La largeur de balayage est (0,49 + 0,71tgθ)°. Les intensités ont été corrigées des facteurs de Lorentz et de polarisation. La structure a été résolue par la méthode de l'atome lourd (*SHELXS*86; Sheldrick, 1990) puis affinée par la méthode des moindres carrés (*SHELXL*93; Sheldrick, 1993).

Collection des données: *CAD*-4-*EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992). Affinement des paramètres de la maille: *CAD*-4-*EXPRESS*. Reduction des données: *MolEN* (Fair, 1990). Les graphiques moleculaires: *ATOMS* (Dowty, 1993).

Les listes des facteurs de structure et des facteurs d'agitation thermique anisotrope ont été déposées au dépôt d'archives de l'UICr (Référence: DU1162). On peut en obtenir des copies en s'adressant à: The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.

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NaYP$_2$O$_7$

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Abstract

Sodium yttrium diphosphate crystallizes in the non-centrosymmetric space group $P2_1$. The structure consists of corner-sharing YO$_6$ octahedra and P$_2$O$_7$ groups forming an alternate stacking of octahedral and phosphate layers. The framework delimits intersecting tunnels where the Na$^+$ cations are located. The P$_2$O$_7$ groups show a nearly staggered configuration intermediate between that in KYP$_2$O$_7$ [Hamady, Zid & Jouini (1994). *J. Solid State Chem.* **113**, 120–124] and that in α-NaTiP$_2$O$_7$ [Leclaire, Benmoussa, Borel, Grandin & Raveau (1988). *J. Solid State Chem.* **77**, 299–305].

Comment

The many structural investigations devoted to the $A^{\rm I}M^{\rm III}$P$_2$O$_7$-type diphosphates in the last 15 years have shown the existence of five structural types.

The compounds of type I exhibit the KAlP$_2$O$_7$ structure (Nam Ng & Calvo, 1973), whereas those of type II are isotypic with NaFeP$_2$O$_7$ (Gabélica-Robert, Goreaud, Labbé & Raveau, 1982). The lithium-containing compounds form the third family and adopt the LiFeP$_2$O$_7$ structure (Genkina, Maksimov, Timofeeva, Bykov & Mel'nikov, 1985; Riou, Nguyen, Benloucif & Raveau, 1990). The fourth type is only represented by α-NaTiP$_2$O$_7$ (Leclaire, Benmoussa, Borel, Grandin & Raveau, 1988). A fifth type occurs for the KYP$_2$O$_7$ structure which we have reported recently (Hamady, Zid & Jouini, 1994). The diphosphates of rare earth metals and yttrium, obtained with an alkali metal larger than K, belong to structural type I (Gabélica-Robert & Tarte, 1982). In contrast, little is known about the structural type adopted by rare earth and Y compounds with smaller cations, *i.e.* Li and Na. The present structural investigation of NaYP$_2$O$_7$, reveals a new structural arrangement.

The three-dimensional framework of NaYP$_2$O$_7$ is built up from corner-sharing YO$_6$ octahedra and P$_2$O$_7$ groups (Fig. 1). The structure can be described as a stacking of alternating octahedral and phosphate layers parallel to (10$\bar{1}$), (101) and (010), leading to the formation of intersecting tunnels where the Na$^+$ ions reside (Fig. 2). The P$_2$O$_7$ group has an almost staggered C_s symmetry, with the plane containing the P—O—P bridge, approximately parallel to (010), as the pseudo-

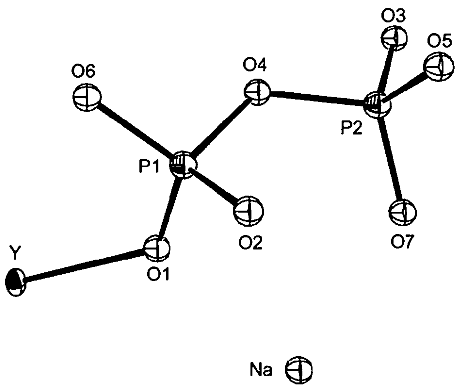

Fig. 1. *ORTEP* (Johnson, 1965) plot of the asymmetric unit of NaYP$_2$O$_7$ showing the labelling scheme. Displacement ellipsoids are shown at the 50% probability level.

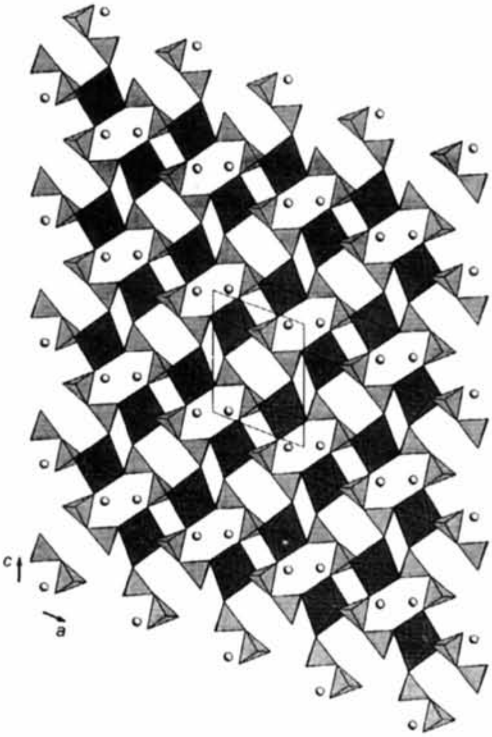

Fig. 2. The structure of $NaYP_2O_7$ projected along the b axis.

mirror plane. The long axis of the P_2O_7 groups is parallel to $[10\bar{1}]$ and perpendicular to [101] and [010]. The YO_6 octahedron shares its six corners with six different P_2O_7 groups. The $P2O_4$ tetrahedron is slightly more distorted than the $P1O_4$ tetrahedron (Table 2).

Within a range of 3 Å, the Na atom has a sixfold coordination. Both YO_6 and NaO_6 octahedra are distorted. The structure of $NaYP_2O_7$ is closely related to those of α-$NaTiP_2O_7$ and KYP_2O_7. The structural relations between the three forms are more evident if one considers the stacking of alternating octahedral and phosphate layers. The configuration of the P_2O_7 group of $NaYP_2O_7$ is intermediate between the really staggered configuration in α-$NaTiP_2O_7$ and the perfectly eclipsed configuration in KYP_2O_7.

Experimental

The title compound was prepared by heating a mixture of Na_2CO_3, Y_2O_3 and $(NH_4)_2HPO_4$ (molar ratio Na:Y:P of 1:0.1:1) at 873 K for 4 d. The temperature was then slowly reduced to 823 K and finally quenched to room temperature. Hexagonal prisms of $NaYP_2O_7$ were isolated by washing the product in boiling water.

Crystal data

$NaYP_2O_7$
$M_r = 285.84$
Monoclinic
$P2_1$
$a = 7.004\ (1)$ Å
$b = 5.3740\ (8)$ Å
$c = 8.691\ (1)$ Å
$\beta = 110.18\ (1)°$
$V = 307.04\ (7)$ Å^3
$Z = 2$
$D_x = 3.092$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 7$–$14°$
$\mu = 10.073$ mm^{-1}
$T = 293\ (2)$ K
Hexagonal prism
$0.03 \times 0.02 \times 0.02$ mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.741$, $T_{\max} = 0.746$
589 measured reflections
553 independent reflections

399 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0262$
$\theta_{\max} = 25°$
$h = -9 \rightarrow 0$
$k = 0 \rightarrow 7$
$l = -11 \rightarrow 12$
1 standard reflection monitored every 400 reflections frequency: 120 min intensity decay: 0.94%

Refinement

Refinement on F^2
$R(F) = 0.0425$
$wR(F^2) = 0.0910$
$S = 1.159$
553 reflections
51 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0255P)^2 + 4.47P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.011$
$\Delta\rho_{\max} = 1.431$ e Å^{-3}
$\Delta\rho_{\min} = -0.875$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.003 (3)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = 0.10 (4)

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

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Y	0.2074 (2)	−0.0043 (4)	0.7523 (2)	0.0117 (5)
P1	0.5491 (5)	0.477 (1)	0.8137 (4)	0.011 (1)
P2	0.8742 (5)	0.503 (2)	0.6854 (4)	0.0076 (8)
Na	0.8316 (9)	−0.009 (3)	0.9457 (7)	0.023 (2)
O1	0.506 (2)	0.201 (2)	0.810 (1)	0.018 (3)
O2	0.713 (2)	0.549 (3)	0.971 (1)	0.017 (3)
O3	0.870 (1)	0.518 (5)	0.512 (1)	0.016 (2)
O4	0.641 (1)	0.527 (3)	0.671 (1)	0.013 (2)
O5	0.980 (3)	0.734 (4)	0.786 (2)	0.018 (5)
O6	0.356 (2)	0.629 (3)	0.771 (2)	0.029 (3)
O7	0.963 (3)	0.273 (4)	0.776 (2)	0.015 (5)

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

Y—O3$^{\rm i}$	2.172 (9)	P2—O3	1.501 (9)
Y—O6$^{\rm ii}$	2.208 (14)	P2—O5	1.55 (2)
Y—O5$^{\rm iii}$	2.22 (2)	P2—O4	1.602 (9)
Y—O1	2.265 (12)	P1—P2	2.863 (4)
Y—O2$^{\rm iv}$	2.291 (10)	Na—O5$^{\rm ii}$	2.43 (2)
Y—O7$^{\rm v}$	2.33 (2)	Na—O1	2.449 (15)
P1—O2	1.500 (11)	Na—O7	2.50 (2)
P1—O6	1.510 (14)	Na—O2$^{\rm ii}$	2.55 (2)

P1—O1	1.511 (15)	Na—O5^{vi}	2.60 (2)
P1—O4	1.604 (9)	Na—O7^{vi}	2.62 (2)
P2—O7	1.48 (2)		
O3^{i}—Y—O6^{ii}	93.8 (7)	O2^{iv}—Y—O7^{v}	75.4 (5)
O3^{i}—Y—O5^{iii}	104.3 (7)	O2—P1—O6	114.8 (8)
O6^{ii}—Y—O5^{iii}	76.6 (6)	O2—P1—O1	110.9 (7)
O3^{i}—Y—O1	94.6 (5)	O6—P1—O1	111.9 (7)
O6^{ii}—Y—O1	92.3 (5)	O2—P1—O4	106.2 (6)
O5^{iii}—Y—O1	158.6 (5)	O6—P1—O4	106.4 (7)
O3^{i}—Y—O2^{iv}	169.7 (7)	O1—P1—O4	106.1 (8)
O6^{ii}—Y—O2^{iv}	95.5 (5)	O7—P2—O3	116.1 (12)
O5^{iii}—Y—O2^{iv}	82.3 (6)	O7—P2—O5	109.6 (6)
O1—Y—O2^{iv}	80.5 (4)	O3—P2—O5	111.4 (12)
O3^{i}—Y—O7^{v}	97.9 (6)	O7—P2—O4	109.9 (10)
O6^{ii}—Y—O7^{v}	154.9 (6)	O3—P2—O4	104.5 (5)
O5^{iii}—Y—O7^{v}	79.0 (3)	O5—P2—O4	104.6 (10)
O1—Y—O7^{v}	108.7 (6)	P1—O4—P2	126.5 (7)

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

Data were corrected for Lorentz and polarization effects. The scan width was $(0.61 + 0.79\tan\theta)^\circ$. Refinement was by full-matrix least-squares method on F^2 using all reflections with $I_{hkl} > 0$. An attempt at anisotropic refinement of all the atoms (five observations per parameter) led to negative values for the displacement coefficients of P2 and O7. This is attributed to the very small crystal size which allowed us to obtain only 399 observable reflections [$I > 2\sigma(I)$]. Only the Y atom was therefore refined anisotropically.

Data collection: *CAD*-4 *Express* (Duisenberg, 1992; Macíček & Yordanov, 1992). Cell refinement: *CAD*-4 *Express*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ATOMS* (Dowty, 1993) and *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BR1148). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A New Langbeinite: Dipotassium Dimanganese Tetrafluoroberyllate

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Abstract

The structure of the cubic phase of a new langbeinite, $K_2Mn_2(BeF_4)_3$, has been determined at 293 K from X-ray diffraction data. Differential scanning calorimetry measurements in the temperature range 100–300 K indicated a new phase transition at 213 K, which has been confirmed by precession X-ray diffractograms, revealing a new type of structure different to those generally expected for the low-temperature phases of langbeinites.

Comment

The langbeinite $K_2Mn_2(BeF_4)_3$ belongs to the family of compounds with the common chemical formula $A_2B_2(XY_4)_3$, where A is a monovalent cation such as Cs, Tl, Rb, NH_4 or K, B is a divalent cation such as Mg, Ni, Co, Zn, Fe, Mn, Cd or Ca, and XY_4 represents the divalent tetrahedral group SO_4 or BeF_4. The sulfates within this family have attracted much interest because of their ferroelastic and ferroelectric behaviour and the nature of their structural phase transitions. All of them have cubic symmetry (space group $P2_13$) in the high-temperature phase and many of them show successive phase transitions as the temperature is lowered. These transitions can be classified as two types according to the transition scheme. Crystals that exhibit a series of phase transitions from cubic ($P2_13$) to orthorhombic ($P2_12_12_1$) across two intermediate, monoclinic ($P2_1$) and triclinic ($P1$), phases belong to type I (Brezina & Glogarova, 1972; Ikeda & Yasuda, 1975; Yamada & Kawano, 1977; Hikita, Chubachi & Ikeda, 1978). Crystals of type II undergo a single phase transition

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