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Neutron Powder Diffraction Study of Solid Solution $Li_{1+x}Ti_{2-x}In_xP_3O_{12}$

I. $0.0 \leq x \leq 0.4$

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Two polycrystalline samples of $Li_{1+x}Ti_{2-x}In_xP_3O_{12}$ prepared with compositions $x = 0.25$ and $x = 0.40$ have been analyzed by powder neutron diffraction. The x values found in the refinement were systematically lower, 0.12 and 0.15, respectively, than those required by chemical analysis. The discrepancy in the x values is explained by formation of a parasitic phase coexisting with the main phase. The structure framework of the analyzed samples (actually $x = 0.12$ and 0.15) is of the NASICON type, with Ti and In atoms randomly distributed among octahedral sites. Lithium atoms are distributed over octahedral and eight-coordinated sites. The octahedral Li(1) site is almost filled, with a relatively large Li(1)–O distance, 2.29 Å, leaving Li(1) ions enough room to jump into Li(2) sites. The latter sites are only partially occupied by Li(2) ions. A large temperature factor associated with a split position inside the eight-coordinated cavity suggests that the Li(2) ions are in a highly disordered configuration.

Introduction

The discovery (*1*, *2*) of high sodium ion mobility in the $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ (NASICON) system focused wide scientific interest on this system as a potential solid electrolyte material for fuel cell and sensor devices and as a convenient system for studying the correlation between alkali ion mobility and the structure of the host, three-dimensional framework. The dependence of the ion mobility upon the distortion of the $[Zr_2Si_xP_{3-x}O_{12}]$ framework that is induced by substitution of phosphorus for silicon has been widely demonstrated by numerous structural analyses and electrical measurements (*3–7*), which have shown the following: (a) The conductivity, which is 10^{-5} $(\Omega\ cm)^{-1}$ in the rhombohedral $R\bar{3}c$ end member, $NaZr_2P_3O_{12}$, increases by four orders of magnitude to reach a maximum value, 10^{-2} $(\Omega\ cm)^{-1}$ at 300°C, for the monoclinic phase, $Na_3Zr_2SiP_2O_{12}$. (b) The structural transition, $R\bar{3}c$ to $C2/c$, is due to rotation of the tetrahedral group, which enlarges the size of the openings for Na ion diffusion. The rotation of the tetrahedral group does not basically change the NASICON structure type; the $[Zr_2Si_2P_3O_{12}]$ framework in the monoclinic phase is still closely related to the rhombohedral structure of $NaZr_2P_3O_{12}$ (*8*).

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Recently (*9*) it was reported that Li^+ exhibits high mobility in the $Li_{1+x}Ti_{2-x}In_xP_3O_{12}$ system, reaching a maximum ionic conductivity for $x \approx 0.35$. On the basis of X-ray powder patterns, Li *et al.* have suggested that for moderate substitution of Ti^{4+} for In^{3+} ($0 \leq x \leq 0.4$) an $R\bar{3}c$, NASICON-type structure is formed in $Li_{1+x}Ti_{2-x}In_xP_3O_{12}$ and further substitution ($x \geq 0.4$) of In^{+3} induces, similar to the NASICON system, a distortion leading to monoclinic symmetry. More detailed electrical measurements performed on carefully sintered pellets have shown that the conductivity curve of this solid solution actually has two maxima: 2×10^{-2} $(\Omega\ cm)^{-1}$ at $x \approx 0.35$, and 8×10^{-3} $(\Omega\ cm)^{-1}$ at $x \approx 1.8$ (*10, 11*). Structural studies using single crystals of composition $x = 0.0$, 0.06, 1.0, 1.8, and 2.0 have unambiguously shown that insertion of In into the solid solution induces structural changes in its framework much more complicated than previously stated. $Li_{1+x}Ti_{2-x}In_xP_3O_{12}$ compounds adopt, depending on the x value, three structure types, corresponding to three different phases: phase I, $0 \leq x \leq 0.4$, is rhombohedral (or may be slightly monoclinic); phase II, $0.4 < x \leq 1.0$, is orthorhombic, $Pbca$; and phase III, $1.0 < x \leq 2.0$, is monoclinic $P2_1/n$. In contrast with the NASICON system, the transitions from phase I to phase II and from phase II to phase III correspond to structural changes in the framework. The rhombohedral $R\bar{3}c$ structure in phase I is of the NASICON type. In the orthorhombic phase the internal bond pattern in the basic $[Ti_{2-x}In_xP_3O_{12}]$ unit is still conserved, but the external bonds in the network linking different basic units are broken, leading to a new structure type (*12*), and, finally, in the structure of $Li_3In_2P_3O_{12}$, the end member of phase III, the rotation of this basic unit is such that the large, eight-coordinated cavity that characterizes the NASICON-type structure is destroyed (*13*). Throughout the structural changes from phase I through phase II to phase III, the basic unit is conserved.

Our aim in this study was to determine the locations of the Li ions in the framework in order to determine the influence of the structural framework change on Li mobility in $Li_{1+x}Ti_{2-x}In_xP_3O_{12}$ solid solutions. Rietveld analysis of neutron powder diffraction data is used for a better determination of Li ion distribution, because it is very difficult to control the composition in growing single crystals with the desired ratio of In to Ti. It is shown in this work that even with the powder samples obtained by solid-state reaction, the Ti/In ratio due to the formation of a parasitic phase is always lower than expected.

Experimental

The polycrystalline sample used in this study was prepared from a stoichiometric mixture of pure Li_2CO_3, TiO_2, In_2O_3, and $NH_4H_2PO_4$. About 28 g of this mixture was finely ground, placed in a large, covered Pt crucible, progressively heated up to 1000°C, held there for 5 h, and, finally, heated to 1150°C and held there for 3 h. To complete the reaction, several cycles of heating to 1150° followed by grinding operations were repeated for compounds with nominal compositions $x = 0.25$ and $x = 0.40$ (called Ia and Ib, respectively). The final compounds were identified by powder X-ray analysis: almost all diffraction lines of the two samples could be indexed assuming space group $R\bar{3}c$ and unit cell parameters taken from previous single-crystal studies (*12*). Some extremely weak reflections at small angles could not, however, be indexed, even by allowing the rhombohedral unit cell to distort into monoclinic symmetry. These weak reflections originate from neither TiO_2 nor In_2O_3. Attempts to eliminate these extra reflections by changing thermal treatments were unsuccessful.

Powder neutron diffraction data from Ia

and Ib were collected at room temperature using the five-detector diffractometer at the National Bureau of Standards (NBS) research reactor *(14)*. The thermal neutrons used, λ = 1.549 Å, were monochromated by reflection from the (220) planes of a Cu crystal. The mosaic spread of the Cu monochromator was estimated to be 15 arcmin and the divergence in the diffraction plane of the beams before and after the monochromator and of the diffracted beam were 10, 20, and 10 arcmin, respectively. A vanadium can of 8-mm diameter was used as the sample container. The diffraction profile was recorded in steps of 0.05° 2θ for the range $12° \le 2\theta \le 120°$. The intensities from the five counters were processed using NBS versions of the Rietveld programs *(15)*.

TABLE I

RESULTS OF REFINEMENTS OF $Li_{1+x}Ti_{2-x}In_xP_8O_{12}$

	$x = 0.12$	$x = 0.15$
Space group	$R\bar{3}c$	$R\bar{3}c$
Unit cell parameters	8.5476(2), 20,9512(7)	8.5604(2), 21,0219(10)
Peak shape used	Gaussian	Gaussian
Number of reflections	250	250
R_1 (int)	3.02 (3.72)[a]	5.15 (6.70)[a]
R_2 (profile)	6.98 (6.99)	6.77 (6.79)
R_3 (weighted profile)	9.36 (9.36)	9.05 (9.06)
R (estimated)	7.62	6.47 (6.47)
$(N\text{-}P\text{-}C)$	2826	2775
x		
By chemical analysis	0.25	0.40
By refinement	0.12	0.15
Observed occupancy factor		
In 6*b* site	0.95	0.95
In 18*e* site	0.06	0.06

[a] Values in parentheses are the R factors obtained excluding Li(2) and Li(3) from the refinement.

Refinement of the Structure

As previously mentioned, some very weak extra reflections appeared on the neutron powder pattern. They were excluded from the refinement. The background was assumed to be a straight line for each detector, and its constant and slope were therefore refined. The unit cell and the positional parameters of the starting model were taken from a previous single-crystal study *(12)*: P and O atoms are located at 18*e* and 36*f* positions, respectively, and Ti or In is at the 12*c* position with an occupancy factor based on the appropriate x value (x = 0.25 and 0.4). Different types of peak shape were tried, but a Gaussian shape appeared to fit the observed profile satisfactorily. The first series of refinements, which included positional, isotropic (later anisotropic), and thermal factors of all atoms (except for the lithium), cell constants, and profile parameters, converged to the agreement factors summarized in Table I.

A difference Fourier map based on the refined framework gave two negative peaks: one, relatively well defined, was located at the 6*b* position, and the other, rather large and ill defined, was situated in the 18*e* position. This latter site corresponds to the large cavity in NASICON structure framework.

Final refinements including the lithium (which, in terms of scattering power, represents less than 3% of the total) and the framework atoms confirmed the locations of Li ions at 6*b* and 18*e* positions. Table II gives the positional parameters, temperature, and occupancy factors of Ia and Ib. Table III gives some selected bonds and angles. The agreement between observed and calculated profile diagrams is shown in Fig. 1. Figure 2 shows a view of the structure along (001), and Fig. 3 shows Li(2) coordination.

Results and Discussion

The atomic coordinates (Table II) indicate that the structure framework of $Li_{1+x}Ti_{2-x}In_xP_3O_{12}$ is of the NASICON type, in which the $[M_2P_3O_{12}]$ framework consists of three P tetrahedra spanning the corners of two MO_6 octahedra ($M = Ti^{4+}$ or In^{3+}). The octahedral sites are randomly occupied by

TABLE II

POSITIONAL PARAMETERS AND OCCUPANCY AND THERMAL FACTORS FOR $Li_{1+x}Ti_{2-x}In_xP_3O_{12}$

Atom	Position	Occupancy factor	x	y	z	Biso.
O(1)	36*f*	1[a]	0.1860(4)	0.9950(3)	0.1903(1)	1.27(5)
		1[b]	0.1862(4)	0.9941(4)	0.1908(1)	1.78(8)
O(2)	36*f*	1	0.1892(3)	0.1652(3)	0.0813(1)	1.07(6)
		1	0.1893(4)	0.1657(3)	0.0816(1)	1.45(7)
P	18*e*	1/2	0.2918(4)	0	1/4	0.82(4)
		1/2	0.2917(5)	0	1/4	0.98(5)
Ti	12*f*	0.313(4)	0	0	0.1422(4)	1.36(6)
		0.308(5)	0	0	0.1441(4)	1.72(6)
In[c]	12*f*	0.020	0	0	0.1422	1.36
		0.025	0	0	0.1441	1.72
Li(1)	6*b*	0.158(6)	0	0	0	3.98(64)
		0.161(6)	0	0	0	5.98(97)
Li(2)[d]	18*e*	0.015(6)	−0.3128(6)	0	1/4	9.0(1.5)
		0.015(7)	−0.3036(7)	0	1/4	9.3(1.7)
Li(3)[d]	18*e*	0.015	−0.3668(8)	0	1/4	9.0
		0.015	−0.3704(9)	0	1/4	9.3

[a] $x = 0.12$.

[b] $x = 0.15$.

[c] All parameters of In are constrained.

[d] Occupancy factors are constrained with respect to the above chemical formula.

Ti^{4+} and In^{3+}. The average M–O distance is slightly shorter in Ia than in Ib (Table III), consistent with the fact that there is more indium in the octahedral site in Ib.

The stoichiometric parameter x deduced from the Ti and In occupancy factors in Table II is significantly lower than it should be according to chemical analysis for Ia and Ib. The disagreement between structural and chemical analysis reflects a real departure from the intended composition. Indeed, during the synthesis it was assumed that In atoms could react with other constituents, forming a new and unwanted phase which could be the origin of the extra reflections mentioned earlier. Attempts to identify these reflections have lead to the following conclusions: (a) the extra reflections are not due to In_2O_3; (b) they cannot be indexed using a unit cell of lower symmetry, corresponding to any maximal, nonisomorphic subgroup of $R\bar{3}c$—$C2/c$ $P2_1/c$, etc.; (c) a set of unit cell parameters, 7.09, 18.33, 16.85, $\beta \approx 90.5$, is consistent with the angular positions of the five extra reflections. Unfortunately, to our knowledge, this unit cell does not correspond to any reported compound.

The mean tetrahedral bond lengths, P–O, are 1.525 and 1.520 Å in Ia and Ib, respectively. These values are slightly smaller than the average values observed in other monophosphates. Contraction of the P–O distance with respect to the mean value (1.536 Å) would indicate the presence of pseudosymmetry (*6*).

Lithium ions, whose mobility is the origin of high ionic conductivity in the solid solution $Li_{1+x}Ti_{2-x}In_xP_3O_{12}$, are distributed over octahedral and eight-coordinated sites. The Li(1)–O separation imposed by site symmetry $\bar{3}$ is substantially longer, by 0.2 Å, than the sum of ionic radii for Li^{VI} and O; the large departure of the O–Li(1)–

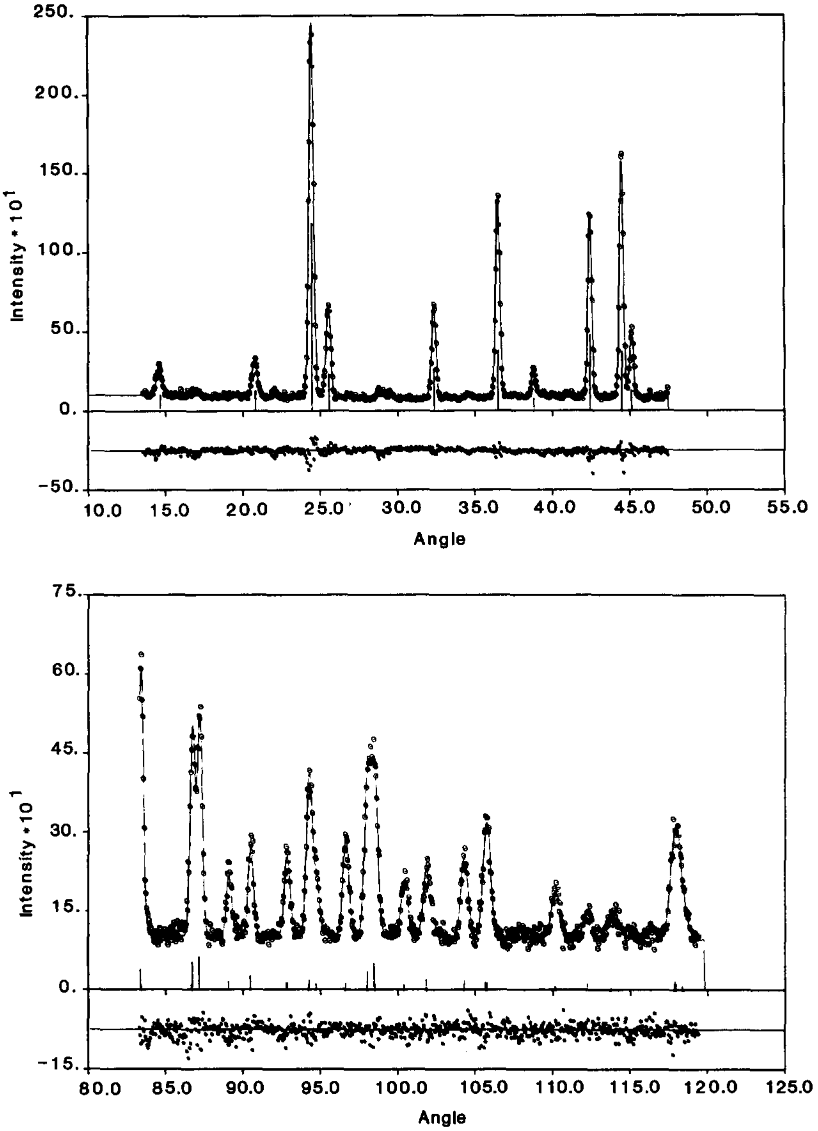

FIG. 1. Observed (circlet) and calculated (line) profile intensities for $Li_{1+x}Ti_{2-x}In_xP_8O_{12}$, $x = 0.12$.

O angle (Table III) from 90° suggests that the so-called octahedral site actually has an antiprismatic form. The Li(2)–O bonds in the eightfold cavity (actually tenfold cavity if the two Li–O distances longer than 2.7 Å are considered) are also slightly larger than those usually observed for eightfold coordinated Li. The occupancy factor for Li(1) shows that this site is almost filled, 95% of the site capacity, whereas the Li(2) site is partially filled, 6%. This result, in agreement with previous studies, seems to be general and confirms that in NASICON-like compounds the octahedral site is energetically more stable than the eight-coordinated site. The preference for the

TABLE III

SELECTED INTERATOMIC DISTANCES AND ANGLES FOR THE RHOMBOHEDRAL $R\bar{3}c$ STRUCTURES OF $Li_{1+x}Ti_{2-x}In_xP_3O_{12}$

	$x = 0.12$	$x = 0.15$
P–O(1)	1.529(5) × 2	1.523(5) × 2
P–O(2)	1.522(4) × 2	1.518(5) × 2
Average	1.525(5)	1.520(5)
M–O(1)	1.899(6) × 3	1.898(6) × 3
M–O(2)	1.986(5) × 3	2.013(6) × 3
Average	1.942(6)	1.956(6)
Li(1)–O(2)	2.287(9)	2.298(8)
Li(2)–O(1)	2.677(10) × 2	2.630(10) × 2
Li(2)–O(1)	2.614(9) × 2	2.553(10) × 2
Li(2)–O(1)	2.611(7) × 2	2.652(8) × 2
Li(2)–O(2)	2.291(9) × 2	2.302(8) × 2
Li(2)–O(2)	2.802(9) × 2	2.875(9) × 2
Average	2.599(9)	2.602(9)
Li(3)–O(1)	3.022(10) × 2	3.055(9) × 2
Li(3)–O(1)	2.956(11) × 2	2.975(10) × 2
Li(3)–O(1)	2.504(8) × 2	2.513(10) × 2
Li(3)–O(2)	2.398(9) × 2	2.333(10) × 2
Li(3)–O(2)	2.321(10) × 2	2.373(8) × 2
Average	2.640(10)	2.645(10)
O(2)–Li(1)–O(2)	70.42(6)	70.43(6)
O(2)–Li(1)–O(2)	109.58(7)	109.57(6)

octahedral site may, however, be reversed, as pointed out by Bauer *et al.* who show that in $Na_3Zr_2Si_2PO_{12}$, at high temperature, the occupancy factor in the eight-coordinated Na(2) site is higher than in the octahedral Na(1) site (*6*). The high occupancy factor of Li(1), tending to inhibit it from ionic movement, suggests that Li diffusion via the Li(1) site is improbable at least at room temperature. The large opening resulting from the long Li(1)–O distance, however, is a favorable geometrical factor for Li(1) diffusion. Consequently, it would be interesting to verify at high temperature (i.e., in the highly conducting state) whether there is effectively a transfer of Li ions from the octahedral site to the eight-coordinated site. As mentioned above, the difference Fourier map clearly indicates that some Li ions are located in the eight-coordinated cavity (in the 18*e* position). Unfortunately, the high-temperature factor of Li(2) makes the determination of its occupancy factor and its location uncertain. Least-squares refinement, however, has strongly suggested an Li(2) configuration that consists of Li(2) splitting into two positions, Li(2) and Li(3), at $-1/3 \pm 0.03$, 0, 1/4. The coordination is eightfold for both Li(2) and Li(3), with Li–O distances quite acceptable for eight-coordinated lithium.

It is unknown whether this disorder is dynamic or static, and it is not possible to determine this by diffraction methods, because the diffracted intensities are necessarily due to time-averaged distributions. To provide some insight into the nature of

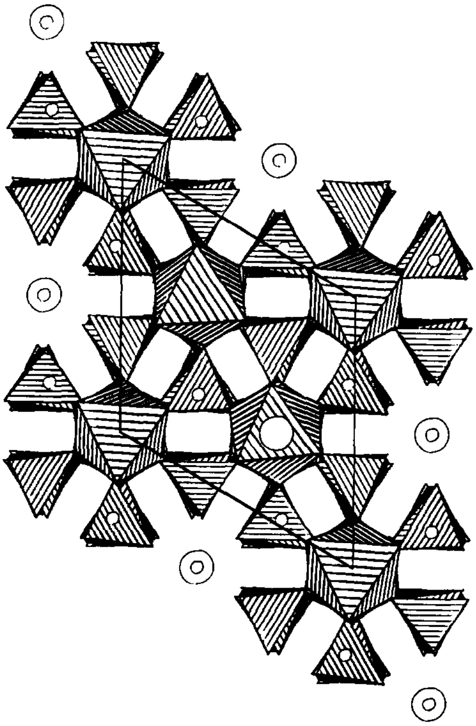

FIG. 2. General view (*16*) along (001) of $Li_{1+x}Ti_{2-x}In_xP_8O_{12}$, $x = 0.12$ or 0.15. Large circle: Li(1); small circle: Li(2) and Li(3).

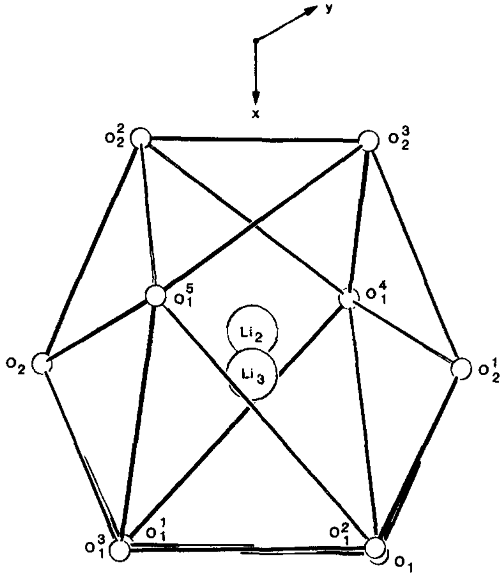

FIG. 3. Coordination polyhedra of Li(2) and Li(3). The Li–O distances are listed in Table III. O_1 $(1 - y, 1 + x - y, z)$; O_1^1 $(\bar{1} + y - x, \bar{x}, z)$; O_1^2 $(\bar{1} + y, x, 1/2 - z)$ O_1^3 $(\bar{x}, \bar{1} + y - x, \frac{1}{2} - z)$; O_1^4 $(\bar{4}/3 + y, \bar{2}/3 + y - x, 1/3 - z)$; O_1^5 $(\bar{2}/3 + x, 2/3 + x - y, 1/6 + z)$; O_2 $(\bar{2}/3 + x, \bar{1}/3 + x - y, 1/6 + z)$; O_2^1 $(\bar{1}/3 + y, 1/3 + y - x, 1/3 - z)$; O_2^2 $(\bar{2}/3 + y - x, \bar{1}/3 + y, 1/6 + z)$; O_2^3 $(\bar{1}/3 - x, 1/3 - y, 1/3 - z)$.

mobile ion disorder, a temperature dependence study of phase Ib is under way.

Conclusions

Neutron Rietveld refinements of powder neutron data of the $Li_{1+x}Ti_{2-x}In_xP_3O_{12}$ system indicate that an unknown phase, still identified, coexists with this high-conducting solid solution, at least for low values of x. Distortion induced by substitution of small amounts of Ti^{4+} by larger In^{3+} ions, up to $x \approx 0.35$, distorts the structure framework, but does not destroy its NASICON-type structure. Li ions occupy both octahedral and eight-coordinated sites. Li ions occupy 95% of the available octahedral sites, whereas the remaining lithium, much more labile, resides in the large cavity, and is presumably in a highly disordered configuration.

Acknowledgments

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