High - Performance Ferrite Magnets: M - Type Sr - Ferrite Containing Lanthanum and Cobalt

K. Iida, Y. Minachi, K. Masuzawa, M. Kawakami, H. Nishio, and H. Taguchi

Materials Research Center, TDK Corporation
570-2 Matsugashita, Minami-Hatori, Narita, Chiba 286-8588, Japan
(Received October 14 1998; Accepted January 21 1999)

Magnetic properties of anisotropic M-type Sr-ferrite containing La and Co ($\text{Sr}_{1-x}\text{La}_x\text{Co}_x\text{Fe}_{12-x}\text{O}_{19}$) was investigated in detail. At a composition of $x = 0.3$, the magnetic properties for permanent magnets were much improved, with the highest values of $B_r = 4.45$ kG, $H_cJ = 4.82$ kOe, and $(BH)_{\max} = 4.86$ MGOe. The temperature dependence of the coercivity was also much improved, with $\Delta H_cJ/H_cJ/\Delta T = 0.1\%$ /°C.

Key words: M-type ferrite magnet, SrM-ferrite, substitution, La, Co, coercivity, temperature coefficient, magnetocrystalline anisotropy

1. Introduction

Ever since the discovery of M-type hexagonal ferrites with chemical formula $\text{BaFe}_{12}\text{O}_{19}$ (BaM) by Went et al. in 1952¹⁾ and $\text{SrFe}_{12}\text{O}_{19}$ (SrM) by Cochardt in 1963²⁾, tremendous efforts have been made in improving their magnetic capabilities, especially from a commercial standpoint. In order to improve the fundamental magnetic properties of hexaferrites, many studies have been also reported concerning cationic substitution.

Some experiments, which used light rare-earth ions such as La and Pr and other metal cations in substitution for Sr (Ba) and Fe, were designed to maintain total electroneutrality while taking into account the ionic radius of the elements. These lead to the synthesis of $\text{Ba}_{1-x}\text{La}_x\text{Zn}_x\text{Fe}_{12-x}\text{O}_{19}$ ³⁾, $\text{LaFe}_{12}\text{O}_{19}$ ⁴⁾, and $\text{Ba}_{1-x}(\text{L.R.E.})_x\text{Co}_x\text{Fe}_{12-x}\text{O}_{19}$ ⁵⁾ type ferrites. However, these studies did not show clearly the magnetic properties of sintered magnets.

Recently, we reported that the saturation magnetization of $\text{Sr}_{0.7}\text{La}_{0.3}\text{Zn}_{0.3}\text{Fe}_{11.7}\text{O}_{19}$ can be improved by more than 4%, although the magnetocrystalline anisotropy constant (K_1) decreases by 10%⁶⁾. With this study of Sr-ferrite containing La and Zn as a starter, we have investigated the effects of other ions instead of La or Zn. In this paper, the effects of Co and La on the magnetic properties of anisotropic Sr-ferrite were reported.

2. Experimental

La_2O_3 , SrCO_3 , CoO_x , $\alpha\text{-Fe}_2\text{O}_3$ powders were used as starting materials. These materials were weighed in nominal composition of Sr : La : Co : Fe = $1-x$: x : x : $12-x$, where x varies from 0 to 1 with 0.1 or 0.2 increment. Mixtures of these raw materials were attrition-milled in

water for 2 hours, dried, granulated, and then calcined at 1200°C for 3 hours in air. The calcined granules were pulverized by a dry-vibratory rod-mill with additives of SiO_2 (0.6 wt%) and CaCO_3 (1.4 wt%) and then ball-milled in xylene with oleic acid (1.3 wt%). After adjusting the slurry content, the slurry was wet-pressed into pellets of $30\phi \times 15\text{mmh}$ under a magnetic field of approximately 10 kOe. This wet-process using an organic solvent and surfactant together with a magnetic field is very effective for achieving high orientation for submicron-sized particles⁷⁾. Finally, the pressed pellets were sintered at 1180~1240°C for 1 hour in air. The sintered samples were characterized with respect to their phase contents, lattice constants, and magnetic properties.

Thermomagnetic analysis (VSM) of cylindrically cut samples ($5\phi \times 6.5\text{mmh}$), was carried out to determine the Curie temperature (T_c) and temperature dependence of H_cJ and B_r . Magnetocrystalline anisotropy field (H_a) of cubically cut samples ($10 \times 10 \times 10\text{mm}$) was determined by magnetization curves parallel and perpendicular to the easy magnetization axis, using a D.C. recording fluxmeter.

3. Results and discussion

The primary particle size of the calcined granules was estimated at around 0.5 μm on average by SEM observation in the compositional range 0 to 1.0. Table 1 shows the phase composition of these calcined granules determined by XRD and T_c analysis. In the range of $x = 0 \sim 0.2$, only a single M-phase was detected. For the samples of $x \geq 0.3$, spinel and / or ortho-ferrite was also detected. The results obtained from sintered compounds made from these calcined powders are described below.

3.1. Phase identification by XRD and T_c analysis

Table 2 shows the phase composition of sintered samples (1200°C). In the range of $x = 0 \sim 0.4$, only a single M-phase was detected. For $x = 0.6$, two phases were identified as $\alpha\text{-Fe}_2\text{O}_3$ (trace) and M-phase. For $x = 0.8$, ortho-ferrite and spinel-ferrite phases were also observed. For $x = 1.0$ ($\text{LaCoFe}_{11}\text{O}_{19}$), no M-phase was detected even when the sintering temperature was as high as 1240°C. According to literature⁸⁻⁹⁾, $\text{LaFe}_{12}\text{O}_{19}$ with M-structure is stable above 1350°C in air. The difference between Table 1 and Table 2 could thus be explained by the proceeding of the reaction.

Fig. 1 shows the relationship between lattice constants

and composition (x). The hexagonal lattice constant a did not change significantly, whereas the lattice constant c decreased linearly as a function of composition. This slight decrease in the lattice constant c may have been caused by the difference between the ionic radii of La^{3+} (1.17Å) and Sr^{2+} (1.32Å) and, between Co^{2+} (0.69Å) and Fe^{3+} (0.79Å). By using above data, X-ray densities were calculated as shown in Table 3. Decrease of the lattice constant c and increase of the formula weight with x lead to an increase of theoretical density.

Fig. 2 shows the compositional dependence of the Curie temperature (T_c) of anisotropic samples sintered at 1200°C. The T_c decreased linearly with increasing x -value. At the composition of $x = 0.8$, T_c of 420°C and 520°C were recorded. The latter corresponds to the spinel-phase. Judging from the change of lattice constants and T_c , it can be assumed that in the range of $x = 0 \sim 0.6$ La and Co enter the lattice and substitute for Sr and Fe, respectively.

Table 1 Phase composition of calcined granules ($\text{Sr}_{1-x}\text{La}_x\text{Co}_x\text{Fe}_{12-x}\text{O}_{19}$), determined by XRD and T_c analysis. Calcined temp. = 1200°C.

x	Phases
0	M
0.1	M
0.2	M
0.3	M+S
0.4	M+S
0.6	M+S+H (trace)
0.8	M+H+S+O
1.0	H+S+O

M: Magnetoplumbite, H: Hematite, S: Spinel
O: Orthoferrite

Table 2 Phase composition of sintered compounds ($\text{Sr}_{1-x}\text{La}_x\text{Co}_x\text{Fe}_{12-x}\text{O}_{19}$), determined by XRD and T_c analysis. Sintering temp. = 1200°C.

x	Phases
0	M
0.1	M
0.2	M
0.3	M
0.4	M
0.6	M+H (trace)
0.8	M+H+S+O
1.0	H+S+O

M: Magnetoplumbite, H: Hematite, S: Spinel
O: Orthoferrite

Fig. 1 Compositional dependence of the lattice constants of sintered compounds ($\text{Sr}_{1-x}\text{La}_x\text{Co}_x\text{Fe}_{12-x}\text{O}_{19}$). Sintering temp. = 1200°C.

Table 3 Lattice constants, formula weight (FW), and theoretical density as a function of composition. Sintering temp. = 1200°C.

x	a (Å)	c (Å)	FW (g/mol)	ρ (g/cm ³)
0	5.89	23.05	1061.8	5.10
0.1	5.88	23.04	1067.2	5.14
0.2	5.89	23.03	1072.7	5.16
0.3	5.89	23.00	1078.1	5.19
0.4	5.88	23.01	1083.5	5.22

Fig. 2 Compositional dependence of the Curie temperature of sintered compounds ($\text{Sr}_{1-x}\text{La}_x\text{Co}_x\text{Fe}_{12-x}\text{O}_{19}$). Sintering temp. = 1200°C.

3.2. Magnetic properties at room temperature

Fig. 3 shows the magnetic properties of the anisotropic samples sintered at 1200°C. In the compositional range from $x = 0$ to $x = 0.4$, the remanence (B_r) gradually increased. Then, at the composition of $x = 0.6$, B_r abruptly decreased.

Fig. 3 Magnetic properties of sintered compounds ($\text{Sr}_{1-x}\text{La}_x\text{Co}_x\text{Fe}_{12-x}\text{O}_{19}$). Sintering temp. = 1200°C.

It is well-known that Br is determined by the product of saturation magnetization ($4\pi J_s$), orientation degree (J_r/J_s), and bulk density (ρ). In the compositional range from 0 to 0.4, the orientation degree (J_r/J_s) and sintered density (ρ) kept constant at about 97~98%. Fig. 4 shows the relationship between $4\pi J_s$ and Br . It is obvious that high Br at the compositions of $x = 0 \sim 0.4$ is due to the enhancement of the saturation magnetization ($4\pi J_s$).

By contrast with these slight increase of Br (4.4 kG $\rightarrow$ 4.5 kG) in the compositional range $x = 0$ to 0.4, HcJ drastically changed (3.8 kOe $\rightarrow$ 4.8 kOe) before it abruptly decreased for the compositions $x \geq 0.4$. In order to investigate the origin of the high HcJ value at $x = 0.3$, microstructures of the sintered samples were observed by SEM. Fig. 5 shows the grain size distribution of sintered samples determined from the SEM micrographs. The grain size distribution at $x = 0.3$ was comparable to that of $x = 0$. The critical diameters of the single domain state were calculated as around 0.97 μm for $x = 0$ and 1.03 μm for $x = 0.3$, respectively. From these results, it is clear that high HcJ at $x = 0.3$ cannot be due to a microstructure with fine grains.

Fig. 6 shows the relationship between magnetocrystalline anisotropy field (H_a) and HcJ of sintered samples (1200°C, 1220°C, and 1240°C). Although H_a -values are almost the same, and are independent of sintering temperature, HcJ decreased at higher sintering temperatures due to grain growth. The H_a -values are strongly dependent on the composition (x). H_a at $x = 0.4$ increased more than 20% compared to the undoped composition ($x = 0$) and has a maximum value. However, HcJ at $x = 0.4$ decreased despite this large H_a -value. From SEM observation, the thickness of the basal plane (i. e. the grain size in the c direction) at x

Fig. 4 Relationship between saturation magnetization ($4\pi J_s$) and Br of sintered compounds ($\text{Sr}_{1-x}\text{La}_x\text{Co}_x\text{Fe}_{12-x}\text{O}_{19}$).

Fig. 5 Particle size distribution of sintered compounds ($\text{Sr}_{1-x}\text{La}_x\text{Co}_x\text{Fe}_{12-x}\text{O}_{19}$). Sintering temp. = 1200°C.

Fig. 6 Relationship between the anisotropy field (H_a) and coercivity (HcJ) for sintered compounds ($\text{Sr}_{1-x}\text{La}_x\text{Co}_x\text{Fe}_{12-x}\text{O}_{19}$).

= 0.4 decreased, resulting in a large aspect ratio as shown in Table 4, which could enhance the demagnetizing factor and thus reduce HcJ .

Table 4 Average grain size (GS) and aspect ratio (a/c) of sintered compounds ($\text{Sr}_{1-x}\text{La}_x\text{Co}_x\text{Fe}_{12-x}\text{O}_{19}$) determined from SEM micrographs, counting 120 grains. Sintering temp. = 1200°C.

x	Average GS (μm); a	Average GS (μm); c	Average aspect ratio (a/c)
0	0.92	0.63	1.61
0.3	0.86	0.62	1.71
0.4	0.86	0.47	1.85

3.3. Temperature dependence of H_cJ and Br

Fig. 7 shows the compositional and temperature dependence of coercivity of anisotropic samples sintered at 1200°C. Besides the change of H_cJ at room temperature, the temperature coefficient of H_cJ ($\Delta H_cJ/H_cJ/\Delta T$) was extremely changed. In the range of $x = 0.6 \sim 1.0$, the sign of the temperature coefficient of H_cJ reversed from positive to negative.

The temperature coefficient of Br ($\Delta Br/Br/\Delta T$) was $-0.19\%/\text{°C}$ which was the same as that of conventional SrM-ferrite in the range of $0 < x < 0.4$.

Fig. 7 Compositional and temperature dependence of coercivity for sintered compounds ($\text{Sr}_{1-x}\text{La}_x\text{Co}_x\text{Fe}_{12-x}\text{O}_{19}$) Sintering temp. = 1200°C.: ■ $x = 0$, ● $x = 0.1$, ▲ $x = 0.2$, ◆ $x = 0.3$, □ $x = 0.4$, ○ $x = 0.6$, △ $x = 0.8$ and ◇ $x = 1.0$.

3.4. High performance ferrite magnet

As a result of this study, it was found that anisotropic Sr-ferrite with chemical formula $\text{Sr}_{0.7}\text{La}_{0.3}\text{Co}_{0.3}\text{Fe}_{11.7}\text{O}_{19}$ gave the highest magnetic properties for permanent magnets as shown in Table 5. These excellent magnetic properties are due to the improvement of the fundamental magnetic properties as shown in Table 6. Further study on the origin of this improvement will be continued.

Table 5 Magnetic properties of the developed material ($x = 0.3 \text{ Sr}_{1-x}\text{La}_x\text{Co}_x\text{Fe}_{12-x}\text{O}_{19}$). The temperature coefficients of Br and H_cJ were determined from J - H hysteresis loops over the temperature range -80°C to 80°C .

	Br (kG)	H_cJ (kOe)	J_t/J_s (%)	H_k/H_cJ (%)	$(BH)_{\text{max}}$ (MGOe)
$x = 0$	4.39	3.93	97.4	95.5	4.73
$x = 0.3$	4.45	4.82	97.5	83.0	4.86

$\Delta H_cJ/H_cJ/\Delta T$ (%)	$\Delta Br/Br/\Delta T$ (%)
0.29	-0.19
0.10	-0.19

Table 6 Fundamental properties of the developed material ($x = 0.3 \text{ Sr}_{1-x}\text{La}_x\text{Co}_x\text{Fe}_{12-x}\text{O}_{19}$). ρ represents the theoretical density. The appropriateness of the estimation of the anisotropy was investigated at the same time¹⁰⁾.

	H_a (kOe)	$4\pi J_s$ (kG)	T_c (°C)	a (Å)	c (Å)	ρ (g/cm ³)
$x = 0$	19.5	4.61 ^{††}	458	5.89	23.05	5.10
$x = 0.3$	24.3	4.70 ^{††}	440	5.89	23.00	5.19

[†], estimation at $\rho = 5.10 \text{ g/cm}^3$

^{††}, estimation at $\rho = 5.19 \text{ g/cm}^3$

4. Conclusions

Magnetic properties of La and Co doped SrM type ferrites ($\text{Sr}_{1-x}\text{La}_x\text{Co}_x\text{Fe}_{12-x}\text{O}_{19}$) were investigated. As a result, we found, for the first time, that superior magnetic properties for permanent magnets were obtained at the composition of $x = 0.3$.

References

- 1) J. J. Went, G. W. Rathenau, E. W. Gorter and G. W. van Oosterhout: *Philips Tech. Rev.*, **13**, 194 (1952).
- 2) A. Cochardt: *J. Appl. Phys.*, **34**, 1273 (1963).
- 3) A. H. Mones and E. Banks: *J. Phys. Chem. Solids*, **4**, 217 (1958).
- 4) V. N. Mulay and A. P. B. Sinha: *Indian J. Pure & Appl. Phys.*, **8**, 412 (1970).
- 5) G. A. Smolenskii and A. A. Andreev: *Phys. Ser.*, **125**, 1405 (1961).
- 6) H. Taguchi, T. Takeishi, K. Suwa, K. Masuzawa and Y. Minachi: Proceedings of The Seventh International Conference on Ferrites (ICF 7), C1-311 (Bordeaux, 1997).
- 7) H. Taguchi, F. Hirata, T. Takeishi and T. Mori: Proceeding of The Sixth International Conference on Ferrites (ICF 6), p.118 (Tokyo, 1992).
- 8) F. K. Lotgering: *J. Phys. Chem. Solids*, **35**, 1633 (1974).
- 9) V. L. Moruzzi and M. W. Shafer: *J. Am. Ceram. Soc.*, **43**, 369 (1960).
- 10) H. Nishio, K. Iida, Y. Minachi, K. Masuzawa, M. Kawakami and T. Tguchi: DIGESTS OF THE 22ND ANNUAL CONFERENCE ON MAGNETICS, p. 93 (Japan, 1998).