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The Crystal Structure of $Li_{3.75}Si_{0.75}P_{0.25}O_4$ and Ionic Conductivity in Tetrahedral Structures*

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The crystal structure of $Li_{4-x}Si_{1-x}P_xO_4$ (x = 0.25), a member of the solid solution series between Li_4SiO_4 and Li_3PO_4, was determined by X-ray diffraction and refined to an R = 0.038 for 478 F_{obs}. The space group is $P12_1/m1$ and the cell constants are a = 5.1157(6), b = 6.1162(9), c = 5.3088(8) Å and β = 90.40(1)°. It is isostructural with disordered Li_4SiO_4 and with the substructure of ordered Li_4SiO_4. The ionic conductivity of $Li_{3.75}Si_{0.75}P_{0.25}O_4$ is more than three orders of magnitude higher than for ordered Li_4SiO_4 for which it is $10^{-5}(\Omega m)^{-1}$ at room temperature. All Li sites are only partially occupied. The highest probability of close Li–Li approaches exists between the octahedral site and an adjoining tetrahedral location. These two sites define a lithium pathway parallel to the b-direction in the structure.

Introduction

Solid solutions between Li_4SiO_4 and Li_3PO_4 show high Li ion conductivity and low activation energies for the lithium ions (*1–4*). An interpretation of the mobility of lithium in these ionic conductors in terms of their crystal structure is only possible after the details of the structures are known. Therefore, the crystal structure of one of these solid solutions, $Li_{3.75}Si_{0.75}P_{0.25}O_4$, was investigated by single crystal X-ray diffraction methods.

The two end members of the solid solution series are not isostructural. In the phosphate compound all cations are in tetrahedral oxygen coordination. The oxygen atoms themselves are arranged in a slightly distorted hexagonal closest packing (hcp). If more than one tetrahedron per close packed oxygen atom is filled in hcp the tetrahedra must share faces with each other. Since this is energetically not favorable, the excess Li atoms in Li_4SiO_4 occupy some nontetrahedral positions with oxygen coordinations for Li of five and six.

Both end members are reported to occur in high and low temperature forms. Dubey and West (*5*) gave cell constants and symmetry information based on X-ray powder diffraction data for high (above 700°C) and low Li_4SiO_4 (Table I). The structure of an ordered form of Li_4SiO_4 was recently solved by Tranqui *et al.* (*6*). It has a cell volume seven times as large (a = 11.546(3), b = 6.090(2), c = 16.645(3) Å, β = 99.5(1)° and with space group $P12_1/m1$) as the cell volume given for the low temperature form (*5*) and for the structure determined by Völlenkle *et al.* (*7*), in which the Li atoms are statistically distributed over six different

* Dedicated to Professor A. F. Wells on his 70th birthday.

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TABLE I

CHEMICAL AND CRYSTALLOGRAPHIC DATA FOR SEVERAL Li ORTHOSILICATES AND ORTHOPHOSPHATES[a]

Compound	Form	Space Group	a (Å)	b (Å)	c (Å)	β	ϵ	Reference
Li_4SiO_4	L	—	5.16(1)	6.12(1)	5.30(1)	90.1(1)	0.843	*5*
Li_4SiO_4 (subcell)	L?	$P1\frac{2_1}{m}1$	5.147(1)	6.094(1)	5.293(1)	90.33(2)	0.843	*6* and This work
Li_4SiO_4 (at 800°C)	H	—	5.23(1)	6.32(1)	5.45(2)	90.8(1)	0.829	*5*
Li_4SiO_4	H?	$P1\frac{2_1}{m}1$	5.14	6.10	5.30	90.5	0.841	*7*
$Li_{3.75}Si_{0.75}P_{0.25}O_4$	—	—	5.107(2)	6.106(2)	5.301(2)	90.36(4)	0.835	*1*
$Li_{3.8}Si_{0.8}P_{0.2}O_4$	—	—	5.142	6.105	5.292	90.25	0.842	*3*
$Li_{3.75}Si_{0.75}P_{0.25}O_4$	—	$P1\frac{2_1}{m}1$	5.1157(6)	6.1162(9)	5.3088(8)	90.40(1)	0.835	This work
Li_3PO_4	L	$P2_1mn$	4.8554(10)	6.1150(10)	5.2394(11)	90	0.798	*8*
Li_3PO_4	H	$P\frac{2_1}{c}\frac{2_1}{m}\frac{2_1}{n}$	4.9228(5)	6.1147(5)	10.475(1)	90	0.810	*9*

[a] H = high temperature form; L = low temperature form; the value ϵ is the ratio between the thickness of one hexagonal layer and the mean diameter of one atom within such layer, taken as $(b/2 + c/\sqrt{3})/2$: the ideal value for hcp is $\sqrt{2/3} = 0.8165$. Estimated standard deviations are listed here and elsewhere in this paper in parentheses, following the value, in units of the least significant digit.

sites. The available experimental data are insufficient to prove it, but it is conceivable that the crystal structure described by Völlenkle *et al.* is a quenched form of the high temperature modification of Li_4SiO_4 reported by Dubey and West. The subcell of the ordered modification is essentially identical with the cell found for the disordered form of Li_4SiO_4 (Table I).

The low temperature polymorph of Li_3PO_4(LT) (below 502°C), as described by Keffer *et al.* (*8*), is simply a lower symmetry ordered derivative of the wurtzite type structure. Since wurtzite crystallizes in a polar space group ($P6_3mc$) all coordination tetrahedra are pointing in the same direction. In the high temperature form of Li_3PO_4(HT) [determined in 1960 (*10*) and recently refined (*11*)], which crystallizes in a centric space group with a cell volume twice as large as the low temperature form, the coordination tetrahedra are pointing alternatively in opposite directions, as they do in Li_4SiO_4. However, the up–down patterns are different for Li_3PO_4(HT) and Li_4SiO_4. Actually, the space group, unit cell size, and the orientation pattern of the tetrahedra of Li_3PO_4(HT) correspond to the olivine type, Mg_2SiO_4. However, in olivine the Mg atoms are in octahedral coordination, while the Si are tetrahedrally coordinated. For all the compounds listed in Table I, except for Li_4SiO_4(HT) at 800°C, the maximum deviation between the b cell constant is 0.02 Å, while it is 0.07 Å for c and 0.30 Å for the a constant. In the setting used here cell constant a corresponds to the pseudohexagonal direction, while b and c are lying in the pseudohexagonal plane. The small a constant for Li_3PO_4(LT) is only partly related to the chemical composition of the compound. It is also due to the small ϵ-value of Li_3PO_4(LT), which, however, is typical for oxide structures derived from the wurtzite type (*12*). For these the ϵ-values range from 0.746 to 0.808. Typical for

the olivine-related types (with tetrahedra pointing in opposite directions) are values from 0.783 to 0.843, that is, they are close to the ideal value (0.817).

Experimental

The sample of $Li_{3.75}Si_{0.75}P_{0.25}O_4$ used for the structural studies was prepared by Shannon *et al.* (*1*) by pulling from the melt. It corresponds most closely to the vacuum melted specimen [see Fig. 15 in (*1*)] used for measurements of ionic conductivity. The bulk of the sample consisted of crystals with polysynthetically twinned lamellae which, when viewed in a polarizing microscope, were extinguishing under crossed polarizers in different positions. Such crystals, when studied on the precession camera, were invariably composed of many different crystallites, with apparently random relative orientations. The crystal selected for quantitative X-ray work had the approximate dimensions of 0.23 × 0.13 × 0.075 mm, was clear and transparent, and displayed for the bulk of its volume a uniform extinction under crossed polarizers. Precession camera studies showed it to be a twinned crystal with the two components related by a mirror in plane $(10\bar{1})$ or a twofold axis in [101]. Consequently all reflections of planes with indices for which $h + l = 0$ are directly superimposed for the two parts. Because β is close to 90°, reflections for planes with indices $h + l = |1|$ and $|2|$ could not be resolved. The cell constants determined at room temperature by the setting of 13 reflections (2θ from 24 to 47°) on a computer-controlled (*13*) X-ray diffractometer are within 0.01 Å of the values determined by X-ray powder diffraction for the corresponding sample (*1*); however, the differences are statistically significant. The cause of the discrepancy is not known, due either to a systematic error in the measurement (where the values more likely to be viewed with suspicion are those from our single crystal determination) or to a real difference in the materials. After all, the crystal selected for single crystal study is *not* representative of the large mass of the sample.

A plot of all available precise cell constants for chemical compositions $Li_{4-x}Si_{1-x}P_xO_4$ between the subcell of Li_4SiO_4 and high temperature Li_3PO_4 shows that a discontinuity exists between the x values 0.4 and 0.5 (Fig. 1). The chemical composition of our sample and its cell constants place it clearly to the left of the discontinuity. The cell constants determined for our specimen correspond to the subcell observed for Li_4SiO_4. Single crystal photographs with exposure times up to 135 hr failed to show superstructure reflections

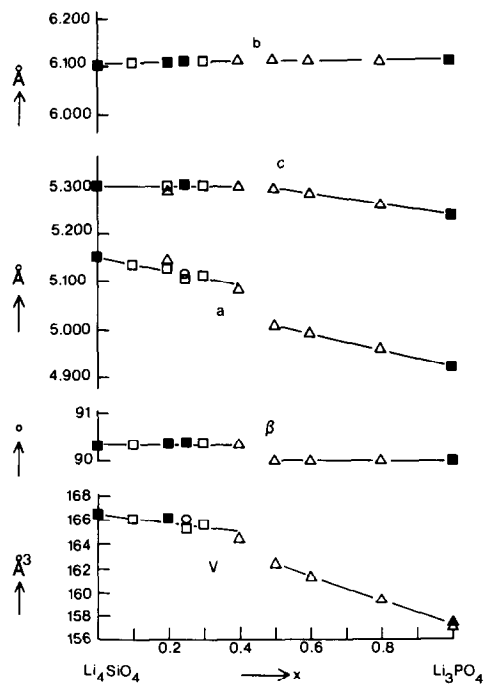

FIG. 1. Cell constants, angle β, and cell volume for the solid solution series $Li_{4-x}Si_{1-x}P_xO_4$. Data are: △ from Hu *et al.* (*3*); □ from Shannon *et al.* (*1*); ▲ from Swanson *et al.* (*9*); ○, this work; overlapping multiple points are indicated by ■. In order to make the values comparable, the c cell length entered here is for $x > 0.5$ one-half of the actual value.

which would be evidence for any larger unit cell, for instance, such one as was observed for ordered Li_4SiO_4 (*6*). Within the precision of our experiment we cannot find evidence for a larger unit cell.

Three-dimensional X-ray diffraction intensities were collected in two quadrants up to $\sin\theta/\lambda$ = 0.9 Å^{-1} on a computer-controlled four-circle diffractometer using graphite-monochromatized Mo$K\alpha$ radiation (λ = 0.71069 Å). For details of data-measuring procedures and for a list of computer programs used in the course of this work, see Ref. (*14*). The total number of measured reflections was 2309. After averaging symmetrically equivalent intensities and applying the Lorentz-polarization correction, this resulted in 1111 F_{obs}, of which 733 were smaller than 3σ. The remaining 478 F_{obs} were used for the refinement. During the course of intensity data collection, the crystal suffered radiation damage, and could not be used for further experiments.

Cell constants and space groups are given in Table I, the cell volume is V = 166.1 Å^3, the number of formula units in the unit cell Z = 2, the calculated density D_x = 2.377 Mgm^{-3}, the formula weight M_r = 118.82, the absorption coefficient is μ(Mo$K\alpha$) = 0.554 mm^{-1}, the general positions are $\pm$ (x, y, z; x, $\frac{1}{2} - y$, z).

Starting with the positional parameters for disordered Li_4SiO_4 (*7*) the refinement proceeded smoothly to an $R = \Sigma||F_0|-|F_c||/\Sigma|F_0|$ of 0.038 for 478 F_{obs}. The corresponding weighted $R_w = [\Sigma w(|F_0|-|F_c|)^2/\Sigma wF_0^2]^{1/2}$ was 0.041. The scattering curve used (*15*) for the atom at the Si,P position was taken as $Si_{0.75}P_{0.25}$. Refinement of anisotropic temperature factors was success-

TABLE II

POSITIONAL COORDINATES, MULTIPLICITIES, SITE SYMMETRIES, AND ISOTROPIC TEMPERATURE FACTORS, A^2 ($B_{equivalent}$ FOR (Si,P), Si, AND O, B FOR Li ATOMS) IN $Li_{3.75}Si_{0.75}P_{0.25}O_4$ (1) AND IN THE SUBSTRUCTURE OF Li_4SiO_4 (2)

Atom	Multiplicity	Site symmetry	x	y	z	B
			1			
$Si_{0.75}P_{0.25}$	2	m	0.6696(2)	$\frac{1}{4}$	0.3252(2)	0.87(2)
O(1)	4	1	0.7763(3)	0.0334(3)	0.1863(3)	1.24(5)
O(2)	2	m	0.3531(4)	$\frac{1}{4}$	0.3162(4)	1.20(7)
O(3)	2	m	0.7705(4)	$\frac{1}{4}$	0.6143(4)	1.22(7)
Li(1)	4	1	0.174(1)	0.003(1)	0.175(1)	1.0(1)
Li(2)	2	m	0.396(6)	$\frac{1}{4}$	0.703(5)	1.5
Li(3)	2	m	0.179(2)	$\frac{1}{4}$	0.638(2)	2.1(3)
Li(4)	4	1	0.398(2)	0.963(3)	0.148(3)	2.7(3)
Li(5)	4	1	0.066(4)	0.051(5)	0.459(5)	2.0(6)
Li(6)	2	m	0.031(6)	$\frac{1}{4}$	0.988(6)	1.5
			2			
Si	2	m	0.66515(8)	$\frac{1}{4}$	0.32600(7)	0.84(1)
O(1)	4	1	0.7745(2)	0.0302(1)	0.1841(1)	0.97(2)
O(2)	2	m	0.3479(2)	$\frac{1}{4}$	0.3149(2)	1.00(3)
O(3)	2	m	0.7672(2)	$\frac{1}{4}$	0.6204(2)	1.03(3)
Li(1)	4	1	0.1651(7)	0.0047(6)	0.1721(6)	1.00(4)
Li(2)	2	m	0.3930(16)	$\frac{1}{4}$	0.6999(14)	2.08(10)
Li(3)	2	m	0.1680(14)	$\frac{1}{4}$	0.6363(13)	1.14(9)
Li(4)	4	1	0.4010(11)	0.9650(9)	0.1502(9)	1.60(6)
Li(5)	4	1	0.0666(18)	0.0372(17)	0.4601(16)	1.49(12)
Li(6)	2	m	0.0183(23)	$\frac{1}{4}$	0.9553(21)	3.35(18)

TABLE III

ANISOTROPIC TEMPERATURE FACTORS FOR THE HEAVY ATOMS IN $Li_{3.75}Si_{0.75}P_{0.25}O_4$ (1) AND IN THE SUBSTRUCTURE OF Li_4SiO_4 (2)[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
			1			
Si,P	0.0117(2)	0.0043(2)	0.0066(2)	0	−0.0007(2)	0
O(1)	0.0141(4)	0.0078(4)	0.0095(4)	0.0025(3)	−0.0007(4)	−0.0014(3)
O(2)	0.0121(6)	0.0061(6)	0.0124(6)	0	−0.0015(6)	0
O(3)	0.0162(7)	0.0062(5)	0.0092(5)	0	−0.0044(6)	0
			2			
Si	0.0121(1)	0.00345(6)	0.00653(8)	0	−0.0009(1)	0
O(1)	0.0092(2)	0.0047(1)	0.0110(2)	0.0008(2)	0.0014(2)	−0.0012(1)
O(2)	0.0084(3)	0.0055(2)	0.0115(3)	0	0.0003(2)	0
O(3)	0.0124(3)	0.0051(2)	0.0090(2)	0	−0.0036(2)	0

[a] The form of the temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

ful for the heavy atoms (Si,P) and O, while for the Li atoms it led to divergence of the refinement. Consequently, only isotropic temperature factors and population parameters were refined for all Li atoms except for Li(2) and Li(6), where high correlations between the isotropic temperature factors and the very small population parameters resulted in diverging refinements as well. Therefore, for Li(2) and Li(6), the temperature factors, B, were kept constant at the arbitrary value of 1.5 Å^2. The highest peak in the final difference synthesis has a density of 0.4 electrons/Å^3. It is located halfway between the Si,P and O(1) atoms. The final coordinates, temperature factors, and occupancies are listed in Tables II, III, and IV.

For comparative purposes we are reporting here also the substructure refinement of Li_4SiO_4. The crystal used was from the same preparation as the one used for determining the superstructure of Li_4SiO_4 (*6*). Cell constants (see Table I) were obtained by computer controlled centering of 15 reflections, followed by least-squares refinement of the setting angles. Systematic absences were observed for $k = 2n + 1$ for $0k0$ reflections. Intensity collection was carried out on a crystal with dimensions of about

TABLE IV

OCCUPANCY FACTORS IN Li_4SiO_4 AND IN $Li_{3.75}Si_{0.75}P_{0.25}O_4$

	Disordered Li_4SiO_4, Völlenkle *et al.* (*7*)	Substructure of ordered Li_4SiO_4, constrained, this work	Occupied over available sites in ordered Li_4SiO_4 (*6*)	Disordered $Li_{3.75}Si_{0.75}P_{0.25}O_4$, this work
Li(1)	$\frac{2}{3}$	0.567(6)	$\frac{4}{7} = 0.571$	0.59(2)
Li(2)	$\frac{1}{2}$	0.530(10)	$\frac{4}{7} = 0.571$	0.20(2)
Li(3)	$\frac{1}{2}$	0.414(10)	$\frac{3}{7} = 0.429$	0.56(4)
Li(4)	$\frac{1}{3}$	0.472(6)	$\frac{3}{7} = 0.429$	0.44(3)
Li(5)	$\frac{1}{3}$	0.247(6)	$\frac{2}{7} = 0.286$	0.20(3)
Li(6)	$\frac{1}{3}$	0.484(12)	$\frac{3}{7} = 0.429$	0.21(2)

0.20 × 0.22 × 0.22 mm. The $\theta - 2\theta$ scan technique was used on a computer-controlled four-circle diffractometer with graphite-monochromatized Mo$K\alpha$ radiation (λ = 0.71073 Å) up to 2θ = 80° at varying scan rates (2 to 4° min^{-1}). Background counts were taken for time periods as long as the scan time at both ends of the scan range [2θ(Mo$K\alpha_1$) − 1° to 2θ(Mo$K\alpha_2$) + 1°]. Total number of reflections measured was 1294, of which 1207 were independent. Absorption corrections were not applied. A total of 890 F_{obs} which had $F^2_{obs} > 3\sigma(F^2_0)$ were used for the refinement starting with the parameters reported by Völlenkle *et al.* (*7*). The final positional, thermal, and occupancy parameters (Tables II, III, and IV) yielded an R of 0.033 and an $R(w)$ of 0.058. The occupancy factors were refined by constraining the total contents of the asymmetric unit to two Li atoms. Interatomic distances are listed in Table V. The F_0 and F_c tables for both refinements are deposited.[1]

Discussion

(Si,P)O_4 Group

The geometry of the (Si,P)O_4 group is hardly distorted, both in its (Si,P)–O distances and in its O–(Si,P)–O angles (Table V). The observed mean P–O distance in Li_3PO_4(HT) is 1.551 Å (*11*), the observed mean Si–O distance in the substructure of ordered Li_4SiO_4 is 1.638 Å (*6*). By linear interpolation this should result in a mean ($Si_{0.75}P_{0.25}$)–O distance of 1.616 Å, in excellent agreement with the observed value of 1.615 Å. Since the mean coordination numbers (CN_m) of the oxygen atoms of the SiO_4, PO_4, and $Si_{0.75}P_{0.25}O_4$ groups are different in these compounds, it is preferable to compare the observed mean distance with a calculated distance based on predictive equations for SiO_4 and PO_4. According to a regression equation (*16*), the mean Si–O distance in $Li_{3.75}Si_{0.75}P_{0.25}O_4$ should be: $d(\text{Si–O})_m = 1.554 + 0.034\text{NSEC}_m +$

TABLE V

SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) FOR $Li_{3.75}Si_{0.75}P_{0.25}O_4$ (1) AND THE SUBSTRUCTURE OF Li_4SiO_4 (2)

		1	
(Si,P)–O(1) × 2	1.613(2)	O(1)–(Si,P)–O(1)	110.4(1)
(Si,P)–O(3)	1.616(2)	O(1)–(Si,P)–O(3) × 2	109.1(1)
(Si,P)–O(2)	1.619(3)	O(1)–(Si,P)–O(2) × 2	109.1(1)
Mean (Si,P)–O	1.615	O(3)–(Si,P)–O(2)	109.9(1)
		Mean O–(Si,P)–O	109.5
Li(1)–O(2)	1.917(6)	Li(2)–O(3)	1.98(3)
Li(1)–O(3)	1.929(6)	Li(2)–O(1) × 2	2.03(2)
Li(1)–O(1)	1.949(6)	Li(2)–O(2)	2.06(3)
Li(1)–O(1)	2.044(5)	Mean Li(2)–O	2.03
Mean Li(1)–O	1.960		
Li(3)–O(2)	1.932(11)	Li(4)–O(1)	1.98(2)
Li(3)–O(1) × 2	1.981(5)	Li(4)–O(2)	1.98(2)
Li(3)–O(3)	2.093(10)	Li(4)–O(1)	1.99(1)
Mean Li(3)–O	1.997	Li(4)–O(3)	2.01(2)
		Mean Li(4)–O	1.99
Li(5)–O(2)	2.06(3)	Li(6)–O(1) × 2	2.14(2)
Li(5)–O(3)	2.06(3)	Li(6)–O(1) × 2	2.20(2)
Li(5)–O(1)	2.07(2)	Li(6)–O(3)	2.38(3)
Li(5)–O(1)	2.11(3)	Li(6)–O(2)	2.39(3)
Li(5)–O(3)	2.11(3)	Mean Li(6)–O	2.24
[Li(5)–O(2)	3.07(3)]		
Mean Li(5)–O	2.08		
		2	
Si–O(2)	1.634(1)	Li(4)–O(2)	1.963(5)
Si–O(1) × 2	1.637(1)	Li(4)–O(1)	1.971(6)
Si–O(3)	1.642(1)	Li(4)–O(1)	1.982(5)
Mean	1.638	Li(4)–O(3)	1.988(5)
		Mean	1.976
Li(1)–O(2)	1.919(4)		
Li(1)–O(1)	1.924(3)	Li(5)–O(3)	1.995(10)
Li(1)–O(3)	1.932(4)	Li(5)–O(1)	2.090(9)
Li(1)–O(1)	2.018(4)	Li(5)–O(1)	2.091(9)
Mean	1.948	Li(5)–O(2)	2.093(10)
		Li(5)–O(3)	2.189(10)
Li(2)–O(3)	1.974(8)	[Li(3)–O(2)	3.011(10)]
Li(2)–O(1) × 2	2.011(4)	Mean	2.092
Li(2)–O(2)	2.050(8)		
Mean	2.012	Li(6)–O(1) × 2	2.146(7)
		Li(6)–O(3)	2.188(11)
Li(3)–O(2)	1.942(7)	Li(6)–O(1) × 2	2.203(9)
Li(3)–O(1) × 2	1.976(4)	Li(6)–O(2)	2.543(12)
Li(3)–O(3)	2.065(7)	Mean	2.238
Mean	1.990		

[1] See NAPS document No. 03990 for seven pages of supplementary material. Order from ASIS/NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, New York 10017. Remit in advance for each NAPS Acession number. Institutions and organizations may use purchase orders when ordering: however, there is a billing charge for this service. Make checks payable to Microfiche Publications. Photocopies are $7.75. Microfiche are $4.00. Outside the U.S. and Canada, postage is $3.00 for a photocopy or $1.50 for a fiche.

$0.0045CN_m = 1.643(6)$ Å, since in this case the secant value (NSEC) is set equal to 2.0 and $CN_m = 4.64$. The corresponding equation for the mean P–O distance (*17*) is: $d(P–O)_m = 1.496 + 0.012CN_m + 1.46DI = 1.552(6)$ Å, because CN_m has the same value as above, while the distortion index (DI) is close to zero. By linear interpolation we obtain an estimated mean $(Si_{0.75}P_{0.25})$–O distance 1.620(6) Å, again in good agreement with the observed value. Thus, the two different estimates for the mean (Si,P)–O value are consistent with the experimental value for a chemical composition $Li_{3.75}Si_{0.75}P_{0.25}O_4$.

The observed mean Si–O distance of 1.638 Å for the substructure refinement of Li_4SiO_4 agrees reasonably well with the estimated value of 1.646(6) Å obtained from the predictive equation (*16*).

Lithium Content

A summation of the individual occupancies of the six Li position in $Li_{3.75}Si_{0.75}P_{0.25}O_4$ yields 3.43(24) Li per formula unit. This is less than the assumed lithium content of 3.75, but the deficit amounts only to slightly more than one standard deviation. Considering the atomic number of lithium and its probable formal oxidation state, a fractional occupation of a site by 0.2 Li should scatter X rays less than one hydrogen atom would.

In view of the difficulty of determining precisely such small electron densities, the agreement between the total Li occupancy of 3.43(24) atoms and the nominal value of 3.75 is sufficient.

Lithium Oxygen Coordinations

The distances from the Li atoms to the surrounding oxygen atoms in $Li_{3.75}Si_{0.75}P_{0.25}O_4$ are very similar (usually within a few hundredths of an Angstrom) to the distances observed in disordered Li_4SiO_4 (*7*) and in the refined subcell data of ordered Li_4SiO_4 (Table V). Few of the observed differences are statistically significant. Consequently the coordinations around the various Li atom positions are the same as in the Li_4SiO_4 structures: Li(5) is five-coordinated, Li(6) is six-coordinated, while the remaining Li atoms are four-coordinated by oxygen atoms. The grand mean distance from these four-coordinated Li atoms to the oxygen atoms ($Li^{[4]}$–O) measures 1.99 Å and is thus similar to the mean $Li^{[4]}$–O distances (1.98 Å) in high and low temperature Li_3PO_4 (*8, 11*) and to the distance expected from Shannon's (*18*) radii (1.98 Å). The mean $Li^{[5]}$–O distance of 2.08 Å is similar to the value of 2.06 Å observed for $Li^{[5]}$–O in $LiAlPO_4(OH,F)$ (*19*). However, the mean $Li^{[6]}$–O distance of 2.24 Å in $Li_{3.75}Si_{0.75}P_{0.25}O_4$ is clearly longer than the value of 2.15 Å expected from effective ionic radii (*18*). One could correlate this longer $Li^{[6]}$–O distance with the partial occupancy of Li(6) on its site (*18*). However, by the same token the observed $Li^{[4]}$–O and $Li^{[5]}$–O distances should then also be longer than they have been observed to be, since all the Li positions here are only partially populated. Obviously the lengthening of Li–O distances due to partial occupations of the Li sites is not uniform in $Li_{3.75}Si_{0.75}P_{0.25}O_4$. Apparently the size of the octahedral Li coordination is determined by the surrounding tetrahedral coordinations. The interstice in which the five coordinated Li(5) atom is residing is of about the same size and shape as the octahedral coordination. Except that Li(5) is located on one side of the octahedral void, close to one O(2) atom (2.06 Å) and much further from the opposing O(2) atom (3.07 Å), thus forming a square pyramidal coordination. The mean Li(5)–O distance including the farther O(2) contact measures 2.25 Å, that is essentially the same as the mean Li(6)–O distance. Similarly long $Li^{[6]}$–O distances of 2.34 and 2.19 Å have been observed in $Li_{3.5}Zn_{0.25}GeO_4$ (*20*) and in $Li_3Zn_{0.5}GeO_4$, where one Li atom is close to a triangular face of an octa-

hedron, however, its mean octahedral $Li^{[6]}$–O distance is 2.4 Å (*21*).

Conductivity Pathways

In ordered Li_4SiO_4 (*6*) all Li–Li distances are longer than 2.30 Å, the various Li coordination polyhedra share only corners and edges with each other and all Li positions are fully occupied. The ionic conductivity of pure Li_4SiO_4 is at room temperature smaller than $10^{-5}(\Omega m)^{-1}$ (*1, 3*). Compositions such as $Li_{3.75}Si_{0.75}P_{0.25}O_4$ or $Li_{3.6}Si_{0.6}P_{0.4}O_4$ have ionic conductivities three or four orders of magnitude higher than that (*1, 3*).

Occupancy factors for the Li sites were reported for disordered Li_4SiO_4 (*7*), but seem to be of low precision. In ordered Li_4SiO_4 one can compare the number of occupied Li sites with the total number of available corresponding Li sites in the subcell (Table IV). These theoretical site occupancies are similar to the site occupancies obtained by a refinement of the subcell diffraction data of ordered Li_4SiO_4. Some of the experimental occupancy factors of $Li_{3.75}Si_{0.75}P_{0.25}O_4$ differ significantly from both of these. Atoms Li(2) and Li(6) have lower Li populations in the solid solution than in Li_4SiO_4, atom Li(3) contains more Li, while Li(1), Li(4), and Li(5) remain about the same.

Most of the short Li–Li distances in $Li_{3.75}Si_{0.75}P_{0.25}O_4$ are across shared faces of coordination polyhedra (Table VI). Since the occupancy factors (Table IV) for all the Li positions are less than 1.0, the short distances do not necessarily mean that any two Li atoms must approach each other as closely as the distances would indicate. The maximum probability that Li atom 1 will have as a close contact a particular Li atom 2 is equal to the product of the occupancy factor of atom 1 multiplied by the sum of the site occupancies of all neighboring atoms 2. If there is any local order in the

TABLE VI

EDGE AND FACE-SHARING BETWEEN Li-POLYHEDRA IN $Li_{3.75}Si_{0.75}P_{0.25}O_4$[a]

Atom 1	CN	Atom 2	Mult.	Distance (Å)	Shared elements	p_a	
Li(1)	4	Li(4)		1.18(1)	F,tt	0.26	0.63
		Li(5)		1.64(3)	F,ts	0.12	
		Li(6)		1.95(2)	F,to	0.25	
		Li(6)		2.06(2)	F,to		
Li(2)	4	Li(3)		1.16(3)	F,tt	0.11	0.29
		Li(4)	×2	1.85(3)	E,tt	0.18	
Li(3)	4	Li(2)		1.16(3)	F,tt	0.11	0.45
		Li(5)	×2	1.65(3)	F,ts	0.22	
		Li(6)		2.01(3)	F,to	0.12	
Li(4)	4	Li(1)		1.18(1)	F,tt	0.26	0.54
		Li(2)		1.85(3)	E,tt	0.09	
		Li(4)		1.95(2)	E,tt	0.19	
Li(5)	5	Li(5)		1.02(4)	F,ss	0.04	0.27
		Li(1)		1.64(3)	F,st	0.12	
		Li(3)		1.65(3)	F,st	0.11	
Li(6)	6	Li(3)		2.01(3)	F,ot	0.12	0.62
		Li(1)	×2	1.95(2)	F,ot	0.50	
		Li(1)	×2	2.06(2)	F,ot		

[a] This list includes all Li–Li contacts shorter than 2.28 Å. CN = coordination number, Mult. = multiplicity of element per polyhedron, E = edge, F = face, t = tetrahedron, s = square pyramid, o = octahedron, p_a = maximum probability of approach between the Li atoms.

arrangements of Li atoms, then the actual probability of such close encounters can be lower. In the structure of ordered Li_4SiO_4, for example, the probability of an occurrence of Li–Li distances shorter than 2.30 Å is zero. In the solid solution the highest probability for short Li–Li distances exists around Li(6) for Li(6)–Li(1) approaches (Table VI). It is likely that the Li(6) and Li(1) sites play a central role in the ionic conductivity of $Li_{3.75}Si_{0.75}P_{0.25}O_4$. An Li(6) atom located at about 2.0 Å from an Li(1) atom should be in an energetically unfavorable position and, therefore, likely to jump into an adjoining vacant Li(1) site, thus contributing to the instability of another neighboring Li(6) atom. The Li(6) and Li(1) site define together a potential ion conducting pathway parallel [010] through the structure. Another instance of an hcp-based ionic conductor where some of the Li atoms are in tetrahedral positions and some in octahedral positions is $Li_{3.5}Zn_{0.25}GeO_4$ (*20*). Since the tetrahedrally located Li are sharing the same positions with Zn, it is probable that only the octahedral Li atoms are participating in the ion transport. In Na_2MgSiO_4, the parent compound of several ionic conductors (*22*), only tetrahedral sites are occupied by the conducting Na ions. All potential conductivity pathways in that tetrahedral structure, which is also based on a hexagonal closest packing of oxygen atoms, lead through an octahedral site (*23*). Therefore, it is not surprising to find that in $Li_{3.75}Si_{0.75}P_{0.25}O_4$ the octahedral Li(6) site has a high probability of being involved in the conduction pathway as well.

Ion Transport in Tetrahedral Structures

There are three closely related groups of tetrahedral structures which are based on hexagonal closest packing of oxygen atoms or on distortions of it:

(1) The wurtzite derivatives are obtained by ordered substitution of cations. They are of lower symmetry than wurtzite or zincite, ZnO, itself. All coordination tetrahedra point in the same direction, they crystallize in polar space groups. Examples are low temperature Li_3PO_4 (*8*) or Na_2MgSiO_4 (*23*). They cannot have more cations than anions in their chemical formula.

(2) The dipolar tetrahedral types are obtained from the wurtzite-type by substituting some cations into tetrahedral positions which are vacant in wurtzite itself. The tetrahedra can now point either way, the symmetry is centric. Examples are: high temperature Li_3PO_4 (*11*), $Li_{3.5}Zn_{0.25}GeO_4$ (*20*), or Li_4SiO_4 (*6, 7*). This type can accommodate more cations than anions, but the excess cations must move into octahedral positions.

(3) The rutile-related tetrahedral types are based on an anion packing obtained by a distortion of hexagonal closest packing. In this rutile-type packing each oxygen atom has 11 oxygen neighbors, not 12 as in hcp (*24*). An example is Li_4GeO_4 (*25*). This packing has, in its ideal form, two types of tetrahedral interstices and can accommodate 25% more tetrahedral cations than it has anions. Therefore, all cations (Li and Ge) are in tetrahedral coordinations in Li_4GeO_4.

A stoichiometric and ordered tetrahedral structure based on hcp with only four tetrahedral cations per four oxygen atoms is unlikely to be a good ionic conductor. The interesting compounds are those with disorder and/or excess cations, that is, they are found mostly in the second and third groups. Good ionic conductivity is exhibited by the solid solutions between compounds belonging to different but related structure types, which all are based on either hcp or rutile packing. Examples for such solid solutions between nonisostructural compounds are: Li_4SiO_4–Li_3PO_4 (*1, 3*), Li_4SiO_4–$LiAlO_2$ (*1*), Li_4SiO_4–Li_4GeO_4 (*26*), Li_4GeO_4–Li_2ZnGeO_4–Li_3PO_4 (*27*), Li_4GeO_4–Li_3VO_4 (*28*), or Li_4GeO_4–Zn_2GeO_4 (*29*). In all cases the crystal struc-

tures of the poorly ion conducting end member phases are known. Their solid solutions exhibiting fast ion transport properties have been hardly investigated structurally. Except for $Li_{3.75}Si_{0.75}P_{0.25}O_4$, only $Li_{3.5}Zn_{0.25}GeO_4$ (*20*) and $Li_{3.0}Zn_{0.5}GeO_4$ (*21*) have been studied by single crystal methods. Because of the complexities of solid solutions between nonisostructural end members one cannot interpolate the structure of an intermediate composition. It is probable that further structural work on these compounds will yield surprises similar to the one found in $Li_3Zn_{0.5}GeO_4$ (*21*), where Li was encountered in three-coordination, while in the closely related structure of $Li_{3.5}Zn_{0.25}GeO_4$ (*20*), it is located in the center of an octahedron.

The crystal structure of $Li_{3.75}Si_{0.75}P_{0.25}O_4$ is representative of the solid solutions between Li_4SiO_4 and Li_3PO_4 to the left of the discontinuity (Fig. 1), that is for values of x up to 0.4. The solid solutions with x from 0.5 to 1.0 must have crystal structures similar to high temperature Li_3PO_4, that is they should be orthorhombic and have a doubled c unit cell constant compared with Li_4SiO_4 (*3*). The composition $Li_{3.5}Si_{0.5}P_{0.5}O_4$ might have a similar Li distribution as $Li_3Zn_{0.5}GeO_4$ (*21*) has because the ratio of cations to anions is the same in both compounds ($A_{4.5}X_4$). Incidentally, in the composition studied here, that ratio is the same as in $Li_{3.5}Zn_{0.25}GeO_4$ (*20*), namely, $A_{4.75}X_4$, but symmetry and unit cell dimensions are different for these two solid electrolytes.

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