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► To cite this version:

H. Taguchi. Recent Improvements of Ferrite Magnets. Journal de Physique IV Proceedings, 1997, 07 (C1), pp.C1-299-C1-302. 10.1051/jp4:19971118 . jpa-00254758

HAL Id: jpa-00254758

<https://hal.science/jpa-00254758>

Submitted on 1 Jan 1997

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Recent Improvements of Ferrite Magnets

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Abstract This paper overviews recent improvements in the properties of ferrite magnets from two viewpoints. First, new processes for submicron-sized particles, for high orientation and for high density were studied in detail. As a result, high performance Sr-ferrite magnets with $B_r=0.44T$ (4.4kG) and $H_{cJ}=320kA/m$ (4.0kOe) were developed. Furthermore, by means of SiO_2 -SrO or SiO_2 -BaO addition, high performance Ba-ferrite magnets with $B_r=0.43T$ (4.3kG), $H_{cJ}=290kA/m$ (3.6kOe) were obtained. At the same time, we discovered that it is possible to make equal the shrinkage ratio in the a - and c -axes. Second, (LiFe)ZnW-ferrite and Zn-substituted M -ferrite were investigated. Consequently, LaZn substituted SrM ferrite magnets were developed with extremely good properties, viz. $B_r=0.46T$ (4.6kG) and $(BH)_{max}=41kJ/m^3$ (5.2MGOe).

1. INTRODUCTION

More than 40 years have passed since the first announcement of Ba-ferrite by Philips [1]. Since then hexa-ferrite magnets have become widely used in many electronic products, which is explained mainly by their unsurpassed cost efficiency. Another advantage is the chemical stability of these oxides which makes them environmentally safe, further establishing their continued use. On the other hand, a great number of attempts have been made to improve the properties. These technics or methods are classified into two groups. First is the processing technic for obtaining submicron sized powder, high orientation and density for micro- and nano-structure control. Second is the *spin-structure* control technic to improve fundamental properties such as saturation magnetization and/or magnetic anisotropy. This paper overviews studies at TDK employing these two approaches.

2. PROCESS FOR HIGH PERFORMANCE FERRITE MAGNETS

2.1 Process for submicron powder

It is assumed that coercivity in ferrite magnets originates in the magnetic behavior of single domain particles with uniaxial magneto crystalline anisotropy [2]. The critical diameter, below which a single domain is stable, is estimated at around $1\mu m$ for SrM -ferrite. Therefore, control of grain size to under a micron is significant for achieving high H_{cJ} .

Taking into account grain growth, ferrite particles should be around $0.3\mu m$ before sintering. However, particles prepared by the co-precipitation method, hydrothermal synthesis or by glass crystallization are too small (under $0.1\mu m$) to be orientated well in a magnetic field. Research at TDK has therefore centered on "ceramic-method" for obtaining submicron particles having adequate size ($0.1\sim 1\mu m$) to produce sintered magnets. From this point of view, raw materials having small particle size should be mixed very well and calcination temperatures lowered; the molar ratio Fe_2O_3/SrO should be around stoichiometric (6.0) to inhibit grain growth.

In the first place, the wet mixing method for raw materials (Fe_2O_3 at $0.3\mu m$ and precipitated fine $SrCO_3$ at $0.02\mu m$) was studied as the ideals [3]. As a result of further investigation, submicron particles were obtained using even commercial-grade raw materials. Figure 1 shows SEM images of mixed and wet-milled raw materials (after drying) and Sr-ferrite particles calcined at $1200^\circ C$ (size of the primary particles= $0.2\sim 0.8\mu m$, $\sigma_s=71$ emu/g, $H_{cJ}=5.3kOe$). Furthermore, very similar powders were also obtained by a dry mixing process using no liquid [4].

Figure 1: SEM images of mixed raw materials and calcined submicron Sr-ferrite particles.

2.2 Process for high orientation

At the pressing stage, submicron sized particles are usually oriented with great difficulty in a magnetic field. It is essentially believed that the single domain particles attract each other magnetically creating agglomerates thus preventing orientation. Figure 2 shows an expected B - H hysteresis curve of one hard-ferrite particle. Magnetic flux density at the working point (B_1), which is determined by the particle shape, relates to the magnetic agglomeration force. Therefore, the surface flux density of the particle must be reduced ($B_1 \rightarrow B_2$) by reducing HcB . On the other hand, the magnetic moment of the particle in a magnetic field (Hex) is proportional to B_s , which is best maximized. It was found that dry-vibrating pulverization in particular was effective in reducing the Hc values ($HcJ=5.5kOe, (HcB=4.6kOe) \rightarrow HcJ(HcB)=2.5kOe$) as shown in table 1, by introducing lattice defects [5]; meanwhile the decrease of σ_s (saturation magnetization per gram; $\propto B_s$) was within 10%.

Figure 2: BH hysteresis curve of one Sr-ferrite particle.

Table 1: Change of specific surface area (SBET), σ_s and HcJ of dry vibration-pulverized powder. Line half-width (L.H.W.) was measured at (205) plane by XRD. Lattice strain and crystallite size was determined using the Warren and Averbach method [6].

Milling time (min.)	SBET (m ² /g)	σ_s (emu/g)	HcJ (kOe)	L.H.W (deg.)	Lattice strain	Crystallite size (Å)
0	2.9	70.7	5.54	0.108	7.87e-6	1376
5	3.4	68.0	3.52	0.126	7.27e-5	315
20	4.9	66.5	2.73	0.217	2.28e-4	215

Furthermore, the wet-process using an organic solvent (e.g. toluene or xylene) and surfactant (e.g. stearic acid or oleic acid) made a remarkable improvement in the degree of orientation for submicron particles as shown in fig.3, thus achieving high performance, anisotropic sintered magnets, with $Br=0.44T$ (4.4kG) and $HcJ=320kA/m$ (4.0kOe) [7].

Figure 3: XRD pattern of submicron Sr-ferrite particles.

Figure 4: Dependence of Br , HcJ and shrinkage ratio of Ba-ferrite on amount of $SrCO_3$.

2.3 Additives for microstructure control and equal shrinkage ratio

Addition of SiO_2 and $CaCO_3$ (or CaO) is conventionally employed to Ba- or Sr-ferrite in order to achieve high density and to inhibit grain-growth at the same time during final sintering. It is predicted that Sr or Ba can substitute for Ca without difficulty because they have similar characters. Therefore, the addition of alkaline-earth elements and silica to M-type alkaline-earth-elements-ferrite was systematically investigated [8]. As fig.4 shows, the addition of adequate amounts of $SrCO_3$ and SiO_2 to Ba-ferrite improved HcJ and decreased the shrinkage ratio. Thus, the highest performance Ba-ferrite magnets ($Br=0.43T$ (4.3kG), $HcJ=290kA/m$ (3.6kOe)) were obtained. It also becomes possible to make equal the shrinkage ratio in the a - and c -axes as shown in fig.5. Applying this material to multi-pole ring magnets (e.g. 24 or 36 poles), which are pressed under alternative magnetic field along the circumference, yielded a smooth surface after sintering as shown in fig.6.

Figure 5: Shrinkage vs. sintering temperature of anisotropic Ba-ferrite with Si-Ca and Si-Sr.

Figure 6: Comparison of the surface deformation of multi-pole ring magnets measured by a round tester.

These distinctive features were due to the inhibition of grain-growth along the a -axis, resulting in a small aspect ratio of the grains. According to TEM-EDS analysis, Ba segregation was found at the grain boundaries (triple points) besides Si and Sr, as shown in table 2. This suggests the reaction between grains (Ba-ferrite) and glassy additives (Sr-silicates) during sintering. Furthermore, only when $\text{SiO}_2\text{-SrCO}_3$ or $\text{SiO}_2\text{-BaCO}_3$ were added to Ba-ferrite were increases in H_cJ and an equal shrinkage ratio observed, as shown in table 3.

Table 2: Content ratio of triple-points to Ba-ferrite grains. Concentration of the elements were analyzed by TEM-EDS at more than 4 points. Bold figures represent obvious segregation at triple-points.

	Si	Ca	Ba	Sr	Fe
Si-Ca addition	51.2	39.4	0.9	1.0	0.4
Si-Sr addition	46.3	8.0	1.9	8.0	0.3

Table 3: Combination of additives and M-ferrite. Anisotropic ferrite magnets with equal shrinkage ratio and higher H_cJ are indicated by $\bigcirc$.

	Si-Ca	Si-Sr	Si-Ba
Sr-ferrite	-	-	-
Ba-ferrite	-	$\bigcirc$	$\bigcirc$
Ca-ferrite	-	-	-

3. STUDY OF CRYSTAL STRUCTURE FOR HIGH PERFORMANCE FERRITE MAGNETS

3.1 W-type ferrite

W-type ferrite magnets became the subject of much attention since the first announcement by Philips in 1980 [9]. They showed that BaFe^{2+}W has a magnetization ($4\pi Is=5.1\text{ kG}$) 10% higher than BaM , and the anisotropy field is about equal ($HA=18\text{ kOe}$). Nevertheless, it is difficult to control the micro-structure, especially for high H_c , because Fe^{2+}W -phase formation requires a reducing atmosphere and higher temperature during sintering, followed by grain growth. Recently, SrFe^{2+}W with noticeable improvement by means of carbon addition has been reported [10].

On the other hand, Zn^{2+}W -type ferrite can be synthesized in air, but the anisotropy field is considerably low ($HA=12\text{ kOe}$). Thus, with the aim of improving HA , substitution of magnetic ions (such as $\text{Li}^+ + \text{Fe}^{3+} \rightarrow \text{Zn}^{2+}$) were studied at first, taking into consideration of the previous studies [11,12]. Consequently, the difference of the crystal stability between Sr- and Ba- $(\text{LiFe})\text{ZnW}$ after long milling was discovered, resulting in the divergent magnetic properties (Ir/Is , H_k/H_cJ) as shown in table 4 [13]. When using Ba- $(\text{LiFe})\text{ZnW}$, a high Br value (4.6 kG) was achieved, but H_c remained low (less than 1 kOe).

Table 4: Magnetic properties of $(\text{LiFe})\text{ZnW}$ -type ferrite magnets.

	$4\pi Is$ (kG)	T_c ($^{\circ}\text{C}$)	K_1 ($\times 10^6$ erg/cc)	Br (kG)	H_cJ (kOe)	Ir/Is (%)	H_k/H_cJ (%)
$\text{Sr}(\text{LiFe})\text{ZnW}$	4.69	440	2.3	4.32	0.64	92.1	57.9
$\text{Ba}(\text{LiFe})\text{ZnW}$	4.78	430	2.0	4.60	0.60	96.1	94.0

3.2 M-type ferrite

The practical limit of Br and $(BH)_{\text{max}}$ in M-type ferrite magnets was considered to be around 4.4 kG and 4.7 MGOe , respectively. Despite of a great number of studies concerning cation substitution in the M-structure, very few attempts to increase magnetization have succeeded. As is well known in spinel ferrites, saturation magnetization increase when non-magnetic ions such as Zn occupy tetrahedral $4f_1$ sites in the M-structure because Fe^{3+} at $4f_1$ sites has a down-spin. As shown below, there are three possible ways of compensating for the difference in valency ($\text{Zn}^{2+} \rightarrow \text{Fe}^{3+}$):

- (1) $1/2\text{Zn}^{2+} + 1/2\text{M}^{4+} \rightarrow \text{Fe}^{3+}$ (M: Sn, Ti, Zr, Mn) or
 $2/3\text{Zn}^{2+} + 1/3\text{M}^{5+} \rightarrow \text{Fe}^{3+}$ (M: V, Sb, Nb, Ta) or
 $3/4\text{Zn}^{2+} + 1/4\text{M}^{6+} \rightarrow \text{Fe}^{3+}$ (M: W, Mo)
 (2) $\text{SrFe}^{3+}_{12-x}\text{Zn}^{2+}_x\text{O}^{2-}_{19-x}\text{F}^-_x$
 (3) $\text{Sr}^{2+}_{1-x}\text{R}^{3+}_x\text{Fe}^{3+}_{12-x}\text{Zn}^{2+}_x\text{O}_{19}$ (R: Y, La, Nd, Sm, Bi) or
 $\text{Sr}^{2+}_{1-x}\text{R}^{4+}_{3x/4}\text{Fe}^{3+}_{12-x}\text{Zn}^{2+}_x\text{O}_{19}$ (R: Ce, Pr)

Despite of many studies [14], method-(1) dose not obviously improve saturation magnetization because M ions may also occupy upper-spin sites. The problem with method-(2) is the vaporization of fluorine thus (F-substituted) single M-phase is difficult to obtain.

Research at TDK therefore has recently focused on method-(3). Among Lanthanoids, La was the most suitable for substitution for Sr because it has similar ionic radius [15]; a small amounts of Na, K, Rb and Bi were also included besides Lanthanoids. The properties of sintered anisotropic samples substituted with La and Zn were studied in detail and presented in this conference [16]. Figure 7 shows the I - H hysteresis curve of newly developed material ($x=0.3$) which indicates the highest (BH)_{max} value obtained.

4. CONCLUSION

Processes for preparing submicron-sized particles, for high orientation and for high density are significant for obtaining high performance ferrite magnets. Outstanding high performance Sr- and Ba-ferrite magnets were obtained, having $B_r=0.44\text{T}$ (4.4kG), $H_{cJ}=320\text{kA/m}$ (4.0kOe) and $B_r=0.43\text{T}$ (4.3kG), $H_{cJ}=290\text{kA/m}$ (3.6kOe), respectively. Furthermore, by the addition of SiO_2 -SrO or SiO_2 -BaO, we succeeded in making equal the shrinkage ratio in the a - and c -axes of anisotropic Ba-ferrite.

By the *spin-control* approach to increasing magnetization, La and Zn substituted Sr-ferrite magnets were developed with extremely high value of $B_r=0.46\text{T}$ (4.6kG) and $(BH)_{\text{max}}=41\text{kJ/m}^3$ (5.2MGoe). These materials are compared with conventional materials (FB-series) in fig.8.

Figure 7: Magnetic properties of developed materials.

Figure 8: Magnetic properties of developed materials.

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