

# New barium niobium sulfides. I. Compound with approximate composition $\text{BaNb}_{5.67}\text{S}_{10.8}$

Masanobu Saeki, Hiroshi Nozaki, Mitsuko Onoda

*National Institute for Research in Inorganic Materials, 1-1, Namiki, Tsukuba, Ibaraki, 305, Japan*

Received 17 March 1995; in final form 5 August 1995

## Abstract

A new barium niobium sulfide has been prepared by controlling the partial pressure of sulfur. The single phase of the sulfide could be synthesized at 1000°C when the chemical composition was maintained at  $x = 5.67$  in  $\text{BaNb}_x\text{S}_y$  and the sulfur partial pressure at 23.7 kPa. This sulfide has a homogeneity range with the variation of the Ba and Nb ratio. The range of the homogeneity varies with the sulfur partial pressure in the preparation. The X-ray powder diffraction pattern of this sulfide could be indexed on the basis of a hexagonal cell with the lattice parameters of  $a = 0.33363(2)$  nm and  $c = 1.7680(2)$  nm. The electron diffraction pattern, however, reveals superspots which are diffuse in the  $a^*-b^*$  plane and streak in the  $c^*$  axis. The sulfide exhibits temperature independent paramagnetism. In addition to this sulfide, six more new sulfides were found in the composition of  $2.8 < x < 10.1$  in  $\text{BaNb}_x\text{S}_y$ . The preparation of those compounds with single phase has not succeeded yet.

**Keywords:** Barium niobium sulfide; Barium sulfide; Niobium sulfide

## 1. Introduction

Several sulfides consisting of Ba and Nb have been reported so far. They are denoted as A, B, C, D and E, and listed in Table 1. The structures of all sulfides, except for A, have been determined by Donohue and Weiher [1], Swinnea et al. [2,3], and Saeki and Onoda [4]. Their structures are related to the  $\text{BaNiO}_3$  type structure.

The purpose of this paper is to describe the preparation of an unknown sulfide, the chemical composition of which is represented as  $\text{BaNb}_{5.67}\text{S}_{10.8}$ .

## 2. Experimental

Preparation of an unknown sulfide is as follows. The starting materials,  $\text{BaCO}_3$  (99.9%) and  $\text{Nb}_2\text{O}_5$  (99.9%), are dried in air at 100°C for 2 days to remove adsorbed moisture. The starting materials are mixed in a calculated amounts, and then heated at 750°C for 3 days in  $\text{CS}_2$  atmosphere. The  $\text{CS}_2$  vapour is carried with  $\text{N}_2$  gas into the furnace. The sulfide obtained thus (which is denoted as a starting sulfide) is placed in a crucible. The crucible is sealed with a small amount of the extra

sulfur in an evacuated silica tube of 400 mm in length and 10 mm in inner diameter as shown in Fig. 1. The silica tube is placed in a temperature gradient furnace. The high temperature side where the specimen is heated is fixed at 1000°C, and the temperature at the low temperature side is changed to regulate the sulfur pressure in the silica tube. The starting sulfide at the high temperature side absorbs or evolves sulfur depending on the sulfur pressure in the tube. The sulfur pressure in the tube is always maintained at sulfur vapour pressure at the temperature of the low temperature side, and is calculated from the following equation [5]

$$\log(P/\text{kPa}) = -4830T^{-1}/\text{K}^{-1} - 5.0 \log(T/\text{K}) + 23.01$$

where  $P$  is the sulfur vapour pressure, and  $T$  is the temperature at the low temperature side. After heating for 5 days, the tube is quenched in cold water.

The determination of the chemical composition was as follows. The amounts of Ba and Nb were calculated from that of the starting materials. It has been confirmed that these metals do not evaporate in the process of the sulfurization [4]. The sulfur content in the starting sulfide was obtained from the change in

Table 1  
Compounds in the Ba–Nb–S system

Formula	Crystal system	Lattice parameters	Electric property	Ref.
A BaNb <sub>2</sub> S <sub>5</sub>	h	$a = 0.333\text{nm}$ , $c = 2.52\text{nm}$	M	[6–8]
B BaNbS <sub>3</sub>	h	$a = 0.685\text{nm}$ , $c = 0.574\text{nm}$	S	[1]
C Ba <sub>16.5</sub> Nb <sub>9</sub> S <sub>39</sub>	h-axis	$a = 0.688\text{nm}$ , $c = 4.18\text{nm}$	I	[3]
D Ba <sub>2</sub> NbS <sub>5</sub>	h	$a = 0.693\text{nm}$ , $c = 4.94\text{nm}$	I	[2]
E Ba <sub>9</sub> NbS <sub>21</sub>	h	$a = 0.696\text{nm}$ , $c = 2.16\text{nm}$	I	[4]

h, hexagonal cell; I, insulator; S, semiconductor; M, metallic.

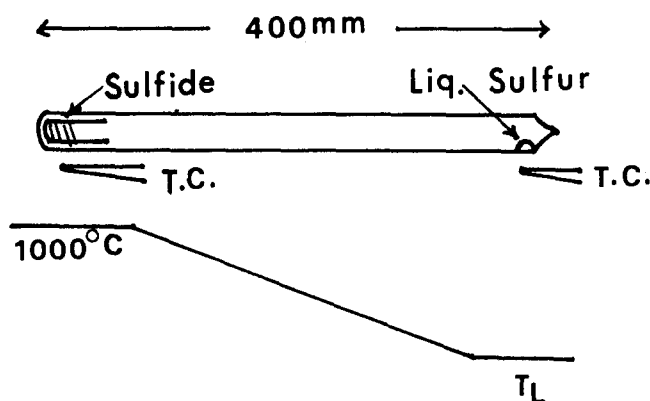


Fig. 1. Temperature at the high temperature side is 1000°C, and temperatures at the low temperature side are set at 260, 300, 360 and 400°C to control the sulfur vapour pressure.

weight of the starting materials and sulfide produced in CS<sub>2</sub> atmosphere. The sulfur content of the starting sulfide prepared in CS<sub>2</sub> atmosphere could be represented by BaS<sub>x</sub>NbS<sub>1.81</sub> in spite of the metal ratio in the range  $x = 5.54$ – $5.99$ . The variation in the sulfur content is observed when the starting sulfide is heated at 1000°C under regulated sulfur pressure. This variation in the sulfur content is calculated from the weight change before and after the heating process at 1000°C.

X-ray powder diffraction data were collected with a stepscan procedure on a Philips PW 1800 diffractometer using automatic divergence slit and counter-side monochromatized Cu K $\alpha$  radiation. Silicon was employed as the standard of the lattice parameters. Electron diffraction patterns were obtained for crushed particles using a 100 kV electron microscope (Hitachi 500-type).

The density of the specimen was obtained by measuring buoyancy in carbon tetrachloride. About 0.5 g of the specimen with fine particles was placed in a bottle, the volume of which was about 2 cm<sup>3</sup>, and the weight of which was 1.5 g. The bottle and the specimen in carbon tetrachloride were kept at reduced pressure to remove the bubbles adsorbed to the specimen and on the surface of the bottle. The buoyancy was obtained by measuring the weight of the specimen in air and in carbon tetrachloride at  $25 \pm$

0.1°C. To examine the accuracy of this method, the density of the fine powder silicon was measured. The results were 2.31 and 2.32 g cm<sup>−3</sup> (two measurements) compared with the literature value of 2.33 g cm<sup>−3</sup>.

### 3. Results

The starting sulfide prepared in CS<sub>2</sub> atmosphere was heated at 1000°C in an evacuated silica tube with an extra amount of sulfur. The powder X-ray diffraction pattern of the specimen obtained thus gave a very complex pattern and poor reproducibility. The complex pattern can be interpreted as the mixture of several structures, and the poor reproducibility is related to a little difference in the amount of added sulfur and to the difficulty in attaining an equilibrium state. All of the diffraction patterns could be explained with the assumption that in the composition of  $2.8 < x < 10.1$  there are seven unknown sulfides denoted as F, G, H, I, J, K and L in descending order of Nb content. The isolation of these sulfides is difficult, but only sulfide H could be prepared as a pure phase by the following method.

The requirement for the preparation of the pure H is to control (1) the preparation temperature, (2) the sulfur pressure in the preparation, and (3) the metal ratio of the starting material. In this experiment, (1) the preparation temperature was fixed at 1000°C. (2) The sulfur pressure was maintained between 2 and 24 kPa, in order to prepare pure H (see Table 2). At a sulfur pressure lower than 2 kPa, the X-ray diffraction pattern of the H gives broad diffraction peaks. At higher than 49 kPa, pure H was no longer obtained at any metal ratio. The results are listed in Table 2. (3) The metal ratio to prepare pure H is dependent on the sulfur pressure. For example, pure H is obtained at  $x = 5.54$ – $5.99$  when the sulfur pressure is  $P = 6.2$  kPa. The specimen was contaminated by NbS<sub>2</sub> at  $x > 5.99$ , and contaminated by the sulfide K at  $x < 5.54$ . At a sulfur pressure of 23.7 kPa, pure H was obtained at  $x = 5.54$ – $5.67$ , as shown in Table 2.

The sulfur content of the pure H was measured for the  $x = 5.67$  material, which was prepared at various

Table 2  
Sulfur pressure ( $P$ ) and metal ratio ( $x$ ) to prepare pure H

$x$	$T_L$ (°C): $P$ (kPa):	260 2.1	300 6.2	360 23.7	400 49.3
6.14		H*	H + NbS <sub>3</sub>		
5.99		H	H	H + G + K + I + NbS <sub>2</sub>	G + K + I + NbS <sub>2</sub>
5.90		H	H	H + G + K + I + NbS <sub>2</sub>	H + F + G + I + NbS <sub>2</sub>
5.76		H	H	H + G + K + I + NbS <sub>2</sub>	H + G + K + I + NbS <sub>2</sub>
5.67		H	H	H	H + G + K + I + NbS <sub>2</sub>
5.54		H	H	H	H + G + I + NbS <sub>2</sub>
5.33		H	H + K	H + G + K + I + NbS <sub>2</sub>	G + K + I + NbS <sub>2</sub>
4.71		H + K			

$T_L$ , temperature at low temperature side;  $P$ , vapour pressure of sulfur at  $T_L$ ;  $x$ , Nb/Ba; H\*, X-ray diffraction pattern contains broad peaks which do not belong to H; F, G, K, I: unknown sulfides.

sulfur pressures. At a sulfur pressure of 23.7 kPa, the sulfur content,  $y$  in BaNb<sub>5.67</sub>S <sub>$y$</sub> , was 10.8, which is the average of four measurements of 10.9, 10.7, 10.8 and 10.7. The  $y$  values were 10.7 and 10.6, respectively, when the sulfur pressures were 6.2 kPa and 2.1 kPa. No variation of the sulfur content was, therefore, observed within the experimental error, in spite of the preparation under different sulfur pressures.

The homogeneity range from  $x = 5.54$  to  $x = 5.99$  was observed, as was described above; nevertheless little variation of the lattice parameters was detected with the variation of the metal ratio and sulfur pressure in the preparation.

Fig. 2 is a powder X-ray diffraction pattern of BaNb<sub>5.67</sub>S<sub>10.8</sub>. All peaks can be indexed on the basis of a hexagonal cell with the lattice parameters of  $a = 0.33363(2)$  nm and  $c = 1.7680(2)$  nm. Table 3 gives the observed and calculated  $d$  values, and observed intensities of the peaks. As can be seen in the table, the peak intensities of  $00l$  are strong compared with the others. This suggests that the compound has a layered structure and takes a preferred orientation.

As is seen in Table 2, a mixture of several unknown sulfides was observed at a sulfur pressure of 48 kPa. This suggests that these sulfides are difficult to bring to

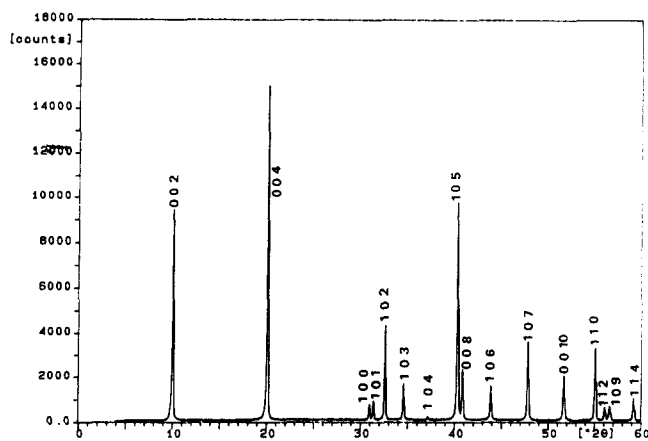


Fig. 2. X-ray powder diffraction pattern of BaNb<sub>5.67</sub>S<sub>10.8</sub>.

Table 3  
Indices, calculated and observed values of  $d$  spacings, and observed intensities for BaNb<sub>5.67</sub>S<sub>10.8</sub> ( $a = 0.33363(2)$  nm,  $c = 1.7680(2)$  nm)

$h$	$k$	$l$	$d_{\text{calc}}$	$d_{\text{obs}}$	$I_{\text{obs}}$
0	0	2	0.88	0.879	63
0	0	4	0.442	0.441	100
1	0	0	0.2889	0.2884	4
1	0	1	0.2852	0.2847	5
1	0	2	0.2746	0.2742	29
1	0	3	0.2594	0.2591	10
1	0	4	0.2418	0.2414	1
1	0	5	0.2237	0.2236	65
0	0	8	0.2210	0.2207	15
1	0	6	0.2063	0.2062	10
1	0	7	0.1902	0.1901	23
0	0	10	0.17680	0.17669	13
1	1	0	0.16682	0.16673	20
1	1	2	0.16392	0.16385	3
1	0	9	0.16245	0.16239	4
1	1	4	0.15607	0.15601	6
1	0	10	0.15081	0.15076	14
0	0	12	0.14733	0.14727	16
2	0	0	0.14447	0.14441	1
2	0	1	0.14399	0.14393	1
2	0	2	0.14258	0.14250	4
2	0	3	0.14031	0.14031	4
2	0	5	0.13374	0.13371	11
1	0	12	0.13125	0.13123	1
2	0	6	0.12972	0.12969	1
2	0	7	0.12540	0.12540	5
1	1	10	0.12133	0.12134	6
2	0	9	0.11638	0.11637	1
1	0	14	0.11571	0.11571	1
2	0	10	0.11187	0.11187	4
1	1	12	0.11043	0.11043	13
1	0	15	0.10913	0.10914	6
2	1	2	0.10838	0.10837	4
2	1	3	0.10738	0.10739	3
2	1	5	0.10434	0.10435	11
2	0	12	0.10315	0.10316	1
2	1	6	0.10240	0.10241	1
1	1	14	0.10069	0.10070	1
2	1	7	0.10024	0.10025	6
1	0	17	0.09785	0.09787	6
3	0	0	0.09631	0.09634	4
3	0	2	0.09574	0.09576	1
3	0	4	0.09410	0.09412	1

an equilibrium state, probably because of the layer structure. When a structure which is not a stable form under the conditions is formed in the reaction process, high activation energy may be necessary for the transformation to a stable form because of a synchronous atom movement of the whole layer. Therefore, the specimen, sometimes, contains four or five structures.

The electron diffraction patterns shown in Fig. 3 were taken by rotating a crystal fragment around principal axes. In addition to the strong spots, many weak diffuse spots are observed as in Fig. 3(a) and 3(b). All of the strong spots are indexed by a hexagonal cell with  $a = 0.33$  nm and  $c = 1.76$  nm, which gave excellent agreement with the cell dimension obtained by X-ray powder diffraction. Weak streaks along  $c^*$  are observed in Fig. 3(b), and they are diffuse in the  $a^*-b^*$  plane shown in Fig. 3(a). They suggest that microdomains of two-dimensional superstructure exist

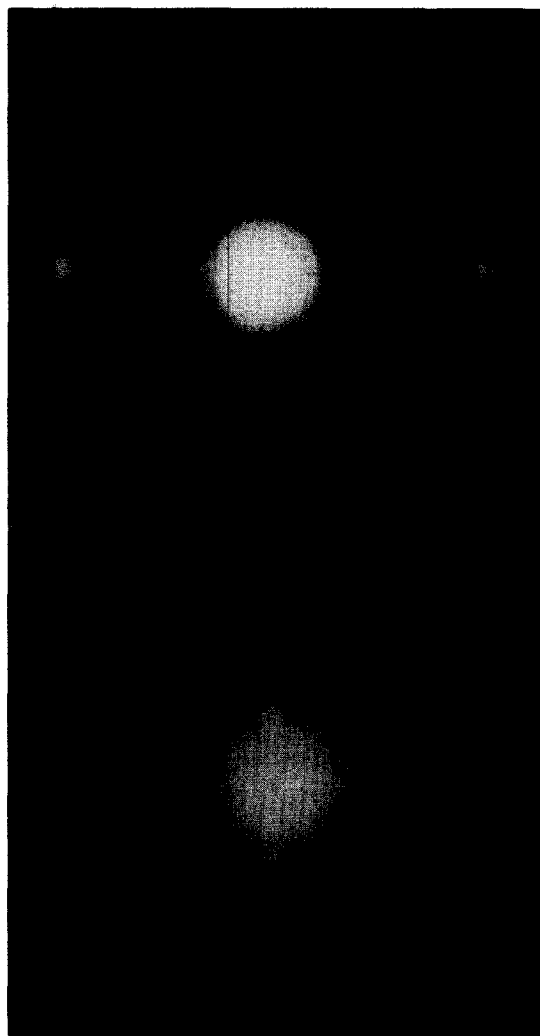


Fig. 3. Electron diffraction patterns. The diffraction spots are indexed with the subcell.

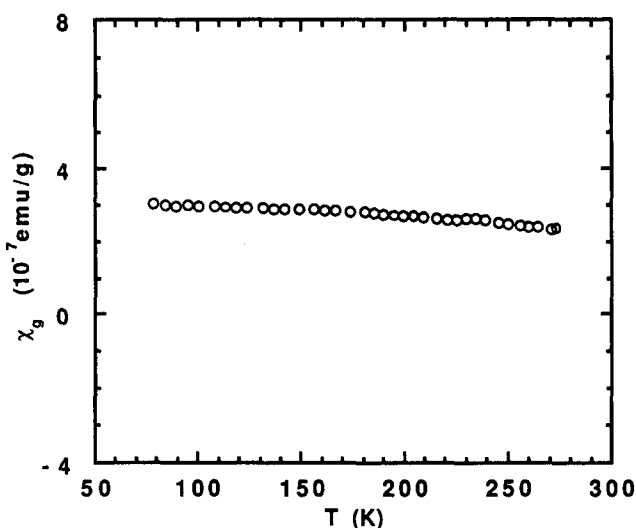


Fig. 4. Magnetic susceptibility vs. temperature.

in the  $a$ - $b$  plane and they stack randomly in the  $c$ -direction, while the subcell maintains regular periodicity. The super spots may be sharp under particular conditions of temperature and chemical composition.

Fig. 4 shows the magnetic susceptibility in the temperature range 77 K to room temperature. It exhibits paramagnetism with  $2.3 \times 10^{-7}$  emu  $g^{-1}$  at 273 K and  $3.0 \times 10^{-7}$  emu  $g^{-1}$  at 78 K, without any magnetic transition in the temperature range.

#### 4. Discussion

As is noticed from the result described above, the chemical composition of this sulfide is similar to that of an intercalation compound  $Ba_xNbS_2$  if it exists. The density was measured in order to determine whether or not this sulfide is a Ba intercalated  $NbS_2$ . If this sulfide is a Ba intercalated  $NbS_2$ , two sandwiches should be contained in the subcell, because of the  $c$ -axes of 1.7680 nm. In this case,  $2Ba_{0.176}NbS_2$  is contained in the subcell of  $0.170$  nm<sup>3</sup>. The calculated density is, therefore,  $3.57$  g cm<sup>-3</sup> for  $V = 0.170$  nm<sup>3</sup> and for the chemical formula  $2Ba_{0.176}NbS_2$ . The measured density was, on the other hand,  $4.71$  g cm<sup>-3</sup>, which is the average value of three measurements of 4.76, 4.70 and 4.67 g cm<sup>-3</sup>. The density does not support the supposition that this sulfide is a Ba intercalated  $NbS_2$ .

The experimental density tells us that the chemical formula contained in the subcell is given by  $Ba_{Q.48}Nb_{2.71}S_{5.16}$  from the data of  $Z = 1$ ,  $V = 0.170$  nm<sup>3</sup>, density =  $4.71$  g cm<sup>-3</sup>,  $x = 5.67$ ,  $y = 10.8$  in  $BaNb_xS_y$ .

## 5. Conclusion

Seven unknown sulfides were found in the Ba–Nb–S system. One of them, whose chemical composition is  $\text{BaNb}_{5.67}\text{S}_{10.8}$ , could be prepared as a single pure phase by controlling the partial pressure of sulfur. The powder X-ray diffraction pattern could be indexed on the basis of a hexagonal cell. The electron diffraction pattern exhibits diffuse superspots. The sulfide showed temperature independent paramagnetism.

## References

- [1] P.C. Donohue and J.F. Weiher, *J. Solid State Chem.*, **10** (1974) 142.
- [2] J.S. Swinnea, H. Steinfink, L.E. Rendon-Diazmiron and M. Comezdaze, *J. Solid State Chem.*, **46** (1983) 367.
- [3] J.S. Swinnea, H. Steinfink, L.E. Rendon-Diazmiron and L. Banos-Lopez, *J. Solid State Chem.*, **56** (1985) 249.
- [4] M. Saeki and M. Onoda, *Bull. Chem. Soc. Jpn.*, **64** (1991) 2923.
- [5] H. Braune, S. Peter and V. Neveling, *Z. Naturforsch.*, **6a** (1951) 32.
- [6] M. Saeki, *Ceramics Japan*, **26** (1991) 1300.
- [7] M. Saeki, M. Onoda and M. Ohta, *Mater. Res. Bull.*, **28** (1993) 279.
- [8] K. Matsuura, T. Wada, T. Nakamizo, H. Yamauchi and S. Tanaka, *J. Solid State Chem.*, **94** (1991) 294.