N1···O27^{i}	3.09 (3)	O4WB···O20^{x}	2.70 (14)
N1···O1W^{ii}	2.91 (4)	O4WB···O22^{ix}	2.61 (14)
O1W···O4^{iii}	3.15 (3)	O4WB···O24^{xi}	2.91 (14)
O1W···O16^{iv}	3.06 (3)	O4WB···O29^{ix}	3.15 (14)
O1W···O18^{ix}	2.97 (3)	O4WB···O5WB	2.36 (14)
O1W···O23^{v}	2.75 (3)	O5WA···O19^{xii}	2.74 (5)
O1W···O24^{v}	3.17 (4)	O5WA···O25^{ii}	2.94 (5)
O1W···O4WA^{vi}	2.57 (5)	O5WA···O29^{ix}	2.73 (5)
O1W···O4WB^{vi}	2.81 (14)	O5WB···O19^{xii}	2.84 (7)
O2W···O20^{vii}	3.14 (4)	O5WB···O20^{x}	3.12 (7)
O2W···O21^{iii}	3.07 (4)	O5WB···O22^{ix}	2.83 (7)
O2W···O24	2.72 (4)	O5WB···O29^{ix}	2.89 (7)
O2W···O27^{iii}	2.79 (4)		

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

Two lattice water molecules, designated O4WA, O4WB, O5WA and O5WB, showed disorder. In the final refinement, the site-occupancy factors of O4WA and O5WA were assigned to be 0.7, and those of O4WB and O5WB 0.3, according to the refinement results. There were 12 O atoms of paradodecatungstate and two disordered O atoms (O$W4B$ and O5WB) became 'non-positive-definite' when all atoms were refined anisotropically. The N and O atoms were then refined isotropically in the final refinement. The isotropic displacement parameters of the 12 O atoms ranged from 0.008 to 0.030 Å^2, which are comparable with those of the other O atoms in the paradodecatungstate (0.011–0.027 Å^2). The largest residual electron-density peaks were located around W atoms.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992). Cell refinement: *CAD-4-PC Software*. Data reduction: *XCAD4* (Harms, 1997). Program(s) used to solve structure: *SHELX97* (Sheldrick, 1997). Program(s) used to refine structure: *SHELX97*. Molecular graphics: *SCHAKAL92* (Keller, 1992) and *ORTEX* (McArdle, 1993). Software used to prepare material for publication: *SHELXL97*.

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K₂NbAlO₂[(As,Nb)O₄]₂, isostructural with KTiOPO₄

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Abstract

The title compound, potassium niobium aluminium arsenate (KNAA), is isostructural with KTiOPO₄ (KTP). In KNAA, the site corresponding to the Ti1 sites of KTP is occupied mostly by Nb atoms, the Ti2 site is occupied predominantly by Al atoms, and the As1 and As2 tetrahedral sites are occupied mostly by As atoms. The $M1O_6$ octahedron is more distorted and the $M2O_6$ octahedron is less distorted than that of KTP.

Comment

Recently, many crystals isostructural with KTiOPO₄ (KTP) (Tordjman *et al.*, 1974) have been synthesized because they have interesting non-linear optical properties. For example, KTP crystals are used effectively for second harmonic generation. The structures of the compounds with the general formula (K,Rb,Tl,Na)TiO-(P,As)O₄ have been determined by single-crystal X-ray or neutron diffraction methods (Haidouri *et al.*, 1990; Mayo *et al.*, 1994; Thomas *et al.*, 1990, 1992).

In this study, a new compound with the chemical formula K₂NbAlO₂[(As,Nb)O₄]₂ (KNAA) has been synthesized by a flux method and the structure was refined using single-crystal X-ray diffraction data. The atomic coordinates, site occupancies and equivalent displacement factors are given in Table 1, the interatomic distances and angles are given in Table 2 and a projection of KNAA parallel to the *c* axis is shown in Fig. 1.

The structure of KNAA, isostructural with that of KTP, has six kinds of cation site, namely *M*1, *M*2,
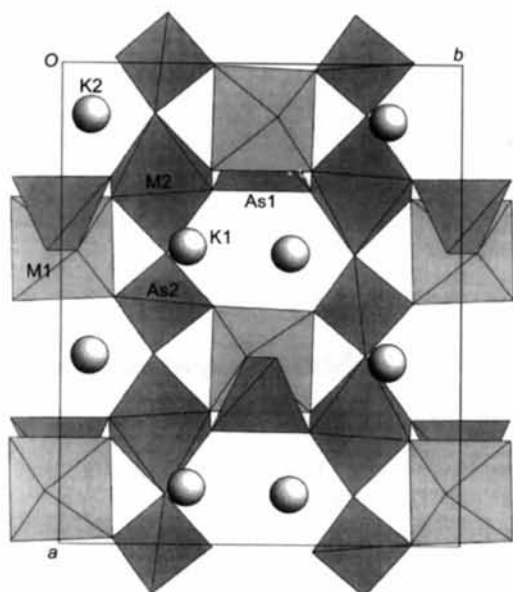
$K_2NbAlO_2[(As_{0.8}Nb_{0.2})O_4]_2$

Fig. 1. A view of the KNAA structure along the [001] direction. The structure of KNAA, isostructural with KTP, has six kinds of cation site, namely $M1$, $M2$, As1, As2, K1 and K2 sites. The structure consists of $M1O_6$ and $M2O_6$ octahedra, and $As1O_4$ and $As2O_4$ tetrahedra forming a three-dimensional corner-sharing network.

As1, As2, K1 and K2 sites. The structure consists of $M1O_6$ and $M2O_6$ octahedra, and $As1O_4$ and $As2O_4$ tetrahedra forming a three-dimensional corner-sharing network, with K1 and K2 occupying the vacancy in the network.

For the octahedral sites, the Nb atoms with higher valence and larger ionic radius and the Al atoms occupy 98 and 2% of the $M1$ sites, respectively, and 2 and 98% of the $M2$ sites, respectively. In the $M1O_6$ octahedron, $M1$—$OM1$ and $M1$—$OM2$ distances are 1.823 (5) and 1.815 (5) Å, respectively, and the remaining $M1$—O1, $M1$—O2, $M1$—O5 and $M1$—O6 distances range from 2.035 (4) to 2.094 (5) Å. The difference of the former short $M1$—O distances from the latter long $M1$—O distances is ca 0.2 Å. On the other hand, in the $M2O_6$ octahedron, the $M2$—O3, $M2$—O4, $M2$—$OM1$, $M2$—$OM2$, $M2$—O7 and $M2$—O8 distances range from 1.858 (6) to 1.972 (4) Å, the difference of the maximum and the minimum $M2$—O distances is ca 0.1 Å and all $M2$—O distances are almost the same. In the KTP structure, both $Ti1O_6$ and $Ti2O_6$ octahedra have one short, one long and four intermediate Ti—O distances. The $M1O_6$ octahedron is more distorted than the TiO_6 octahedra and the $M2O_6$ octahedron is less distorted.

For the As1 and As2 sites, As and Nb atoms occupy 80 and 20%, respectively. The As1 site is four-coordinated by O1, O2, O3 and O4 at distances between 1.677 (4) and 1.694 (6) Å, with one longer and three shorter As1—O distances. The As2 site is four-coordinated by O5, O6, O7 and O8 at distances

between 1.668 (5) and 1.701 (4) Å, with two longer and two shorter As2—O distances. The $As1O_4$ and $As2O_4$ tetrahedra are slightly distorted compared with those in KTP.

Experimental

The crystal of KNAA was synthesized by a flux method (Chani $et\ al.$, 1997). The chemical composition was analysed using an energy-dispersive X-ray analyser (EDX). The EDX data expressed in oxides was 18.0 (6) wt% K_2O, 35.8 (9) wt% Nb_2O_5, 11.6 (17) wt% Al_2O_3 and 34.8 (12) wt% As_2O_5. The chemical composition, $K_{1.97(8)}Nb_{1.38(5)}Al_{1.0(3)}As_{1.63(8)}O_{10}$, calculated on the basis of ten O atoms, was assumed to be $K_{2.0}Nb_{1.4}Al_{1.0}As_{1.6}O_{10}$, taking into account the s.u.'s.

Crystal data

$K_2NbAlO_2[(As_{0.8}Nb_{0.2})O_4]_2$	Mo $K\alpha$ radiation
$M_r = 515.12$	$\lambda = 0.71069$ Å
Orthorhombic	Cell parameters from 80
$Pn2_1a$	reflections
$a = 13.006\,(1)$ Å	$\theta = 10–26°$
$b = 10.648\,(1)$ Å	$\mu = 8.57$ mm^{-1}
$c = 6.619\,(1)$ Å	$T = 293\,(2)$ K
$V = 916.7\,(3)$ Å^3	Sphere
$Z = 4$	0.093 (5) mm (radius)
$D_x = 3.733$ Mg m^{-3}	Colourless
D_m not measured	

Data collection

Rigaku AFC-7 diffractometer	2365 reflections with $F > 3\sigma(F)$
ω–2θ scans	$R_{int} = 0.013$
Absorption correction:	$\theta_{max} = 34.96°$
spherical (modified $PTPHI$	$h = -18 \rightarrow 18$
program in PW1100	$k = -14 \rightarrow 14$
software)	$l = -10 \rightarrow 9$
$T_{min} = 0.269$, $T_{max} = 0.353$	3 standard reflections
8491 measured reflections	every 200 reflections
2598 independent reflections	intensity decay: none

Refinement

Refinement on F	$\Delta\rho_{max} = 0.723$ e Å^{-3}
$R = 0.023$	$\Delta\rho_{min} = -0.628$ e Å^{-3}
$wR = 0.034$	Extinction correction: Becker
$S = 1.991$	& Coppens (1974)
2365 reflections	Extinction coefficient:
147 parameters	0.334 (10)
$w = 1/[\sigma^2(F_o)]$	Scattering factors from
$(\Delta/\sigma)_{max} < 0.001$	$International\ Tables\ for$
	$Crystallography$ (Vol. C)

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

$$U_{eq} = (1/3)\sum_i\sum_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
K1	0.38020 (12)	0.3147 (2)	0.7809 (2)	0.0283 (4)
K2	0.10640 (11)	0.0724 (2)	0.6956 (2)	0.0287 (4)
$M1$_Nb†	0.36839 (2)	0	0.49994 (9)	0.00426 (8)
$M1$_Al‡	0.36839	0	0.49994 (9)	0.00426

M2_Nb‡	0.24700	0.2473	0.2528	0.0043
M2_Al†	0.24700	0.2473	0.2528	0.0043
As1_As§	0.49872 (5)	0.2519 (1)	0.32209 (6)	0.0062 (9)
As1_Nb¶	0.49872	0.2519	0.32209	0.0062
As2_As§	0.18725 (3)	0.50045 (12)	0.50368 (10)	0.0072 (10)
As2_Nb¶	0.18725	0.50045	0.50368	0.0072
O1	0.4870 (4)	0.1323 (5)	0.4882 (9)	0.0140 (13)
O2	0.5043 (4)	0.3811 (5)	0.4693 (11)	0.0107 (11)
O3	0.3930 (3)	0.2645 (6)	0.1779 (6)	0.0118 (11)
O4	0.6027 (3)	0.2332 (4)	0.1751 (6)	0.0062 (10)
OM1	0.2231 (4)	0.6249 (5)	−0.0559 (10)	0.0100 (13)
OM2	0.2204 (4)	0.3735 (5)	0.0585 (9)	0.0076 (12)
O5	0.1114 (3)	0.5397 (5)	0.3054 (6)	0.0103 (9)
O6	0.1088 (3)	0.4644 (4)	0.7011 (6)	0.0087 (10)
O7	0.2644 (4)	0.6224 (5)	0.5489 (10)	0.0091 (13)
O8	0.2616 (4)	0.3762 (5)	0.4538 (10)	0.0104 (13)

† Site occupancy = 0.980 (2).   ‡ Site occupancy = 0.020 (2).   § Site occupancy = 0.800 (10).   ¶ Site occupancy = 0.200 (10).

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

M1—OM1'	1.823 (5)	M2—O4"	1.942 (4)
M1—OM2'	1.815 (5)	M2—O3	1.972 (4)
M1—O6"	2.035 (4)	As1—O4	1.677 (4)
M1—O5'	2.082 (4)	As1—O1	1.683 (6)
M1—O2'''	2.094 (5)	As1—O3	1.679 (4)
M1—O1	2.091 (5)	As1—O2	1.694 (6)
M2—OM1'	1.858 (6)	As2—O7	1.668 (5)
M2—OM2	1.892 (6)	As2—O8	1.671 (6)
M2—O7"	1.900 (6)	As2—O6	1.701 (4)
M2—O8	1.921 (6)	As2—O5	1.694 (4)

OM1'—M1—OM2'	99.8 (2)	OM1'—M2—O4"	88.9 (3)
OM1'—M1—O6"	91.9 (2)	OM2—M2—O4"	92.7 (4)
OM2'—M1—O6"	99.3 (2)	O7"—M2—O4"	92.6 (3)
OM1'—M1—O5'	97.4 (2)	O8—M2—O4"	88.8 (4)
OM2'—M1—O5'	91.3 (2)	OM1'—M2—O3	91.5 (4)
O6"—M1—O5'	164.4 (2)	OM2—M2—O3	86.9 (4)
OM1'—M1—O2'''	167.7 (2)	O7"—M2—O3	87.7 (4)
OM2'—M1—O2'''	96.0 (2)	O8—M2—O3	90.9 (4)
O6"—M1—O2'''	71.6 (2)	O4"—M2—O3	179.5 (5)
O5'—M1—O2'''	96.1 (2)	O4—As1—O1	111.1 (2)
OM1'—M1—O1	89.0 (2)	O4—As1—O3	109.9 (2)
OM2'—M1—O1	82.3 (2)	O1—As1—O3	111.2 (3)
O6"—M1—O1	89.0 (2)	O4—As1—O2	113.1 (2)
O5'—M1—O1	78.8 (2)	O1—As1—O2	104.0 (3)
O2'''—M1—O1	77.9 (2)	O3—As1—O2	107.0 (3)
OM1'—M2—OM2	178.1 (4)	O7—As2—O8	107.7 (3)
OM1'—M2—O7"	90.3 (3)	O7—As2—O6	113.5 (3)
OM2—M2—O7"	89.9 (4)	O8—As2—O6	108.7 (3)
OM1'—M2—O8	90.2 (4)	O7—As2—O5	107.3 (3)
OM2—M2—O8	89.0 (5)	O8—As2—O5	112.3 (3)
O7"—M2—O8	178.3 (4)	O6—As2—O5	107.6 (2)

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

Possible space groups assigned from X-ray photographs are *Pnma* and *Pn2₁a* for systematic absences $h = 2n + 1$ for $hk0$ and $k + l = 2n + 1$ for $0kl$. In this study, the same space group as KTP (*Pn2₁a*; Tordjman *et al.*, 1974) was assumed as the correct space group. The structure parameters of KTP were adopted as the initial parameters of KNAA. The Friedel pairs were averaged and 2698 reflections were obtained.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSC/AFC Diffractometer Control Software*. Program(s) used to refine structure: modified from the 1977 *ORXFLS4* version of *ORFLS* (Busing *et al.*, 1962).

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Zinc cadmium thiocyanate (ZCTC)

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Abstract

The title complex, zinc cadmium tetrathiocyanate, [ZnCd(SCN)$_4$]$_n$, contains slightly flattened ZnN$_4$ and CdS$_4$ tetrahedra. The –S═C═N– bridges connect Zn and Cd atoms, forming infinite three-dimensional –Cd—S═C═N—Zn– networks, and are essentially linear at C and N, but bent at S. The structure exhibits a high non-linear optical property, and physical and chemical stability.

Comment

Recently, organometallic and coordination complexes have emerged as potential building blocks for second-order non-linear optical (NLO) materials (Long, 1995; Tian *et al.*, 1997). Compared with organic molecules,