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► To cite this version:

H. Taguchi, T. Takeishi, K. Suwa, K. Masuzawa, Y. Minachi. High Energy Ferrite Magnets. Journal de Physique IV Proceedings, 1997, 07 (C1), pp.C1-311-C1-312. 10.1051/jp4:19971122 . jpa-00254763

HAL Id: jpa-00254763

<https://hal.science/jpa-00254763>

Submitted on 1 Jan 1997

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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 $\text{Sr}_{0.7}\text{La}_{0.3}\text{Fe}_{11.7}\text{Zn}_{0.3}\text{O}_{19}$, 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 (B_r) and maximum energy product ($(BH)_{\text{max}}$) 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 $\text{R}^{4+} \rightarrow \text{Sr}^{2+}$) is one way to compensate for the decrease in positive charge ($\text{Zn}^{2+} \rightarrow \text{Fe}^{3+}$). Among the Lanthanoids, La^{3+} has the largest solubility limit in M-type ferrite [2]. The formula of $\text{Ba}_{1-x}\text{La}_x\text{Fe}_{12-x}\text{M}_x\text{O}_{19}$ ($\text{M}=\text{Zn}$ or Mg) was first made public in 1958 [3]. Compounds with the basic formula $\text{LaM}^{2+}\text{Fe}_{11}\text{O}_{19}$ ($\text{M}=\text{Cu}$, Cd , Zn , Ni , Co or Mg) were studied in 1970 [4]. Taking into consideration these references, the possibility of using $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}\text{Zn}_x\text{O}_{19}$ 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 $1150 \sim 1250^\circ\text{C}$ in air, followed by drying and granulating. The powder calcined at 1200°C 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 $30\phi \times 15\text{mmh}$ 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 achieving high orientation for submicron-sized particles under a magnetic field [5]. The wet-pressed pellets were sintered at $1180 \sim 1240^\circ\text{C}$ in air. I - H hysteresis curves were measured using a $30\text{mm}\phi$ 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 $5\phi \times 2\text{mmh}$ (a-axis and c-axis were both in the radial plane). H_A was calculated using the formula $H_A = 2K_1/l_s$. 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°C for $0 \leq x < 0.5$. At lower temperatures, or $x \geq 0.5$, hematite (H), LaFeO_3 (Ortho-ferrite:O) and spinel ferrite (S) were detected besides the M phase. At higher than 1250°C , undesirable grain growth (over a few microns) occurred. After calcination at 1200°C , almost all the primary particles were observed to be under $1\mu\text{m}$ by SEM.

Table 1 Phases of the compounds $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}\text{Zn}_x\text{O}_{19}$ calcined at various temperature for 1 hour in air.

X	1150°C	1200°C	1250°C
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 (T_c) and HA decreased monotonically as shown in fig.1. K_1 at $x=0.3$ was $3.3 \times 10^6 \text{ erg/cc}$, 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 T_c 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. $23.05 \rightarrow 22.95 \text{ \AA}$. This can be explained by the differences between the ionic radii of La^{3+} (1.17 $\text{\AA}$), Sr^{2+} (1.32 $\text{\AA}$), Zn^{2+} (0.74 $\text{\AA}$) and Fe^{3+} (0.79 $\text{\AA}$). X-ray density was calculated at around 5.20 g/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 $(BH)_{\text{max}}$ value. $4\pi I_s$, Br and Hk/HcJ increased, while HcJ decreased. When sintered at 1220°C , maximum values of Br and $(BH)_{\text{max}}$ were obtained for the composition with $x=0.3$, viz.,

$$4\pi I_s = 4.70 \text{ kG}, \text{Br} = 4.60 \text{ kG}, \text{HcB} = 2.54 \text{ kOe}, \text{HcJ} = 2.62 \text{ kOe}, \text{Hk/HcJ} = 94\%$$

$$(\text{BH})_{\text{max}} = 5.2 \text{ MGOe}, \Delta \text{Br/Br}/\Delta T = -0.20\%/^\circ\text{C}, \Delta \text{HcJ/HcJ}/\Delta T = 0.31\%/^\circ\text{C}$$

The density of the sample was 5.06 g/cm^3 (97.3%). The mean diameter of the grains was around $0.8 \mu\text{m}$ 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 $0.97 \mu\text{m}$ for $x=0$ and $0.90 \mu\text{m}$ 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 4 kOe (at $x=0$) to 2.6 kOe ($x=0.3$). 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 41 kJ/m^3 (5.2 MGOe).

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

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

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

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