JOURNAL OF MATERIALS SCIENCE 23 (1988) 588–592

Synthesis of barium hexaferrite for magnetic recording media using the KCl flux system

KAZUO HIGUCHI, SHINAKO TAKAHASHI, HIDEAKI ITOH, SHIGEHARU NAKA
Synthetic Crystal Research Laboratory, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, Japan

Individual and fine crystals of barium hexaferrite were prepared by a modified flux method using the KCl flux system. Co^{2+}–Ti^{4+}-substituted barium hexaferrite with a homogeneous composition was synthesized at 950° C for 5 h or at 1000° C for 1 h from a mixture of $BaCO_3$, Fe_2O_3, CoO and TiO_2 with 30 wt% KCl added. Laboratory-prepared fine Fe_2O_3 was preferred because it gave ferrite particles with diameters of 0.2 to 0.4 μm. Magnetic properties were controlled by the Co–Ti content in hexaferrite crystals. Coercive force and Curie temperature decreased with the degree of Co–Ti substitution with saturation magnetization held at high value. The present process, from which individual and fine barium hexaferrite crystals can be prepared by using the KCl flux system, is recommended as a means of mass-production of ferrite powders with controlled magnetic properties for use in magnetic recording media.

1. Introduction

A flux method is one of the most promising techniques to prepare individual crystals with their inherent habits. Several works have reported the preparation of barium hexaferrite single crystals by the flux method [1–4]. By means of a skilful choice of flux system and by controlling the synthetic conditions, both large crystals [1, 2] and individual fine crystals [3, 4] were obtained by this method. The synthetic procedure is relatively simple compared with the hydrolysis method [5] or the glass ceramic method [6–8] where a careful post-heat-treatment is indispensable. No paper has been published on the control of magnetic properties of ion-substituted barium hexaferrites obtained by the flux method.

In the present paper, a modified flux method was applied to the preparation of well-dispersed and fine barium hexaferrite crystals for a perpendicular magnetic recording media. The coercive force was controlled by means of the substitution of Fe^{3+} with Co^{2+}–Ti^{4+}, which has been applied to the glass ceramic method [6–8] or the hydrothermal method [9].

According to the selection direction of the flux system, which was proposed by Oishi [10], the following fluxes were considered to be appropriate for the synthesis of barium hexaferrite; K_2O–Fe_2O_3, Bi_2O_3, HgO, PbO, KF and KCl. In the present study, chlorides such as KCl, NaCl, $BaCl_2$ were chosen as the flux system, because they could be removed from the products by washing with water after the synthetic reaction, which would be done more easily in the chloride flux system than the oxide flux system. In addition, such chloride fluxes would not be incorporated into the ferrite crystals.

2. Experimental details

2.1. Starting materials

Five kinds of iron oxides (α-Fe_2O_3) were examined as starting materials of iron source; i.e. as-received iron oxide reagent or iron oxides prepared in the laboratory by a thermal decomposition of salts. $Fe(NO_3)_3 9H_2O$ and $Fe_2(SO_4)_3 xH_2O$ were thermally decomposed to prepare α-Fe_2O_3 for 2 h at 400° C and at 650 to 700° C, respectively. As-decomposed α-Fe_2O_3 was ultrafiltrated carefully by washing in distilled water and was then dried at 90° C. $BaCO_3$, CoO and TiO_2 were commercial reagents with purities of 99%. The following flux systems were used: KCl (melting point = 776° C), NaCl (800° C), 43 mol % KCl–57 mol % $BaCl_2$ (645° C) and 50 mol % KCl–50 mol % NaCl (680° C).

2.2. Experimental procedure

A calculated amount of these materials for the composition of $BaFe_{12-2x}Co_xTi_xO_{19}$ (x = 0, 0.5, 0.75, 1.0) were mixed well with 10 to 70 wt % flux in the agate mortar. The pellets (1 cm diameter), formed by pressing the mixture under a load of 1 ton, were heated at $10° C\,min^{-1}$ and held for 1 to 5 h at various soaking temperatures of 700 to 1000° C in an electric furnace. After cooling the specimens in the furnace, they were crushed and ultrasonically treated by washing in distilled water to remove the residual flux. The particles thus obtained were dried at 90° C.

2.3. Characterization

X-ray powder diffraction analysis, using Cu$K\alpha$ radiation with a graphite monochrometer, was carried out for product identification. The particle size and morphology of the powders were examined by scanning electron microscopy and transmission electron

0022–2461/88 $03.00 + .12

TABLE I Specific surface area of starting iron oxide and particle size of prepared $BaFe_{11}Co_{0.5}Ti_{0.5}O_{19}$

Thermal decomposition temperature (° C)	Specific surface area ($m^2 g^{-1}$)	Particle size of barium hexaferrite* (μm)
Reagent Fe_2O_3	2.4	0.3–1.0
Decomposed Fe_2O_3		
$Fe_2(SO_4)_3$, 700	15.1	0.1–0.3
$Fe_2(SO_4)_3$, 680	32.2	0.2–0.5
$Fe_2(SO_4)_3$, 650	64.1	0.2–0.4
$Fe(NO_3)_3$, 400	35.1	0.2–0.4

*$BaFe_{11}Co_{0.5}Ti_{0.5}O_{19}$ composition, KCl 30 wt %, 950° C, 1 h.

microscopy. Specific surface area was measured by an automatic surface area analyser. X-ray fluorescence analysis using a germanium target, was conducted to identify the elements in the products. The coercive force ($_iH_c$) and saturation magnetization (σ_s) were measured by a vibrating-sample magnetometer at room temperature. Curie temperatures were evaluated from thermomagnetic curves measured by a Faraday-type magnetic balance.

3. Results and discussion

3.1. Formation process and morphology of barium hexaferrite

3.1.1. Particle size of starting iron oxide

The specific surface area of the starting iron oxide is given in Table I. In contrast to the diameter of more than 1 μm for as-received reagent, laboratory-prepared iron oxides were very small, being several tens of nanometres as shown in Fig. 1. The particle sizes of $BaFe_{11}Co_{0.5}Ti_{0.5}O_{19}$, which was prepared using KCl flux (30 wt %) at 950° C for 1 h, are also shown in Table I. The particle sizes were measured by SEM observation. Barium hexaferrites with smaller particle size and narrower size distribution were prepared from laboratory-prepared iron oxides compared with those of the as-received reagent. There was no remarkable difference in particle size of the barium hexaferrite crystals obtained from the four kinds of laboratory-prepared iron oxides. It was seen that small iron oxide particles with large specific surface areas were favourable for the preparation of barium hexaferrite with a small particle size.

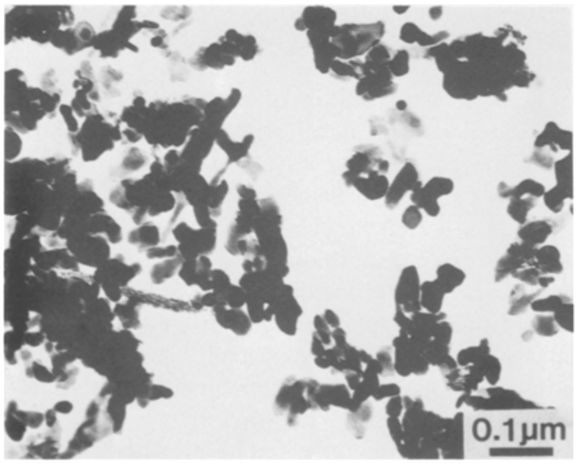

Figure 1 TEM photograph of laboratory-prepared α-Fe_2O_3 ($Fe(NO_3)_3$, 400° C, 2 h).

TABLE II Correlation between composition and particle size of barium hexaferrite

Heat treatment	x in $BaFe_{12-2x}Co_xTi_xO_{19}$	Specific surface area ($m^2 g^{-1}$)	Particle size (μm)
950° C, 5 h	0	2.9	0.5–0.8
	0.5	3.9	0.2–0.4
	0.75	3.8	0.2–0.4
	1.0	3.8	0.2–0.4
1000° C, 1 h	0	–	–
	0.5	4.1	0.2–0.3
	0.75	4.4	0.2–0.3
	1.0	5.1	0.2–0.3

Flux: 30 wt % KCl.

Amongst the four starting iron oxides, however, iron oxide, which was prepared from ferric nitrate, was suited as a starting material to form a single phase of barium hexaferrite. In some cases of iron oxides from ferric sulphate, a consumption of Ba^{2+} by residual sulphate ion resulted in the coexistence of unreacted iron oxide with barium hexaferrite after the heat treatment. Therefore, unless otherwise noted, laboratory-prepared iron oxide from ferric nitrate was used in the present study in order to prepare a single phase of finer barium hexaferrite crystals.

3.1.2. Composition of starting materials

Table II shows the correlation between the composition x in $BaFe_{12-2x}Co_xTi_xO_{19}$ and the particle size of barium hexaferrite prepared under two different heat-treatment conditions, 950° C for 5 h and 1000° C for 1 h. The decrease in particle size with the degree of Co–Ti substitution suggests that the substitution hinders grain growth of hexaferrite microcrystals. A similar effect was observed in the case of ion-substituted barium hexaferrite prepared by hydrolysis [11, 12]. This effect of hindered grain growth by Co–Ti substitution was favourable for controlling the particle size and coercive force.

3.1.3. Composition of flux

The flux systems of KCl–$BaCl_2$ and KCl–NaCl were not so effective on decreasing the formation temperature of hexaferrites as was the KCl flux system. In addition, the KCl–$BaCl_2$ flux tended to give larger crystals than the KCl flux. In the flux system of KCl, temperatures higher than 900° C were required in order to prepare barium hexaferrite in single phase.

Observation of the phases formed after heat-treatment of two different systems, i.e. KCl flux system and non-flux system, suggested that a flux such as KCl promoted the formation reaction of barium hexaferrite. The particle size of barium hexaferrite prepared using the KCl flux, increased with the amount of flux in the range of more than 50 wt %, which was caused by grain growth of the crystals in the melt. On the other hand, an incomplete reaction of starting materials led to the coexistence of iron oxide when the flux content was less than 20 wt %. Well-defined hexagonal plate-like particles were difficult to find. In order to obtain single phase barium hexaferrite with finer particle sizes, the appropriate amount of KCl flux required seems to be in the range 20 to 40 wt %. At the

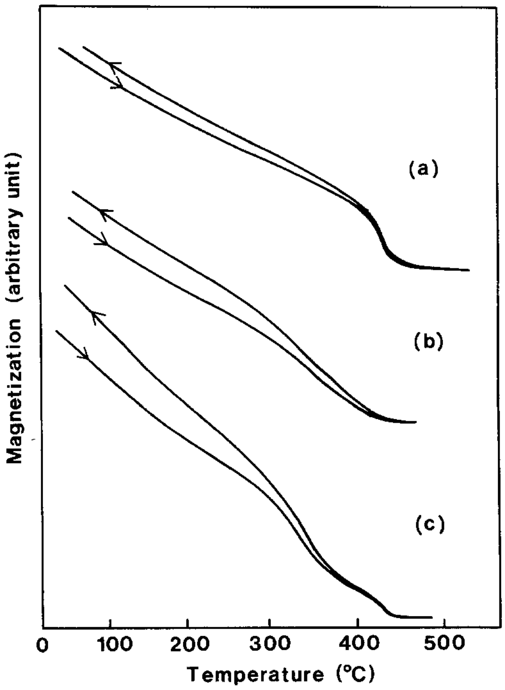

Figure 2 Thermomagnetic curves with various Co^{2+}–Ti^{4+} content in $BaFe_{12-2x}Co_xTi_xO_{19}$ prepared with 30 wt %-KCl at 950° C for 1 h; (a) $x = 0$, (b) $x = 0.5$ and (c) $x = 1.0$.

optimum amount of flux (30 wt % $\simeq$ 53 vol %), it is considered that every barium hexaferrite particle would be surrounded by the molten flux at elevated temperatures. The well-defined hexagonal plate-like crystals could be prepared in this discrete state of the growing microcrystals.

3.1.4. Heat-treatment condition

Fig. 2 shows the thermomagnetic curves of the specimens with various Co–Ti contents, x, in $BaFe_{12-2x}Co_xTi_xO_{19}$ which were prepared with 30 wt % KCl at 950° C for 1 h. The Curie temperature of the pure barium hexaferrite ($x = 0$) was found at 450° C, which agreed with the reported value [13]. However, the shape of the curves of Co–Ti substituted specimens differs from that of pure barium hexaferrite and exhibits two kinds of remarkable change in magnetization, which would result from the compositional inhomogeneity in the specimens. In other words, the specimen with $x = 1$ includes barium hexaferrite with two kinds of composition: almost pure barium hexaferrite ($x \simeq 0$) and that with a large amount of Co–Ti content. This inhomogeneity was removed by extending the heat-treatment duration or by raising the treatment temperature. Co–Ti-substituted barium hexaferrite with a homogeneous composition ($x = 1$) was prepared under the condition of 950° C for 5 h or 1000° C for 1 h, as seen by a single Curie temperature in the thermomagnetic curves in Fig. 3. Consequently, the heat-treatments at these conditions were necessary to prepare Co–Ti-substituted barium hexaferrite with a homogeneous composition in the present synthetic process using the KCl flux.

Fig. 4 shows TEM photographs of Co–Ti-substituted barium hexaferrite with the composition of $BaFe_{10}CoTiO_{19}$, which was prepared under the above conditions. Well-defined hexagonal crystals with particle size in the range 0.2 to 0.4 μm can be observed in these specimens. These crystals were considered to be single magnetic domain particles.

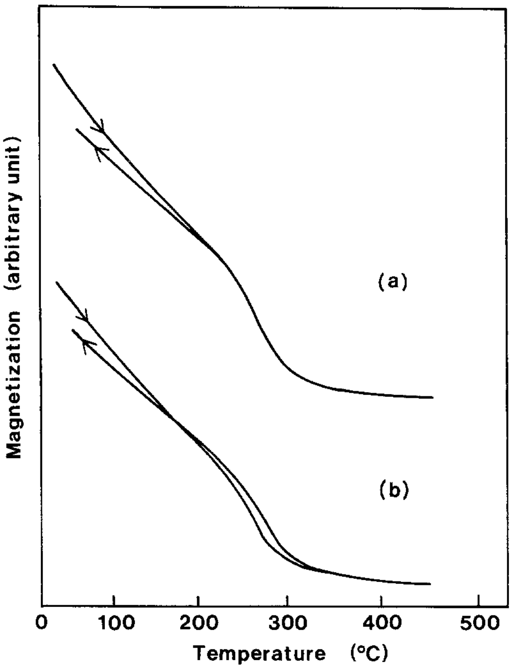

Figure 3 Thermomagnetic curves of $BaFe_{10}CoTiO_{19}$ prepared with 30 wt %-KCl (a) at 950° C for 5 h and (b) at 1000° C for 1 h.

3.1.5. X-ray fluorescence analysis of prepared powder

By means of X-ray fluorescence analysis, the chemical species of prepared Co–Ti-substituted barium hexaferrite were examined. Only the constituting elements, barium, iron, cobalt and titanium, were found in the specimen with no potassium detected. It was found that no contamination of barium hexaferrite by potassium occurred in the modified flux method using the KCl flux.

3.2. Magnetic properties of barium hexaferrite prepared using the KCl flux

Variation of Curie temperature of Co–Ti-substituted barium hexaferrite with Co–Ti content is shown in Fig. 5 for three kinds of heat-treatment conditions. The Curie temperature decreased with Co–Ti content because of the lowered superexchange interaction by the substitution of Fe^{3+} with Co^{2+}–Ti^{4+}. This result is consistent with that for Co–Ti-substituted barium hexaferrite prepared by hydrolysis method of organometallic compounds [5].

Fig. 6 shows a variation of coercive force of Co–Ti-substituted barium hexaferrite with Co–Ti content. The coercive force at a given composition shows almost the same value, regardless of different heat-treatment conditions, so that the coercive forces at the respective compositions are considered to be intrinsic values. The decrease in the coercive force with Co–Ti substitution could be explained by a lowered magnetocrystalline anisotropy, because each particle was considered to have a single magnetic domain size. Although the coercive force seemed to be somewhat lower than that for Co–Ti-substituted barium hexaferrite prepared by the other method, the coercive force for barium hexaferrite prepared by the flux method could be controlled

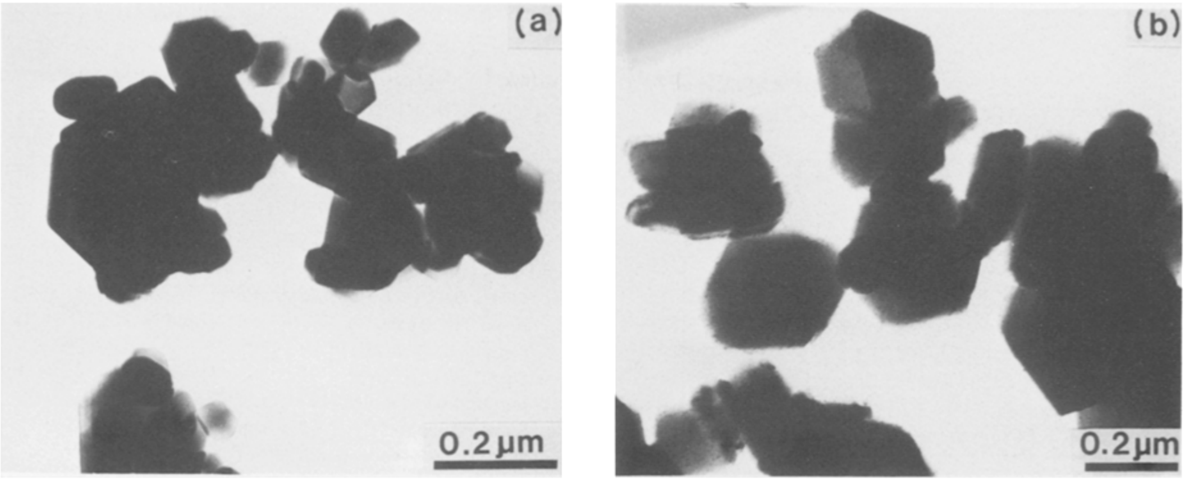

Figure 4 TEM photographs of $BaFe_{10}CoTiO_{19}$ prepared with 30wt%-KCl at (a) 950° C for 5h, and (b) 1000° C for 1h.

by Co–Ti substitution over a fairly wide range of Co–Ti content.

On the other hand, the saturation magnetization of the specimens treated at various conditions had high values (over 60e.m.u. g^{-1} up to $x = 0.75$ in $BaFe_{12-2x}Co_xTi_xO_{19}$) as shown in Fig. 7.

These fine particles of Co–Ti-substituted barium hexaferrites with high magnetization and controlled coercive force of the manageable level were considered to be suitable for the magnetic recording media.

3.3. Evaluation of performances of barium hexaferrites prepared by the modified flux method

From a viewpoint of the magnetic properties, barium hexaferrites prepared by this flux method are considered to be suitable for perpendicular magnetic recording media, because the coercive force of barium hexaferrite can be controlled over a wide range by composition of $BaFe_{12-2x}Co_xTi_xO_{19}$ with the magnetization held at a high value (see Section 3.2).

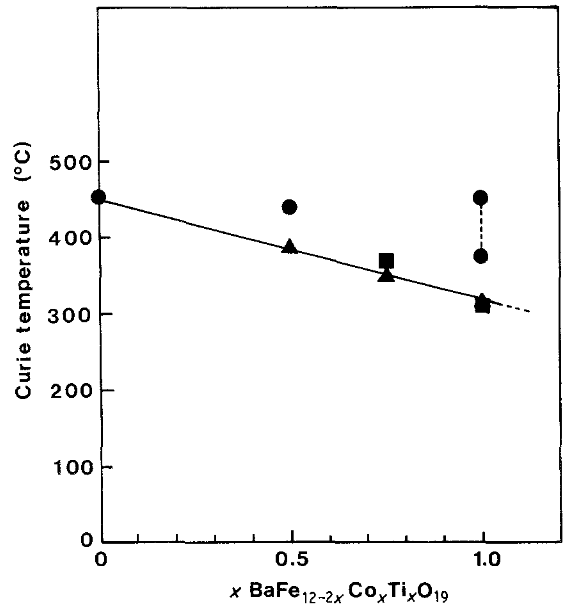

Figure 5 Variation of Curie temperature with Co^{2+}–Ti^{4+} content for Co–Ti-substituted barium hexaferrite prepared under various heat-treatment conditions: (●) 950°C, 1h, (▲) 950°C, 5h, (■) 1000°C, 1h.

As far as the morphology of barium hexaferrite particles is concerned, the flux method, by which individual crystals can be grown by a simple process, would be a desirable technique for the mass production of recording media, provided that barium hexaferrite with a finer particle size could be prepared.

The manufacturing costs of barium hexaferrite by the flux methods would be lower than by the other methods except for the conventional ceramic method by solid state reaction. The ceramic method, however, is not favourable for preparing fine crystals for magnetic recording media. Therefore, the present method should be a promising way for practical mass-production of barium hexaferrite powders for the recording media.

4. Conclusion

Fine barium hexaferrite crystals with controlled

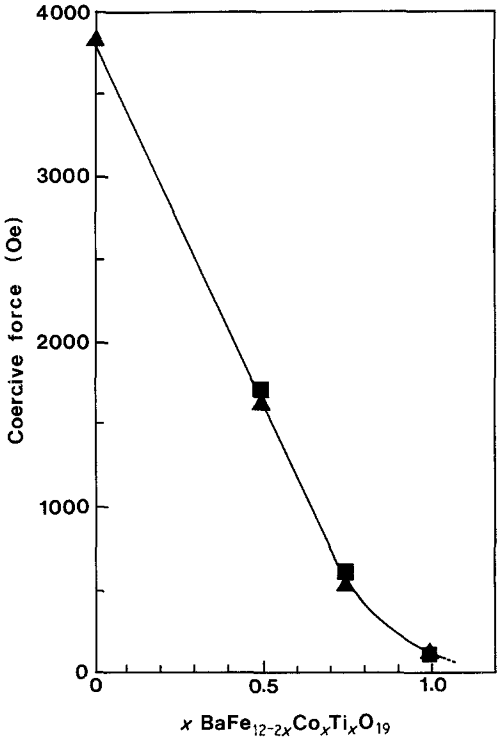

Figure 6 Variation of coercive force of Co–Ti-substituted barium hexaferrite with Co^{2+}–Ti^{4+} content: (▲) 950°C, 5h, (■) 1000°C, 1h.

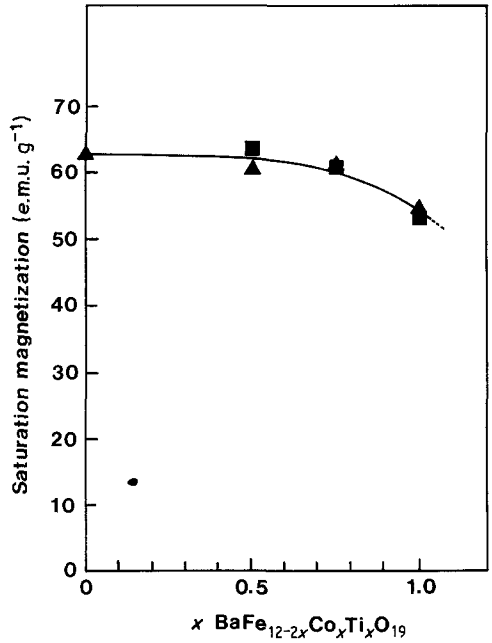

Figure 7 Variation of saturation magnetization of Co–Ti-substituted barium hexaferrite with Co^{2+}–Ti^{4+} content: (▲) 950° C, 5 h, (■) 1000° C, 1 h.

magnetic properties were readily prepared by a modified flux method using the KCl flux system. Heat-treatment at 950° C for 5 h or at 1000° C for 1 h was required to obtain plate-like Co–Ti-substituted barium hexaferrite crystals with 0.2 to 0.4 μm particle size and homogeneous composition.

In order to prepare finer barium hexaferrite crystals, it was preferable to use iron oxide powder with small grain sizes as the starting material and to add CoO and TiO$_2$ to the system with 30 wt % KCl flux. Magnetic properties were controlled by the Co–Ti content in hexaferrite crystals. Coercive force was readily controlled by the composition over a wide range with holding saturation magnetization at high value.

The modified flux method is a promising way to mass-produce barium hexaferrite powders for magnetic recording media.

References

1. L. H. BRIXNER, *J. Amer. Chem. Soc.* **81** (1959) 3841.
2. J. AIDELBERG, J. FLICSTEIN and M. SCHIEBER, *J. Crystal Growth* **21** (1974) 195.
3. D. G. WICKHAM, "Ferrites", Proceedings of the International Conference (1970) p. 105.
4. R. H. ARENDT, *J. Solid State Chem.* **8** (1973) 339.
5. K. HIGUCHI, S. NAKA and S. HIRANO, to be published.
6. O. KUBO, T. IDO and H. YOKOYAMA, *IEEE Trans. Mag.* **MAG-18** (1982) 1122.
7. T. FUJIWARA, M. ISSHIKI, Y. KOIKE and T. OGUCHI, *ibid.* **MAG-18** (1982) 1200.
8. M. KIYAMA, T. TAKADA, N. NAGAI and N. HOSHI, "Advances in Ceramics" (The American Ceramic Society, Columbus, Ohio, 1985) p. 51.
9. O. KUBO, T. IDO, H. YOKOYAMA and Y. KOIKE, *J. Appl. Phys.* **57** (1985) 4280.
10. S. OISHI, Thesis, Nagoya University (1984).
11. K. HIGUCHI, S. HIRANO and S. NAKA, in "Advances in Ceramics" (The American Ceramic Society, Columbus, Ohio, 1985) p. 73.
12. K. HIGUCHI, S. NAKA and S. HIRANO, *Adv. Ceram. Mater.* **1** (1986) 104.
13. J. SMIT and H. P. J. WIJIN, "Ferrites" (Philips' Technical Library, International, 1965) p. 177.

Received 30 March
and accepted 16 June 1987