

## Mössbauer Study of the Thermal Decomposition Products of BaFeO<sub>4</sub>

TOSHIO ICHIDA\*

*Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu, Japan*

Received September 5, 1972

A pure sample of a hexavalent iron compound, BaFeO<sub>4</sub>, was decomposed at temperatures below 1200°C at oxygen pressures from 0.2 to 1500 atm. In addition to the already known BaFeO<sub>x</sub> ( $2.5 \leq x < 3.0$ ) phases with hexagonal and triclinic symmetry, two new phases were obtained as decomposition products at low temperatures. One of the new phases, with composition BaFeO<sub>2.61-2.71</sub>, has tetragonal symmetry; lattice constants are  $a_0 = 8.54 \text{ \AA}$ ,  $c_0 = 7.29 \text{ \AA}$ . The phase is antiferromagnetic with Néel temperature estimated to be  $225 \pm 10 \text{ K}$ . Two internal fields observed on its Mössbauer spectra correspond to Fe<sup>3+</sup> and Fe<sup>4+</sup>. In the other new phase, with composition BaFeO<sub>2.5</sub>, all Fe<sup>3+</sup> ions had the same hyperfine field; it too is antiferromagnetic with a Néel temperature of  $893 \pm 10 \text{ K}$ . Mössbauer data on the hexagonal phase coincided with earlier results of Gallagher, MacChesney, and Buchanan [*J. Chem. Phys.* **43**, 516 (1965)]. In the triclinic-I BaFeO<sub>2.50</sub> phase, internal magnetic fields were observed at room temperature, and it was supposed that there were four kinds of Fe<sup>3+</sup> sites. The phase diagram of BaFeO<sub>x</sub> system was determined as functions of temperature and oxygen pressure.

### Introduction

For compounds containing Fe<sup>2+</sup> or Fe<sup>3+</sup> ions, numerous investigations have been made. Only a few compounds containing tetra- or hexavalent iron ions have been reported. K<sub>2</sub>FeO<sub>4</sub>, SrFeO<sub>4</sub> and BaFeO<sub>4</sub>, containing hexavalent iron, have been synthesized and their physical properties, particularly magnetic ones, measured (1-6). Compounds containing tetravalent iron include cubic and tetragonal SrFeO<sub>x</sub> ( $2.5 < x \leq 3.0$ ) phases with perovskite structure and several phases in the BaFeO<sub>x</sub> ( $2.5 < x < 3.0$ ) system.

The present author, with others, earlier reported the preparation and magnetic properties of some pure hexavalent iron compounds (5-7). A study of the decomposition products of K<sub>2</sub>FeO<sub>4</sub> (7) showed no intermediate valence states between Fe<sup>6+</sup> and Fe<sup>3+</sup>.

In this paper, the decomposition products of BaFeO<sub>4</sub> will be reported. A few results have been described previously (3, 8, 9). Scholder et al. (3, 8) reported that BaFeO<sub>3</sub> with perovskite structure was obtained by heating BaFeO<sub>4</sub> at

temperatures from 750 to 800°C in an oxygen atmosphere. The compound BaFeO<sub>x</sub> ( $2.5 \leq x < 3.0$ ), so-called "barium orthoferrate," has been investigated by several authors (10-22). Van Hook (12) studied the phase relations of the BaFeO<sub>x</sub> ( $2.5 \leq x < 3.0$ ) system by X-ray powder patterns and by thermogravimetric methods. His samples were prepared by ordinary ceramic methods from reaction of BaCO<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> at various oxygen pressures and temperatures. He found that the hexagonal phase, which is isomorphous with the high-temperature polymorph of BaTiO<sub>3</sub>, was stable at low temperatures over a wide range of oxygen pressures. It transforms to an unidentified phase of composition BaFeO<sub>2.50</sub> at higher temperatures (above 915°C in air). Gallagher, MacChesney, and Buchanan (13), and MacChesney et al. (14) prepared hexagonal compounds with various oxygen contents ranging from BaFeO<sub>2.83</sub> to BaFeO<sub>2.95</sub>. They studied susceptibility, and resistivity properties of these phases at various temperatures. They identified the phase BaFeO<sub>2.50</sub> as being isomorphous with orthorhombic brownmillerite. Subsequently, Mori (15) found that the powder pattern of BaFeO<sub>2.50</sub> could be indexed well in terms of triclinic symmetry, and named this the triclinic-I

\* On leave from Kawasaki Steel Corporation. Present address: Research Laboratories, Kawasaki Steel Corp., 1, Kawasaki-cho, Chiba, Japan.

phase. Besides the hexagonal and triclinic-I phase, he prepared new phases of triclinic-II and cubic-tetragonal BaFeO<sub>x</sub> by annealing the triclinic-I BaFeO<sub>2.50</sub> phase at lower temperatures.

It is found in these reports that the crystal structure of BaFeO<sub>x</sub> compounds obtained by annealing at temperatures lower than about 500°C depends on the starting BaFeO<sub>x</sub> phase. Though true equilibrium product phases must be independent of the starting material, metastable phases often appear at low temperatures. In addition to being interested in the iron valency in the decomposition products of BaFeO<sub>4</sub>, the present investigation was made to determine the low-temperature equilibrium phases in the BaFeO<sub>x</sub> system. As a starting material, BaFeO<sub>4</sub> has definite merits. The atomic ratio of Ba to Fe is equal to that in the decomposition products BaFeO<sub>x</sub>, and the equilibrium state should be attained more rapidly in BaFeO<sub>4</sub> fine particles than with other reagents previously used.

This paper describes experimental phase relations of products obtained by the thermal decomposition of BaFeO<sub>4</sub> heated under oxygen pressures from 0.2 to 1500 atm at temperatures below 1200°C. After confirming that each of products consisted of a single phase belonging to BaFeO<sub>x</sub> ( $2.5 \leq x < 3.0$ ), the formation range of each phase was determined as functions of temperature and oxygen pressures. In addition to the hexagonal and the triclinic-I phases, two kinds of new BaFeO<sub>x</sub> phases were found at low temperatures. By observing transformations among the four phases, the equilibrium formation diagram was determined. X-Ray diffraction and Mössbauer effect measurements were made to characterize each of the products.

### Sample Preparation and Measurements

The starting material BaFeO<sub>4</sub> was prepared according to the method of Scholder et al. (3) from a pure sample of K<sub>2</sub>FeO<sub>4</sub> obtained by a previously reported procedure (6, 7). A solution of K<sub>2</sub>FeO<sub>4</sub> in 2% KOH was added to a solution of Ba(CH<sub>3</sub>COO)<sub>2</sub>, and the precipitated BaFeO<sub>4</sub> was washed well with distilled water. All reactions were made at about 0°C to avoid reduction of Fe<sup>6+</sup> ions. Distilled water with no trace of CO<sub>2</sub> was used to prevent forming BaCO<sub>3</sub>. The precipitate was isolated from water by using a centrifugal separator and dried in a desiccator. BaFeO<sub>4</sub> particles were granular with a diameter

of about 0.05 μm. By X-ray diffraction, the sample was confirmed to be a single phase of BaFeO<sub>4</sub>. Measurements of magnetization and Mössbauer effect at 80 K confirmed the absence of ferromagnetic impurities and of any iron valence state other than hexavalent (6).

The pure samples of BaFeO<sub>4</sub> were heated under oxygen pressures from 0.2 to 1500 atm. In the case of heating in air or oxygen at 1 atm, the samples were spread thinly on a boat made of porcelain or platinum and heated below 1200°C for 50 hr before rapid cooling to room temperature. Though the heating period was prolonged to 1500 hr, no difference was detected in the products. In the case of heating under high oxygen pressures, the samples were held in a test tube of silica or gold and were put in a cone-sealed hydrothermal reaction vessel made of Stellite. These samples were quenched in cold water with the reactor under pressure after being kept at temperatures below 900°C for 50 hr under oxygen pressures of less than 1500 atm.

Phase identifications of the obtained products were made by X-ray diffraction techniques. Mössbauer effect measurements were carried out using an apparatus consisting of Elron's driving unit, AME-20, and Northern Scientific Co.'s 1024 channel pulse height analyzer, NS-600. The temperature of the absorber was varied between 4.2 and 903 K. The gamma ray source, <sup>57</sup>Co in Cu metal, was always kept at room temperature. Calibration of the velocity scale was made using pure Fe and α-Fe<sub>2</sub>O<sub>3</sub> as standard absorbers. Isomer shift is expressed relative to pure Fe metal. The ratios of Fe<sup>3+</sup> to Fe<sup>4+</sup> ions, isomer shifts, quadrupole splittings and other magnetic properties of the products were estimated from these <sup>57</sup>Fe Mössbauer spectra by using Curve Resolver-310 (Du Pont Co.).

### Results and Discussion

#### 1. X-Ray Diffraction Measurements

By X-ray analysis, it was found that four kinds of compounds were obtained by heating BaFeO<sub>4</sub> at temperatures below 1200°C in air. X-Ray diffraction patterns of these four compounds are shown in Fig. 1. The identification was made by comparing these diffraction patterns with reported data (10, 11, 14-22). It was found that the compound obtained at temperatures above 950°C in air was the triclinic-I BaFeO<sub>2.50</sub>, indexed by Mori (15), and the compound obtained between 750 and 900°C

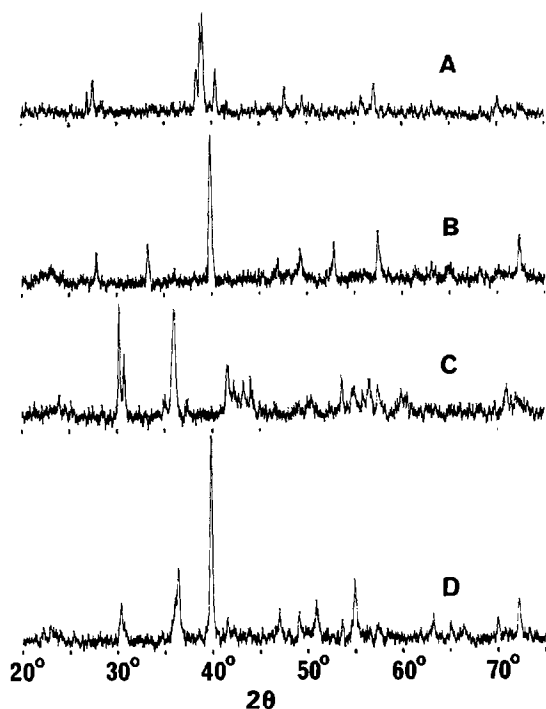


FIG. 1. X-Ray diffraction powder patterns of the products obtained by heating  $\text{BaFeO}_4$  in air at 1100°C(A), 800°C(B), 600°C(C) and 400°C(D). Fe- $K\alpha$  radiation.

was the hexagonal  $\text{BaFeO}_x$  ( $2.5 < x < 3.0$ ) reported as isomorphous with high temperature  $\text{BaTiO}_3$  (11). Gallagher, MacChesney, and Buchanan (13), and MacChesney et al. (14) had reported that the compound  $\text{BaFeO}_{2.50}$  obtained by heating  $\text{BaFeO}_x$  at temperatures above 915°C in air was isomorphous with brownmillerite ( $4\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ ) with space group  $Pcmn$  ( $16O_{2h}$ ). The present data are inconsistent with his result, but agree with the result by Mori. The other two phases, formed at lower temperatures, have not been previously reported. As shown in Table I, the X-ray powder pattern of the lower temperature phase can be indexed in the tetragonal system. The powder pattern of the other unknown phase, formed in the temperature range between 520 and 700°C in air, could not be indexed as cubic, tetragonal or hexagonal. It was confirmed, however, by careful examination of its X-ray pattern that the relative intensities of the X-ray diffraction peaks were always constant and any other barium compound such as barium oxide did not exist in the products obtained between 520 and 700°C in air. As

TABLE I  
X-RAY DIFFRACTION POWDER DATA OF THE TETRAGONAL  
 $\text{BaFeO}_{2.71}^a$

$2\theta_{\text{obs}}$ ( $^\circ$ ) <sup>b</sup>	$1/d_{\text{obs}}^2$	$1/d_{\text{cal}}^2$	(h k l)
30.298	0.0728	0.0736	(2 0 1)
36.370	0.1038	0.1026	(1 1 2)
39.772	0.1233	0.1233	(3 0 0)
46.970	0.1693	0.1693	(0 0 3)
49.085	0.1839	0.1830	(1 0 3)
50.860	0.1965	0.1967	(1 1 3)
54.980	0.2274	0.2241	(2 0 3)
57.340	0.2453	0.2466	(3 3 0)
63.220	0.2928	0.2926	(3 0 3)
		0.2928	(4 2 1)
65.020	0.3079	0.3081	(4 1 2)
66.400	0.3196	0.3218	(3 3 2)
70.040	0.3510	0.3492	(4 2 2)
72.240	0.3704	0.3750	(5 1 1)

<sup>a</sup>  $a_0 = 8.54 \text{ \AA}$ ;  $c_0 = 7.29 \text{ \AA}$ .

<sup>b</sup> Fe $K\alpha$  radiation.

described below, it was proved by Mössbauer effect measurements that only one kind of iron compound existed in the product. Therefore, it was concluded that the product obtained between 520 and 700°C in air consisted of single phase with lower symmetry than tetragonal or hexagonal.

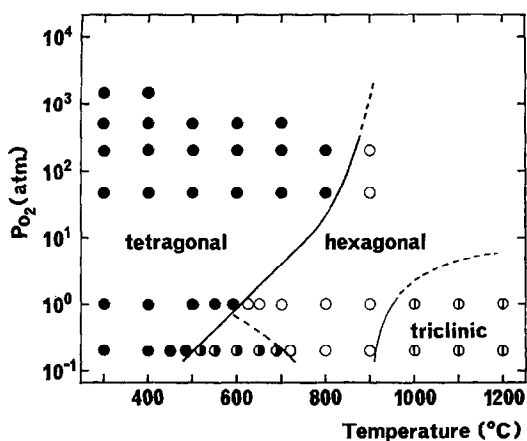


FIG. 2. Formation diagram of the products obtained by heating  $\text{BaFeO}_4$  at various temperatures and oxygen pressures. (●) tetragonal phase; (⊙) low temperature  $\text{BaFeO}_{2.5}$  phase; (○) hexagonal phase; (⊖) triclinic-I phase.

All of the products obtained under high-oxygen pressures were identified by X-ray diffraction as one of the four kinds of decomposition products obtained in air. The formation range of each phase is given in Fig. 2 as functions of temperature and oxygen pressure. It was confirmed by careful examination of X-ray patterns that each of the four compounds was a single phase. As described below, the atomic ratio of Ba and Fe is unity in all of the four phases, i.e., they belong to the BaFeO<sub>x</sub> system.

## II. Mössbauer Effect Measurements

1. *Tetragonal phase.* Mössbauer spectra of the tetragonal compounds formed by heating at various conditions are shown in Fig. 3 and Fig. 4. Mössbauer spectra measured at 4.2 K exhibit magnetic hyperfine interactions with two sets of six lines. According to previously reported

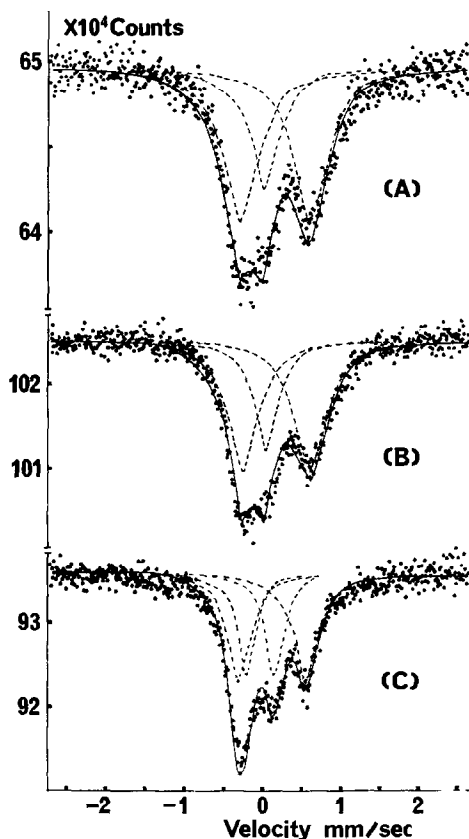


FIG. 3. Mössbauer absorption spectra of <sup>57</sup>Fe measured at room temperature in the tetragonal compounds obtained by heating BaFeO<sub>4</sub> at 400°C in air(A), in 1 atm of oxygen(B) and under the oxygen pressures of 1500 atm(C).

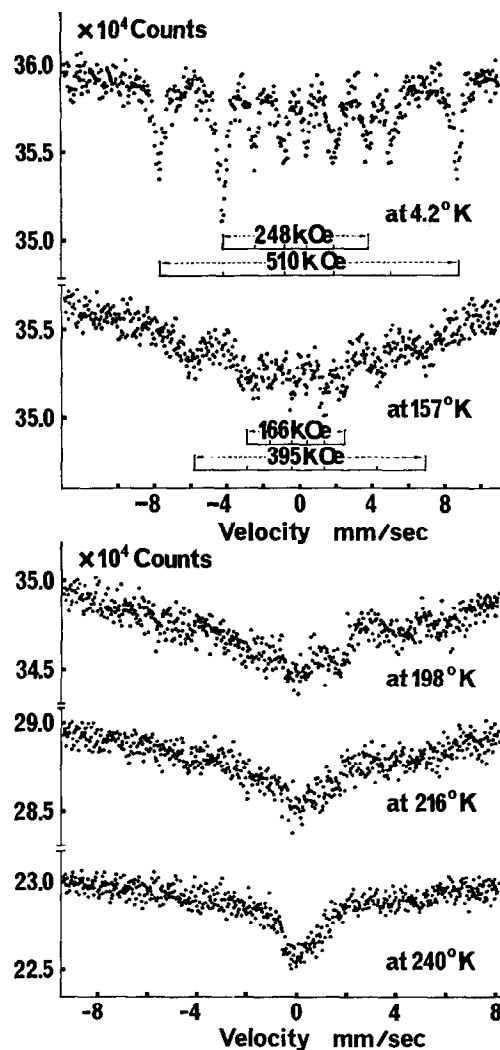


FIG. 4. Mössbauer absorption spectra of <sup>57</sup>Fe in the tetragonal BaFeO<sub>2.71</sub> measured at various temperatures.

data, the magnitudes of internal magnetic field of Fe<sup>6+</sup>, Fe<sup>4+</sup> and Fe<sup>3+</sup> are 130–140 kOe (5, 6), 160–330 kOe (13, 23, 24) and 450–550 kOe, respectively. Shimony and Kundsén (25) summarized the correlation between the isomer shift and the valency state of the iron as follows: The isomer shifts of Fe<sup>6+</sup>, Fe<sup>4+</sup>, Fe<sup>3+</sup> and Fe<sup>2+</sup> are  $-0.85 \pm 0.03$  mm/sec,  $-0.02 \pm 0.03$  mm/sec,  $+0.4 \pm 0.2$  mm/sec and  $+1.25 \pm 0.1$  mm/sec, respectively. Judging from the internal magnetic fields and isomer shifts, two sets of six lines observed in the tetragonal compounds correspond to the absorptions of Fe<sup>3+</sup> and Fe<sup>4+</sup> ions, respectively. The internal magnetic field of 510

kOe is due to  $\text{Fe}^{3+}$  ions and the other of 248 kOe to  $\text{Fe}^{4+}$ . As is shown in Fig. 3, the ratio of  $\text{Fe}^{3+}$  to  $\text{Fe}^{4+}$  ions in the tetragonal compounds was determined by measuring the areas under the Mössbauer peaks with Lorentzian curves using Curve Resolver-310 (Du Pont Co.). According to these curve resolutions, the amount of  $\text{Fe}^{4+}$  in the tetragonal phase obtained by heating at  $400^\circ\text{C}$  in air or oxygen atmosphere is 22% of total Fe, while that obtained at  $400^\circ\text{C}$  and oxygen pressures of 1500 atm is 42%.

Oxygen analyses were attempted by a thermo-balance, but weight loss was large and reliable data were not obtained because of absorbed water, gas, and such anions as carbonate and acetate in the sample.

The paramagnetic spectra of  $\text{Fe}^{3+}$  ions in all the tetragonal compounds showed a quadrupole splitting of  $0.85 \pm 0.03$  mm/sec and an isomer shift of  $+0.20 \pm 0.03$  mm/sec. The spectra of  $\text{Fe}^{4+}$  ions in the tetragonal compounds formed at high-oxygen pressures showed a quadrupole splitting of  $0.35 \pm 0.03$  mm/sec and an isomer shift of  $0.00 \pm 0.03$  mm/sec. Spectra of the same phase formed at lower oxygen pressure were singlet. All previous spectra of  $\text{Fe}^{4+}$  ions showed no quadrupole splitting (13, 23–25), because  $\text{Fe}^{4+}$  ions are normally surrounded by an oxygen octahedron with cubic symmetry. The magnetic transition temperature of the tetragonal compound containing 42%  $\text{Fe}^{4+}$  was determined by measuring the temperature variation of Mössbauer spectra. The results are shown in Fig. 4. Though the spectra were not always very clear, the vanishing point of internal magnetic fields suggest that both the Fe ions have the same magnetic transition temperature, corresponding to a Néel point of  $225 \pm 10$  K.

**2. Low-temperature  $\text{BaFeO}_{2.5}$  phase.** As before mentioned, another new compound with unknown crystal structure was obtained by heating  $\text{BaFeO}_4$  in air in the temperature range between  $520$  and  $700^\circ\text{C}$  (Fig. 2). As the color of the particles is pale brown, it was suspected that the compound contains no  $\text{Fe}^{4+}$ . The Mössbauer spectrum obtained at room temperature is shown in Fig. 5. Judging from the isomer shift and the internal magnetic field (470 kOe at room temperature), it is concluded that all of Fe ions are in a trivalent state; accordingly, the composition of this phase is  $\text{BaFeO}_{2.5}$ . Hereafter, we call this phase the low-temperature  $\text{BaFeO}_{2.5}$  phase. To determine the magnetic transition temperature of the new phase, temperature variation of

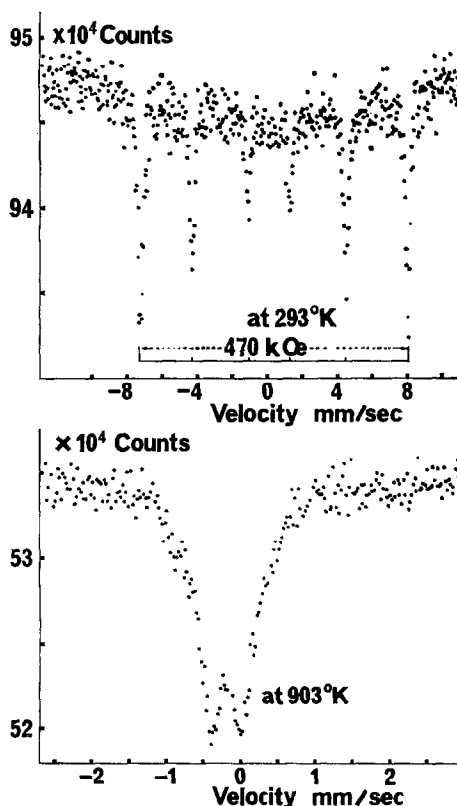


FIG. 5. Mössbauer absorption spectra of  $^{57}\text{Fe}$  in the low-temperature  $\text{BaFeO}_{2.5}$  phase measured at 293 and 903 K.

Mössbauer spectra was measured. The paramagnetic spectrum obtained at 903 K is shown in Fig. 5 and a temperature vs internal magnetic field curve is shown in Fig. 6. The Néel temperature of this phase is estimated to be  $893 \pm 10$  K.

**3. Hexagonal phase.** Gallagher, MacChesney, and Buchanan (13) reported Mössbauer spectra of the hexagonal  $\text{BaFeO}_x$  phase. Our Mössbauer data for this phase are in good agreement with theirs. The spectra of the phase obtained by heating at  $800^\circ\text{C}$  in oxygen atmosphere are shown in Fig. 7. From magnetic measurements, Mori (15) had predicted that some of  $\text{Fe}^{3+}$  and  $\text{Fe}^{4+}$  ions in the hexagonal phase were in a low-spin state. In the Mössbauer spectra observed on the hexagonal  $\text{BaFeO}_x$  phase at 4.2 K (Fig. 7), only two kinds of internal magnetic fields appeared. In either case of tetrahedral and octahedral coordination, the spin values of  $\text{Fe}^{3+}$  in a low- and high-spin state are  $1/2$  and  $5/2$ , respectively. On the other hand, those of octahedrally coordinated  $\text{Fe}^{4+}$  in a low- and

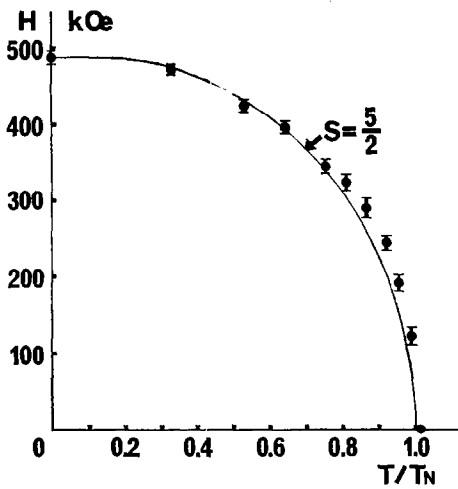


FIG. 6. The temperature dependence of the internal magnetic field in the low-temperature BaFeO<sub>2.5</sub> phase.  $T_N$  is 893 K. (—) the Brillouin function for  $S = 5/2$ .

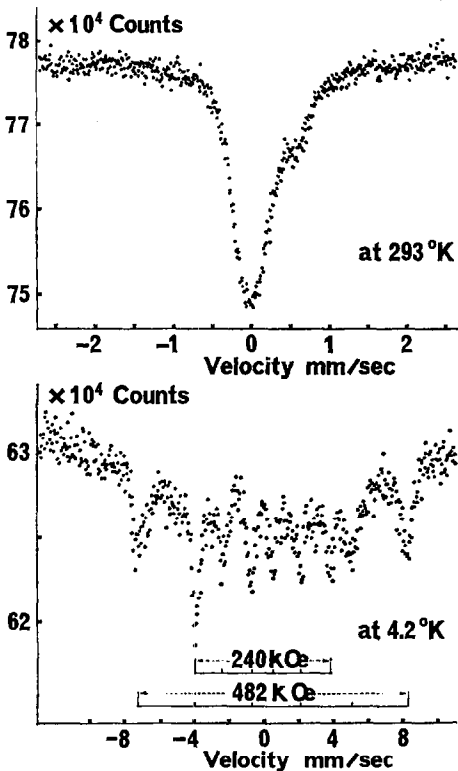


FIG. 7. Mössbauer absorption spectra of <sup>57</sup>Fe measured at 293 and 4.2 K in the hexagonal BaFeO<sub>x</sub> obtained by heating BaFeO<sub>4</sub> at 800°C in 1 atm of oxygen.

high-spin state are 1 and 2, respectively. There has been no report, however, on the existence of Fe<sup>4+</sup> ions in a low-spin state. Judging from the magnitude of internal magnetic fields (482 kOe for Fe<sup>3+</sup> and 240 kOe for Fe<sup>4+</sup> ions), it seems that both Fe<sup>3+</sup> and Fe<sup>4+</sup> are in high-spin states. The observed value for Fe<sup>4+</sup> ions is smaller than the usual ratio of 110 kOe/ $\mu_B$ , which is observed in the case of ionic Fe<sup>2+</sup> or Fe<sup>3+</sup> compounds. The reduction is possibly due to the covalent bond formation between Fe<sup>4+</sup> ion and surrounding oxygens. Such reductions of internal magnetic field resulting from the covalency have been reported in the case of Fe<sup>6+</sup> (5, 6) and Fe<sup>4+</sup> compounds (13, 23, 24).

4. *Triclinic-I phase.* Mössbauer spectra of the triclinic-I phase measured at room temperature and 4.2 K are shown in Fig. 8. The magnitude of isomer shifts and internal magnetic fields suggests all the iron ions in the triclinic-I phase are trivalent; this is consistent with the phase's brown color. The composition is concluded to be BaFeO<sub>2.5</sub>. The Mössbauer spectra of the triclinic-I phase can be divided into two groups of six line absorptions. One of the outermost absorptions splits into a triplet; so, there might be four kinds of Fe sites in the triclinic-I phase.

III. Interchange Among Decomposition Products

Among the four kinds of compounds obtained in this work by heating BaFeO<sub>4</sub> at various

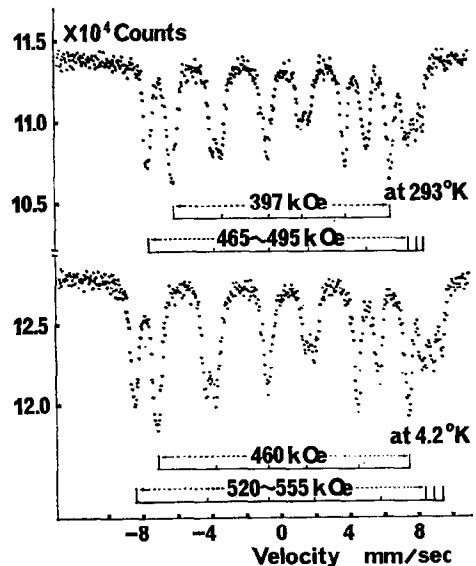


FIG. 8. Mössbauer absorption spectra of <sup>57</sup>Fe in the triclinic-I BaFeO<sub>2.50</sub> phase measured at 293 and 4.2 K.

conditions, only the triclinic-I and hexagonal phases have been previously identified in the  $\text{BaFeO}_x$  ( $2.5 \leq x < 3.0$ ) system. X-Ray diffraction and Mössbauer effect measurements on the other compounds obtained by low-temperature decomposition of  $\text{BaFeO}_4$  verify that they are single phase and belong to the same  $\text{BaFeO}_x$  ( $2.5 \leq x < 3.0$ ) system. The basis for these conclusions are as follows: It was proved by Mössbauer effect measurements that only one kind of iron compound existed in each product. The relative intensities of X-ray diffraction peaks in each product were independent of the heating conditions and no other barium compound was detected by X-ray diffraction.

The changes from the tetragonal phase and the low-temperature  $\text{BaFeO}_{2.5}$  phase to the hexagonal  $\text{BaFeO}_x$  phase are completed within a few hours at such low temperatures as  $620^\circ\text{C}$  in oxygen atmosphere and  $720^\circ\text{C}$  in air, respectively. These rapid low-temperature changes can be explained in that both of the new phases belong to  $\text{BaFeO}_x$  ( $2.5 \leq x < 3.0$ ) system; that is, the changes are analogous to phase transformations.

Since the atomic ratio of Fe and Ba is always unity in each of the decomposition products, the number of components in this system can be taken as two: (BaFe) and O. In a case where one solid phase exists in an equilibrium state, there are two degrees of freedom; and where two solid phases coexist, the freedom is one. According to Gibb's phase rule, a product equilibrated at certain temperature and oxygen pressure is of single phase and there is a univariant equilibrium between two solid phases in the temperature-pressure diagram of the  $\text{BaFeO}_x$  system. As mentioned above, the present experimental data follow the phase rule.

The phase transformations between adjacent  $\text{BaFeO}_x$  phases in Fig. 2 were examined by heating each phase under conditions favoring formation of adjacent phases. The results are shown in Fig. 9. By heat treatment, the tetragonal phase was transformed to the low-temperature  $\text{BaFeO}_{2.5}$  phase in air at temperature between  $520$  and  $700^\circ\text{C}$ ; this is consistent with the stability fields shown in Fig. 2. Both low-temperature phases could be transformed to the hexagonal phase by subjecting them to any condition indicated in Fig. 2 as being in the equilibrium range of the hexagonal phase. Each of the phase transformations represented in Fig. 9 took place reproducibly at the appropriate phase

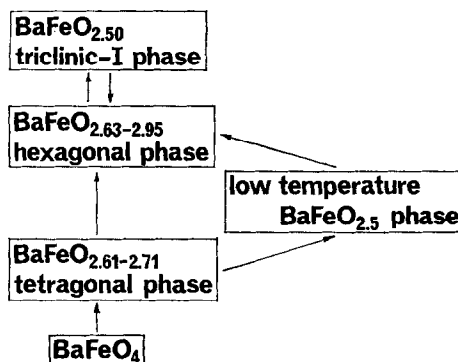


FIG. 9. Phase transformations among several  $\text{BaFeO}_x$  phases. Each arrow shows the direction of phase transition.

boundary of Fig. 2. It is well known that the formation range of a metastable phase is usually indefinite and its phase transformation does not take place reproducibly. Accordingly in this sense, it seems that both of the new phases are equilibrium phases in the low-temperature range.

However, no reversed transformation was detected by subjecting the hexagonal phase to any condition in the formation range of either low-temperature phase of Fig. 2. Similarly, the low-temperature  $\text{BaFeO}_{2.5}$  phase was not transformed by subjecting it to any condition in the formation range of the tetragonal phase. Moreover, the low-temperature  $\text{BaFeO}_{2.5}$  phase which was obtained by heating  $\text{BaFeO}_4$  at between  $520$  and  $700^\circ\text{C}$  in air was not transformed to the hexagonal phase even at  $800^\circ\text{C}$  and oxygen pressures of  $200$  atm although it was transformed at  $620^\circ\text{C}$  in  $1$  atm of oxygen or at  $720^\circ\text{C}$  in air. Because no reversible transformation is observed between the tetragonal phase, the low-temperature  $\text{BaFeO}_{2.5}$  phase or the hexagonal phase, the formation ranges in Fig. 2 may not exactly correspond to the true phase boundaries for the phase diagram of the  $\text{BaFeO}_x$  ( $2.5 \leq x < 3.0$ ) system. Presumably, the absence of reversible transformations is because the high temperature phases, i.e., hexagonal or triclinic-I, undergo grain growth which further inhibits solid state diffusion at lower temperatures.

The discovery of the two new low-temperature phases in the present work can be attributed to the atomic-scale distribution of Ba and Fe in the fine grains of starting material  $\text{BaFeO}_4$ . This assumes that these phases have not been

previously obtained by ordinary ceramic methods because of low diffusion rates at the requisite low temperatures. Bando (26) and Kachi, Bando, and Higuchi (27) have shown that, particularly in cases of the order-disorder phenomena and phase transformations, atomic diffusion takes place more rapidly in fine particles than in large grains because vacancy concentrations are typically higher.

It can be concluded that both the hexagonal and triclinic-I phases obtained at high temperatures are in equilibrium. Although no phase transformation was detected by annealing the hexagonal phase at lower temperatures (12), several phases were formed in the case of annealing the triclinic-I phase (15). From X-ray analysis, it is obvious that the triclinic-I phase and all its low-temperature derivatives, such as the cubic, tetragonal and triclinic-II phases, are related to the perovskite structure. As is often the case with metastable phases, for example,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, the formation ranges of low-temperature derivatives are not definite. So, it is supposed that the previously reported derivatives of triclinic-I are also metastable phases formed as a result of minor diffusion within the perovskite framework.

Considering the advantages of the starting material BaFeO<sub>4</sub> for realizing equilibrium phases at low temperatures and the reproducible experimental results of forming both low-temperature phases under definite conditions, it is concluded that both are equilibrium phases.

### Acknowledgments

The author expresses his hearty thanks to Professor T. Takada for prominent guidance during the course of this work. The author also thanks Professor Y. Bando, Dr. T. Shinjo and Dr. M. Kiyama for their continuous guidance and helpful discussions. Thanks are due to Dr. M. Imai and Dr. K. Sanbongi of Research Laboratories, Kawasaki Steel Corp. for warm encouragement. He also thanks Kawasaki Steel Corp. for giving an opportunity to study at Kyoto University.

### References

1. H. J. HROSTOWSKI AND A. B. SCOTT, *J. Chem. Phys.* **18**, 105 (1956).
2. G. W. THOMPSON, L. T. OCKERMAN, AND J. M. SCHREYER, *J. Amer. Chem. Soc.* **73**, 1379 (1951).
3. V. R. SCHOLDER, H. V. BUNSEN, F. KINDERVATER, AND W. ZEISS, *Z. Anorg. Allg. Chem.* **282**, 268 (1955).
4. G. K. WERTHEIM AND R. H. HERBER, *J. Chem. Phys.* **36**, 2497 (1962).
5. T. SHINJO, T. ICHIDA, AND T. TAKADA, *J. Phys. Soc. Jap.* **26**, 1547 (1969).
6. T. SHINJO, T. ICHIDA, AND T. TAKADA, *J. Phys. Soc. Jap.* **29**, 111 (1970).
7. T. ICHIDA, *Bull. Chem. Soc. Jap.*, **46**, 79 (1973).
8. V. R. SCHOLDER, F. KINDERVATER, AND W. ZEISS, *Z. Anorg. Allg. Chem.* **283**, 338 (1956).
9. U. N. PANYUSHKIN, G. DE PASQUALI, AND H. G. DRICKARMER, *J. Chem. Phys.* **51**, 3305 (1969).
10. M. ERCHAK, JR., I. FANKUCHEN, AND R. WARD, *J. Amer. Chem. Soc.* **68**, 2085 (1946).
11. W. W. MALINOFSKY AND H. KEDESZY, *J. Amer. Chem. Soc.* **76**, 3090 (1954).
12. H. J. VAN HOOK, *J. Phys. Chem.* **68**, 3786 (1964).
13. P. K. GALLAGHER, J. B. MACCHESNEY, AND D. N. E. BUCHANAN, *J. Chem. Phys.* **43**, 516 (1956).
14. J. B. MACCHESNEY, J. F. POTTER, R. C. SHERWOOD, AND H. J. WILLIAMS, *J. Chem. Phys.* **43**, 3317 (1965).
15. S. MORI, *J. Phys. Soc. Jap.* **28**, 44 (1970).
16. Y. GOTO AND T. TAKADA, *J. Amer. Ceram. Soc.* **43**, 150 (1960).
17. C. OKAZAKI, S. MORI, AND F. KANAMARU, *J. Phys. Soc. Jap.* **16**, 119 (1961).
18. S. W. DERBYSHIRE, A. C. FRAKER, AND H. H. STADELMAIER, *Acta Crystallogr.* **14**, 1293 (1961).
19. A. C. FRAKER, *J. Phys. Chem.* **69**, 4395 (1965).
20. T. NEGAS AND R. S. ROTH, *J. Res. Nat. Bur. Stand., Sect. A* **73**, 425 (1969).
21. C. DO-DINH, E. F. BERTAUT, AND J. CHAPPERT, *J. Phys. (Paris)* **30**, 566 (1969).
22. C. GLEITZER, M. ZANNE, AND C. ZELLER, *C. R. Acad. Sci.* **270**, 1496 (1970).
23. P. K. GALLAGHER, J. B. MACCHESNEY, AND D. N. E. BUCHANAN, *J. Chem. Phys.* **41**, 2429 (1964).
24. P. K. GALLAGHER, J. B. MACCHESNEY, AND D. N. E. BUCHANAN, *J. Chem. Phys.* **45**, 2466 (1966).
25. U. SHIMONY AND J. M. KUNDSSEN, *Phys. Rev.* **144**, 361 (1966).
26. Y. BANDO, *Trans. Jap. Inst. Metals* **5**, 137 (1964).
27. S. KACHI, Y. BANDO, AND S. HIGUCHI, *Jap. J. Appl. Phys.* **1**, 307 (1962).