# The Crystal Chemistry of Phases in the Ba–Fe–S and Se Systems*

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The crystal structures of a number of new phases synthesized in the Ba–Fe–S and Se systems were investigated by X-ray diffraction techniques. $Ba_2FeS_3$ is orthorhombic, $Pnma$, $a = 12.087(5)$ Å, $b = 4.246(2)$ Å, $c = 12.359(5)$ Å, $\rho_{meas} = 4.0$ g/cm$^3$, $\rho_{calc} = 4.47$ g/cm$^3$, $Z = 4$, mp >1300°C. The compound is isostructural with $Ba_2ZnS_3$ and the structure consists of $FeS_4$ tetrahedrons sharing corners to form an infinite linear chain. $Ba_2FeSe_3$ is isostructural with the sulfide and its parameters are $a = 12.350(7)$ Å, $b = 4.439(2)$ Å, $c = 12.921(5)$ Å. $BaFe_2S_3$ is orthorhombic, $Cmcm$, $a = 8.7835(9)$ Å, $b = 11.219$ Å, $c = 5.2860$ Å, $\rho_{meas} = 4.0$ g/cm$^3$, $\rho_{calc} = 4.40$ g/cm$^3$, $Z = 4$, mp $765 \pm 10$°C. Three-dimensional X-ray diffraction data were used to refine the structure which consists of two $FeS_4$ tetrahedrons sharing edges and this binuclear unit in turn shares edges with others to form an infinite chain. The structure of $BaFe_2Se_3$ is essentially the same as that of the sulfide but they are not isostructural. The selenide is orthorhombic, $Pnma$, $a = 11.878(3)$ Å, $b = 5.447(2)$ Å, $c = 9.160(2)$ Å, $\rho_{calc} = 5.44$ g/cm$^3$, $Z = 4$; decomposes above 750°C. $Ba_6Fe_8S_{15}$ is tetragonal, $I4/m$, $a = 11.408(2)$ Å, $c = 10.256(2)$ Å, $\rho_{meas} = 4.30$ g/cm$^3$, $\rho_{calc} = 4.36$ g/cm$^3$, $Z = 2$, mp $880 \pm 10$°C. The structure was determined from three-dimensional X-ray diffraction data and consists of a tetranuclear unit formed by 4 $FeS_4$ tetrahedrons sharing corners and these units then share edges to form an infinite column. $Ba_3Fe_3Se_7$ is hexagonal, $P6_3mc$, $a = 10.843(3)$ Å, $c = 7.384(2)$ Å, $\rho_{calc} = 5.00$ g/cm$^3$, $Z = 2$. The structure was determined using three-dimensional single crystal X-ray diffraction data and consists of isolated trinuclear units formed by edge sharing of three $FeSe_4$ tetrahedrons. In the several compounds the Fe–Fe distances between chains are 6 Å, and vary from 2.6 to 4.2 Å within the chains. The Fe–S distances are 2.3–2.4 Å, the S–Fe–S angles are tetrahedral and the Ba–S distances are essentially equal to the sum of the ionic radii. The corresponding distances in the selenides reflect the larger size of the anion.

## Introduction

A series of new compounds has been synthesized in the barium–first row transition metal–sulfur and selenium systems which is based on a common structural scheme consisting of tetrahedrons linked by corner and edge sharing into linear chains or columns.

The crystal structure of $Ba_7Fe_6S_{14}$ *(1)* and the structure and magnetic behavior of $Ba_2MnS_3$ and $Ba_2MnSe_3$ *(2)* have been reported; and a preliminary account of the structures of the other phases has been given *(3)*. In this paper, we present a detailed discussion of new structures that have been found in the Ba–Fe–S and Se systems.

## Experimental Section

BaS, BaSe, Fe, S, and Se constitute the starting materials for the ternary compound preparations. Commercial, yellow BaS, containing free S, was heated at 500°C for 4–5 hr under a current of $H_2$. BaSe was prepared by the reduction of $BaSeO_3$ under a current of $H_2$ at 500°C for 4–5 hr. After treatment, the X-ray powder diffraction patterns of the white BaS and BaSe showed no extraneous lines. The Fe, S, and Se powders were nominally 99.9% pure; and no impurities were detected on examination of their X-ray powder patterns. Different ratios of BaS, BaSe, Fe, S, or Se were mixed in a graphite tube and sealed under vacuum of $10^{-3}$ to $10^{-4}$ mm in Vycor tubing and preheated at temperatures of 300°C for sulfides and 350°C for selenides for

4–5 hr. The temperature was then raised and kept in the range of 750 to 1050°C for 2 days. At the end of the reaction, the sample was slowly cooled to room temperature by cutting off the power to the furnace or was quenched by dropping it into ice water. The ampoule with the reacted material was first examined under an optical microscope to see if some of the starting materials still remained unreacted; BaS or BaSe can be easily recognized by its white crystals. If the sample looked homogeneous, a X-ray powder diffraction pattern was obtained to study the phases produced. Frequently, free sulfur was found condensed on the walls of the Vycor tubing and a freshly prepared mixture was then reheated at a higher temperature. If free sulfur remained after several treatments, it was assumed that it was an excess component in the mixture.

The powder diffraction patterns of the products were examined for peaks from the starting materials, from the known binary compounds, and from the known, related, ternary compounds. If the pattern indicated that a new phase had formed, then the assumption was made that the stoichiometry corresponded to the ratio of starting materials and the literature was searched for possible isostructural compounds. If this procedure was unsuccessful, then a single crystal was selected and a complete crystal structure analysis was carried out.

Melting points of the compounds were obtained by selecting single crystals and placing them on a thermocouple junction to which an ac voltage was applied. Melting temperatures were obtained by observing the crystals microscopically. A X-ray powder diffraction diagram was obtained after the material had solidified to check whether melting had occurred congruently.

Densities of the compounds were obtained by the liquid displacement method using benzene; and the experimental errors are 10%.

### Structures of $Ba_2FeS_3$ and $Ba_2FeSe_3$

The initial mixtures of $2BaS:Fe:S$ and $2BaSe:Fe:Se$ were heated at 850–870° for 2 days. The X-ray powder patterns of the two products were quite similar indicating that they were probably isostructural. Weissenberg and precession diagrams of a single crystal selected from the selenide showed diffraction symmetry $mmm$, systematic absences for $0kl$, $k + l = 2n + 1$ and for $hk0$, $h = 2n + 1$, consistent with space groups $Pnma$ or $Pn2_1a$. Measured $2\theta$ values of

reflections from several levels of Weissenberg photographs were used in a least-squares refinement for obtaining the lattice parameters $a = 12.350(7)$ Å, $b = 4.439(2)$ Å, $c = 12.921(5)$ Å. The powder pattern of $Ba_2FeS_3$ was also indexed on the basis of an orthorhombic cell and a least-squares refinement of $2\theta$ values obtained from these patterns gave lattice constants $a = 12.087(5)$ Å, $b = 4.246(3)$ Å, and $c = 12.359(7)$ Å. With an assumed stoichiometry based on the initial composition and a knowledge of the lattice constants and space group it was found that the compounds could be isostructural with $Ba_2ZnS_3$ (4). A calculation of the powder intensities for $Ba_2FeS_3$ and single crystal intensities for $Ba_2FeSe_3$ using the atomic coordinates of $Ba_2ZnS_3$ gave good qualitative agreement and confirmed that the structures were identical. The measured density of $Ba_2FeS_3$ is 4.02 g/cm³, calculated $\rho = 4.47$ g/cm³, $Z = 4$ formula weights per unit cell; mp > 1300°C.

The projection of the structure of $Ba_2FeS_3$ on (010) is shown in Fig. 1. A linear infinite tetrahedral iron chain, formed by corner sharing, exists parallel to the $b$ axis and the Fe–Fe distance between shared tetrahedrons is 4.246(3) Å, the $b$ axis dimension of the unit cell. In $Ba_2FeSe_3$, this distance is 4.439(2) Å. Bond distances were calculated on the basis of the $Ba_2ZnS_3$ parameters and the Fe–S distance where S is shared between two Fe ions is 2.45 Å, considerably longer than the other Fe–S distances of 2.30 and 2.38 Å. One $Ba^{2+}$ is surrounded by six S ions at the corners of a trigonal prism and an additional S ion is approximately centered above one rectangular face. Seven S ions surround the other $Ba^{2+}$ forming a distorted trigonal prism with one face capped. $Ba_2FeS_3$ is isostructural with $Ba_2ZnS_3$, $K_2CuCl_3$, $(NH_4)_2CuBr_3$, $Cs_2AgCl_3$, $Cs_2AgI_3$, and $CuPbBiS_3$ (5). We also synthesized $Ba_2CoS_3$, $Pnma$, $a = 11.87$ Å, $b = 4.20$ Å, $c = 12.30$ Å and it, too, is isostructural with $Ba_2FeS_3$. The structure of $Ba_2FeS_3$ is similar to, but not isostructural with, $Ba_2MnS_3$ (2).

### Crystal Structure of $BaFe_2S_3$

A mixture of $BaS:2Fe:2S$ was prepared and heated at 790°C for 2 days and then slowly cooled to room temperature. The material was black and highly crystalline and the X-ray powder pattern showed no lines which could be ascribed to the starting materials or to the known iron sulfide compounds.
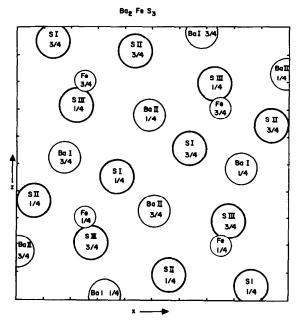
Ba₂ Fe S₃



FIG. 1. The projection of $Ba_2FeS_3$ on (010): (numbers inside circles) fractional heights along the $b$ axis.

Weissenberg and precession pictures obtained from a single crystal selected from the product showed that the diffraction symmetry was *mmm*, with systematic absences $hkl$, $h + k = 2n + 1$ and $h0l$, $l = 2n + 1$ consistent with space groups $C2cm$, $Cmc2_1$ and $Cmcm$. The lattice constants obtained from the films were $a = 8.78$ Å, $b = 11.22$ Å, and $c = 5.28$ Å. An examination of lattice constants and space groups for compounds with stoichiometry $AB_2C_3$ (5) showed that $CsCu_2Cl_3$ might be isostructural with the unknown phase.

A crystal measuring $0.037 \times 0.037 \times 0.129$ mm, was mounted parallel to the $c$ axis and placed on a GE goniostat. Thirty reflections were carefully centered on the $K_{\alpha_1}$ and $K_{\alpha_2}$ components of the molybdenum radiation ($\lambda_1 = 0.70926$ Å, $\lambda_2 = 0.71354$ Å) using a 1° takeoff angle and a 0.02° slit. The $2\theta$ measurements were used in a least-squares refinement for the determination of the lattice constants $a = 8.7835(9)$ Å, $b = 11.219(1)$ Å, and $c = 5.2860(5)$ Å. The measured density is 4.00 g/cm³, $\rho_{calc} = 4.40$ g/cm³, $Z = 4$; mp $= 765 \pm 10$°C. Reflection intensities were collected with the goniostat at a 5° takeoff angle and a wide aperture in front of the counter, using the stationary crystal–stationary counter method with balanced filters for molybdenum radiation. Independent reflections (336) were measured to $2\theta = 60$° and the data were reduced to $F(hkl)$ by applying Lorentz, polarization, and absorption corrections. Standard deviations were estimated using the expression

TABLE I

ATOMIC PARAMETERS AND THEIR STANDARD DEVIATIONS IN PARENTHESES
($\times 10^4$) FOR $BaFe_2S_3$[a]

| Atom | $x$ | $y$ | $z$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Ba | $\frac{1}{4}$ | 1859(3) | $\frac{1}{4}$ | 66(3) | 41(2) | 94(9) | 0 | 0 | 0 |
| Fe | 3464(4) | $\frac{1}{4}$ | 0 | 26(4) | 14(3) | 33(11) | 0 | 0 | 0 |
| S(I) | $\frac{1}{4}$ | 6147(9) | $\frac{1}{4}$ | 35(12) | 10(7) | 70(34) | 0 | 0 | 0 |
| S(II) | 2074(9) | 3768(7) | $\frac{1}{4}$ | 52(9) | 41(7) | 50(23) | 0 | 0 | 0 |

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

$\sigma(F) = \frac{1}{2}\{K(1 + I_Y/I_{Zr})/(1 - I_Y/I_{Zr})\}^{1/2}$ where $I_Y$ is the background, $I_{Zr}$ is the peak count and $K$ is the product of the Lorentz, polarization, absorption, $\alpha$ splitting, and tube current corrections. The transmission factors ($\mu_l = 136.6$ cm$^{-1}$) varied from 0.350 to 0.406.

The atomic parameters for $CsCu_2Cl_3$ (6), space group $Cmcm$, were used as starting parameters for a least-squares refinement of the structure and after 3 cycles with anisotropic temperature factors $R$ was 0.064 and $wR$ was 0.067; ($R = \sum||F_0| - |F_c||/\sum|F_0|$, $wR = [\sum w(F_0 - F_c)^2/\sum wF_0^2]^{1/2}$). The standard deviation of a reflection of unit weight, $[\sum w(F_0 - F_c)^2/(n_o - n_v)]^{1/2}$ is 3.37 where $n_0$ is the number of observations and $n_v$ the number of variables. A three-dimensional Fourier difference map showed no physically meaningful peaks and the largest one was 1.0 e/Å$^3$. Atomic scattering factors with $\Delta f'$ and $\Delta f''$ corrections for Fe and Ba were used (7). The final parameters are shown in Table I; the observed and calculated structure factors are available[1] and bond distances and angles are shown in Table II.

## Discussion of the Structure

Two $FeS_4$ tetrahedrons share an edge with the line formed by the two Fe ions parallel to the $a$ axis of the unit cell, Fig. 2. This unit of two tetrahedrons, in turn, shares edges with another unit above it and parallel to the $c$ axis and forms an infinite chain along [001], shown stereoscopically in Fig. 3. The $Ba^{2+}$ is coordinated to 8 sulfur ions, 6 are located at the corners of a trigonal prism at 3.29 and 3.45 Å and two are approximately above the rectangular faces at 3.35 Å. Two additional sulfur atoms are located near the third rectangular face of the prism but at 3.92 Å and cannot be considered as part of the coordination sphere.

## Crystal Structure of $BaFe_2Se_3$

A mixture of BaSe:2Fe:Se was heated at 790°C for 2 days, followed by slow cooling. The X-ray powder pattern of the material showed

### TABLE II

BOND DISTANCES AND ANGLES IN $BaFe_2S_3{}^a$

| Distances (Å) | | | |
|---|---|---|---|
| $2^b$Fe–S$_1$ | 2.28(1) | 4Ba–S$_2$ | 3.29(1) |
| 2Fe–S$_2$ | 2.27(1) | 2Ba–S$_2$ | 3.35(1) |
| Fe–Fe | 2.643(5) | 2Ba–S$_2$ | 3.92(1) |
| Fe–Fe | 2.699(5) | 2S$_2$–S$_1$ | 3.69(1) |
| Ba–Fe | 3.998(5) | S$_1$–S$_1$ | 3.69(1) |
| 2Ba–S$_1$ | 3.46(1) | 2S$_2$–S$_1$ | 3.70(1) |
| | | S$_2$–S$_2$ | 3.82(1) |

| Angles (°) | |
|---|---|
| S$_2$–Fe–S$_1$ | 108.1(4) |
| S$_1$–Fe–S$_1$ | 107.6(4) |
| S$_1$–Fe–S$_2$ | 108.1(4) |
| S$_2$–Fe–S$_2$ | 114.9(4) |
| S$_2$–Fe–S$_1$ | 108.9(4) |
| S$_1$–Fe–S$_2$ | 108.9(4) |

$^a$ Standard deviations are shown in parentheses.

$^b$ The number in front of a bond length indicates how frequently this length occurs.

great similarity to $BaFe_2S_3$ and initially these two compounds appeared to be isostructural. A single crystal was selected from the black, crystalline material and Weissenberg and precession pictures showed that the diffraction symmetry was $mmm$ with systematic absences $0kl$, $h + l = 2n + 1$ and $hk0$, $h = 2n + 1$ consistent with space group $Pnma$ or $Pn2_1a$; approximate lattice constants were $a = 11.90$ Å, $b = 5.41$ Å, $c = 9.22$ Å. The different space group showed that this compound was not isostructural with $BaFe_2S_3$ and a search of lattice constants and space groups for compounds with stoichiometry $AB_2C_3$ (5) indicated that constants for $CsAg_2I_3$ were similar to those of the unknown phase. A single crystal structure determination was undertaken on the assumption that the compound was $BaFe_2Se_3$ and was isostructural with $CsAg_2I_3$.

A single crystal[2] of ellipsoidal shape with dimensions $0.078 \times 0.104 \times 0.182$ mm was mounted on a four circle diffractometer and 12 reflections in the range of 25–39° $2\theta$ were carefully centered on the $AgK_\beta$ radiation ($\lambda = 0.49701$ Å). Least-squares refinement gave lattice constants at $24 \pm 0.5$°C of $a = 11.878(3)$ Å, $b = 5.447(2)$ Å, and $c = 9.160(2)$ Å; $\rho_{calc} = 5.44$
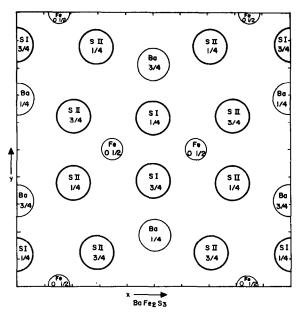
FIG. 2. The projection of the structure of $BaFe_2S_3$ on (001).

g/cm$^3$, $Z = 4$; decomposes above 750°C. Intensities were collected in the range $3° \leqslant 2\theta \leqslant 50°$ using unfiltered Ag$K$ radiation and a scintillation counter. The integrated intensities of 1160 reflections were obtained by step scanning in intervals of 0.01°, counting for 2 sec at each step, over an angular range of 0.55° and with the instrument at a 1.5° takeoff angle. The background was measured on each side of the peak for 60 sec. A standard reflection, (040), was measured after every 20 reflections throughout the data collection and the range of counts was 121 600–131 200. All reflection intensities in a given interval were multiplied by the appropriate ratio so that they were referred to a single value of the (040) intensity. The data were corrected for Lorentz, polarization, and absorption effects ($\mu = 164.9$ cm$^{-1}$); the transmission factors varied from 0.292 to 0.384.

The atomic parameters for $CsAg_2I_3$ were used as starting parameters for a least-squares refinement using ORFLS (8). The quantity refined was $\sum w(F_0{}^2 - F_c{}^2)^2$ with weights equal to the reciprocal of the variances which were estimated from the empirical equation

$$\sigma^2(F_0{}^2) = \{T + B + [0.05(T - B)]^2\}/A(Lp)^2,$$

where $T$ is total counts, $B$ is background counts, $A$ is the absorption correction, and $Lp$ are the Lorentz and polarization factors. The scattering factors for the neutral atoms were taken from Cromer and Waber (9) and all atoms were corrected for the real and imaginary contributions of anomalous dispersion. After four cycles of refinements using anisotropic temperature factors, $R$ was 0.0725 for 983 reflections greater than $\sigma$ and $R = 0.0891$ for all 1160 reflections. The standard deviation of a reflection of unit weight



FIG. 3. Stereoscopic drawing of the double tetrahedral chain in $BaFe_2S_3$: (horizontal direction) [100]; and (vertical [001].

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## TABLE III

ATOMIC PARAMETERS AND THEIR STANDARD DEVIATIONS IN PARENTHESES
$(\pm 10^4)^a$ for $Ba\,Fe_2\,Se_3$

| Atom | $x$ | $y$ | $z$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|------|-----|-----|-----|----------|----------|----------|----------|----------|----------|
| Ba | 1847(1) | $\frac{1}{4}$ | 5185(1) | 49(1) | 89(3) | 69(0) | 0 | 15(1) | 0 |
| Fe | 4947(1) | 3(3) | 3515(1) | 28(1) | 76(4) | 31(1) | −2(1) | −0(1) | 0(2) |
| SeI | 3590(1) | $\frac{1}{4}$ | 2272(2) | 40(1) | 71(4) | 45(2) | 0 | −21(1) | 0 |
| SeII | 6259(1) | $\frac{1}{4}$ | 4915(1) | 28(1) | 66(4) | 34(1) | 0 | 0(1) | 0 |
| SeIII | 3976(1) | $\frac{1}{4}$ | 8125(2) | 47(1) | 92(5) | 53(2) | 0 | 28(1) | 0 |

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

is 1.73. The final parameters are shown in Table III; the observed and calculated structure factors are available[3] and bond distances and angles are shown in Table IV.

## TABLE IV

BOND DISTANCES AND ANGLES IN $BaFe_2Se_3{}^a$

### Distances (Å)

| | | | |
|------|---------|-------|----------|
| Fe–Se$_1$ | 2.396(2) | Ba–Se$_3$ | 3.455(1) |
| Fe–Se$_3$ | 2.399(2) | Ba–Se$_3$ | 3.455(1) |
| Fe–Se$_2$ | 2.434(2) | Ba–Se$_1$ | 3.377(2) |
| Fe–Se$_2$ | 2.444(2) | Ba–Se$_3$ | 3.694(2) |
| Fe–Fe | 2.721(3) | Ba–Se$_3$ | 3.745(2) |
| Fe–Fe | 2.726(3) | Se$_1$–Se$_3$ | 3.988(2) |
| Ba–Fe | 3.963(2) | Se$_1$–Se$_2$ | 3.418(2) |
| Ba–Se$_1$ | 3.368(1) | Se$_1$–Se$_2$ | 3.753(2) |
| Ba–Se$_1$ | 3.368(1) | Se$_3$–Se$_2$ | 3.999(2) |
| Ba–Se$_2$ | 3.534(1) | Se$_3$–Se$_2$ | 3.906(2) |
| Ba–Se$_2$ | 3.534(1) | Se$_2$–Se$_2$ | 3.826(2) |

### Angles (°)

| | |
|------|----------|
| Se$_1$–Fe–Se$_3$ | 112.55(8) |
| Se$_1$–Fe–Se$_2$ | 111.32(6) |
| Se$_1$–Fe–Se$_2$ | 101.67(7) |
| Se$_3$–Fe–Se$_2$ | 107.83(7) |
| Se$_3$–Fe–Se$_2$ | 111.35(6) |
| Se$_2$–Fe–Se$_2$ | 112.13(6) |

$^a$ Standard deviations in the last decimal place in parentheses.

[3] A table of observed and calculated structure factors has been deposited as Document No. NAPS-01691 with the ASIS National Auxiliary Publications Service, c/o CCM Information Corp., 909 Third Avenue, New York, NY 10022. A copy may be secured by citing the document number and by remitting $5.00 for photocopies or $2.00 for microfiche. Advance payment is required. Make check or money order payable to ASIS-NAPS.

## Discussion of the Structure

The structure shown in projection on (010) in Fig. 4 is basically identical with that of $BaFe_2S_3$ but sufficient distortions exist to change the symmetry operations relating the atoms and the coordination of the $Ba^{2+}$ is thereby affected. The $Ba^{2+}$ is surrounded by 6 $Se^{2-}$ at the corners of a trigonal prism with Ba–Se distances of 3.368, 3.455, and 3.534 Å. Two additional $Se^{2-}$ are above the centers of two rectangular faces of the prism at distances of 3.377 and 3.694 Å from $Ba^{2+}$. The corresponding Ba–S distances in $BaFe_2S_3$ are equal. A ninth $Se^{2-}$ is near the third rectangular face at a distance of 3.745 Å while the tenth selenium atom is at a distance of 4.47 Å. If the $Ba^{2+}$ coordination is taken as 8 in $BaFe_2S_3$ then it can be considered as 9 in $BaFe_2Se_3$. In the former compound the coordination polyhedron is also more symmetric.

## Crystal Structure of $Ba_6Fe_8S_{15}$

The crystal, which eventually was shown to have this stoichiometry, was found in the product obtained from a quench of a starting mixture having the composition BaS:2Fe:2S which had been held at 800°C for 2 days. It was evident from the X-ray powder pattern that the product was polyphasic. A single crystal was selected and Weissenberg and precession photographs showed diffraction symmetry $4/m$ and systematic absences of spectra were observed for $hkl$, $h + k + l = 2n + 1$, consistent with space groups $I\bar{4}$, $I4$, and $I4/m$. A crystal measuring approximately 0.31 × 0.044 × 0.092 mm was mounted on a quarter circle single crystal orienter with the $c$ axis (0.092 mm) parallel to the $\phi$ axis of the instrument. Thirty-four reflections having $2\theta > 27°$ were centered on $MoK_{\alpha_1}$ and $MoK_{\alpha_2}$ with the instrument set to fine conditions as previously described
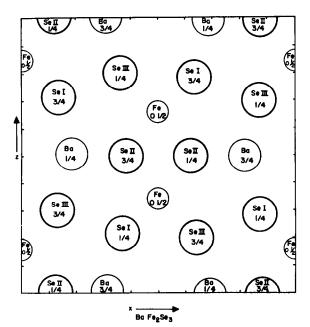
FIG. 4. The projection of the crystal structure of $BaFe_2Se_3$ on (010).

and the least-squares refinement using the measured $2\theta$ values gave $a = 11.408(2)$ Å, $c = 10.256(2)$ Å; $Z = 2$, $\rho_{cal} = 4.36$ g/cm$^3$, $\rho_{meas} = 4.30$ g/cm$^3$; the compound melts congruently at $880 \pm 10°$C (the number of formula weights and calculated density are based on the subsequently determined stoichiometry).

Three-dimensional data to $2\theta = 60°$ were collected with Mo$K$ radiation using the procedure described for the data collection used for the $BaFe_2S_3$ crystal. A total of 1033 reflections was measured, of which 956 were considered to be above background. The shape of the crystal was approximated by 6 planes for the calculation of an absorption correction on the intensities after the structure had been determined. The linear absorption coefficient is 143 cm$^{-1}$ and the transmission factors varied from 0.125 to 0.500.

Structure determination

A three-dimensional Patterson map was calculated and the Harker section $P(00w)$ showed several strong interactions. Wilson statistics were also calculated based on the formula $BaFe_2S_3$ since the reaction mixture from which these crystals were selected was BaS:2Fe:2S. The statistics followed a centric distribution and therefore these two indications led us to the selection of $I4/m$ as the proper space group. The sequence of computer programs FAME–

MAGIC–LINK–SYMPL ($10$) was used to generate about 300 phases from five symbol assigned reflections. A three-dimensional $E(hkl)$ map showed peaks which could be interpreted as due to two Ba and one Fe atoms. The Patterson map peaks were used as a check on the selected positions. A three-dimensional electron density map calculated with signs obtained with these positions revealed additional peaks which were due to S and it became evident that the compound had the formula $Ba_6Fe_8S_{15}$. The final parameters shown in Table V were obtained by a least-squares refinement using the procedures described previously. The atomic scattering factors of Ba and Fe were corrected for $\Delta f'$ and $\Delta f''$. The final $R = 0.0800$, $wR = 0.0678$ for 1034 reflections and $R = 0.0714$, $wR = 0.0673$ for 928 reflections greater than $\sigma$. The standard deviation of a reflection of unit weight is 1.48. A three-dimensional difference map showed no physically meaningful peaks and the largest one was 1.5 $e/$Å$^3$. The final set of observed and calculated structure factors is available.[4]

[4] A table of observed and calculated structure factors has been deposited as Document No. NAPS-01691 with the ASIS National Auxiliary Publications Service, c/o CCM Information Corp., 909 Third Avenue, New York, NY 10022. A copy may be secured by citing the document number and by remitting $5.00 for photocopies or $2.00 for microfiche. Advance payment is required. Make check or money order payable to ASIS-NAPS.

TABLE V

FINAL ATOMIC PARAMETERS AND THEIR STANDARD DEVIATIONS IN PARENTHESES
($\times 10^4$) FOR $Ba_6Fe_8S_{15}$[a]

| Atom | $x$ | $y$ | $z$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|------|-----|-----|-----|----------|----------|----------|----------|----------|----------|
| $Ba_1$ | 0 | 0 | 3044(2) | 14(1) | 14(1) | 25(2) | 0 | 0 | 0 |
| $Ba_2$ | 2484(1) | 1304(1) | 0 | 15(1) | 15(1) | 38(1) | 0(1) | 0 | 0 |
| Fe | 1537(2) | 4384(2) | 1365(2) | 13(1) | 14(1) | 25(2) | 0(1) | −1(1) | 1(1) |
| $S_1$ | 790(3) | 2700(3) | 2266(4) | 17(2) | 14(2) | 31(3) | 3(2) | 6(2) | 4(2) |
| $S_2$ | 3035(5) | 3951(4) | 0 | 17(3) | 15(3) | 25(5) | 0 | 0 | 0 |
| $S_3$ | 0 | $\frac{1}{2}$ | 0 | 12(5) | 13(5) | 28(7) | 4(4) | 0 | 0 |
| $S_4$ | 0 | 0 | 0 | 16(8) | 16(8) | 16(9) | 0 | 0 | 0 |

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

## Discussion of the Structure

Once the stoichiometry of the compound was known the preparative conditions required for single phase material were investigated. A mixture of $6BaS:8Fe:9S$ preheated as previously described and then heated at 760°C for 2 days, followed by quenching, yields single phase material of $Ba_6Fe_8S_{15}$ as judged by the X-ray powder diffraction diagram and microscopic examination. The product is black and highly crystalline with many small crystals visible in the powder.

The [001] projection of the structure is shown in Fig. 5. Four $FeS_4$ tetrahedrons share corners and their arrangement can be described with reference to an octahedron. Two opposing faces of the upper half of an octahedron, (111) and ($\bar{1}\bar{1}1$), form the bases for two tetrahedrons and they share a corner which is the apex of the octahedron; two opposing faces of the lower half of the octahedron, ($1\bar{1}\bar{1}$) and ($\bar{1}1\bar{1}$), form the bases of the other two tetrahedrons and they share a corner which is the lower apex of the octahedron. The sets of two tetrahedrons share corners which are the 4 points 100, 010, $\bar{1}$00, and 0$\bar{1}$0 of the octahedron. This unit of 4 $FeS_4$ tetrahedrons is propagated by mirror planes perpendicular to [001] into an infinite column parallel to the
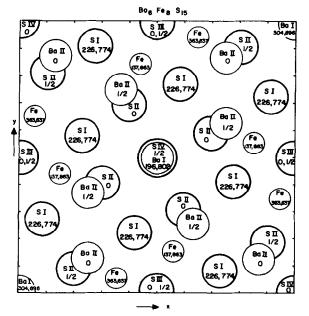


FIG. 5. The projection of the structure of $Ba_6Fe_8S_{15}$ on (001).

FIG. 6. Stereoscopic view of the infinite column of tetrahedra in $Ba_6Fe_8S_{15}$. The vertical direction is [001] of the unit cell.

$c$ axis as illustrated in Fig. 6. The Fe–Fe distances between edge sharing tetrahedrons are 2.81 Å and are 3.34, 3.54, and 3.78 Å for Fe–Fe distances when tetrahedrons share corners. The Fe–Fe distance between atoms in adjacent chains is 6.10 Å. The Ba ions are in ninefold coordination. Eight S ions form a square antiprism around $Ba_1$ and the ninth atom, $S_4$, is in the center of one square

TABLE VI

BOND DISTANCES AND ANGLES IN $Ba_6Fe_8S_{15}$[a]

| Distances (Å) | | | |
|---|---|---|---|
| Fe–$S_2$ | 2.27(1) | $Ba_1$–$S_2$ | 3.23(1) |
| Fe–$S_1$ | 2.29(1) | $Ba_1$–$S_2$ | 3.23(1) |
| Fe–$S_1$ | 2.30(1) | $Ba_1$–$S_1$ | 3.31(1) |
| Fe–$S_3$ | 2.36(1) | $Ba_1$–$S_1$ | 3.31(1) |
| $Ba_2$–$S_2$ | 3.09(1) | $Ba_1$–$S_1$ | 3.31(1) |
| $Ba_2$–$S_3$ | 3.23(1) | $Ba_1$–$S_1$ | 3.31(1) |
| $Ba_2$–$S_4$ | 3.20(1) | $S_2$–$S_1$ | 3.74(1) |
| $Ba_2$–$S_1$ | 3.34(1) | $S_1$–$S_3$ | 3.95(1) |
| $Ba_2$–$S_1$ | 3.34(1) | $S_2$–$S_3$ | 3.67(1) |
| $Ba_2$–$S_1$ | 3.36(1) | $S_1$–$S_3$ | 3.61(1) |
| $Ba_2$–$S_1$ | 3.36(1) | $S_2$–$S_1$ | 3.61(1) |
| $Ba_2$–$S_1$ | 3.61(1) | $S_1$–$S_1$ | 3.95(1) |
| $Ba_2$–$S_1$ | 3.61(1) | Fe–Fe | 2.811(7) |
| $Ba_1$–$S_4$ | 3.119 | Fe–Fe | 3.539(7) |
| $Ba_1$–$S_2$ | 3.23(1) | Fe–Fe | 3.783(7) |
| $Ba_1$–$S_2$ | 3.23(1) | Fe–Fe | 3.342(7) |
| | | Fe–Fe | 6.102(7) |

| Angles (°) | |
|---|---|
| $S_2$–Fe–$S_1$ | 110.3(3) |
| $S_1$–Fe–$S_3$ | 115.8(3) |
| $S_1$–Fe–$S_1$ | 118.8(3) |
| $S_2$–Fe–$S_3$ | 104.9(3) |
| $S_1$–Fe–$S_3$ | 102.1(3) |
| $S_2$–Fe–$S_1$ | 104.2(3) |
| Fe–$S_1$–Fe | 100.8(3) |
| Fe–$S_3$–Fe | 106.8(1) |
| Fe–$S_1$–Fe | 108.8(3) |

[a] Standard deviations in the last decimal place in parentheses.

face, along the $c$ axis. The $S_4$ atom is not part of a $FeS_4$ tetrahedron. The polyhedron around $Ba_2$ consists of a capped trigonal prism. The Ba–S distances are essentially equal to the sum of the ionic radii. The bond distances and angles are listed in Table VI.

The formula of this compound can be written as $Ba_6Fe_2(III)Fe_6(II)S_{15}$ and, since the Fe ions are crystallographically indistinguishable, we can consider the average oxidation number as 2.25. There is a possibility that electrical conduction can occur via a hopping mechanism and that this material should display conductivity in one dimension similar to the recently reported mixed valence square planar complexes (11).

### Crystal Structure of $Ba_3Fe_3Se_7$

In addition to $Ba_2FeSe_3$, an unknown phase was occasionally observed in the reacted material obtained from an initial mixture of $2BaSe:Fe:Se$. The unknown phase, which was later found to be $Ba_3Fe_3Se_7$, consisted of black hexagonally shaped crystals.

Weissenberg and precession photographs showed diffraction symmetry $6/mmm$ and the only systematic absences of spectra were $hhl$, $l =$ odd, consistent with space groups $P\bar{6}2c$, $P6_3mc$, and $P6_3/mmc$. A hexagonally shaped crystal measuring approximately $0.03 \times 0.03 \times 0.07$ mm was mounted on a quarter circle single crystal orienter with the $c$ axis (0.07 mm) parallel to the $\phi$ axis of the instrument. Thirty-one reflections having $11° < 2\theta < 39°$ were carefully centered on the $K_{\alpha_1}$ and $K_{\alpha_2}$ components of Mo radiation ($\lambda_1$ 0.70926 Å, $\lambda_2$ 0.71354 Å) using a $1°$ takeoff angle and a $0.02°$ slit. The $2\theta$ measurements, made at room temperature, $25 \pm 0.5°$, were used in a least-squares refinement for the determination of the lattice parameters $a$ 10.843(3) Å, $c = 7.384(2)$ Å; $Z = 2$, $\rho_{cal} = 5.00$ g/cm³.

Peak height intensities were obtained with

<div align="center">

TABLE VII

FINAL ATOMIC PARAMETERS AND THEIR STANDARD DEVIATIONS IN PARENTHESES
$(\times 10^4)$ FOR $Ba_3Fe_3Se_7$[a]

</div>

| Atom | $x$ | $y$ | $z$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|------|-----|-----|-----|----------|----------|----------|----------|----------|----------|
| Ba | 1911(2) | 3822(2) | 0 | 21(2) | 21(2) | 69(4) | −6(2) | 0 | 0 |
| Fe | 2458(6) | 4916(6) | 486(1) | 38(7) | 38(7) | 5(1) | 36(5) | 0 | 0 |
| $Se_1$ | 4573(5) | 9146(5) | 3110(7) | 35(5) | 35(5) | 50(7) | 25(4) | 0 | 0 |
| $Se_2$ | 1252(4) | 2504(4) | 5895(7) | 23(5) | 23(5) | 73(8) | 13(4) | 0 | 0 |
| $Se_3$ | $\frac{1}{3}$ | $\frac{2}{3}$ | 738(1) | 17(7) | 17(7) | 30(1) | 0 | 0 | 0 |

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

balanced filters and $MoK_\alpha$ radiation as previously described. A total of 455 independent reflections was measured of which 397 were considered observed on the basis that the peak measurement exceeded background by 4 counts in 10 sec. The shape of the crystal was approximated by 8 planes for the calculation of an absorption correction on the intensities after the structure was solved. The linear absorption coefficient is 289.5 $cm^{-1}$ and the transmission factors varied from 0.259 to 0.292.

Structure Determination

A three-dimensional Patterson function was calculated. If a mirror plane exists perpendicular to the $c$ axis then a large number of interactions should be observed on the Harker section $P(00w)$ and this was not the case. Thus we began to interpret the Patterson map on the basis of an acentric space group. The Harker section $P(u,0,0)$ showed many interactions and space group $P6_3mc$ was therefore chosen. The positions of one Ba and one Se were located from the Patterson map and phases were calculated. A three-dimensional electron density map based on these phases revealed positions for one Fe and two additional Se atoms. It was evident now that the compound was $Ba_3Fe_3Se_7$. The atomic coordinates were refined by least squares (8) and the function minimized was $\sum w(KF_0 - F_c)^2$

with $w = 1/\sigma^2$. After three cycles of refinements with anisotropic temperature factors and using 381 reflections greater than $\sigma$, $R$ was 0.0704, $wR = 0.071$; for all 455 reflections $R = 0.0887$, $wR = 0.0725$. The scattering factors used were for neutral atoms and the Ba and Fe values were corrected for $\Delta f'$ and $\Delta f''$ (7). The final atomic parameters are shown in Table VII and structure factors are available.[5] A three-dimensional electron density difference map calculated with the final parameters showed no physically significant peaks; the largest peak was 1.5 $e/Å^3$. The standard deviation of a reflection of unit weight, $[\sum w(KF_0 - F_c)^2/(n_0 - n_v)]^{1/2}$, is 0.897 ($n_0 =$ number of observations, 455; and $n_v =$ number of variables, 57).

Discussion of the Structure

The structure of $Ba_3Fe_3Se_7$ consists of isolated trinuclear units formed by three $FeS_4$ tetrahedrons sharing edges, Fig. 7. The Fe–Fe distances within the unit are 2.85 Å and are

[5] A table of observed and calculated structure factors has been deposited as Document No. NAPS-01691 with the ASIS National Auxiliary Publications Service, c/o CCM Information Corp., 909 Third Avenue, New York, NY 10022. A copy may be secured by citing the document number and by remitting $5.00 for photocopies or $2.00 for microfiche. Advance payment is required. Make check or money order payable to ASIS-NAPS.



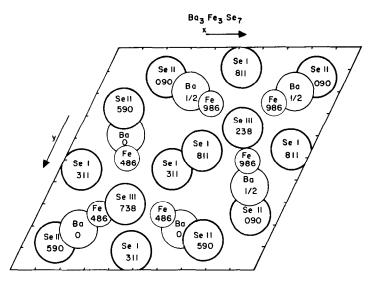FIG. 7. Stereoscopic view of 3 $FeSe_4$ tetrahedrons forming the trinuclear unit in $Ba_3Fe_3Se_7$.

FIG. 8. Projection of the structure of $Ba_3Fe_3Se_7$ on (001).

5.91 Å between iron ions of different units. Ba is in eightfold coordination consisting of a distorted trigonal prism which is capped on two rectangular faces. The (001) projection of the structure is shown in Fig. 8. The Fe and Ba ions lie in planes at $z = 0.486$ and $z = 0$, respectively, and they are separated by sulfur lying in planes at $z = 0.311$

and 0.590. The bond distances and angles of interest are shown in Table VIII. The formula can be expressed as $Ba_3Fe_2(III)Fe(II)Se_7$ and the crystallographically equivalent Fe can be considered to have the average oxidation number 2.66.

## TABLE VIII

BOND DISTANCES AND ANGLES IN $Ba_3Fe_3Se_7$[a]

### Distances (Å)

| | | | |
|---|---|---|---|
| Fe–Se$_1$ | 2.44(1) | Ba–Se$_3$ | 3.30(1) |
| Fe–Se$_2$ | 2.39(1) | Ba–Se$_2$ | 3.27(1) |
| Fe–Se$_3$ | 2.48(1) | Ba–Se$_2$ | 3.26(1) |
| Fe–Se$_1$ | 2.44(1) | Ba–Se$_2$ | 3.26(1) |
| Fe–Fe | 2.85(1) | Se$_1$–Se$_3$ | 3.92(1) |
| Ba–Fe | 3.84(1) | Se$_1$–Se$_2$ | 3.98(1) |
| Fe–Fe | 5.91(1) | Se$_2$–Se$_3$ | 4.06(1) |
| Ba–Se$_1$ | 3.75(1) | Se$_1$–Se$_1$ | 4.03(1) |
| Ba–Se$_1$ | 3.75(1) | Se$_1$–Se$_3$ | 3.92(1) |
| Ba–Se$_1$ | 3.41(1) | Se$_1$–Se$_2$ | 3.98(1) |
| Ba–Se$_1$ | 3.41(1) | | |

### Angles (°)

| | |
|---|---|
| Se$_1$–Fe–Se$_3$ | 105.5(5) |
| Se$_1$–Fe–Se$_2$ | 110.8(5) |
| Se$_2$–Fe–Se$_3$ | 112.8(5) |
| Se$_1$–Fe–Se$_1$ | 111.2(5) |
| Se$_1$–Fe–Se$_3$ | 105.5(5) |
| Se$_1$–Fe–Se$_2$ | 110.8(6) |

[a] Standard deviations in the last decimal place in parentheses.

## Summary

The crystal structures of the compounds synthesized in the Ba–Fe–S and Se systems are based on the articulation of $FeS_4$ tetrahedrons. The structures reported to date are essentially linear polymers in which corner and edge sharing tetrahedrons form infinite chains and columns which are held together laterally by barium ions. The only exception is $Ba_3Fe_3Se_7$ in which 3 tetrahedrons share edges to form an isolated trinuclear unit. In $Ba_2FeS_3$, $Ba_2FeSe_3$ and the Mn and Co analogues the tetrahedra share corners to form the chain; in $BaFe_2S_3$ and $BaFe_2Se_3$, two tetrahedrons share an edge and this binuclear unit in turn shares edges to form an infinite column; a trinuclear unit which consists of a central tetrahedron sharing two opposite edges with two other tetrahedrons and each of these outside tetrahedrons then shares corners with another trinuclear unit to form an infinite zigzag chain makes up the structure of $Ba_7Fe_6S_{14}$ (1); an infinite column built by edge sharing of a tetranuclear unit which consists of four tetrahedrons sharing corners constitutes the structure of $Ba_6Fe_8S_{15}$. A linear chain formed by successive edge sharing of one tetrahedron is found in $KFeS_2$ (12);

and preliminary evidence indicates that one of the unknown phases on which work is in progress has this type of structure.

The Fe–Fe distances between chains is about 6 Å and within a chain varies from about 2.6 to 4.2 Å. The Fe–S distances vary from 2.3 to 2.4 Å depending on the linkage in which the S atom participates. The S–Fe–S angles are essentially tetrahedral and the Ba–S distances are close to the sum of the ionic radii. The corresponding distances in the selenides reflect the larger size of the anion.

## Acknowledgment

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