Preparation and Crystal Structure of $K_2YNb_5O_{15-\delta}$

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Single crystals of new reduced potassium yttrium niobate, $K_2YNb_5O_{15-\delta}$, were prepared in a H_2 atmosphere at 1200°C. Potassium yttrium niobate crystallizes in the orthorhombic space group *Cmmm* with $a = 10.316(1)$, $b = 15.257(1)$, and $c = 3.914(1)$ Å, $Z = 2$, and the final R factors are $R = 0.046$ and $R_w = 0.047$ for 1077 unique reflections. The crystal structure is built up by corner-sharing of NbO_6 octahedra and the three-dimensional framework formed by the Nb_5O_{15} units is same as that of the $NaNb_6O_{15}F$-type structure. The Y^{3+} ion is located in a distorted perovskite-like cavity and the K^+ ion is in a pentagonal tunnel. Reduced potassium yttrium niobate, $K_2YNb_5O_{15-\delta}$, is oxidized without deterioration in crystallinity at about 450°C, and the oxidized phase, $K_2YNb_5O_{15}$, transforms to the tetragonal tungsten bronze-type structure at 1150°C. © 1996 Academic Press, Inc.

INTRODUCTION

Niobium can adopt various oxidation states and many reduced complex niobates have been reported (1–10). Reduced complex niobates can be divided into two groups; strongly reduced complex niobates with metal–metal bonding and weakly reduced ones without metal–metal bonding. Many of the strongly reduced complex niobates are characterized by having the $[Nb_6O_{12}]O_6$ cluster as found in complex niobates such as $Rb_{1.51}Nb_{10}O_{15}$ (1), $NaNb_{10}O_{18}$ (2), $Rb_4Al_2Nb_{35}O_{70}$ (3), etc. Recently we discovered a strongly reduced rubidium niobate, $Rb_{1.51}Nb_{10}O_{15}$ (1), and attempted soft-chemical reaction of this niobate (11). On the other hand, perovskite-type compounds, A_xNbO_3 (A = Sr, Ba, Eu) (4–6), and phosphatoniobates such as $KNb_3P_3O_{15}$ (7), $K_3Nb_6P_4O_{26}$ (8), and $K_3Nb_8O_{21}$ (9) are known as the weakly reduced complex niobates. Reduced strontium rare-earth niobates, (Sr, Ln)$Nb_2O_{6-\delta}$ (Ln = La, Nd, Pr, Ce), were reported to be superconductors with $T_c \sim 12$ K (10), but Istomin *et al.* could not confirm the superconductivity (12).

During the investigation of new reduced complex niobates we found a new phase, $K_2YNb_5O_{15-\delta}$. Its three-dimensional framework is similar to that of the $NaNb_6O_{15}F$-type structure (13) and can be related to those of the

$TlCa_2Ta_5O_{15}$-type structure (14–16) and the tetragonal tungsten bronze-type structure (17, 18), having a basic structural unit of M_5O_{15} (M = Nb,Ta). In these structural types large ions are accommodated in hexagonal or pentagonal tunnels while ions with medium size, such as Ca^{2+} and Y^{3+}, are found in distorted perovskite-like cavities. We describe here the crystal structure of $K_2YNb_5O_{15-\delta}$ and its thermal behavior.

EXPERIMENTAL

Sample Preparation

Black single crystals of $K_2YNb_5O_{15-\delta}$ were obtained as follows. A mixture of K_2CO_3, Y_2O_3, and Nb_2O_5 with a molar ratio of 4:1:8 was heated in a stream of hydrogen at 1200°C for 1 h. The products always contained a large amount of colorless crystals and water-soluble phases in addition to $K_2YNb_5O_{15-\delta}$. The colorless crystals were removed by decantation and the water-soluble phases were dissolved with distilled water. Powder samples were identified by X-ray powder diffraction using Cu$K\alpha$ radiation. Thermal stability was investigated by TG-DTA with a heating rate of 10°/min.

Structure Determination

Single crystal X-ray diffraction data were collected by using a Rigaku AFC-7R four-circle diffractometer with graphite monochromated Mo$K\alpha$ radiation using the ω-2θ scan technique ($D\omega = (1.00 + 0.30 \tan \theta)°$). The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by using ψ scans. The crystal structure was solved and refined with the computer programs from the TEXSAN crystallographic software package (19). The lattice parameters were determined from 20 reflections measured by the four-circle diffractometer. Details of the data collection and refinement are summarized in Table 1. The atomic positions of Nb, Y, and K were determined by direct methods and subsequent Fourier analysis revealed the positions of the oxygen atoms.

The facts that the color of the crystals is black and the weight gain is observable in the TG curve as mentioned

TABLE 1
Crystal Data and Intensity Collection for K₂YNb₅O₁₅₋δ

Color	Black
Size (mm)	$0.10 \times 0.10 \times 0.30$
Crystal system	Orthorhombic
Space group	*Cmmm* (No. 65), $Z = 2$
Lattice parameters (Å)	$a = 10.316(1)$
	$b = 15.257(1)$
	$c = 3.914(1)$
Volume (Å³)	616.1(3)
Formula weight	871.63
Calculated density (g/cm³)	4.70
Diffractometer	Rigaku AFC-7R
Radiation	Graphite monochromated
Mo$K\alpha$	($\lambda = 0.71069$ Å)
Temperature (°C)	23
μ (Mo$K\alpha$) (cm⁻¹)	97.54
Maximum 2θ (°)	90
Scan mode	φ-2θ
Scan speed (°/min)	16
Number of data collected	1477
Number of unique data	1077 ($I > 3.00\sigma(I)$)
Absorption correction	Ψ scans
Transmission factors	0.94–0.98
Refinement method	Full-matrix least-squares on $|F|$
Number of parameters	45
R	0.046
R_w	0.047
Goodness of fit	1.87

TABLE 2
Positional and Anisotropic Thermal Parameters (Å²) for K₂YNb₅O₁₅₋δ

Atom	Site	x	y	z	B_{eq}*[a]	Occupancy
Nb(1)	8q	0.19126(4)	0.12908(3)	1/2	0.700(5)	1
Nb(2)	2c	1/2	0	1/2	2.38(3)	1
Y	2a	0	0	0	2.12(3)	1
K	4i	1/2	0.2053(1)	0	1.98(3)	1
O(1)	8q	0.3672(4)	0.0917(3)	1/2	2.9(1)	1
O(2)	8p	0.1703(8)	0.1197(4)	0	2.9(1)	1
O(3)	4f	1/4	1/4	1/2	1.3(1)	1
O(4)	4h	0.1321(5)	0	1/2	1.0(1)	1
O(5)	2b	0	1/2	0	4.1(3)	1
O(6)	4j	0	0.1557(5)	1/2	3.4(2)	1

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nb(1)	0.0105(1)	0.0063(1)	0.0097(1)	−0.0019(1)	0	0
Nb(2)	0.0199(5)	0.0088(4)	0.062(1)	0	0	0
Y	0.0137(5)	0.059(1)	0.0081(4)	0	0	0
K	0.039(1)	0.0164(7)	0.0198(9)	0	0	0
O(1)	0.006(1)	0.011(1)	0.094(6)	0.003(1)	0	0
O(2)	0.083(5)	0.024(2)	0.005(1)	−0.013(3)	0	0
O(3)	0.014(2)	0.007(2)	0.029(3)	−0.002(2)	0	0
O(4)	0.008(2)	0.006(2)	0.024(3)	0	0	0
O(5)	0.023(5)	0.13(2)	0.001(3)	0	0	0
O(6)	0.008(2)	0.016(3)	0.105(9)	0	0	0

[a] B_{eq}* $= (8\pi^{2/3})\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* a_i a_j$.

later imply that some of oxygen atoms are deficient. Therefore, the occupancies of all oxygens were refined at first, and then that of O(3) was revealed to be less than unit and the final R factors were $R = 0.046$ and $R_\text{w} = 0.047$ for 1077 unique reflections. However, the final R factors did not change when the occupancies of all oxygens were fixed to be unit, and the positional parameters did not change significantly compared with those for the oxygen deficient model. Probably the extent of oxygen deficiency was so small that any significant difference did not result from the two models. The position and extent of oxygen deficiency cannot be clarified from the structural analysis using single crystal X-ray diffraction data. The final positional and anisotropic thermal parameters are summarized in Table 2. Selected interatomic distances and angles are listed in Table 3.

RESULTS AND DISCUSSION

Preparation of K₂YNb₅O₁₅₋δ

Tetragonal tungsten bronze-type K₂YNb₅O₁₅, (denoted as TTB-K₂YNb₅O₁₅ hereafter) (20) is prepared by heating a stoichiometric mixture of K_2CO_3, Y_2O_3, and Nb_2O_5 at 1200°C in air. Attempts to prepare the reduced potassium yttrium niobate, K₂YNb₅O₁₅₋δ, by reducing TTB-K₂YNb₅O₁₅ in a H_2 atmosphere were unsuccessful; TTB-

TABLE 3
Selected Interatomic Distances (Å) and Angles (°) for K₂YNb₅O₁₅₋δ

|			
Nb(1)–O(1)	1.903(4)	O(1)–O(2)	2.853(7)
–O(2)	1.974(1) × 2	O(1)–O(3)	2.701(4)
–O(3)	1.9419(4)	O(1)–O(4)	2.799(6)
–O(4)	2.062(2)	O(2)–O(3)	2.909(4)
–O(6)	2.015(2)	O(2)–O(4)	2.705(4)
		O(2)–O(6)	2.687(6)
		O(3)–O(6)	2.953(4)
		O(4)–O(6)	2.739(7)
Nb(2)–O(1)	1.958(4) × 4	O(1)–O(1)	2.797(9)
–O(5)	1.959(1) × 2	O(1)–O(1)	2.740(9)
		O(1)–O(5)	2.768(3)
K–O(1)	2.952(4) × 4	Y–O(2)	2.534(7) × 4
–O(2)	3.197(7) × 2	–O(4)	2.385(3) × 4
–O(2)	3.644(8) × 2	–O(6)	3.078(6) × 4
–O(3)	3.3086(5) × 4		
–O(5)	3.132(2)		
–O(6)	2.885(6) × 2		
O(1)–Nb(1)–O(2)	94.7(3)	O(1)–Nb(1)–O(3)	89.3(1)
O(1)–Nb(1)–O(4)	89.3(2)	O(2)–Nb(1)–O(4)	84.1(2)
O(2)–Nb(1)–O(3)	95.9(2)	O(2)–Nb(1)–O(6)	84.7(3)
O(3)–Nb(1)–O(6)	96.5(2)	O(4)–Nb(1)–O(6)	84.4(3)
O(1)–Nb(2)–O(1)	88.8(3)	O(1)–Nb(2)–O(5)	90.0
Nb(1)–O(4)–Nb(1)	145.6(3)	Nb(1)–O(1)–Nb(2)	151.9(3)
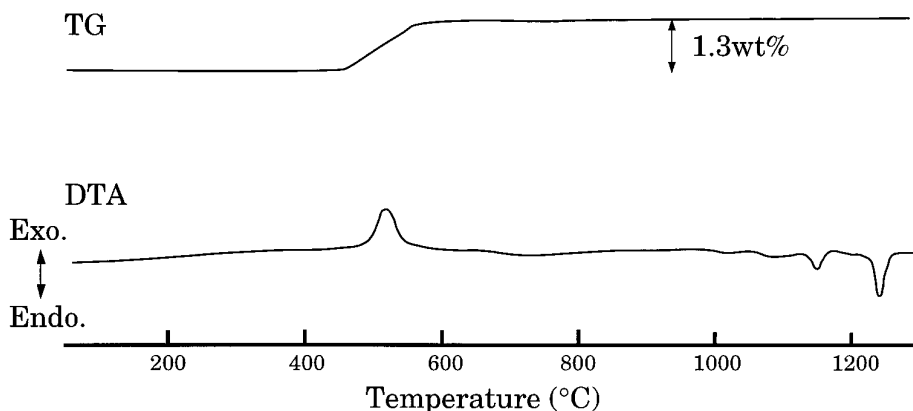
FIG. 1. TG-DTA curves of $K_2YNb_5O_{15-\delta}$.

$K_2YNb_5O_{15}$ remained intact at 1000°C and decomposed to NbO_2 and unknown phases at 1200°C. Heating the stoichiometric mixture in a H_2 atmosphere resulted in the formation of blue unknown phases with low crystallinity at 1000°C or the formation of a mixture of NbO_2 and TTB-$K_2YNb_5O_{15}$ at 1200°C. Thus the reduced potassium yttrium niobate, $K_2YNb_5O_{15-\delta}$, cannot be prepared by heating a stoichiometric mixture in a H_2 atmosphere or by reducing TTB-$K_2YNb_5O_{15}$, while single crystals of the new potassium yttrium niobate, $K_2YNb_5O_{15-\delta}$, are obtained by heating a mixture of K_2CO_3, Y_2O_3, and Nb_2O_5 with a molar ratio of $4:1:8$ at 1200°C in a H_2 atmosphere. Probably a large excess of K_2CO_3 plays an important role in preparation of the new reduced potassium yttrium niobate.

Thermal Behavior and Oxygen Deficiency of $K_2YNb_5O_{15-\delta}$

As shown in Fig. 1, $K_2YNb_5O_{15-\delta}$ is oxidized by heating in air, accompanied with an endothermic peak and a weight gain of 1.3 wt% at about 450°C. Black $K_2YNb_5O_{15-\delta}$ turns to colorless above 500°C. The oxidized product shows a very similar X-ray powder pattern to that of $K_2YNb_5O_{15-\delta}$ and can be regarded as $K_2YNb_5O_{15}$ isostructural with $K_2YNb_5O_{15-\delta}$. Then the oxidized product of $K_2YNb_5O_{15-\delta}$ is denoted as O-$K_2YNb_5O_{15}$ hereafter. Lattice parameters for O-$K_2YNb_5O_{15}$ were determined to be $a = 10.295(1)$, $b = 15.253(1)$, and $c = 3.903(1)$ Å, indicating a volume decrease of 0.51% during the oxidation. In accordance with this small volume change, a black single crystal of $K_2YNb_5O_{15-\delta}$ was found to change to a colorless single crystal of O-$K_2YNb_5O_{15}$. The colorless crystal is reversibly converted into the black one by heating at 1000°C in a H_2 atmosphere, in contrast to the behavior of TTB-$K_2YNb_5O_{15}$ mentioned above.

The X-ray powder pattern for the sample heated up to 1200°C in air is identified with that for the tetragonal tungsten bronze-type $K_2YNb_5O_{15}$ (20). Upon the transforma-

tion from O-$K_2YNb_5O_{15}$ to TTB-$K_2YNb_5O_{15}$, the volume decrease is calculated to be 1.75% and the crystals are deteriorated. The weak endothermic peak at 1150°C in the DTA curve probably corresponds to the transformation to the tetragonal tungsten bronze-type structure and the strong endothermic peak at 1240°C to the melting of the sample.

Structural analysis of a single crystal of O-$K_2YNb_5O_{15}$, which was selected from colorless crystals obtained by oxidizing crystals of $K_2YNb_5O_{15-\delta}$ at 1000°C in air, leads to $R = 0.055$ and $R_w = 0.057$ for 1465 unique reflections and indicates no major change of crystallographic parameters from those for $K_2YNb_5O_{15-\delta}$.

The oxygen deficiency for $K_2YNb_5O_{15-\delta}$ could be calculated to be $\delta = 0.70$ from the weight gain of 1.3 wt%. However, this value is overestimated, because the samples measured always contained small amounts of oxidizable impurities. The amount of oxygen deficiency could not be also determined precisely by the TG measurement. The exact extent of oxygen deficiency remains ambiguous at this moment of time.

Crystal Structure of $K_2YNb_5O_{15-\delta}$

The three-dimensional framework in the crystal structure of $K_2YNb_5O_{15-\delta}$ is built up by corner-sharing of NbO_6 octahedra as shown in Fig. 2. The Nb_5O_{15} structural unit in $K_2YNb_5O_{15-\delta}$ is formed by one $Nb(2)O_6$ octahedron and four $Nb(1)O_6$ octahedra as depicted in Fig. 3. Each octahedron shares O(2) or O(5) at the top and bottom of the octahedron along the crystallographic c axis. The $Nb(1)O_6$ octahedra are connected to the adjacent Nb_5O_{15} unit by sharing O(6) on the horizontal plane of the octahedra along the a axis. The infinite Nb_5O_{15} slabs are orientated perpendicular to the b axis and stacked along the b axis, connected by O(3). All Nb–O distances are in the range 1.9–2.0 Å, in agreement with the Nb–O distance found for pentavalent niobium with octahedral coordina-
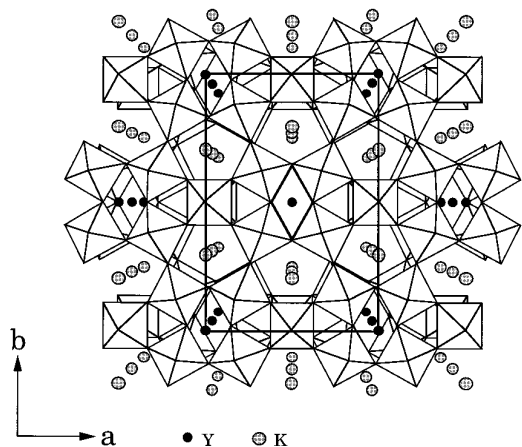
FIG. 2. Crystal structure of $K_2YNb_5O_{15-\delta}$.

FIG. 4. ORTEP drawing of coordination of yttrium ion.

tion (16). The O–Nb(1)–O angles are 84.1°–96.5° and O–Nb(2)–O angles are 88.8° and 90.0°. The NbO_6 octahedra in $K_2YNb_2O_{15-\delta}$ are considered to be not significantly distorted from a regular octahedron.

As seen in Fig. 2, Y^{3+} and K^+ ions in $K_2YNb_5O_{15-\delta}$ are accommodated in the cavities formed by the linkage of the Nb_5O_{15} units. An Y^{3+} ion is surrounded by four O(4) at a distance of 2.385(3) Å, four O(2) at a distance of 2.534(7) Å, and four O(6) at a long distance of 3.078(6) Å as shown in Fig. 4. As the last distance is too far for O(6) to coordinate to the Y^{3+} ion, the coordination of the Y^{3+} ion with oxygen atoms can be regarded as 8-fold rather than 12-fold. A K^+ ion is coordinated by 15 oxygen atoms at distances which range from 2.885(6) to 3.644(8) Å (mean 3.175 Å) as shown in Fig. 5.

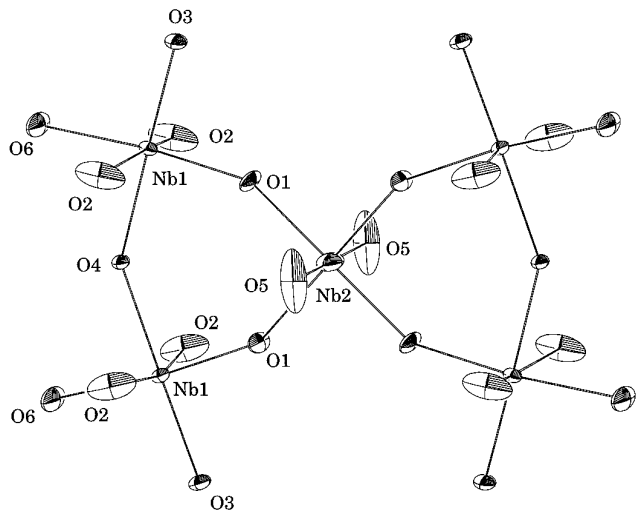The framework of $K_2YNb_5O_{15-\delta}$ conforms to that of $NaNb_6O_{15}F$ (13) or $Ba_4CoTa_{10}O_{30}$ (21). Especially the structures of $K_2YNb_5O_{15-\delta}$ and $Ba_4CoTa_{10}O_{30}$ are isostructural with each other, although only a half of the sites for Y^{3+} ions in $K_2YNb_5O_{15-\delta}$ are occupied by Co^{2+} ions in $Ba_4CoTa_{10}O_{30}$. The structure of $K_2YNb_5O_{15-\delta}$ can also be related to those of the $TlCa_2Ta_5O_{15}$-type structure (14–16) and the tetragonal and hexagonal tungsten bronze-type structures (17, 18), since all of these structures are composed of the Nb_5O_{15} basic units. In Fig. 6 schematic structures of $K_2YNb_5O_{15-\delta}$, $TlCa_2Ta_5O_{15}$-type, and tetragonal and hexagonal tungsten bronzes are projected along the c axis. These structural types are characterized by the basic structural unit of M_5O_{15} unit which is indicated by rectangles with thick line in Fig. 6. The hexagonal tungsten bronze-type is exceptional in this group of structural types, because the M_5O_{15} units are linked with the additional structural unit of an octahedron, while in other structural types the M_5O_{15} units share oxygen atoms of the octahedron at every corner of the rectangle with each other. The rectangles are arranged parallel along the a axis in $K_2YNb_5O_{15-\delta}$ and $TlCa_2Ta_5O_{15}$ so that the rectangles are
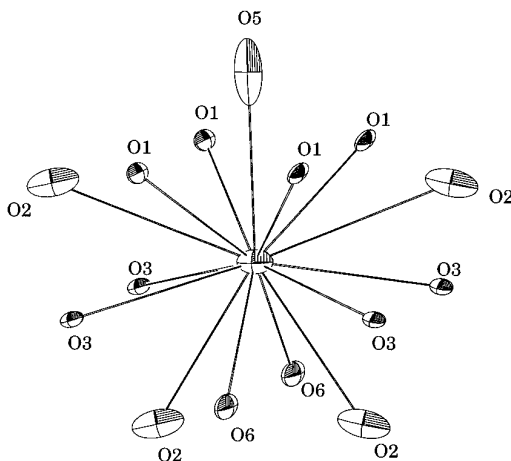

FIG. 3. ORTEP drawing of Nb_5O_{15} basic unit in $K_2YNb_5O_{15-\delta}$.

FIG. 5. ORTEP drawing of coordination of potassium ion.

$NaNb_6O_{15}F$-type structure

Tetragonal tungsten bronze-type structure

$TlCa_2Ta_5O_{15}$-type structure
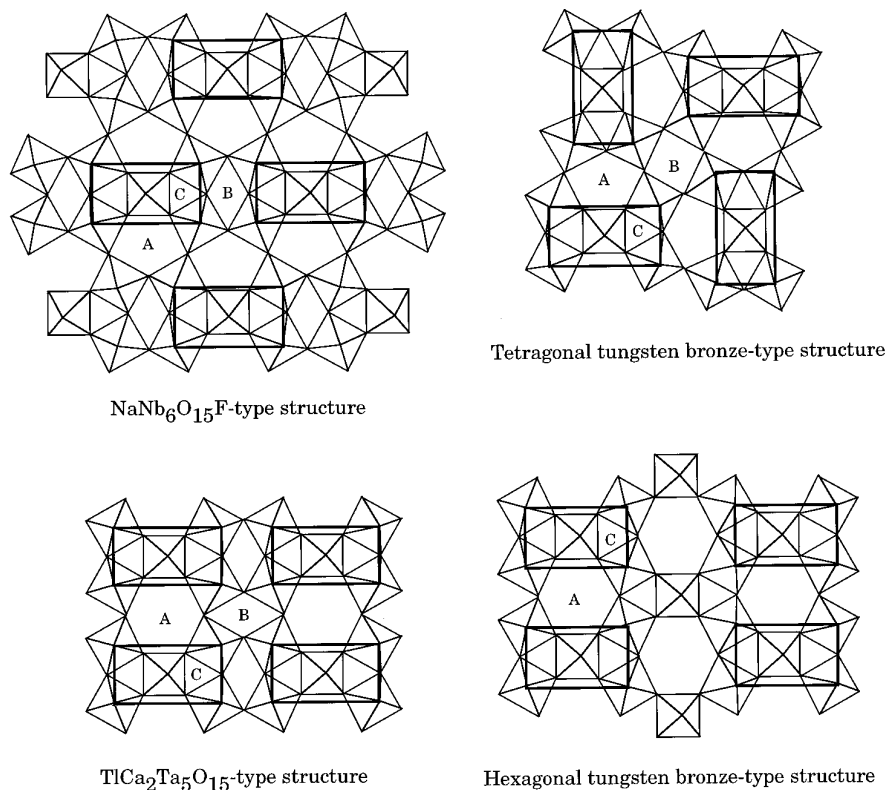

Hexagonal tungsten bronze-type structure

FIG. 6. Schematic structures of $NaNb_6O_{15}F$-type, $TlCa_2Ta_5O_{15}$-type, and the tetragonal and hexagonal tungsten bronze-types.

superposed along the b axis in $TlCa_2Ta_5O_{15}$ but staggered in $K_2YNb_5O_{15-\delta}$. In the tetragonal tungsten bronze-type structure the rectangles are perpendicular to each other.

There are three types of crystallographic sites in the cavities formed by linkage of the M_5O_{15} units: types A, B, and C. The coordination numbers for the A, B, and C sites in idealized structures of these structural types are summarized in Table 4. There is no B site in the hexagonal tungsten bronze-type structure. The C site in the tricapped trigonal prism can be occupied only by very small ions such as the Li^+ ion (22) or the M^{5+} ion (M = Nb, Ta) (23, 24). The A site is occupied by large cations as found for K^+ ions with a coordination number of 15 in the pentagonal

tunnel of $K_2YNb_5O_{15-\delta}$. A similar A site is also reported for large ions in the tetragonal tungsten bronzes, $NaNb_6O_{15}F$ and $Ba_4CoTa_{10}O_{30}$ (21). In the case of the $TlCa_2Ta_5O_{15}$-type structure, the site with a coordination number of 18 in the hexagonal tunnel is referred to as the A site. The B site is located in the perovskite-like cavity (distorted cuboctahedron) and is occupied by cations with medium size. When the perovskite-like cavity is rather regular, a cation residing there is expected to have a coordination number of 12 as found in the tetragonal tungsten bronze-type structure. However, as mentioned above, the Y^{3+} ion in $K_2YNb_5O_{15-\delta}$ has the coordination number of 8 at the B site, because the perovskite cavity is deformed very much. Similarly the Co^{2+} ion in $Ba_4CoTa_{10}O_{30}$ (21) and the Ca^{2+} ion in $TlCa_2Ta_5O_{15}$ (21) are located at the B site in the deformed perovskite cavity with the coordination number of 8.

As seen in Fig. 6, the structure of $K_2YNb_5O_{15-\delta}$ can be derived from the $TlCa_2Ta_5O_{15}$-type structure by translation of the rectangle by $a/2$ so that one of B sites with small coordination number remains as it is in the $TlCa_2Ta_5O_{15}$-type structure and two A sites in the pentagonal tunnel are formed instead of one A site in the hexagonal tunnel and one B site. As discussed by Dion *et al.* (15), the $TlCa_2Ta_5O_{15}$-type structure is stabilized by large cations such as

TABLE 4

The Coordination Numbers for the A, B, and C Sites in Idealized Structures of the Tetragonal Tungsten Bronze-(TTB), $TlCa_2Ta_5O_{15}$-, and $NaNb_6O_{15}F$-Type Structures

Site	TTB	$TlCa_2Ta_5O_{15}$	$NaNb_6O_{15}F$
A	15	18	15
B	12	8	8
C	9	9	9

Cs$^+$, Rb$^+$, and Tl$^+$, and in the series of RbLnNaTa$_5$O$_{15}$ (Ln = rare earth metal) the structural type changes from the TlCa$_2$Ta$_5$O$_{15}$-type to the tetragonal tungsten bronze-type when the B site cation becomes large enough to be adapted for the A site with a large coordination number of the latter. From the view point of ionic size and ratio of number of large and medium ions, it seems to be preferable for K$_2$YNb$_5$O$_{15-\delta}$ to have the structure with the cation arrangement similar to the tetragonal tungsten bronze-type structure. However, difference in size of the ion at the B site determines whether the tetragonal tungsten bronze or K$_2$YNb$_5$O$_{15-\delta}$-type structure would be adopted. The Y^{3+} ion in K$_2$YNb$_5$O$_{15-\delta}$ and the Co^{2+} ion in Ba$_4$Co Ta$_{10}$O$_{30}$ are rather small compared with the rare earth ions in K$_2$$LnNb_5O_{15}$ (Ln = rare earth metal) with the tetragonal tungsten bronze-type structure (20).

CONCLUSION

A new reduced potassium yttrium niobate, K$_2$YNb$_5$O$_{15-\delta}$, was prepared in a H$_2$ atmosphere at 1200°C and its crystal structure was determined by using single crystal X-ray diffraction data. The crystal structure is built up by corner-sharing of the Nb$_5$O$_{15}$ unit and can be compared with that of the same structural unit. Reversible oxidation and reduction can be observed as long as the structure of K$_2$YNb$_5$O$_{15-\delta}$ is kept. However, after the transformation of O-K$_2$YNb$_5$O$_{15}$ to the tetragonal tungsten bronze-type structure reduction to K$_2$YNb$_5$O$_{15-\delta}$ with the tetragonal tungsten bronze-type structure was not observed.

REFERENCES

1. N. Kumada, N. Kinomura, R. Wang, and A. W. Sleight, *Mater. Res. Bull.* **29**, 41 (1994).
2. J. Köhler and A. Simon, *Z. Anorg. Allg. Chem.* **572**, 7 (1989).
3. M. J. Geselbracht and A. M. Stacy, *J. Solid State Chem.* **110**, 1 (1989).
4. K. Isawa, J. Sugiyama, K. Matsuura, A. Nozaki, and H. Ymauchi, *Phys. Rev. B* **47**, 2849 (1993).
5. B. Hessen, S. A. Sunshine, T. Siegrist, and R. Jimenez, *Mater. Res. Bull.* **26**, 85 (1991).
6. K. Ishikawa, G. Adachi, and J. Shiokawa, *Mater. Res. Bull.* **18**, 653 (1983).
7. A. Leclaire, M. M. Borel, A. Grandin, and B. Raveau, *J. Solid State Chem.* **83**, 245 (1989).
8. A. Benabbas, M. M. Borel, A. Grandin, A. Leclaire, and B. Raveau, *J. Solid State Chem.* **84**, 365 (1990).
9. A. Benabbas, M. M. Borel, A. Grandin, A. Leclaire, and B. Raveau, *Acta. Crystallogr. Sect. C* **49**, 439 (1993).
10. J. Akimitsu, J. Amano, H. Sawa, O. Nagase, K. Gyoda, and M. Kogai, *Jpn. J. Appl. Phys.* **30**, L1155 (1991).
11. N. Kumada, M. Ohtsuka, N. Kinomura, and A. W. Sleight, *Mater. Res. Bull.* in press.
12. S. Y. Istomin, O. G. D'yachenko, E. V. Antipov, G. Svensson, and M. Nygren, *Mater. Res. Bull.* **29**, 743 (1994).
13. S. Andersson, *Acta Chem. Scand.* **19**, 2285 (1965).
14. M. Ganne, M. Doin, A. Verbaere, and M. Tournoux, *J. Solid State Chem.* **29**, 9 (1979).
15. M. Doin, M. Ganne, and M. Tournoux, *Mater. Res. Bull.* **15**, 121 (1980).
16. M. Doin, M. Ganne, M. Tournoux, and J. Ravez, *J. Solid State Chem.* **53**, 422 (1984).
17. A. Magneli, *Ark. Kemi* **1**, 213 (1949).
18. F. Takusagawa and R. A. Jacobson, *J. Solid State Chem.* **18**, 163 (1976).
19. Molecular Structure Corporation, "TEXSAN." The Woodlands, TX, 1993.
20. B. A. Scott, E. A. Giess, G. Burns, and D. F. O'Kane, *Mater. Res. Bull.* **3**, 831 (1968).
21. B. J. Tönnies and H. M. Buschbaum, *Mh. Chem.* **115**, 1151 (1984).
22. A. F. Wells, "Structural Inorganic Chemistry," p. 508. Clarendon Press, Oxford, 1975.
23. M. Lundberg and M. Sundberg, *J. Solid State Chem.* **62**, 216 (1986).
24. A. A. Awadalla and B. M. Gatehouse, *J. Solid State Chem.* **23**, 349 (1978).