Phase Relations of Ternary Compounds in the Ba–Fe–S System

T. P. PERNG, N. KIMIZUKA,* AND H. STEINFINK

*Materials Science Laboratories, Department of Chemical Engineering,
The University of Texas, Austin, Texas 78712*

The phase relations of the ternary phases at 900 and 700°C were determined by heating mixtures in the regions BaS–FeS–FeS_2 and Fe–FeS–BaS and identifying the products by powder X-ray diffraction. The stable ternary phases at 900°C are $BaFe_2S_3$, Ba_2FeS_3, $Ba_6Fe_8S_{15}$, a solid solution $BaFeS_2$–$Ba_7Fe_6S_{14}$, Ba_2FeS_4, the infinitely adaptive series $Ba_3Fe_{1+x}S_5$, $\frac{1}{3} \leq x \leq \frac{2}{3}$, and $Ba_9Fe_{16}S_{32}$ which belongs to the infinitely adaptive series $Ba_{1+x}Fe_2S_4$. At 700°C the stable ternary phases are: $BaFe_2S_3$, Ba_2FeS_3, $BaFeS_2$–$Ba_7Fe_6S_{14}$ (solid solution), $Ba_6Fe_8S_{15}$, Ba_2FeS_4, $Ba_5Fe_4S_{11}$, and two infinitely adaptive series: $Ba_3Fe_{1+x}S_5$ and $Ba_{1+x}Fe_2S_4$. A stable ternary phase at 700 and 900°C with probable composition $Ba_2Fe_4S_5$ was found in the Fe–FeS–BaS section.

Introduction

Extensive research has been carried out for nearly 10 years on compounds that form in the Ba–Fe–S system (*1*). However, no systematic investigation of the phase relations among the many reported compounds has been published. Grey reported a series of experiments in which he investigated the dependence of the value of x on temperature and sulfur vapor pressure for the infinitely adaptive series of compounds $Ba_{1+x}Fe_2S_4$ (*2*). Swinnea and Steinfink (*3*) described the preparation and crystal structure of β-$BaFe_2S_4$, the end member of this series, and also provided additional data for the preparations of compounds with $x > 0$ (*4*). Cohen *et al.* (*5*), in the discussion of the crystal structure of $Ba_5Fe_4S_{11}$, also reported on the stability range of this com-

pound. Information concerning the preparation of the high-pressure phases, Ba_3FeS_5 and a polymorph, $Ba_9Fe_3S_{11}(S_2)_2$, is presented in the discussions of their crystal structures (*6, 7*). This paper reports the results of a systematic investigation of the phase relations at 700 and 900°C. Most of the previously reported compounds can be considered to occur in the pseudoternary system BaS–FeS–FeS_2. Nonstoichiometric $Fe_{1-x}S$ is stable below 1190°C (*8*); the melting point of BaS is above 1200°C and FeS_2 decomposes to $Fe_{1-x}S$ and a liquid phase at 743°C under normal pressure (*8*). Thus the 700°C isotherm represents the phase relations in the subsolidus region, while the 900°C isotherm explores the phase diagram in the presence of a liquid phase.

Experimental

FeS, FeS_2, and BaS were used as the starting materials. FeS and FeS_2 were prepared from iron metal powder (99.99%) and

sulfur (99.9%). BaS was purchased from Apache Chemicals, Inc., as a yellow powder with a stated purity of 98–99%. FeS was prepared by reacting a mixture of Fe : S = 1.000 : 1.000 atomic weight ratio in an evacuated Pyrex glass tube at about 150°C for 1 week. The product from this reaction was crushed under acetone in an agate mortar, resealed in an evacuated Vycor tube, heated at 500°C for 10 days and then cooled. A powder X-ray diffraction pattern showed that the material was single-phase troilite, FeS.

To prepare FeS_2 a mixture of Fe : S = 1.000 : 2.000 (atomic weight ratio) was sealed in a Pyrex glass tube and heated at about 150°C for 1 month. The product was crushed under acetone in an agate mortar, resealed in a Vycor tube, and heated at 500°C for 1 week and 700°C for 2 weeks. A powder X-ray diffraction pattern showed that the final product was single-phase pyrite, FeS_2.

An X-ray diffraction powder pattern showed that the commercial BaS had BaS_2 admixed with it. The yellow material was treated with H_2 at 650°C for 2 days and the resultant white product was single-phase BaS as judged by an X-ray diffraction pattern.

Resistance heated, horizontal tube furnaces were used for carrying out the reactions. The temperature was controlled by a Research, Inc. controller which held the temperature fluctuations to ±1.5°C in a constant temperature zone about 5 cm in length at 900°C.

About 800 mg of a starting mixture was placed into a capped carbon crucible about 40 mm long that was machined from spectroscopically pure graphite rods. The crucible was then sealed in an evacuated Vycor tube 7 mm i.d. and 85 mm long. In order to minimize the dead volume in a sample tube, Vycor glass powder was packed into the sample ampoule (9). No solid-state reaction between the carbon crucible and the sulfide material was observed and the weight difference of the carbon crucible before and after a reaction was zero, within experimental error. At the end of the reaction the ampoule was carefully opened and reweighed. The maximum weight loss was 0.5%, calculated on the basis of sample weight. This loss was ascribed to the presence of S vapor, and indeed it was observed that the weight loss of the condensed phases increased as the FeS_2 component in the reaction mixture increased.

All samples were quenched by dropping them into water. To ascertain the equilibrium state of the reaction products, the process of sample heating, quenching in water, crushing under acetone in an agate mortar, identification by the X-ray powder diffraction method, reheating, etc. was repeated. When the intensities and positions of the lines of the X-ray diffraction pattern became invariant, we concluded that the reaction had attained equilibrium. All products were also examined under an optical microscope. Even though the ternary compounds are black, it is possible to detect the presence of a liquid phase in the mixture on the basis of morphology.

X-Ray powder diffraction patterns obtained with a diffractometer fitted with a diffracted beam graphite monochromator and $CuK\alpha$ radiation were used to identify the phases. Powder patterns were calculated and drawn by computer for all known phases, and these standard patterns were used to identify the phases in the reaction products by direct comparison with the standards. This procedure was exceptionally well suited for the identification of minor constituents in these very complex powder diffraction patterns. It is estimated that under favorable conditions as little as 1% of a phase could be seen.

The 900°C Isotherm

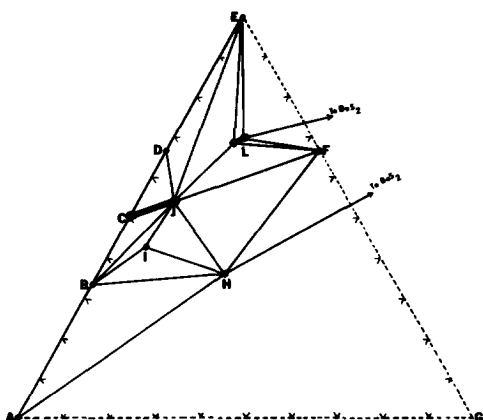The phase relations among the stable phases at 900°C shown in Fig. 1 were

FIG. 1. Phase relations at 900°C, A = FeS, B = BaFe$_2$S$_3$, C = BaFeS$_2$, J = Ba$_7$Fe$_6$S$_{14}$, and C–J denotes a solid solution; D = Ba$_2$FeS$_3$, E = BaS, F = Ba$_2$FeS$_4$, G = FeS$_2$, H = Ba$_{1.125}$Fe$_2$S$_4$, I = Ba$_6$Fe$_8$S$_{15}$, L = infinitely adaptive series, Ba$_3$Fe$_{1+x}$S$_5$. Intervals on the diagram are in 10%.

established from the results of about 150 equilibrium experiments. An abbreviated list of experimental results, which are essential for the establishment of the phase relations, is shown in Table I.

In the pseudobinary system BaS–FeS two stable ternary phases, Ba$_2$FeS$_3$ and BaFe$_2$S$_3$, occur and they have been described previously (10). When the reaction product from a mixture of 1BaS : 1FeS (sample 4) was examined after repeated heating a single phase was finally observed which had an X-ray powder diffraction pattern identical to that of Ba$_7$Fe$_6$S$_{14}$ (11). A sample consisting of BaFe$_2$S$_3$: Ba$_2$FeS$_3$ = 1 : 1 did not attain equilibrium after heating for 7 days and showed three phases, BaFe$_2$S$_3$, Ba$_2$FeS$_3$, and "BaFeS$_2$," which had the same X-ray diffraction pattern as Ba$_7$Fe$_6$S$_{14}$. Only after repeated grinding and heating did the starting compounds disappear. When a mixture of BaS and FeS is reacted and cooled, and the ampoule is opened it is evident that the product was formed under pressure. This pressure is probably less than 20 atm or the ampoule would have exploded. If the product is

reground and reheated then any subsequent opening of the ampoule indicates that no pressure greater than atmospheric is present. These observations imply that the S vapor activity is an important parameter in the reaction kinetics. Initially this S activity is due to the formation of nonstoichiometric Fe$_{1-x}$S. Once BaFe$_2$S$_3$ and Ba$_2$FeS$_3$ have formed, or if they constitute the starting mixture, the subsequent approach to equilibrium becomes lengthy. To prove this inference, we heated a mixture of 1BaS : 1FeS continuously for 7 days and found that single-phase material was obtained. We also reacted a mixture of 1Fe : 1Ba$_7$Fe$_6$S$_{14}$, and after 7 days the X-ray powder pattern showed BaFe$_2$S$_3$, Ba$_2$FeS$_3$ and "BaFeS$_2$." No free Fe was seen in the pattern, nor was there any magnetic evidence for its presence. The product was reheated for an additional week and "BaFeS$_2$" became the major phase. We are certain that eventually single-phase material would have been produced, but the slow approach to equilibrium is most likely due to the effect previously discussed.

Single crystals were selected from several "BaFeS$_2$" preparations and the X-ray patterns yielded the identical lattice constants and space group reported for Ba$_7$Fe$_6$S$_{14}$, and it also had the identical Mössbauer spectrum (11, 12).

The results from an energy-dispersive X-ray analysis indicated Ba : Fe ≈ 1 : 1 but did not permit the assignment of a definite stoichiometry. Atomic absorption results for Ba and Fe and S determined as SO$_2$ using ir absorption indicated a formula Ba$_{0.9}$FeS$_{2.0}$. We conclude that this phase has a homogeneity range from Ba$_7$Fe$_6$S$_{14}$ to BaFeS$_2$ and is shown as such in Fig. 1. It is noteworthy that the first report on this compound stated its composition as Ba$_5$Fe$_5$S$_{12}$ (13).

In the ternary system BaS–FeS–FeS$_2$ the known phases Ba$_6$Fe$_8$S$_{15}$ (10) and Ba$_7$Fe$_6$S$_{14}$ were observed. In contrast to the difficulty

TABLE I

PHASE RELATIONS AT 900°C

No.	Composition BaS : FeS : FeS₂			Reaction time (days)	Reaction products	No.	Composition BaS : FeS : FeS₂			Reaction time (days)	Reaction products
1	3	1	0	4	BaS, 2 – 1 – 3[a]	19	5	12	3	3	1 – 2 – 3, 9 – 16 – 32, FeS
2	2	1	0	3	2 – 1 – 3	20	6	1	1	4	BaS, 9 – 4 – 15
3	3	2	0	3 + 3 + 4[b]	2 – 1 – 3, 7 – 6 – 14[c]	21	9	2	2	4	9 – 4 – 15
4	1	1	0	3 + 5.5 + 3 + 3	1 – 1 – 2[c]	22	10	3	3	3 + 3	2 – 1 – 4, 15 – 7 – 25, 7 – 6 – 14
5	2	3	0	7	1 – 2 – 3, 7 – 6 – 14[c]	23	3	1	1	3 + 4	2 – 1 – 4, 7 – 6 – 14
6	1	2	0	3	1 – 2 – 3	24	46	17	17	3	2 – 1 – 4, 7 – 6 – 14, 9 – 16 – 32
7	1	3	0	4	FeS, 1 – 2 – 3	25	1	1	1	4	9 – 16 – 32
8	62.49	33.33	4.18	3	2 – 1 – 3, 7 – 6 – 14, BaS	26	1	2	2	3	9 – 16 – 32, FeS
9	21	17	2	5	7 – 6 – 14[c]	27	27	1	9	3.5 + 3	9 – 4 – 15, BaS, BaS₂
10	6.44	6.44	1	4	7 – 6 – 14, 6 – 8 – 15	28	13	4	3	3 + 4	7 – 6 – 14, 15 – 7 – 25, 2 – 1 – 4
11	7	5	1	4	7 – 6 – 14	29	5	1	2	3 + 3	2 – 1 – 4, 7 – 6 – 14
12	6	7	1	4	6 – 8 – 15	30	5	2	4	3 + 3.5	2 – 1 – 4, 9 – 16 – 32, BaS₂
13	8	11	1	4.5	6 – 8 – 15, 1 – 2 – 3	31	7	3	10	3	9 – 16 – 32, BaS₂
14	31	6	3	3	BaS, 15 – 7 – 25, 7 – 6 – 14	32	4	0	1	3	BaS, 9 – 4 – 15, BaS₂
15	6	3	3	3	7 – 6 – 14, 15 – 7 – 25	33	32.3	0	11.8	2.5 + 3	9 – 4 – 15, BaS₂
16	19	20	1	9	1 – 2 – 3, 7 – 6 – 14[c]	34	9	0	4	3	9 – 4 – 15, 2 – 1 – 4, BaS₂
17	9	4	3	4 + 3	7 – 6 – 14, 9 – 16 – 32	35	2	0	1	2	2 – 1 – 4
18	17	17	6	4 + 4 + 4 + 4 + 3	7 – 6 – 14, 9 – 16 – 32, 6 – 8 – 15	36	21.5	0	19	2	9 – 16 – 32, BaS₂

[a] X–Y–Z denotes the stoichiometry $Ba_XFe_YS_Z$.
[b] Heating for 3 days, regrinding and heating for 3 days, regrinding and heating for 4 days.
[c] 1 – 1 – 2 ↔ 7 – 6 – 14: any composition in the solid solution range.

in achieving an equilibrium product from a mixture that yields "BaFeS$_2$" the reaction of a 7BaS : 5FeS : 1FeS$_2$ mixture (sample 11) proceeds rapidly and yields single-phase material. The infinitely adaptive series Ba$_3$Fe$_{1+x}$S$_5$ (14) and Ba$_{1+x}$Fe$_2$S$_4$ (15) are also observed. The values of x for the former lie between $\frac{2}{3}$ and $\frac{1}{3}$ but only one compound from the latter series, Ba$_9$Fe$_{16}$S$_{32}$ (Ba$_{1.125}$Fe$_2$S$_4$) was observed under the experimental conditions at 900°C. The dependence of x on the vapor pressure of sulfur in the series Ba$_{1+x}$Fe$_2$S$_4$ has been investigated in detail (4, 16).

In the pseudobinary system BaS–FeS$_2$ only one stable phase is observed with the nominal stoichiometry Ba$_2$FeS$_4$. The X-ray powder diffraction pattern of this material was identical with that from a compound which had been labeled α-Ba$_9$Fe$_4$S$_{15}$ (14). The stoichiometry based on the published crystal structure yields a formula Ba$_9$Fe$_4$S$_{16.7}$ and in conjunction with the thermochemical results the designation α-Ba$_9$Fe$_4$S$_{15}$ and the description of this phase as a low-temperature polymorph of β-Ba$_9$Fe$_4$S$_{15}$ are incorrect (14). Several single crystals were selected from the single-phase product "Ba$_2$FeS$_4$" and the lattice constants and space group were identical to the previously described "α-Ba$_9$Fe$_4$S$_{15}$." A complete set of three-dimensional X-ray diffraction data was collected and the crystal structure redetermined. It was precisely the same as previously reported (14). Also, the Mössbauer spectrum was identical to that previously reported for "α-Ba$_9$Fe$_4$S$_{15}$." Mixtures of BaS : FeS$_2$ = 2 : 1 consistently yielded single-phase material but mixtures of 9 : 4 yielded a product whose diffraction pattern showed the presence of BaS$_2$, β-Ba$_9$Fe$_4$S$_{15}$ (Ba$_3$Fe$_{1.333}$S$_5$) and "α-Ba$_9$Fe$_4$S$_{15}$." Energy dispersive X-ray analyses were carried out on the Ba$_2$FeS$_4$ material and the Ba : Fe ratio was about 2. Atomic absorption analysis for Ba and Fe and S determined as SO$_2$ yielded a

formula Ba$_2$Fe$_{1.06}$S$_{4.03}$. A density measurement gave ρ = 3.98 ± .03 g/cm^3; calculated ρ = 3.83 g/cm^3 for Ba$_2$FeS$_4$ and 4.17 g/cm^3 for "α-Ba$_9$Fe$_4$S$_{16.7}$." On the basis of the thermochemical and analytical results we have used the point corresponding to Ba$_2$FeS$_4$ for drawing the phase fields of Fig. 1. It is recommended that the letter β be omitted for the member of the infinitely adaptive series Ba$_9$Fe$_4$S$_{15}$ (Ba$_3$Fe$_{1.333}$S$_5$) (14).

The 700°C Isotherm

About 150 equilibrium experiments were carried out to establish the phase relations shown in Fig. 2 and in Table II the phases obtained at equilibrium from 33 compositions are summarized. In general, the solid-state reaction rate between FeS, FeS$_2$ and BaS is slow and to assure that equilibrium was reached three approaches were used: (1) Starting mixtures of BaS, FeS, and FeS$_2$ were reacted at 700°C. (2) Starting mixtures of BaS, Fe, and S were reacted at 250°C and then heated at 700°C. (3) Starting mixtures of BaS, FeS, and FeS$_2$ were reacted at 900°C and after a suitable interval the temperature was lowered to 700°C. At the end of the reaction the samples were quenched in water.
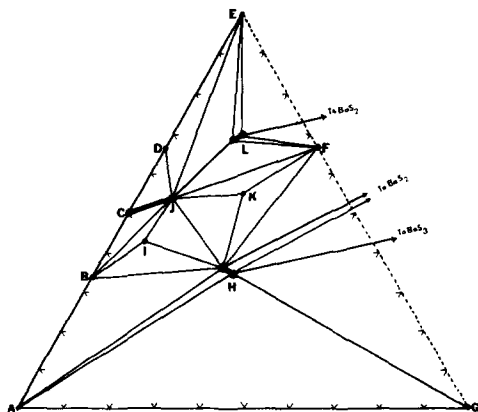

FIG. 2. Phase relations at 700°C. The symbols retain the same meaning, except H is the infinitely adaptive series Ba$_{1+x}$Fe$_2$S$_4$ and K = Ba$_5$Fe$_4$S$_{11}$.

TABLE II

PHASE RELATIONS AT 700°C

No.	Composition BaS : FeS : FeS$_2$			Reaction time (days)	Reaction products
1	3	1	0	10	BaS, 2 – 1 – 3
2	2	1	0	12	2 – 1 – 3
3	1	1	0	25	1 – 1 – 2
4	1	2	0	10	1 – 2 – 3
5	1	3	0	11	1 – 2 – 3, FeS
6	31	6	3	15	BaS, 7 – 6 – 14, 15 – 7 – 25
7	14	5	1	10	BaS, 7 – 6 – 14
8	15	4	3	10	15 – 7 – 25
9	25	14	1	17	2 – 1 – 3, 7 – 6 – 14
10	6	3	1	10	15 – 7 – 25, 7 – 6 – 14
11	7	5	1	10	7 – 6 – 14
12	6.44	6.44	1	10	6 – 8 – 15, 7 – 6 – 14
13	19	19	2	15	1 – 2 – 3, 7 – 6 – 14
14	8	11	1	12	1 – 2 – 3, 6 – 8 – 15
15	40	44.5	15.5	15	9 – 16 – 32, 6 – 8 – 15
16	7	9	4	10	(1 + x) – 2 – 4, 1 – 2 – 3
17	4	12	3	7	(1 + x) – 2 – 4, FeS

No.	Composition BaS : FeS : FeS$_2$			Reaction time (days)	Reaction products
18	9	8	2	15	(1 + x) – 2 – 4, 7 – 6 – 14, 6 – 8 – 15
19	6	1	1	15	BaS, 9 – 4 – 15
20	26	7	7	15	2 – 1 – 4, 15 – 7 – 25, 7 – 6 – 14
21	58	21	21	15	7 – 6 – 14, 5 – 4 – 11, 2 – 1 – 4
22	5	1	2	10	7 – 6 – 14, 2 – 1 – 4
23	5	2	2	15	5 – 4 – 11
24	3	2	1	12	7 – 6 – 14, 5 – 4 – 11, 9 – 16 – 32
25	1	1	1	8	(1 + x) – 2 – 4
26	1	2	2	9	(1 + x) – 2 – 4, FeS, FeS$_2$
27	7	3	10	7	FeS$_2$, (1 + x) – 2 – 4, BaS$_3$
28	4	0	1	7	BaS, BaS$_3$, 9 – 4 – 15
29	7	0	3	7	2 – 1 – 4, BaS$_3$, 9 – 4 – 15
30	2	0	1	10	2 – 1 – 4
31	3	0	2	10	(1 + x) – 2 – 4, 2 – 1 – 4, BaS$_2$
32	1	0	1	7	(1 + x) – 2 – 4, BaS$_2$, BaS$_3$
33	1	0	4	7	FeS$_2$, (1 + x) – 2 – 4, BaS$_3$

In the pseudobinary system BaS–FeS three stable ternary phases, Ba_2FeS_3, $BaFe_2S_3$, and $BaFeS_2$ were observed. In the pseudobinary system BaS–FeS$_2$, one stable ternary phase is found, which we now designate as Ba_2FeS_4. In the ternary system BaS–FeS–FeS$_2$ two infinitely adaptive series are observed with the general formulas $Ba_3Fe_{1+x}S_5$ and $Ba_{1+x}Fe_2S_4$; the values of x for the first series lie between $\frac{2}{3}$ and $\frac{1}{3}$ and in particular the phases $Ba_{15}Fe_7S_{25}$ ($x = 0.4$) and $Ba_9Fe_4S_{15}$ ($x = \frac{1}{3}$) are easily observed although other compositions were also seen. For the latter series compounds with $0.072 \leq x \leq 0.125$ were seen. Three additional stable phases are $Ba_8Fe_8S_{15}$, $Ba_5Fe_4S_{11}$, and $Ba_7Fe_6S_{14}$. A detailed discussion of the stability range of $Ba_5Fe_4S_{11}$ is given by Cohen et al. (5).

Fe–FeS–BaS

When we investigated the binary relations between BaS and FeS we observed X-ray diffraction powder lines which could not be assigned to known phases. The intensities among the unknown lines varied depending on the composition of the starting mixtures. This led us to the conclusion that two unknown phases were present and that they may be iron rich; i.e., in the triangle Fe–FeS–BaS. Furthermore, regrinding and reheating at 900°C eliminated these unknown phases. We reacted mixtures of Fe, BaS, and FeS at 900°C with compositions which placed them in the region Fe–Ba$_2$FeS$_3$–BaS and we observed these two unknown phases after the reaction product was examined for the first time. Upon repeated grinding and heating of the products these phases disappeared leading us to the conclusion that they are metastable at 900°C. We are certain that the tie lines between Fe and BaS and Fe and Ba$_2$FeS$_3$ exist at 900°C.

We expanded the experiments to the region Fe–FeS–Ba$_2$FeS$_3$ and the very first result showed powder diffraction lines ascribable to a third unknown phase. Samples 6, 7, and 8 were subjected to the procedures shown in Table III and evidently this unknown phase is stable.

The results of the reactions from samples 10, 13, 14, 15, 17, and 19 place the composition of this phase in the shaded region of Fig. 3. The products from samples 4, 7, 11, 12, and 16 lead to the conclusion that the composition is near the line Fe–BaFe$_2$S$_3$. We observed that this phase is also stable between 700 and 1000°C and that it coexists with BaFe$_2$S$_3$. We experienced great difficulty in bringing the reactions to thermodynamic equilibrium and most reactions did not reach equilibrium. We could never prepare this compound as a single phase. A small single crystal was selected for X-ray diffraction analysis. The compound is orthorhombic, $a = 4.016$, $b = 9.616$, $c = 6.514$ Å, $Pmmn$. A three-dimensional X-ray crystal structure analysis refined to $R = 0.031$ and led to a probable stoichiometry $Ba_2Fe_4S_5$. The idealized crystal structure leads to the formula $BaFe_2S_3$ but one S has a very large thermal parameter. The refinement on the occupancy factor converges to a value of 0.5 so that the formula becomes $BaFe_2S_{2.5}$. A complete description

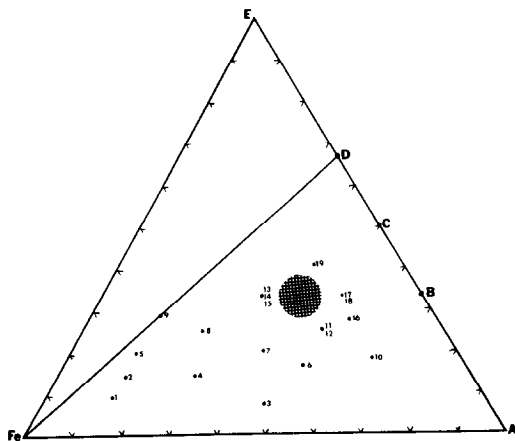FIG. 3. Experimental points investigated to determine the stability range for "Ba$_2$Fe$_4$S$_5$."

TABLE III

REACTIONS IN THE SYSTEM Fe–Ba$_2$FeS$_3$–FeS^a

No.	Composition BaS : FeS : Fe			Temperature (°C)	Reaction condition (days)	Products
1	2	3	17	900	4 + 3	$1 - 2 - 3 \approx x_2,^b$ Fe
2	1	1	5	900	4 + 3	$1 - 2 - 3 \approx x_2 >$ Fe, $2 - 1 - 3$
3	1	6	6	900	4 + 4	FeS $> x_2$, $1 - 2 - 3$, Fe
4	1	2	4	900	3.5 + 4	$1 - 2 - 3 > x_2$, Fe
5	3	2	10	900	4	$2 - 1 - 3 \approx$ Fe $> x_2$
6	1	3	2	900	3.5 + 4.5	FeS, $1 - 2 - 3 >$ Fe, x_2
				700	+ 7	$x_2 > 1 - 2 - 3$, FeS, Fe
				700	+7 + 7	$x_2 \gg 1 - 2 - 3$, FeS
7	BaFe$_2$S$_3$: Fe			700	7	$x_2 >$ Fe, $1 - 2 - 3$
	= 1 : 2			900	+ 7	$x_2 \gg$ Fe, FeS $> 1 - 2 - 3$
8	1	1	2	900	4.5	$2 - 1 - 3 \approx 1 - 2 - 3 >$ Fe, x_2
				700	+7 + 7	$x_2 \gg 2 - 1 - 3 > 1 - 2 - 3$, Fe
					+ 7	$x_2 \gg 2 - 1 - 3$, Fe
9	2	1	4	900	4	$2 - 1 - 3$, Fe
10	2	7	2	900	6	$x_2 >$ FeS, Fe
11	1	2	1	900	3.5 + 6	$x_2 \gg 1 - 2 - 3$, Fe
12	1	2	1	750	6	
				900	+ 8	$x_2 \gg 1 - 2 - 3$, Fe
13	1	1	1	900	3 + 3	$x_2 \gg 2 - 1 - 3$, Fe
14	1	1	1	1000	3	$x_2 \gg 2 - 1 - 3$, Fe
15	1	1	1	750	8	$x_2 \gg 2 - 1 - 3$, Fe
16	3	6	2	900	9.5	$x_2 > 1 - 2 - 3 \gg$ FeS, Fe
17	2	3	1	900	6 + 6	$1 - 2 - 3 \approx x_2$
18	2	3	1	700	9	$x_2 \gg$ FeS, $2 - 1 - 3$, BaS
19	9	9	4	900	3.5	$x_2 \approx 2 - 1 - 3$

^{a} Relative quantities of compounds as judged from X-ray diffraction patterns are shown by: $\approx$, about equal; $>$, greater than; $\gg$, very much larger.

^{b} x_2 is new phase.

of the crystal structure will be published (17). Energy dispersive X-ray analysis, as well as atomic absorption spectroscopy for Ba and Fe, and S determined as SO$_2$ indicate a composition BaFe$_2$S$_{2.1-2.5}$.

Discussion

The stable ternary phases at 900°C are BaFe$_2$S$_3$, Ba$_2$FeS$_3$, Ba$_6$Fe$_8$S$_{15}$, a solid solution BaFeS$_2$–Ba$_7$Fe$_6$S$_{14}$, Ba$_9$Fe$_{16}$S$_{32}$, which is a member of the infinitely adaptive series Ba$_{1+x}$Fe$_2$S$_4$, the infinitely adaptive series Ba$_3$Fe$_{1+x}$S$_5$ with end members Ba$_9$Fe$_4$S$_{15}$ and Ba$_{15}$Fe$_7$S$_{25}$, Ba$_2$FeS$_4$, and BaFe$_2$S$_{2.5}$. At 700°C the stable ternary phases are

BaFe$_2$S$_3$, Ba$_2$FeS$_3$, Ba$_7$Fe$_6$S$_{14}$–BaFeS$_2$, Ba$_6$Fe$_8$S$_{15}$, Ba$_2$FeS$_4$, Ba$_{1+x}$Fe$_2$S$_4$, Ba$_3$Fe$_{1+x}$S$_5$, Ba$_5$Fe$_4$S$_{11}$, and BaFe$_2$S$_{2.5}$.

The results from the studies at 700 and 900°C have uncovered several problems. The existence of a solid solution BaFeS$_2$–Ba$_7$Fe$_6$S$_{14}$ seems to be fairly certain and the triangles B–C–J and C–J–D in the phase diagram in Figs. 1 and 2 are two-phase regions of BaFe$_{1-x}$S$_2$ + BaFe$_2$S$_3$ and BaFe$_{1-x}$S$_2$ + Ba$_2$FeS$_3$, respectively. The Ba$_2$FeS$_4$ composition has the same crystal structure as determined for a previously designated phase "α-Ba$_9$Fe$_4$S$_{15}$." The only single-phase material that can be prepared is from mixtures having the stoichiometry

Ba_2FeS_4. Further work to clarify these points needs to be done but we will not pursue it further.

When mixtures in the approximate ratios $BaS : FeS : FeS_2 = 4 : 1 : 1$, i.e., in the triangle $Ba_7Fe_6S_{14}$–$Ba_{15}Fe_7S_{25}$–Ba_2FeS_4, were heated at 900°C the initial reaction product showed some diffraction lines that could not be identified and thus are ascribed to an unknown phase. Upon regrinding and reheating this unknown phase disappears. Similarly mixtures in the region $Ba_7Fe_6S_{14}$–Ba_2FeS_4–$Ba_9Fe_{16}S_{32}$ gave rise, occasionally, to some diffraction lines which belonged to a different unknown phase and it also disappeared upon regrinding and reheating of the product. A total of four different unknown, metastable phases were encountered at 900°C, the above mentioned two phases and the two unknown compositions in the Fe–Ba_2FeS_3–BaS region. We do not intend to do further work leading to the identification of these phases.

Acknowledgment

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