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$Li_{1.14}Nb_{0.93}Sc_{0.67}Cr_{0.40}(PO_4)_3$

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Abstract

Lithium niobium scandium–chromium tris(monophosphate) presents a large domain of homogeneity by cationic substitution: $Nb^V = Sc^{III}(Cr^{III}) + 2Li^I$. Basic structural units comprise two MO_6 octahedra linked by three PO_4 tetrahedra, as in the Nasicon-type structure, with partial ordering of the M atoms (M = Nb, Sc, Cr). Li^+ cations partially occupy interstices of two kinds, connected by channels along the c axis with small windows which limit the ionic mobility.

Comment

Compounds forming Nasicon (the acronym for Na superionic conductor) or related structures constitute a very large class of solid-state compounds because Zr in $NaZr_2(PO_4)_3$ can be substituted by many cations.

In the course of studies concerning Nasicon-type Li ionic conductors, three extremes of cationic conductivity values at 573 K were found for $Li_{1+x}Ti_{2-x}In_x(PO_4)_3$, correlated with the existence of three distinct phases: phase I for $0 \leq x \leq 0.4$ (space group $R\bar{3}c$), phase II for $0.4 < x < 1.1$ ($Pbca$) and phase III for $1.1 \leq x \leq 2$ ($P2_1/n$) (Hamdoune, Tran Qui & Schouler, 1986). Phases I and II are found in $Li_{1-x}Ti^{IV}_{2-x}Ti^{III}_x(PO_4)_3$ for $0 \leq x \leq 0.5$ and $0.5 < x < 1.2$, respectively (Wang, Greenblatt, Wang & Hwu, 1993). The covalency of Ti^{IV}—O bonds weakens Li—O interactions and so favours ionic conductivity.

In order to increase covalency of the structural skeleton $[M_2(PO_4)_3]$, we have introduced a cation in a pentavalent oxidation state: $Li_{2(x+y)-1}Nb^V_{2-x-y}Sc^{III}_xCr^{III}_y(PO_4)_3$ presents a large domain of homogeneity for $x + y > 0.5$. We describe the crystal structure of this phase for $x = 0.674$ and $y = 0.394$.

The $[M_2(PO_4)_3]$ framework consists of irregular MO_6 octahedra and PO_4 tetrahedra (Table 2). Like the Nasicon structure (Hagman & Kierkegaard, 1968), the basic unit includes two MO_6 octahedra linked by three PO_4 tetrahedra (Fig. 1). These units are distorted and they reveal partial cationic ordering: Nb and Cr atoms located in $M(1)O_6$ octahedra, Nb and Sc atoms in $M(2)O_6$ octahedra. The M—O distances in the $M(1)O_6$ octahedra are significantly shorter than the M—O distances in the $M(2)O_6$ octahedra, in accord with the values of the ionic radii: $r_{Nb^{5+}} = 0.64$, $r_{Cr^{3+}} = 0.615$ and $r_{Sc^{3+}} = 0.745$ Å (Shannon, 1976). Two parallel units $[M(1)M(2)P_3O_{18}]$ share two corner O atoms, thus constituting double units $[M(1)_2M(2)_2P_6O_{34}]$ (Fig. 1).

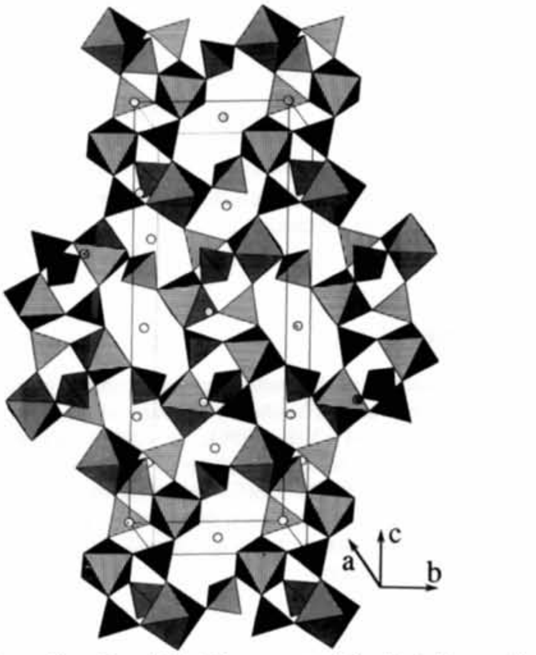

Fig. 1. Perspective view of the title compound. Small circles are Li atoms.

These double units share their free apical O atoms to form the three-dimensional network.

Li atoms partially occupy two interstices: a general position with pseudo-tetrahedral symmetry (occupation factor 0.836) and an inversion centre with pseudo-octahedral symmetry (occupation factor 0.600) (see Table 1).

The structural skeleton is similar to those of $Li_{2.08}Ti_{0.92}In_{1.08}(PO_4)_3$ (Tran Qui & Hamdoune, 1988) and $Li_{1.78}Ti_2(PO_4)_3$ (Wang & Hwu, 1992). However, we note a preference of small cations (Cr^{3+} here) for $M(1)$ sites, whereas in $Li_{2.08}Ti_{0.92}In_{1.08}(PO_4)_3$ the same statistical occupation of $M(1)$ and $M(2)$ sites is proposed in spite of the large difference between the ionic radii of Ti^{4+} ($r = 0.605$ Å) and In^{3+} ($r = 0.800$ Å) (Shannon, 1976).

The main disparity between the structures of these three isotypic phases concerns the Li-atom distribution, which determines the ionic conductivity. In $Li_{2.08}Ti_{0.92}In_{1.08}(PO_4)_3$, two general positions are fully occupied by Li atoms [one position is located at 0.19 Å from the inversion centre corresponding to our Li(2) position]; the remaining Li atoms have not been localized. In $Li_{1.78}Ti_2(PO_4)_3$, the Li atoms are distributed over four sites: general Li(1) and special Li(2) positions are fully occupied whereas Li(3) and Li(4) sites in the channels are partially occupied. In the present compound, the general Li(1) and special Li(2) positions are partially occupied, with a small difference in occupancies, so revealing comparable site energies. Structural studies of the other isotypic phases, $Li_{1+z}M_2(PO_4)_3$ with $z > 0.5$, appear necessary in order to determine if this energetic characteristic is correlated with the presence of pentavalent cations in the framework.

In the present case, the low ionic conductivity ($\sigma_{573\,K} = 2 \times 10^{-4}\,S\,cm^{-1}$) must be related to geometric constraints: 'bottlenecks' of channels are characterized by minimum diagonal O$\cdots$O distances of 3.55 and 3.91 Å, which are significantly smaller than double the usual Li—O distance (2 × 2.15 = 4.30 Å).

Experimental

A powder sample of the compound was prepared by solid-state synthesis from a stoichiometric mixture of Li_2CO_3, Nb_2O_5, Cr_2O_3, Sc_2O_3 and $(NH_4)_2HPO_4$ at 1300 K. Crystals were grown by the flux method: melting of the mixture at 1573 K (sample/$Li_4P_2O_7$: 80/20 mol%) followed by slowly cooling ($2\,K\,h^{-1}$) to 973 K. Elemental quantitative analysis by XRF gave x and y values in good agreement with results of the structure determination.

Crystal data

$Li_{1.14}Nb_{0.93}Sc_{0.67}Cr_{0.40}P_3O_{12}$
$M_r = 430.17$
Orthorhombic
$Pbca$
$a = 8.641\,(1)$ Å
$b = 8.760\,(1)$ Å
$c = 24.335\,(3)$ Å
$V = 1842.0\,(7)$ Å^3
$Z = 8$
$D_x = 3.102$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 24 reflections
$\theta = 16\text{–}17°$
$\mu = 2.639$ mm^{-1}
$T = 293$ K
Parallelepiped limited by {100}, {010} and {001} forms
0.17 × 0.15 × 0.09 mm
Green

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: analytical
$T_{min} = 0.81$, $T_{max} = 0.95$
3083 measured reflections
2678 independent reflections
1910 observed reflections [$I > 3\sigma(I)$]

$\theta_{max} = 30°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 34$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F
$R = 0.030$
$wR = 0.033$
$S = 2.54$
1910 reflections
160 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} < 0.08$

$\Delta\rho_{max} = 0.6$ e Å^{-3}
$\Delta\rho_{min} = -0.7$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2A)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

U_{iso} for Li atoms; $U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for all others.

	x	y	z	U_{iso}/U_{eq}
$M(1)$†	0.49931 (6)	0.28465 (5)	0.43156 (2)	0.0077 (2)
$M(2)$‡	0.50104 (7)	0.21634 (7)	0.18028 (2)	0.0090 (2)
P(1)	0.3486 (1)	0.3666 (1)	0.55307 (4)	0.0092 (5)
P(2)	0.2881 (1)	0.4959 (1)	0.87679 (5)	0.0093 (4)
P(3)	0.1411 (1)	0.3553 (1)	0.19894 (4)	0.0072 (4)
O(1)	0.4264 (4)	0.2688 (4)	0.5088 (1)	0.019 (2)
O(2)	0.1729 (4)	0.3486 (4)	0.5466 (1)	0.016 (2)
O(3)	0.3838 (4)	0.5357 (4)	0.5439 (1)	0.017 (2)
O(4)	0.4029 (4)	0.3153 (4)	0.6086 (1)	0.021 (2)
O(5)	0.1947 (4)	0.3901 (4)	0.8405 (2)	0.026 (2)
O(6)	0.3992 (4)	0.5838 (4)	0.8398 (1)	0.019 (2)
O(7)	0.1854 (4)	0.6012 (4)	0.9107 (2)	0.022 (2)
O(8)	0.3844 (4)	0.4047 (4)	0.9184 (2)	0.023 (2)
O(9)	0.0789 (5)	0.2406 (4)	0.2408 (1)	0.019 (1)
O(10)	0.0821 (4)	0.3020 (4)	0.1429 (1)	0.019 (2)
O(11)	0.0855 (4)	0.5167 (4)	0.2123 (1)	0.016 (1)
O(12)	0.3183 (4)	0.3535 (4)	0.2008 (1)	0.017 (2)
Li(1)§	0.039 (2)	0.467 (2)	0.7144 (5)	0.036 (3)
Li(2)¶	1/2	1/2	0	0.052 (7)

† $M(1)$ sites are randomly occupied by $(Nb_{0.606} + Cr_{0.394})$.
‡ $M(2)$ sites are randomly occupied by $(Nb_{0.326} + Sc_{0.674})$.
§ Occupation factor of Li(1) site: 0.836.
¶ Occupation factor of Li(2) site: 0.600.

Table 2. *Selected geometric parameters* (Å, °)

$M(1)$	O(1)	O(2^{i})	O(30^{ii})	O(7^{iii})	O(8^{iv})	O(10^{v})
O(1)	1.987 (2)	2.723 (6)	2.696 (6)	2.816 (7)	2.698 (7)	3.940 (7)
O(2)	86.8 (1)	1.974 (3)	2.785 (7)	3.920 (9)	2.680 (6)	2.801 (5)

O(3^{ii})	86.1 (1)	90.1 (1)	1.963 (3)	2.888 (7)	3.912 (9)	2.813 (5)
O(7^{iii})	91.3 (2)	174.4 (7)	95.1 (2)	1.951 (3)	2.733 (6)	2.786 (7)
O(8^{iv})	86.3 (2)	85.9 (1)	171.5 (4)	88.7 (2)	1.960 (3)	2.902 (7)
O(10^{v})	177.0 (8)	91.0 (1)	91.8 (1)	91.1 (2)	95.7 (2)	1.954 (2)

M(2)	O(4^{iv})	O(5^{i})	O(6^{ii})	O(9^{v})	O(11^{vi})	O(12)
O(4^{iv})	1.959 (3)	2.885 (6)	2.935 (7)	3.998 (7)	2.923 (5)	2.785 (5)
O(5^{i})	94.1 (2)	1.981 (3)	2.803 (7)	2.863 (5)	2.860 (6)	4.018 (9)
O(6^{ii})	95.3 (2)	89.2 (1)	2.012 (3)	2.865 (5)	3.228 (5)	2.690 (6)
O(9^{v})	173.1 (4)	90.6 (2)	89.8 (1)	2.046 (3)	2.677 (6)	2.841 (7)
O(11^{vi})	93.4 (1)	90.2 (2)	171.3 (4)	81.5 (1)	2.055 (3)	3.078 (7)
O(12)	88.1 (1)	172.1 (5)	83.0 (1)	87.9 (1)	97.3 (1)	2.046 (3)

P(1)	O(1)	O(2)	O(3)	O(4)
O(1)	1.532 (2)	2.477 (6)	2.516 (6)	2.471 (4)
O(2)	107.7 (2)	1.535 (3)	2.452 (6)	2.512 (5)
O(3)	110.6 (2)	106.3 (2)	1.529 (3)	2.497 (5)
O(4)	109.2 (2)	111.8 (2)	111.1 (2)	1.499 (2)

P(2)	O(5)	O(6)	O(7)	O(8)
O(5)	1.513 (2)	2.450 (6)	2.519 (6)	2.509 (6)
O(6)	107.5 (2)	1.525 (2)	2.532 (6)	2.477 (6)
O(7)	112.1 (2)	112.4 (2)	1.523 (3)	2.440 (6)
O(8)	110.8	108.1 (2)	105.9 (2)	1.535 (3)

P(3)	O(9)	O(10)	O(11)	O(12)
O(9)	1.528 (2)	2.443 (4)	2.517 (6)	2.491 (6)
O(10)	106.0 (2)	1.529 (2)	2.528 (5)	2.521 (5)
O(11)	110.8 (2)	111.6 (2)	1.528 (3)	2.484 (6)
O(12)	109.0 (2)	110.9 (2)	108.5 (2)	1.532 (3)

Li(1)	O(6^{vii})	O(9^{viii})	O(11^{ix})	O(12^{x})
O(6^{vii})	2.06 (2)	3.786 (8)	3.228 (5)	2.690 (6)
O(9^{viii})	140.7 (4)	1.96 (2)	2.677 (6)	3.638 (8)
O(11^{ix})	102.2 (2)	82.8 (4)	2.09 (1)	3.442 (7)
O(12^{x})	82.3 (5)	131.8 (3)	113.6 (8)	2.03 (2)

Li(2)	O(1^{iv})	O(1^{xi})	O(2^{v})	O(2^{iii})	O(8^{xii})	O(8^{ii})
O(1^{iv})	2.448 (4)	4.90 (1)	2.723 (6)	3.890 (9)	2.698 (7)	4.00 (1)
O(1^{xi})	180	2.448 (4)	3.890 (9)	2.723 (6)	4.00 (1)	2.698 (7)
O(2^{v})	69.9 (1)	110.1 (1)	2.297 (4)	4.59 (1)	2.680 (6)	3.83 (1)
O(2^{iii})	110.1 (1)	69.9 (1)	180	2.297 (4)	3.83 (1)	2.680 (6)
O(8^{xii})	68.0 (1)	112.0 (1)	70.0 (1)	110.0 (1)	2.374 (5)	4.75 (1)
O(8^{ii})	112.0 (1)	68.0 (1)	110.0 (1)	70.0 (1)	180	2.374 (5)

Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (ii) $1-x, 1-y, 1-z$; (iii) $\frac{1}{2}-x, 1-y, z-\frac{1}{2}$; (iv) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (v) $\frac{1}{2}+x, y, \frac{1}{2}-z$; (vi) $\frac{1}{2}-x, y-\frac{1}{2}, z$; (vii) $x-\frac{1}{2}, y, \frac{3}{2}-z$; (viii) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (ix) $-x, 1-y, 1-z$; (x) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; (xi) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (xii) $x, y, z-1$.

The ω scan width was $(0.8+0.345\tan\theta)^\circ$ with a variable ω scan speed of 1.2–20° min^{-1} and a background/peak counting time ratio of 0.5. Data were corrected for Lorentz and polarization effects. *SHELXS*86 (Sheldrick, 1985) was used to solve the structure by direct methods, and *CRYSTALS* (Watkin, Carruthers & Betteridge, 1987) was used to refine the structure on a MicroVAXII. *MOLVIEW* (Cense, 1990) was used to prepare the view of the structure on a Macintosh LC.

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: DU1115). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Lead(II) Hydrogenselenite

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Abstract

The title structure, $Pb(HSeO_3)_2$, consists of layers of Pb—O polyhedra connected into a two-dimensional network by Se atoms. The layers are parallel to the *bc* plane and are not interconnected by chemical bonds. Hydrogen bonding between layers is improbable. The coordination polyhedron of Pb consists of eight O atoms in the form of a square antiprism, with all Pb—O distances less than 3.0 Å. There is no apparent lone-pair effect on the lead ion.

Comment

The coordination geometry of the Pb^{II} ion is interesting because of the stereochemical effects occasionally exhibited by the lone electron pair, either as an apparent gap or as other distortions in the coordination geometry (Lawton & Kokotailo, 1972). Sometimes the effect is not detected, as in the lead(II)–carboxylate compound $Pb[O_2(CH_3)_2](18\text{-crown-}6).3H_2O$, where the lead ion is decacoordinate, or in lead(II) aminosquarate, $Pb(C_4O_3HNH_2)_2(OH_2)_2$, where it is octacoordinate, while in $PbSe_2O_5$ with a 6 + 2 coordination scheme the effect is clearly manifested (Shin, Hampden-Smith, Kodas & Duesler, 1993; Narinesingh, Ramcharitar, Hall & Williams, 1994; Koskenlinna & Valkonen, 1995). In $PbSeO_3$, the lone-pair effect is also evident (Koskenlinna & Valkonen, 1977). As part of this study, we prepared lead(II) hydrogenselenite, $Pb(HSeO_3)_2$, and now describe its structure.