The Ba ions, which lie on diad axes, are each surrounded by ten (*i.e.* five pairs of) O atoms. These are: O(4) (ketonic) at 2·73, O(6) (water) at 2·80, O(2) (ketonic) at 2·89, O(1) and O(3) (carboxylic) at 2·87 and 3·06 Å respectively.

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Sodium Neodymium Metaphosphate $NaNdP_4O_{12}$

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Abstract. Monoclinic, $P2_1/n$ (C_{2h}^5); $a=9{\cdot}907$ (4), $b=13{\cdot}10$ (1), $c=7{\cdot}201$ (3) Å, $\beta=90{\cdot}51$ (3)°; $Z=4$, $D_m=3{\cdot}45$, $D_c=3{\cdot}43$ g cm^{-3}; μ(Mo $K\alpha$)$=63{\cdot}8$ cm^{-1}. The structural framework consists of helical chains of $(PO_3)_\infty$ along the c axis. Nd^{3+} and Na^+ ions alternate linearly in a direction surrounded by four $(PO_3)_\infty$ chains. NdO_8 dodecahedra and Na polyhedra form zigzag chains sharing faces. The refinement converged to $R=0{\cdot}028$, $R_w=0{\cdot}031$ for 2592 independent observed reflexions.

Introduction. Following the development of an efficient laser material $LiNdP_4O_{12}$ (Yamada, Otsuka & Nakano, 1974), another new Nd phosphate crystal $NaNdP_4O_{12}$ was found in our laboratory (Nakano, Otsuka & Yamada, 1976). The cell dimensions of the crystal are similar to those of the other alkaline Nd metaphosphate previously reported (Table 1).

Specimens were selected from crystals grown from the melt of $33Na_2O$–$7Nd_2O_3$–$60P_2O_5$ by the Kyropoulos technique (Nakano *et al.*, 1976). Precession and Weissenberg photographs exhibited $2/m$ Laue symmetry with the following systematic absences: $h0l$ when $h+l=2n+1$, $0k0$ when $k=2n+1$.

Table 1. *The axial relations for three alkaline* Nd *metaphosphates*

Crystal	Space group	a	b	c	β	Z
$LiNdP_4O_{12}$[a]	$I2/c$	9·844 Å	7·008 Å	13·25 Å	90·1°	4
$LiNdP_4O_{12}$[b]	$C2/c$	16·408	7·035	9·729	126·38	4
$NaNdP_4O_{12}$[c]	$P2_1/n$	9·907	13·10	7·201	90·51	4
$KNdP_4O_{12}$[d]	$P2_1$	7·266	8·436	8·007	91·97	2

(*a*) Koizumi (1976); (*b*) Hong (1975*a*); (*c*) this work; (*d*) Hong (1975*b*).

A prismatic crystal $0{\cdot}15\times0{\cdot}20\times0{\cdot}65$ mm was mounted with its c axis along the φ axis of the Rigaku Denki automatic four-circle X-ray diffractometer. Reflexions within $(\sin\theta/\lambda)=0{\cdot}72$ Å^{-1} were measured using the ω–2θ scan technique with a Ge monochromator. The intensities were corrected for Lorentz–polarization, absorption and extinction effects.

The location of atoms, except oxygen, was determined by the three-dimensional Patterson method assuming a similarity to the $LiNdP_4O_{12}$ structure (Koizumi, 1976). Structure factors based on the Patterson coordinates gave the conventional R value of 0·283. Successive Fourier syntheses clearly revealed the oxygen positions indicating tetrahedral coordination around the P atom.

All the atomic parameters were refined by the full-matrix least-squares method (Busing, Martin & Levy, 1962) to give $R=0{\cdot}028$, $R_w=0{\cdot}031$. The final atomic parameters are listed in Table 2.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31747 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Positional and thermal parameters obtained in the final least-squares refinement*

Estimated standard deviations are given in parentheses. Anisotropic thermal factors ($\times 10^5$) are given by the expression: $T=\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2kl\beta_{23}+2hl\beta_{13})]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Nd	0·0238 (1)	0·2174 (1)	0·9868 (1)	301 (2)	180 (1)	523 (3)	4 (1)	15 (1)	−1 (1)
P(1)	0·1943 (1)	0·3722 (1)	0·3548 (2)	343 (9)	178 (5)	553 (17)	3 (5)	0 (10)	0 (7)
P(2)	0·2561 (1)	0·4001 (1)	0·7509 (2)	366 (9)	174 (5)	552 (17)	−13 (6)	8 (10)	−1 (7)
P(3)	0·3037 (1)	0·0896 (1)	0·2305 (2)	371 (9)	175 (5)	574 (17)	19 (5)	28 (10)	−7 (8)
P(4)	0·2360 (1)	0·1145 (1)	0·6197 (2)	348 (9)	179 (5)	592 (17)	−6 (5)	62 (10)	8 (7)
Na	0·4338 (2)	0·2787 (2)	0·0001 (3)	553 (21)	454 (14)	964 (38)	37 (14)	−75 (23)	145 (19)
O(1)	0·1049 (3)	0·2897 (3)	0·2845 (4)	481 (31)	215 (17)	649 (53)	−54 (19)	−60 (33)	−45 (25)
O(2)	0·3417 (3)	0·3671 (3)	0·3192 (4)	387 (29)	261 (18)	707 (54)	53 (18)	30 (32)	73 (25)
O(3)	0·2055 (4)	0·3350 (3)	0·9057 (5)	483 (5)	227 (19)	748 (58)	−72 (19)	29 (34)	74 (25)
O(4)	0·4035 (3)	0·3937 (3)	0·7143 (5)	361 (29)	230 (17)	749 (56)	−11 (18)	17 (32)	−58 (25)
O(5)	0·1327 (3)	0·4782 (2)	0·2834 (5)	433 (31)	164 (16)	933 (62)	1 (18)	−55 (35)	68 (25)
O(6)	0·1674 (3)	0·3769 (3)	0·5718 (4)	363 (30)	256 (18)	614 (54)	−11 (19)	−115 (32)	−31 (25)
O(7)	0·2120 (4)	0·1102 (3)	0·0701 (5)	545 (33)	273 (19)	641 (55)	106 (20)	−74 (34)	−2 (26)
O(8)	0·4180 (3)	0·1607 (3)	0·2614 (5)	522 (33)	240 (18)	732 (58)	−112 (20)	60 (34)	−55 (26)
O(9)	0·3470 (3)	0·1896 (3)	0·6328 (5)	449 (31)	211 (17)	721 (56)	−88 (18)	81 (33)	−37 (25)
O(10)	0·1016 (3)	0·1418 (3)	0·6929 (5)	414 (30)	253 (18)	712 (55)	41 (19)	82 (32)	−12 (35)
O(11)	0·2908 (3)	0·0140 (3)	0·7134 (5)	471 (31)	182 (17)	850 (58)	0 (18)	20 (33)	38 (25)
O(12)	0·2119 (3)	0·0806 (3)	0·4107 (5)	455 (31)	271 (18)	611 (55)	−70 (19)	59 (33)	−67 (25)

Discussion. Bond distances and angles are given in Table 3 and Fig. 3. Views of the structure projected along the *c* and *b* axes are shown in Figs. 1 and 2, respectively.

The NdO_8 dodecahedron is considerably distorted, as in NdP_5O_{14} (Hong, 1974). The dodecahedron shares all its oxygen atoms with the corners of neighbouring PO_4 tetrahedra and with the faces of neighbouring Na polyhedra (Fig. 2).

The relative arrangement of Nd^{3+} and Na^+ resembles that of the other alkaline Nd metaphosphates, in which the displacement of the alkaline ion from the axis of the Nd^{3+}–M^+ (M^+ stands for alkaline metal ion) zigzag chain increases with the ionic radius and coordination number of M^+ [Table 4, Fig. 3(*c*)].

The Na polyhedron is also quite irregular, as are the K polyhedra in the $KNdP_4O_{12}$ structure (Hong, 1975*b*). Five O atoms constitute the first coordination sphere around the Na^+ ion at distances approximately equal to the sum of the atomic radii, 2·40∼2·57 Å. The sixth bond makes the polyhedron into an octahedron and is substantially longer: 2·72 Å

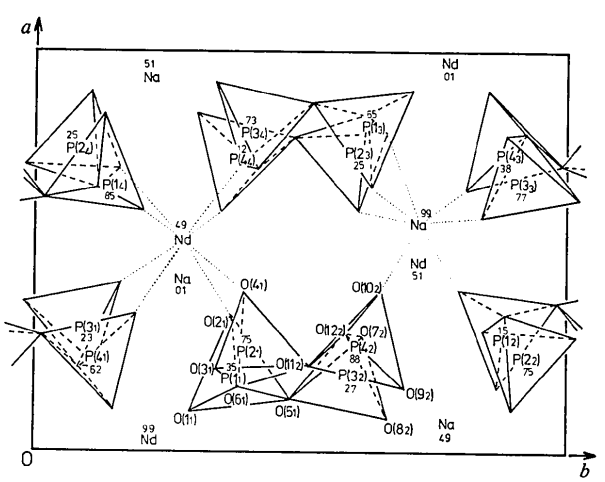

Fig. 1. Projection of the $NaNdP_4O_{12}$ structure along [010].

Table 3. *Bond distances* (Å) *and angles* (°) *with standard errors in* $NaNdP_4O_{12}$

Dodecahedron around Nd [for Nd–O see Fig. 3(*a*)]		Polyhedron around Na [for Na–O see Fig. 3(*b*)]	
O(1)–O(3)	2·965 (5)	O(1)–O(9)	2·801 (4)
O(1)–O(7)	3·002 (5)	O(2)–O(8)	2·836 (6)
O(1)–O(9)	2·801 (4)	O(2)–O(10)	2·728 (4)
O(2)–O(4)	2·936 (5)	O(3)–O(4)	2·508 (5)
O(2)–O(8)	2·838 (6)	O(3)–O(9)	3·067 (5)
O(2)–O(10)	2·728 (4)	O(4)–O(9)	2·795 (6)
O(3)–O(8)	3·041 (5)	O(8)–O(9)	2·785 (5)
O(4)–O(9)	2·795 (6)		
O(7)–O(10)	2·972 (5)	Nd—Nd	5·719 (1)
O(8)–O(9)	2·785 (5)		6·209 (1)
Tetrahedron around P(1)		**Tetrahedron around P(2)**	
P(1)–O(1)	1·489 (4)	P(2)–O(3)	1·487 (4)
P(1)–O(2)	1·482 (3)	P(2)–O(4)	1·484 (3)
P(1)–O(5)	1·603 (3)	P(2)–O(6)	1·596 (3)
P(1)–O(6)	1·584 (3)	P(2)–O(11)	1·583 (4)
O(1)–P(1)–O(2)	119·8 (2)	O(3)–P(2)–O(4)	115·2 (2)
O(1)–P(1)–O(5)	106·2 (2)	O(3)–P(2)–O(6)	108·2 (2)
O(1)–P(1)–O(6)	105·6 (2)	O(3)–P(2)–O(11)	108·8 (2)
O(2)–P(1)–O(5)	111·2 (2)	O(4)–P(2)–O(6)	113·3 (2)
O(2)–P(1)–O(6)	109·2 (2)	O(4)–P(2)–O(11)	111·7 (2)
O(5)–P(1)–O(6)	102·8 (2)	O(6)–P(2)–O(11)	98·5 (2)
Tetrahedron around P(3)		**Tetrahedron around P(4)**	
P(3)–O(5)	1·593 (3)	P(4)–O(9)	1·479 (3)
P(3)–O(7)	1·500 (4)	P(4)–O(10)	1·482 (4)
P(3)–O(8)	1·485 (4)	P(4)–O(11)	1·578 (4)
P(3)–O(12)	1·582 (4)	P(4)–O(12)	1·589 (4)
O(5)–P(3)–O(7)	110·0 (2)	O(9)—P(4)–O(10)	117·7 (2)
O(5)–P(3)–O(8)	106·4 (2)	O(9)—P(4)–O(11)	105·6 (2)
O(5)–P(3)–O(12)	102·0 (2)	O(9)—P(4)–O(12)	111·4 (2)
O(7)–P(3)–O(8)	118·1 (2)	O(10)–P(4)–O(11)	112·5 (2)
O(7)–P(3)–O(12)	107·3 (2)	O(10)–P(4)–O(12)	105·6 (2)
O(8)–P(3)–O(12)	110·9 (2)	O(11)–P(4)–O(12)	103·1 (2)

Table 4. *The relations between the ionic radius (r) and the displacement of the alkaline ion* (M^+) *from the axis of the* Nd^{3+}–M^+ *zigzag chain (d) in the* $MNdP_4O_{12}$ *structure*

	Li^+	Na^+	K^+
r(Å)	0·60	0·95	1·33
d(Å)	0	0·46	0·79
Coordination number (n)	4	6+1	7

(*International Tables for X-ray Crystallography*, 1962). Another oxygen atom [O(9)] lies at a distance of 3·02 Å [Fig. 3(*b*)]. This type of coordination around Na^+ can also be seen in the structures of $[Na_3H(PO_3)_4]_x$ (Jost, 1968) and Na_2ZrSiO_5 (Treushnikov, Ilyukhin & Belov, 1970). The weaker bonds to Na^+ cause a larger thermal motion (B_{eq}^{Na}: 2·43) compared with those of the other atoms (B_{eq}: 1·17 ~ 1·78). Such tendencies are also reported in the above-mentioned structures.

The helical $(PO_3)_\infty$ chains in the $NaNdP_4O_{12}$ structure are similar to those of the other alkaline Nd metaphosphates, in which the chains run along the shortest unit-cell directions. In the present structure the chain axis deviates considerably from the centre of each quarter cell and results in the formation of a larger tunnel along the c axis than is found in the $LiNdP_4O_{12}$ structure.

It is to be noted that the adjacent NdO_8 polyhedra do not share any oxygen atom as in the structures of $LiNdP_4O_{12}$ and $KNdP_4O_{12}$. Although the shortest Nd–Nd distance (5·719 Å) is somewhat longer than that in $LiNdP_4O_{12}$ (5·644 Å), the laser characteristics of the present crystal are less prominent than the latter (Hong, 1975*a*). This is related to the lower symmetry of the NdO_8 dodecahedron and $(PO_3)_\infty$ chains and, moreover, the larger interaction between Nd^{3+} and the alkaline ion (Na^+).

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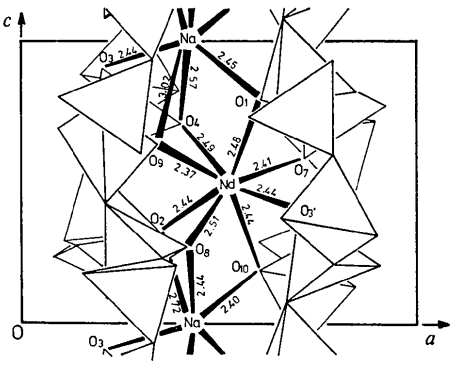
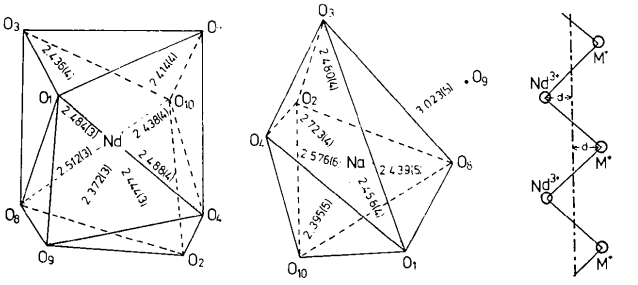


Fig. 2. Schematic view of the $-Nd^{3+}-Na^+-$ chain in the [010] direction.



(*a*) (*b*) (*c*)

Fig. 3. Schematic illustration of (*a*) the NdO_8 dodecahedron, (*b*) the sodium coordination polyhedron and (*c*) the $-Nd^{3+}-M^+-$ zigzag chain in alkaline Nd metaphosphate.

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