

## Preparation and Properties of New Potassium-Barium Ferrite with Mixed $\beta$ -Alumina and Magnetoplumbite Structure

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A new hexaferrite (ideal composition:  $\text{KBaFe}_{23}\text{O}_{36}$ ) with mixed  $\beta$ -alumina and magnetoplumbite structure was synthesized by the solid-state reaction of the mixture  $0.45\text{K}_2\text{CO}_3 \cdot 0.55\text{BaCO}_3 \cdot 6\text{Fe}_2\text{O}_3$  at 1300 to 1350°C. The alternate stacking structure of half cells of  $\text{K}^+$ - $\beta$ -ferrite and Ba hexaferrite was proposed based on the X-ray powder diffraction pattern of this ferrite. A similar compound was also found in the  $\text{Rb}_2\text{O}-\text{BaO}-\text{Fe}_2\text{O}_3$  system. The saturation magnetization of the K-Ba ferrite was very small (1.6 emu/g at 25°C) compared to that of the Ba hexaferrite. The electronic conductivity of the K-Ba ferrite was  $0.3 \text{ S} \cdot \text{cm}^{-1}$  at 300°C, which was too high to measure the ionic conductivity based on the  $\beta$ -alumina structure, but the electronic conduction was reduced by MgO doping. The ionic conductivity of Mg-doped K-Ba ferrite ( $0.45\text{K}_2\text{O} \cdot 0.55\text{BaO} \cdot 5.7\text{Fe}_2\text{O}_3 \cdot 0.3\text{MgO}$ ) was  $6 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$  at 300°C, comparable to that of  $\text{K}^+$ - $\beta$ -ferrite. © 1990 Academic Press, Inc.

### Introduction

Structures of magnetoplumbite-type barium ferrite ( $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ ) and  $\beta$ -alumina-type potassium ferrite ( $\text{K}^+$ - $\beta$ -ferrite,  $(1+x)\text{K}_2\text{O} \cdot 11\text{Fe}_2\text{O}_3$  ( $x = 0$  to 1)) are made of spinel blocks separated by mirror planes containing  $\text{K}^+$  or  $\text{Ba}^{2+}$  ions. The space group of these compounds is  $P6_3/mmc$ . The difference between their structures lies in the mirror planes, which are loose-packed in  $\text{K}^+$ - $\beta$ -ferrite and close-packed in Ba hexaferrite. The slight difference in the structure of the mirror plane leads to a striking difference in the properties of the two compounds. The Ba hexaferrite is well-known as a ferromagnetic compound, while the  $\text{K}^+$ - $\beta$ -ferrite shows antiferromagnetic behavior (1) and mixed conduction of  $\text{K}^+$  ion and electron (2, 3). The ionic conduction

of  $\text{K}^+$ - $\beta$ -ferrite is comparable to that of  $\beta$ -alumina.

In the past several years, new types of hexaaluminates have been discovered in  $\text{Na}_2\text{O}-\text{Ln}_2\text{O}_3-\text{Al}_2\text{O}_3$  (SLnA) (4-7) and  $\text{BaO}-\text{Ln}_2\text{O}_3-\text{Al}_2\text{O}_3$  (BLnA) (8) systems, where Ln is La or Nd. The structure of these compounds is described as an alternate stacking of half a  $\beta$ -alumina unit cell and half a magnetoplumbite unit cell. The space group of these aluminates is not  $P6_3/mmc$  but  $P\bar{6}m2$ . A compound having a similar structure is expected to exist also in the  $\text{K}_2\text{O}-\text{BaO}-\text{Fe}_2\text{O}_3$  system. If such a new hexaferrite is obtained, the magnetic structure and electrical conductivity of this compound may be interesting. In this paper, we report on the preparation and properties of a new type of hexaferrite in the  $\text{K}_2\text{O}-\text{BaO}-\text{Fe}_2\text{O}_3$  system.

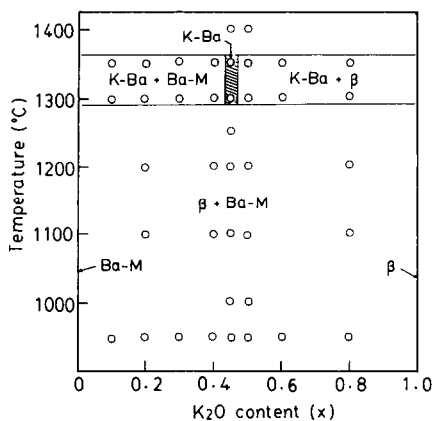


FIG. 1. Formation region of the new hexaferrite in the  $K_2O$ - $BaO$ - $Fe_2O_3$  system ( $xK_2O \cdot (1-x)BaO \cdot 6Fe_2O_3$ ).  $\beta$ ,  $\beta$ -ferrite;  $Ba-M$ ,  $Ba$  hexaferrite;  $K-Ba$ , new  $K-Ba$  ferrite.

### Experimental Procedure

Starting powders of  $K_2CO_3$ ,  $BaCO_3$ , and  $\alpha-Fe_2O_3$  were mixed with a composition of  $xK_2O \cdot (1-x)BaO \cdot 6Fe_2O_3$  ( $0 \leq x \leq 1$ ). The mixture was charged into a porcelain crucible (9 ml) and then calcined at  $950^\circ C$  for 1 hr. The resulting powder was pressed under 100 MPa to form a tablet 11 mm in diameter and 3 mm in thickness. This tablet was embedded in powder of the same composition and heated at different temperatures between 950 and  $1400^\circ C$  for 30 min to 1 hr.

The product was identified by the X-ray powder diffraction method. The composition of the product was determined by atomic absorption and flame analyses. The saturation magnetization was measured by B-H curve tracer (Riken Denshi Co., Ltd., Model BHU-60A) at  $25^\circ C$ , applying a magnetic field of 5 kOe. In order to obtain the electrical conductivity, gold wire electrodes were bonded on both sides of the tablet with gold paste. The electrical conductivity was measured by an impedance analyzer (YHP 4192A), applying 5 Hz to 13 MHz of alternating current (9, 10). The dc resistance was

also measured by means of four-probe technique to obtain the electronic conductivity.

### Results and Discussion

#### (1) Formation of New Hexaferrite and Structure

The phase-identification results are shown in Fig. 1. Below  $1200^\circ C$ , mixed phases of  $Ba$  hexaferrite and  $K^+-\beta$ -ferrite were formed over all compositions. However, a new compound was found at 1300 to  $1350^\circ C$ . The single phase of this compound was obtained in a range of composition close to  $0.45K_2O \cdot 0.55BaO \cdot 6Fe_2O_3$ . Figure 2 shows the X-ray pattern of this new  $K-Ba$  ferrite, together with that of  $K^+-\beta$ -ferrite. The  $K-Ba$  ferrite seems to have the mixed  $\beta$ -alumina and magnetoplumbite structure, because the diffraction pattern completely corresponds to that of the  $Na-Ln$  hexaaluminate reported by Rafaoui *et al.* (5). The lattice constants of the  $K-Ba$  ferrite were  $a_0 = 5.913 \text{ \AA}$  and  $c_0 = 23.48 \text{ \AA}$ , which are close to those of  $Ba$  hexaferrite ( $a_0 = 5.889 \text{ \AA}$  and  $c_0 = 23.194 \text{ \AA}$ ) or  $K^+-\beta$ -ferrite ( $a_0 = 5.93 \text{ \AA}$  and  $c_0 = 23.78 \text{ \AA}$ ). A number of peaks are associated with the reflections of  $Ba$  hexaferrite or  $K^+-\beta$ -ferrite. However, this pattern has some strong (00 $l$ ) lines with  $l = 2n + 1$ . These (00 $l$ ) lines are not allowed

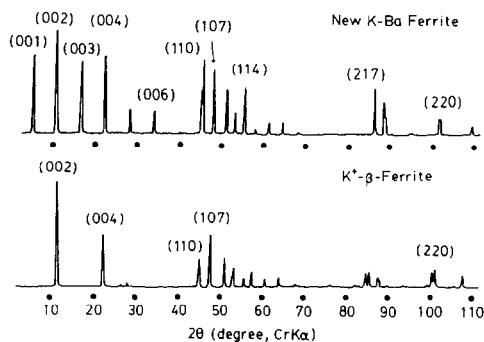


FIG. 2. X-ray diffraction patterns of new  $K-Ba$  hexaferrite and  $K^+-\beta$ -ferrite.

by the  $P6_3/mmc$  space group of magnetoplumbite or  $\beta$ -alumina structure. Therefore, this compound has a lower symmetry compared to that of Ba hexaferrite or  $K^+-\beta$ -ferrite. This lowering of symmetry suggests that the two (00 $l$ ) planes containing the large cations ( $K^+$  and  $Ba^{2+}$ ) are not equivalent; that is,  $K^+$  ions and  $Ba^{2+}$  ions are located in different (00 $l$ ) planes. It is proposed that the K-Ba ferrite has an alternate stacking structure of half unit cells of magnetoplumbite structure and  $\beta$  structure, as shown in Fig. 3, in which  $K^+$  ions and  $Ba^{2+}$  ions would be in  $\beta$  and magnetoplumbite lattices, respectively. Table I shows the X-ray powder diffraction data for the K-Ba ferrite. The calculated intensities were obtained by referring the atomic parameters for the Na-Nd aluminate (7). The calculated intensities agreed approximately with those observed, which supports the essential correctness of the proposed structure.

According to atomic absorption and flame analyses, the resulting composition of the product with starting composition  $x = 0.45$  was determined to be  $0.40 K_2O \cdot 0.55 BaO \cdot 6Fe_2O_3$ . The loss of  $K_2O$  content is due to the vaporization of potassium during the

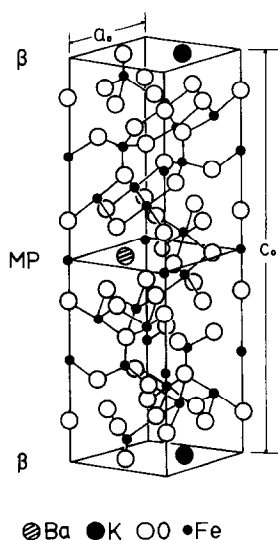


Fig. 3. Probable unit cell of K-Ba ferrite.

TABLE I  
X-RAY POWDER DIFFRACTION DATA FOR  
K-Ba FERRITE

$hkl$	$d_o(\text{\AA})$	$d_c(\text{\AA})$	$I/I_o$	$I/I_c$
001	23.57	23.48	81	85
002	11.78	11.74	100	116
003	7.85	7.83	61	62
004	5.88	5.87	56	35
102	}4.70	4.69	}23	13
005		4.70		11
006	3.920	3.913	15	13
007	3.360	3.354	2	1
110	2.958	2.957	44	26
008	2.938	2.935	13	10
107	2.809	2.805	62	69
114	2.641	2.641	48	57
009	2.612	2.609	2	1
200	2.558	2.560	3	9
203	2.432	2.433	23	26
0010	2.350	2.348	2	1
205	2.248	2.248	11	13
206	2.143	2.143	16	16
207	2.037	2.035	2	4
217	1.676	1.676	32	28
2011	}1.640	1.640	}25	24
304		1.639		12
306	1.565	1.565	5	4
219	1.555	1.554	4	1
220	1.478	1.478	33	44
312	1.408	1.410	6	2

Note.  $a = 5.913 \text{ \AA}$ ;  $c = 23.48 \text{ \AA}$ ;  $d_o$  and  $I/I_o$ , observed;  $d_c$  and  $I/I_c$ , calculated.

solid-state reaction. This experimental formula,  $0.40K_2O \cdot 0.55BaO \cdot 6Fe_2O_3$  ( $K_{1.53}Ba_{1.05}Fe_{23.0}O_{36.3}$ ) has excess  $K^+$  ions compared to the ideal composition  $KBaFe_{23}O_{36}$  which is expected from the crystal structure in Fig. 3. This may be due to non-stoichiometry in  $\beta$ -alumina-type structure, as in the case of  $K^+-\beta$ -ferrite (11).

The  $\beta$ -alumina-type ferrite is also obtained by the solid-state reaction of  $Rb_2O$  and  $Fe_2O_3$  or  $Cs_2O$  and  $Fe_2O_3$  (10). In addition, the isomorphs of magnetoplumbite-type hexaferrite are also formed in  $SrO-Fe_2O_3$  and  $PbO-Fe_2O_3$  systems (12). Therefore, preparations of new hexaferrites

TABLE II  
PREPARATION OF NEW HEXAFERRITE IN OTHER SYSTEMS

Starting materials	Temp. (°C)	Phase
0.45Na <sub>2</sub> O · 0.55BaO · 6Fe <sub>2</sub> O <sub>3</sub>	1350	NaFeO <sub>2</sub> , α-Fe <sub>2</sub> O <sub>3</sub> , MP
0.45Rb <sub>2</sub> O · 0.55BaO · 6Fe <sub>2</sub> O <sub>3</sub>	1350	Rb-Ba hexaferrite
0.45Cs <sub>2</sub> O · 0.55BaO · 6Fe <sub>2</sub> O <sub>3</sub>	1350	β, MP
0.45Na <sub>2</sub> O · 0.55SrO · 6Fe <sub>2</sub> O <sub>3</sub>	1200-1350	NaFeO <sub>2</sub> , α-Fe <sub>2</sub> O <sub>3</sub> , MP
0.45K <sub>2</sub> O · 0.55SrO · 6Fe <sub>2</sub> O <sub>3</sub>	950-1350	β, (β <sup>''</sup> ), <sup>a</sup> MP
0.45K <sub>2</sub> O · 0.55PbO · 6Fe <sub>2</sub> O <sub>3</sub>	1200-1350	β, MP

Note. β, β-ferrite; MP, magnetoplumbite type ferrite; β<sup>''</sup>, β<sup>''</sup>-ferrite.  
<sup>a</sup> β<sup>''</sup> phase formed at below 1200°C.

have been tried in other systems. The results are shown in Table II. The Rb<sub>2</sub>O-BaO-Fe<sub>2</sub>O<sub>3</sub> system was the only one exhibiting new hexaferrites, except for the K<sub>2</sub>O-BaO-Fe<sub>2</sub>O<sub>3</sub> system. The lattice constants of the Rb-Ba hexaferrite were  $a_0 = 5.91 \text{ \AA}$  and  $c_0 = 23.73 \text{ \AA}$ .

### (2) Magnetic Structure of K-Ba Hexaferrite

The saturation magnetization of the K-Ba ferrite was 1.6 emu/g at 25°C. This value is very small compared to the magnetization value of Ba hexaferrite. This low magnetization may be explained on the basis of the crystal structure of the K-Ba ferrite. According to Gorter (1), the magnetic structures of Ba hexaferrite and K<sup>+</sup>-β-ferrite are as shown in Figs. 4a and 4b, respectively. In Ba hexaferrite, pairs of adjacent Fe<sup>3+</sup> ions on both sides of the mirror plane have parallel ionic moments, while the pairs in K<sup>+</sup>-β-ferrite have antiparallel ionic moments due to the large magnetic interaction of Fe<sup>3+</sup>-O-Fe<sup>3+</sup> with an angle of 180°. The resultant moments of the spinel block in Ba hexaferrite are parallel to those of the adjacent block, but those in K<sup>+</sup>-β-ferrite are antiparallel. Therefore, the magnetic structure of the K-Ba ferrite is expected to be described as in Fig. 4c; that is, the spinel blocks on both sides of the Ba plane have

parallel moments, while the blocks on both sides of the K plane have antiparallel moments (at the present stage, the direction of easy magnetization is unclear). Consequently, the sum of the magnetic moments in this structure must be zero. The magnetization of 1.6 emu/g may be due to a small amount of magnetic impurity. However, further magnetic measurements will be required to obtain the detailed magnetic structure.

### (3) Electrical Conductivity of K-Ba Hexaferrite

K<sup>+</sup>-β-ferrite reveals the ionic conduction of alkali ions based on the alkali layer of the β-alumina structure. However, β-ferrite exhibits an electronic conduction based on the hopping of electrons as well as Ba hexaferrite (13). The line (a) in Fig. 5 shows the electronic conductivity of a K-Ba ferrite tablet fired at 1350°C for 30 min (relative density 83%). The electronic conductivity was 0.3 S · cm<sup>-1</sup> at 300°C. The ac conductivity was almost equal to the dc conductivity and revealed only a very slight dependence on frequency. This indicates that the electronic conductivity is much higher than the ionic conductivity.

Takahasi *et al.* (2) reported that the electronic conduction of K<sup>+</sup>-β-ferrite was de-

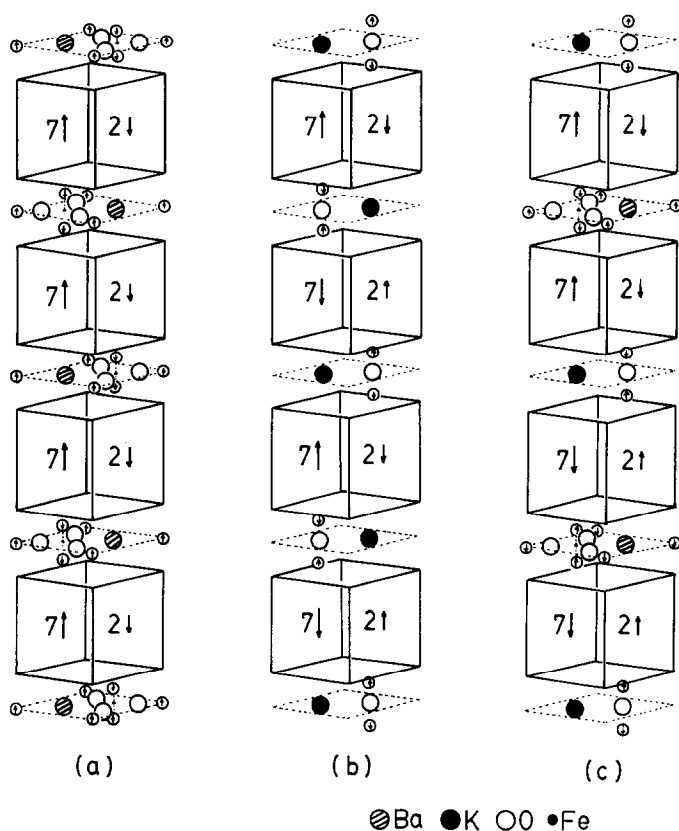


FIG. 4. Schematic representations of the magnetic structure of (a) Ba hexaferrite, (b)  $K^+$ - $\beta$ -ferrite, and (c) K-Ba ferrite (arrow: magnetic moment).

creased by doping with a divalent metal oxide such as MgO, ZnO, and NiO, but the ionic conduction was unaltered. In order to reduce the electronic conduction of K-Ba ferrite and to measure the ionic conductivity, the tablet of Mg-doped K-Ba ferrite (relative density 88%) was prepared by the solid-state reaction of  $0.45K_2O \cdot 0.55BaO \cdot 5.7Fe_2O_3 \cdot 0.3MgO$  at  $1350^\circ C$  for 30 min. The X-ray powder diffraction pattern showed that the product was a single phase of K-Ba ferrite. The electronic conductivity of Mg-doped K-Ba ferrite is shown as line (b) in Fig. 5, which was  $10^2$ - $10^3$  times lower than that of undoped K-Ba ferrite. The concentration of  $Fe^{2+}$  ions in the spinel blocks

should be decreased by doping of  $Mg^{2+}$  ions, as in the case of  $K^+$ - $\beta$ -ferrite (2). The ionic conductivity of Mg-doped ferrite was obtained by the complex impedance method (9, 10) and is shown as line (c) in Fig. 5. The ionic conductivity at  $300^\circ C$  was  $6 \times 10^{-3} S \cdot cm^{-1}$ . This value is comparable to that of  $K^+$ - $\beta$ -ferrite (sintered body) reported by Takahashi *et al.* (2) ( $3.5 \times 10^{-3} - 1.5 \times 10^{-2} S \cdot cm^{-1}$  at  $300^\circ C$ ) or Dudley and Steele (3) ( $5 \times 10^{-3} - 2 \times 10^{-2} S \cdot cm^{-1}$  at  $300^\circ C$ ). In addition, the activation energy in ionic conduction of Mg-doped ferrite was 0.18 eV, which was lower than that of  $K^+$ - $\beta$ -ferrite (0.259 eV (3)). The undoped ferrite should also have a high ionic conduction.

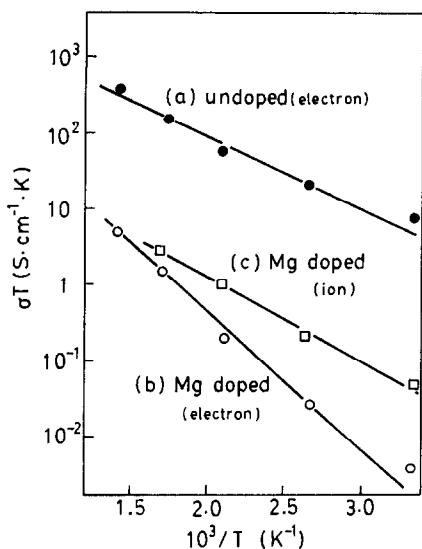


FIG. 5. Electrical conductivities of K-Ba ferrites. (a) Electronic conductivity of undoped K-Ba ferrite; (b) electronic and (c) ionic conductivities of Mg-doped K-Ba ferrite.

### Summary

A new hexaferrite with mixed  $\beta$ -alumina and magnetoplumbite structure was synthesized by the solid-state reaction of the mixture of  $0.45\text{K}_2\text{CO}_3 \cdot 0.55\text{BaCO}_3 \cdot 6\text{Fe}_2\text{O}_3$  at 1300 to 1350°C. The alternate stacking structure of half cells of  $\text{K}^+$ - $\beta$ -ferrite and Ba hexaferrite was proposed from the X-ray powder diffraction pattern of this ferrite. A similar compound was also found in the  $\text{Rb}_2\text{O}-\text{BaO}-\text{Fe}_2\text{O}_3$  system.

The saturation magnetization of the K-Ba ferrite was very small compared to that of Ba hexaferrite.

The electronic conductivity of K-Ba ferrite was  $0.3 \text{ S} \cdot \text{cm}^{-1}$  at 300°C, which was too high to permit measurements of the ionic conductivity based on the  $\beta$ -alumina structure. However, the electronic conductivity of Mg-doped K-Ba ferrite ( $0.45\text{K}_2\text{O} \cdot 0.55\text{BaO} \cdot 5.7\text{Fe}_2\text{O}_3 \cdot 0.3\text{MgO}$ ) was  $10^2$ – $10^3$  times lower than that of the undoped ferrite. The ionic conductivity of Mg-doped K-Ba ferrite, which is thought to be equal to that of undoped ferrite, was  $6 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$  at 300°C, comparable to that of  $\text{K}^+$ - $\beta$ -ferrite.

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