impedance spectroscopy up to >340 K where Li7Zn0.5SiS6 is in the fast-motional regime, resulting in an averaging of the dipolar interaction and giving rise to narrow spectra with line widths of

\[ 4083 \times 10^{-8} \, \text{S cm}^{-1} \]

The conductivity in the high-temperature cubic structure (\( >411 \, \text{K} \)) has a significant impact on Li ion mobility with an activation energy approximately half (0.34(eV)) of the room-temperature conductivity \( \sigma_{303} \) of Li7Zn0.5SiS6 measured at 303 K with the circuit used to model the data shown in the inset. (b) Arrhenius plot of the total conductivity of Li7Zn0.5SiS6 in the temperature range of 303–503 K with activation energies extracted from the plotted data. (c) \(^{7}\)Li NMR spectra of Li7Zn0.5SiS6 under static conditions plotted in the temperature range of 140–410 K. Data above the phase transition to cubic \( F43m \) symmetry have not been recorded. (d) Motional narrowing of the line width (full width at half-maximum) of the central \(^{7}\)Li NMR transition of tetragonal Li7Zn0.5SiS6. The solid line is a sigmoidal regression fit and is a guide to the eye. The onset temperature of motional narrowing (\( T_{\text{onset}} \)) is indicated with a dashed line. Pseudo-octahedral Li¹ cages centered around the 4c Wyckoff position in \( F43m \) (e) Li7Zn0.5SiS6 and (f) Li6.6P0.4Ge0.6S5I,34 highlighting the comparable site occupancies between both materials and the extensively delocalized distribution of Li in the high-temperature \( F43m \) Li7Zn0.5SiS6 structure. Double-headed arrows compare distances between sites likely involved in forming an extended conduction pathway.
temperature F43m regime (Li$_{7}$Zn$_{0.5}$SiS$_{6}$, $\sigma_{300\text{K}}$ 4.3×10$^{-3}$ S cm$^{-1}$) is an order of magnitude higher than that of F43m Li$_{5}$PS$_{6}$ (5.9×10$^{-5}$ S cm$^{-1}$) and Li$_{6}$PS$_{5}$I (1.3×10$^{-5}$ S cm$^{-1}$) at the same temperature. This result from the more delocalized distribution of Li in the high-temperature F43m structure (Figure 8e) compared against Li$_{5}$PS$_{6}$ and Li$_{7}$PS$_{6}$, in which only two sites (T5 and T5a) and one site (T5) are occupied, respectively. Interestingly, the low temperature ordered structures of argyrodites such as Li$_{5}$PS$_{6}$ (Pnma) and Li$_{7}$PS$_{6}$ (Cc) exhibit lower activation energies than their higher temperature F43m polymorphs. This is not the case for Li$_{7}$Zn$_{0.5}$SiS$_{6}$. The activation energy of F43m Li$_{7}$Zn$_{0.5}$SiS$_{6}$ (0.34(1) eV) aligns well with the range reported (0.15–0.42 eV) for several superionic argyrodite conductors such as Li$_{6.35}$P$_{0.65}$Si$_{0.35}$Br and Li$_{6.15}$Al$_{0.15}$Si$_{1.35}$S$_{5}$O$_{0.266}$. indicating that, in the high-temperature F43m regime of Li$_{7}$Zn$_{0.5}$SiS$_{6}$, comparable Li ion mobility is possible likely due to the availability of extensively delocalized Li sites that form part of the diffusion pathways. Though Li$_{7}$Zn$_{0.5}$SiS$_{6}$ and Li$_{6.6}$P$_{0.4}$Ge$_{0.6}$S$_{5}$I both exhibit simultaneous occupation of the T5, T5a, T2, and T4 sites, specific site occupancies and distances between these sites that form part of the extended conduction pathway are considerably different. In F43m Li$_{7}$Zn$_{0.5}$SiS$_{6}$, the T5 sites are occupied by 0.405(8) Li and 0.0414(5) Zn with T5 site occupied by 0.318 Li and T5a site, by 0.358 Li. The T5 sites at higher temperatures in Li$_{7}$Zn$_{0.5}$SiS$_{6}$ compared to that (1.93 Å) for Li$_{6.6}$P$_{0.4}$Ge$_{0.6}$S$_{5}$I, (1.51 Å) in Li$_{6.6}$P$_{0.4}$Ge$_{0.6}$S$_{5}$I and Li$_{7}$PS$_{6}$ (5.9×10$^{-5}$ S cm$^{-1}$) at the same temperature. Anion disorder in argyrodites is known to impact significantly on Li ion conductivity by influencing the energy landscape for Li$^{+}$ ion mobility. Disorder on the anion sublattice, which can be controlled through anionic or cationic substitutions or the synthesis method, yields an inhomogeneous distribution of charge density generating spatially diffuse and delocalized distributions of Li$^{+}$ ions, resulting in higher ion mobility. Li$_{7}$Zn$_{0.5}$SiS$_{6}$ has a single cation (Si$^{4+}$) on the 4b position and is a single anion (S$^{2-}$ only) system; however, it achieves a highly delocalized Li distribution in the F43m regime comparable to that of the highest conducting argyrodites. It is possible through additional substitution chemistry that the disordered F43m structure of Li$_{7}$Zn$_{0.5}$SiS$_{6}$ could be stabilized to lower temperatures or a more inhomogeneous charge density distribution could be achieved to further improve the ionic conductivity.

4. CONCLUSIONS

Li$_{7}$Zn$_{0.5}$SiS$_{6}$, the first argyrodite with a tetragonal (I4) crystal structure has been synthesized and characterized through a combination of X-ray, neutron powder diffraction, NMR, and impedance spectroscopy. Li$_{7}$Zn$_{0.5}$SiS$_{6}$ is a rare example of an argyrodite with >7 mobile cations, and the incorporation of a small amount (6.7%) of Zn into the Li sublattice stabilizes a complex tetragonal superstructure of F43m argyrodites with a unique Li distribution previously unseen in these materials. At high temperatures, Li$_{7}$Zn$_{0.5}$SiS$_{6}$ adopts a F43m cubic argyrodite structure with simultaneous occupation of the 48f (T5), 24e (T5a), 48h (T2), and 16e (T4) sites, a unique site distribution that provides a range of possible pathways for ion hopping, yielding a higher conductivity than other Li-only materials such as Li$_{5}$PS$_{6}$, that show order–disorder behavior. This combination of sites leads to an extensively delocalized Li distribution forming a continuous face-sharing tetrahedral pathway for Li ions that is accessible in F43m Li$_{7}$Zn$_{0.5}$SiS$_{6}$. This is achieved via incorporation of Zn and overloading of the mobile cation content, which has a profound effect on the structure of Li$_{7}$Zn$_{0.5}$SiS$_{6}$. This significantly impacts the Li ion conductivity and reveals how property-controlling cation ordering in argyrodites arises from compositional control. The realization of this unique ordering pattern offers new routes to tuning and further understanding the unexplored chemistries of argyrodite materials, in particular the unexpected increase in conductivity in the high-temperature disordered form compared to some lithium-only argyrodites.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.2c00320.

Further details on the synthetic isolation and structural characterization (diffraction, NMR, Raman) of Li$_{7}$Zn$_{0.5}$SiS$_{6}$, impedance results, elemental analysis (ICP), and tables of bond distances and angles in high-temperature F43m and room-temperature I4 structures (PDF)

Li$_{7}$Zn$_{0.5}$SiS$_{6}$ powder CIF for HT structure (CIF)
Li$_{7}$Zn$_{0.5}$SiS$_{6}$ powder CIF for RT structure (CIF)
Li$_{7}$Zn$_{0.5}$SiS$_{6}$ RT structure only, with dummy atoms used for bond distance restraints during refinement (CIF)

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Notes  
The authors declare no competing financial interest.  
Room-temperature and high-temperature crystal structures of Li$_7$Zn$_{0.5}$Si$_6$S$_{14}$ are deposited with ICSD numbers 2144376-2144384 and 2144370-2144373, respectively. Underlying data collected as part of this work is available via the University of Liverpool data repository at https://datacat.liverpool.ac.uk/id/eprint/1603.

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Dedication  
This paper is dedicated to Professor John Goodenough.

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