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Crystal Structure of the Lithium Ion Conductor, $Li_{3.4}Ga_{0.2}SiO_4$

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The crystal structure of $Li_{3.4}Ga_{0.2}SiO_4$ has been determined by Rietveld refinement of time-of-flight neutron HRPD data. A total of 67 position, thermal, occupancy, and instrument parameters were refined to a final $R_{wp} = 5.24\%$, $R_{ex} = 4.20\%$. The structure is related to that of monoclinic, disordered Li_4SiO_4. It contains isolated SiO_4 tetrahedra, six sets of partially occupied sites for lithium, and gallium with partial occupancy on one of the tetrahedral lithium sites. The similarities between this structure and those of rutile and β-BeO are discussed. © 1990 Academic Press, Inc.

Introduction

Li_4SiO_4 is the parent structure for a group of lithium ion conducting solid–solutions that form by aliovalent substitution (*1*). Most attention has focused on materials with partial replacement of Si by pentavalent cations and concomitant creation of lithium ion vacancies (*2–8*):

$$\mathrm{Li + Si \rightleftharpoons P, As, V}$$

Recently, we (*9–11*) have shown that lithium may be replaced extensively by trivalent ions according to

$$\mathrm{3\,Li \rightleftharpoons Al, Ga}$$

and that dramatic increases in lithium ion conductivity occur. Conductivities pass through a maximum of 2×10^{-5} ohm^{-1} cm^{-1} (Ga system) and 5×10^{-4} ohm^{-1} cm^{-1} (Al system) at 100°C for compositions $x \approx 0.20$–0.25 in the solid–solution series, $Li_{4-3x}(Al,Ga)_xSiO_4$.

We have now carried out structural studies on one of the solid–solutions in the Ga system, with $x = 0.20$, by refinement of powder neutron diffraction data. This had the objectives of locating the substitutional Ga ions, determining the lithium ion distribution over the various available sites, and understanding the mechanism of lithium ion conduction. The crystal structure of Li_4SiO_4 is complex. Some crystals appear to contain lithium ions in partially occupied 4-, 5-, and 6-coordinate sites (*12, 13*). Other crystals possess a large supercell in which the various 4-, 5-, and 6-coordinate sites are fully occupied (*14*).

Experimental

Samples of $^7Li_{3.4}Ga_{0.2}SiO_4$ were prepared by solid state reaction of $^7Li_2CO_3$ (AERE, Harwell Stable Isotope Unit, 99.99% ^7Li), Ga_2O_3 (Aldrich, 99.99%), and SiO_2 (Thermal Syndicate quartz powder, particle size < 100 μm, 99.98%) in three stages. Initially, $^7Li_4SiO_4$ and $^7LiGaSiO_4$ were prepared, 18.5

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hr at 890°C and 18.5 hr at 950°C, respectively. From these, $^7Li_5GaSi_2O_8$ was prepared, 1 day at 950°C and 2 days at 1000°C. $^7Li_{3.4}Ga_{0.2}SiO_4$ was then prepared by reacting $^7Li_4SiO_4$ and $^7Li_5GaSi_2O_8$ at 950°C for 8 days. At all stages, the samples were reground daily and the course of reaction monitored by X-ray powder diffraction. The above multistage procedure was preferred since it gave a phase pure final product. This was not the case for a sample prepared by direct reaction of the oxides and carbonates.

A high resolution time of flight powder neutron diffraction profile was collected on the high resolution powder diffractometer, HRPD at ISIS, Rutherfold Appleton Laboratory. This instrument possesses a theoretical resolution $\Delta d/d$ of 5×10^{-4} and can measure d-spacings over the range 0.4 to 6 Å. Approximately 15 g of powdered $^7Li_{3.4}Ga_{0.2}SiO_4$ were placed in a cylindrical vanadium can which was positioned 1 m in front of the bank of back-scattering detectors in the HRPD diffractometer. Data were collected over the time of flight range 20,000–120,000 μsec, corresponding to a d-spacing range of 0.5 to 2.5 Å, for $4\frac{1}{2}$ hr. A data set in the time of flight range 100,000–200,000 μsec (d-spacings 2–4 Å) was also collected for $\frac{1}{2}$ hr in order to have data on the large d-spacings for precise lattice parameter and space group determination. The data from the concentric rings of detectors were summed and normalized; the region 28,000–95,000 μsec time of flight was used for profile refinement. The profile was fitted using a modified Rietveld method, with the peak shape modeled by a convolution of a Gaussian and two exponential functions (*15*). In the later stages of refinement, a convolution of a Voigt and two exponential functions was found to model more accurately the observed peak shape. Scattering lengths used were Li, -0.220×10^{-12} cm; Ga, 0.729×10^{-12} cm; Si, 0.4149×10^{-12} cm; and O, 0.5805×10^{-12} cm (*16*).

Results and Discussion

Structure Refinement

Structure refinement was carried out in the monoclinic space group $P2_1/m$ (No. 11) (*17*). The monoclinic unit cell determined from X-ray Guinier Hägg powder patterns was confirmed by the autoindexing program VISSER (*18*) and showed orthorhombic pseudo-symmetry. The starting structural model used for the refinement was that of disordered Li_4SiO_4 (*12*); there was no evidence of supercell reflections in the X-ray powder patterns, the neutron diffraction profile, or the selected area electron diffraction photographs. A previous structure refinement on $Li_{3.75}Si_{0.75}P_{0.25}O_4$, also with the Li_4SiO_4 structure, showed no evidence for the presence of a superstructure (*13*). It was concluded, therefore, that no supercell was present in $Li_{3.4}Ga_{0.2}SiO_4$.

In the initial stages of the refinement, the scale factor, instrumental zero point correction, unit cell parameters, and five background parameters were varied, followed by the Gaussian part of the peak shape. The oxygen and silicon positional and thermal parameters were then refined, followed by positional, thermal, and site occupational factors for lithium. At this stage, examination of difference Fourier maps and the temperature factors and site occupancies for lithium, gave no indication as to the location of the Ga atoms. Consideration of the crystal structures of Li_4SiO_4 and $Li_5GaSi_2O_8$ (presumed similar to γ-$LiAlO_2$ (*19*) led to the suggestion that the Ga could be located in the Li(1) sites, which are equivalent to some of the Al sites in γ-$LiAlO_2$. Accordingly, Ga was placed on this site, with a partial occupancy given by the overall formula. The Li atoms were then allowed to refine over the six Li sites of the Li_4SiO_4 structure, including the Li(1) sites that are partially occupied by Ga. The total, refined Li content agreed very well with that expected from the chemical formula. Anisotropic temperature factors were successfully refined for Si and O. Because of the low occupancy of some of the Li sites, individual temperature factors could not be refined satisfactorily for all the Li atoms, and, therefore, a single isotropic temperature factor was refined for the Li(1)/Ga, Li(4), Li(5), and Li(6) sites. The Li(2) and Li(3) sites had sufficient occupancies for their isotropic temperature factors to be refined separately.

With $x = 0.2$, a total lithium content of 6.8 atoms per unit cell is expected. The total refined lithium content is 6.6(2) atoms per cell, which is in very good agreement considering the small scattering cross section and disordered nature of the lithium atoms in this material.

On examination of the fitted profile, it was found necessary to use a peak shape modeled by a convolution of a Voigt and two exponential functions to accurately fit the observed peak shape. The final refinement contained four peak shape parameters (two Gaussian, two Lorentzian) and a peak center parameter, as well as the previously refined instrumental and sample-variable parameters.

Refinement terminated with $R_{wp} = 5.24\%$, $R_{ex} = 4.20\%$, $\chi^2 = 1.56$ for 7445 data points and 67 variable parameters (for definition of R-factors, see Ref. (*20*). The final refined atomic parameters are given in Table I with selected bond distances and angles in Table II. A projection of the structure is given in Fig. 1. The complete, fitted diffraction profile is shown in Fig. 2.

Placement of gallium onto the Li(1) site seems fully justified from consideration of bond lengths (Table II). This distorted tetrahedral site has the shortest metal–oxygen bond distances, which compare reasonably well with a typical value of 1.87 Å for tetrahedral gallium and 1.99 Å for tetrahedral lithium (*21*). The bond distances given for this site in Table II represent an average, although the individual Li(1)–O and Ga–O distances are likely to differ somewhat from these average values.

Description of the Structure

The structure may be regarded as derived from the parent, disordered Li_4SiO_4 structure by substitution of Ga onto Li(1) sites and reduction in some of the Li site occupancy factors. The SiO_4 tetrahedra are isolated from each other and contain all the oxygens in the structure. Sites for Li and Ga are therefore created by the way in which the SiO_4 tetrahedra are arranged. All the cation sites apart from Si are partially occupied.

The oxygen array caused by the disposition of the SiO_4 tetrahedra is very similar to that found in rutile (*22*) and β-BeO (*23*) and may be regarded as a distorted form of tetragonal packing (*24*). Cation ordering along the unique axis (*c* in rutile, β-BeO; *b* in $Li_{3.4}Ga_{0.2}SiO_4$) causes a doubling of this cell edge in $Li_{3.4}Ga_{0.2}SiO_4$ to 6.13 Å, instead of 3 Å. The different sizes of the SiO_4 and LiO_n polyhedra also lead to a distortion of the oxygen arrangement from that found in rutile/β-BeO.

The structures of rutile/β-BeO may be regarded as a framework formed by columns of edge-sharing octahedra/pairs of edge-sharing tetrahedra (Fig. 3). Between the columns are distorted channel sites which are empty in rutile/β-BeO. In $Li_{3.4}Ga_{0.2}SiO_4$, a similar framework forms but the construction of the columns is intermediate between that of rutile and β-BeO. Two types of columns are present. In one, pairs of edge-sharing SiO_4 and $Li(2)O_4$ tetrahedra are present, similar to the BeO_4 pairs in β-BeO, but the Li(2) sites are only partially occupied. In the other, pairs of $(Li(1),Ga)O_4$ tetrahedra are present but these also share faces with $Li(6)O_6$ octahedra; all these sites are partially occupied. These latter columns have features of both the rutile and β-BeO structures, therefore.

TABLE I

UNIT CELL PARAMETERS AND ATOMIC COORDINATES FOR $Li_{3.4}Ga_{0.2}SiO_4$

Space group $P2_1/m$ (No. 11)
$a = 5.1478(4)$, $b = 6.1316(5)$, $c = 5.2505(4)$ Å, $\beta = 89.7948(5)°$

Atom	Position	x	y	z	Site	B_{iso}
Si	2*e*	0.6695(3)	0.25(−)	0.3271(3)	1.0	—
O(1)	4*f*	0.7873(2)	0.0299(1)	0.1873(2)	1.0	—
O(2)	2*e*	0.3518(3)	0.25(−)	0.3029(3)	1.0	—
O(3)	2*e*	0.7501(3)	0.25(−)	0.6271(2)	1.0	—
Ga	4*f*	0.178(1)	0.010(2)	0.166(2)	0.1(−)	2.0(2)
Li(1)	4*f*	0.178(1)	0.010(2)	0.166(2)	0.66(1)	2.0(2)
Li(2)	2*e*	0.341(2)	0.25(−)	0.685(2)	0.47(2)	2.2(3)
Li(3)	2*e*	0.180(2)	0.25(−)	0.638(2)	0.39(2)	1.4(4)
Li(4)	4*f*	0.398(2)	0.962(2)	0.131(2)	0.25(1)	2.0(2)
Li(5)	4*f*	0.059(3)	0.028(3)	0.444(3)	0.16(1)	2.0(2)
Li(6)	2*e*	0.027(3)	0.25(−)	0.980(3)	0.26(1)	2.0(2)

Anisotropic temperature factors

	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Si	1.39(8)	1.01(6)	1.51(7)		−0.98(6)	
O(1)	1.94(4)	1.18(4)	1.83(4)	−0.20(3)	−0.01(3)	−0.01(3)
O(2)	1.27(6)	0.85(6)	2.59(7)		−0.44(5)	
O(3)	3.50(7)	0.68(5)	1.66(6)		−1.11(5)	

The channel sites in $Li_{3.4}Ga_{0.2}SiO_4$ are partially occupied by Li(3), Li(4), and Li(5) in distorted tetrahedral and trigonal bipyramidal environments. The distinction between the tetrahedral coordination of Li(3), Li(4) and the trigonal bipyramidal coordination of Li(5) is not great and rests on a comparison of bond distances: 1.95 (2×), 1.97 and 2.22 Å in Li(3)–O; 1.93, 1.97, 2.00, and 2.07 Å for Li(4)–O; 1.95, 2.00, 2.12, 2.16, and 2.30 Å for Li(5)–O. These compare with 1.96 (2×), 2.01 and 2.12 Å for tetrahedral Li(2)–O and 2.13 (2×), 2.15 (2×), 2.34, and 2.38 Å for octahedral Li(6)–O.

The channels are of two types. One type is occupied by Li(4) atoms and the Li(4)–O tetrahedra share edges with each other. The other type contains Li(3) and Li(5) atoms. The Li(5)O_5 trigonal bipyramids share faces both with each other and with Li(3)O_4 tetrahedra. In addition to edge- or face-sharing of polyhedra within the channels and within the framework, edge- and face-sharing between channel and framework sites also occurs. For example, Li(4)O_4 and (Li(1),Ga)O_4 tetrahedra share faces; Li(4)O_4 and SiO_4 tetrahedra share edges.

Electrostatic repulsions between adjacent cations in edge-/face-sharing polyhedra place limitations on the types of linkage that are feasible. Edge-sharing of tetrahedra is clearly allowable since fully occupied SiO_4 tetrahedra share edges with partially occupied Li(2)O_4 tetrahedra. However, tetrahedra that share faces give cation–cation distances that are too short for both sites to be occupied simultaneously. This principle was confirmed during the refinement of the lithium site occupancies since it was found that the combined occupancy of face-sharing tetrahedral sites never exceeded unity. Hence, although the structure contains ex-

TABLE II

Selected Bond Distances and Angles for $Li_{3.4}Ga_{0.2}SiO_4$

Si coordination	
Si–O(1)	1.651(1) ×2
–O(2)	1.641(2)
–O(3)	1.630(2)
O(1)–Si–O(1′)	109.7(1)
–O(2)	109.3(1) ×2
–O(3)	109.6(1) ×2
O(2)–Si–O(3)	109.4(1)
Ga/Li(1) coordination	
Ga/Li(1)–O(1)	2.019(7)
–O(1′)	1.879(8)
–O(2)	1.867(9)
–O(3)	1.964(9)
O(1)–Ga/Li(1)–O(1′)	98.8(3)
–O(2)	114.2(4)
–O(3)	102.0(4)
O(1′)–Ga/Li(1)–O(2)	116.0(4)
–O(3)	115.0(5)
O(2)–Ga/Li(1)–O(3)	109.6(4)
Li(2) coordination	
Li(2)–O(1)	1.958(4) ×2
–O(2)	2.006(8)
–O(3)	2.124(10)
O(1)–Li(2)–O(1′)	122.4(5)
–O(2)	110.6(3) ×2
–O(3)	112.5(3) ×2
O(2)–Li(2)–O(3)	80.5(3)
Li(3) coordination	
Li(3)–O(1)	1.952(4) ×2
–O(2)	1.968(9)
–O(3)	2.215(11)
O(1)–Li(3)–O(1′)	123.0(4)
–O(2)	112.4(3) ×2
–O(3)	95.7(3) ×2
O(2)–Li(3)–O(3)	114.9(4)
Li(4) coordination	
Li(4)–O(1)	2.068(11)
–O(1′)	1.928(10)
–O(2)	1.999(10)
–O(3)	1.969(10)
O(1)–Li(4)–O(1′)	127.0(5)
–O(2)	82.6(4)
–O(3)	114.5(5)
O(1′)–Li(4)–O(2)	108.0(5)
–O(3)	112.6(5)
O(2)–Li(4)–O(3)	104.2(4)
Li(5) coordination	
Li(5)–O(1)	1.947(15)
–O(1′)	2.122(15)
–O(2)	2.159(15)
–O(3)	2.004(16)
–O(3′)	2.300(15)
O(1)–Li(5)–O(1′)	154.6(9)
–O(2)	105.1(7)
–O(3)	103.1(7)
–O(3′)	77.8(7)
O(1′)–Li(5)–O(2)	99.1(6)
–O(3)	81.0(6)
–O(3′)	88.8(6)
O(2)–Li(5)–O(3)	97.5(6)
–O(3′)	104.6(6)
O(3)–Li(5)–O(3′)	156.8(8)
Li(6) coordination	
Li(6)–O(1)	2.126(12) ×2
–O(1′)	2.150(10) ×2
–O(2)	2.384(16)
–O(2′)	2.343(15)
O(1)–Li(6)–O(1)	78.8(5)
–O(1)	87.6(1) ×2
–O(1′)	166.4(6) ×2
–O(2)	92.5(5) ×2
–O(3)	92.9(6) ×2
O(1′)–Li(6)–O(1′)	105.9(7)
–O(2)	88.8(5) ×2
–O(3)	87.0(4) ×2
O(2)–Li(6)–O(3)	173.0(8)

amples of face-sharing tetrahedra, only one site of each pair is occupied at any particular time.

The situation with face-sharing tetrahedra and octahedra is similar to that of face-sharing tetrahedra. The refinement indicates that the combined occupancy of the tetrahedral (Li(1),Ga)O_4 and octahedral Li(6)O_6 sites is 1.02, very close to unity, as also is the combined occupancy of the (Li(1), Ga)O_4, and Li(4)O_6 sites. This indicates that either the octahedral sites or the tetrahedral sites are occupied, but not both simultaneously. The possibility exists that occupancy of these sites is not random, but that alternate domains form in which

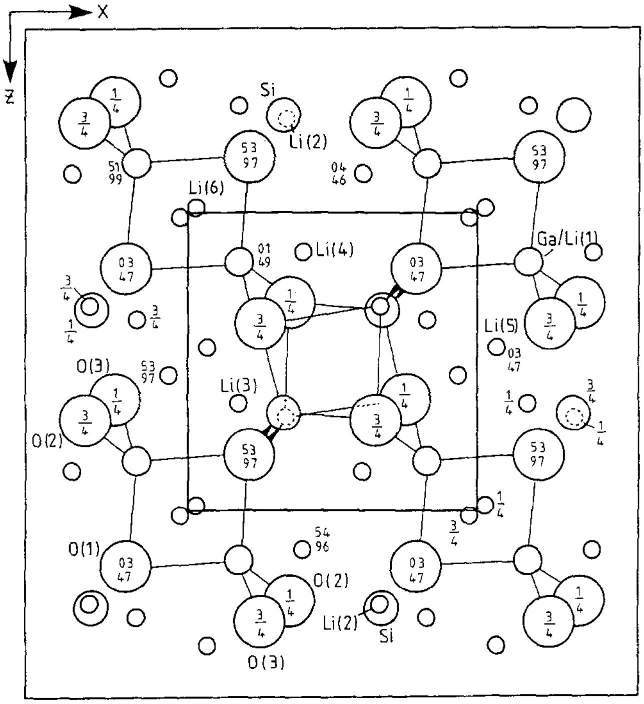

FIG. 1. Projection of the crystal structure of $Li_{3.4}Ga_{0.2}SiO_4$ along [010].

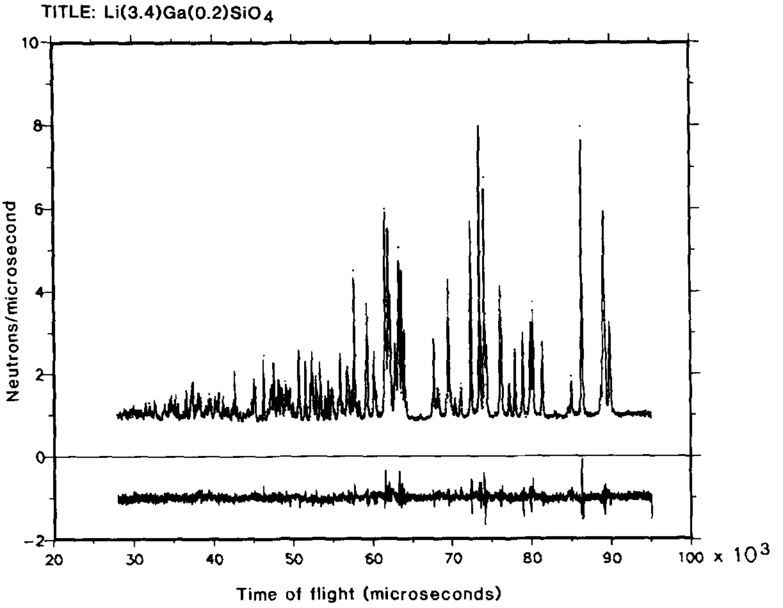

FIG. 2. Fitted powder neutron diffraction profile for $Li_{3.4}Ga_{0.2}SiO_4$ with difference (obsd-calcd) shown below.

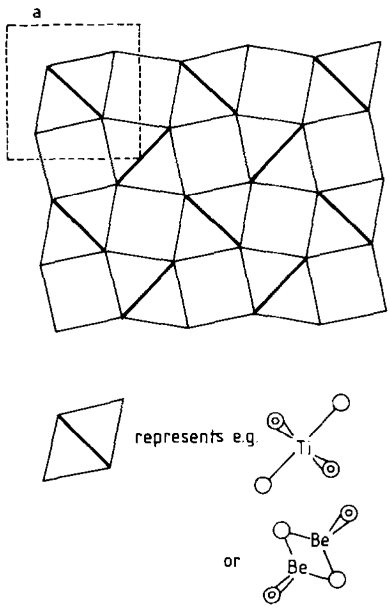

FIG. 3. Schematic projection of the structures of rutile and β-BeO showing columns of edge-sharing octahedra/pairs of edge-sharing tetrahedra.

one type of domain contains fully occupied Li(6) sites forming columns of edge-sharing octahedra, as in rutile. In the other type of domain fully occupied pairs of edge sharing $(Li(1),Ga)O_4$ tetrahedra link at their corners to form columns as in β-BeO and γ-$LiAlO_2$. Examination of lithium occupancies in stoichiometric Li_4SiO_4 (*12, 13*) indicates that similar domains could also be present in it.

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