

## Structure of the Orthorhombic Phase of $\text{Li}_{1+x}\text{Ti}_{2-x}\text{In}_x\text{P}_3\text{O}_{12}$ , $x = 1.08$

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**Abstract.**  $\text{Li}_{1+x}\text{Ti}_{2-x}\text{In}_x\text{P}_3\text{O}_{12}$  is orthorhombic for  $0.4 < x < 1.1$ ; *Pbca*, for  $x = 1.08$ :  $M_r = 467.42$ ,  $a = 8.647$  (2),  $b = 8.807$  (2),  $c = 24.328$  (3) Å,  $Z = 4$ ,  $V = 1852.7$  Å<sup>3</sup>,  $D_x = 3.35$  Mg m<sup>-3</sup>, Mo *K*α,  $\lambda = 0.7107$  Å,  $\mu = 1.94$  mm<sup>-1</sup>,  $F(000) = 872$ ,  $T = 298$  K,  $R = 4.7\%$  for 1265 observed reflections. The structure of the title compound consists of basic units: three  $\text{PO}_4$  tetrahedra spanning the six corners of two  $\text{MO}_6$  octahedra; the basic units are in turn linked together forming a three-dimensional  $[\text{Ti}_{2-x}\text{In}_x\text{P}_3\text{O}_{12}]$  framework in which the *M* site is randomly occupied by  $\text{Ti}^{4+}$  and  $\text{In}^{3+}$ . This arrangement is locally similar to that of the Nasicon framework. However, the orthorhombic structure is actually an intergrowth of Nasicon and anti-Nasicon blocks.

**Introduction.** It has previously been reported that the  $\text{Li}_{1+x}\text{Ti}_{2-x}\text{In}_x\text{P}_3\text{O}_{12}$  solid solution, hereafter referred to as LTIP, exhibits ionic conductivity *via* the Li mobility in the three-dimensional  $[\text{Ti}_{2-x}\text{In}_x\text{P}_3\text{O}_{12}]$  framework (Li Shi-Chun & Lin Zu-Xiang, 1983).

X-ray powder studies have suggested that compounds in the LTIP system adopt, depending on the  $x$  value, three distinct structures corresponding to three different phases: phase I,  $0 < x < 0.4$ , is  $R\bar{3}c$  (or probably monoclinic  $C2/c$  for  $x$  near to 0.4); phase II,  $0.4 < x < 1.1$ , is orthorhombic, *Pbca*; and phase III,  $1.1 < x < 2.0$ , is monoclinic  $P2_1/n$  (Hamdouné, Tran Qui & Schouler, 1986).

Electrical measurements performed on polycrystalline samples showed that the conductivity curve of the LTIP system as a function of  $x$  has three extrema: a maximum,  $2.56 \times 10^{-2}$  ( $\Omega \text{ cm}$ )<sup>-1</sup> at  $x = 0.3$ , a minimum,  $3 \times 10^{-3}$  ( $\Omega \text{ cm}$ )<sup>-1</sup> at  $x = 0.9$  and another maximum,  $7 \times 10^{-2}$  ( $\Omega \text{ cm}$ )<sup>-1</sup>, at  $x = 1.8$  (Hamdouné, 1987) suggesting that phase transitions between I, II and III correspond to major changes in the  $[\text{Ti}_{2-x}\text{In}_x\text{P}_3\text{O}_{12}]$  framework. In order to correlate the structural framework and ionic conductivity in the LTIP system the structures of phases I and III have recently been reported (Tran Qui & Hamdouné, 1987). We now describe the crystal structure of phase II.

**Experimental.** Crystals were grown by the method previously described (Hamdouné *et al.*, 1986). Single crystal used for this study was an approximate

parallelepiped,  $0.12 \times 0.08 \times 0.07$  mm. Enraf–Nonius CAD-4 diffractometer; cell parameters from 25 reflections,  $8 < \theta < 25^\circ$ ; graphite-monochromatized Mo *K*α radiation,  $\omega/2\theta$  scan. Three reflections every two hours as intensity and orientation control; no observable intensity decay. 6700 reflections in the range  $4 < 2\theta < 60^\circ$ , averaged to  $1265 > 3\sigma(F)$ ; range of *hkl*:  $-9 < h < 9$ ,  $0 < k < 10$ ,  $0 < l < 27$ . Lorentz–polarization correction, no absorption correction. The Ti/In, P and four O atoms were located by direct methods (*MULTAN80*; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and the remaining O and Li atoms by difference Fourier syntheses. Isotropic and anisotropic full-matrix least-squares refinement using NRC VAX *Crystal Structure System* (Larson, Lee, Le Page & Gabe, 1982). Another series of refinement including the occupancy factor of the Ti/In site gave a substitutional parameter  $x = 1.08$  implying an average excess of 0.08 of Li per unit cell which cannot, however, be localized by difference Fourier synthesis. Function minimized  $\sum w(|F_o| - |KF_c|)^2$ ,  $w = [\sigma^2(F_o) + 0.01|F_o|^2]^{-1}$ .  $f$ ,  $f'$  and  $f''$  from *International Tables for X-ray Crystallography* (1974). Final  $R = 0.047$  ( $wR = 0.052$ ) for 1265 reflections; max shift/e.s.d. 0.5 for O(7)  $z$  parameter; maximum and minimum  $\Delta\rho \leq 0.25$  e Å<sup>-3</sup>; VAX 780 computer.\*

**Discussion.** Fractional coordinates and equivalent isotropic temperature factors of atoms in the asymmetric unit cell are given in Table 1 and selected bond lengths in Table 2. The  $[\text{Ti}_{0.92}\text{In}_{1.08}\text{P}_3\text{O}_{12}]$  framework and lithium sites are illustrated in Fig. 1. This framework consists of two  $\text{MO}_6$  octahedra, of which three vertices of each are linked by a  $\text{PO}_4$  tetrahedron forming a basic unit of two octahedra and three tetrahedra; this basic unit is denoted  $[\text{O}-T_3-\text{O}]$ . The two remaining vertices of each tetrahedron which do not span the parallel faces of the octahedra are linked to the top and bottom, respectively, of two neighbouring basic units giving rise to an infinite string of basic units,

\* Lists of structure factors, anisotropic thermal parameters and interatomic angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44951 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> (Å <sup>2</sup> )
M(1)†	0.49870 (6)	0.79281 (3)	0.43007 (2)	0.874 (6)
M(2)	0.50048 (4)	0.21574 (3)	0.32154 (1)	0.903 (5)
P(1)	0.2915 (1)	0.4925 (1)	0.62107 (4)	1.07 (2)
P(2)	0.1418 (1)	0.1438 (1)	0.79968 (4)	0.94 (2)
P(3)	0.3434 (1)	0.3679 (1)	0.94828 (4)	1.18 (2)
O(1)	0.2012 (4)	0.3889 (4)	0.6582 (2)	3.55 (7)
O(2)	0.0950 (4)	0.0768 (4)	0.6572 (1)	2.47 (6)
O(3)	0.3892 (4)	0.3270 (5)	0.8914 (1)	3.78 (8)
O(4)	0.3864 (4)	0.5357 (3)	0.9598 (1)	2.23 (6)
O(5)	0.3115 (4)	0.4026 (4)	0.0882 (2)	3.44 (7)
O(6)	0.4262 (4)	0.2329 (3)	0.4893 (1)	2.83 (7)
O(7)	0.3812 (4)	0.4021 (4)	0.5787 (2)	3.43 (7)
O(8)	0.5834 (4)	0.2623 (3)	0.7407 (1)	2.43 (6)
O(9)	0.4191 (3)	0.4874 (3)	0.7839 (1)	1.77 (5)
O(10)	0.0822 (4)	0.1945 (5)	0.1444 (1)	2.79 (6)
O(11)	0.3175 (3)	0.1391 (3)	0.2014 (1)	1.90 (5)
O(12)	0.1693 (3)	0.1513 (4)	0.4565 (1)	2.28 (6)
Li(1)	0.0380 (10)	0.038 (1)	0.2881 (4)	2.0 (2)
Li(2)	0.4785 (8)	0.501 (2)	0.5020 (5)	3.6 (6)

† M sites are randomly occupied by (Ti<sub>0.92</sub> + In<sub>1.08</sub>).

Table 2. Selected bond lengths (Å) with standard deviations in parentheses

P(1)—O(1)	1.504 (2)	P(2)—O(8)	1.520 (2) <sup>b</sup>	P(3)—O(3)	1.484 (3)
P(1)—O(2)	1.511 (2) <sup>a</sup>	P(2)—O(9)	1.524 (2) <sup>a</sup>	P(3)—O(4)	1.531 (2)
P(1)—O(5)	1.512 (2) <sup>f</sup>	P(2)—O(10)	1.522 (2) <sup>f</sup>	P(3)—O(6)	1.512 (2) <sup>b</sup>
P(1)—O(7)	1.519 (2)	P(2)—O(11)	1.520 (2)	P(3)—O(12)	1.528 (2) <sup>b</sup>
Average	1.511 (2)	Average	1.521 (2)	Average	1.514 (3)
M(1)—O(4)	1.980 (1) <sup>e</sup>	M(2)—O(1)	2.026 (3) <sup>a</sup>		
M(1)—O(5)	1.956 (1) <sup>d</sup>	M(2)—O(2)	2.068 (2) <sup>a</sup>		
M(1)—O(6)	2.077 (1) <sup>e</sup>	M(2)—O(3)	1.988 (2) <sup>b</sup>		
M(1)—O(7)	2.013 (1) <sup>e</sup>	M(2)—O(8)	2.102 (2) <sup>b</sup>		
M(1)—O(10)	1.945 (1) <sup>f</sup>	M(2)—O(9)	2.130 (2) <sup>b</sup>		
M(1)—O(12)	2.018 (1) <sup>a</sup>	M(2)—O(11)	2.109 (2) <sup>b</sup>		
Average	1.998 (1)	Average	2.070 (2)		
Li(1)—O(2)	2.029 (8) <sup>a</sup>	Li(2)—O(6)	2.43 (1)		
Li(1)—O(8)	1.933 (7) <sup>f</sup>	Li(2)—O(7)	2.22 (1)		
Li(1)—O(9)	2.045 (7) <sup>a</sup>	Li(2)—O(7)	2.46 (1) <sup>a</sup>		
Li(1)—O(11)	2.015 (7) <sup>f</sup>	Li(2)—O(12)	2.45 (1) <sup>a</sup>		
Average	2.005 (7)	Average	2.35 (1)		

Symmetry code: (a)  $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$ ; (b)  $x, \frac{1}{2}-y, \frac{1}{2}+z$ ; (c)  $x, \frac{1}{2}-y, -\frac{1}{2}+z$ ; (d)  $1-x, \frac{1}{2}+y, \frac{1}{2}-z$ ; (e)  $1-x, \frac{1}{2}+y, 1-z$ ; (f)  $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$ ; (g)  $\frac{1}{2}-x, \frac{1}{2}+y, z$ ; (h)  $-\frac{1}{2}+x, y, \frac{3}{2}-z$ ; (i)  $-\frac{1}{2}+x, y, z$ ; (j)  $-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$ .

[Ti<sub>2-x</sub>In<sub>x</sub>P<sub>3</sub>O<sub>12</sub>], hereafter referred to as [O—T<sub>3</sub>—O]<sub>∞</sub>. The P—O bond lengths and O—P—O angles (Table 2) show that the monophosphate groups are fairly regular and that the MO<sub>6</sub> octahedra are slightly distorted with an average M—O distance significantly longer than that observed in the Ti-rich rhombohedral compounds, consistent with the presence of In<sup>3+</sup> in the M sites. The thermal factor values for O atoms in this compound are rather large compared to those observed in the two end members, LiTi<sub>2</sub>P<sub>3</sub>O<sub>12</sub> and Li<sub>3</sub>In<sub>2</sub>P<sub>3</sub>O<sub>12</sub>, of the LTIP system. This feature may be explained, in the present case, by the compositional proximity of this compound

to the orthorhombic—monoclinic transition region which causes some distortion in the framework.

In order to relate the structure of the orthorhombic phase with the Nasicon-type arrangement we describe the [Ti<sub>2-x</sub>In<sub>x</sub>P<sub>3</sub>O<sub>12</sub>] framework of both phases as formed alternatively by an infinite [O—T<sub>3</sub>—O]<sub>∞</sub> string parallel to the orthorhombic *b* axis and its centrosymmetric image. Two adjacent strings are grouped together forming double strings. In the Nasicon framework the double strings are identical and stacked parallel to the C<sub>2</sub>/c monoclinic *c* axis creating characteristic antiprismatic and eightfold polyhedral cavities while in the orthorhombic framework the stacking is alternatively made by a double string parallel to the *b* axis and its mirror image. Thus, the orthorhombic [Ti<sub>2-x</sub>In<sub>x</sub>P<sub>3</sub>O<sub>12</sub>] framework can be regarded as an intergrowth between Nasicon and anti-Nasicon blocks, represented by A + A' + B + B'... in Fig. 1 [as examples of Nasicon and 'anti-Nasicon' structures one is referred to the structure of Na<sub>3</sub>Sc<sub>2</sub>P<sub>3</sub>O<sub>12</sub> reported by Efremov & Kalinin (1978) and Hong (1979), respectively]. The alkali antiprismatic and eightfold polyhedral sites, which are critical for fast-ion diffusion in the Nasicon-type compounds, are destroyed in the orthorhombic framework. Li ions are trapped in two

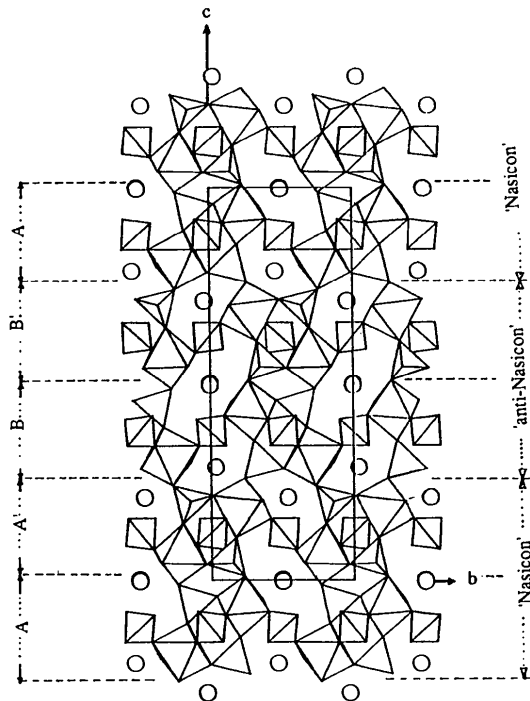


Fig. 1. Computer drawing (Fischer, 1985) of the [Ti<sub>2-x</sub>In<sub>x</sub>P<sub>3</sub>O<sub>12</sub>] framework of the orthorhombic phase; Li atoms are represented by circles. For clarity only atoms with  $-0.4 < x < 0.4$  are represented; A is the infinite string of (O—T<sub>3</sub>—O), A' is the centrosymmetric image of A. (A + A') is of Nasicon type, its mirror image is (B + B').

different tetrahedral sites: one with average Li(1)—O distance of 2.00 Å and another, larger and more mobile, with average Li(2)—O distance of 2.35 Å.

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## Structures of Trisodium Hexakis(formato)chromate(III) Tetrahydrate and Trisodium Hexakis(formato)molybdate(III)

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**Abstract.** Na<sub>3</sub>[Cr(CHO<sub>2</sub>)<sub>6</sub>].4H<sub>2</sub>O, *M<sub>r</sub>* = 463.15, triclinic, *P* $\bar{1}$ , *a* = 6.463 (1), *b* = 7.678 (2), *c* = 8.741 (2) Å,  $\alpha$  = 101.46 (1),  $\beta$  = 97.26 (1),  $\gamma$  = 78.74 (1)°, *V* = 415.2 (2) Å<sup>3</sup>, *Z* = 1, *D<sub>x</sub>* = 1.852 Mg m<sup>-3</sup>, Mo *K*α,  $\lambda$  = 0.71073 Å,  $\mu$  = 0.824 mm<sup>-1</sup>, *F*(000) = 235, 298 K, *R*(*F*) = 0.023 for 2221 reflexions [*I* > 3σ(*I*)] and 149 variables. Na<sub>3</sub>[Mo(CHO<sub>2</sub>)<sub>6</sub>], *M<sub>r</sub>* = 435.02, orthorhombic, *Pccn*, *a* = 14.630 (6), *b* = 6.383 (2), *c* = 13.888 (5) Å, *V* = 1296.9 (8) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 2.228 Mg m<sup>-3</sup>, Mo *K*α,  $\lambda$  = 0.71073 Å,  $\mu$  = 1.143 mm<sup>-1</sup>, *F*(000) = 852, 293 K, *R* = 0.026 for 1524 reflexions [*I* > 3σ(*I*)] and 113 variables. In both complexes the metal atom is bonded to six formate ions, two with *M*—O—C—O*t* in the *sp* and four in the *ap* conformation. [Cr(CHO<sub>2</sub>)<sub>6</sub>]<sup>3-</sup> is centrosymmetric with Cr—O distances of 1.973 (1), 1.979 (1) and 1.992 (1) Å; the long Cr—O bond is to an O atom which is hydrogen bonded to water. [Mo(CHO<sub>2</sub>)<sub>6</sub>]<sup>3-</sup> has twofold symmetry; the Mo—O distances are 2.116 (1), 2.113 (1) and 2.110 (1) Å. In both cases, the coordination octahedra are distorted, the r.m.s. deviations of the angles from ideality being 2.4° for CrO<sub>6</sub> and 5.2° for MoO<sub>6</sub>.

**Introduction.** Compounds of the type Na<sub>3</sub>[M<sup>III</sup>(CHO<sub>2</sub>)<sub>6</sub>] seem only to be known for four metals, Fe (Weinland & Reihlen, 1913), V (Barbieri, 1916), Cr (Stiasny & Walther, 1928) and Mo (Brorson & Schäffer, 1986). The structures of several formate

complexes of divalent metals are known which contain [M<sup>II</sup>(CHO<sub>2</sub>)<sub>6</sub>] octahedra but in most of these (Weber, 1980, and references therein) the formates are bridges between the metal atoms. Formate groups can be bonded with *M*—O—C—O*t* (O*t* = terminal O atom) in the *sp* or *ap* conformation, *i.e.* the torsion angle can be 0 or 180°, an extreme case of the former is when the formate is bidentate as in [Mo(CO)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>(CHO<sub>2</sub>)<sub>2</sub>] (Brower, Winston, Tonker & Templeton, 1986). The structures of the Cr and the Mo complexes are reported here.

**Experimental.** The chromium compound was synthesized by M. Brorson and C. Schäffer of Copenhagen University using Stiasny & Walther's (1928) method and recrystallized by adding ethanol to an aqueous solution. A lath-shaped crystal, 0.45 × 0.22 × 0.18 mm, was mounted on a Picker FACS-1 diffractometer. Cell dimensions were determined from the setting angles of 25 reflections with 13 ≤ θ ≤ 20°. Intensities were measured out to [(sin θ)/λ]<sub>max</sub> = 0.7 Å<sup>-1</sup> using an ω-2θ scan and Nb-filtered Mo *K*α radiation, scan width (2.0 + 0.692 tan θ)°, step length 0.04°, 1 s step<sup>-1</sup>. Reflexions with 0 ≤ *h* ≤ 9, -10 ≤ *k* ≤ 10, -12 ≤ *l* ≤ 12 measured giving 2421 independent reflexions of which 2221 had *I* > 3σ<sub>cs</sub>(*I*). Reflexions 400 and 222 were monitored every 60 reflexions, the overall fall off in intensity was 3.7%. No correction was made for absorption.