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

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

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Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: BR1105). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$K_2NiWO_2(PO_4)_2$: a New Structure Type Related to $KTiOPO_4$ (KTP)

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Abstract

Substitution of the two symmetrically unrelated Ti^{4+} ions in the structure of the well known non-linear optical crystal $KTiOPO_4$ (potassium titanyl phosphate, KTP, space group $Pna2_1$) by Ni^{2+} and W^{6+} ($2Ti^{4+} \rightarrow Ni^{2+} + W^{6+}$) leads to the new compound $K_2NiWO_2(PO_4)_2$ [dipotassium nickel bis(monophosphato)tungstate, KNiWP], which forms a new structure type. The main structural characteristic of tetragonal KNiWP (space group $P4_{1,3}2_12$) is helical chains of corner-linked alternate $[WO_6]$ and $[NiO_6]$ octahedra along [001] connected *via* phosphate groups. Structural and metric relationships exist between the KNiWP and KTP structure types.

Comment

The majority of crystal–chemical investigations carried out on the $KTiOPO_4$ (KTP) structure family during the past ten years have focused on a simple substitution of K, Ti and P by crystal–chemically related constituents. In this way, a great number of compounds have been synthesized that are isostructural with KTP. All these attempts have been made in the hope of further improving the physical properties for applications in the field of laser optics (Stucky, Phillips & Gier, 1989).

Recently, during the search for further members of the KTP group, a new family of compounds with the general formula $K_2M^{2+}M^{6+}O_2(PO_4)_2$ ($M^{2+} = Ni^{2+}, Co^{2+}, Mg^{2+}$; $M^{6+} = W^{6+}$) was found (Wostrack, 1993). These compounds can be derived from KTP by substitution of the two symmetrically unrelated Ti^{4+} ions by two cations with different valencies ($2Ti^{4+} \rightarrow M^{2+} + M^{6+}$). X-ray powder and single-crystal investigations of members of this family have shown that these compounds do not form superstructures of KTP (Wostrack, Peuchert, Schneider, Liebertz & Bohatý, 1993). As one result of our studies, the crystal structure of $K_2NiWO_2(PO_4)_2$ (KNiWP) is presented.

Both Ni^{2+} and W^{6+} occupy the special Wyckoff site 4(*a*) of space group $P4_12_12$ ($P4_32_12$) and are octahedrally surrounded by three pairs of symmetrically dependent O atoms. The $[WO_6]$ octahedra are quite distorted [W—O distance range: 1.752 (2)–2.068 (2) Å] while, by comparison, the $[NiO_6]$ octahedra differ only slightly from ideal shape [Ni—O distance range: 2.029 (2)–2.104 (2) Å]. Both types of octahedra are alternately linked with each other *via* one common O atom, O(5), forming helical chains along [001]. In the chain ...Ni—O(5)—W—O(5)—Ni... the symmetrically related O(5) atoms form short bonds with the W atom [W—O(5) = 1.752 (2), Ni—O(5) = 2.046 (2) Å]. The bridging O(5) atoms, corresponding to the titanyl O atoms of the KTP structure, are in *cis* positions relative to Ni^{2+} and W^{6+}. In contrast to this *cis–cis* arrangement in KNiWP, the titanyl O atoms of KTP are in alternating *cis–trans* positions (Fig. 1).

Quite regular phosphate tetrahedra [P—O distance range: 1.513 (2)–1.578 (2) Å] link the two octahedral chains in the unit cell to form a three-dimensional network. The K^+ ions occupy cavities within the framework, which provides irregular eightfold coordination by O atoms [K—O distance range: 2.621 (3)–3.169 (2) Å] (Fig. 2).

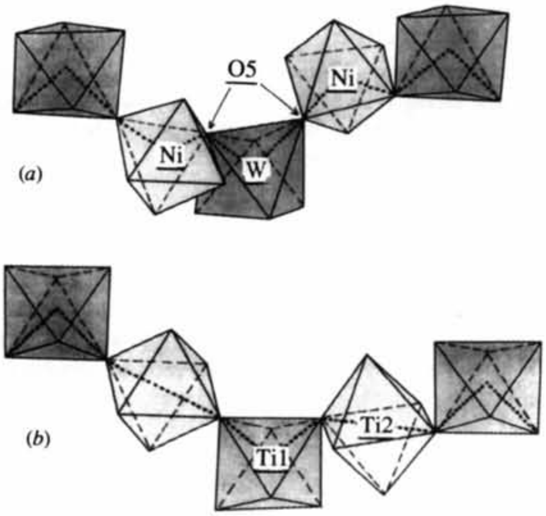

Fig. 1. Connection of octahedra in the KNiWP and KTP structure types (dotted lines): (*a*) KNiWP, ...*cis–cis–cis*...; (*b*) KTP, ...*cis–trans–cis*... (*ATOMS*; Dowty, 1989).

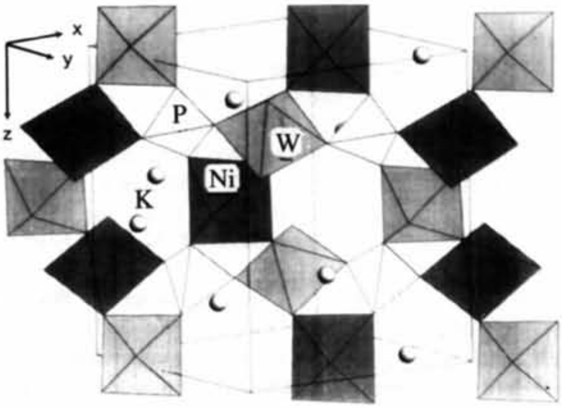

Fig. 2. Part of the KNiWP structure showing the connection of octahedral chains *via* phosphate groups. Cavities are occupied by K^+ ions (*ATOMS*; Dowty, 1989).

A comparison of KNiWP and KTP shows that there is a significant metric relationship between both types of structures: $a_{\rm KNiWP} \simeq a_{\rm KTP}/\sqrt{2}$, $b_{\rm KNiWP} \simeq b_{\rm KTP} \times \sqrt{2}$, $c_{\rm KNiWP} \simeq c_{\rm KTP}$.

The stability range of KNiWP was studied by optical and thermoanalytical methods. Between 100 and 870 K no phase transition was observed. In contrast with KNiWP, the compounds $K_2CoWO_2(PO_4)_2$ (KCoWP) and $K_2MgWO_2(PO_4)_2$ (KMgWP) undergo structural phase transitions. KCoWP is isostructural with KNiWP above 383 K and KMgWP is isostructural with KNiWP above 533 K. In addition, KMgWP exhibits at least two more phase transitions near 433 K (Wostrack, Peuchert, Schneider, Liebertz & Bohatý, 1993) and 633 K. More detailed investigations, mainly concerning the phase transitions indicated above, are currently being undertaken.

Experimental

Crystals of KNiWP were grown from KPO_3 flux. A stoichiometric mixture of KPO_3, $Ni_2(CO_3)(OH)_2$ and WO_3 (analytical grade) and the KPO_3 flux (molar ratio compound/flux = 2.5:1) was ground, placed in a platinum crucible and heated to 1123 K. After one day at fixed temperature the liquid was slowly cooled to 973 K at a constant rate of 1 K h^{-1} followed by faster cooling to room temperature (~20 K h^{-1}). Light-green optically perfect KNiWP crystals up to 1 × 1 × 1 mm, bounded by the forms {111} and {100}, were obtained. It was not difficult to separate the crystals mechanically from the brownish glass matrix. For X-ray single crystal investigations, spheres (diameter $\leq$ 0.2 mm) were prepared using a bond mill.

Crystal data

$K_2NiWO_2(PO_4)_2$
$M_r = 542.7$
Tetragonal
$P4_12_12$
$a = 9.161\ (1)$ Å
$c = 10.678\ (2)$ Å
$V = 896.1\ (2)$ Å^3
$Z = 4$
$D_x = 4.022$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 13.57–25.05°$
$\mu = 16.254$ mm^{-1}
$T = 293\ (2)$ K
Sphere
0.1 mm (radius)
Light green

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*MolEN*; Fair, 1990)
$T_{\min} = 0.956$, $T_{\max} = 0.999$
4466 measured reflections
1969 independent reflections
1857 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0238$
$\theta_{\max} = 34.97°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 14$
$l = -17 \rightarrow 17$
3 intensity and 2 orientation control reflections;
orientation control every 200 reflections
intensity control every 120 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0173$
$wR(F^2) = 0.0330$
$S = 1.117$
1969 reflections
75 parameters
$w = 1/[\sigma^2(F_o)^2 + (0.01P)^2 + 0.72P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.07$ e Å^{-3}
$\Delta\rho_{\min} = -1.01$ e Å^{-3}

Extinction correction: $F_c^* = F_ck[1 + (0.001\chi \times F_c^2\lambda^3/\sin 2\theta)]^{1/4}$
Extinction coefficient: $\chi = 0.0077\ (2)$
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)
Absolute configuration: $\chi = -0.006\ (7)$ (Flack, 1983)

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	$U_{\rm eq}$
W	0.1099 (1)	x	0	0.003 (1)
Ni	0.6381 (1)	x	0	0.005 (1)
P	0.3302 (1)	0.8228 (1)	0.0031 (1)	0.004 (1)
K	0.0001 (1)	0.7103 (1)	0.0475 (1)	0.026 (1)
O(1)	0.2190 (2)	0.2398 (3)	0.1278 (2)	0.008 (1)
O(2)	0.2839 (2)	−0.0138 (2)	0.0279 (2)	0.007 (1)
O(3)	0.7614 (3)	0.2448 (3)	0.1075 (2)	0.009 (1)
O(4)	0.8153 (2)	0.4934 (2)	0.0174 (2)	0.008 (1)
O(5)	−0.0059 (2)	0.0447 (2)	0.1179 (2)	0.009 (1)

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

W—O(5$^{\rm i}$)	1.752 (2)	P—O(4$^{\rm i}$)	1.513 (2)
W—O(5)	1.752 (2)	P—O(3$^{\rm i}$)	1.524 (2)
W—O(2$^{\rm i}$)	1.978 (2)	P—O(1$^{\rm v}$)	1.548 (2)
W—O(2)	1.978 (2)	P—O(2$^{\rm vi}$)	1.578 (2)
W—O(1)	2.068 (2)	K—O(3$^{\rm v}$)	2.621 (3)
W—O(1$^{\rm i}$)	2.068 (2)	K—O(4$^{\rm vii}$)	2.630 (2)
Ni—O(3$^{\rm ii}$)	2.029 (2)	K—O(1$^{\rm v}$)	2.708 (2)
Ni—O(3$^{\rm iii}$)	2.029 (2)	K—O(3$^{\rm i}$)	2.825 (3)
Ni—O(5$^{\rm iv}$)	2.046 (2)	K—O(4$^{\rm viii}$)	3.000 (2)
Ni—O(5$^{\rm v}$)	2.046 (2)	K—O(3$^{\rm viii}$)	3.107 (3)
Ni—O(4$^{\rm i}$)	2.104 (2)	K—O(5$^{\rm vi}$)	3.156 (2)
Ni—O(4)	2.104 (2)	K—O(5$^{\rm ix}$)	3.169 (2)
O(5$^{\rm i}$)—W—O(5)	95.9 (1)	O(3$^{\rm iii}$)—Ni—O(4)	88.9 (1)
O(2$^{\rm i}$) –W—O(2)	161.1 (1)	O(5$^{\rm v}$)—Ni—O(4)	97.6 (1)
O(1)—W—O(1$^{\rm i}$)	83.1 (1)	O(3$^{\rm i}$)—P—O(4$^{\rm i}$)	112.2 (1)
O(5)—W—O(2)	100.6 (1)	O(3$^{\rm i}$)—P—O(2$^{\rm vi}$)	110.0 (1)
O(2)—W—O(1)	80.9 (1)	O(4$^{\rm i}$)—P—O(2$^{\rm vi}$)	109.4 (1)
W—O(5)—Ni$^{\rm x}$	135.4 (1)	O(3$^{\rm i}$)—P—O(1$^{\rm v}$)	107.8 (1)
O(5$^{\rm iv}$)—Ni—O(5$^{\rm v}$)	88.9 (1)	O(4$^{\rm i}$)—P—O(1$^{\rm v}$)	112.6 (1)
O(3$^{\rm ii}$)—Ni—O(3$^{\rm iii}$)	97.2 (1)	O(2$^{\rm vi}$)—P—O(1$^{\rm v}$)	104.5 (1)
O(4$^{\rm i}$)—Ni—O(4)	168.5 (1)		

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

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: SH1105). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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CsNbOB$_2$O$_5$: the Basic Structure Type of the Borates $A M$OB$_2$O$_5$ (A = K, Rb, Cs, Tl; M = Nb, Ta)

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Abstract

A new anhydrous borate, CsNbOB$_2$O$_5$ (caesium niobatodiborate), has been found in the ternary system Cs$_2$O–Nb$_2$O$_5$–B$_2$O$_3$. The compound belongs to the already known AMOB$_2$O$_5$ family (originally reported as AMB$_2$O$_6$) with A = K, Rb, Cs, Tl; M = Nb, Ta. These published members exhibit superstructures, the length of the superperiod depending on the chemical composition A and M. The structure of CsNbOB$_2$O$_5$ reported here has the smallest possible unit cell and represents the basic structural type for the family.

Comment

The present work is a part of a systematic search for non-centrosymmetric compounds, especially borates, to obtain new materials for application in nonlinear optics. The first members of the borates AMOB$_2$O$_5$ (A = Rb, Tl and M = Nb, Ta) were described by Gasperin (1974) and Baucher & Gasperin (1975). They found them to be non-centrosymmetric with very similar crystal structures [space group Pn for RbNbOB$_2$O$_5$ (Baucher, Gasperin & Cervelle, 1976), $Pn2_1a$ for TlNbOB$_2$O$_5$ (setting $a\bar{c}b$) and $Pn2_1m$ (setting bca) for the other compounds]. The lattice constants are given as $a = 2 \times 3.91$, $b = 9.48$, $c = 7.40$ Å for TlNbOB$_2$O$_5$, $a = 5 \times 3.86$, $b = 9.50$, $c = 7.44$ Å for TlTaOB$_2$O$_5$, $a = 5 \times 3.94$, $b = 9.49$, $c = 7.42$ Å for RbNbOB$_2$O$_5$, and $a = 5 \times 3.88$, $b = 9.52$, $c = 7.44$ Å for RbTaOB$_2$O$_5$. The multiplying factors of the a lattice constants result from the superstructures of the members of the family. These data are in good agreement with our results. Further members of this crystal family, KNbOB$_2$O$_5$, KTaOB$_2$O$_5$ and CsNbOB$_2$O$_5$, were synthesized for the first time in our laboratory and show similar superstructures with cell dimensions of $a = 7.318(1)$, $b = 8 \times 3.904(1)$, $c = 9.219(1)$ Å for KNbOB$_2$O$_5$, $a = 7.333(1)$, $b = 8 \times 3.843(1)$, $c = 9.313(1)$ Å for KTaOB$_2$O$_5$, and a