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Preparation and Crystal Structure of a New Barium Niobium Sulfide, $Ba_9Nb_4S_{21}$

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A new barium niobium sulfide, $Ba_9Nb_4S_{21}$, was prepared by the reaction of CS_2 with a mixture of $BaCO_3$ and Nb_2O_5. Powder X-ray diffraction peaks and electron diffraction spots for the compound were indexable on the basis of a hexagonal cell with lattice parameters of a=6.9743(6) and c=21.599(2) Å. Refinement based on powder X-ray diffraction data suggested that the crystal structure belongs to the same series with those of $Ba_{16.5}Nb_9S_{42}$ and Ba_2NbS_5 reported by Swinnea et al.[1,2]

Three compounds, $BaNbS_3$, $Ba_{16.5}Nb_9S_{42}$, and Ba_2NbS_5 have been reported in the Ba–Nb–S system. $BaNbS_3$ is isostructural with $BaNiO_3$. According to Donohue,[3] this compound has a composition of $BaNb_{0.8}S_3$ with niobium vacancies, and the Nb atom has a formal charge of +5.

The existence of $Ba_{16.5}Nb_9S_{42}$ and Ba_2NbS_5 was reported by Swinnea.[1,2] The structures of these compounds will be described later in this paper.

In the Ba–Ta–S system, six compounds are reported as listed in Table 1. (In what follows these compounds are designated **a**, **b**, **c**, **d**, **e**, and **f**, for brevity). In the Ba–Nb–S system, types **b**, **d**, and **e** ($BaNbS_3$, $Ba_{16.5}Nb_9S_{42}$, and Ba_2NbS_5) have been found so far but types **a**, **c**, and **f** have not been reported yet. From the analogy of the chemical properties of tantalum and niobium, it is suggested that there is a possibility for the existence of those types of compounds in the Ba–Nb–S system. For this reason, the preparation of new barium niobium sulfides were attempted with the result that types **a** and **f** existed but type **c** was not found. This paper aims to report the preparation and crystal structure of type **f**, $Ba_9Nb_4S_{21}$, which has been unknown until now. The compound of type **a**, the structure of which has not yet been determined, will be described elsewhere.

Experimental

Preparation. The starting materials, $BaCO_3$ (purity 99%) and Nb_2O_5 (99.9%), were mixed in a ratio of Ba/(Ba+Nb)= 0.703. The mixture was placed in a furnace and kept at 750 °C for 3 d in an atmosphere of CS_2 carried by N_2 gas. After cooling to room temperature, the specimen was sealed in an evacuated silica tube with sulfur (1.4 wt%) and kept at 900 °C for 18 h. It was quenched in water.

Chemical Analysis. Chemical analysis was performed for Ba and Nb. The details are as follows. To determine Nb and Ba contents, about 1 g of the specimen was dissolved in 0.8 equiv HCl. Hydrogen sulfide gas was evolved as the specimen dissolved. Ba was dissolved in the solution while Nb remained as solid. The resulting precipitate consisting of the Nb-compound was separated from the solution by filtration, and was then ignited in air at 1000 °C to produce Nb_2O_5. The Nb content was obtained from the weight of Nb_2O_5.

The Ba ion in the solution was precipitated as $BaSO_4$ by adding 1 equiv H_2SO_4. The $BaSO_4$ was separated from the solution and weighed to obtain the Ba content.

The sulfur content was determined from the weight of the specimen and analytical values of Ba and Nb.

Diffraction Data. Powder X-ray diffraction data were collected with a step-scan procedure on a Rigaku RAD-2B-type diffractometer using counter-side monochromatized Cu $K\alpha$ radiation. Measurements were performed from $2\theta=5°$ to 100° with an interval of 0.02°. It took 35 seconds to measure one point. Electron diffraction patterns were taken for crushed particles using a 100 kV electron microscope (Hitachi 500-type).

Density. The density of 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 ml, and the weight of which was 1.5 g.

Table 1. Compounds in the Ba–Ta–S System

Type	a	b	c	d	e	f
Formula	$BaTa_2S_5$	$BaTaS_3$	$Ba_3Ta_2S_8$	$Ba_{16.5}Ta_9S_{39}$	Ba_2TaS_5	$Ba_9Ta_4S_{20}$
Crystal system	H	H	M	R	H	H
Lattice const. (Å)	a= 3.33 c=25.2	a=6.85 c=5.74	a=12.6 b= 6.85 c=11.9 β=108.9°	a= 6.88 c=41.8 (Hexagonal axis)	a= 6.93 c=49.4	a= 6.96 c=21.6
Electric property	Me	S	I	I	I	I
Ref.	4	3,5	6	7	8	9

H: Hexagonal, M: Monoclinic, R: Rhombohedral, Me: Metallic, S: Semiconductor, I: Insulator.

The bottle and the specimen in carbon tetrachloride were kept at reduced pressure to remove the bubbles attached on the specimen and on the surface of the bottle. The buoyancy was obtained by measuring weights in air and in carbon tetrachloride at 25±0.1 °C.

Results

The specimen obtained was of a pure single phase, and the powder X-ray diffraction pattern did not correspond to any known barium niobium sulfides. But the diffraction pattern was very close to that of type **f** in the Ba–Ta–S system, ($Ba_9Ta_4S_{20}$), with different peak intensities. This suggests that the type **f** compound also exists in the Ba–Nb–S system.

The spots of the electron diffraction patterns were indexed on the basis of a hexagonal cell.[10] The lattice parameters were calculated from the distances between two appropriate spots, resulting in a=7 Å and c=22 Å.

In the powder X ray diffraction patterns,[10] all the peaks that were detected were indexable on the basis of a hexagonal cell with lattice parameters a=6.9743(6) and c=21.599(2) Å. These values are in excellent agreement with those from the electron diffraction.

Table 2. Chemical Composition

Element	Ba/wt%	Nb/wt%	S/wt%
Experimental	54.1, 54.6, 54.6, 54.7, 54.7	15.7, 15.7, 15.8, 15.8, 15.5	
Average	54.5	15.7	29.8
Calcd for $Ba_9Nb_4S_{21}$	54.2	16.3	29.5

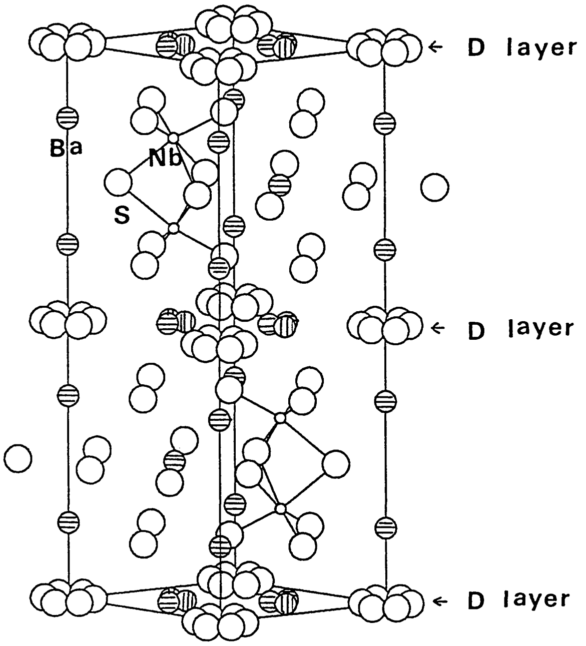

Fig. 1. Crystal structure of $Ba_9Nb_4S_{21}$.
(Niobium atoms are indicated by the small circles, barium atoms by hatched circles, and sulfur atoms by large circles.)

The results of chemical analysis of the compound are presented in Table 2. They agree with the calculated values of $Ba_9Nb_4S_{21}$ within experimental error. From the results, the compound is represented as $Ba_9Nb_4S_{21}$.

Observed densities were 4.25, 4.26 and 4.26 (g cm^{-3}), compared with the calculated one (4.16 g cm^{-3}, Z=1, V=910 Å). The specimen is an insulator, brown black in color, and generates H_2S gas by the reaction with water.

Discussion

We attempted to determine the crystal strucrure of the product ($Ba_9Nb_4S_{21}$) by refinement based on the powder X-ray diffraction pattern, which was similar to those of types **d** ($Ba_{16.5}Nb_9S_{42}$) and **e** (Ba_2NbS_5). This suggests that these three compounds belong to the same structure series.

The structures of types **d** and **e** reported by Swinnea and coworkers[1,2] are based on the stacking of BaS_3 layers in the sequence DABABDBCBCDCACA for type **d** ($Ba_{16.5}Nb_9S_{42}$) and CBDBABDBCBCDCACDCB for type **e** (Ba_2NbS_5), where the A, B, and C layers are hexagonal BaS_3 layers with Ba at (0,0,z), (2/3,1/3,z), and (1/3,2/3,z), respectively, and the D layer is a Ba-rich disordered layer in which Ba and S sites are partly occupied. The Nb atoms occupy interstices between A and B, B and C, and C and A layers, but there is no Nb atom between D and A, D, and B, and D and C layers. The structures are described in space group $R\bar{3}m$ for **d** ($Ba_{16.5}Nb_9S_{42}$) and $P6_3/mmc$ for **e** (Ba_2NbS_5).

It is assumed that the structure of $Ba_9Nb_4S_{21}$ belongs to the same series with types **d** and **e**. The structure, therefore, should have the same rule with those in stacking sequence. In addition, from the unit cell value in the c direction, it is found that 8 layers are contained in a unit cell. The chemical composition reveals that two of them are the D-layers. This information leads us to a single possible structure for $Ba_9Nb_4S_{21}$ shown in Fig. 1.

The structure refinement of the compound was attempted using a total pattern fit program RIETAN[11] based on the Rietveld method.[12] The refinement was performed for the powder X-ray diffraction pattern of $Ba_9Nb_4S_{21}$ based on the structure model given in Fig. 1, and performed for regions from d=4.4 to d=1.0 Å with 9 positional parameters, one overall temperature factor and one scaling factor. The diffraction peaks with d-values larger than 4.4 Å were ignored because it was impossible to obtain accurate intensities experimentally. The calculated pattern without the correction for the preferred orientation was in agreement with that observed (R_{wp}=16.0%, R_p=12.5%, R_I=9.1%, R_F=7.3%). See Ref. 13 for the definitions of the reliability factors R_{wp}, R_p, R_I, and R_F. Tables 3 and 4 give final values of the structure parameters and the interatomic distances.

Table 3. Crystal Data and Atomic Parameters for $Ba_9Nb_4S_{21}$

Crystal data (Hexagonal, space group $P6_3/mmc$ (No. 194)) a=6.9743(6) Å, c=21.599(2) Å, V=910 Å^3, Z=1 (According to the formula $Ba_9Nb_4S_{21}$)

Atomic parameters

Atom	Occupation	x	y	z
Nb	1.0	1/3	2/3	0.1686(8)
Ba(1)	1.0	0	0	0.1363(6)
Ba(2)	1.0	1/3	2/3	3/4
Ba(3)	0.25	0.367(2)	$2x$	−0.0070(6)
S(1)	1.0	0.494(3)	$2x$	0.120(1)
S(2)	1.0	0.159(4)	$2x$	1/4
S(3)	0.25	0.078(5)	$2x$	0.002(8)

$B(\mathrm{Nb})=B(\mathrm{Ba})=B(\mathrm{S})=3.4(2)$ Å^2.

Table 4. Selected Interatomic Distances (Å) in $Ba_9Nb_4S_{21}$[a)]

Nb–S1	3×2.21(4)	S1–Nb	3×2.21(4)
–S2	3×2.75(4)	–Ba1	6×3.51(4)
Ba1–S1	6×3.51(4)	–Ba2	6×3.49(4)
–S2	3×3.12(3)	–Ba3	[1]×3.02(4)
–S3	[3]×3.08(18)	–Ba3	[2]×3.39(4)
–S3	[3]×3.10(18)	–Ba3	[1]×3.07(4)
Ba2–S1	6×3.51(4)	–Ba3	[2]×3.46(4)
–S2	6×3.49(3)		

a) Distances between Ba3 and S3 are omitted because their sites are statistically occupied.

The diffraction profile observed was compared with the calculated one.[10)] The intensities calculated on the atomic parameter were compared with the integrated intensities obtained from the pattern.[10)]

The structure is based on the stacking of the D- and BaS_3-layers with a sequence DABADACA. Ba and S atoms are distributed statistically at the respective sites in the D-layer. The Nb atoms occupy interstices between A and B, B and C, and C and A layers, but there is no Nb atom between D and A, D and B, and D and C layers. The structure is described in the space group $P6_3/mmc$ (No. 194) with the atomic positions given in Table 3.

$Ba_9Ta_4S_{20}$,[9)] the structure of which has not yet been reported, is probably isostructural with this compound. (The refinement with the same structure model on the powder X-ray diffraction pattern of $Ba_9Ta_4S_{20}$ gave R_{wp}=12.7%, R_p=9.6%, R_I=10.8%, and R_F=6.6%).

The sulfur content in type **f** has different values in the Ba–Nb–S and Ba–Ta–S system, i.e., $Ba_9Nb_4S_{21}$ and $Ba_9Nb_4S_{20}$. They probably contain an identical amount of sulfur. The difference came from the experimental error.

From the results described above, it is concluded that there exists a previously unreported barium niobium sulfide, the chemical composition of which is $Ba_9Nb_4S_{21}$, and the refinement on the powder X-ray diffraction pattern supported the structure which belongs to the same series with the other compounds in the Ba–Nb–S system.

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