The Crystal Structure of the 42-Å Subcell of a Layer Structure with Approximate Composition $Ba_4Nb_2S_9$

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Platy crystals from the products of a mixture 4 Bas : 2 Nb : 5 S reacted at 1000°C have cell constants a = 13.754(3) Å, c = 83.73(2) Å, $R\bar{3}m$. The reciprocal lattice had a pronounced subcell with dimensions a = 6.877(1) Å, c = 41.84(1) Å, same space group. Three dimensional X-ray diffraction data were collected using monochromatized Mo$K\alpha$ radiation and of 5051 measured intensities 1892 were considered observed. From the set of observed intensities 611 reflections having all even indices were used to refine the crystal structure of the 42 × 7-Å subcell. The final R = 0.036 and ωR = 0.052 for the 611 observed amplitudes and R = 0.046, ωR = 0.052 for all 711 amplitudes of the subcell. The structure is based on the stacking of hexagonal BaS_3 layers with the sequence $D\,A\,B\,A\,B\,D\,B\,C\,B\,C\,D\,C\,A\,C\,A\,D$. The D layer denotes a disordered level and occurs at $z = 0$, $\frac{1}{3}$, and $\frac{2}{3}$. The different letters for the ordered layers are based on the Ba positions in that layer. The Nb ions occupy octahedral interstices and form a unit of three face sharing octahedra parallel to c. The column is terminated above and below by disordered levels. The Nb–Nb distances are 3.22 Å, causing displacement of Nb from the centers of the two outside octahedra. One Ba is in the center of a triangular orthobicupola formed by 12 S atoms. The other Ba is in the center of a hexagon of 6 S with 3 additional S above this layer forming $\frac{1}{2}$ of a cuboctahedron. The lower half consists of a disordered layer of atoms. The Nb–S distances are 2.279, 2.433, and 2.683 Å; Ba–S distances vary between 3.1 and 3.5 Å. The subcell content based on the ordered structure only is $Ba_{12}Nb_9S_{36}$. The placement of disordered Ba and S at $z = 0$, $\frac{1}{3}$, and $\frac{2}{3}$ levels of the subcell leads to the unlikely composition $Ba_{16.5}Nb_9S_{42}$. The ordered structure most likely has a composition $Ba_4Nb_2S_9$, $z = 36$, so that the subcell composition should be $Ba_{18}Nb_9S_{40.5}$. The completely ordered structure has not been solved.

Introduction

The structures of the compounds in the ternary system Ba–M–X (M = Nb, Ta; X = S, Se) have not been well documented. Aslanov (*1, 2*) described the synthesis of BaTaSe$_3$ and BaTaS$_3$ and indexed their X-ray powder diffraction patterns based on

hexagonal unit cells and suggested that they were isostructural with CsNiCl$_3$, $P6_3/mmc$. Gardner *et al.* (*3*) reported the crystal structure of BaTaS$_3$, $P6_3/mmc$, from single crystal X-ray data. This structure was based on the hexagonal close packing of BaS$_3$ layers with the tantalum cations in one fourth of the octahedral voids between

the close-packed layers. This packing leads to infinite chains of face sharing TaS_6 octahedra with 2.872 Å Ta–Ta interatomic distances, less than the 2.98-Å intermetallic contact for tantalum. Donohue and Weiher (*4*) reported the preparation of several Ba–Ta–S and Ba–Ta–Se compounds with various stoichiometries near $BaTaX_3$. They also reported the occurrence of a compound in the Ba–Nb–S system, $BaNb_{0.8}S_3$, and gave the hexagonal cell parameters, a = 6.831 Å, c = 5.764 Å, but did not provide any structural information. We have prepared a phase which, when analyzed by energy dispersive X-ray fluorescence, yielded an approximate stoichiometry $Ba_4Nb_2S_9$. The crystals were excellent and we report here the results of a single crystal X-ray structure investigation.

Experimental

BaS, Nb, and S constituted the starting materials for the synthesis of this ternary compound. Yellow BaS, containing free S, was treated under a current of H_2 at 500°C for 2 days. After treatment, the X-ray powder diffraction pattern of now white BaS showed no extraneous lines. The Nb and S used were nominally 99.9% pure. A mixture of BaS, Nb, and S in the ratio 4 : 2 : 5 was placed in a graphite ampoule which was in turn sealed in an evacuated vycor tube. The mixture was heated at 1000°C for several days and then allowed to cool to room temperature by turning off power to the furnace. Microprobe analysis of platy single crystals picked from the black, highly crystalline reaction product confirmed the approximate composition, $Ba_4Nb_2S_9$. The powder diffraction pattern of this material did not correspond to any known phase. The density of several pieces was measured by immersion in benzene and was 4.16(5) g/cc.

Weissenberg and Buerger precession photographs of a single crystal taken from

the reaction product showed that the diffraction symmetry of this compound is $\bar{3}m$, with systematic absences $hkil$, $-h + k + 1 \neq 3$ n, consistent with space groups $R3m$, $R32$, or $R\bar{3}m$. The photographs also revealed the presence of a pronounced subcell of dimensions $a_{subcell} = a/2 \simeq 6.9$ Å and $c_{subcell} = c/2 \simeq 42$ Å. This crystal was transferred to a Syntex P2₁ single crystal diffractometer and three-dimensional X-ray diffraction data were collected to sin θ/λ = 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 30 reflections whose 2θ values were precisely determined in the range $25° < 2\theta < 30°$ yielded the lattice parameters a = 13.754(3) Å, c = 83.73(2) Å; the subcell parameters were $\frac{1}{2} a$ and $\frac{1}{2} c$. The measured intensities were transformed into structure factors through application of Lorentz, polarization, and absorption corrections using μ_l = 132 cm⁻¹. The absorption correction ranged from 0.30 to 0.65. Estimated errors of the intensities were calculated from

$$\sigma(F^2) = S \sqrt{I_p + 1/R^2(I_{B_1} + I_{B_2})}$$

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, and R = ratio of total background counting time/scan time. Of the 5051 measured intensities, 1892 were considered observed on the basis that the structure factor F exceeded $2\sigma(F)$.

Structure Determination of Subcell

Of the 1892 observed intensities, 611 reflections having all even Miller indices were used in the refinement of the 42 × 7-Å subcell. After the indices of these reflections were halved, the direct method employing the program Multan was used to calculate

TABLE I

$Ba_{16.5}Nb_9S_{42}$ SUBCELL POSITIONAL PARAMETERS AND THERMAL VIBRATIONS $(\times 10^5)^a$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ba(1)	0	0	20057(3)	1198(19)	1198(19)	48.4(.8)	599(10)	0	0
Ba(2)	0	0	7052(3)	1359(19)	1359(19)	19.3(.6)	679(10)	0	0
Nb(1)	0	0	42137(5)	1791(35)	1791(35)	38(1)	895(17)	0	0
Nb(2)	0	0	$\frac{1}{4}$	1717(44)	1717(44)	31(1)	858(22)	0	0
S(1)	49723(20)	−49723(20)	20138(7)	1469(51)	1469(51)	44(2)	1089(57)	−15(4)	15(4)
S(2)	50300(26)	−50300(26)	6289(11)	1793(65)	1793(65)	119(4)	1162(74)	74(7)	−74(7)
Ba(3)[b]	4156(25)	−4156(25)	33119(6)	2024(65)	2024(65)	24(1)	362(59)	−14(4)	14(4)
S(3)[c]	−8892(74)	8892(74)	16(22)	2860(214)	2860(214)	26(4)	2068(209)	−10(14)	10(14)

Note. The temperature factor is $\exp(-(B_{11}H^2 + B_{22}K^2 + B_{33}L^2 + 2(B_{12}HK + B_{13}HL + B_{23}KL)))$

[a] Standard deviations are in parentheses.

[b] The occupancy of Ba(3) is 0.249(1)

[c] The occupancy of S(3) is 0.332(4)

phases for an initial electron density map which revealed two of the barium positions. Phases based on these positions were generated and used in the calculation of the next Fourier map which revealed the locations of the remaining ordered atoms in the subcell. A subsequent Fourier map revealed additional scattering matter at $z = 0$ and at the symmetry related levels $z = \frac{1}{3}, \frac{2}{3}$. This density was interpreted as due to two crystallographically disordered atoms labeled Ba3 and S3 in Table I. A full matrix least squares refinement minimizing $\Sigma\omega(F_0 - F_c)^2$ with $\omega = [\sigma(F_0)^2]^{-1}$ using the University of Texas modified Doeden–Ibers program NUCLS was carried out using isotropic temperature factors and values of the scattering factors for neutral atoms corrected for the real and imaginary parts of dispersion (5). For the 611 observed reflections, R was 0.095 and ωR was 0.115. Changing to anisotropic temperature factors lowered R to 0.036 and ωR to 0.052 for the observed reflections and R to 0.046 and ωR to 0.052 for all 711 reflections of the subcell. The observed and calculated subcell structure factor amplitudes are listed in Table II.[1] This listing contains also the com-

[1] See NAPS document No. 04046 for 24 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00

plete set of 5051 reflections with their standard deviations. A final difference electron density map showed random peaks and depressions with the highest values being ± 1.9 e$Å^{-3}$. Table I lists the final atomic parameters and the final stoichiometry of the subcell as $Ba_{16.5}Nb_9S_{42}$. This unit cell content corresponds to a calculated density of 4.31 g/cc.

Discussion

The subcell or average structure of $Ba_{16.5}Nb_9S_{42}$ is shown in Fig. 1 and Table III gives the most important interatomic distances and angles. The Ba–S distances are essentially due to ionic interactions. The Ba2–S3 and Ba3–S distances cannot be considered as meaningful because of the disorder of the $z = 0, \frac{1}{3}$, and $\frac{2}{3}$ levels in which Ba3 and S3 are located.

The structure is based on the stacking of hexagonal BaS_3 layers as follows (numbers in parentheses are $z \times 10^3$): D (0), A (063), B

DISORDER Z=1

A

C

A

C

DISORDER Z=2/3

C

B
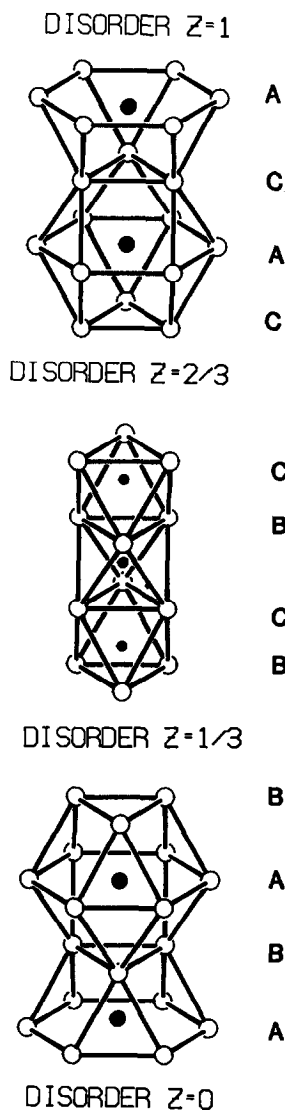
C

B

DISORDER Z=1/3

B

A

B

A

DISORDER Z=0

FIG. 1. The structure of the 42-Å subcell. The c axis is vertical and the view is along the a axis. Layer types are indicated by A, B, C. Open circles represent S, large filled circles Ba, and the small filled circles are Nb.

(123), A (202), B (267), D (333), B (398), C (465), B (535), C (600), D (667), C (728), A (799), C (868), A (934), D (1000), where D is a disordered layer; A is a layer with barium at 0, 0, z and sulfurs at $\frac{1}{3}$, 0, z; $\frac{1}{3}$, $\frac{1}{3}$, z; and 0, $\frac{1}{3}$, z; B is a layer with barium at $\frac{2}{3}$, $\frac{1}{3}$, z and sulfurs at $\frac{1}{3}$, $\frac{1}{3}$, z; $\frac{1}{3}$, $\frac{2}{3}$, z; and $\frac{2}{3}$, $\frac{2}{3}$, z; and C

represents a layer with barium at $\frac{1}{3}$, $\frac{2}{3}$, z and sulfurs at $\frac{1}{3}$, $\frac{1}{3}$, z; $\frac{2}{3}$, $\frac{1}{3}$, z; and $\frac{2}{3}$, $\frac{2}{3}$, z.

The coordination polyhedron around Ba(1) consists of 12 sulfur atoms at the vertices of a triangular orthobicupola with the cation in the center of the sulfur hexagon (Fig. 1). Ba(2) is coordinated by 9 ordered sulfurs and by disordered atoms at $z = 0$, $\frac{1}{3}$, and $\frac{2}{3}$. Thus, this cation is at the center of an incomplete triangular orthobicupola and would require 3 more ordered sulfurs to complete this type of coordination polyhedron. To complete the coordination polyhedron in this space group, two different BaS$_3$ layer types would be required at the same level of z, e.g., both B and C type layers at $z = 0$. This leads to inconsistencies at $z = 0$, $\frac{1}{3}$, and $\frac{2}{3}$ and thus to disordered Ba–S layers at these levels.

The niobium ions occupy octahedral interstices in the sulfur framework. Columns

TABLE III

BOND DISTANCES AND ANGLES FOR THE SUBCELL STRUCTURE

Bond distances (Å)			
Ba(1)–6S(1)	3.439(1)	Nb(2)–6S(1)	2.433(2)
3S(1)	3.511(3)		
3S(2)	3.513(3)	Ba(3)– S(2)	3.119(4)
		S(2)	3.568(2)
Ba(2)–3S(1)	3.267(2)	S(2)	2.930(4)
6S(2)	3.454(1)	S(2)	3.388(2)
3S(3)	3.142(5)	S(3)	3.467(2)
3S(3)	3.129(5)	S(3)	3.233(3)
		S(3)	3.407(2)
Nb(1)–3S(1)	2.683(2)	S(3)	2.700(1)
3S(2)	2.280(2)		
		Nb(1)–Nb(2)	3.291(20)
		Ba(3)–Ba(3)	0.858(1)
		–Ba(3)	2.986(1)

Angles (°)	
S(1)–Nb(1)–S(1)	78.16(7)
S(1)–Nb(1)–S(2)	89.66(6)
S(1)–Nb(1)–S(2)	164.2 (1)
S(2)–Nb(1)–S(2)	100.35(8)
S(1)–Nb(2)–S(1)	88.06(7)
S(1)–Nb(2)–S(1)	180.00(8)

of three face sharing NbS_6 octahedra are formed and are terminated above and below by disordered sulfur levels. While Nb(2) is located at the center of the central octahedron, Nb(1) are displaced from the centers of the outer octahedra by 0.39 Å. This arrangement makes the Nb–Nb interatomic distance 3.22 Å instead of 2.87 Å, which is the distance between octahedral centers, and is less than the 2.98-Å intermetallic contact distance for niobium. Thus, this structure does not suffer from the same short metal–metal distance problem that Gardner's $BaTaS_3$ structure exhibits. The 3.26-Å Nb–Nb distance also limits to three the number of face sharing octahedra that can be accommodated. Increasing the number of octahedra in the column to 5 instead of 3 would require octahedral faces at $z = 0$, $\frac{1}{5}$, and $\frac{3}{5}$ (disorder levels) and the 3.26-Å Nb–Nb distance would place niobiums at a distance of only 0.4 Å from this hypothetical face giving much too short Nb–S distances of about 2 Å and a displacement of the niobiums of about 1 Å from the octahedral centers.

The disordered "average" structure is obtained by folding the entire cell of this compound into $\frac{1}{8}$ of the volume. The entire cell, with a volume eight times that of the averaged structure, must contain fully ordered atoms. Several models of an "unfolded" structure were used and refinement using the full set of 1892 X-ray intensities were carried out but without success. It may well be that the atoms labeled barium and sulfur in the disordered layers are interchanged in the subcell structure for the following reason. In the subcell there are the following ordered atoms: 12Ba, 9Nb, and 36S. In the disordered layer there are a total of 10.5 atoms in two positions, 4.5 of one type and 6 of the other. The magnetic susceptibility of this compound was measured using a Faraday balance and the compound is diamagnetic indicative of pentavalent Nb. The following equations can be formu-

lated to balance charge and total number of atoms:

$$x + 6 = 10.5$$
$$2x - 2y + 12(2) + 9(5) - 36(2) = 0$$

or

$$x - y = \frac{3}{2}$$

where x is the number of barium atoms and y is the number of sulfur atoms in the disordered layer. Solving these two equations simultaneously gives $x = 6$ and $y = 4.5$ or the composition $Ba_{18}Nb_9S_{40.5}$. This composition would correspond exactly to the $Ba_4Nb_2S_9$ stoichiometry obtained by microprobe analysis, and the contents of the 84 Å cell would then be $Ba_4Nb_2S_9$, $z = 36$. Such an approach was tried in the subcell refinement but instead of converging to $Ba_{18}Nb_9S_{40.5}$, the refinement converged to $Ba_{28.7}Nb_9S_{37.6}$ with 16.7 disordered Ba atoms and 1.6 disordered S atoms.

The unfolding of the averaged structure will be difficult. Assuming that the Ba–S layers of the unfolded structure remain the same as in the subcell, one finds that these layers become Ba_4S_{12} layers and contain Ba atoms at 0, 0, z and $\frac{1}{3}$, $\frac{1}{3}$, z or positions 6c and 18h in $R\bar{3}m$ and S atoms at $\frac{1}{4}$, $-\frac{1}{4}$, z, (18h); $-\frac{1}{4}$, $\frac{1}{4}$, z (18h); and $\frac{1}{4}$, $\frac{1}{4}$, z (36i). This leads to three different types of layers at z and $-z$, $z + \frac{1}{3}$ and $-(z + \frac{2}{3})$, and $z + \frac{2}{3}$ and $-(z + \frac{1}{3})$. Two stacking sequences for these layer types have been tried in order to "build" the 84-Å structure. The first assumed that Nb(2) remains at 0, 0, 0.500 and is at the center of a 3-unit octahedral chain, and the center of the next 3-unit chain is located at 0, 0, 0. The second stacking sequence assumed that the disordered layers remained at $z = 0$ and appear again at $z = 0.500$, and the 3-unit octahedral chains are centered about $z = 0.250$ and 0.750. Both attempts lead to good agreement for the subcell reflections ($R \simeq 0.1$ with isotropic temperature factors), but poor agreement for the reflections containing odd Miller in-

dices ($R \simeq 0.3$). None of the models in which Ba and S are placed in fixed positions at the levels which exhibit disorder could be refined. The agreement between calculated and observed $F(hkl)$, for h, k, and l all even is almost unaffected by different arrangements of Ba and S at the disordered levels, i.e., the subcell structure, as expected, determines these amplitudes and phases. The perturbation caused by the correct, unfolded structure for these reflections is negligible. However, for the other type of reflections these atoms are essentially the only ones that affect amplitudes and phases. No further work is intended on this structure.

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