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The Crystal Structure of $Na_3Nb_{12}O_{31}F$

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The oxide $Na_3Nb_{12}O_{31}F$ is tetragonal (space group $P4$), with unit cell dimensions $a = b = 17.494(1)$ and $c = 3.9442(2)$ Å. The structure of $Na_3Nb_{12}O_{31}F$ was preliminarily determined by X-ray diffraction and refined to $R = 0.140$ for 1628 observed reflections.

Introduction

The tetragonal potassium tungsten bronze structure K_xWO_3 ($0.48 < x < 0.54$) (*1*) consists of a framework of corner-shared MO_6 octahedra with three types of interstitial sites, in which a variety of cations can be accommodated. A number of compounds are structurally related to that of the tetragonal potassium tungsten bronze and the differences between these structures depend on the number of sites occupied and on the size and charge of the metal atoms (*2–4*). Among these, the a and b axes of $BaO \cdot 2Ta_2O_5$ (*2*) are related to the tungsten bronze-type a axis by a factor $\sqrt{2}$. In this paper, a single crystal X-ray analysis has been carried out on $Na_3Nb_{12}O_{31}F$, which is considered to have a superstructure based on the tetragonal tungsten bronze in which some of the pentagonal tunnels are occupied by Nb and O atoms.

Experimental

Mixtures with gross compositions $NaF \cdot 8Nb_2O_5$ were sealed in platinum capsules, heated at 1200°C for 3 days, and then quench cooled in water. A Guinier powder pattern of the sample confirmed the presence of two phases, N–Nb_2O_5 and $Na_3Nb_{12}O_{31}F$, the formulas of which were derived from the final least-squares refinement. The colors of N–Nb_2O_5 and $Na_3Nb_{12}O_{31}F$ are blue and colorless, respectively. A small colorless tetragonal needle-like crystal of dimension $0.034 \times 0.035 \times 0.129$ mm was selected, using an optical microscope, transferred to a glass fiber with the longest axis parallel to the fiber axis, and then mounted on a goniometer head. Preliminary oscillation and Weissenberg photographs indicated that the crystal was tetragonal and had no systematic absences. These results suggested that the most probable space group was $P4$ or $P4/m$. Refinement by least squares of 34 single-indexed lines of a powder pattern obtained in a Guinier–Hägg focusing camera using Cu$K\alpha_1$ radiation gave the lattice parameters $a = b = 17.494(1)$ and $c = 3.9442(4)$ Å. Data collection was made with a Nicolet $P\,3m$ four-circle diffractometer using graphite monochromated Mo$K\alpha$ radiation. The integrated intensities of 2132

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reflections having 2 θ values from 3 to 50° were measured. Measured intensities were corrected for Lorentz polarization effects and intensities with $I < 6\sigma_c(I)$ were excluded from the refinements.

Structure Determination and Refinement

Neutral scattering factors for all atoms and anomalous dispersion corrections for Nb were taken from "International Tables for X-ray Crystallography" (*5*). The positions of the Nb atoms were derived from a three-dimensional Patterson map computed with the DRF program by assuming the space group to be *P*4. The following three-dimensional difference Fourier map based on phases determined by the Nb atoms only showed the positions of the 16 oxygen and 2 sodium atoms with very different peak heights. Initially, the coordinates of the 6 independent niobium and 16 oxygen atoms were refined by the full-matrix least-squares method using the LUPALS program in the space group *P*4 with isotropic temperature factors for both niobium and oxygen atoms. After several cycles of refinement, the *R* factor decreased to 0.21. At this stage, anisotropic temperature factors of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2C^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]h$ were introduced for the Nb atoms, and the *R* factor decreased to 0.143. Finally, two Na atoms were introduced but the refinement did not change the *R* values significantly; the *R* factor decreased to 0.140 where $R = \Sigma(||F_0| - |F_c||)/\Sigma|F_0|$. We found no indications of Na atoms in the tetragonal tunnels. The final atomic coordinates with their estimated standard deviations in parentheses are given in Table I.

The question then arises, Why is the *R* value so high? One explanation is that there is disorder along the *c* axis in the crystals as seen by the high temperature factors in the *C* direction (U_{33} is about 20 times higher than U_{11} and U_{22}). Another reason for the high *R* value is that data to very high resolution are included. Although the *R* value is quite high this has not made the structure determination less accurate than normal. The atomic coordinates are determinated with a standard deviation of about 0.003 Å for the Nb atoms in the *a* and *b* directions and 0.02 Å along *c*.

TABLE I

ATOMIC COORDINATES

Atom	Position	*x/a*	*y/b*	*z/c*
Nb(1)	4(d)	0.0704(1)	0.1393(2)	0.0550(37)
Nb(2)	4(d)	0.0676(2)	0.3689(2)	0.0608(42)
Nb(3)	4(d)	0.2506(2)	0.0785(1)	0.0474(45)
Nb(4)	4(d)	0.2496(2)	0.2663(2)	0.0945(37)
Nb(5)	4(d)	0.4321(1)	0.1450(1)	0.0711(40)
Nb(6)	4(d)	0.4382(2)	0.3588(2)	0.0510(0)
O(1)	4(d)	0.1357(10)	0.0448(10)	0.113(7)
O(2)	4(d)	0.3722(12)	0.0430(13)	0.093(12)
O(3)	4(d)	0.1826(13)	0.1696(13)	0.033(12)
O(4)	4(d)	0.3173(10)	0.1770(10)	0.121(7)
O(5)	4(d)	0.0428(12)	0.2473(12)	0.025(11)
O(6)	4(d)	0.4707(13)	0.2453(13)	0.091(13)
O(7)	4(d)	0.1696(14)	0.3464(14)	0.021(10)
O(8)	4(d)	0.3332(16)	0.3277(17)	0.135(10)
O(9)	4(d)	0.0865(13)	0.4718(13)	0.101(12)
O(10)	4(d)	0.3993(22)	0.4645(21)	0.121(14)
O(11)	4(d)	0.0688(16)	0.1340(15)	0.574(16)
O(12)	4(d)	0.2502(13)	0.0766(13)	0.553(17)
O(13)	4(d)	0.4308(19)	0.1419(19)	0.551(23)
O(14)	4(d)	0.2503(33)	0.2649(36)	0.552(40)
O(15)	4(d)	0.0634(21)	0.3668(21)	0.564(24)
O(16)	4(d)	0.4362(28)	0.3542(27)	0.562(28)
Na(1)	4(d)	0.2588(53)	0.4239(34)	0.533(28)
Na(2)	2(c)	0.5000(0)	0.0000(0)	0.670(90)

Description of the Structure

The crystal structure is shown in Fig. 1, and the interatomic distances in Table II. The structure is built up by NbO_6 octahedra sharing corners and NbO_7 pentagonal bipyramids sharing edges with five octahedra. The octahedra join together at their vertices to form four- and five-sided tunnels. Five Nb atoms are surrounded by six oxygen atoms at the corners of an octahedron, respectively, and the mean Nb–O distance in the five octahedra is 1.977 Å with a range from 1.808 to 2.176 Å. The O–Nb–O octrahedral axes are parallel to

TABLE II

INTERATOMIC DISTANCES

Nb(1)	O(11)	1.89(6)	Nb(4)	O(14)	1.80(15)
	O(5)	1.95(2)		O(8)	1.82(3)
	O(1)	2.02(1)		O(4)	1.96(1)
	O(1)	2.03(1)		O(7)	2.00(2)
	O(3)	2.03(2)		O(3)	2.07(2)
	O(11)	2.05(6)		O(14)	2.13(15)
Nb(2)	O(7)	1.83(2)	Nb(5)	O(6)	1.88(2)
	O(9)	1.83(2)		O(13)	1.89(9)
	O(2)	1.94(2)		O(9)	1.97(2)
	O(15)	1.96(9)		O(13)	2.05(9)
	O(15)	1.98(9)		O(2)	2.07(2)
	O(5)	2.17(2)		O(4)	2.09(1)
Nb(3)	O(12)	1.95(7)	Nb(6)	O(10)	1.86(3)
	O(3)	1.99(2)		O(16)	1.92(11)
	O(12)	1.99(7)		O(8)	1.94(3)
	O(4)	2.10(1)		O(10)	1.99(3)
	O(1)	2.11(1)		O(16)	2.01(11)
	O(5)	2.12(2)		O(6)	2.07(2)
	O(2)	2.22(2)			

the c axis. The Nb(3) atom at the center of a pentagonal bipyramidal coordination polyhedron was surrounded by seven oxygen atoms. The mean Nb(3)–O distance is 2.071 Å with a range from 1.950 to 2.225 Å. The Na(2) atom was situated within the

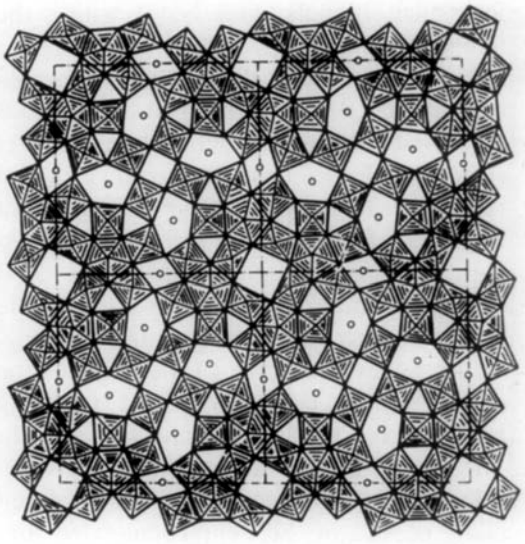

FIG. 1. Crystal structure of $Na_3Nb_{12}O_{31}F$ projected along [001]. Unit (2 × 2) cells are outlined. The structure, made up mainly of NbO_7 pentagonal bipyramids surrounded by five NbO_6 octahedra, is a new type of GTB-like structure.

TABLE III

TEMPERATURE FACTORS (SUPPLEMENT)

Atom	B	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nb(1)		0.00063(9)	0.00008(8)	0.0825(53)	0.00009(6)	0.0063(9)	−0.0068(9)
Nb(2)		0.00075(9)	0.00045(9)	0.0583(4)	0.00018(6)	0.0020(10)	−0.0014(10)
Nb(3)		0.00020(8)	0.00059(9)	0.0742(49)	0.00022(6)	−0.0017(9)	−0.0024(10)
Nb(4)		0.00060(9)	0.00030(8)	0.0584(51)	0.00022(6)	−0.0015(9)	−0.0035(7)
Nb(5)		−0.00010(7)	0.00068(9)	0.0591(41)	0.00005(6)	−0.0023(9)	−0.0001(10)
Nb(6)		0.00127(12)	0.00107(11)	0.0668(52)	−0.00021(8)	0.0044(12)	−0.0041(11)
Na(1)		0.0057(24)	0.02115(63)	0.174(78)	−0.0038(33)	0.024(13)	−0.003(25)
Na(2)		0.0226(116)	0.0063(40)	0.618(434)	−0.0089(59)		
O(1)	−0.55(30)						
O(2)	0.35(36)						
O(3)	0.42(41)						
O(4)	−0.85(28)						
O(5)	−0.01(37)						
O(6)	0.28(35)						
O(7)	0.51(42)						
O(8)	1.04(53)						
O(9)	0.42(40)						
O(10)	2.74(77)						
O(11)	1.24(48)						
O(12)	0.63(37)						
O(13)	1.88(57)						
O(14)	5.69(151)						
O(15)	2.58(71)						
O(16)	4.16(99)						

four-sided tunnels, and Na(1) within the five-sided tunnels.

This structure has the Gatehous tungsten bronze (GTB)-like structure. The GTB (*6, 7*) and TTB (tetragonal tungsten bronze) structural elements are quite similar in that both are composed of four pentagons of NbO_6 octahedra, with neighboring pentagons sharing one octahedra. In the GTB structures there is a niobium atom in the center of each pentagon, forming a pentagonal bipyramid. In the TTB structures the center of the pentagon is not filled by niobium so a pentagonal tunnel is formed. The $Na_3Nb_{12}O_{31}F$ structure can be considered as a consequence of the ordered filling of half of the pentagonal-sided tunnels of the TTB structure with Nb and O atoms. Therefore the structure of the $Na_3Nb_{12}O_{31}F$, made up mainly of NbO_7 pentagonal bipyramids, surrounded by five NbO_6 octahedra, is a new type of GTB-like structure.

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