JOURNAL OF SOLID STATE CHEMISTRY 36, 9–19 (1981)

Studies on the Compounds in Ba–Fe–S System. III. Phase Relation of $Ba_{1+x}Fe_2S_4$ with Infinitely Adaptive Structure

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Received December 31, 1979; in revised form March 10, 1980

Samples of the infinitely adaptive phase $Ba_{1+x}Fe_2S_4$ (or $Ba_p(Fe_2S_4)_q$; p, q: integer) were carefully prepared by changing the nominal composition and annealing temperature T_a. The single-phase materials, defined in this paper as a member of the infinitely adaptive series $Ba_p(Fe_2S_4)_q$, were obtained by the addition of excess sulfur in the nominal composition range $0.05 \leq x \leq 0.20$ at T_a ranging from 650 to 880°C. X-Ray powder diffraction showed the existence of many members of the $Ba_p(Fe_2S_4)_q$ series. The supercell periodicity was markedly dependent on T_a. The composition of reaction products estimated from X-ray diffraction, the method proposed by Grey based on crystallographic considerations, deviated in practice from the nominal composition. This fact suggests random distribution of Ba and Fe vacancies.

Introduction

The $Ba_{1+x}Fe_2S_4$ phase in the ternary Ba–Fe–S system was first reported by Grey (*1*), and the homologous series of compounds $Ba_p(Fe_2S_4)_q$ (p, q: integer) have been known in the composition range $0.0625 \leq x \leq 0.143$ ($x = p/q - 1$). Crystal structure analysis by single-crystal X-ray diffraction was reported in detail for the two members of the series, $Ba_5Fe_9S_{18}$ (*2*) and $Ba_9Fe_{16}S_{32}$ (*3*).[1] The average structure of these phases can be described as superstructures based on the NH_4CuMoS_4-type structure (*4*). There are two chains, a Ba chain with c_1 unit length and a $(FeS_2)_\infty$ edge shared tetrahedron chain with unit length c_2, along the c axis. The c dimension of the unit cell is equal to the least common multiple of c_1 and c_2.

$$c = q\,c_1 = p\,c_2. \qquad (1)$$

When c_1 is equal to c_2, the lattice is isostructural with NH_4CuMoS_4, which corresponds to the compound "$BaFe_2S_4$."[2] As the Ba content x changes, the periodicity of two chains, c_1 and c_2, changes and the lattice parameter c of the supercell changes following relation (1). The relation between the composition and the supercell periodicity is expressed by the formula

$$1 + x = p/q = c_1/c_2. \qquad (2)$$

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[1] These structures may be considered as the average structure with the average composition of $Ba_5Fe_9S_{18}$ and $Ba_9Fe_{16}S_{32}$. As will be published in later papers many members of the $Ba_p(Fe_2S_4)_q$ series exist in a microscopic scale.

[2] According to a personal communication, Professor Steinfink's group has succeeded in synthesis and crystal structure analysis of "$BaFe_2S_4$," results of which have been published (*5*).

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Seven members of the $Ba_p(Fe_2S_4)_q$ series have been prepared so far in the composition range $0.0625 \leq x \leq 0.143$ (*1*, *3*). Relation (2) implies that the slight change of Ba concentration results in the formation of new supercell. In this sense, the $Ba_{1+x}Fe_2S_4$ phase is known as an example of an "infinitely adaptive structure" proposed by J. S. Anderson (*6*).

Grey (*1*) obtained $Ba_{1+x}Fe_2S_4$ samples by heating the stoichiometric starting mixture, BaS + 2Fe + 3S : $BaFe_2S_4$, always accompanied by impurity phases such as $BaFe_2S_3$, $Fe_{1-x}S$ and/or FeS_2. It was pointed out that the supercell periodicity principally depends on the annealing temperature T_a (*1*). In relation to the "infinitely adaptive structure" of these phases, careful sample preparation is needed to characterize these complex phases. This paper describes the preparation of samples changing nominal composition and also annealing temperature in order to investigate the phase relation and the effect of heat treatment on the superstructure. The present authors propose the possibility of nonstoichiometric infinitely adaptive phase $Ba_{p'}Fe_{2q'}S_4$ with random distribution of Fe and Ba vacancies ($q \neq 1$).

Experimental

Samples were prepared by heating the mixture of BaS, Fe, and S in evacuated silica tubes. To avoid reaction between BaS and silica, the charges were enclosed in graphite crucibles. Here, we define the nominal composition α as the atomic ratio in the starting mixture of 2Ba to Fe, both of which are reasonably assumed to be perfectly retained in the reaction products. The nominal composition was selected variously in the range $1 \leq 2Ba/Fe \leq 1.5$ and $1/6 \leq Ba/S \leq \alpha/4$ (both given in atomic ratio). The mixtures were heated at 350°C for 1 day and the temperature was then raised. Several annealing temperatures T_a were selected in the range $500°C \leq T_a \leq 1000°C$. The annealing period was varied from 2 to 5 weeks and then the samples were quenched in cold water. Obtained products were examined by an X-ray diffractometer using Cu$K\alpha$ radiation. For the determination of lattice parameters, the step scan method was employed, and the silicon powder was used as an internal standard.

Effect of Sulfur Composition

Reaction products having nominal composition $Ba_\alpha Fe_2S_4$ (stoichiometric composition) were always accompanied with impurity phases such as $BaFe_2S_3$ or $Fe_{1-x}S$. This implies that the equilibrium sulfur vapor pressure is rather high, and the expected single phase of $Ba_{1+x}Fe_2S_4$ might not be obtained. When excess sulfur was added, we could obtain impurity-free products. To make clear the effect of excess sulfur on the phase of products, six kinds of starting mixture with the same nominal ratio of Ba to Fe ($\alpha = 1.10$) varying the ratio of Ba to S, 1/4, 1/5, 1/6, 1/9, 1/15 and large excess sulfur (the ratio for the stoichiometry is 1.10/4) were heated at 700°C for 3 weeks. Within experimental error, the amount of starting material (500 mg) and the volume of the closed silica tube (8 ml) were kept constant in each experiment. In the first five cases, there remained no liquid sulfur at T_a. In the last case, however, the sulfur existed as liquid phase, and therefore the sulfur vapor pressure is equal to the saturated vapor pressure of liquid sulfur at T_a. The results are summarized in Table I. In the sulfur excess region from Ba/S = 1/4 to 1/6, pure $Ba_{1+x}Fe_2S_4$ phase, which has constant values of the lattice parameters within experimental error, was obtained. In this case the equilibrated vapor pressure of sulfur must increase with increase of starting sulfur content, although the exact value of the pressure is unknown. The calculated

TABLE I

THE CHANGE OF REACTION PRODUCTS BY THE EXCESS SULFUR COMPOSITION (T_a = 700°C)

Ba/S (Atomic ratio)	Nominal composition in atomic ratio Ba	Fe	S	Reaction products	Lattice parameters of $Ba_{1+x}Fe_2S_4$ (Å)
1/4	1.1	2	4.4	$Ba_{1+x}Fe_2S_4$	$a = 7.762\ (\pm 0.002)$ $c/p = 5.09\ (\pm 0.005)$ $c/q = 5.49\ (\pm 0.005)$ $p/q = 1.078\ (\pm 0.005)$
1/5	1.1	2	5.5	$Ba_{1+x}Fe_2S_4$	$a = 7.761, c/p = 5.08$ $c/q = 5.48, p/q = 1.078$
1/6	1.1	2	6.6	$Ba_{1+x}Fe_2S_4$	$a = 7.758, c/p = 5.10$ $c/q = 5.48, p/q = 1.075$
1/9	1.1	2	9.9	$Ba_{1+x}Fe_2S_4$ + FeS_2 + BaS_3	—
1/15	1.1	2	16.5	FeS_2 + BaS_3 + $Ba_{1+x}Fe_2S_4$	—
1/∞	1.1	2	30	BaS_3 + FeS_2	—

sulfur vapor pressure is at most about 3 atm even in the case of 1/6. Present experiment shows that in such a low-pressure region of sulfur vapor the value of p/q[3] ($\simeq 1.078 \pm 0.005$) is almost independent on sulfur vapor pressure within experimental error. Accordingly, in this paper the quantity of sulfur was chosen to be in the range of 1/4 to 1/6 for the ratio of Ba to S, keeping the weight of charges and the volume of the closed silica tubes constant within experimental error. It is noted, however, that the sulfur content of the solid phase in the isoratio of Ba/Fe has to increase with increasing sulfur vapor pressure from consideration of the Gibbs phase rule.

Effect of Annealing Period

In order to discuss the phase diagram, it is necessary for the reaction products to attain final chemical equilibrium. To confirm this, the change of the X-ray powder diffraction pattern with annealing period (T_a = 700°C) was investigated by use of step scan method. As an example, the results of the reaction products with nominal composition $\alpha = 1.10$ and the ratio Ba/S equal to 1/4 are shown in Fig. 1. The fresh mixtures with the same weight were prepared for each run. The reaction product annealed at 350°C for 1 day was the mixture of BaS_2, $Fe_{1-x}S$, and FeS_2. That annealed at 700°C for 1 hr was mainly $Ba_{1+x}Fe_2S_4$ with some impurity phases such as FeS_2 remaining. The peak position of the X-ray powder diffractogram slightly changed as the annealing period increased up to 1 day. The product annealed at 700°C for 2 weeks did not show any diffraction peaks of impurity phases. (As for the diffraction line, marked by arrows in Fig. 1, see Final Remarks.) Thus, 2 weeks as an annealing period is enough to get final chemical equilibrium in the present experiments.

Results and Discussion

Lattice Parameters of Obtained $Ba_{1+x}Fe_2S_4$

X-Ray powder diffraction patterns of the $Ba_{1+x}Fe_2S_4$ phase obtained agree well with

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[3] As for the value p/q, see below.

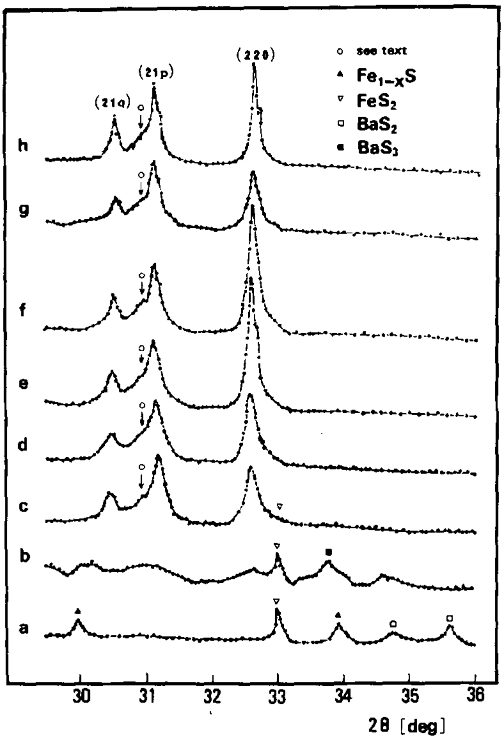

FIG. 1. X-Ray (Cu$K\alpha$) diffraction profiles vs annealing period. The nominal composition is $Ba_{1.1}Fe_2S_{4.4}$. The annealing temperature was first kept at 350°C for 1 day and then raised to 700°C. The diffraction peaks of impurity phases are indicated in the figure. As for the diffraction peak marked by an arrow, see the text. The annealing period is as follows: (a) 350°C, 1 day; (b) 700°C, 10 min; (c) 700°C, 1 hr; (d) 700°C, 2 hr; (e) 700°C, 6 hr; (f) 700°C, 1 day; (g) 700°C, 1 week; (h) 700°C, 2 weeks.

those reported by Grey (*1*). They could be indexed as a tetragonal system. Strong ($hk0$) reflections and relatively weak superlattice reflections (hkl) ($l \neq 0$) were observed. The diffraction lines (especially those with $l \neq 0$) of some samples were somewhat broader than usual. This indicates coexistence of different members of the $Ba_p(Fe_2S_4)_q$ series. The superlattice reflections were indexed as ($h\ k\ np$) or ($h'\ k'\ nq$), where n is 1 or 2, following Grey's report (*1*). Using these superlattice reflections and the lattice parameter a calculated from the ($hk0$) reflections, c/p and c/q were determined. It is apparent from Eq. (1) that c/p and c/q correspond to the unit length of the Ba chain (c_2) and the $(FeS_2)_\infty$ tetrahedron chain (c_1), respectively.

Lattice parameters a, c/p (c_2), c/q (c_1) of $Ba_{1+x}Fe_2S_4$ samples with different nominal compositions are shown together in Fig. 2a as a function of annealing temperature T_a. Lattice parameters are likely to depend on the annealing temperature rather than the nominal composition. Lattice parameters a and c/q (c_1) increase as the annealing temperature is raised, while c/p (c_2) decreases. The c dimension of the lattice can be determined as the least common multiple of c_1 (c/q) and c_2 (c/p), following Eq. (1). It is, however, convenient to describe the periodicity along the c axis with the value p/q ($=c_1/c_2$), which corresponds to the ratio of 2Ba to Fe. (Eq. (2)). Strictly speaking, the value p/q describes "the ratio of Ba *sites* to Fe *sites*" in the $Ba_p(Fe_2S_4)_q$ cell, and it may be called "*structural*" composition (see below). Figure 2b shows the p/q values at several annealing temperatures. The value of p/q increases with an increase of the annealing temperature. The observed values range from 1.060 to 1.150 in the annealing temperature range 600°C $\leq T_a \leq$ 900°C. The typical values of (p, q) pairs with small integers are also indicated at the right of the figure. The previously reported seven members of the $Ba_p(Fe_2S_4)_q$ series are included in the present experiment. Furthermore, new phases with (p, q) = (11, 10), (13, 12), (15, 14), etc. have been confirmed as members of the $Ba_p(Fe_2S_4)_q$ series. The p/q values seem to change continuously with annealing temperature or nominal composition. This behavior is consistent with the infinitely adaptive structure (*6*).

Phase Relation of $Ba_{1+x}Fe_2S_4$

In Fig. 3, the relation among T_a, nominal composition α, and obtained products is shown as a phase diagram. In this figure,

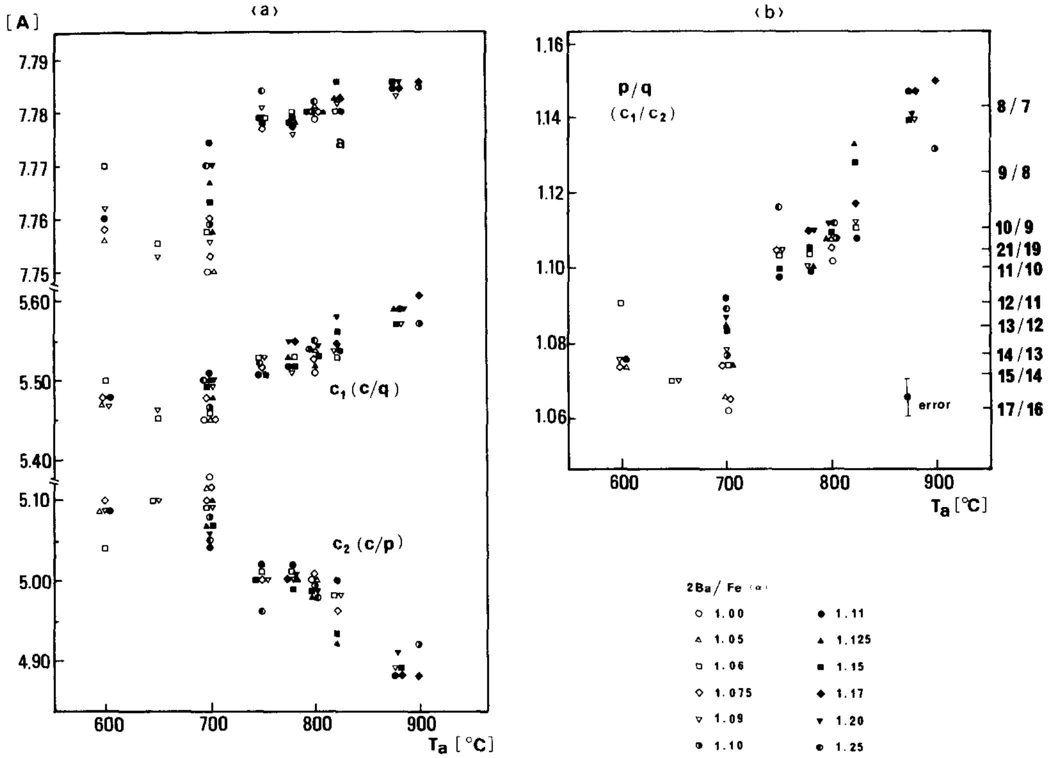

FIG. 2. Lattice parameters a, c_1 (c/q), c_2 (c/p), and the composition p/q, estimated by Eq. (1) ("structural" composition), of obtained $Ba_{1+x}Fe_2S_4$ samples. (a) The plot of a, c/q, and c/p vs annealing temperature T_a. The nominal composition α is shown by different marks. The experimental errors are ±0.001 Å for a and ±0.005 Å for c/q and c/p. (b) The plot of p/q vs T_a. The experimental error for p/q (±0.005 Å) is shown in the figure. Note the strong dependence of p/q on T_a rather than nominal composition.

the composition of the obtained $Ba_{1+x}Fe_2S_4$ phase, p/q, estimated from X-ray diffraction (see Eq. (1), *"structural"* composition) was indicated as the small figure $1000 \times (p/q - 1)$. The ratio of Ba to S in the starting mixture was always 1/4 except for those marked by asterisks (Ba/S = 1/5). The addition of excess sulfur up to Ba/S = 1/6 did not much change the phase relation shown in Fig. 3. The main product in these nominal-composition ($1.10 \leq \alpha \leq 1.50$) and annealing-temperature (500°C $\leq T_a \leq$ 1000°C) ranges were members of the $Ba_p(Fe_2S_4)_q$ series. Impurity phases detected by X-ray powder diffraction are also shown in the figure. The impurity phase was $BaFe_2S_3$ at high annealing temperatures. At low temperatures, iron sulfides, $Fe_{1-x}S$ or FeS_2, appeared as impurity phases. When Ba content was increased, BaS_2, BaS_3, or $Ba_6Fe_8S_{15}$ (7) appeared. Products of $Ba_{1+x}Fe_2S_4$ free from impurity phase[4] were obtained in the nominal composition range $1.00 \leq \alpha \leq 1.20$ and in the annealing temperature range 600°C $\leq T_a \leq$ 900°C.

Effect of Annealing Temperature

As shown in Figs. 2 and 3, the "structural" composition p/q of reaction prod-

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[4] The samples were examined by a transmission electron microscope and were confirmed their "single phase" character.

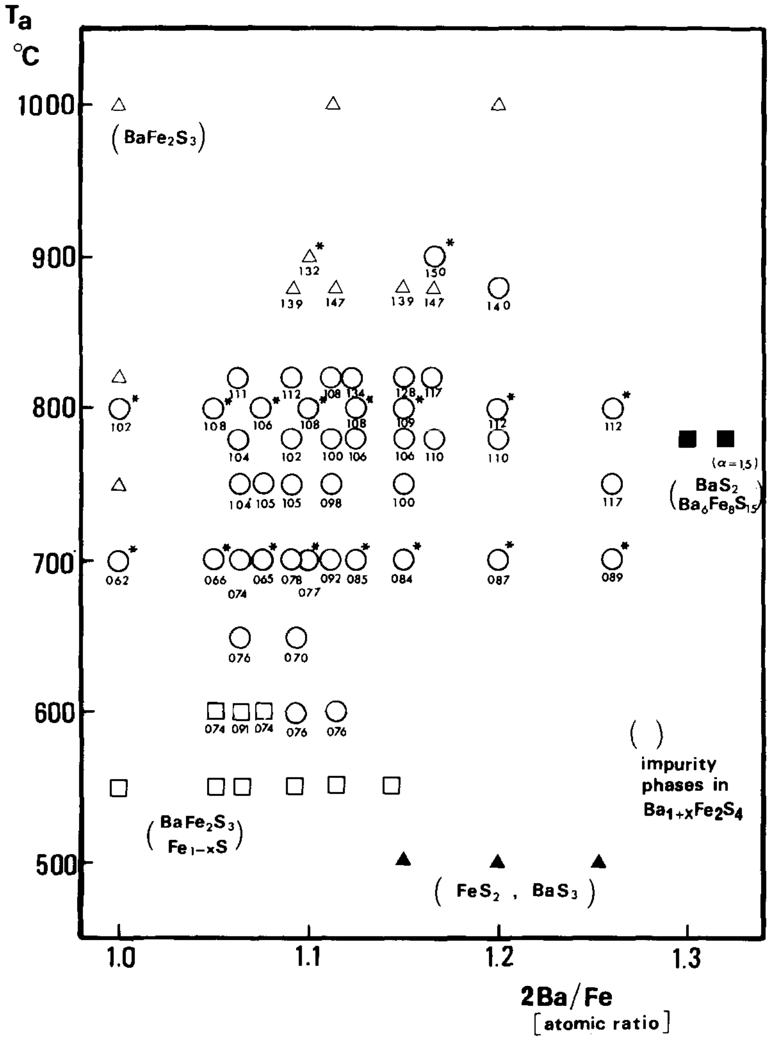

FIG. 3. The relation of annealing temperature T_a, nominal composition α (=2Ba/Fe), and obtained products. The main product in this composition and annealing temperature range is $Ba_{1+x}Fe_2S_4$. The single-phase products of $Ba_{1+x}Fe_2S_4$ are shown by circles and products containing impurity phases are shown by other marks. The composition p/q ("structural" composition) of $Ba_{1+x}Fe_2S_4$ estimated by Eq. (1) is indicated by small figures in the form of $1000 \times (p/q - 1)$ for single-phase products (○) and products with relatively small amount of impurity phases. The impurity phases contained in $Ba_{1+x}Fe_2S_4$ are also shown in the figure. Those marked by asterisk are products with the starting Ba/S atomic ratio of $\frac{1}{5}$, and others are products with Ba/S = $\frac{1}{4}$.

ucts, deduced from Eq. (1), usually deviates from the nominal composition α. The value of p/q (=1 + x) depends on the annealing temperature T_a, as pointed out by Grey (*1*) for the first time. This result was reconfirmed by the following experiment. A mixture with α = 1.10 and Ba/S = 1/5 was heated at 700°C for 2 weeks. The p/q value of the product was 1.078. Then the product (starting material) was divided into three batches, (a), (b), and (c). Sample (a) was heated again at 700°C for 5 weeks; sample (b), at 800°C; and sample (c) at 900°C. In this experiment, a small amount of excess sulfur was added, because the equilibrium sulfur vapor condensed on an inner wall of the silica tube when the first product with $p/q = 1.078$ was quenched in cold water. The p/q value of the former (a) was 1.077, which was the same as the starting material. The p/q values of the latter two were 1.108 and 1.132, respectively, which are different from the starting material. It is, however, noted that only sample (c) annealed at 900°C contains a small amount of $BaFe_2S_3$. Sample (b), then, was heated at 700°C for 5 weeks with a small addition of sulfur. The value of p/q of this sample (1.083) returned to that of sample (a), within experimental error (± 0.005 in p/q). These processes are displayed by powder diffraction patterns in Fig. 4. This experiment firmly confirmed that the value of p/q depends on the annealing temperature T_a and that the change in p/q is reversible. This experiment also has made it clear that there is no change in α during recycled heat treatment. According to the Gibbs phase rule, the number of degrees of freedom of the system is 2 in one solid phase + one gas phase (sulfur) in the ternary Ba–Fe–S system at a fixed temperature. The sulfur content in the solid has to change with equilibrium vapor pressure of sulfur under the condition of fixed ratio of Ba to Fe and at finite temperature. In this sense, this experiment is benefitted by the fact that the p/q value of the phase with the same value of α hardly depends on the sulfur vapor pressure in the low pressure region.

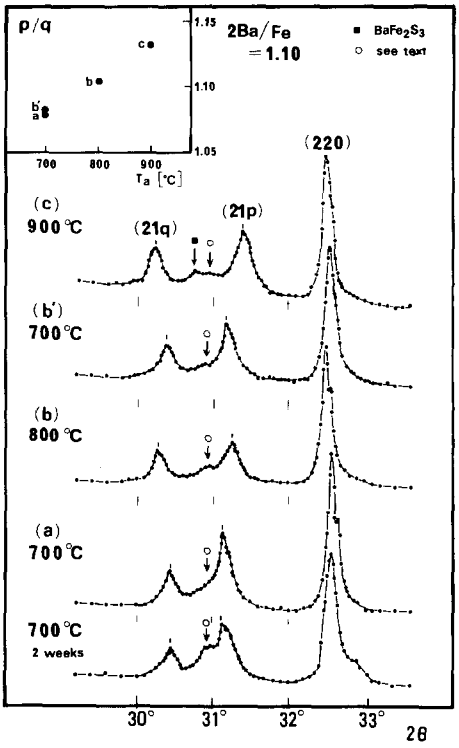

FIG. 4. X-Ray (Cu$K\alpha$) powder diffraction pattern of products with the same nominal composition (α = 1.10) but with different heat treatments. The starting mixture was heated at 700°C for 2 weeks. The product was divided into three batches, (a), (b), and (c). They were annealed for 5 weeks with slight excess sulfur added at 700°C, 800°C, and 900°C, respectively. Product (b) was again annealed at 700°C for 5 weeks (b'). In the inset, the "structural" composition p/q are shown as a function of T_a. Product (c) contained $BaFe_2S_3$ as an impurity phase. As for the diffraction peaks marked by arrow, see text.

On the Compound "$BaFe_2S_4$"

Figure 5 shows the p/q vs c_1, c_2, and a curves. Each axis is almost linearly proportional to the p/q value, although each of the samples has different nominal composition and is also heat treated at different T_a. The extrapolation of p/q ("structural" composition) to 1.00 gives the unit cell parameters $a = 7.70$ Å and $c = 5.30$ Å (tetragonal) for the compound "$BaFe_2S_4$." The fact that the lengths of c_1 and c_2 have the same value (5.30 Å) by extrapolation of p/q to 1.00 again verified the model proposed by Grey (*1*).

According to personal communication from Professor H. Steinfink, "$BaFe_2S_4$" was prepared at 800°C under sulfur vapor

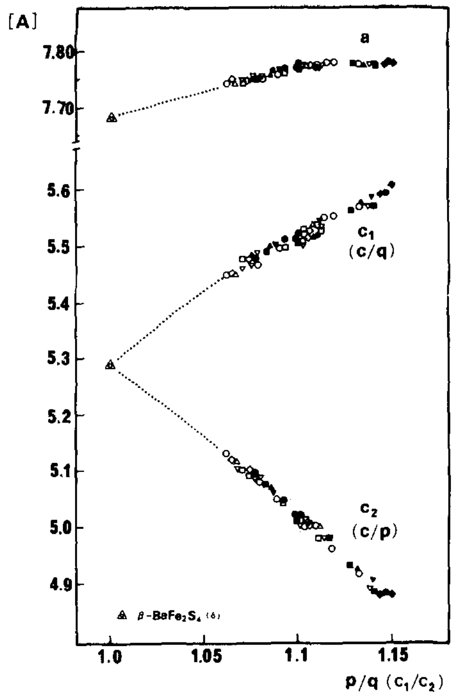

FIG. 5. The plots of lattice parameters a, c_1, c_2 vs p/q ("structural" composition). They show nearly linear relation. Nominal compositions are shown by marks used in Fig. 2. The extrapolation of the relation to p/q = 1.00 gives good agreement with the lattice parameters, a and c ($c_1 = c_2$) of β-$BaFe_2S_4$ (5).

pressure of 6.7 atm (5). The lattice parameters a and c are 7.678 and 5.292 Å, respectively, which is in excellent agreement with values obtained by the extrapolation of p/q to 1.00 in the present experiment.

Existence of Ba or Fe Vacancies

As repeatedly mentioned above, the most interesting result obtained in this experiment is that the value of p/q ("structural" composition) does not coincide with the value of α (nominal composition) and, moreover, depends on T_a. If there are no vacancies in each site for Ba, Fe and S, the p/q values have to be coincident with α. In view of these facts, it is obvious that the system here treated is not the pseudobinary system as expresses by $Ba_p(Fe_2S_4)_q$ or $Ba_{1+x}Fe_2S_4$ which indicates that the ratio of Fe/S is always equal to 1/2 in atomic ratio. Here, we have to use the general chemical formula $Ba_{p''}Fe_{q''}S_{r''}$. From the basic structure of this system, it is reasonably accepted that the framework of the crystal structure consists of sulfur ions, and therefore there exist no vacancies in sulfur ion sites. Then the chemical composition is correctly expressed as $Ba_{p'}Fe_{2q'}S_4$, where $\alpha = p'/q'$. The values of (p, q) determined by X-ray diffraction correspond to the number of available sites for Ba or Fe are occupied or not. Thus we have the relation

$$\alpha = p'/q' = \alpha_1 p/\alpha_2 q \qquad (0 \leq \alpha_1, \alpha_2 \leq 1), \quad (3)$$

where α_1 and α_2 and the occupation probabilities of Ba and Fe, respectively. As an example, we analyze the data for an α vs p/q curve of samples annealed at 700°C for 5 weeks, which is shown in Fig. 6. At the point where $\alpha = p/q$, indicated by an arrow in Fig. 6, the ratio β of α_1 to α_2 is equal to 1 ($\alpha_1 = \alpha_2$). It is assumed that at this point, there are no vacancies on either of the sites ($\alpha_1 = \alpha_2 = 1$). This assumption was made to minimize the total numbers of vacancies. There is a possibility of simultaneous existence of Ba and Fe vacancies, and so the absolute value of α has to be determined by experiment. On the left side of this point, Ba vacancies increase with a decrease of α, reaching about 6% vacancies ($[Ba_{1.0}\square_{0.06}]Fe_2S_4$), while Fe vacancies keep constant ($\alpha_2 = 1$). On the right side of this point, Fe vacancies increase with increase of α, reaching about 13% vacancies ($Ba_{1.25}[Fe_2\square_{0.3}]S_4$), while Ba vacancies keep constant ($\alpha_1 = 1$). We could not observe a definite effect of vacancies on lattice parameters of (p, q) values.

The p/q dependence on annealing temperature with constant value of α (p'/q' ratio) shown in Fig. 4 can be also explained by the concept of occupation probability (random vacancies). Sample (a) annealed at

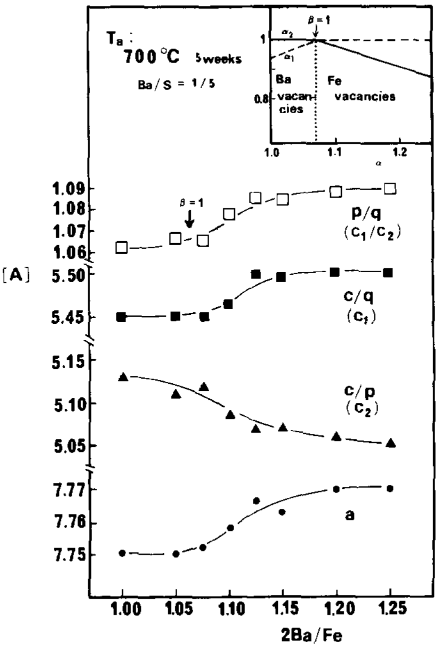

FIG. 6. The plots of lattice parameters a, c_1, c_2, and p/q of samples annealed at 700°C vs their nominal composition. The inconsistency between "structural" composition p/q and nominal composition α can be explained by the existence of Ba or Fe vacancies as shown in the text.

700°C has about 2% of Fe vacancies ($Ba_{1.1}[Fe_2\square_{0.04}]S_{4.08}$) and sample (b) annealed at 800°C has about 1% of Ba vacancies ($[Ba_{1.1}\square_{0.01}]Fe_2S_4$).

Thus, we could explain the following two characteristics observed in the $Ba_{1+x}Fe_2S_4$ system by the concept of occupation probabilities of α_1 and α_2:

(i) the difference between the value of nominal composition α and "structural" composition p/q.

(ii) the temperature dependence of p/q value of the samples with constant α.

Final Remarks

Here, we point out some problems to be solved in the future. So far, the crystal structures of the members of the $Ba_p(Fe_2S_4)_q$ series were determined to be tetragonal (1–3). Recently, the present authors have examined these samples by electron microscopy, and have found that the structure is a superstructure based on the NH_4CuMoS_4-type structure and also that the real supercell is monoclinic or triclinic (*8*). From observations of the orientation and spacing anomalies, we concluded that this system is an example of a modulated structure, which may have close correlation to the above-mentioned structure with vacancies.

Another interesting fact is that the "$BaFe_2S_4$" phase always coexists in the $Ba_{1+x}Fe_2S_4$ phase. The weak diffraction peak between the (21p) and (21q) peaks, marked by an arrow in Figs. 1 and 4, can be indexed as the (211) peak of "$BaFe_2S_4$" ($p = q = 1$). Other peaks corresponding to "$BaFe_2S_4$" were hardly observed in powder X-ray diffraction patterns. This means that the unit length a of the "$BaFe_2S_4$" mixed in $Ba_{1+x}Fe_2S_4$ is the same as that of $Ba_{1+x}Fe_2S_4$, and only c is different. In order to confirm whether two coexisting phases are in chemical equilibrium, the annealing period was varied from 2 to 12 weeks at 700°C for the sample with $\alpha = 1.10$. As a result, the p/q value of the $Ba_{1+x}Fe_2S_4$ phase and the diffraction angle and intensity of the (211) peak of "$BaFe_2S_4$" were not changed. Thus, two-phase coexistence seems to be intrinsic in this system. Figure 7 shows a high-resolution electron micrograph of a sample of $\alpha = 1.10$ with $p/q = 1.075$ annealed at 700°C for 12 weeks. This shows coherent irregular intergrowth of "$BaFe_2S_4$" in the $Ba_{1+x}Fe_2S_4$ matrix. In the $Ba_{1+x}Fe_2S_4$ matrix, the wide lattice fringes corresponding to $c/2$ of the supercell were observed in addition to the fine contrast corresponding to the basic structure. (region A). In region B, wide fringes were absent and only fine contrast was observed. This region B can be assigned to

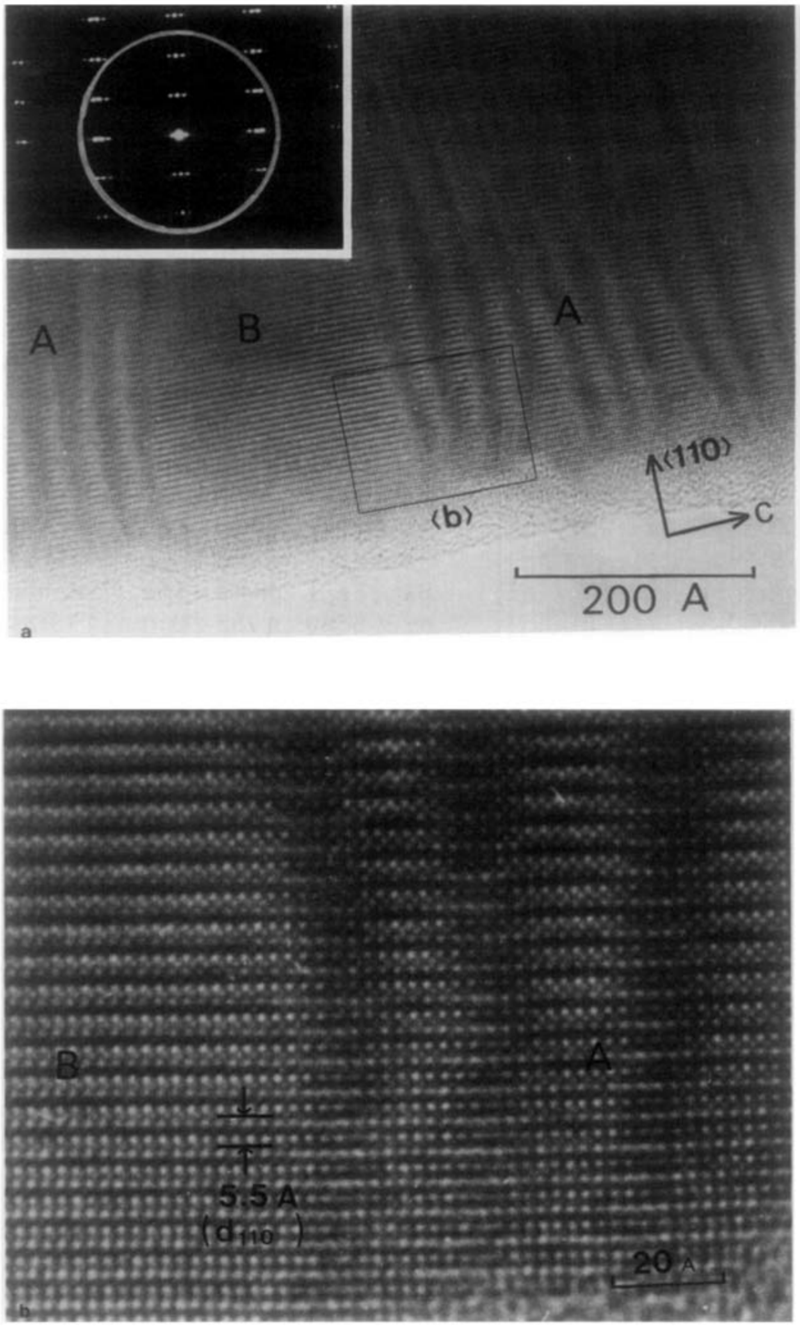

FIG. 7. A high-resolution electron micrograph showing the coherent intergrowth of $BaFe_2S_4$ (region *B*) in the $Ba_{1+x}Fe_2S_4$ matrix (region *A*). (110) incidence. The corresponding diffraction pattern and the objective-aperture size are also shown in the figure. The micrograph (b) is the enlargement of the region indicated in (a). In region A, lattice fringes corresponding to the supercell periodicity along *c* axis of $Ba_{1+x}Fe_2S_4$ were imaged. In region B, such wide lattice fringes were not observed. The fine contrast corresponding to the basic structure was observed in both region A and region B. Note the coherency of the contrast, especially lattice fringes with spacing corresponding to *d*(110), in regions A and B.

"$BaFe_2S_4$." Moreover, the lattice fringes corresponding to $d(110)$ show the coherency in both region A and region B. This coherent intergrowth of "$BaFe_2S_4$" in $Ba_{1+x}Fe_2S_4$ suggests that the two-phase coexistence is different from the usual one. Also, this electron microscopic observation agrees with the results of X-ray diffraction. It is noted that the vacancy model is right in principle, even if the "$BaFe_2S_4$" phase always coexists in the $Ba_{1+x}Fe_2S_4$ phase. At present, we have no explanation from the viewpoint of thermodynamics or phase rule for the coexistence of $Ba_{1+x}Fe_2S_4$ and "$BaFe_2S_4$." To make the phase relations more clear, data on the relation of temperature, composition, p/q value, and equilibrium sulfur vapor pressure are necessary. Experiments are now under way to obtain these data.

Acknowledgment

The authors express their thanks to Professor H. Steinfink (University of Texas at Austin) for sending us the preprint entitled "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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