

PO₄ tetrahedra and P₂O₇ groups allowing the formula K(MoO)₂(PO₄)(P₂O₇) and delimiting various tunnels.

Each K⁺ ion is statistically distributed over two positions. In the half occupied K(1) sites, potassium is distributed at random in the six-sided tunnels, two adjacent sites which correspond to each other by a symmetry center not being occupied simultaneously. In the larger tunnels two identical cages are available for one K(2) ion so that the latter is distributed at random over these two equivalent sites which are half occupied.

This main difference from the rubidium and caesium molybdenophosphate is easily explained by the size of K⁺ which is smaller than Rb⁺ and Cs⁺. This cation, unlike the other alkaline cations, does not induce any distortion of the β-Mo₂PO₃O₁₃ framework; consequently, as higher crystal symmetry is observed, no ordering of the K⁺ ions in the tunnels is obtained, in contrast to Rb⁺ and Cs⁺ for which the two sorts of cages exhibit a different size and geometry.

The MoO₆ octahedra correspond to those observed in the literature for Mo^v with one very short Mo—O bond, four medium ones and a very long one (Table 2).

The P(3)—O distances correspond to those of a monophosphate, *i.e.* four almost equal distances. The P(1)—O and the P(2)—O distances correspond to those observed in the tetrahedra of the diphosphate groups, *i.e.* one long distance and three medium ones (Table 2).

K(1) is surrounded by ten O atoms with K—O distances ranging from 2.863 (4) to 3.344 (4) Å and K(2) is bonded to seven O atoms with 2.724 (4) < K—O < 3.344 (4) Å (Table 2).

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Structure of (Na_{2/3}Zr_{1/3})₂P₂O₇

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Abstract. Sodium zirconium diphosphate, $M_r = 265.4$, orthorhombic, $Fddd$, origin on $\bar{1}$, $a = 6.867$ (5), $b = 12.345$ (4), $c = 27.527$ (5) Å, $V = 2333$ (2) Å³, $Z = 16$, $D_x = 3.022$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.70107$ Å, $\mu = 17.76$ cm⁻¹, $F(000) = 2037.33$, $T = 293$ K, $R = 0.07$ for 420 independent reflections. The asymmetric unit contains a single, disordered metal site. In the crystal, two thirds of these sites are occupied by Na⁺ ions and the remainder by Zr⁴⁺ ions. Each metal site is surrounded by a distorted octahedron of diphosphate O atoms. The two PO₄ tetrahedra in each diphosphate anion are related by a diad axis passing through the O atom linking the P

atoms. The structure can be described as a piling up of slices parallel to (001) with thickness $c/8$. In each slice, diphosphate anions are aligned parallel to $\langle 110 \rangle$ and distributed in a pseudotrigonal grid ($b/a \approx 3^{1/2}$). (Na,Zr) octahedra form strips parallel to $\langle 110 \rangle$ by sharing edges, and connect three different anions in the slice and two anions in adjacent slices.

Introduction. Crystals of the title compound were prepared in teflon liners by the hydrothermal method using Morey-type autoclaves at 423 K and 15 MPa. A typical starting mixture consisted of NaOH (5 g), ZrOCl₂ (1 g) and 85% H₃PO₄ (12 ml). The resulting

dipyramidal crystals of (Na_{2/3}Zr_{1/3})₂P₂O₇ varied in size from 0.1 to 2 mm and were found to be interesting superionic conductors.

Experimental. Dipyramidal crystal with isometric dimensions of 0.2 mm. Enraf-Nonius CAD-4 diffractometer, graphite monochromator, $\omega/2\theta$ scans, scan rate depending on intensity of preliminary scan, scan width 0.8° (ω), 518 unique intensities with $1 < \theta < 25^\circ$ were collected, of which 98 with $I < 3\sigma(I)$ were considered unobserved. 25 reflections in the range $3.6 < \theta < 14.7^\circ$ were used for measuring lattice parameters. No absorption correction was applied. h 0–8, k 0–14, l 0–32.

Standard reflections 260, 177 and 266 were measured every hour, no significant variation was observed. Structure was solved by direct methods using the *MULTAN* system of programs (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980).

Refinements were carried out by the program *SHELX76* (Sheldrick, 1976). Scattering factors for neutral atoms and f' , f'' were from *International Tables for X-ray Crystallography* (1974). O atoms were refined isotropically and the remainder anisotropically.

Final R values: $R = 0.072$ ($wR = 0.076$). The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(F_o)/82.571$. Max. $\Delta/\sigma = 0.06$. Max. and min. peak

Table 1. Atomic coordinates ($\times 10^4$) and B_{eq} (\AA^2) of (Na_{2/3}Zr_{1/3})₂P₂O₇

$B_{eq} = (8\pi^2/3)(U_{11} + U_{22} + U_{33})$ for the orthogonalized U_{ij} tensor.

	x	y	z	B_{eq}
P	7842 (2)	4816 (1)	521 (1)	0.59
Na,Zr	2758 (4)	5171 (3)	756 (1)	4.74
O(1)	9326 (8)	5360 (4)	843 (2)	1.24
O(2)	7249 (7)	5427 (4)	64 (2)	1.05
O(3)	6007 (7)	4461 (4)	806 (2)	0.97
O(4)			282 (2)	0.55

heights in final difference synthesis 0.94 and $-1.10 e \text{\AA}^{-3}$. Occupancy factors for Na and Zr were fixed to fulfil stoichiometry. Final atomic coordinates and B_{eq} are reported in Table 1.*

Discussion. The angles and interatomic distances in the diphosphate anions (Table 2) show no special features. (Na,Zr)—O bonding distances are intermediate between typical Na—O distances in similar ionic conductors (2.6 Å) (Subramanian, Rudolf & Clearfield, 1985; Rudolf, Subramanian & Clearfield, 1985), and those encountered in ZrO₆ octahedra (2.15 Å) (Shannon & Prewitt, 1969). B_{eq} for the disordered metal site is high, compared with those of the other atoms, as observed in other ionic conductors.

The composition of the present compound is to be compared with the so called NASICONs (sodium, zirconium, scandium phosphosilicates) (Subramanian, Rudolf & Clearfield, 1985). In both cases the ratio Na/(Zr,Sc) is 3/2 but in the present structure Na and Zr atoms share the same crystallographic position. It is possible that Si could partially substitute P in the structure to give a compound similar in composition to the non-stoichiometric NASICONs described by Rudolf, Subramanian & Clearfield (1985). Indeed, (Na_{2/3}Zr_{1/3})₂P₂O₇ may well be the orthorhombic structure type synthesized by the above authors as a precursor of the non-stoichiometric Na_{2.88}(Na_{0.32}Zr_{1.68})Si_{1.84}P_{1.16}O_{11.54}.

The structure consists of an arrangement of anions and (Na,Zr) octahedra in slices parallel to (001) with thickness $c/8$ (Fig. 1). In each slice, the anions parallel to $\langle 110 \rangle$ are linked together by chains

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52982 (4 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Main interatomic distances (\AA) and bond angles ($^\circ$) of (Na_{2/3}Zr_{1/3})₂P₂O₇

(Na,Zr) octahedron						
(Na,Zr)	O(1 ⁱ)	O(1 ⁱⁱ)	O(1 ⁱⁱⁱ)	O(2 ^{iv})	O(3 ^v)	O(3 ^{vi})
O(1 ⁱ)	2.381 (6)	90.3 (4)	90.5 (4)	97.1 (3)	161.8 (4)	77.2 (4)
O(1 ⁱⁱ)	3.465 (8)	2.506 (6)	78.4 (4)	165.8 (3)	82.6 (4)	94.3 (4)
O(1 ⁱⁱⁱ)	3.437 (8)	3.138 (7)	2.458 (6)	113.6 (3)	104.3 (4)	165.7 (4)
O(2 ^{iv})	3.566 (7)	4.845 (7)	4.045 (7)	2.375 (4)	86.7 (3)	75.6 (3)
O(3 ^v)	4.722 (8)	3.241 (8)	3.838 (8)	3.279 (7)	2.401 (6)	86.7 (4)
O(3 ^{vi})	3.231 (8)	3.877 (8)	5.193 (8)	3.173 (7)	3.564 (8)	2.776 (6)
P ₂ O ₇ anion (asymmetric unit)						
P	O(1)	O(2)	O(3)	O(4)		
O(1)	1.508 (5)	116.5 (3)	112.3 (3)	110.2 (3)		
O(2)	2.577 (8)	1.524 (5)	109.9 (3)	99.8 (3)		
O(3)	2.537 (8)	2.514 (8)	1.547 (5)	107.0 (2)		
O(4)	2.549 (7)	2.389 (7)	2.530 (7)	1.599 (3)		
P—O(4)—P ^{vi}	131.3 (4)					

Symmetry code: (i) x, y, z ($\bar{1}, 0, 0$); (ii) $\frac{1}{4} - x, y, \frac{1}{4} - z$ ($1, 0, 0$); (iii) $\frac{1}{4} - x, \frac{1}{4} - y, z$ ($1, 1, 0$); (iv) $-x, -y, -z$ ($1, 1, 0$); (v) x, y, z ($0, 0, 0$); (vi) $\frac{1}{4} - x, \frac{1}{4} - y, z$ ($\frac{1}{2}, \frac{1}{2}, 0$); (vii) $\frac{1}{4} - x, \frac{1}{4} - y, z$ ($\frac{3}{2}, \frac{1}{2}, 0$).

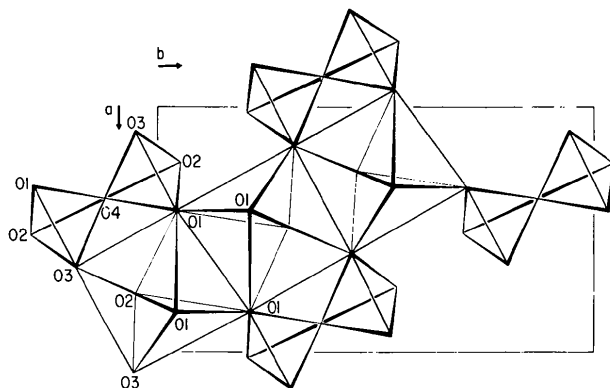


Fig. 1. Projection of one $c/8$ thickness slice of the structure, down the c axis, showing the interconnections of the PO_4 tetrahedra and $(\text{Na,Zr})\text{O}_6$ octahedra. For clarity, P and (Na,Zr) sites are omitted.

$(\text{Na,Zr})\text{O}_6$ octahedra. Each octahedron is connected to five P_2O_7 anions: three of them in the slice, through atoms O(1) and O(3), and the other two in adjacent slices through atoms O(1) and O(2). In consecutive slices related by twofold axes, chains of octahedra in directions $[110]$ and $[1\bar{1}0]$ share edges defining a distorted tetrahedron formed by O(1) atoms around the empty $8(a)$ Wyckoff position with symmetry 222 (Fig. 2). The angle between $[110]$ and adjacent $[1\bar{1}0]$ chains of octahedra is near 60° . The blocks (thickness $c/4$) formed by two such slices are connected through O(2) atoms.

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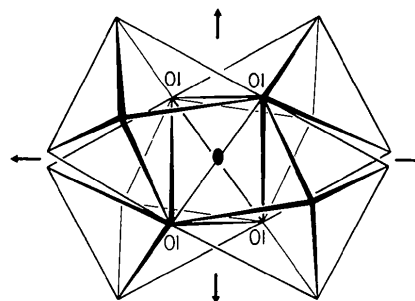


Fig. 2. Detail of the intersection of $(\text{Na,Zr})\text{O}_6$ octahedra chains in directions $[110]$ and $[1\bar{1}0]$ around the 222 empty Wyckoff position. The orientation is the same as in Fig. 1.

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Synthesis and Crystal Structures of Two Novel Selenites, $\text{NaY}(\text{SeO}_3)_2$ and $\text{NaLa}(\text{SeO}_3)_2$

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Abstract. Sodium yttrium diselenite, $M_r = 365.8$, orthorhombic, $P2_1cn$, $a = 5.397(2)$, $b = 8.525(2)$, $c = 12.765(2)$ Å, $V = 587.3$ Å³, $Z = 4$, $D_x = 4.132$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 237.2$ cm⁻¹, $F(000) = 664$, room temperature, $R = 0.027$ for 805 observed reflections with $I > 3\sigma(I)$. Lanthanum sodium diselenite, $M_r = 415.8$, monoclinic, $P2_1/n$, $a = 6.696(4)$, $b = 6.761(4)$, $c =$

$13.199(5)$ Å, $\beta = 101.51(3)^\circ$, $V = 585.5$ Å³, $Z = 4$, $D_x = 4.716$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 196.75$ cm⁻¹, $F(000) = 736$, room temperature, $R = 0.056$ for 1312 observed reflections with $I > 3\sigma(I)$. Both compounds were prepared hydrothermally at 532 K. Both structures contain discrete SeO_3 groups and pentacoordinate sodium. The yttrium atom in $\text{NaY}(\text{SeO}_3)_2$ is coordinated by seven oxygens in a