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A new potassium niobate, KNb_5O_{13}

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(Nb–O) = 0.002 Å
R factor = 0.019
wR factor = 0.045
Data-to-parameter ratio = 13.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The structure of KNb_5O_{13} consists of two-dimensional slabs of edge- and corner-sharing NbO_6 octahedra, and these slabs are interconnected to form the three-dimensional framework. The K^+ cations reside in the empty channels. Among the three crystallographically independent Nb atoms, the coordination around the Nb atom bridging the slabs is more regular than those of the other Nb atoms. A bond-valence calculation indicates that the charge balance should be represented by $[K^+][Nb^{5+}]_5[O^{2-}]_{13}$.

Comment

During the investigation of the K/Nb/Cd/Se system, single crystals of KNb_5O_{13} were obtained. This phase is a new member of the large family formed between K_2O and Nb_2O_5, *viz*. $KNbO_3$ (Katz & Megaw, 1967), KNb_3O_8 (Gasperin, 1982), $K_4Nb_6O_{17}$ (Gasperin & le Bihan, 1982), $K_3Nb_7O_{19}$ (Sundberg & Lundberg, 1987) and $K_2Nb_{14}O_{36}$ (Hu *et al.*, 1992). KNb_5O_{13} is isotypic with previously reported KTa_5O_{13}, which was considered as a 'chemical twin' of α-PbO_2 (Awadalla & Gatehouse, 1978).

The structure of KNb_5O_{13} can be described in terms of edge- and corner-sharing NbO_6 octahedra linked to form slabs, as found in the α-PbO_2-type structure (Fig. 1). These two-dimensional slabs lie parallel to the *ab* plane and are interconnected along the *c* direction through the O atoms

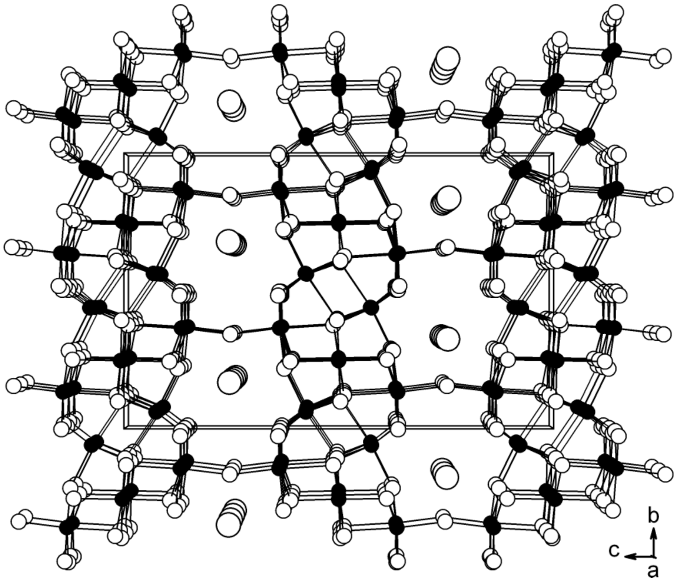

Figure 1
The structure of KNb_5O_{13}, viewed down [100]. Large open circles are K atoms, small filled circles are Nb atoms and small open circles are O atoms.

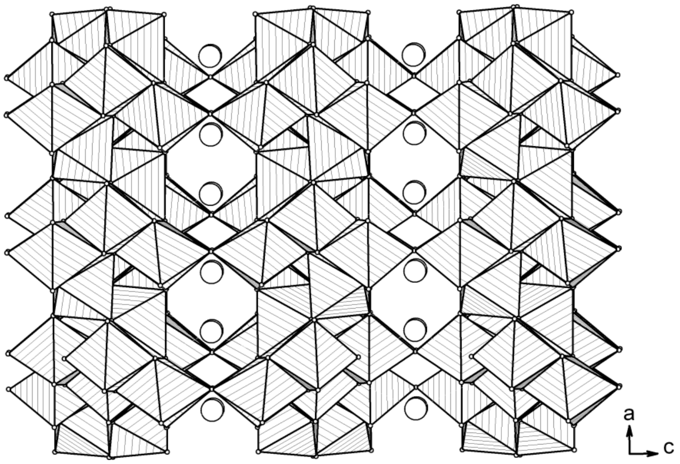

Figure 2
The structure of KNb_5O_{13}, viewed down [010].

shared by NbO_6 octahedra *via* Nb2—O7—Nb2 bridges. This linking mode produces tunnels extended only parallel to the *ab* plane (Fig. 2). The K^+ cations residing in the empty channels are each surrounded by seven O atoms (K—O < 3.0 Å) and are stabilized by electrostatic interactions between the K and O atoms. The octahedra centred by Nb2, which connect the slabs, are more regular [Nb2—O = 1.885 (2)–2.087 (2) Å] than those of Nb1 [1.838 (2)–2.213 (2) Å] and Nb3 [1.910 (2)–2.234 (2) Å]. This structural feature is also found in KTa_5O_{13}. The Nb—O distances correspond to the usual values found for pentavalent Nb in octahedral coordination (Benabbas *et al.*, 1993) and are also comparable with the Ta—O distances [1.86 (2)–2.17 (2) Å] found in KTa_5O_{13} (Awadalla & Gatehouse, 1978).

The bond valence sums calculated for the present structure (Adams, 2001) are 4.979, 5.040, and 4.985 for Nb1, Nb2 and Nb3, respectively, 1.098 for K, and 1.942–2.083 for the O atoms; these values are in good agreement with the estimated oxidation states from the classical charge balance, $[K^+][Nb^{5+}]_5[O^{2-}]_{13}$. The global instability index (GII) is 0.052 v.u., which is a typical value for an unstrained structure (Adams, 2001).

Experimental

KNb_5O_{13} was prepared by the reaction of elemental Nb, Cd and Se with the use of the halide flux technique. Powders of Nb (Cerac, 99.8%), Cd (Cerac, 99.5%) and Se (Cerac, 99.95%) were mixed in silica tubes in an Nb:Cd:Se atomic ratio of 2:1:5, and then KBr was added in an 'Nb_2CdSe_5':KBr weight ratio of 1:2. The tubes were evacuated to 10^{-2} Torr (1 Torr = 133.322 Pa), sealed, and heated gradually (5 K h^{-1}) to 973 K in a tube furnace, where they were kept for 24 h. The tubes were cooled slowly to room temperature at a rate of 5 K h^{-1}. The excess halides were removed with distilled water and black needle-shaped crystals up to 0.2 mm in length were obtained. The crystals are stable in air and water. Qualitative analysis of the crystals with an EDAX-equipped scanning electron microscope indicated the presence of K, Nb and O. No other element was detected. The source of the oxygen is believed to be the water molecule included in the hygroscopic alkali metal halide fluxes.

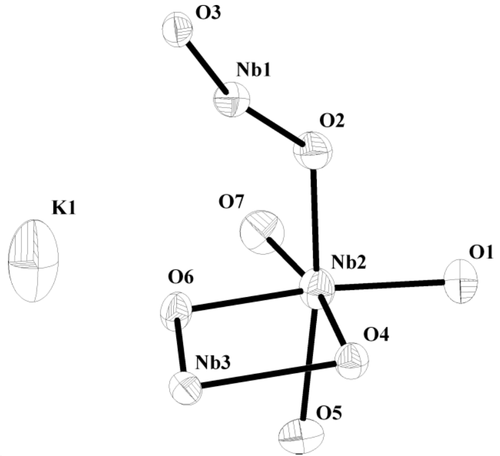

Figure 3
The asymmetric unit in KNb_5O_{13}, with displacement ellipsoids shown at the 90% probability level.

Crystal data

KNb_5O_{13}
$M_r = 711.65$
Orthorhombic, *Pbcm*
$a = 5.672$ (2) Å
$b = 10.737$ (5) Å
$c = 16.742$ (6) Å
$V = 1019.7$ (7) Å^3
$Z = 4$
$D_x = 4.636$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 9114 reflections
$\theta = 3.1$–$27.5°$
$\mu = 5.93$ mm^{-1}
$T = 150$ (2) K
Needle, black
0.20 × 0.04 × 0.04 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: numerical (Higashi, 2000)
$T_{\min} = 0.750$, $T_{\max} = 0.790$
9248 measured reflections

1205 independent reflections
1147 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.035$
$\theta_{\max} = 27.5°$
$h = -7 \rightarrow 7$
$k = -13 \rightarrow 13$
$l = -21 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.046$
$S = 1.19$
1205 reflections
91 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0113P)^2 + 3.9558P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.59$ e Å^{-3}
$\Delta\rho_{\min} = -0.73$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00360 (19)

Table 1
Selected interatomic distances (Å).

K1—O6	2.682 (2)	Nb2—O1	1.885 (2)
K1—O6$^{\rm i}$	2.682 (2)	Nb2—O7	1.9175 (9)
K1—O1$^{\rm ii}$	2.855 (3)	Nb2—O2	1.989 (2)
K1—O1$^{\rm iii}$	2.855 (3)	Nb2—O6	1.989 (2)
K1—O2$^{\rm iv}$	2.872 (2)	Nb2—O5	2.015 (2)
K1—O2$^{\rm v}$	2.872 (2)	Nb2—O4	2.087 (2)
K1—O7	2.996 (4)	Nb3—O6	1.910 (2)
Nb1—O5$^{\rm iii}$	1.838 (2)	Nb3—O6$^{\rm vi}$	1.910 (2)
Nb1—O2	1.881 (2)	Nb3—O3$^{\rm ix}$	1.915 (2)
Nb1—O4$^{\rm vi}$	1.972 (2)	Nb3—O3$^{\rm x}$	1.915 (2)
Nb1—O1$^{\rm vii}$	1.984 (2)	Nb3—O4	2.234 (2)
Nb1—O3	2.182 (2)	Nb3—O4$^{\rm vi}$	2.234 (2)
Nb1—O3$^{\rm viii}$	2.213 (2)		

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

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Data collection: *RAPID-AUTO* (Rigaku, 2005); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: locally modified version of *ORTEPII* (Johnson, 1965); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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