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Occurrence of the Tetragonal Tungsten Bronze Structure Type in the $KF-Nb_2O_5$ System

LI DE-YU,* MONICA LUNDBERG, PER-ERIK WERNER and MARIANNE WESTDAHL

Department of Inorganic Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden

Three intermediate phases, KNb_2O_5F, $KNb_4O_{10}F$ and $KNb_6O_{15}F$, have been investigated in the system $KF-nNb_2O_5$ ($1 \leq n \leq 4$) at temperatures between 850 and 1000 °C. The samples were studied by X-ray powder diffraction methods. The cell parameters and the structural relations to tetragonal tungsten bronze are discussed. The polyhedral framework of the two most niobium-rich phases contains niobium atoms not only in octahedral but also in pentagonal bipyramids. In the structure of KNb_2O_5F, potassium atoms are located with full occupancy in five-sided tunnels and with 50 % occupancy in four-sided tunnels.

A large variety of structures have been found in the K–Nb–O and K–Nb–O–F systems. Among those, the tetragonal tungsten bronze-type (TTB), M_xWO_3, appears as a non-stoichiometric phase with a unit cell containing a constant number of Nb atoms.[1,2]

The TTB structure[3] contains MX_6-octahedra sharing corners in three dimensions so as to form three-, four- and five-member rings, marked A, B and C, respectively, in Fig. 1. It has an anion-to-transition metal ratio equal to 3. Compositional deviations may be regulated by insertion of equal amounts of transition metal atoms and anions in the pentagonal tunnels. The MX_7 pentagonal bipyramids formed in this process share their equatorial edges with the five MX_6 octahedra surrounding the pentagonal tunnel. A stack of these building units has been called a pentagonal column (PC),[4] observable in, e.g., the TTB-related compound $Nb_{16}W_{18}O_{94}$,[5] which has a unit cell three times the size of the TTB-cell, and an oxygen-to-metal ratio of 2.76. To compensate for the oxygen deficiency, 4 out of 12 pentagonal tunnels have transformed into PC's arranged in an ordered way.

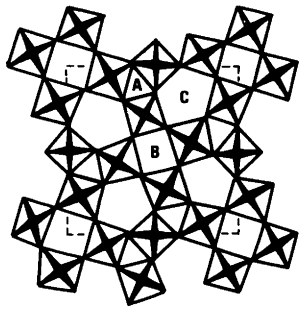

Fig. 1. The TTB structure type viewed along [001]. The three-, four- and five-sided tunnels are marked A, B and C, respectively.

In the present investigation the addition of niobium atoms in the TTB-lattice has been studied in the system $KF-Nb_2O_5$, especially the influence on the niobium coordinations and the effects on the cell parameters.

EXPERIMENTAL

Starting materials were Nb_2O_5 (Merck, optipure), purified from oxide fluorides by several hours' heating at 1100 °C, $KNbO_3$, obtained by heating stoichiometric amounts of K_2CO_3 (BDH,

* On leave from the Shanghai Institute of Ceramics, Chinese Academy of Sciences, 865 Chang-ning Road, Shanghai 200050, China.

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laboratory reagents) and Nb_2O_5 in a platinum crucible at 900 °C for 5 h, and NbO_2F prepared by dissolving Nb_2O_5 in HF according to Ref. 6. Thoroughly ground mixtures of Nb_2O_5, $KNbO_3$ and NbO_2F were kept in sealed platinum tubes at temperatures between 850–1000 °C for 3–5 days. The samples were rapidly cooled to room temperature.

X-ray powder photographs were taken in a focusing camera of Guinier-Hägg type, using strictly monochromatized Cu$K\alpha_1$ radiation. Silicon (a/λ=3.525176)[7] was added as internal standard. The films were analyzed with a film scanner measuring system.[8] The unit cell parameters were refined by the program PIRUM.[9] Profile refinement of the Rietveld type has been performed with the programs described in Ref. 10.

The densities were determined by observing the apparent loss of weight in n-hexane. The density of the liquid was calibrated with a germanium crystal (ρ=5.3267 g cm^{-3} at 298 K).

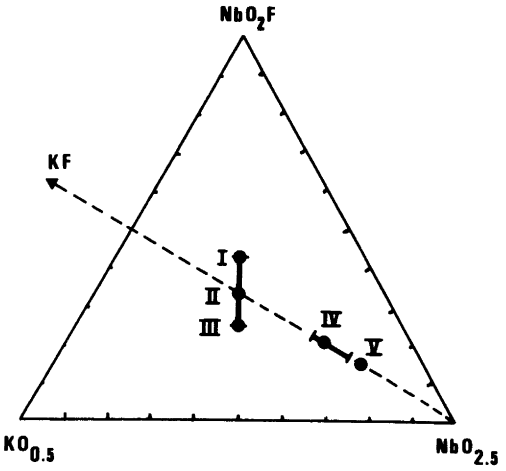

Fig. 2. A partial phase diagram showing the TTB-related structures discussed in the text. The numbers I–V refer to the compositions listed in Table 1.

Table 1. Unit-cell parameters for $K_xNbO_{2+x}F_{1-x}$ and $KNb_{2n}O_{5n}F$. Standard deviations are given within parentheses.[a]

$K_xNbO_{2+x}F_{1-x}$ [b]	I x=0.4	II x=0.5	III x=0.6
a/Å	12.5856(3)	12.6089(3)	12.6418(2)
c/Å	3.9168(2)	3.9415(2)	3.9522(1)
a/c	3.21	3.20	3.20
V/Å^3	620.42	626.63	631.62
d_{obs}/g cm^{-3}	4.22	4.26	4.34
d_{calc}/g cm^{-3}	4.24	4.29	4.35
Fig. of merit (16,17)	M(20)=33 F(85)=52(0.011, 159)	M(20)=58 F(67)=58(0.008,145)	M(20)=104 F(80)=87(0.006,166)

$KNb_{2n}O_{5n}F$ [c]	IV 1.8≤n≤2.6	n=2	V n=3
a/Å	12.480(1)–12.451(1)	12.4605(6)	17.686(3)
b/Å			
c/Å	3.9606(4)–3.9646(8)	3.9606(4)	3.9629(5)
a/c		3.15	3.15[c]
V/Å^3	614.50–616.87	614.94	1232.2
d_{obs}/g cm^{-3}		4.49	4.57
d_{calc}/g cm^{-3}		4.55[b]	4.61
Fig. of merit (16,17)		M(20)=40 F(66)=37(0.012,146)	M(20)=7 F(30)=(0.013,376)

[a] The indexed Guinier powder patterns are deposited with the authors. [b] Based on model I (see text). [c] Calculated for the subcell.

RESULTS OF THE PHASE ANALYSIS

Several samples with the compositions KF-nNb$_2$O$_5$ ($1 \leq n \leq 4$) and K$_x$NbO$_{2+x}$F$_{1-x}$ ($0.4 \leq x \leq 0.6$) were prepared. According to the Guinier powder photographs three main phases could be distinguished (*cf.* Fig. 2). They all have structures related to the tetragonal tungsten bronze type (TTB).

KNb$_2$O$_5$F (n=1). The compound KNb$_2$O$_5$F (n=1) was reported by Magnéli and Nord[1] to be isomorphous with the tetragonal potassium tungsten bronze K$_x$WO$_3$.[3] This phase has a region of homogeneity expressed by the general formula K$_x$NbO$_{2+x}$F$_{1-x}$ with $0.42 \leq x \leq 0.60$ according to de Pape *et al.*[2] Cell parameters have been determined for x=0.4, 0.5 and 0.6 and are shown in Table 1.

The distribution of the potassium atoms in the four- and five-sided tunnels (B and C in Fig. 1) was studied by means of X-ray powder profile refinements. Crystals of KNb$_2$O$_5$F grow as very thin needles parallel to the c-axis, causing considerable orientation effects especially in the 00l reflexions. However, the least-squares refinements converged, giving standard deviations in bond lengths about 0.03 Å, although the resulting R-value, 0.17, is rather high.

Five potassium atoms are distributed over six sites in the unit cell. In the space group *P4/mbm* this corresponds to one twofold and one fourfold position. The fourfold position, equivalent to the C-site (the pentagonal tunnels), proved to be fully occupied within $\pm 1.5\sigma$, while the B-site was found to be occupied to 50 %. The high R-value obtained in the structure refinement may also be due to the fact that potassium is statistically distributed over the B-sites. A similar result was obtained by Kihlborg and Klug, 1973,[12] who found the potassium content of K$_{0.37}$WO$_3$ to be 10 % in the B-site and 88 % in the C-site. The atomic positions given for K$_{0.37}$WO$_3$ remain almost unchanged in KNb$_2$O$_5$F and will therefore not be given in this paper.

KF-nNb$_2$O$_5$ for 1.8≤n≤2.6. According to the Guinier films a non-stoichiometric phase appears within the range $1.8 \leq n \leq 2.6$. The powder patterns show large similarities with the ones obtained for KNb$_2$O$_5$F and could be fully indexed using tetragonal symmetry (*cf.* Table 1). No traces of other compounds could be found. The a-axis decreases with increasing niobium content, while the value of the c-axis increases slightly, so that the cell volume remains relatively constant (*cf.* Table 1).

The sample KNb$_4$O$_{10}$F (n=2) was chosen for more detailed studies. The Guinier films indicated the basic octahedral framework to be of the same kind as the TTB structure, with a unit cell composition of Nb$_{10}$X$_{30}$. The phase has a niobium content exceeding the amount required to occupy the octahedral positions. The excess of niobium atoms may appear in two different polyhedral environments, either as a pentagonal bipyramid formed by introducing equal numbers of niobium atoms and anions in the five-sided tunnels (C) (Model I), or as tricapped trigonal prisms, when niobium atoms are located at the A-sites (Model II).

To express the structural character of KNb$_4$O$_{10}$F, the chemical formula may be written either as K$_{2.9}$(NbX)$_{1.4}$Nb$_{10}$X$_{30}$ (Model I) or as K$_{2.8}$Nb$_{0.9}$Nb$_{10}$X$_{30}$ (Model II), where model I comprises 1.4 seven-coordinated Nb atoms in PC's and model II contains 0.9 nine-coordinated Nb atoms. However, the latter localization of Nb would result in some rather long Nb–X bonds.

The unit cell content suggested for model I yields a calculated density of 4.55 g cm^{-3}, while the corresponding value for model II is 4.34 g cm^{-3}. The observed density of KNb$_4$O$_{10}$F is 4.49 g cm^{-3}, which makes model I the most probable one. However, the structure of a similar compound, K$_6$Ta$_{10.8}$O$_{30}$, has been reported to accommodate 0.8 Ta atoms at the A positions.[13]

Attempts were therefore made to verify the proposed structure by profile refinement. Unfortunately, the prospects were not the best, since the lines in the photographs were somewhat broadened. This was possibly due to lattice variation caused by disorder, and the intensities were affected by preferred orientation. However, the two proposed structure models including the occupancy parameter for the extra Nb atoms were tested. From a number of least-squares refinements it was concluded that the model with Nb in pentagonal bipyramids is the most correct one. The value of the occupational factor obtained corresponds to 1.2±0.2 Nb atoms distributed over one fourfold position, in reasonable agreement with the observed density. The model with Nb in tricapped trigonal prisms was rejected because the occupancy parameter decreased to a value close to zero and the R_F-value was larger, (25 %), than in the former case (18 %).

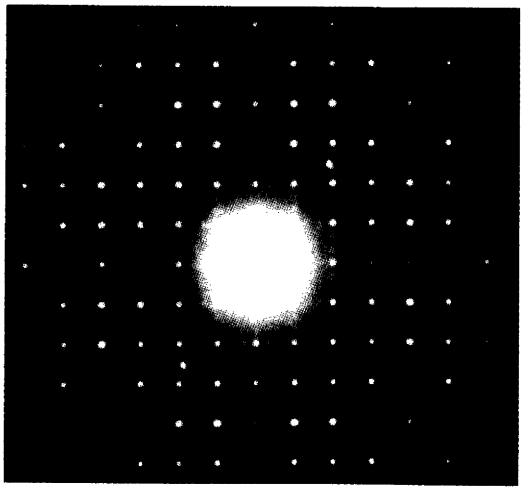

Fig. 3. Electron diffraction pattern taken from $KNb_4O_{10}F$. Superlattice spots in twin orientation can be seen.

In order to check these conclusions, an electron microscopy investigation was started. Preliminary results show that the compound $KNb_4O_{10}F$ has a superstructure with a unit cell three times the TTB cell. The electron diffraction patterns also indicated twinning (see Fig. 3), which was confirmer by lattice images. This type of supercell was first found for the crystal structure of $Nb_{16}W_{18}O_{94}$[5] containing four PC's in the unit cell (see above). Since there were no traces of superlattice reflexions in strongly exposed X-ray powder photographs, an X-ray powder pattern was calculated for $KNb_4O_{10}F$, using the triple unit cell and the atomic parameters from the structure determination of $Nb_{16}W_{18}O_{94}$. According to this calculation, weak superstructure lines should have been visible in the films. Therefore it would be reasonable to assume some kind of disorder in the arrangement of the pentagonal bipyramids as well as of the potassium atoms. This is also reflected in the width of the observed lines, as mentioned above.

$KNb_6O_{15}F$ (n=3). The third phase, $n=3$, in the system is orthorhombic and seems to be a stoichiometric phase. The cell parameters (*cf.* Table 1) give a cell volume approximately twice as large as that of the TTB cell. The cell parameters have been identified by electron diffraction patterns from the same sample.[14]

The composition $KNb_6O_{15}F$ with $Z=4$ yields a calculated density of 4.61 g cm^{-3} in good agreement with the observed value 4.57 g $cm.^{-3}$

The appearance of the powder pattern indicates a structure related to the TTB structure type, although the composition implies that 4 out of 24 Nb atoms are situated in pentagonal bipyramids, and the formula can be written as $K_4(NbX)_4Nb_{20}X_{60}$. The larger unit cell suggests, however, a different distribution of the pentagonal bipyramids than for the nonstoichiometric phase discussed above.

This type of doubling of the TTB-type unit cell has been observed in several systems, intensely studied because of their dielectric properties. An example is $K_3Li_2Ta_5O_{15}$,[15] a compound with the alkali metal atoms located in both four- and five-sided tunnels.

Guinier films of all preparations with n-values in between the three phases described above were indexed as two-phase samples, using the cell parameters obtained from KNb_2O_5F and $KNb_{3.6}O_9F$, and $KNb_{5.2}O_{13}F$ and KNb_6O_{15} respectively.

The somewhat shorter c-axis in KNb_2O_5F (*cf.* Table 1) is probably due to the fact that no pentagonal bipyramids are present in this structure. As can be seen from Table 1, the cell volume of the substructure is almost independent of the number of pentagonal bipyramids. The system has been further investigated by high resolution electron microscopy. These investigations include structural studies of the $n=3$ phase, which will be published elsewhere (14).

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