High Energy Ferrite Magnets

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Abstract Lanthanum and zinc substitution in M-type hexaferrite was studied in detail in order to increase the saturation magnetization. For the composition $Sr_{0.7}La_{0.3}Fe_{11.7}Zn_{0.3}O_{19}$, the saturation magnetization was increased by more than 4% and the uniaxial anisotropy constant (K_1) was almost the same as that of non-substituted Ba-ferrite. Furthermore, high energy ferrite magnets having more than 40kJ/m^3(5MGOe) were obtained for the first time by the new process for high orientation, high density and submicron-sized grains.

1. INTRODUCTION

M-type ferrite magnets are widely used throughout the world. The practical limit of flux density (Br) and maximum energy product ((BH)max) are around 0.44T(4.4kG) and 37kJ/m^3(4.7MGOe), respectively. Despite numerous studies concerning cation substitution in the M-structure, very few attempts have proved successful improving their fundamental properties. According to Gorter [1], one can expect that saturation magnetization will increase when non-magnetic ions such as Zn occupy tetrahedral 4f1 sites in the M-structure, as is true in spinel ferrite. This is because Fe^{3+} at the 4f1 sites have a down-spin and Zn^{2+} have a strong tetrahedral-site-preference. A Lanthanoid substitution for strontium (R^{3+} or $R^{4+} \rightarrow Sr^{2+}$) is one way to compensate for the decrease in positive charge ($Zn^{2+} \rightarrow Fe^{3+}$). Among the Lanthanoids, La^{3+} has the largest solubility limit in M-type ferrite [2]. The formula of $Ba_{1-x}La_xFe_{12-x}M_xO_{19}$ (M=Zn or Mg) was first made public in 1958 [3]. Compounds with the basic formula $LaM^{2+}Fe_{11}O_{19}$ (M=Cu, Cd, Zn, Ni, Co or Mg) were studied in 1970 [4]. Taking into consideration these references, the possibility of using $Sr_{1-x}La_xFe_{12-x}Zn_xO_{19}$ compounds as permanent magnets was investigated.

2. EXPERIMENTAL PROCEDURE

Mixtures of Fe_2O_3, $SrCO_3$, ZnO and La_2O_3 were attrition-milled in water and calcined at 1150～1250℃ in air, followed by drying and granulating. The powder calcined at 1200℃ was first pulverized using a dry vibratory rod-mill with SiO_2 and $CaCO_3$, then ball-milled in xylene with oleic acid. After adjusting the slurry content, pellets of 30$\phi\times$15mm*h* were wet-pressed while applying a magnetic field of up to 12kOe in the thickness direction. This newly developed wet-process using organic solvent (xylene) and surfactant (oleic acid) is very effective in acheiving high orientation for submicron-sized particles under a magnetic field [5]. The wet-pressed pellets were sintered at 1180～1240℃ in air. *I-H* hysteresis curves were measured using a 30mmϕ search coil in a field of up to 25kOe. σ-T curves were measured using a VSM. K_1 values were measured using a torque magneto-meter after grinding to cylindrical shapes of 5$\phi\times$2mm*h* (a-axis and c-axis were both in the radial plane). H_A was calculated using the formula H_A=2K_1/Is. Mossbauer spectra were taken and compared with published data for M-type ferrite. Micro- and nano-structure was investigated by SEM and TEM-EDS.

3. RESULTS AND DISCUSSION

3.1 Properties of the calcined powder

Table 1 shows the phases obtained at various calcination temperatures, detected using XRD. Single M-phase was obtained at over 1200℃ for $0 \leqq x < 0.5$. At lower temperatures, or $x \geqq 0.5$, hematite (H), $LaFeO_3$ (Ortho-ferrite:O) and spinel ferrite (S) were detected besides the M phase. At higher than 1250℃, undesirable grain growth (over a few microns) occurred. After calcination at 1200℃, almost all the primary particles were observed to be under 1μm by SEM.

Table 1 Phases of the compounds $Sr_{1-x}La_xFe_{12-x}Zn_xO_{19}$ calcined at various temperature for 1 hour in air.

X	1150℃	1200℃	1250℃
0, 0.1, 0.2	M +H	M	M
0.3, 0.4	M +H+S+O	M	M
0.5	M +H+S+O	M +H+O	M +(H)trace
over 0.6	M +H+S+O	M +H+S+O	M +H+S+O

H: hematite, O: $LaFeO_3$ (Ortho-ferrite), S: spinel ferrite

3.2 Fundamental properties of LaZn-substituted Sr-ferrite

Up to a 4% increase of magnetization per mole (NB) at room temperature was achieved, while the Curie temperature (Tc) and HA decreased monotonicaly as shown in fig.1. K1 at x=0.3 was 3.3×10^{6}erg/cc, the same as that of M-type Ba-ferrite. The increase of magnetization suggests Zn^{2+} substituted for Fe^{3+} at the 4f1 sites. The decrease of Tc and HA is explained by the substitution of non-magnetic ions (Zn^{2+}) for magnetic ions (Fe^{3+}). The lattice constant (c) decreased slightly, e.g. 23.05→ 22.95Å. This can be explained by the differences between the ionic radii of La^{3+} (1.17Å), Sr^{2+} (1.32Å), Zn^{2+} (0.74Å) and Fe^{3+} (0.79Å). X-ray density was calculated at around 5.20g/cm^3 for x=0.3. Mossbauer spectra of ^{57}Fe had obviously changed but a decrease in intensity from 4f1 sites was not established because of the ambiguity of fitting based on references [6-7].

3.3 Properties of anisotropic magnets

Figure 2 shows the magnetic properties at the optimum sintering temperature giving highest $(BH)_{max}$ value. 4πIs, Br and Hk/HcJ increased, while HcJ decreased. When sintered at 1220℃, maximum values of Br and $(BH)_{max}$ were obtained for the composition with x=0.3, viz.,.

4πIs=4.70kG, Br=4.60kG, HcB=2.54kOe, HcJ=2.62kOe, Hk/HcJ=94%
$(BH)_{max}$=5.2MGOe, ⊿Br/Br/⊿T=-0.20%/℃, ⊿HcJ/HcJ/⊿T=0.31%/℃

The density of the sample was 5.06g/cm^3 (97.3%). The mean diameter of the grains was around 0.8μm and a considerable number of over-micron sized grains, regarded as multi-domain grains, were observed by SEM (Fig.3). The critical diameter for single domain isolated particles is calculated as 0.97 μm for x=0 and 0.90μm for x=0.3. Thus the low ratio of single domain grains, as well as the decrease of HA value, resulted in a decrease of HcJ value from 4kOe (at x=0) to 2.6kOe (x=0.3). The Hk/HcJ value suggests that LaZn-substitution promotes the homogeneity of micro structure. According to TEM-EDS analysis, neither La nor Zn was found to have segregated at the grain boundaries.

4. CONCLUSION

A small amount of La and Zn substitution (x=0.3) was very effective in increasing saturation magnetization of M-type Sr-ferrite, while the decrease of magnetic anisotropy was within 10%. By producing submicron particles and orienting them in a magnetic field, we succeeded in achieving outstanding magnet properties of 41kJ/m^3(5.2MGOe).

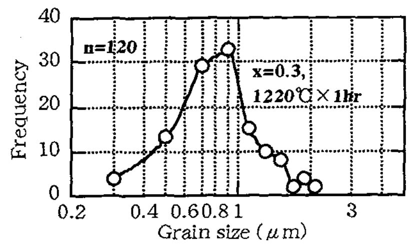

Figure 3: Grain size distribution of LaZn-substituted Sr-ferrite.

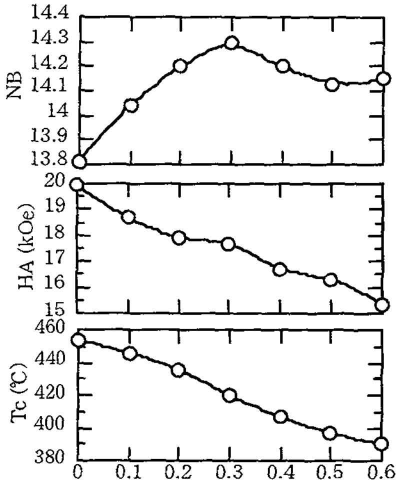

Figure 1: Dependence of magnetization (NB), anisotropic field (HA) and Curie temperature (Tc) on the composition of substitution.

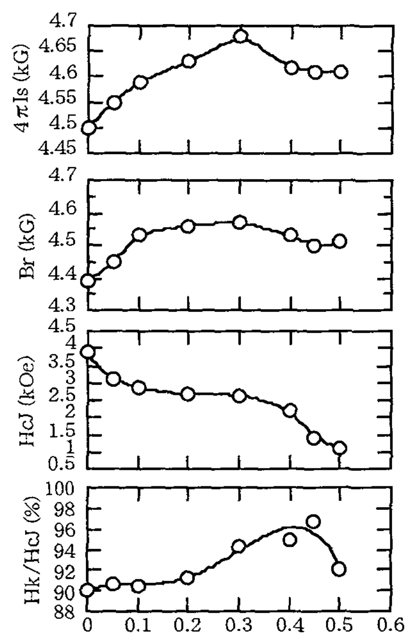

Figure 2: Magnetic properties of anisotropic ferrite magnets by substitution of La and Zn.

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