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The Crystal Structure of β-$BaFe_2S_4$: The First Member in the Infinitely Adaptive Series $Ba_p(Fe_2S_4)_q$

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Single crystals of the compound β-$BaFe_2S_4$, the first member in the infinitely adaptive series of compounds $Ba_p(Fe_2S_4)_q$, were synthesized in a solid-state reaction by heating 1 BaS and 2Fe at 800 ± 3°C and 6.7 atm sulfur vapor pressure. The 108 nonequivalent X-ray diffraction intensities were collected with an automatic single-crystal diffractometer. The compound is tetragonal, $I4/m$, $a = b = 7.678(2)$ Å, $c = 5.292(4)$ Å, $z = 2$. The structure was refined with anisotropic temperature factors to $R = wR = 0.031$. The $(FeS_2)_\infty$ framework is formed by isolated columns of edge-sharing FeS_4 tetrahedra with Ba location between the columns at $z = 0$ and $\frac{1}{2}$. The Ba is in 12-fold coordination at the center of a capped tetragonal prism.

Introduction

The crystal structure of the infinitely adaptive series $Ba_{1+x}Fe_2S_4$ or $Ba_p(Fe_2S_4)_q$ with p and q integral has been described in detail by several investigators (*1–3*). The synthesis of the end member of the series $BaFe_2S_4$ has proven to be difficult. Boller (*4, 5*) reported the synthesis of two polymorphs of $BaFe_2S_4$ by ion exchanging K^+ in $KFeS_2$ using aqueous $BaCl_2$ solutions. The two structures differed only in the packing of the $(FeS_2)_\infty$ edge-sharing chains; the α phase transformed slowly at about 300°C to the denser β, and it is the latter which is the end member of the series. This preparative method yielded only fibers, and the lattice constants, space groups, and crystal structures of the two phases were obtained from intensity data measured from X-ray diffraction fiber photographs. Boller's analysis of β-$BaFe_2S_4$ confirmed the space group $I4/m$ predicted by Hoggins and Steinfink (*3*) but yielded a Ba z parameter of 0.0991 as opposed to the predicted $z = 0$. Grey (*1*) had postulated a structure for $BaFe_2S_4$ which was isostructural with NH_4CuMoS_4, and the Ba z parameter was also zero. We were able to prepare excellent single crystals of β-$BaFe_2S_4$ in a solid-state reaction, and we report its structure in this paper.

Experimental

To reproduce Boller's preparation of β-$BaFe_2S_4$, we prepared $KFeS_4$ following the procedure described in "*Inorganic Synthesis*" (*6*). The product consisted of aggregates of tiny needles in nearly parallel alignment and the X-ray diffraction powder pattern showed it to be single-phase $KFeS_2$. These crystals were soaked in saturated $BaCl_2$ solutions several times, and the product consisted of distended fibrous aggregates, as shown in Fig. 1a. The X-ray

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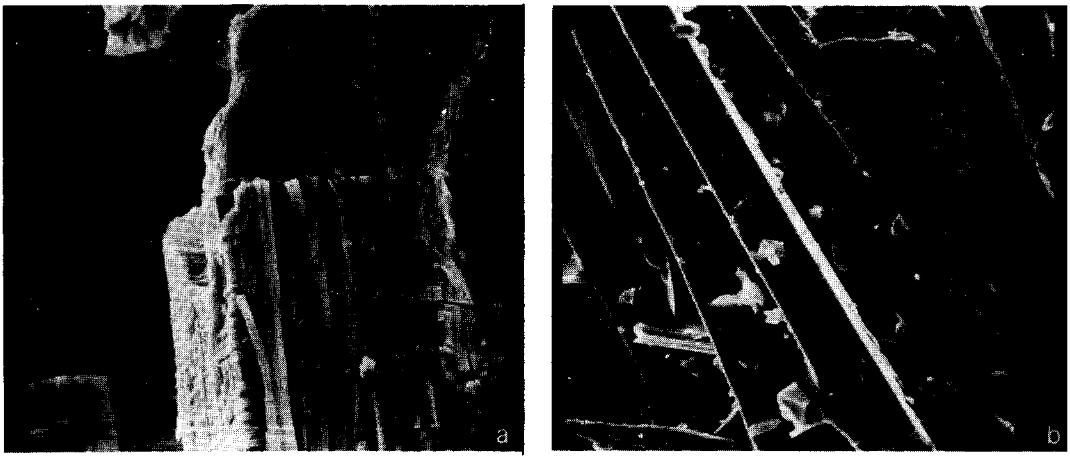

FIG. 1. (a) Scanning electron micrograph of α-$BaFe_2S_4$ obtained by ion exchange of $KFeS_2$. (×600). (b) Scanning electron micrograph of β-$BaFe_2S_4$ obtained by a solid-state reaction using 6.7 atm sulfur vapor pressure. (×600).

diffraction powder pattern was that of α-$BaFeS_4$. This material was heated for 1 week in an evacuated Vycor tube at 300°C, and the resultant powder X-ray diffraction pattern could be ascribed to a phase $Ba_{1.156}Fe_2S_4$ or $Ba_{37}(Fe_2S_4)_{32}$. Boller (*5*) prepared his β-$BaFe_2S_4$ by heating the α phase in a continuously evacuated system at about 280°C, although some decomposition occurred during this process. He also remarks that heating the α phase in evacuated and sealed Vycor tubes leads to phases with $x > 0$, e.g., $Ba_{1.091}Fe_2S_4$ and other products. Evidently the experimental conditions for the $\alpha \rightarrow \beta$ transformation are rather critical, and Boller notes that after heating for only 45 hr at 280°C several phases are observed in the transformed sample.

Our results, as well as Boller's, convinced us that this procedure would not yield single crystals of suitable quality for structure analysis. We decided, therefore, to investigate systematically the dependence of x on the vapor pressure of sulfur in a solid-state reaction and we will report those results later. However, one of the conditions did yield excellent crystals of the desired β-$BaFe_2S_4$ and a structural analysis was done with X-ray diffraction data obtained from this product.

Purified BaS, metallic Fe with nominal purity 99.9%, and S, nominally 5 9's pure, were sealed in an evacuated quartz ampoule. The barium sulfide and iron mixture in the ratio 1 : 2 was contained in a graphite boat at one end of the quartz tube and a large excess of sulfur was placed at the other end of the tube. Heating took place in a gradient furnace with the BaS and Fe charge at 800 ± 3°C and S at 598 ± 3°C, which produced a 6.7-atm vapor pressure of sulfur in the tube. The reaction was carrried out under these conditions for 2 days and the product was quenched in ice water. Very well-crystallized, black material was obtained and the X-ray powder diffraction pattern indicated lines only from the $BaFe_2S_4$ phase (*1*). Many needle-shaped crystals could be seen in the scanning electron microscope (Fig. 1b). Most of them were aggregates with good parallel alignment but others, very thin, appeared to be single. A crystal 12 × 230 μm was mounted and Weissenberg and precession diagrams showed it to be of excellent quality. The single-crystal X-ray diffraction diagrams were consistent with the space groups $I4/m$, $I4$, or $I\bar{4}$.

This crystal was transferred to an automated Picker diffractometer equipped with a graphite monochromator; Cu$K\alpha$ radiation was used for all further work. Even though no evidence for split reflections was seen on the photographs, which would indicate deviation from the $x = 0$ stoichiometry, ω scans were carried out on the 211, 112, and 101 reflections. The half-widths at maximum were, respectively, 0.22°, 0.19°, and 0.21°, and the lineshapes were symmetric with no evidence of splitting. We were satisfied that, indeed, this was the desired $BaFe_2S_4$ phase. Seven reflections with $20° < 2\theta < 51°$ were precisely centered and lattice constants $a = 7.678(2)$ Å, $c = 5.292(4)$ Å were obtained from a least-squares refinement of the data ($\lambda = 1.5405$). A $\theta - 2\theta°$ scan mode was utilized to collect diffraction intensities for a $\frac{1}{8}$ sphere of reciprocal space to $\sin\theta/\lambda = 0.57$ Å^{-1}. Equivalent intensities, after correction for absorption, were averaged and the final data set consisted of 108 reflections greater than 2.5 $\sigma(I)$. The standard deviations were calculated from

$$\sigma(F) = S\left[\frac{P}{t_1^2} + 4\frac{B_1 + B_2}{t_2^2}\right]^{1/2},$$

where S = scan width, P = peak counts, t_1 = peak scan time, t_2 = background scan time, B_1 and B_2 = background counts. The intensities were transformed into structure factor amplitudes by the application of Lorentz, polarization, and absorption corrections ($\mu_l = 975\ \mathrm{cm}^{-1}$ (crystal shape approximated as a tetragonal prism), transmission factors 0.215–0.356). The expression $[ALp + BLp(\cos^2 2\theta)]$ was used for the polarization effect for the monochromator where

$$ALp = \frac{F_M}{1 + \cos^2 2\theta_M} + \frac{1 - F_M}{1 + \cos 2\theta_M}$$

and

$$BLp = \frac{F_M \cos^2 2\theta_M}{1 + \cos^2 2\theta_M} + \frac{(1 - F_M)\cos 2\theta_M}{1 + \cos^2 \theta_M},$$

where F_M was set to 0.5 and θ_M to 13.3°. The atomic scattering factors, including the real and imaginary corrections for anomalous scattering, were taken from Cromer and Liberman (*7*).

Structure Determination

A three-dimensional Patterson function was calculated and checked against the models proposed by Grey (*1*) and Hoggins and Steinfink (*3*). It was evident that the proposed S position at $x = 0.16$, $y = 0.34$, $z = \frac{1}{2}$ (*3*) was not correct. Instead, an interaction corresponding to the S position $x = 0.195$, $y = 0.390$, $z = 0$ was observed, i.e., a 90° rotation of the $(FeS_2)_\infty$ edge-sharing tetrahedral chains from the previously proposed structure. A least-squares refinement

TABLE I

FINAL ATOMIC PARAMETERS AND STANDARD DEVIATIONS ($\times 10^4$) FOR β-$BaFe_2S_4$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ba	0	0	0	75(6) [220(20)][a]	75 [220(20)]	486(18) [690(30)]	—	—	—
Fe	0	$\frac{1}{2}$	$\frac{1}{4}$	58(7) [170(20)]	58 [170(20)]	68(14) [100(20)]	—	—	—
S	6196(4)	1986(4)	0	63(6) [190(20)]	70(6) [210(20]	114(15) [160(21)]	16(4) [50(10)]	—	—

[a] $[U_{ij}(\sigma U_{ij})]$.

with isotropic temperature factors was carried out using the program NUCLS(*8*), minimizing $\sum \omega(F_0 - F_c)^2$ with $\omega = [\sigma(F_0)^2]^{-1}$. For the 108 observed structure amplitudes, R was 0.099 and wR was 0.075. Five cycles of refinement, changing to anisotropic temperature factors, converged to $R = 0.036, wR = 0.037$, and the inclusion of an extinction coefficient (*9*), $c = 1.409 \times 10^{-5}$, yielded $R = wR = 0.031$. The standard deviation of a reflection of unit weight is 1.47. Table I contains a listing of the final atomic parameters and Table II of observed and calculated F. The highest peak

TABLE II

OBSERVED AND CALCULATED F (×10) FOR β-$BaFe_2S_4$[a]

H	K	F_{obs}	F_{calc}	H	K	F_{obs}	F_{calc}	H	K	F_{obs}	F_{calc}	H	K	F_{obs}	F_{calc}
	***	$L = 0$	***	1	8	407	394	2	8	33	37<	5	2	76	111<
1	1	176	179	2	1	488	492	3	1	1856	1871	5	4	279	261
1	3	75	49≥	2	3	521	548	3	3	735	729	6	1	285	292
1	5	114	92	2	5	468	491	3	5	749	738	6	3	85	110≥
1	7	440	445	2	7	433	418	3	7	601	584	7	0	11	57<
2	0	1484	1405	3	0	709	686	4	0	248	221	7	2	318	325
2	2	1536	1545	3	2	474	470	4	2	10	53<		***	$L = 4$	***
2	4	1773	1853	3	4	607	606	4	4	66	116<	0	0	1332	1362
2	6	551	567	3	6	797	813	4	6	11	80<	1	1	286	290
2	8	555	553	3	8	72	74≥	5	1	659	659	1	3	243	216
3	1	905	906	4	1	673	657	5	3	905	880	1	5	42	105<
3	3	250	283	4	3	1090	1105	5	5	1045	980	2	0	590	567
3	5	10	20<	4	5	110	149≥	6	0	82	58≥	2	2	690	683
3	7	49	70<	4	7	323	315	6	2	431	405	2	4	1019	1004
4	0	1113	1088	5	0	1117	1106	6	4	209	230	2	6	243	242
4	2	1156	1177	5	2	274	268	7	1	464	487	3	1	337	338
4	4	846	867	5	4	440	430	7	3	615	598	3	3	365	360
4	6	799	817	5	6	274	277	8	0	51	36≥	3	5	200	153
5	1	182	210	6	1	463	475	8	2	155	174	4	0	492	477
5	3	160	161	6	3	236	239		***	$L = 3$	***	4	2	572	560
5	5	429	441	6	5	457	444	1	0	378	358	4	4	420	417
5	7	199	206	7	0	160	145	1	2	1066	1084	5	1	342	306
6	0	979	992	7	2	465	485	1	4	117	121≥	5	3	11	47<
6	2	1297	1311	7	4	612	609	1	6	158	180	6	0	500	520
6	4	485	489	8	1	578	612	2	1	188	229	6	2	748	762
6	6	620	599	8	3	119	131	2	3	294	290		***	$L = 5$	***
7	1	71	108<		***	$L = 2$	***	2	5	316	289	1	0	14	91<
7	3	11	85<	0	0	932	873	2	7	296	269	1	2	550	591
7	5	42	63<	1	1	1196	1235	3	0	409	377	1	4	12	63<
8	0	646	661	1	3	1090	1102	3	2	221	232	2	1	72	36<
8	2	398	411	1	5	908	920	3	4	374	373	2	3	69	75<
	***	$L = 1$	***	1	7	1020	983	3	6	590	590	3	0	139	124<
1	0	758	712	2	0	336	309	4	1	403	388	3	2	31	42<
1	2	1744	1749	2	2	92	57≥	4	3	785	780	4	1	181	149
1	4	307	306	2	4	502	547	4	5	35	59<		***	$L = 6$	***
1	6	315	339	2	6	292	287	5	0	763	781	0	0	14	174<

[a] The symbol ≥ specifies that $\sigma(F) < F_{obs} \leq 2.5\,\sigma(F)$ and < means $F_{obs} < \sigma(F)$.

in the final difference electron density map was 0.67 e Å^{-3}, and was within a ring of density around the Ba position in the $z = 0$ plane.

Discussion

The bond distances and angles are shown in Table III and are as expected. Barium is in 12-fold coordination and the sulfur atoms form a capped tetragonal prism.

Hoggins and Steinfink (*3*) had predicted the sulfur atom coordinates to be $x = 0.34$, $y = 0.16$, $z = 0$ for the β-$BaFe_2S_4$ compound. Boller (*5*) used these coordinates in his refinement of the diffraction intensities and reports a final $R = 0.10$. The major difference between his results and the predicted structure was the movement of Ba^{2+} to $z = 0.099$ from $z = 0$. We used Boller's parameters in a least-squares refinement with our F values, and after three cycles the temperature factor for S rose to 12.3, effectively eliminating it; the z parameter of Ba became 0.021, $B = 1.65$, and the temperature factor for Fe became −0.74; the R value rose to 0.36. It is difficult to carry out a refinement using our parameters and Boller's data, because in fiber photographs reflections (hkl) and (khl) cannot be measured separately and in a crystal with diffraction symmetry $4/m$ they have different intensities. Further superposition of intensities occurs when $h^2 + k^2$ is the same for two different reflections, e.g., (431) and (501). We converted our $F(hkl)$ to $F^2(hkl)$ and compared the resultant values with Boller's $(I/LP)_0$ (*5*). Good qualitative agreement was observed for all reflections except (112) and (202). Boller's intensities are nearly equal, while in our data set $F^2(112) \gg F^2(202)$. The possibility exists that this difference implies that the β-$BaFe_2S_4$ obtained by heating the α phase which was prepared by ion exchange of $KFeS_2$ has a different structure from the material we prepared, and may be an intermediate form between α and β. It should be emphasized that, except for these two reflections, all others agree and that the lattice constants and space groups also agree.

Boller's structure has a statistical distribution of Ba in position 4e of $I4/m$, while we successfully refined the structure with Ba in the 2a position. However, the β_{33} parameter is inordinately large, and this points to the possibility that the true Ba positions are displaced from $z = 0$, i.e., they are not located precisely in the center of the tetragonal prism. We undertook, therefore, a refinement of the structure in space group $I4$, fixing the orientation of the $(FeS_2)_\infty$ chain and placing Ba in the 2a position. After five

TABLE III

BOND DISTANCES AND ANGLES FOR β-$BaFe_2S_4$

Distance (Å)		Angle (deg)	
8Ba–S	3.634(<1)	3S–Fe–S	110.9(>1)
4Ba–S	3.295(3)	3S–Fe–S	106.7(>1)
4Fe–S	2.218(<1)		
Fe–Fe	2.646(<1)		
S–S	3.522(5)		
S–S	3.652(<1)		
S–S	3.560(5)		
S–S	3.411(<1)		

cycles of refinement, R was 0.032, $wR = 0.030$, and for Ba, $z = 0.0063(37)$, $\beta_{11} = 0.0076(6)$, $\beta_{33} = 0.0477(19)$. The z parameter does not differ significantly from zero and β_{33} remained large. This may simply reflect the fact that there are no near neighbors along the c axis and the vibrational ellipsoid is, thus, very anisotropic. The occupancy factor for Ba was also varied in this refinement and was 2.024(16), i.e., it does not significantly vary from full occupancy.

It is concluded that the centric structure is correct, that the centers of the capped tetragonal prisms formed by 12 sulfur anions are fully occupied by barium ions, and that this is the structure of β-$BaFe_2S_4$, the $p = q = 1$ member of the infinitely adaptive series of compounds $Ba_p(Fe_2S_4)_q$.

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