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Crystal Chemistry of the Ba–Nb–S System: A Layer Structure of Approximate Composition $Ba_2NbS_4(S_2)_{0.5}$

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Black platy crystals from the product of a reaction mixture of 6BaS : 3Nb : 7S reacted at 1000°C were hexagonal with $a = 6.909(4)$ Å, $c = 49.25(2)$ Å, $P6_3/mmc$, $Z = 10$. A pronounced subcell with $a = 6.91$ Å, $c = 5.5$ Å indicated that this was a layer structure consisting of stacking of close-packed BaS_3 layers. Three dimensional X-ray diffraction data were collected from a single crystal using monochromatized Mo$K\alpha$ radiation. From the 1535 measured reflections, 782 unique structure amplitudes were obtained of which 608 greater than $2\sigma(F)$ were used to solve the structure. The final $R = 0.1065$, $\omega R = 0.0793$; for 91 reflections with $l = 9n$, $R = 0.0397$ and for the 517 reflections $l \neq 9n$, $R = 0.138$. The structure is based on the stacking of close-packed BaS_3 layers with the sequence CBDBABDBC BCDCACDCB, where D designates a disordered layer. The disordered layers contain two crystallographically independent Ba with partial site occupancies and disordered S_2 and S ions. Nb occupy octahedral interstices and form two different arrangements; a unit consisting of 3 face-sharing octahedra and a unit of 2 face-sharing octahedra. These octahedral units are separated by the disordered layers. The Nb–Nb distances in the chain of 3 are 3.29 Å and they are 3.57 Å in the double unit.

Introduction

An ongoing program to investigate the phases formed in the Ba–Nb–S system has led to the recent report on the layer structure of a phase with approximate composition $Ba_4Nb_2S_9$ (*1*). A review of the literature by Swinnea *et al.* (*1*) concluded that the stoichiometries and crystal structures of the Ba–Ta and Ba–Nb chalcogenides are very uncertain. They appear to be layer structures formed by stacking of close-packed layers of BaX_3 with the transition metals occupying octahedral interstices. The structural investigation reported here is of a phase with approximate composition Ba : Nb : S = 2 : 1 : 5, very close to the previously reported composition 2 : 1 : 4.5.

The reaction conditions were identical to those described previously (*1*). A mixture in the ratio 6BaS : 3Nb : 7S contained in a graphite crucible was sealed in a Vycor ampule and heated at 1000°C for several days. The reaction product showed many well-formed, black platy crystals very similar to those of the $Ba_4Nb_2S_9$ phase as well as other irregular black crystal fragments. The powder diffraction diagram of the reaction

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product was complex, apparently a composite of several phases, none of which could be matched with the powder pattern of $Ba_4Nb_2S_9$. Several plates were selected and analyzed in an electron-beam microprobe. The results indicated a composition Ba : Nb : S approximately 2 : 1 : 3. A single crystal was mounted and Weissenberg and precession diagrams showed a hexagonal unit cell $a = 6.9$ Å and $c = 49$ Å. The a axis is essentially equal to the subcell a parameter of $Ba_4Nb_2S_9$ but c differs. The diffraction diagrams showed that this was also a layer structure and pronounced subcell reflections were observed indicating a c' parameter of 5.5 Å or $\frac{1}{9}c$. The subcell parameters are very similar to those reported for a phase $BaNb_{0.8}S_3$ for which no structural information is available (*2*). The similarity of the structural motif to that of $Ba_4Nb_2S_9$ was sufficiently compelling to us to determine the layer arrangement in detail. We were also very interested to learn whether the previous observation that only 3 face-sharing NbS_6 octahedra can exist contiguously in a layer structure will hold in this compound. We therefore proceeded with the crystal structure solution.

Structure Determination

Weissenberg and precession photographs of a single crystal showed the diffraction symmetry of this compound to be *6/mmm* with systematic absence $hhl: l = 2n + 1$, consistent with space groups $P6_3/mmc$, $P6_3mc$, and $P\bar{6}2c$. The first two space groups frequently occur for close-packed systems (*3*) and we decided to build a structure in the centrosymmetric group; an effort which was subsequently shown to be justified. A single crystal shaped like a pentagonal trapezoid with a base whose edges varied from 0.0128 to 0.0229 cm, the top face edges varied from 0.0088 to 0.0109 cm, and the height was 0.0074 cm, was mounted on an automated single-crystal diffractometer and data were collected to $\sin\theta/\lambda = 0.70$ using Mo$K\alpha$ radiation monochromatized with a graphite crystal. The diffractometer was operated in the ω-scan mode with scan rates varying from 1.5 to 5° min^{-1}. A least-squares refinement of 15 reflections whose 2θ values were precisely determined in the range 19–27° yielded the lattice parameters $a = 6.909(4)$ Å and $c = 49.25(2)$ Å. The measured intensities were transformed in the usual manner to structure factors and included an absorption correction $\mu_l = 12.3$ mm^{-1} based on an assumed unit cell content $Ba_{20}Nb_{10}S_{50}$. The transmission factors ranged from 0.32 to 0.51. Estimated errors of the intensities were calculated from

$$\sigma(F^2) = S[I_\mathrm{p} + 1/R^2(I_{\mathrm{B}_1} + I_{\mathrm{B}_2}) + (\mathrm{p}I)^2]^{1/2},$$

where I_p = number of counts accumulated during the scan of the peak, I_{B_1} = background counts on low 2θ side, I_{B_2} = background counts on high 2θ side, S = speed of scan in deg min^{-1}, R = ratio of total background counting time/scan time, $p = 0.02$. Of the 1535 reflections measured in $\frac{1}{12}$ of the reciprocal space volume 81 *hhl* had zero intensity due to the space group absence. Equivalent reflections contained in the remaining 1454 reflections were averaged to produce 782 unique reflections with $R = 0.039$. The structure was solved using 608 structure amplitudes greater than $2\sigma(F)$.

A direct methods procedure for $P6_3/mmc$ showed an E map which was consistent with close-packed BaS_3 layers with the alternating sequence CBCB . . . and Nb in the interstitial octahedral sites, yielding the stoichiometry $BaNbS_3$.[1] As expected, only the subcell reflections $hkl: l = 9n$ entered into this calculation and the true structure necessarily must differ from such an arrangement. There are 14 possible stacking sequences for close-packed BaS_3 layers in

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[1] The layer notation follows that in Ref. (*3*); an A layer has Ba in the 00z position, a B layer has Ba at $\frac{2}{3}\,\frac{1}{3}\,z$, and a C layer has Ba at $\frac{1}{3}\,\frac{2}{3}\,z$.

TABLE I

ATOMIC PARAMETERS (×10^4) AND TEMPERATURE PARAMETERS (×10^3) FOR $Ba_2NbS_4(S_2)_{0.5}$. (STANDARD DEVIATIONS IN PARENTHESES)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}[b] (Å^2)	Occupancy
Ba1	0	0	$\frac{1}{4}$	84(4)	84[a]	45(4)	42	0	0	71(2)	
Ba2	$\frac{1}{3}$	$\frac{2}{3}$	7001(1)	41(2)	41	19(2)	20	0	0	34(1)	
Ba3	$\frac{1}{3}$	$\frac{2}{3}$	5809(1)	30(1)	30	12(1)	15	0	0	24(1)	
Ba4	$\frac{1}{3}$	$\frac{2}{3}$	4713(1)	24(1)	24	45(2)	12	0	0	31(1)	
Ba5	$\frac{1}{3}$	$\frac{2}{3}$	3615(1)	110(5)	110	33(3)	55	0	0	84(3)	3.20(7)
Ba6	563(6)	$2x$	3562(1)	26(3)	49(5)	30(3)	25(3)	−3(2)	−6	33(3)	3.59(8)[c]
Nb1	0	0	$\frac{1}{2}$	32(3)	32	12(3)	16	0	0	26(2)	
Nb2	0	0	668(1)	42(2)	42	26(3)	21	0	0	36(2)	
Nb3	$\frac{1}{3}$	$\frac{2}{3}$	2862(1)	46(3)	46	48(4)	23	0	0	47(2)	
S1	4952(16)	$2x$	$\frac{1}{4}$	65(8)	51(10)	32(6)	25	0	0	51(6)	
S2	8354(11)	$2x$	6924(3)	49(5)	31(7)	153(11)	15(3)	8(5)	17	79(5)	
S3	8340(12)	$2x$	5878(2)	55(5)	48(8)	88(7)	24(4)	16(4)	32	64(5)	
S4	8359(8)	$2x$	4707(1)	27(3)	9(4)	37(4)	4(2)	−4(3)	−8	26(2)	
S5	$\frac{1}{3}$	$\frac{2}{3}$	1916(4)							5(8)[d]	2.00(18)
S6	4168(38)	$2x$	6406(7)							12(17)[d]	2.27(44)
S7	2448(24)	$2x$	6404(4)							28(11)[d]	4.44(49)

Note. The temperature factor is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2(U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*))]$.

[a] The omission of a standard deviation indicates a symmetry related quantity, i.e., $U_{22} = U_{11}$, $U_{11} = 2U_{12}$, $U_{13} = 2U_{23}$.

[b] $\frac{1}{3}$ (Trace of orthogonalized U_{ij} matrix).

[c] Based on occupancy of a 00z position.

[d] Isotropic refinement.

this space group (*4*) and we calculated R values for all possibilities. The values ranged from 52 to 72%. A number of electron density maps were calculated for stacking sequences having R values 52–60%. After many false starts a sequence having the Zhdanov symbol 211(1)112 seemed to offer the greatest promise for a successful solution of the structure (*3*). As expected Nb appeared in octahedral interstices forming a sequence of 3 face-sharing octahedra alternating with, and separated from, two face-sharing octahedra. The layers separating the Nb occupied octahedral sequences showed electron density due to disordered atoms, reminiscent of the observations in the crystal structure of $Ba_4Nb_2S_9$ (*1*). Electron density also appeared in the unoccupied trigonal site of the $Ba(2)S_3$ layers (see atom labeling in Table I). The peaks were assigned to Ba or S on the basis of their location in the structure and near neighbor environment. Least-squares refinements converged to the parameters shown in Table I. For 608 structure amplitudes greater than $2\sigma(F)$, $R = 0.1065$ and $\omega R = 0.0793$, $\omega = 4.2649/\sigma^2(F)$; for 91 reflections $hkl: l = 9n$ $R = 0.0397$ and for 517 reflections $hkl: l \neq 9n, R = 0.138$. The maximum $\Delta/\sigma = 0.023$. The scattering factors were for neutral atoms corrected for the real and imaginary parts of dispersion (*5*). The final difference electron density map showed a maximum peak of about 5 e^- Å^{-3} and a hole of about the same extent. Calculations were carried out using the program SHELX-76 and bond distances and angles were calculated using the program

BADTEA (*6*). Table II contains a list of observed and calculated structure factors.[2]

Discussion

The layers . . . CBDBABDBC . . . (D = disordered level) in the first half of the unit cell occur at the idealized values of $z = \frac{1}{36}, \frac{3}{36}, \ldots \frac{17}{36}$. The observation of electron density in the D levels at A and C sites leads to the inference that the true structure could have the sequence CBABABCBC. Models based on this arrangement would not refine. We also attempted to construct models in space group $P6_3mc$ for which seven possibilities exist (*4*), but none could be refined successfully. The structure as finally determined and illustrated in Fig. 1 consists of close-packed BaS_3 layers, $Ba(1)S_3$, $Ba(2)S_3$, $Ba(3)S_3$, and $Ba(4)S_3$. However, the stacking is not continuous along the *c* axis. Layers are bridged by Ba5 and Ba6 in trigonal prismatic coordination and apparently by disulfide and sulfide ions, S6–S7, and S7, respectively.

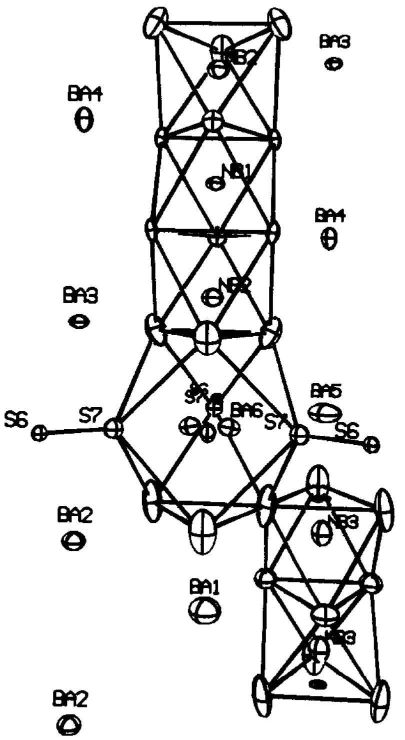

FIG. 1. View of the structure. The *c* axis is vertical and Nb1 is at 00½. The disordered level shown is at $z = 0.3615$. The disk represents S5. S atoms within a BaS_3 layer have the same designation as the Ba.

An examination of bond distances listed in Table III shows that S6–S7 is 2.06 Å and S2–S5 is 2.02 Å, typical of the S_2^{2-} ion. Electron density and difference electron density maps always showed scattering matter of about 8 electrons at $\frac{1}{3}\ \frac{2}{3}\ 0.1915$, labeled S5, in the center of a triad of S2 atoms. The S(2) atoms have a large U_{33} value which together with the density labeled S5 may be indicative of a disorder in the S(2) sites. The Nb3 ion occupies the octahedron formed by three S2 and three S1. The U_{33} thermal parameter for Nb3 is 58×10^{-3} which is 2 U_{33} for Nb2 and 3 U_{33} for Nb1 and may be due to the postulated disorder around the Nb3 site. Refinements in which the occupancy factor of Nb3 was allowed to vary always yielded full occupancy. It is also possible that the unexplained scattering density is due to an interstitial oxygen atom which could have been introduced occasionally into the structure. The local environment around Nb(3) could be drastically changed and perhaps become tetrahedral with either an oxygen at the apex or a S_2 ion formed by S_2–S_5 (*7*).

In order to test the significance of the scattering densities labeled S5, S6, and S7 a *R* factor ratio test was calculated for the hypothesis that some or all of these atoms are unnecessary. Eight models were examined at a significance level $\alpha = 0.005$, $n - m = 500$ (*5*) and the results are shown in Table IV. It is evident that S5, S6, and S7 repre-

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[2] See NAPS Document No. 04250 for 4 pages of supplementary materials from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, New York 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid.

TABLE III

BOND DISTANCES IN ÅNGSTROMS

6Ba1–S1	3.455(14)	6Nb1–S4	2.437(7)
6 –S2	3.454(12)	3Nb2–S3	2.241(12)
3Ba2–S1	3.203(11)	3 –S4	2.693(8)
6 –S2	3.475(9)	3Nb3–S1	2.632(13)
3 –S6	3.091(32)	3 –S2	2.278(12)
3 –S7	3.126(20)	1 –S5	1.094(19)
6Ba3–S3	3.472(10)		
3 –S4	3.248(7)		
3 –S6	3.108(32)	2S1–S1	3.356(29)
3 –S7	3.117(20)	2 –S1	3.554(29)
3Ba4–S3	3.533(11)	4 –S2	3.459(14)
6 –S4	3.455(7)	2 –S5	3.467(18)
3 –S4	3.504(8)	2S2–S2	3.413(19)
3Ba5–S2	3.337(11)	2 –S2	3.496(19)
3 –S3	3.198(11)	2 –S6	3.673(34)
3 –S6	2.994(38)	2 –S7	3.640(23)
6 –S7	3.580(20)	3 –S5	2.019(11)
1 –S5	2.618(19)	2S3–S3	3.440(22)
3 –Ba6	3.327(7)	2 –S3	3.469(22)
1Ba6–S2	2.723(13)	2 –S4	3.493(12)
2 –S2	3.376(13)	2 –S6	3.706(33)
2 –S3	3.651(12)	2 –S7	3.660(22)
1 –S3	3.053(12)	2S4–S4	3.492(12)
2 –S6	3.170(22)	2 –S4	3.401(14)
2 –S6	3.473(31)	2 –S4	3.509(14)
2 –S7	2.661(22)	2S6–S6	1.726(66)
1 –S7	3.604(26)	2 –S7	1.031(40)
2 –Ba6	1.166(11)	1 –S7	2.059(46)
		1 –S5	3.907(38)
		2S7–S7	1.839(44)
		Nb1–Nb2	3.288(5)
		Nb3–Nb3	3.562(11)

sent significant scattering densities although assignments to an atom species are uncertain.

The peak heights in the electron density maps which were eventually labeled Ba5 and Ba6 were always lower than those for the other Ba positions. Indeed, they are present on a statistical basis in the trigonal prismatic interstices formed by the Ba(2)S(2)$_3$ and Ba(3)S(3)$_3$ levels and serve to tie the close-packed levels together. The disulfide ion S(6)–S(7) or the sulfide ion S(7) cap the 3 rectangular faces of the trigonal prism (Fig. 1). The Ba6 appears disordered around the threefold axis, slightly displaced from the (00z) position. If it were located on the threefold axis then Ba5–Ba6 becomes about 4 Å while the distance to the displaced Ba6 atom furthest from Ba5 is 4.4 Å.

The disorder as reflected in the various occupancy factors is thought to be due to the choice of $P6_3/mmc$. The true crystal system is probably not hexagonal and may well be triclinic. The close-packed layers, BaS$_3$, and the Nb ions are located in the structure consistent with $P6_3/mmc$. The other atoms are forced to become "disordered" because their equipoints in the structure are not consistent with the chosen space group symmetry elements. The weighted reciprocal lattice was very carefully examined and no inconsistency with $P6_3/mmc$ was observed. Since the major part of the scattering matter in the unit cell is consistent with $P6_3/mmc$ this is not surprising.

The S_2^{2-} ion formed by S6–S7 in the disordered level has its center of gravity on the threefold axis and only one of the 3 orientations can be occupied in a given unit cell. Only one orientation is shown in Fig. 1. There are four such levels in the unit cell. The occupancy factors for S6 and S7 produce a total of about 7 atoms in the unit cell. If it is assumed that one S$_2$ exists at

TABLE IV

R-RATIO TEST FOR 8 MODELS CONTAINING COMBINATIONS OF ATOMS S5, S6, AND S7 AT $\alpha = 0.005$ AND $n - m = 500$

Atoms	*R*	ω*R*	b^a	*R*(calc.)	*R*(theor.)
All	0.1065	0.0793	0	1.0	
S5,S6	0.1254	0.0986	3	1.243	1.013
S6,S7	0.1326	0.1047	3	1.320	1.013
S5,S7	0.1159	0.0875	3	1.103	1.013
S5	0.1388	0.1112	6	1.402	1.019
S6	0.1435	0.1173	6	1.479	1.019
S7	0.1382	0.1088	6	1.372	1.019
None	0.1547	0.1267	9	1.598	1.024

[a] Definition: $b = N_{p_1} - N_{p_2}$, $N_{p_1} = 66$.

each level the occupancy factors should have been equal and provided for 8 atoms in the unit cell. The 2:1 ratio of S7:S6 could imply that at the temperature of the reaction only sulfide exists but during the slow-cooling process S_2 ions can be introduced. The difficulties of interpreting the meaning of the statistically occupied sites prevent the assignment of a definite stoichiometry to this compound.

The octahedra around Nb share faces. Nb1 and Nb2 form a trinuclear cluster. Nb1 is at the center of the octahedron with equal Nb–S distances of 2.43 Å. The Nb2 and Nb2′ are displaced 0.6 Å from the center so that Nb1–Nb2 becomes 3.29 Å. This was also observed in the structure of $Ba_4Nb_2S_9$ and it may be a general principle that this displacement must occur because of the electrostatic repulsion between two in line Nb^{5+} and limits such a cluster to at most 3 octahedral units. Nb3 and its mirror related atom Nb3′ are located in face-sharing octahedra but displaced from the center by 0.44 Å so that Nb3–Nb3′ is 3.57 Å.

If electrostatic repulsion prevents Nb^{5+} or Ta^{5+} from being closer than about 3.3 Å then the reported structure for $BaTaS_3$ (*8*) may only be realizable for tetravalent cations. Its space group is $P6_3/mmc$ with a = 6.846 Å and c = 5.744 Å and the structure consists of stacking of BCBC . . . layers of BaS_3 with Ta in octahedral interstices of face-sharing octahedra forming an infinite chain. The Ta–Ta distances are 2.872 Å. The authors remark on the fact that unlike $BaVS_3$ which has the same structure and is metallic, $BaTaS_3$ is a semiconductor.

Donohue and Weiher (*2*) observe that "Single phase material was obtained only when starting cation ratios were Ba/0.8 Ta or Ba/0.8 Nb," i.e., pentavalent transition metal cations. The mixtures in which the ratio of barium to transition metal was 1:1 always yielded a two-phase product. Unfortunately no single-crystal X-ray study was carried out on this phase and it would be of great interest to determine this structure.

Acknowledgments

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