Acta Chemica Scandinavica, 1993: 47: 789–792
Printed in Belgium – all rights reserved

ACTA
CHEMICA SCANDINAVICA
ISSN 0904-213X

A Bismuth Niobium Oxide, $BiNb_{5.4}O_{15}$, with a *TTB*-Related Structure

Ingrid Bryntse

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

Bryntse, I., 1993. A Bismuth Niobium Oxide, $BiN_{5.4}O_{15}$, with a *TTB*-Related Structure. – Acta Chem. Scand. 47: 789–792.

An orthorhombic compound [$a = 17.676(2)$, $b = 17.207(2)$, $c = 3.9610(4)$ Å, $z = 4$], with the approximate composition $BiNb_{5.4}O_{15}$ has been synthesized. The structure is related to tetragonal tungsten bronze (*TTB*), and it seems to be identical with $Bi_2Nb_{10}O_{28}$, first reported by Roth and Waring. It has been studied with X-ray powder diffraction, high-resolution electron microscopy and energy dispersive spectrometry analyses (EDS). A probable space group is *Cmmm*. The Nb atoms are situated in a *TTB*-type network of oxygen octahedra, and the Bi atoms are located in every second one of the five-cornered tunnels. $BiNb_{5.4}O_{15}$ has a superstructure of *TTB*, of the same type as *H*-KNb_3O_8.

In the course of investigations of the system Bi_2O_3–CuO–Nb_2O_5,[1] it was noticed that a green tetragonal tungsten bronze (*TTB*)-type phase with the approximate metal ratio Bi : Nb = 1 : 5 was formed. The compound also has a very low copper content, probably below 2 at. % out of the metal atoms. Since most of the *d*-values of this phase agreed with those reported by Roth and Waring for an unindexed powder pattern of $Bi_2Nb_{10}O_{28}$,[2] it was decided to prepare and analyze this compound without copper.

There are many publications of studies in the Bi_2O_3–Nb_2O_5 system. Besides $Bi_2Nb_{10}O_{28}$, the following phases were reported by Roth and Waring: α- and β-$BiNbO_4$, $Bi_3Nb_{17}O_{47}$, $Bi_5Nb_3O_{15}$ and $Bi_8Nb_{18}O_{57}$.[2] X-Ray diffraction data for a phase with the composition $Bi_{1.70}Nb_{0.30}O_{3.30}$ have also been published.[3] Keve and Skapski have reported a single-crystal study of $Bi_3Nb_{17}O_{47}$,[4] which was found to crystallize as a superstructure of tetragonal tungsten bronze (*TTB*).[5] High-resolution electron microscopy studies of this system can also be found[6,7] in which phases such as $Bi_5Nb_3O_{15}$, with stepped Aurivillius structures, have been observed.

Experimental

Samples were prepared from mixtures of Bi_2O_3 (Baker's, analyzed, preheated in air at 600°C) and Nb_2O_5 (Carl Roth, puriss. 99.9%, preheated in air at 1100°C). The oxides were weighed in the ratios $Bi_2O_3 : Nb_2O_5 =$ 0.90 : 5.00, 0.95 : 5.00, 1.00 : 5.00, 1.05 : 5.00 and 1.10 : 5.00. The powders were ground in propanone in an agate mortar, dried and pelletized. The pellets were placed in alumina crucibles in an open furnace, heated stepwise at 600°C for 1 h, 700°C for 1 h, 800°C for 1 h, 900°C for 1 h and 1000°C for at least 24 h, and then cooled to room temperature outside the furnace. This procedure was repeated twice with intermediate regrindings.

Two experiments were carried out to grow larger crystals from an already prepared sample with the composition 1.05 Bi_2O_3 : 5.00 Nb_2O_5. In the first attempt, the powder was placed in a closed platinum ampoule and heated for a long time at 1080°C, just below the dissociation temperature (1090°C, according to Roth and Waring);[2] it was then slowly cooled to room temperature. The particles of the powder did not grow significantly, however. In the second experiment, the sample was heated at 650°C together with a flux of $Ba(NO_3)_2$ in a closed quartz tube. This experiment was also unsuccessful, since it resulted in a reaction between the flux and the quartz tube.

X-Ray powder diffraction patterns of all specimens were recorded with Cu$K\alpha_1$ radiation ($\lambda = 1.540\,5981$ Å) in a Guinier–Hägg focusing camera with subtraction geometry. Finely powdered silicon ($a = 5.430\,880$ Å at 25°C[8] was used as internal standard. The films were evaluated by means of an automatic film scanner.[9] The unit cell parameters were refined with the program PUDER.[10]

Three types of electron microscopes were used for characterizing the samples: a Jeol 820 scanning electron microscope with microanalysis equipment (LINK QX200) and two transmission electron microscopes, viz. Jeol 200CX and 2000FX. The second was used for high-resolution electron microscopy (HREM) investigations. The third was equipped with an energy-dispersive

spectrometry system (LINK QX200), with the detector in the high-angle (70°) position. To verify the high-resolution images, theoretical calculations were performed with the SHRLI program package.[11]

Results

From the Guinier powder patterns a main phase could be identified, having an orthorhombic *C*-centered unit cell with the parameters $a = 17.676(2)$, $b = 17.207(2)$ and $c = 3.9610(4)$ Å. This cell is related to the tetragonal tungsten bronze, so that $a \approx b \approx \sqrt{2}\, a_{TTB}$ and $c \approx c_{TTB}$. The indexed powder pattern is shown in Table 1. Lines of Nb_2O_5 and $Bi_3Nb_{17}O_{47}$ could also be detected in the pattern. A sample with the starting composition 1.05 Bi_2O_3 : 5.00 Nb_2O_5 showed the weakest Nb_2O_5 reflections, and was studied by microscopy.

Table 1. Indexed powder pattern of $BiNb_{5.4}O_{15}$.

h	*k*	*l*	d_{obs}/Å	d_{calc}/Å	Intensity
1	1	0	12.36641	12.32975	16.5
2	0	0	8.84117	8.83788	6.0
0	2	0	8.61813	8.60373	10.3
1	3	0	5.45817	5.45576	3.1
0	0	1	3.96220	3.96097	100.0
4	2	0	3.93092	3.93079	22.4[a]
2	4	0	3.86695	3.86798	26.3
2	0	1	3.61472	3.61455	24.0[a]
5	1	0	3.46224	3.46283	11.5[a]
1	5	0	3.37824	3.37806	77.4
2	2	1	3.33060	3.33242	4.6
1	3	1	3.20488	3.20529	51.3[a]
4	4	0	3.08127	3.08244	14.3[a]
5	3	0	3.00965	3.00947	94.6[a]
3	5	0	2.97123	2.97169	31.3
4	0	1	2.94812	2.94950	58.6
0	6	0	2.86680	2.86791	24.6
3	3	1	2.85190	2.85203	41.2[a]
6	2	0	2.78737	2.78711	50.8[a]
2	4	1	2.76719	2.76737	7.8[a]
2	6	0	2.72775	2.72788	12.2
5	1	1	2.60799	2.60703	24.9
1	5	1	2.57034	2.57028	6.9
6	4	0	2.43016	2.43064	4.5[a]
5	3	1	2.39506	2.39628	3.7[a]
3	5	1	2.37696	2.37708	39.3
7	3	0	2.31047	2.31107	3.5[a]
2	6	1	2.24796	2.24664	5.8[a]
0	8	0	2.15047	2.15093	10.0
2	8	0	2.09162	2.08993	4.4[a]
4	6	1	2.05562	2.05616	4.2[a]
0	0	2	1.98069	1.98049	52.0
3	7	1	1.96710	1.96863	26.3[a]
1	1	2	1.95534	1.95542	3.8
4	8	0	1.93358	1.93399	25.8
2	2	2	1.88507	1.88558	9.6
3	1	2	1.86611	1.86620	6.1[a]
9	3	0	1.85809	1.85807	19.9
2	8	1	1.84829	1.84841	18.8
3	9	0	1.81859	1.81859	3.8[a]
0	4	2	1.79900	1.79899	6.8[a]
3	3	2	1.78413	1.78414	5.3[a]
10	0	0	1.76757	1.76758	11.1[a]

[a] These reflections may contain scattering from the minority phase $Bi_3Nb_{17}O_{47}$.

Because the scanning electron microscope showed that the crystals were only 1 μm long, transmission electron microscopes were preferred for further analyses. Carefully performed energy-dispersive spectrometry analyses (EDS) showed that the metal ratio of the main phase was Bi : Nb = 2.0(1) : 10.79(6), measured on 10 crystallites. A diffraction pattern in the [001] zone can be seen in Fig. 1. It was obvious that many crystallites were twinned. Moreover, the extinctions and symmetry of the diffraction patterns suggested the space group *Cmmm*, which was used for image simulations.

High-resolution photographs of thin crystallites oriented along the short axis, ***c***, showed that the structure was of the tetragonal tungsten bronze (*TTB*) type.[5] That structure can be described as a framework of octahedra linked so that three-, four- and five-sided tunnels are formed. In the present HREM images a wavy dark pattern along one direction could be seen. It was especially evident at lower magnification, as shown in Fig. 2a. Comparing images at higher magnification with the structure of *TTB* it is obvious that half of the pentagonal tunnels of *TTB* seem to have the same dark contrast as the octahedra network (Fig. 2b). Therefore it was assumed that those five-cornered tunnels were filled so that every second row of them was occupied. It can be seen in the HREM photographs that the longest of the two axes (here chosen to be the ***a***-axis) is parallel to the rows of filled pentagonal columns. The same type of unit cell has been reported for $Cu_{9-x}Ta_{22}O_{64-2x}F_{2x}$.[12]

A model was first made with the Nb atoms inside the oxygen octahedra, building up an NbO_3 network. The larger Bi atoms were assumed to be placed in the five-cornered tunnels (see the proposed structure in Fig. 3). This model was the only one that gave reasonable agreement between observed and calculated images (Fig. 2b).

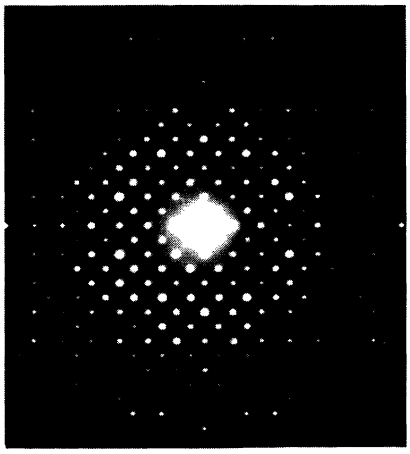
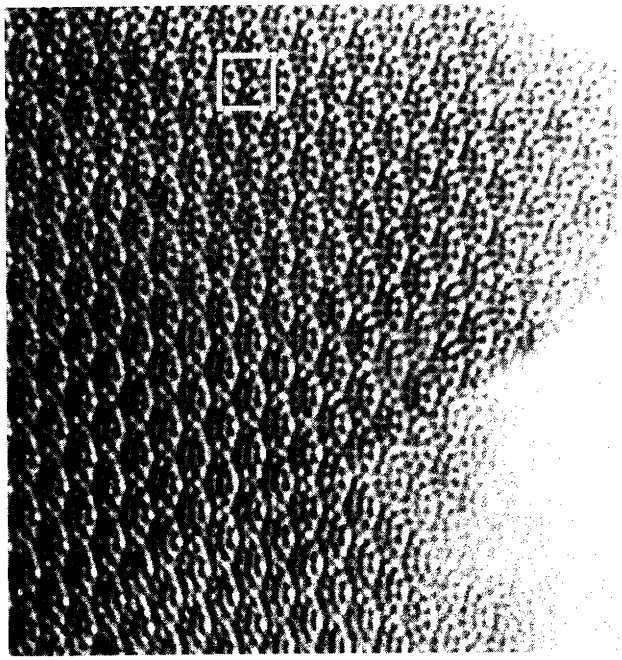


Fig. 1. Electron diffraction pattern in the [001] zone direction of the *TTB*-type phase $BiNb_{5.4}O_{15}$.

(a)



(b)

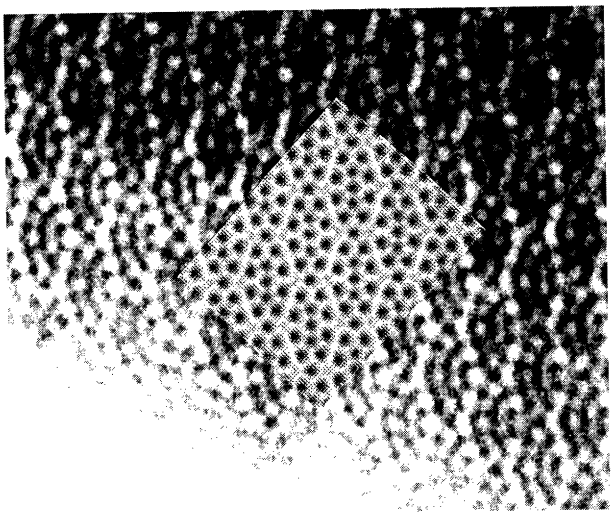


Fig. 2. (a) Low-magnification micrograph of a thin flake of $BiNb_{5.4}O_{15}$ aligned along [001] with one unit cell marked. (b) HREM image of $BiNb_{5.4}O_{15}$ with an inserted calculated image (Defocus −500 Å, slice thickness 20 Å).

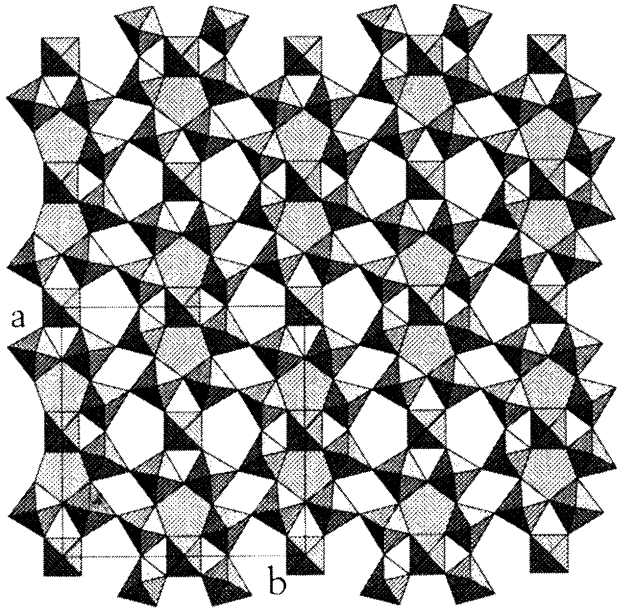


Fig. 3. Proposed structure of $BiNb_{5.4}O_{15}$. The bismuth atoms are situated in the five-cornered tunnels and the niobium atoms are in the oxygen octahedra.

Discussion

The HREM images of the bismuth niobate are very similar to those of the so-called *M-TTB* phases, e.g. *H*-KNb_3O_8 and $KNb_6O_{15}F$, described by Lundberg and Sundberg.[13,14] Also these *M-TTB* phases have been interpreted as having parallel rows of filled tunnels.

The structure model of the bismuth niobium oxide suggested by the HREM investigation (Fig. 3) places 4 Bi, 20 Nb and 60 O atoms per unit cell. Assuming that all oxygen positions at the corners of the octahedra are occupied, and taking into account the metal ratios from the EDS analyses mentioned above as well as the oxidation states of the atoms, an approximate formula $Bi_{4.0}Nb_{21.6}O_{60}$ ($BiNb_{5.4}O_{15}$) is more likely. This gives 1.6 extra niobium atoms per unit cell, which may statistically enter remaining empty tunnels. There is thus a small excess of niobium of the kind reported for other Nb- and Ta-containing *TTB* phases.[15–17] However, the average occupancy of these sites is too low to give any detectable contrast in the HREM images.

Calculations of distances in the proposed structure of $BiNb_{5.4}O_{15}$ show that bismuth atoms at an elevation ($z = 1/2$) other than the niobium atoms ($z = 0$) would have Bi–O distances of *ca.* 3 Å. The Nb–O distances are *ca.* 2 Å.

There are now many types of *TTB*-like structures known for metal oxides, oxyfluorides and fluorides. The *M-TTB*-type phases mentioned above[13,14] have niobium atoms together with oxygen atoms in the five-cornered tunnels, so that so-called pentagonal bipyramids are formed. One pair of Nb^{5+}–O^{2-} per tunnel and unit cell would give the same net charge as one Bi^{3+} without any oxygen.

The most similar phase reported before seems to be $Bi_3Nb_{17}O_{47}$, which was synthesized at a temperature of 1230°C.[4] A crystal of this compound was shown by Keve and Skapski[4] to have a structure of the *3TTB*-type. They found that the bismuth atoms are placed in five- and four-cornered tunnels and that the niobium atoms are mainly inside oxygen octahedra.

$PbNb_2O_6$ is also a *TTB*-related compound.[18] The Pb atoms fill all the five-cornered and half of the four-cornered tunnel sites in this structure. Both Pb^{2+} and Bi^{3+} have a lone pair of *s*-electrons, which may be the reason for the reported non-symmetrical location of them in the tunnels of $Bi_3Nb_{17}O_{47}$ and $PbNb_2O_6$. Probably $BiNb_{5.4}O_{15}$ shows the same assymetry, but this cannot be detected by HREM studies. For a precise structure determination of such a complicated structure one would require untwinned single crystals.

Acknowledgments. I am grateful for discussions with Prof. L. Kihlborg and Dr. B.-O. Marinder and for technical assistance by Mr. Stefan Carlsson. This work is part of a project that has received financial support from the Swedish Natural Science Research Council.

References

1. Bryntse, I. *Eur. Solid State Inorg. Chem. 28* (1991) 481.
2. Roth, R. S. and Waring, J. L. *J. Res. Natl. Bur. Stand. 66A* (1962) 451.
3. Pfoertsch, *JCPDS Grant-in Report*, 1981, JCPDS nr 33-210 (Powder Data File).
4. Keve, E. T. and Skapski, A. C. *J. Chem. Soc. A* (1971) 1280.
5. Magnéli, A. *Arkiv. Kemi 1 24* (1949) 213.
6. Zhou, W., Jefferson, D. A. and Thomas, J. M. *J. Solid State Chem. 70* (1987) 129.
7. Gopalakrishnan, J., Ramanan, A., Rao, C. N. R., Jefferson, D. A. and Smith, D. J. *J. Solid State Chem. 55* (1984) 101.
8. Hubbard, C. R., Swanson, H. E. and Mauer, F. A. *J. Appl. Crystallogr. 8* (1975) 45.
9. Johansson, K. E., Palm, T. and Werner, P.-E. *J. Phys. E 13* (1980) 1289.
10. Eriksson, L. program PUDER (1991).
11. O'Keefe, M., Buseck, P. R. and Iijima, S. *Nature (London) 274* (1978) 322.
12. Lundberg, M. and Sundberg, M. *Micron and Microscopia Acta 22* (1991) 157.
13. Lundberg, M. and Sundberg, M. *J. Solid State Chem. 63* (1986) 216.
14. Lundberg, M. and Sundberg, M. *J. Less Comm. Met. 137* (1988) 163.
15. Kato, K. and Tamura, S. *Acta Crystallogr., Sect. B 31* (1975) 673.
16. Awadalla, A. A. and Gatehouse, B. M. *J. Solid State Chem. 23* (1978) 349.
17. Sundberg, M. and Marinder, B.-O. *J. Solid State Chem. 84* (1990) 23.
18. Labbe, Ph., Frey, M. and Allais, G. *Acta Crystallogr., Sect. B 29* (1973) 2204.

Received January 29, 1993.