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The Crystal Structure of "$Ba_2Fe_4S_5$": A Two-Dimensional Array of FeS_4 Tetrahedra

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The crystal structure of a compound with a nominal composition $Ba_2Fe_4S_5$ was determined from 432 observed structure amplitudes. The lattice constants are a = 4.016(2) Å, b = 9.616(4) Å, c = 6.514(4) Å, *Pmmn*, $Z = 1$. The structure consists of BaS_6 trigonal prisms that share triangular faces to form infinite columns parallel to a. Zig-zag chains of Fe are formed parallel to b by filling the tetrahedral interstices. The structure can also be viewed as an infinite two-dimensional plane of FeS_4 tetrahedra formed by the sharing of two edges of a face in the $\pm a$ directions and connecting by corner sharing in the $\pm b$ directions. The Ba are in the trigonal prismatic interstices. The apical sulfur atom shows an anomalously large temperature factor and has a 50% site occupancy. On the basis of full occupancy of that site the composition corresponds to $BaFe_2S_3$. This structure is closely related to the previously reported $BaFe_2S_3$ and may be an averaged structure due to twinning of a polymorph of $BaFe_2S_3$.

Introduction

During the investigation of the Ba–Fe–S phase diagram, a new phase was observed to crystallize in the triangle BaS–FeS–Fe. Systematic variations in the proportions of reactants BaS, FeS, and Fe showed that the composition could be narrowed to the Fe–FeS–Ba_2FeS_3 triangle. The phase was stable between 700 and 1000°C and coexisted with $BaFe_2S_3$. Thermodynamic equilibrium was never obtained and the compound was not prepared as single-phase material. Numerous experiments in which ratios of starting compositions of Fe, FeS, and BaS were varied yielded the unknown phase as a major component when BaS : FeS : Fe equaled 1 : 1 : 1 (*1*). Energy dispersive X-ray spectroscopy yielded a stoichiometry $BaFe_{1.7}S_2$ while quantitative chemical analysis gave a result of $BaFe_2S_{2.1}$. The Mössbauer spectrum showed only one quadrupole split absorption line with an isomer shift consistent with Fe^{2+} in tetrahedral sulfur environment (*2*). A single crystal was selected from the black, highly crystalline reaction product and a three-dimensional X-ray diffraction structure analysis was carried out.

Structure Determination

Weissenberg and Buerger precession photographs of a single crystal taken from the reaction product showed that the diffraction symmetry of this compound is *mmm*, with systematic absences $hk0$, $h + k = 2n + 1$, consistent with space groups $Pmn2_1$ and *Pmmn*. The crystal was trans-

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TABLE I

"$Ba_2Fe_4S_5$" POSITIONAL PARAMETERS ($\times 10^4$) AND THERMAL VIBRATIONS ($\times 10^5$). STANDARD DEVIATIONS ARE IN PARENTHESES

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ba(1)	$\frac{1}{4}$	$\frac{1}{4}$	5279(1)	106(4)	29(1)	55(1)	0	0	0
Fe(1)	$\frac{1}{4}$	9178(1)	8792(1)	143(5)	29(1)	53(2)	0	0	−9(1)
S(1)	$\frac{1}{4}$	9613(1)	2354(2)	123(7)	31(1)	47(2)	0	0	2(1)
S(2)[a]	$\frac{1}{4}$	$\frac{3}{4}$	7318(9)	387(34)	74(6)	161(12)	0	0	0

[a] The occupancy of S(2) is 0.530(3). The temperature factor is $\exp(-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2(B_{12}hk + B_{13}hl + B_{23}kl)))$.

ferred to a Syntex $P2_1$ single-crystal diffractometer and X-ray data to a value of $2\theta = 60°$ were collected using Mo$K\alpha$ radiation monochromatized with a graphite crystal. A least-squares refinement of 25 reflections whose 2θ values were precisely determined in the range $15° < 2\theta < 30°$ yielded the lattice parameters $a = 4.016(2)$ Å, $b = 9.616(4)$ Å, $c = 6.514(4)$ Å. The measured intensities were corrected for Lorentz polarization, and absorption using $\mu_l = 144$ cm^{-1}. The absorption correction ranged from 0.10 to 0.32. Estimated errors of the intensities were calculated from $\sigma(F^2) = S[I_p + 1/R^2(I_{b_1} + I_{b_2})]^{1/2}$, where I_p is the 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 = scan speed in deg/min, and R = ratio of total background counting time to scan time. Of the 441 measured intensities 432 were considered observed on the basis that F exceeded $2\sigma(F)$.

The 432 observed intensities were used to calculate a three-dimensional Patterson map, and the Harker line $\frac{1}{2}$, $\frac{1}{2}$, w enabled us to locate the position of a barium atom at $\frac{1}{4}$, $\frac{1}{4}$, 0.530. Assumed Ba–Fe interactions permitted the placement of an iron atom in position 4e of $Pmmn$. Phases based on these positions and used in the calculation of an electron density map led to the location of the two remaining sulfur positions. Full-matrix least-squares refinement using the program NUCLS and anisotropic temperature factors for all atoms converged to $R = 0.031$ and $\omega R = 0.038$ for the observed reflections. Values of the scattering factors for neutral atoms, corrected for the real and imaginary parts of dispersion, were used (*3*). A final difference electron density map showed depressions of about 3e Å^{-3} near Ba and of about 1.5e Å^{-3} near Fe positions. Table I lists the final atomic parameters.

The initial structure refinements with full occupancy of the S(2) site produced a very large value of the thermal vibration ellipsoid and R was 0.051, $\omega R = 0.079$. Refinement was then carried out in which the temperature factors of S(2) were set to the same values as those of S(1) and the occupancy of S(2) refined. The resulting R was 0.036, $\omega R = 0.050$, and the occupancy factor converged to 0.4. Varying the occupancy and temperature factors simultaneously led to the results shown in Table I. Table II lists F_{obs} and F_{calc} resulting from these parameters.[1]

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[1] Supplementary material is available from Dr. H. Steinfink and/or NAPS. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 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. Institutions and Organizations may order by purchase order. However, there is a billing and handling charge for this service of \$15. Foreign orders add \$4.50 for postage and handling, for the first 20 pages, and \$1.00 for additional 10 pages of material. \$1.50 for postage of any microfiche orders.

Discussion

The bond distances and angles are listed in Table III. It is evident that Ba–S(2) and Fe–S(2) distances are impossibly short and the stoichiometry $Ba_2Fe_4S_5$, based on the structural analysis, is difficult to accept. The Mössbauer isomer shift of 0.672 mm/sec (with respect to Fe) and $\Delta E = 1.57$ mm/sec as well as the Fe–S(1) distances all indicate Fe^{2+} (*2*).

TABLE III

BOND DISTANCES AND ANGLES

Distances (Å)			
Ba(1)–8S(1)	3.247(0)	S(1)–4S(1)	3.741(0)
–4S(1)	3.367(1)	–4S(1)	4.017(0)
–4S(2)	2.626(0)	–4S(1)	4.059(0)
Fe(1)–4Fe(1)	3.001(0)	–2S(1)	4.065(2)
–2Fe(1)	3.228(1)	–8S(2)	3.433(0)
–4Fe(1)	4.017(0)	–4S(2)	3.820(1)
–2S(1)	2.358(2)	–4S(2)	3.860(1)
–4S(1)	2.438(0)	S(2)–2S(2)	4.017(0)
–4S(2)	1.879(1)		
Angles (°)			
4 S(1)–Fe(1)–S(1)	111.0(0)		
16 S(1)–Fe(1)–S(2)	104.7(0)		
8 S(1)–Fe(1)–S(1)	102.5(1)		

The structure consists of infinite columns of BaS_6 trigonal prisms parallel to *a* formed by sharing of the triangular faces. The *c* axis periodicity encompasses two adjacent columns rotated 180° with respect to each other and displaced by $\frac{1}{2}a$, Fig. 1. Zig-zag chains of Fe parallel to *b* fill the tetrahedral interstices, two at $x = \frac{1}{4}$ and two at $x = \frac{3}{4}$. The stoichiometry of this phase based on full site occupancy by S(2) is $BaFe_2S_3$ so that this would be a polymorph of the previously described $BaFe_2S_3$ structure (*4*, *5*). If alternating rows of BaS_6 prismatic columns are translated by $\frac{1}{2}b$ the prism arrangement matches that of $BaFe_2S_3$. After this translation the Fe atoms at $x = \frac{1}{4}$ and $\frac{3}{4}$ are about 1.5 Å apart along the *c* axis. A shortening of the *c* axis so that the Fe atoms superimpose in the (100) projection will reproduce the $BaFe_2S_3$ structure. The $BaFe_2S_3$ structure

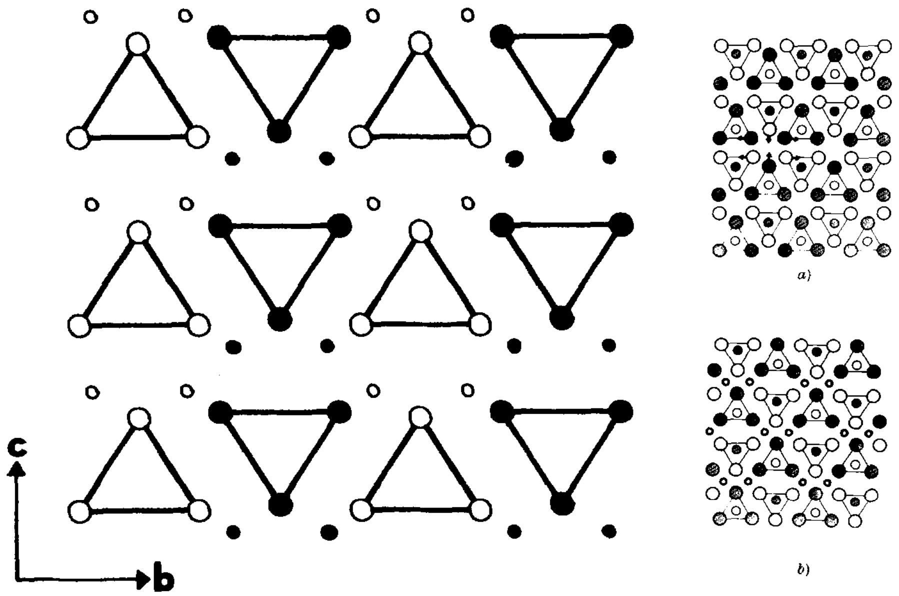

FIG. 1. Projection of the structure along [100]. Large open circles represent S at $x = \frac{1}{4}$, large solid circles are S at $x = \frac{3}{4}$. Smaller open and filled circles are Fe at $x = \frac{1}{4}$ and $x = \frac{3}{4}$, respectively. The inset shows (a) trigonal prisms as arranged in the $SnNi_3$ structure and (b) the $BaFe_2S_3$ structure.

will also be achieved by rotating one row by 180° around an axis parallel to *b* and then compressing *c* to superimpose the Fe atoms.

The structure can also be described in terms of the articulation of FeS_4 tetrahedra, Fig. 2. Infinite planes of tetrahedra are formed by sharing two edges of one face in the $\pm a$ directions and corner sharing via an apical sulfur atom in the $\pm b$ directions. The Ba^{2+} ions are in trigonal prismatic interstices and hold the layers of tetrahedra together into a three-dimensional structure.

The integrity of the structure appears to depend on the presence of S(2) and it is unlikely that ½ of the sites can remain unoccupied and still produce a stable crystal. No diffuse scattering was observed in precession or Weissenberg photographs nor was there any evidence of twinning or of a larger unit cell than reported. If twinning produces exact superposition of the reciprocal lattices it would go undetected and the resultant structure would be an average of the individual structures. The *b* and *c* lattice constants are nearly three times and twice 3.23 Å, respectively. This corresponds to the Fe–Fe separation between atoms along *b* in the same *x* plane. Integral multiples between lattice constants are frequently due to twinning and this observation in conjunction with the 50% S(2) site occupancy leads us to suggest that this is an average structure of a $BaFe_2S_3$ polymorph. It is evident from the impossibly short Ba–S(2) and Fe–S(2) distances that the S(2) spatial parameters represent average values due to twinning of the true structure. Models were constructed in which S(2) was displaced and various space group requirements, e.g., $\bar{1}$, were relaxed. None of these models refined successfully. Since the data are from a composite crystal the inability to converge to a "correct" structure is to be expected. We attempted to search for untwinned crystals and took Weissenberg and precession photographs of a number of different crystals. In all cases the geometry and intensities of the reciprocal lattices were identical. It is noteworthy that we were unable to prepare single-phase material. The highest yield of this material was obtained when the starting composition consisted of BaS : FeS : Fe near 1 : 1 : 1. Some Fe and a considerable amount of $BaFe_2S_3$ were always present (*1*). The equilibrium relationship between this material and $BaFe_2S_3$ remains unknown and we do not intend to pursue this problem further.

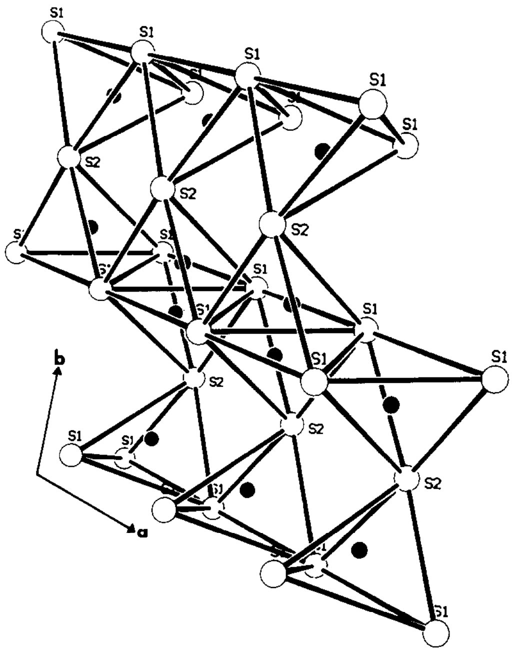

FIG. 2. A two-dimensional layer of FeS_4 tetrahedra. The *b* axis is vertical.

Acknowledgments

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