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LETTERS TO THE EDITOR

$Li_{3-x}Ti_2(PO_4)_3$ ($0 \leq x \leq 1$): A New Mixed Valent Titanium(III/IV) Phosphate with a NASICON-Type Structure

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A new NASICON-related structure of lithium titanium phosphate $Li_{2.72}Ti_2(PO_4)_3$ has been determined. This compound crystallizes in an orthorhombic system, *Pbcn*, with a = 12.064 (3) Å, b = 8.663 (3) Å, c = 8.711 (4) Å, V = 910.4 (8) Å^3, and Z = 4. The single crystal structure of this novel mixed valent titanium(III/IV) phosphate reveals one titanium atom per asymmetric unit. Two lithium sites are characterized by a pair of distorted polyhedra, $Li(1)O_4$ and $Li(2)O_5$, which share a common edge resulting in a short Li(1) . . . Li(2) distance, i.e., 2.29 (5) Å. Magnetic susceptibility and microprobe analysis confirmed the structural composition. The room temperature ionic conductivity is comparable with that of the known $Li_{1+x}Ti^{IV}_{2-x}In^{III}_x(PO_4)_3$, which suggests possible fast ionic conductivity.

Introduction

Since the discovery of fast Na^+-ion transport in $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ (*1*), the NASICON and its structurally related compounds have been extensively studied. Single crystal structure investigations have revealed that compounds with the general formula $A_xM_2(PO_4)_3$, of the NASICON-type, are characterized by a structural framework built up from $M_2(PO_4)_3$ units. Each unit consists of corner-sharing MO_6 octahedra and PO_4 tetrahedra. The A-site cation has demonstrated that it plays an important role in determining the structure type and moreover the size of the openings for ion diffusion. Furthermore, composition (x) of the A-site cation is also a fundamental factor associated with fast ionic conductivity.

Recently, a new system $Li_{1+x}Ti^{IV}_{2-x}In^{III}_x(PO_4)_3$ that exhibits high ionic conductivity was reported (*2*). Detailed studies have concluded that at 300°C the best conductivity measured, i.e., 2×10^{-2} $(\Omega\ \mathrm{cm})^{-1}$ for $x \approx 0.35$ (*3*), is lower by a factor of ten than that of NASICON. The latter has an Na^+-ion conductivity that is competitive with the best β- and β''-alumina (*4*). $Li_{1+x}Ti_{2-x}In_x(PO_4)_3$ compounds adopt one of three structure types depending upon the x value (*5*, *6*). We have discovered that the newly synthesized $Li_{3-x}Ti^{III}_{2-x}Ti^{IV}_x(PO_4)_3$ series with $0 \leq x \leq 1$ may offer an interesting fast ionic conductivity and phase transformation. In this paper, we report the synthesis and structural characterization of a novel compound of reduced lithium titanium phosphate, $Li_{2.72}Ti_2(PO_4)_3$. A solid solution series $Li_{3-x}Ti_2(PO_4)_3$ ($0 \leq x \leq 1$) and its structural transformation are also briefly discussed.

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Experimental

Syntheses. The single crystals of the title compound, $Li_{3-x}Ti_2(PO_4)_3$ ($x = 0.28$), were first obtained from a reduced system of Li_2O–TiO_x–P_2O_5 ($x < 2$). The reaction was carried out by a two-step conventional high temperature solid state reaction. The first step of the synthesis was to prepare a solid state precursor with a mole ratio of Li/Ti/P of 1.40/1.15/2.00. The reaction mixture of Li_2CO_3 (J. T. Baker Chemical Co., 99.9%), TiO_2 (Aldrich, 99.9+%), and $(NH_4)_2HPO_4$ (Fisher Scientific Co., 99.4%) was calcined in air. To prevent the loss of Li_2O, the calcination procedures were carried out at a relatively low temperature, 350°C overnight, followed by 550°C for 5 hr. The synthesis proceeded with a reduction reaction containing an appropriate amount of the precursor and titanium metal powder (Aldrich, 99.9%) in a fused silica tube for 3 days at 900°C. The reaction was slowly cooled at a rate of −5°C/hr to 500°C and −50°C/hr to room temperature. The product was black in color.

High purity polycrystalline samples of $Li_{3-x}Ti_2(PO_4)_3$ ($0 \leq x \leq 1$) were synthesized by the stoichiometric reaction using the same procedure. The yield was ca. 95% according to the powder X-ray diffraction patterns. The DTA curve of the $Li_{2.72}Ti_2(PO_4)_3$ phase revealed two reversible phase transitions at ~165 and 230°C.

Single Crystal X-Ray Structure Determination. A black gem crystal was chosen for the single crystal structure study. Data collection, and general structure determination procedures were the same as previously reported (7). Detailed crystallographic parameters are tabulated in Table I. Weissenberg photographs and the Laue patterns consistently showed a primitive (*mmm*) orthorhombic crystal system. Based on the intensity statistics, systematic extinctions (observed *hkl*: 0*kl* with $k = 2n$, *h*0*l* with $l = 2n$, *hk*0 with $h + k = 2n$), and the successful structure refinement, the space group was determined to be *Pbcn* (No. 60). Three azimuthal scans ($2\theta = 9.37°, 24.27°, 24.29°$) were used for absorption corrections. The atomic coordinates of three cations (Ti, P(1), and P(2)) were found by a direct method. The positional parameters of the six oxygen atoms were located from the calculated Fourier synthesis maps. The structural and thermal parameters were then refined by full-matrix least-squares methods based on F^2 to $R = 0.085$ and $R_w = 0.102$. The positions of two lithium atoms were finally determined by difference maps and reasonable Li–O distances. The occupancy factors for two lithium atoms, Li(1) and Li(2), were initially refined. The resultant value indicated that the latter possesses partial occupancy, e.g., 0.36. The final positional and thermal parameters are given in Table II. (The structure factor table and anisotropic thermal parameters are in Appen-

TABLE I

CRYSTALLOGRAPHIC PARAMETERS FOR $Li_{2.72}Ti_2(PO_4)_3$

Formula mass (amu)	399.59
Space group	*Pbcn* (No. 60)
a (Å)	12.064 (3)
b (Å)	8.663 (3)
c (Å)	8.711 (4)
V (Å^3)	910.4 (8)
Z	4
T (K) of data collection	296
p calc. (g cm^{-3})	2.92
Radiation (graphite monochromated)	Mo$K\alpha$ ($\lambda = 0.71069$ Å)
Crystal shape, color	Gem, black
Crystal size (mm)	0.10 × 0.15 × 0.20
Linear abs. coeff. (cm^{-1}), μ	23.22
Transmission factors	0.98 ~ 1.00
Scan type	$\omega - 2\theta$
Scan speed (degrees/min)	4.0
Scan range (degrees)	−0.7 to 0.7° in ω
Standard reflections	2,1,−1; 2,0,−2; 1,1,−2
Background counts	$\frac{1}{4}$ of scan range on each side of reflection
2θ (max)	55°
Data collected	$\pm h, k, l$
p for σ (F^2)	0.03
No. of unique data ($F_0^2 > 0$)	1048
No. of unique data with $F_0^2 > 3\sigma$ (F_0^2)	778
F_{000}	772.64
R/R_w (F^2)/GOF	0.060/0.070/2.03
R (on F for $F^2 > 3\sigma$ (F_0^2))	0.048
No. of variables	87

TABLE II

POSITIONAL AND ISOTHERMAL TEMPERATURE PARAMETERS FOR $Li_{2.72}Ti_2(PO_4)_3$

Atom	x	y	z	$B_{(eq)}$[a]
Ti	0.39036 (8)	0.2507 (1)	0.0376 (1)	0.72 (4)
P (1)	0.5	0.5393 (3)	0.25	0.94 (9)
P (2)	0.3507 (1)	0.1046 (2)	0.3946 (2)	0.63 (6)
O (1)	0.4251 (4)	0.3553 (7)	−0.1543 (6)	2.3 (2)
O (2)	0.4230 (4)	0.4439 (6)	0.1515 (6)	2.2 (2)
O (3)	0.5320 (3)	0.1552 (5)	0.0675 (5)	1.4 (2)
O (4)	0.2287 (4)	0.3276 (6)	0.0151 (5)	1.5 (2)
O (5)	0.3172 (4)	0.1582 (5)	0.2338 (5)	1.2 (2)
O (6)	0.3407 (4)	0.0697 (5)	−0.0998 (5)	1.2 (2)
Li (1)	0.180 (2)	0.295 (2)	0.225 (2)	4.6 (4)
Li (2)[b]	0.202 (4)	0.078 (5)	0.078 (5)	4 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameters defined as $B_{eq} = \frac{4}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2\,ac\cos\beta)\beta_{13}]$.

[b] Refined occupancy factor is 0.36.

dixes I and II.)[1] The microprobe analysis (see Appendix III)[1] showed that the average composition of the cationic elements is $Li_{2.7}Ti_{2.0}P_{3.1}$, which is comparable (within the experimental error) with the structural composition. Its composition was further confirmed by a various temperature magnetic susceptibility measurement of selected black crystals (see Appendix IV).[1] A Curie constant of 1.0950 emu K/mole gives rise to a 2.97 μ_B which corresponds to 1.72 unpaired electrons per formula unit. This matches with the expected value based on the structural formula, $Li_{2.72}Ti_2(PO_4)_3$.

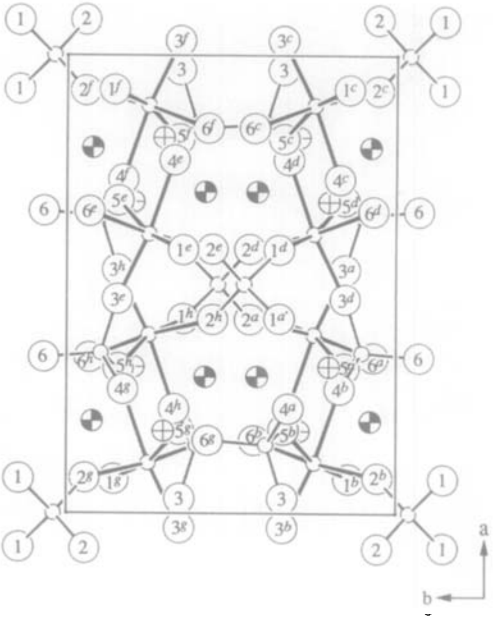

FIG. 1. The ORTEP drawing of the projected unit cell of $Li_{2.72}Ti_2(PO_4)_3$ viewed along c. The octahedrally coordinated TiO_6 bonds are drawn in heavy lines. The titanium and phosphorus atoms are drawn in open circles connected by thick (Ti–O) and thin (P–O) lines to oxygen atoms. The numbered large open circles are oxygens. The cross-hatched and half-filled small circles are Li(1) and Li(2), respectively. Symmetry code: $a = x, y, z$; $b = 1/2 - x, 1/2 - y, 1/2 - z$; $c = 1/2 + x, 1/2 - y, 1 - z$; $d = 1 - x, y, 1/2 - z$; $e = 1 - x, 1 - y, 1 - z$; $f = 1/2 + x, 1/2 + y, 1/2 - z$; $g = 1/2 - x, 1/2 + y, z$; $h = x, 1 - y, 1/2 + z$, $a' = x, y, 1 + z$; $g' = 1/2 - x, 1/2 + y, 1 + z$.

Structure Description and Discussion

In Fig. 1, the projected single crystal structure of the title compound is viewed along c. It contains isolated TiO_6 octahedra (drawn in thick lines) which share each of their six corners with a PO_4 tetrahedron. In the network, there are two lithium atoms per asymmetric unit, e.g., Li(1) and Li(2). The Li(2) site (half-filled circles) is partially occupied in an approximately pentagonal channel structure running along the c-axis (Fig. 2). This partial occupancy may be responsible for the fast ionic conductivity.

Despite the complexity of the structure, it exhibits a great similarity with that of NASICON. Both mixed frameworks are built up from similar $[Ti_2(PO_4)_3]$ structural units. Each unit is composed of two TiO_6

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[1] See NAPS document No. 04830 for 15 pages of supplementary materials. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid.

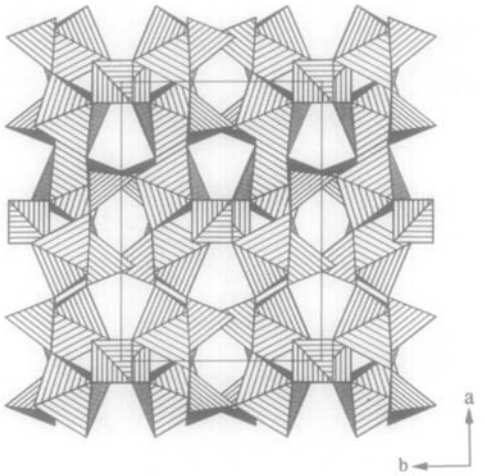

FIG. 2. A STRUPLO 86 polyhedral representation of the structure of $Li_{2.72}Ti_2(PO_4)_3$ is viewed along *c*. The lithium atoms are omitted for clarity. The projected unit cell on the *ab*-plane is outlined.

octahedra linked to each other through three PO_4 tetrahedra, as shown in Fig. 3. Thus, the structure formula of the unit can be written as $Ti_{2/1}(O^{t,o})_{6/2}[P_{1/1}(O^{b})_{2/1}(O^{t,i})_{2/2}]_{3/1}$ (O^{t}, terminal oxygen; O^{b}, bridging oxygen; i, inner; o, outer). $[Ti_2(PO_4)_3]$ units share terminal oxygen atoms, i.e., O(4), to form a two-dimensional slab parallel to the *ac*-plane (Figs. 2 and 3). The slabs are stacked along the *b*-axis and interconnected by sharing the remaining terminal oxygens, i.e., O(1) and O(6). Subsequently, a network structure is formed allowing the lithium cations to be located in cages and channels. Ideally, a half occupied Li(2) site, along with a fully occupied Li(1), would result in a chemical composition, $Li_3Ti_2(PO_4)_3$, in which the titanium cation is trivalent.

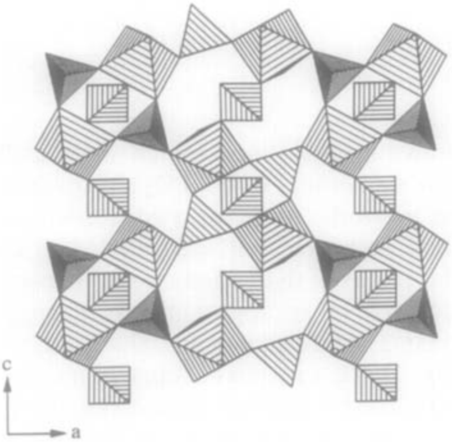

FIG. 3. The slab structure built up from $Ti_2(PO_4)_3$ units is shown by a STRUPLO 86 polyhedral plot. The Li(1) atoms are located in the cage formed by stacked slabs parallel to *ac*-plane. (See text.)

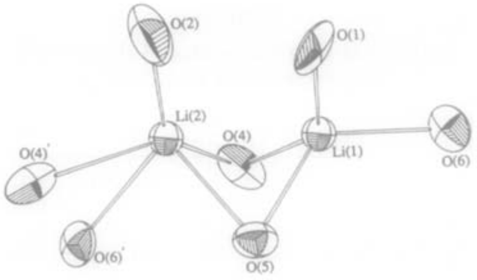

FIG. 4. The ORTEP drawing of the two lithium polyhedra, e.g., $Li(1)O_4$ and $Li(2)O_5$, that share a common edge, O(4)–O(5).

The two lithium cations were found in a pair of greatly distorted polyhedra, $Li(1)O_4$ and $Li(2)O_5$, as shown in Fig. 4. These deformed polyhedral groups share a common edge formed by O(4) and O(5). The Li(1)–O distances (Table III) range from 1.94 to 2.10 Å and are comparable with the sum of tetrahedrally coordinated Shannon crystal radii, i.e., 1.97 Å (*8*). In the $Li(2)O_5$ polyhedron, however, there are three relatively long Li(2)–O distances, i.e., 2.25, 2.28, and 2.39 Å. This indicates that the Li(2) cation is less tightly bonded to the oxide lattice and may therefore be more mobile. Furthermore, the resultant short Li(1)–Li(2) distance, i.e., 2.29(5) Å, is comparable with that in the Li_2O (antifluorite structure), e.g., $d_{\text{Li-Li}} = a/2 = 2.31$ Å (*9*).

One of the major interests in the compound $Li_{3-x}Ti_2(PO_4)_3$ rests on its ionic mo-

TABLE III

IMPORTANT BOND DISTANCES (Å) AND ANGLES (DEGREES)

TiO$_6$ Octahedra			
Ti–O (1)	1.948 (5)	Ti–O (4)	2.070 (4)
Ti–O (2)	1.985 (5)	Ti–O (5)	2.084 (5)
Ti–O (3)	1.917 (4)	Ti–O (6)	2.062 (5)
O (1)–Ti–O (2)	89.7 (2)	O (2)–Ti–O (6)	171.5 (2)
O (1)–Ti–O (3)	97.2 (2)	O (3)–Ti–O (4)	172.7 (2)
O (1)–Ti–O (4)	88.3 (2)	O (3)–Ti–O (5)	95.8 (2)
O (1)–Ti–O (5)	167.0 (2)	O (3)–Ti–O (6)	90.6 (2)
O (1)–Ti–O (6)	85.3 (2)	O (4)–Ti–O (5)	78.6 (2)
O (2)–Ti–O (3)	96.8 (2)	O (4)–Ti–O (6)	85.2 (2)
O (2)–Ti–O (4)	87.9 (2)	O (5)–Ti–O (6)	93.5 (2)
O (2)–Ti–O (5)	89.9 (2)		
PO$_4$ Tetrahedra			
P (1)–O (1)	1.531 (5) (2×)	P (2)–O (3)	1.517 (4)
P (1)–O (2)	1.510 (5) (2×)	P (2)–O (4)	1.538 (4)
O (1)–P (1)–O (1)	106.8 (4)	P (2)–O (5)	1.530 (5)
O (1)–P (1)–O (2)	105.8 (3) (2×)	P (2)–O (6)	1.516 (4)
O (1)–P (1)–O (2)	112.3 (3) (2×)	O (3)–P (2)–O (4)	108.8 (3)
O (2)–P (1)–O (2)	113.7 (4)	O (3)–P (2)–O (5)	111.0 (3)
		O (3)–P (2)–O (6)	110.8 (3)
		O (4)–P (2)–O (5)	110.1 (3)
		O (4)–P (2)–O (6)	108.0 (3)
		O (5)–P (2)–O (6)	108.1 (3)
Li(1)O$_4$ and Li(2)O$_5$ Polyhedra			
Li (1)–O (1)	2.10 (2)	Li (2)–O (2)	2.01 (5)
Li (1)–O (4)	1.94 (2)	Li (2)–O (4)	2.25 (5)
Li (1)–O (5)	2.04 (2)	Li (2)–O (4)′	2.39 (5)
Li (1)–O (6)	1.94 (2)	Li (2)–O (5)	2.07 (5)
		Li (2)–O (6)′	2.28 (5)

bility which is attributed to the existence of an interconnected space of partially occupied lattice sites. In the solid solution series ($0 \leq x \leq 1$) we observed that the cell volume decreases as the lithium composition is reduced. It is noted that a discontinuity in the cell volume appears at x between 0.28 and 0.55. This may be attributed to the fact that the average oxidation state increases as x decreases. That is to say a structural transformation may occur due to the separation of Ti^{4+}/Ti^{3+} sites and/or possibly changing in Li-site distribution. All of these changes will have an interesting effect on the Li-transport property. The detailed structural transformation and ionic conductivity measurements are under way.

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References

1. (a) H. Y.-P. HONG, *Mater. Res. Bull.* **11,** 173 (1976); (b) J. B. GOODENOUGH, H. Y.-P. HONG, AND J. A. KAFALAS, *Mater. Res. Bull.* **11,** 204 (1976).
2. SHI-CHUN LI AND ZU-XIANG LIN, *Solid State Ionics* **10,** 835 (1983).
3. S. HAMDOUNE, D. TRAN QUI, AND E. J. L. SCHOULER, *Solid State Ionics* **19,** 587 (1986).
4. (a) Y.-F. Y. YAO AND J. T. KUMMER, *J. Inorg. Nuclear Chem.* **29,** 2453 (1967);
   (b) M. S. WHITTINGHAM, *J. Chem. Phys.* **54,** 414 (1971);
   (c) J. L. BRIANT AND G. C. FARRINGTON, *J. Solid State Chem.* **33,** 385 (1980).
5. D. TRAN QUI, S. HAMDOUNE, J. L. SOUBEYROUX, AND E. PRINCE, *J. Solid State Chem.* **72,** 309 (1988); and the references cited therein.
6. D. TRAN QUI AND S. HAMDOUNE, *Acta Crystallogr. C* **43,** 397 (1987).
7. S. WANG AND S.-J. HWU, *J. Solid State Chem.* **90,** 31 (1991).
8. R. D. SHANNON, *Acta Crystallogr. A* **32,** 751 (1976).
9. Li_2O, No. 12-254, Joint Committee on Powder Diffraction Standards, Swarthmore, PA.