JOURNAL OF SOLID STATE CHEMISTRY **1**, 368–371 (1970)

The Preparation of a Barium Niobium Bronze

RALPH R. KREISER AND ROLAND WARD

Department of Chemistry, University of Connecticut, Storrs, Connecticut, 06268

Received October 9, 1969

A barium niobium oxide displaying bronze characteristics is found by the reaction of niobium metal with mixtures of barium and niobium oxides with $Ba_5Nb_4O_{15}$. It is a red compound with the cubic perovskite-type structure $a_0 = 4.080$ Å, a good electrical conductor and paramagnetic with Curie–Weiss behavior. The compound was not obtained pure but is believed to have the composition $BaNbO_3$.

The identification of the barium niobium oxide described in this paper was incidental to a search for a ternary oxide containing a metal cluster. Since the structure of NbO can be regarded as octahedral clusters of niobium atoms joined by edge-sharing oxygen atoms in a continuous three-dimensional array, it was thought that it might be possible to isolate the $Nb_6O_{12}^{10-}$ which would be isoelectronic with $Nb_6Cl_{12}^{2+}$ by the use of suitable large cations. The establishment of an oxidation state of $2\frac{2}{3}$ for the niobium seemed to be essential for the purpose. Mixtures of niobium pentoxide with niobium metal and various oxides were used over a temperature range of 800–1200°C. Stoichiometries corresponding to $Th_3ONb_6O_{12}$ and $La_4ONb_6O_{12}$ failed to yield any new phase. The alkaline earth oxides, however, mixtures corresponding to $M_5^{2+}Nb_6O_{12}$ gave rise to unique phases which were first thought to be examples of the cluster compounds. The structures were obviously related to simple cubic configurations, but the presence in all the diffraction patterns of low-intensity lines suggested the more complex structure expected for $M_5Nb_6O_{12}$ (*1*). It turned out that the additional lines were due to impurities. The compounds were probably not obtained completely free from impurities, but the structure can be identified as the perovskite type. Phases of this kind have been reported by Krylov (*2*) as barium-deficient perovskite.

Experimental

The niobium (*5*) oxide was 99.6% Nb_2O_5. This was taken to dryness two times with 43% reagent grade hydrofluoric acid. It was then fumed to dryness two times with reagent-grade concentrated sulfuric acid. After grinding in an agate mortar it was washed thoroughly with distilled water and ignited at 1000°C for 24 h. This treatment was designed to remove any silica and fluoride from niobium pentoxide. It has been demonstrated that fluoride ion is a common impurity in commercial niobium pentoxide (*3*). The presence of traces of fluoride ion in the starting mixtures causes the formation of large crystals of NbO_2. The niobium metal was 325 mesh powder and listed as 99.9% Nb. Before use it was dried for 2 h at 1500°C. A thermogravimetric oxidation of the metal in air indicated that it was at least 99.5% Nb. The major impurity was probably a surface oxide coating. The barium and strontium oxides were freshly prepared before use by heating the peroxides in a vacuum at 1000°C for 1 h. The calcium oxide was listed to be pure and was heated under vacuum at 1000°C for 1 h before use.

Barium Niobium Oxide

Mixtures of barium oxide, niobium (V) oxide and niobium metal were weighed to the nearest 0.1 mg and were pelleted in a stainless-steel die 7 mm in diameter in order to limit the reaction of the sample with the silica container. After heating for another 124 h at 1000°C, the ampul was air quenched and the pellets finely ground in an agate vial on a Spex mixer-mill. With proportions of the reactants corresponding to the formula $Ba_5Nb_6O_{12}$, the product was a red powder but always contained small amounts of niobium metal and other impurities. Samples close to the stoichiometry $BaNbO_3$ gave purer products.

Reduction of the compound $Ba_5Nb_4O_{15}$ also led to the formation of the red phase. The white 5-layer compound $Ba_5Nb_4O_{15}$ was prepared according to the method of Galasso (*4*). This was mixed with 3% by weight of niobium metal, sealed into an evacuated silica ampul, and heated at 1000°C for a 48-h period. The pellet appeared to be red, but when it was crushed it was found that only a thin covering over the entire pellet was red while the center of the pellet was light blue in color. An additional 3% of niobium metal was ground into the sample. This was resealed into a silica ampul and heated at 1000°C for 196 h, after which the ampul was air quenched and opened. The pellet was again found to have a red covering with a darker blue center. A final portion of niobium metal was added to completely convert the starting material to $BaNbO_3$. This was sealed into an evacuated silica ampul, heated at 100°C for 72 h, and air quenched. The entire pellet was red in color. The dark red powder was washed once with 6N sulfuric acid, three times with distilled water, and once with acetone, after which it was air dried.

Similar preparations were made using strontium and calcium oxides in place of barium. The product gave X-ray diffraction patterns resembling that of the barium compound except that the pattern of the calcium niobium oxide was more complex. The lattice parameter for the strontium-niobium oxide prepared in this study was $a_0 = 4.025$ Å, which is close to the upper limit (4.016 Å) reported for the nonstoichiometric phase Sr_xNbO_3 (*5*). The diffraction pattern of the calcium compound is given in Table I.

The ratio of barium to niobium in several preparations varied over the range 1.0–0.6, and the attempts to adjust the oxidation state of the niobium were made by varying the proportion of niobium to niobium pentoxide. The products of these experiments were examined by X-ray powder diffraction. The data were obtained from samples sprinkled on vaseline which was coated on a glass microscope slide. A General Electric XRD-5 Powder Diffractometer was used with copper *K* radiation. For the determination of the lattice parameter, potassium chloride was ground into the sample for an internal standard. Intensities were determined by cutting out the various peaks and weighing them to the nearest 0.1 mg. The calculated intensities were computed on an IBM-360 computer using Hamilton's modification of the Busing–Levy Least-Squares Program. The generated $|F|^2$ were converted to intensities by correcting for multiplicities and for Lorenz polarization effects.

When the mixtures were heated at 1000°C, the samples in which the planned oxidation state of the niobium was between 2 and 4 gave sharp diffraction patterns with the characteristics listed in Table II. Other weak lines were usually observed in the spectra. The dominant lines of the spectra due to the red component (Table II) can be attributed to a cubic perovskite-like phase ($a_0 = 4.080$ Å).

Samples corresponding to composition ranging from $Ba_{0.9}NbO_3$ to $Ba_{0.65}NbO_3$ gave products containing the red phase down to $Ba_{0.7}NbO_3$, but the lattice parameter of the cubic phase was invariant within experimental error. At Ba/Nb = 0.65, none of the red phase was obtained. The X-ray pattern of this product is given in Table III.

Attempts to prepare the pure red phase were not clearly successful in spite of its chemical inertness.

TABLE I

X-RAY DIFFRACTION FOR CALCIUM NIOBIUM OXIDE

hkl	$\sin^2\theta$ (obs)	*I* (obs)
100	0.0377	19.9
110	0.0754[a]	45.5
111	—	—
200	0.1514	21.4
210	0.1864	2.5
—	0.1894	7.8
211	0.2268	11.4
—	0.2304	15.6
220	0.3037	5.2
300	—	—
310	0.3791	12.9

[a] indicates a shoulder.

TABLE II

X-RAY DATA FOR $BaNbO_3$

hkl	$\sin^2\theta$ (obs)	*I* (obs)	$\sin^2\theta$ (calc)	*I* (calc)
100	0.0357	4.4	0.0357	1.9
110	0.0714	162	0.0714	158
111	0.1071	9.3	0.1071	10.1
200	0.1430	51.3	0.1428	51.1
210	0.1791	1.6	0.1785	1.2
211	0.2141	74.8	0.2142	68.2
220	0.2855	35.1	0.2856	31.1
300	0.3208	1.5	0.3213	0.7
310	0.3570	29.5	0.3570	29.2
311	0.3926	2.6	0.3927	2.8
222	0.4284	10.2	0.4284	10.7
320	—	—	—	—
321	0.4997	37.1	0.4998	37.6
400	0.5707	5.9	0.5712	5.5
410	0.6060	0.6	0.6069	0.8
330	0.6423	24.3	0.6426	24.1
420	0.7138	24.3	0.7140	22.2

TABLE III

X-RAY DATA FOR STOICHIOMETRY $Ba_{0.65}NbO_3$

I	*d*
w	3.58
w$^+$	3.48
m	3.25
w	3.14
m	3.04
m$^-$	2.96
w$^+$	2.87
s	2.81
w$^+$	2.63
w	2.34
w	2.19
w$^+$	2.15
w	2.03
m	1.99

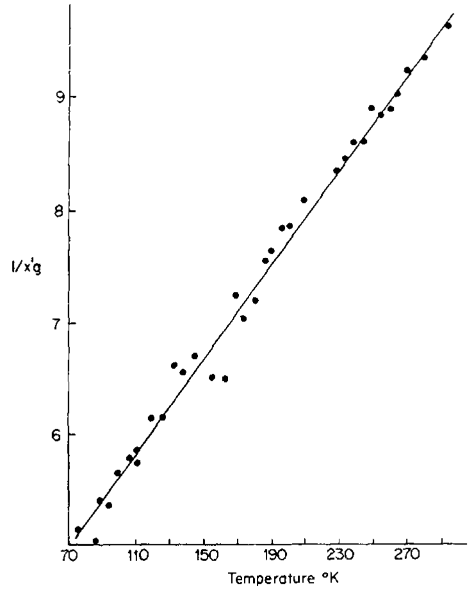

FIG. 1. The magnetic susceptibility of $BaNbO_3$.

The compound appeared to be impervious to attack by sulfuric or hydrochloric acids, aqua regia, or concentrated alkali solutions. It is decomposed by hot hydrofluoric acid.

Efforts were made to obtain single crystals by the use of fluxes and by transport with iodine. The addition of 2% by weight of barium fluoride appeared to improve the intensities of the X-ray diffraction pattern, but no crystals were found in the resulting material. The use of other fluxes seemed to yield oxidized products or disproportionation products. For example, a ratio of ten barium fluoride to one of $BaNbO_3$ yielded crystals of $Ba_3Nb_6Si_4O_{23}$ (*6*). Lead oxide as the fluxing agent yielded white powders of $Ba_5Nb_4O_{15}$ while boric oxide in a ratio of five flux to one yielded crystals of niobium (IV) oxide.

Fluorescense analysis of the solid indicated a barium to niobium ratio of about 0.76. Qualitative tests showed that the compound is an excellent electrical conductor at room temperature.

The magnetic behavior of the compound follows the Curie–Weiss law (Fig. 1).

A high-field nmr spectrum of the compound gives a resonance, whereas the compound $Ba_5Nb_4O_{15}$ does not (*7*). This was taken to indicate that the new compound contained niobium in a site of high symmetry such as could be provided by the cubic perovskite structure. The niobium in $Ba_5Nb_4O_{15}$ was shown to occupy a distorted octrahedral site and would therefore not yield a resonance line. The resonance line of niobium metal was absent thus indicating that the impurity was not present.

Thermogravimetric analysis of a sample which contained no niobium metal as revealed by X-ray showed that reaction with air began at 300°C. The gain in weight was 1.97%. The density of this preparation determined by the buoyancy method was 6.10 g/cc.

Discussion

The analytical results on the barium niobium oxide based upon fluorescence analysis indicated a barium to niobium ratio of 0.76. The perovskite-type structure would suggest a barium-deficient structure $Ba_{0.76}NbO_3$. This corresponds quite well with the thermogravimetric analysis. The gain in weight is close to that required for oxidation to pentavalent niobium (1.67% for $Ba_{0.76}NbO_3$ compared with 1.97% found). Total analysis of a comparable sample involving direct oxygen analysis gave Ba 51.53 ± 0.07, Nb 30.42 ± 0.08, O 18.12 ± 0.02. The major impurity of this sample discernable with X-rays was $Ba_5Nb_4O_{15}$. It is difficult to reconcile these results for the direct analysis indicates an over-all composition corresponding to $BaNb_{0.878}O_{3.02}$ which suggests a mixture of 94 mole% $BaNbO_3$ with 6 mole% $Ba_5Nb_4O_{15}$. The blue phase is probably a very slightly oxygen-deficient $Ba_5Nb_4O_{15-x}$. The TGA of the blue phase gave a negligible weight gain upon oxidation to white stoichiometric compound. The oxygen to barium ratio according to analysis is close to 3, which is in agreement with that of the proposed mixture if the blue phase is only slightly oxygen-deficient.

The production of the red compound appears to occur mainly through the blue phase. The X-ray diffraction pattern obtained after the first few seconds of initial heating during sealing of the ampul showed only one peak of low intensity which could not be assigned. The pattern obtained after 12 h of heating showed that the hexagonal compound $Ba_5Nb_4O_{13}$ was formed in addition to $BaNbO_3$. The observation that the red phase was found on the outside of the pellet may be explained in part by assuming that the barium ion had to be transported out of the pellet to react with the silica, perhaps forming a barium silicate. This could also explain the extensive devitrification of the silica ampul found in the first few heatings of the compound.

The evaluation of the purity of a product by means of X-ray diffraction patterns is difficult. It was established by making mechanical mixtures of the red phase with NbO and NbO_2 that 2% of the former and 4% of the latter could be detected. The reaction products, however, may have a topological relationship which cannot be duplicated by mere mechanical mixing. If the red phase is actually formed on the surface of the blue phase, the latter may be very effectively shielded from the X-rays. In some cases, prolonged exposures with the Debye–Shearer method reveals the presence of impurities which easily escape detection with the diffractometer.

The invariance of the lattice parameter certainly demands that the compound be essentially stoichiometric especially with such a large cation as barium (*2*).

The diffraction patterns of the red phase were very sharp and extended well into the back reflection region. Very small variations in lattice parameter could have been detected. None was observed. Random filling of the *A* sites in the perovskite structure would not require strict stoichiometry unless there were some peculiar stability induced by a mixed state for niobium such as $Ba_{0.75}Nb^{IV}_{0.5}Nb^{V}_{0.5}O_3$. None of the faint additional lines observed in the diffraction pattern could be indexed as an ordering line requiring a multiple cell.

It is not possible to derive strictly quantitative data from the magnetic data given in Fig. 1 since the precise niobium content is not known. Assuming that the composition is not far from that of the analyzed sample, a moment of 0.8 μB can be estimated. A sample containing 6 mole% $Ba_5Nb_4O_{15}$ would be expected to have this moment.

These magnetic properties are comparable to those of the vanadium bronzes (*8*) such as the nonstoichiometric semiconductor $Na_{0.33}V_2O_5$. The magnetic behavior of this compound indicated that the electrons introduced by the sodium are largely in localized V^{4+} centers (*6*).

Attempts to make nonstoichiometric bronzes with alkaline earth *A* cations has been successful only in the case of Sr_xNbO_3 (*5*). No variation in the lattice parameter could be found in the system Sr–Mo–O (*8*). The constancy of the lattice parameter and the absence of ordering lines in the diffraction pattern seem to point conclusively to the formula $BaNbO_3$ for red bronze. The competitive formation of $Ba_5Nb_4O_{15}$ and its slow convertion to the red phase makes the isolation of the compound difficult. The use of high pressures might conceivably offer a route to the direct synthesis of the cubic $BaNbO_3$, since these conditions have been shown to favor the conversion of hexagonal layer structures to the cubic perovskites (*9*).

Acknowledgments

We are indebted to Dr. Carl Moeller for discussion of the magnetic properties and to Dr. E. Dunlop for some of the analytical data. We also wish to acknowledge the financial support provided by Grant No. G.P. 6367 from the National Science Foundation.

References

1. R. R. Kreiser and R. Ward, *Amer. Chem. Soc. Rep.* San Francisco **67** (April 1968).

2. E. I. Krylov and A. A. Sharnin, *Zh. Obshch. Khim.* **25**, 1680 (1955); *J. Gen. Chem. U.S.S.R.* **25**, 1637 (1955); E. I. Krylov, *Dokl. Akad. Nauk S.S.S.R.* **104**, 246 (1955).

3. S. Andersson, *Acta Chem. Scand.* **18**, 2339 (1964).

4. F. Galasso and L. Katz, *Acta Cryst.* **14**, 647 (1961).

5. D. Ridgley and R. Ward, *J. Amer. Chem. Soc.* **77**, 6132 (1955).

6. J. Shannon, Thesis, Univ. of Connecticut, 1968.

7. R. Snodgrass, Univ. of Connecticut, private communication.

8. A. D. Wadsley, *Acta Cryst.* **8**, 695 (1955).

9. M. J. Sienko, *Advan. Chem.* **39**, 224 (1963).

10. W. H. McCarrol, Thesis, Univ. of Connecticut, 1956.

11. J. M. Longo and J. A. Kafalas, *J. Solid State Chem.* **1**, 103 (1969).