

**K<sub>3</sub>(Sc<sub>0.875</sub>Nb<sub>0.125</sub>)Nb<sub>2</sub>O<sub>9</sub>H<sub>1.75</sub>: a new scandium niobate with a unique cage structure**

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Potassium scandium niobate hydroxide, K<sub>3</sub>(Sc<sub>0.875</sub>Nb<sub>0.125</sub>)Nb<sub>2</sub>O<sub>9</sub>H<sub>1.75</sub>, is a new scandium niobate with a unique cage structure. The structure contains two non-equivalent K<sup>+</sup> sites ( $3m$  and  $\bar{6}m2$  site symmetry), one disordered Sc<sup>3+</sup>/Nb<sup>5+</sup> site ( $\bar{3}m$  site symmetry), one Nb<sup>5+</sup> site ( $3m$  site symmetry), two O<sup>2-</sup> sites ( $m$  and  $mm2$  site symmetry) and one H<sup>+</sup> site ( $m$  site symmetry). Both scandium and niobium have octahedral environments, which combine to form cages around potassium. One K atom lies in a cube-like cage built of seven octahedra, while the other K atom is encapsulated by an eight-membered trigonal face-bicapped prism. The cages form sheets that extend along the  $ab$  plane.

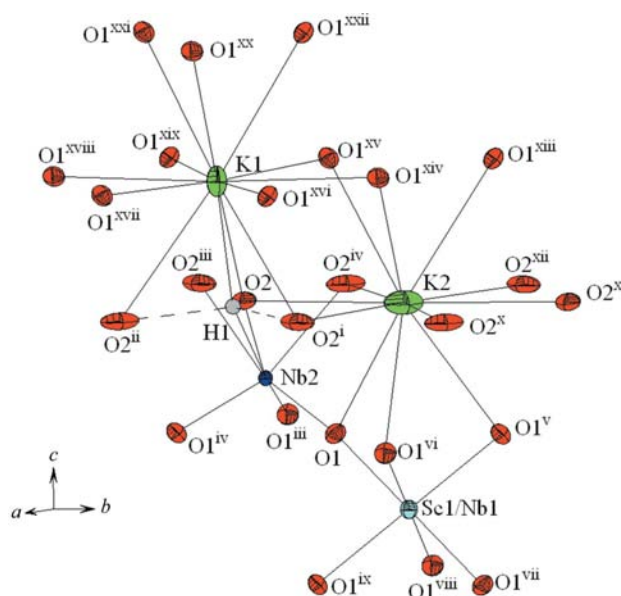
**Comment**

Refractory oxides such as Sc<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, HfO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub> have been a source of much interest over the years owing to their many practical uses, including applications as high-temperature liners, abrasives and laser hosts. In the process of developing these materials, there were preliminary explorations of refractory mixed metal oxides. Because of the difficulty of making high quality samples of these extremely refractory compounds, particularly as single crystals, investigation of these metal oxides has been somewhat neglected.

One relatively unexplored system is that of the scandium niobates, which have generally been limited to powders created by conventional solid-state methods (Rooksby & White, 1963, 1964). Only in one case was single-crystal growth of ScNbO<sub>4</sub> (Ross & Grün, 1990) by chemical vapor deposition reported; however, the crystal size was very small, which prevented complete structural characterization of the material. Hydrothermal solutions have demonstrated the ability to produce single crystals of several classical refractory oxides (Kuznetsov & Sidorenko, 1968). Therefore, a hydrothermal synthesis study of the scandium niobates was undertaken. Using high temperatures, high pressures and extremely basic solutions, the title compound was prepared.

The title structure consists of Sc<sub>0.875</sub>Nb<sub>0.125</sub>O<sub>6</sub> and NbO<sub>3</sub>(OH)<sub>3</sub> octahedral building blocks (Fig. 1). The Sc<sub>0.875</sub>Nb<sub>0.125</sub>O<sub>6</sub> units are corner-sharing *via* atom O1 with the niobium octahedra. An NbO<sub>3</sub>(OH)<sub>3</sub> octahedron occupies the (110) plane and is face-sharing with another niobium octahedron. At 1.867 (3) Å, the three Nb2—O1 bonds are much shorter than the Nb2—O2 bonds of 2.189 (5) Å, distorting the octahedra. This has also been observed in other face-sharing niobium systems (Tyutyunnik *et al.*, 2002; Tarakina *et al.*, 2003). As a result of metal–metal repulsion, the Nb2 atoms are shifted away from each other. The distortion is compounded by the corner-shared O1 atom bound to the lower valent Sc<sup>3+</sup> ion, creating the short Nb2—O1<sup>iii</sup> bond angle of 100.45 (1)°, in contrast to 74.2 (2)° for the O2—Nb2—O2<sup>iii</sup> angle [symmetry code: (iii)  $-x + y, -x + 1, z$ ]. Contrary to the face-sharing niobates, the Sc<sub>0.875</sub>Nb<sub>0.125</sub>O<sub>6</sub> octahedra exhibit no distortion. The combined scandium and distorted niobium environments form a framework that extends along the  $c$  axis.

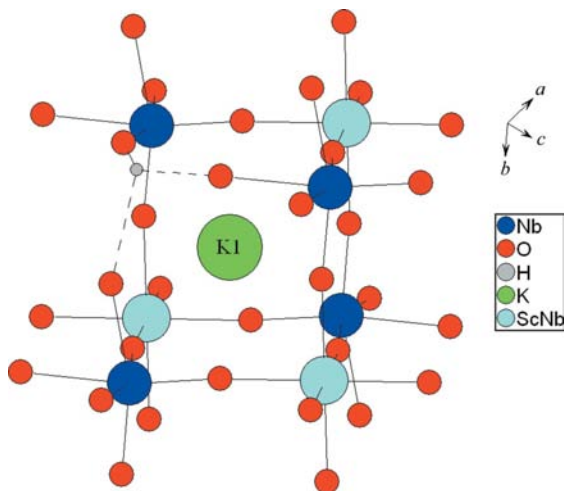
A broad IR stretch located at 3313 cm<sup>-1</sup> indicates the presence of a hydroxy group. In order to locate the hydrogen site, bond valence sums were calculated. This revealed atom O2 [1.366 valence units (v.u.)] as significantly underbonded compared with atom O1 (2.056 v.u.). Therefore, a site located 0.86 Å from atom O2 was designated H1. This has a bifurcated hydrogen bond to atoms O2<sup>i</sup> and O2<sup>ii</sup> [symmetry codes: (i)  $-x + y, -x + 2, z$ ; (ii)  $-y + 2, x - y + 2, z$ ] with distances of 2.491 (7) and 2.486 (7) Å, respectively. The H atom was kept

**Figure 1**

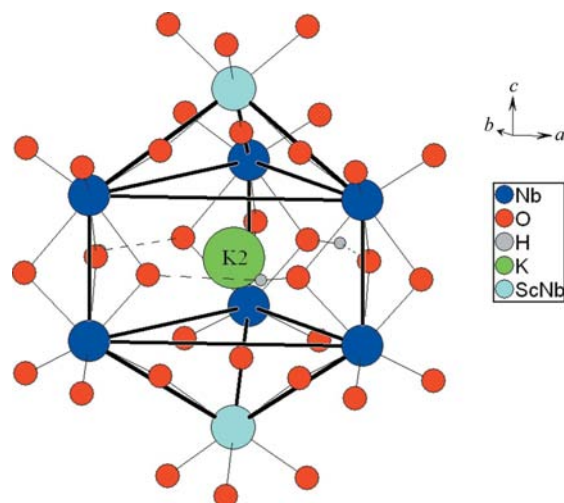
A view of the full coordination environments of scandium, niobium and potassium drawn with 50% probability displacement ellipsoids. [Symmetry codes: (i)  $-x + y, -x + 2, z$ ; (ii)  $-y + 2, x - y + 2, z$ ; (iii)  $-x + y, -x + 1, z$ ; (iv)  $-y + 1, x - y + 1, z$ ; (v)  $-y + 2, x - y + 1, z$ ; (vi)  $-x + y + 1, -x + 2, z$ ; (vii)  $-x + 2, -x + y + 1, -z + 1$ ; (viii)  $y, x, -z + 1$ ; (ix)  $x - y + 1, -y + 2, -z + 1$ ; (x)  $-y + 1, x - y + 2, z$ ; (xi)  $x - 1, y, z$ ; (xii)  $-x + y - 1, -x + 1, z$ ; (xiii)  $-x + y + 1, y, -z + \frac{1}{2}$ ; (xiv)  $-y + 2, -x + 2, -z + \frac{1}{2}$ ; (xv)  $x, x - y + 1, -z + \frac{1}{2}$ ; (xvi)  $-x + y + 1, y + 1, -z + \frac{1}{2}$ ; (xvii)  $x, x - y + 2, -z + \frac{1}{2}$ ; (xviii)  $-y + 1, -x + 2, -z + \frac{1}{2}$ ; (xix)  $-x + y, y, -z + \frac{1}{2}$ ; (xx)  $x - y + 1, x + 1, z - \frac{1}{2}$ ; (xxi)  $-x + 1, -y + 2, z - \frac{1}{2}$ ; (xxii)  $y, -x + y + 1, z - \frac{1}{2}$ ].

fixed with  $U_{\text{iso}} = 0.10 \text{ \AA}^2$  and a partial occupancy to provide an electrically neutral formula. Including the hydrogen environment, a recalculation of the bond valence sum for atom O2 provided an acceptable value of 1.975 v.u. Both hydrogen bonds are considered weak (Brown, 1976) because the bond valence attributed to the acceptor O atoms is less than 0.20 v.u. Furthermore, the  $\text{O2}^{\text{i}} \cdots \text{O2}^{\text{ii}}$  distance is 3.1981 (13) Å. This is much longer than the distance of less than or equal to 2.73 Å that is a requirement of a strong hydrogen bond.

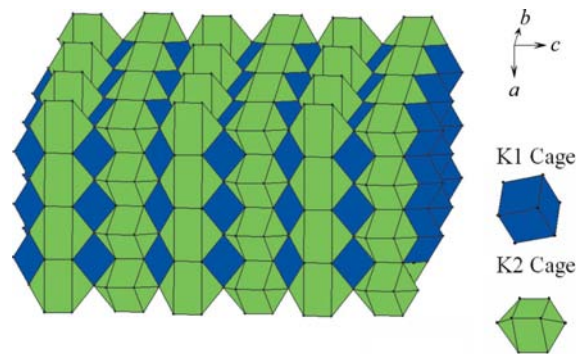
The potassium environments are both 12-coordinate. They have a sixfold coordination of O atoms, which is parallel to the *ab* plane, with a threefold coordination above and below the plane in the *c* direction. The coordination environment is created by two different cage enclosures around atoms K1 and K2, seen in Figs. 2 and 3, respectively. The K1 cage is formed by three scandium and four niobium corner-sharing octahedra. They combine to form a cube-like enclosure with one vertex missing. Atom K1 is centrally located in the cage along the (110) plane. The eighth vertex required to complete the cube



**Figure 2**  
A view of the K1 cage built by scandium and niobium octahedra.



**Figure 3**  
A view of the K2 cage projected slightly off the *ac* plane. The bold lines are not bonds, but are included to aid viewing of the trigonal face-bicapped prism cage.



**Figure 4**  
An extended view of the long-range cage structure projected slightly off the *ac* plane. The lighter polyhedra represent the K1 cage, while the darker units correspond to K2 cages.

is occupied by the bifurcated hydrogen bond. The hydrogen bond also contributes to the K2 cage, but is less pronounced in this case. An eight-membered cage composed of two scandium and six niobium octahedra is oriented to construct a trigonal face-bicapped prism with K2 located along the (100) plane. Scandium octahedra form the face-capping pyramid, while the trigonal prism is built of face-sharing niobium octahedra. A similar permethylpolysilane  $\text{Si}_8\text{Me}_{14}$  cage structure has been reported (West & Carberry, 1975). The most notable difference is the tetrahedral coordination of the silicon *versus* the octahedral scandium and niobium environments. The polysilane cage enclosure is small compared with the large internal volume ( $5.8 \times 5.8 \times 7.3 \text{ \AA}$ ) of the scandium/niobium cage structure. This internal volume created by the octahedral environments provides space for the hydrogen-bond network to interact along the *ab* plane.

The long-range structure (Fig. 4) comprises alternating sheets of the K1 and K2 cage structures extending along the *ab* plane. As the K1 sheets propagate in the *c* direction, they angle themselves as if a mirror plane extends through the middle of the K2 sandwiched sheet. The K2  $\bar{6}m2$  site symmetry causes a  $60^\circ$  rotation from one K2 sheet to the next.

**Experimental**

$\text{K}_3(\text{Sc}_{0.875}\text{Nb}_{0.125})\text{Nb}_2\text{O}_9\text{H}_{1.75}$  was prepared by hydrothermal synthesis. Powders of  $\text{Sc}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_5$  in a 2:1 molar ratio were sealed in a silver ampoule with a solution of 2 M KOH. The ampoule was placed in a 27 ml Inconel autoclave, heated to 848 K and counter-pressured to 17 000 p.s.i. (1 p.s.i. = 6.89 kPa). These conditions were maintained for 10 d, and after this time the ampoule was opened and the contents washed with deionized water. Single crystals of  $\text{KNbO}_3$  were the major constituent, and  $\text{K}_3(\text{Sc}_{0.875}\text{Nb}_{0.125})\text{Nb}_2\text{O}_9\text{H}_{1.75}$  colorless tapering hexagonal rod crystals suitable for single-crystal X-ray diffraction were the minor product. FT-IR:  $3313 \text{ cm}^{-1}$  (broad, s OH).

*Crystal data*

|  |   |
|--|---|
| $\text{K}_3(\text{Sc}_{0.875}\text{Nb}_{0.125})\text{Nb}_2\text{O}_9\text{H}_{1.75}$ | $Z = 2$                                   |
| $M_r = 499.84$   | Mo $K\alpha$ radiation                    |
| Hexagonal, $P6_3/mmc$  | $\mu = 4.92 \text{ mm}^{-1}$              |
| $a = 5.8416 (15) \text{ \AA}$  | $T = 298 \text{ K}$                       |
| $c = 14.604 (5) \text{ \AA}$   | $0.30 \times 0.27 \times 0.25 \text{ mm}$ |
| $V = 431.6 (2) \text{ \AA}^3$  |   |

*Data collection*

Rigaku AFC-8S Mercury CCD diffractometer  
Absorption correction: multi-scan (Jacobson, 1998)  
 $T_{\min} = 0.256$ ,  $T_{\max} = 0.298$

3318 measured reflections  
178 independent reflections  
170 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.028$

*Refinement*

$R[F^2 > 2\sigma(F^2)] = 0.028$   
 $wR(F^2) = 0.081$   
 $S = 1.02$   
178 reflections

21 parameters  
H-atom parameters not refined  
 $\Delta\rho_{\max} = 1.04 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.78 \text{ e } \text{\AA}^{-3}$

**Table 1**Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

| $D-H\cdots A$         | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------|-------|-------------|-------------|---------------|
| $O2-H1\cdots O2^i$    | 0.86  | 2.49        | 3.1981 (13) | 140           |
| $O2-H1\cdots O2^{ii}$ | 0.86  | 2.49        | 3.1981 (13) | 140           |

Symmetry codes: (i)  $-x + y, -x + 2, z$ ; (ii)  $-y + 2, x - y + 2, z$ .

Data collection: *CrystalClear* (Molecular Structure Corporation & Rigaku, 2006); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular

graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LG3008). Services for accessing these data are described at the back of the journal.

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