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The Structure of $Li_{3.4}Si_{0.7}S_{0.3}O_4$ by Powder Neutron Diffraction

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The structure of $Li_{4-2x}Si_{1-x}S_xO_4$ ($x \approx 0.32$) has been determined from neutron powder diffraction studies at room temperature, 350, and 700°C. This compound, which is a member of the series of ionic-conducting solid solutions formed between Li_4SiO_4 and Li_2SO_4, is isostructural with Li_3PO_4. The space group is *Pmnb*, with $a = 6.1701(1)$, $b = 10.6550(2)$, $c = 5.0175(1)$ Å at room temperature. The distribution of lithium ions suggests the occurrence of a defect cluster in which the inclusion of an interstitial lithium ion causes displacements of the adjacent lithium ions of the normal Li_3PO_4 structure. There appears to be little variation of the structure with temperature.

Introduction

Solid solutions derived from Li_4SiO_4 of the type $Li_{4-x}Si_{1-x}P_xO_4$, $Li_{4+x}Si_{1-x}Al_xO_4$, and $Li_{4-2x}Si_{1-x}S_xO_4$ are good lithium ion conductors (*1–4*) although Li_4SiO_4 itself is only poorly conducting. Tranqui *et al.* (*5*) describe an ordered structure for Li_4SiO_4 with a unit cell volume seven times larger than that determined by Völlenkle *et al.* (*6*) in which the lithium ions are disordered over six different sites. The latter arrangement is also found for $Li_{3.75}Si_{0.75}P_{0.25}O_4$ (*7*) although the occupancies of the Li sites are modified. From the observation of the various lithium ion separations, a possible ion conducting pathway has been identified in this compound involving an octahedrally coordinated Li ion (*7*). Other studies on $Li_{3.5}Zn_{0.25}GeO_4$ (*8*) and $Li_3Zn_{0.5}GeO_4$ (*9*) locate lithium ions in tetrahedral, octahedral, and threefold coordination in an orthorhombic structure closely derived from that of Li_3PO_4 (*10, 11*). The present study describes a neutron powder diffraction study at room temperature, 350, and 700°C on $Li_{3.36}Si_{0.68}S_{0.32}O_4$, a member of the series of solid solutions formed between Li_4SiO_4 and Li_2SO_4.

Experimental

Because of the relatively high neutron absorption of natural lithium, isotopically pure $^7Li_2CO_3$ supplied by AERE, Harwell, was used as the source of lithium ion.

The appropriate quantities of SiO_2, Li_2CO_3, and Li_2SO_4 were thoroughly mixed and heated for several hours in a Au crucible to give a nominal composition of $Li_{3.4}Si_{0.7}S_{0.3}O_4$. The sample was contained in a standard thin-walled vanadium sample can and neutron diffraction studies were made at room temperature, 350, and 700°C at a

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wavelength of 1.909 Å on the high-resolution diffractometer D1A at the ILL (Grenoble). Diffraction data were collected in steps of 0.05° over an angular range between 4.5 and 156° in 2θ.

Data Analysis

Indexing of the powder diffraction patterns was assisted by the use of the unit cell refinement program described by Pawley (*12*). This program, in the absence of a structural model, and assuming a Gaussian form for the peak shape, varies the intensity of each possible reflection and the cell parameters, zero point, etc. so as to obtain the best fit between the observed and calculated diffraction profiles. Using this approach it is clear that the unit cell of $Li_{4-2x}Si_{1-x}S_xO_4$ is doubled along *c* with respect to that of Li_4SiO_4 and that the structure is based on an orthorhombic cell similar to Li_3PO_4 (*10*). Several very weak peaks, however, were not consistent with this assignment. Careful scrutiny of these showed that they could be indexed on another orthorhombic cell with dimensions at room temperature of a = 9.385(5), b = 5.402(3), c = 4.654(2) Å. These are very close to those of Li_2SiO_3 (*13*), a likely side product of the sample preparation.

The structural refinements were performed by the Rietveld method (*14*) using the computer program of Thomas and Bendall (*15, 16*) which allows the analysis of a diffraction profile which contains peaks from up to three contributing phases. This program has been previously used to examine, for example, the low-temperature structure of deuterated $HUO_2AsO_4 \cdot 4H_2O$ with contaminating ice (*17*), where details of the relevant procedure may be found. The scattering lengths used were Si = 0.415, S = 0.285, O = 0.580, $^7Li = -0.220 \times$

TABLE I

FINAL PARAMETERS FOR $Li_{4-2x}Si_{1-x}S_xO_4$ AT ROOM TEMPERATURE IN SPACE GROUP *Pmnb*

Atom	Position	Point symmetry	x	y	z	B (Å^2)	N
Si/S	4*c*	*m*	1/4	0.4111(4)	0.3238(5)	—	4
O(1)	8*d*	1	0.0398(2)	0.3418(2)	0.2193(3)	—	8
O(2)	4*c*	*m*	1/4	0.0524(2)	0.2775(4)	—	4
O(3)	4*c*	*m*	1/4	0.9098(2)	0.8587(3)	—	4
Li(1)	8*d*	1	0.0024(8)	0.3334(6)	0.8147(14)	1.7(1)	6.5(1)
Li(2)	4*c*	*m*	1/4	0.5737(7)	0.8109(18)	1.7(1)	3.0(1)
Li(3)	8*d*	1	0.050(5)	0.485(3)	0.941(6)	1.1(7)	0.9(1)
Li(1A)	8*d*	1	−0.042(4)	0.332(2)	0.655(6)	1.1(7)	1.5(1)
Li(2A)	4*c*	*m*	1/4	0.599(3)	0.635(8)	1.1(7)	0.8(1)

Anisotropic temperature parameters (Å^2)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Si/S	0.9(2)	1.0(1)	0.8(1)	0	0	0.1(1)
O(1)	1.4(1)	0.9(1)	1.8(1)	−0.1(1)	−0.3(1)	0.2(1)
O(2)	1.1(1)	1.2(1)	1.6(1)	0	0	−0.3(1)
O(3)	0.8(1)	1.8(1)	1.7(1)	0	0	0.0(1)

Note. Parameters a = 6.1701(1), b = 10.6550(2), c = 5.0175(1) Å. ESD's of refined parameters in parenthesis. The anisotropic temperature factor has the form $T = \exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

10^{-12} cm (*18*). Refinements at the three different temperatures are described.

At 25°C. In the room-temperature diffraction pattern no peaks were visible which could be attributed to a multiple unit cell arising from long-range ordering of Si and S atoms. The refinement, therefore, was based on the Li_3PO_4 structure in space group *Pmnb* (*10*). In Li_3PO_4 there is a roughly hexagonally close-packed array of oxygen ions with phosphorous atoms and two types of lithium ion occupying $\frac{1}{8}$, $\frac{1}{4}$ [Li(1)], and $\frac{1}{8}$ [Li(2)] of the tetrahedral holes, respectively. The arrangement of the PO_4^{3-} tetrahedra is essentially that found in olivine Mg_2SiO_4 (*19*).

Throughout the angular range considered there were 195 reflections arising from $Li_{4-2x}Si_{1-x}S_xO_4$ as well as 83 weak reflections from the contaminating Li_2SiO_3. The latter were accounted for by including a contribution to the diffraction profile using the structural model obtained by single-crystal X-ray diffraction in space group *Cmc*2_1 (*13*). Only an effective scale factor, lattice constants and half-width parameters were refined for this phase; the atom positions and the thermal parameters were fixed at the values found in the X-ray study. For $Li_{4-2x}Si_{1-x}S_xO_4$ an initial model included only Li(1) and Li(2) whose occupancies were allowed to vary. The Si/S ratio was fixed at $x = 0.32$, which is compatible with the presence of a small amount of Li_2SiO_3 impurity. This initial refinement terminated with $R_{wp} = 10.5$, $R_E = 4.3\%$. (For description of the *R* factors see Ref. (*14*).) The occupancy factors for Li(1) and Li(2) indicated nearly fully occupied sites.

A difference Fourier map, however, indicated a number of possible interstitial lithium sites close to the centers of some tetrahedral and octahedral holes in the average close-packed oxygen array. Lithium atoms were thus inserted into the model and various refinements were performed varying their occupancy, isotropic temperature factors, and sometimes the atomic coordinates. Only three additional lithium sites were found to have significant occupancy. The first of these, Li(3), is associated with the octahedral site centered at the position 4*b* (0, 0, $\frac{1}{2}$) which has point symmetry $\bar{1}$ and shares a face with each of two ($\bar{1}$-related)

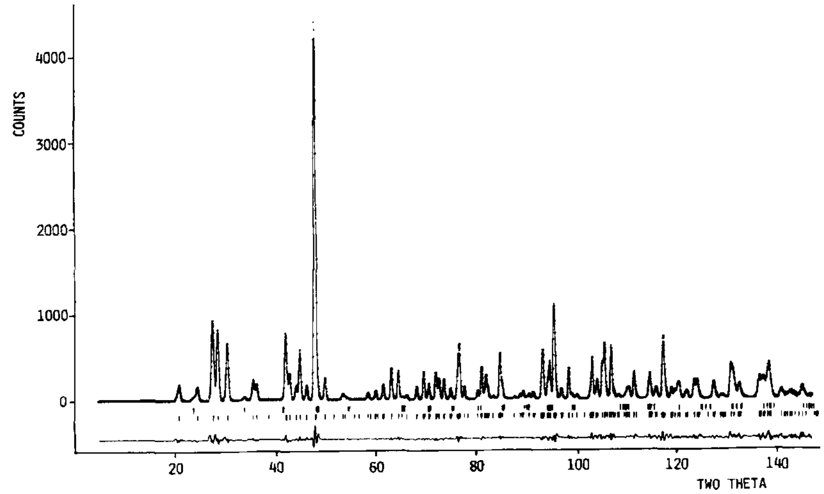

FIG. 1. Observed (points), calculated (full curve), and difference profiles for $Li_{4-2x}Si_{1-x}S_xO_4$ at room temperature. The positions of the Bragg peaks are marked for $Li_{4-2x}Si_{1-x}S_xO_4$ (bottom) and for the impurity phase Li_2SiO_3 (top).

Li(1) sites and two ($\bar{1}$-related) Li(2) sites. The 4*b* position is a large site with 4 equatorial oxygen atoms at distances of 2.03 Å [O(1)] and 1.98 Å [O(2)] from the center and two longer axial bonds of 2.56 Å [O(3)]. Both the Fourier map and the refinement suggest that the lithium ion is displaced from the center of the site by a distance of 0.46 Å toward a position of five-fold coordination. The other two sites, Li(1A) and Li(2A), are tetrahedral and each shares a face with an adjacent Li(1) or Li(2) site, respectively. In addition, Li(1A) also shares an edge with another adjoining Li(1) tetrahedron.

In the final refinement, anisotropic temperature factors for the silicate/sulfate framework were refined. The lithium ions, which are weakly scattering and only partially occupy the available sites, were refined isotropically with a single temperature factor for both Li(1) and Li(2) and another value for the interstitial ions Li(3), Li(1A), and Li(2A). There were, therefore, a total of 47 atomic positional, thermal and lithium occupancy parameters for $Li_{4-2x}Si_{1-x}S_xO_4$ in addition to the normal scale factor, cell constants, half-width, zero point, and asymmetry correction, plus the seven parameters exclusive to the secondary phase Li_2SiO_3. The refinement terminated with $R_{wp} = 7.6$, $R_p = 7.8$, $R_I = 3.8$ and $R_E = 4.3\%$. The final parameters are given in Table I, the observed and calculated profiles in Fig. 1, and important bond distances and angles are in Table II.

Discussion

The refinement shows that the structure of $Li_{4-2x}Si_{1-x}S_xO_4$, which is shown in Fig. 2, closely resembles that of Li_3PO_4 (*10, 11*). The (Si/S)O_4 group is only slightly distorted from a regular tetrahedron with an average (Si/S)–O bond length of 1.587 Å. This value is very near to the value of 1.59 Å obtained by linear interpolation between the mean Si–O distance of 1.635 Å found in Li_4SiO_4 (*5*) and the mean S–O bond distance of 1.50 Å in Li_2SO_4 (*20*) or $Li_2SO_4 \cdot H_2O$ (*21*), even though the structures and lithium ion arrangements are different in all these compounds. Comparison of the Li–O bond lengths and, more particularly, the bond angles with those of Li_3PO_4 (*10*) shows that the environment of the two major lithium ions Li(1) and Li(2) have a close resemblance in both compounds. For Li(1), O–

TABLE II

AVERAGE BOND DISTANCES (Å) AND ANGLES (DEGREES) IN $Li_{4-2x}Si_{1-x}S_xO_4$ AT ROOM TEMPERATURE INCLUDING Li–Li CONTACTS LESS THAN 2.35 Å

(Si/S)–O(1) × 2	1.582(2)	O(1)–(Si/S)–O(1)	110.2(2)
(Si/S)–O(2)	1.589(4)	O(1)–(Si/S)–O(2) × 2	109.6(1)
(Si/S)–O(3)	1.593(3)	O(1)–(Si/S)–O(3) × 2	109.1(1)
Mean (Si/S)–O	1.587	O(2)–(Si/S)–O(3)	109.2(2)
Li(1)–O(1)	1.945(6)	Mean O–(Si/S)–O	109.5
Li(1)–O(1)′	2.045(7)	O(1)–Li(1)–O(1)′	107.6(3)
Li(1)–O(2)	1.985(6)	O(1)–Li(1)–O(2)	117.4(3)
Li(1)–O(3)	1.938(6)	O(1)′–Li(1)–O(2)	98.9(3)
Mean Li(1)–O	1.978	O(1)–Li(1)–O(3)	113.5(3)
Li(2)–O(1) × 2	2.007(4)	O(1)′–Li(1)–O(3)	109.8(3)
Li(2)–O(2)	2.078(9)	O(2)–Li(1)–O(3)	108.6(3)
Li(2)–O(3)	1.944(8)	Mean O–Li(1)–O	109.3
Mean Li(2)–O	2.009	O(1)–Li(2)–O(1)	126.0(4)
Li(3)–O(1)	2.07(3)	O(1)–Li(2)–O(2) × 2	97.1(3)
Li(3)–O(1)′	2.09(3)	O(1)–Li(2)–O(3) × 2	111.7(2)
Li(3)–O(2)	2.01(3)	O(2)–Li(2)–O(3)	109.7(4)
Li(3)–O(2)′	2.07(3)	Mean O–Li(2)–O	108.9
Li(3)–O(3)	2.10(3)	O(1)–Li(3)–O(1)′	154.7(1.7)
Mean Li(3)–O	2.07	O(1)–Li(3)–O(2)	79.0(1.1)
Li(1A)–O(1)	1.88(3)	O(1)–Li(3)–O(2)′	95.6(1.3)
Li(1A)–O(1)′	2.24(3)	O(1)–Li(3)–O(3)	102.6(1.5)
Li(1A)–O(2)	1.88(2)	O(1)′–Li(3)–O(2)	96.9(1.4)
Li(1A)–O(3)	1.98(2)	O(1)′–Li(3)–O(2)′	77.2(1.1)
Mean Li(1A)–O	2.00	O(1)′–Li(3)–O(3)	102.5(1.4)
Li(2A)–O(1) × 2	2.03(2)	O(2)–Li(3)–O(2)′	154.2(1.8)
Li(2A)–O(2)	2.13(4)	O(2)–Li(3)–O(3)	106.2(1.4)
Li(2A)–O(3)	2.01(3)	O(2)′–Li(3)–O(3)	99.6(1.4)
Mean Li(2A)–O	2.05	Mean O–Li(3)–O	106.8
Li(1)–Li(3)	1.76(3)	O(1)–Li(1A)–O(1)′	102.1(1.2)
Li(1)–Li(3)′	2.31(3)	O(1)–Li(1A)–O(2)	126.3(1.4)
Li(1)–Li(1A)	0.85(3)	O(1)–Li(1A)–O(3)	114.1(1.2)
Li(2)–Li(3) × 2	1.68(3)	O(1)′–Li(1A)–O(2)	116.3(1.3)
Li(2)–Li(3)′ × 2	2.32(3)	O(1)′–Li(1A)–O(3)	75.2(9)
Li(2)–Li(2A)	0.92(4)	O(2)–Li(1A)–O(3)	111.1(1.3)
Li(3)–Li(3)′	0.91(5)	Mean O–Li(1A)–O	107.5
Li(3)–Li(1A)	2.25(4)	O(1)–Li(2A)–O(1)′	123.0(1.8)
Li(3)–Li(2A)	2.31(4)	O(1)–Li(2A)–O(2) × 2	115.0(1.0)
Li(1A)–Li(2A)′	2.07(4)	O(1)–Li(2A)–O(3) × 2	107.8(1.0)
		O(2)–Li(2A)–O(3)	77.6(1.2)
		Mean O–Li(2A)–O	107.7

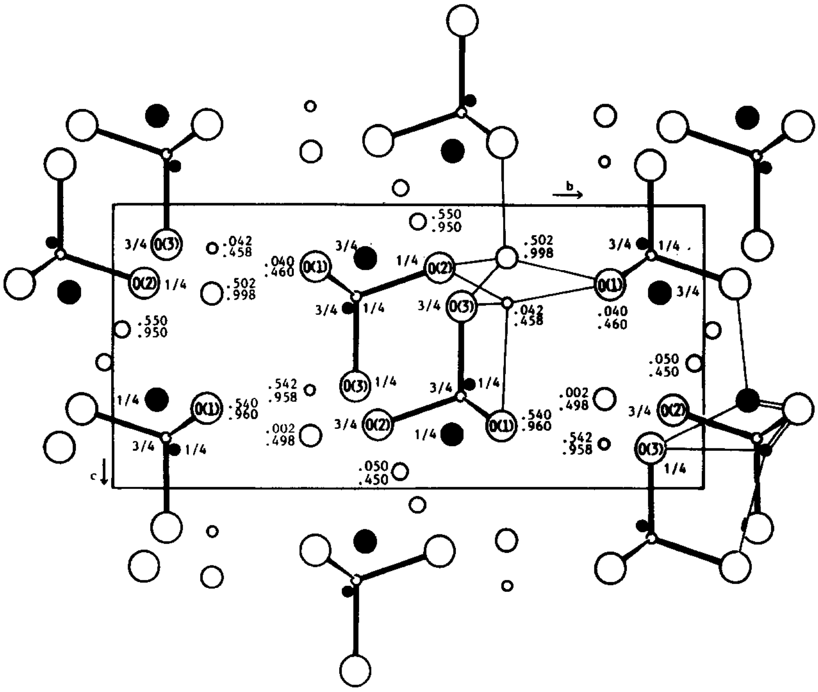

FIG. 2. Projection of the structure of $Li_{4-2x}Si_{1-x}S_xO_4$ parallel to [100]. The tetrahedral coordination of Li(1) [largest open circles], Li(2) [larger black circles], Li(1A) [smallest open circles], and Li(2A) [smaller black circles] is shown. Li(3) [intermediate open circles] is in an octahedral site.

Li–O bond angles vary from 98.9 to 117.4° (97–119° in Li_3PO_4), whereas for Li(2) these angles lie between 97.1 and 126.0° (95–125° in Li_3PO_4). Generally the lengths of the lithium–oxygen bond distances are between 1.88 and 2.24 Å, which is within the ranges of 1.84–2.43 Å for four- and five-coordinate lithium in ordered Li_4SiO_4 (*5*). The Li(1A) coordination is particularly distorted. The lithium ion is displaced away from the center of its site toward the face it shares with the neighboring Li(1) site which is a position resembling trigonal coordination.

Lithium ion distribution. Table II shows that the separations between Li(1) and the neighboring Li(1A), and between Li(2) and Li(2A), are very short at 0.85(3) and 0.92(4) Å, respectively. It is, therefore, most unlikely that both sites of an actual pair could be simultaneously occupied. Indeed, the total refined occupancy of each pair of sites, Li(1)/Li(1A) or Li(2)/Li(2A) is close to 8 and 4, respectively, which is the maximum number of lithium ions which can be accommodated while avoiding energetically unfavorable close contacts between neighboring sites. In ordered Li_4SiO_4 there are no Li–Li distances less than 2.30 Å (*5*).

With $x \approx 0.32$, a total lithium content of 13.4 atoms per unit cell is expected. The total occupancy from the refinement is 12.7(5) which is satisfactory agreement considering the small scattering length and disordered nature of the lithium ions in this compound. However, as the Li(1)/Li(1A) and Li(2)/Li(2A) sites are essentially full, the missing lithium is apparently reflected in the occupancy of Li(3) which is 0.9(1) instead of ≈1.4. This may be an indication that our chosen model is to some extent inadequate because it fails to account, for example, for the anisotropic motion of the

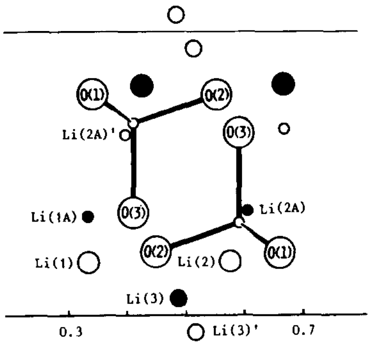

FIG. 3. The proposed short-range ordering of the lithium ions in $Li_{4-2x}Si_{1-x}S_xO_4$. Filled circles, occupied sites; open circles, vacant sites.

lithium atoms, anharmonicity or the effects of Si/S short-range order, and so could lead to inaccuracies in the structural parameters and an underestimation of the calculated errors. If, on the other hand, the occupancy of Li(3) is correctly determined, there must be further Li sites with very small occupancies which we have not detected.

In either case the lithium distribution is fairly well determined and some broad conclusions can be drawn. The various lithium–lithium contact distances are shown in Fig. 3. They suggest a simple scheme whereby the observed lithium site occupancies may at least in part be rationalized. The inclusion of an Li(3) into the Li_3PO_4 structure would bring it into conflict with two neighboring Li(1) and Li(2) atoms (at 1.76(3) and 1.68(3) Å, respectively), if these latter two sites were full. It is not surprising, therefore, that lithium ions are repelled into the adjacent Li(1A) and Li(2A) positions which are at 2.25(4) and 2.32(3) Å and which have occupancies quite similar to those of Li(3). In the case of Li(1A) this ion does not reside at the center of its new site but is displaced toward the triangular face it shares with the vacant adjacent Li(1) position. The Li(1A)–Li(3) distance of 2.25(4) Å, however, is slightly shorter than the minimum value of 2.30 Å for a Li–Li sepa-

TABLE III

FINAL PARAMETERS FOR $Li_{4-2x}Si_{1-x}S_xO_4$ AT 350°C IN SPACE GROUP *Pmnb*

Atom	Position	x	y	z	B (Å^2)	N
Si/S	4*c*	1/4	0.4104(3)	0.3240(5)	—	4
O(1)	8*d*	0.0418(2)	0.3415(1)	0.2196(3)	—	8
O(2)	4*c*	1/4	0.0508(2)	0.2762(4)	—	4
O(3)	4*c*	1/4	0.9094(2)	0.8607(3)	—	4
Li(1)	8*d*	0.0017(9)	0.3344(6)	0.8122(17)	3.4(2)	6.4(2)
Li(2)	4*c*	1/4	0.5729(8)	0.8094(22)	3.4(2)	2.9(1)
Li(3)	8*d*	0.058(7)	0.488(9)	0.940(3)	3.5(7)	0.9(1)
Li(1A)	8*d*	−0.040(10)	0.336(4)	0.657(9)	3.5(7)	1.7(2)
Li(2A)	4*c*	1/4	0.601(5)	0.648(9)	3.5(7)	0.8(1)

Anisotropic temperature parameters (Å^2)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Si/S	1.5(1)	1.9(1)	1.5(1)	0	0	0.0(1)
O(1)	2.5(1)	1.9(1)	2.9(1)	−0.3(1)	−0.4(1)	0.1(1)
O(2)	1.9(1)	2.1(1)	2.7(1)	0	0	−0.4(1)
O(3)	1.8(1)	3.3(1)	2.1(1)	0	0	0.0(1)

$a = 6.2217(1)$; $b = 10.7109(2)$; $c = 5.0571(1)$ Å
$R_{wp} = 7.4$; $R_p = 7.8$; $R_I = 4.2$; $R_E = 4.2\%$

ration which probably reflects the difficulty of accurately defining the positional, thermal, and occupancy parameters of a weakly scattering and disordered atom close to a center of symmetry.

High temperature. The data collected at 350 and 700°C showed a very close resemblance to those obtained at room temperature. The same procedure was followed except that an additional overall temperature factor was refined for the secondary phase Li_2SiO_3. There is little change in the structure of $Li_{4-2x}Si_{1-x}S_xO_4$ between room temperature and 700°C and a very similar arrangement of lithium ions is found. During the refinements it was noted that the weakly occupied interstitial lithium ions became more difficult to define with the increase of their thermal vibrations with temperature. This resulted in a further shortening of the distance between Li(1A) and Li(3) (2.25(4) Å at room temperature). It was thus decided to constrain this distance to be equal to the refined room-temperature value. The introduction of this constraint, at 350 and at 700°C, had only a minor effect on the R-factors. The final parameters are given in Tables III and IV, and some bond lengths in Table V.

Generally it can be seen that, while Li–O bond lengths increase with temperature, as might be expected, the average (Si/S)–O bond length appears to decrease. The anisotropic temperature factors of the oxygen atoms indicate that the principal axes of the thermal ellipsoids are almost perpendicular to the (Si/S)–O bond directions and suggest that the $(Si/S)O_4$ tetrahedra are performing librational motion whose amplitude increases with temperature. The apparent decrease in the (Si/S)–O bond lengths, therefore, is probably not a real effect since, as is well established, bond lengths obtained by diffraction experiments appear foreshortened in librating species (*22*).

TABLE IV

Final Parameters for $Li_{4-2x}Si_{1-x}S_xO_4$ at 700°C in Space Group *Pmnb*

Atom	Position	x	y	z	B (Å^2)	N
Si/S	4*c*	1/4	0.4100(3)	0.3223(6)	—	4
O(1)	8*d*	0.0442(3)	0.3419(1)	0.2195(3)	—	8
O(2)	4*c*	1/4	0.0485(2)	0.2769(5)	—	4
O(3)	4*c*	1/4	0.9086(3)	0.8655(4)	—	4
Li(1)	8*d*	0.0000(10)	0.3340(7)	0.8092(21)	5.1(2)	6.3(2)
Li(2)	4*c*	1/4	0.5677(9)	0.8157(18)	5.1(2)	3.0(1)
Li(3)	8*d*	0.068(21)	0.485(2)	0.925(6)	6.6(8)	1.3(1)
Li(1A)	8*d*	−0.032(2)	0.340(1)	0.633(6)	6.6(8)	1.8(2)
Li(2A)	4*c*	1/4	0.628(3)	0.618(7)	6.6(8)	1.0(1)

Anisotropic temperature parameters (Å^2)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Si/S	1.6(1)	2.4(1)	2.8(2)	0	0	0.6(2)
O(1)	3.5(1)	3.6(1)	3.8(1)	−0.7(1)	−0.7(1)	0.1(1)
O(2)	2.7(1)	3.2(1)	4.4(1)	0	0	−0.1(1)
O(3)	2.9(1)	4.4(1)	2.6(1)	0	0	0.1(1)

$a = 6.2859(2)$; $b = 10.7716(2)$; $c = 5.1059(1)$ Å

$R_{wp} = 7.3$; $R_p = 8.2$; $R_I = 4.5$; $R_E = 4.3\%$

TABLE V

AVERAGE BOND LENGTHS (Å) IN $Li_{4-2x}Si_{1-x}S_xO_4$ AT 350 AND 700°C

	350°C	700°C
(Si/S)–O(1) × 2	1.581(2)	1.577(2)
(Si/S)–O(2)	1.587(4)	1.576(4)
(Si/S)–O(3)	1.595(3)	1.594(3)
Mean (Si/S)–O	1.586	1.581
Li(1)–O(1)	1.960(7)	1.969(8)
Li(1)–O(1)′	2.077(9)	2.115(11)
Li(1)–O(2)	1.999(6)	2.025(7)
Li(1)–O(3)	1.949(7)	1.978(8)
Mean Li(1)–O	1.996	2.022
Li(2)–O(1) × 2	2.039(4)	2.098(5)
Li(2)–O(2)	2.109(11)	2.091(10)
Li(2)–O(3)	1.950(9)	1.947(10)
Mean Li(2)–O	2.034	2.059
Li(3)–O(1)	2.11(8)	2.16(3)
Li(3)–O(1)′	2.10(9)	2.12(5)
Li(3)–O(2)	1.99(5)	2.02(8)
Li(3)–O(2)′	2.13(5)	2.17(12)
Li(3)–O(3)	2.11(5)	2.05(8)
Mean Li(3)–O	2.09	2.10
Li(1A)–O(1)	1.93(4)	2.01(2)
Li(1A)–O(1)′	2.27(5)	2.17(3)
Li(1A)–O(2)	1.88(5)	1.96(2)
Li(1A)–O(3)	1.97(6)	1.92(2)
Mean Li(1A)–O	2.01	2.02
Li(2A)–O(1) × 2	2.03(2)	2.05(2)
Li(2A)–O(2)	2.21(5)	2.19(4)
Li(2A)–O(3)	2.06(6)	2.36(3)
Mean Li(2A)–O	2.08	2.16
Li(1)–Li(3)	1.80(9)	1.79(4)
Li(1)–Li(3)′	2.31(8)	2.41(4)
Li(1)–Li(1A)	0.83(5)	0.92(3)
Li(2)–Li(3) × 2	1.64(7)	1.55(10)
Li(2)–Li(3)′ × 2	2.39(5)	2.46(11)
Li(2)–Li(2A)	0.87(5)	1.20(4)
Li(3)–Li(3)′	0.98(6)	1.19(14)
Li(3)–Li(1A)[a]	2.25	2.25
Li(3)–Li(2A)	2.26(7)	2.47(7)
Li(1A)–Li(2A)′	2.13(6)	1.91(4)

[a] Fixed at room temperature value.

Conclusion

The refinements show that $Li_{4-2x}Si_{1-x}S_xO_4$ adopts a structure which can be interpreted in terms of the lithium phosphate structure with the additional lithium atoms incorporated exclusively (or nearly exclusively) in one site. At the same time, displaced normal lithium ions are observed so that it is plausible to associate the three resulting interstitial lithium ions with a defect cluster in which two normal lithium ions are displaced for each additional Li(3) introduced.

The agreement of the refined lithium site occupancies with this model is certainly not perfect, either because the errors or the occupation numbers are larger than estimated, or because of the presence of a further undetected site. Nevertheless it provides a reasonable first description as Table VI shows.

No major structural changes are observed from room temperature to 700°C, which is in accord with the conductivity (σ) results which show a straight-line log σ vs $1/T$ plot in the temperature range up to 200°C (*1*).

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TABLE VI

COMPARISON OF THE OCCUPATION OF SITES FOR THE SIMPLE CLUSTER MODEL WITH THE OBSERVED VALUES

Site	Model	Observed		
		25°C	350°C	700°C
Vacancy Li(1)	1.4	1.5(1)	1.6(2)	1.7(2)
Vacancy Li(2)	1.4	1.0(1)	1.1(1)	1.0(1)
Li(3)	1.4	0.9(1)	0.9(1)	1.3(1)
Li(1A)	1.4	1.5(1)	1.7(2)	1.8(2)
Li(2A)	1.4	0.8(1)	0.8(1)	1.0(1)

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