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NASICON-type $Li_{2.5}K_{0.16}Na_{0.34}Cr_2(PO_4)_3$

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Key indicators
Single-crystal X-ray study
T = 293 K
Mean σ(P–O) = 0.002 Å
Disorder in solvent or counterion
R factor = 0.025
wR factor = 0.072
Data-to-parameter ratio = 9.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

A new NASICON-type chromium(III) phosphate, $K_{0.16}Na_{0.34}Li_{2.5}Cr_2(PO_4)_3$, lithium sodium potassium dichromate tris(phosphate), has been prepared by solid-state reaction. It consists of CrO_6 octahedra and PO_4 tetrahedra sharing corners to form a three-dimensional framework. The monovalent cations are located in the *M*1 (six-coordinate) and *M*2 (four-coordinate) sites of the framework. The *M*1 site is occupied by Na^+ and K^+ cations with 69 (3) and 31 (3)% occupancy, respectively. The Li^+ ions, Li1 and Li2, are split over two *M*2 sites in general positions, with 60 (2) and 40 (2)% occupancy, respectively. Atom Li2 is disordered around a threefold inversion axis.

Comment

Since the discovery of the ionic conduction properties of NASICON, $Na_3Zr_2Si_2PO_{12}$ (Hong & Chinn, 1976; Goodenough *et al.*, 1976), many investigations have been devoted to similar compounds, such as phosphates with general formula $Na_3M_2^{III}(PO_4)_3$ (M = Cr, Fe, Sc or In). The isostructural phosphates $Na_3M_2^{III}(PO_4)_3$ and $Li_3M_2^{III}(PO_4)_3$ (M = Cr, Fe, Se or In) are also good ionic conductors and have been extensively studied.

The ionic conductivity of some compounds in the *A*–Cr–P/As–O systems (*A* is a monovalent cation), such as $K_3Cr_3(PO_4)_4$ (Kouass & Boughzala, 2005) and $K_3Cr_3(AsO_4)_4$ (Bouzemi *et al.*, 2003), led us to continue this study by total or partial substitution of the ion transporters with others of smaller size. During the course of these studies, we succeeded in isolating $K_{0.16}Na_{0.34}Li_{2.5}Cr_2(PO_4)_3$, which is isostructural with $Li_3Fe_2(PO_4)_3$ (Masquelier *et al.*, 2000), $Li_{3+x}Fe_2(PO_4)_3$ (Eyob *et al.*, 2002) and γ-NASICON. It also shows similar structural features with $Na_3Fe_2(PO_4)_3$ (Masquelier *et al.*, 2000).

The structure of $K_{0.16}Na_{0.34}Li_{2.5}Cr_2(PO_4)_3$ consists of CrO_6 octahedra and PO_4 tetrahedra sharing corners to form a three-dimensional framework with composition $[Cr_2(PO_4)_3]$, the so-called 'lantern units' of the structure (Masquelier *et al.*, 2000), which are stacked along the *c* direction. The monovalent K^+ and Na^+ cations are located in interconnecting cavities and share the same crystallographic site, with 69 (3) and 31 (3)% occupancy, respectively. Li^+ is distributed in the periphery and in the middle of the cavities with 60 (2)% and 40 (2)% occupancy, respectively.

The P atom has a regular tetrahedral coordination, with an average P—O distance of 1.54 (2) Å and an average O—P—O angle of 109.5 (2)°. These values are consistent with those typically observed in phosphates. Both Cr1 and Cr2 octahedral sites appear to be relatively regular, with three short Cr1—O and Cr2—O bond lengths of 1.940 (2) and 1.968 (2) Å,

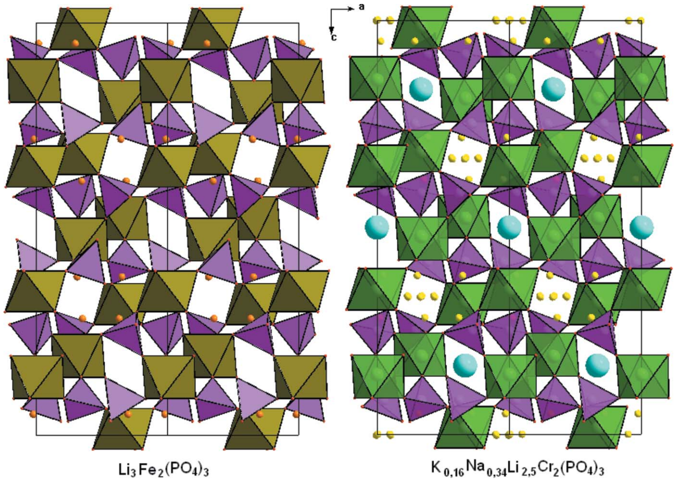

Figure 1
The arrangement of the monovalent cations in the framework of $Li_3Fe_2(PO_4)_3$ and $K_{0.16}Na_{0.34}Li_{2.5}Cr_2(PO_4)_3$. PO_4 tetrahedra are shown in purple, FeO_6 octahedra in olive green and CrO_6 octahedra in green. On the left-hand side, the Li cations are indicated as orange spheres, and on the right-hand side as yellow spheres. The K/Na cations are light blue.

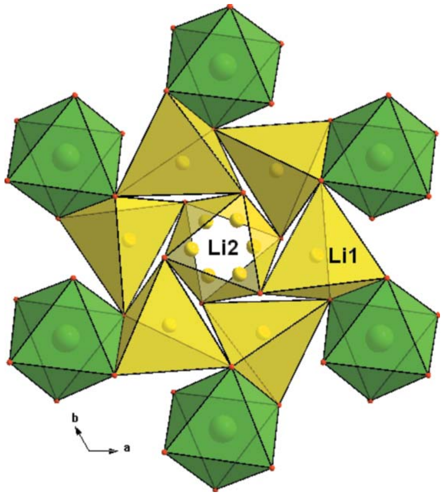

Figure 2
The tetrahedral coordination of the Li1 sites and disorder of the Li2 site within the framework.

respectively, and three longer bonds of 2.008 (2) and 2.000 (2) Å, respectively. Bond-valence analysis (Brown & Altermatt, 1985) of the $K_{0.16}Na_{0.34}Li_{2.5}Cr_2(PO_4)_3$ structure yields adequate bond valence sums for Cr, P and O ions with minor deviations from the expected values.

The anionic framework of $K_{0.16}Na_{0.34}Li_{2.5}Cr_2(PO_4)_3$ is analogous to that of $Li_3Fe_2(PO_4)_3$ (Eyob *et al.*, 2002). The structure shows the same flat elliptical cavities along the *c* axis. The dimensions of the cavities are approximately 6.8 Å in the *ab* plane and 5.4 Å along the *c* axis. There are two types of elliptical cavities, (i) and (ii), and they are connected by windows along the *a* and *b* directions. These cavities are not fully occupied by Li^+ cations due to their small size. In the $Li_3Fe_2(PO_4)_3$ structure, the Li^+ ion is placed at the periphery in order to be near the O corners of the PO_4 and FeO_6 polyhedra, and the cavity centre is thus empty. In the title compound, the first type of cavity, (i), is fully occupied by K^+/Na^+ cations, while the second contains two lithium cations: Li1 occupies the periphery of the cavities, and Li2 is somewhat displaced from the centres of the same cavities due to a disorder around the threefold inversion axis (Fig. 1). Both Li^+ ions are fourfold coordinated by O atoms, with average Li1—O and Li2—O bond lengths of 2.06 (1) and 2.37 (2) Å, respectively (Fig. 2). The disorder of the Li2 ions [shortest Li2—Li2 distance is 0.83 (1) Å] causes the elongation of the Li2—O bonds, which are considerably longer than average Li—O distances observed in similar compounds.

The Na^+/K^+ cations are six-coordinated. The average Na/K—O bond length of 2.75 (2) Å (Fig. 3) is intermediate between those typically observed for fully occupied Na^+ or K^+ ion sites in similar coordination.

The existence of windows interconnecting the cavities where the cations reside, as well as the disorder of the Li^+ ions on their sites, may be favourable for a high mobility of the ion transporters. This would allow interesting properties of ionic conduction. Tests for this behaviour are currently in progress.

Experimental

The synthesis was carried out by solid-state reaction from a mixture of sodium carbonate, lithium carbonate, ammonium hydrogenphosphate and ammonium dichromate in the molar ratio Li/Na/P/Cr = 2.5:0.34:3:2. The reagents were mixed and finely ground and then placed in an alumina crucible. The thermal treatment was carried out in two steps. The first consisted of preheating to 673 K to decompose the ammonium salts and carbonates. The temperature was then raised to 1123 K and maintained for 15 d. After cooling to room temperature, the reaction mixture was washed out with water. It contained green crystals of $K_{0.16}Na_{0.34}Li_{2.5}Cr_2(PO_4)_3$. Qualitative analysis of these crystals by energy-dispersive spectroscopy on a scanning electron microscope revealed the presence of K, Na, Cr, and P. The light atoms Li and O could not be satisfactorily determined with that method, which has been used for previous preparations containing this element.

Crystal data

$Li_{2.5}Na_{0.34}K_{0.16}Cr_2(PO_4)_3$
$M_r = 420.31$
Trigonal, $R\overline{3}$
$a = 8.300$ (2) Å
$c = 22.469$ (5) Å
$V = 1340.5$ (5) Å^3
$Z = 6$
$D_x = 3.124$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10$–16°
$\mu = 3.13$ mm^{-1}
$T = 293$ (2) K
Hexagonal prism, green
0.15 × 0.12 × 0.08 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.644$, $T_{max} = 0.779$
2047 measured reflections
648 independent reflections
572 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 26.9°$
$h = -10 \rightarrow 9$
$k = 0 \rightarrow 10$
$l = -28 \rightarrow 28$
2 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.072$
$S = 1.13$
648 reflections
67 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0328P)^2 + 7.8382P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.89$ e Å^{-3}
$\Delta\rho_{min} = -0.48$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0016 (4)

Table 1
Selected geometric parameters (Å, °).

Cr1—O1	1.940 (2)	Li1—O4	2.031 (10)
Cr1—O2	2.008 (2)	Li1—O2^{iii}	1.983 (10)
Cr2—O4	1.968 (2)	Li1—O3^{iv}	1.991 (10)
Cr2—O3^{i}	1.999 (2)	Li1—O4^{i}	2.221 (10)
P—O1	1.511 (2)	Li2—O2^{iii}	2.145 (17)
P—O2	1.542 (2)	Li2—O2^{v}	2.323 (19)
P—O3	1.545 (2)	Li2—O2^{i}	2.438 (19)
P—O4	1.559 (2)	Li2—O4^{iii}	2.570 (19)
K—O3^{ii}	2.751 (2)		
O1—P—O2	111.44 (13)	O1—P—O4	112.85 (14)
O1—P—O3	108.35 (13)	O2—P—O4	103.92 (12)
O2—P—O3	109.28 (12)	O3—P—O4	110.94 (12)

Symmetry codes: (i) $y - \frac{1}{3}, -x + y + \frac{1}{3}, -z + \frac{1}{3}$; (ii) $x - 1, y - 1, z$; (iii) $-x + y, -x + 1, z$; (iv) $-y + 1, x - y, z$; (v) $-x + \frac{2}{3}, -y + \frac{4}{3}, -z + \frac{1}{3}$.

Except for the two Li atoms, which were refined isotropically, all atoms were refined anisotropically. The sums of the site occupancy factors for the monovalent cations were restrained to unity. The highest peak is located 0.83 Å from Li2 and the deepest hole 0.52 Å from Cr1.

Data collection: *CAD-4 EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

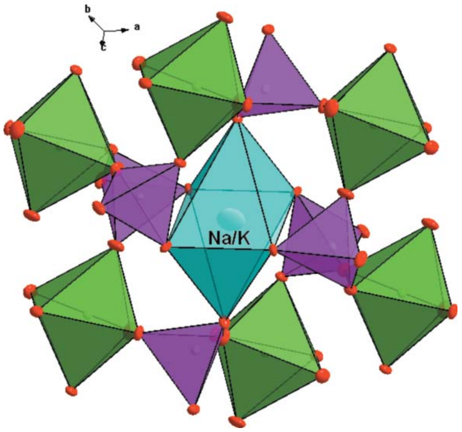

Figure 3
The octahedral coordination of the K/Na site, displayed with 50% probability displacement ellipsoids.

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