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Signficantly improving magnetic properties of Sr-La-Co hexagonal ferrite

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Abstract: The hard magnetic ferrite system of $Sr_{1-X}La_XFe_{12-Y}Co_YO_{19}$ with x = 0.0-0.3 and y = 0.0-0.3 has been prepared by traditional ceramic technology and showed hexagonal crystalline structure of M-Type.The anisotropic sample $Sr_{0.8}La_{0.2}Fe_{11.7}Co_{0.3}O_{19}$ + 0.5% weight SiO_2 sintered at 1280°C/2h has the best hard magnetic properties, namely B_r = 4.66 kG; ${}_BH_C$ = 3.46 kOe and $(BH)_{max}$ = 5.70 MG.Oe. The role of La and Co as well as the reasons leading to these perfect properties of the studied ferrites have been discussed based on the overall studies of structure and characteristics of examined samples.

1. Introduction

In more than a half century from the discovery of hexagonal ferrite, ferrite magnets always used very popular and everywhere in science, technology, life and especially in civil electronics industry, in communications and other different areas due to cheap price as well as simple technology. But still now the problem to improve hard magnetic properties of this kind of materials always attracted the researchers and technologists. We are talking about two main following trends:

- Using different doping elements including 3d and Rare-earth metal oxides with hoping that saturation magnetization and magnetocrystalline anisotropy will be improved [1-4].
- Applying advance technologies such as coprecipitation, sol-gel, high pressure compressing, hot pressing, isostatic pressing ...to manufacture ferrite powder and product [5-8].

In this report we study the structure and magnetic properties of ferrite system $Sr_{1-X}La_XFe_{12-y}Co_yO_{19}$ (x = 0.0-0.3 and y = 0.0-0.3) to improve the quality of hard magnetic ferrite and explain the reasons leading to these results.

2. Experiment

Substitution in our study was the simultaneous doping of La and Co in system $Sr_{1-X}La_XFe_{12-y}Co_yO_{19}$ + 0.5% weight of SiO_2. Raw materials used here are $SrCO_3$, Fe_2O_3, La_2O_3, CoO and SiO_2 with high purity (3 - 4 N). Wet planetary ball mill has been used to provide fine powder with grain size

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around 1μm. The ratio between powder: ball: water was 1: 4: 1. We kept the moisture of powder about 35% for anisotropic pressing. To orientate the particles along the magnetic field, the field strength of 1T and the pressure of 500 kG/cm^2 have been applied. The samples were sintered at temperatures 1260^{o}C, 1270^{o}C, 1280^{o}C and keeping time was 2h. Approximately, the chemical composition of samples was checked by EDS facility. The thermal transitions were performed by DTA- DTG machine. The crystallographic structure of samples was examined by X-ray diffractometer (Siemens D5005 X-ray, Germany). Microstructure of isotropic and anisotropic samples has been studied using SEM (JEOL-JSM5410LV, Japan). Magnetic properties are investigated by VSM (200C Nim, USA), hysteresisgraph (AMH50-20, USA) and magnetometer using high pulse magnetic field to measure SPD curve.

3. Results and discussion

Fig. 1 shows demagnetizing curves of Sr-La-Co anisotropic samples sintered at 1280^{o}C/2h . The main characteristics derived from this figure are presented in Table 1.

Table 1. The main hard magnetic parameters of anisotropic samples sinterd at 1280^{o}C/2h

Sample	Compound	B_r [kG]	$_BH_C$ [kOe]	$_JH_C$ [kOe]	$(BH)_{max}$ [MG.Oe]
M1	$SrFe_{12}O_{19}$	4.60	2.15	2.45	4.78
M2	$Sr_{0.8}La_{0.2}Fe_{12}O_{19}$	4.58	2.73	2.73	5.34
M3	$Sr_{0.7}La_{0.3}Fe_{11.9}Co_{0.1}O_{19}$	4.50	2.90	3.25	5.60
M4	$Sr_{0.8}La_{0.2}Fe_{11.7}Co_{0.3}O_{19}$	4.66	3.46	3.60	5.70

It is clearly seen from this table that with appropriate substitution of La and Co, the magnetic characteristics of sample M4 evidently improved in comparison with pure hexagonal ferrite M1, namely $_BH_C$ increased up to 60% and $(BH)_{max}$ achieved the record value of 5.70 MG.Oe. To understand the reasons leading to so very high quality of this sample, we remember that for materials consisting of single domain particles, the magnetizing process is the rotation process of magnetization vectors of domains and coercivity should be determined by expression:

$$H_C = a\frac{K_1}{I_S} + b(N_1 - N_2)I_S + c\frac{\lambda\tau}{I_S} \quad (1) \quad [9]$$

Here a, b and c are contants, K_1 is magnetocrystalline anisotropic constant, N_1 and N_2 are demagnetization factors determined parallel and perpendicular to the axis of particles, strain and I_S is saturation magnetization. The first term in expression (1) relating with magnetocrystalline anisotropy and normally plays a decided role for creating high coercivity of

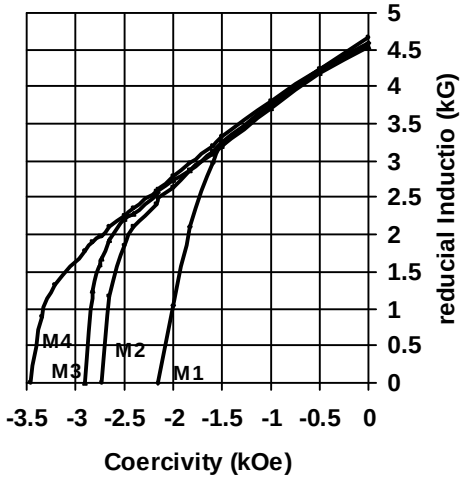

Fig. 1. Demagnetizing curves of anisotropic samples M1- M4.

materials . For this reason almost authors focusing to find the way for increasing K_1 of hexagonal ferrite mainly by substitution effects. The second term in (1) dealing with shape anisotropy of particles forming material and takes part of several tens percent of H_C and finally the last term in (1) determined by magnetic elastic energy and often is small and could be ignored. Apart from above indication, the general orientation to improve hard magnetic properties of hexagonal ferrite is to make raise magnetocrystalline anisotropy, shape anisotropy of particles as well as saturation magnetization

Constant K_1 was measured in magnetometer with high pulse magnetic field using special point detection (SPD) technicque. Fig.2 shows the measurements of M(H) curve and d^2 M/ dH^2(H) curve for sample M4 .

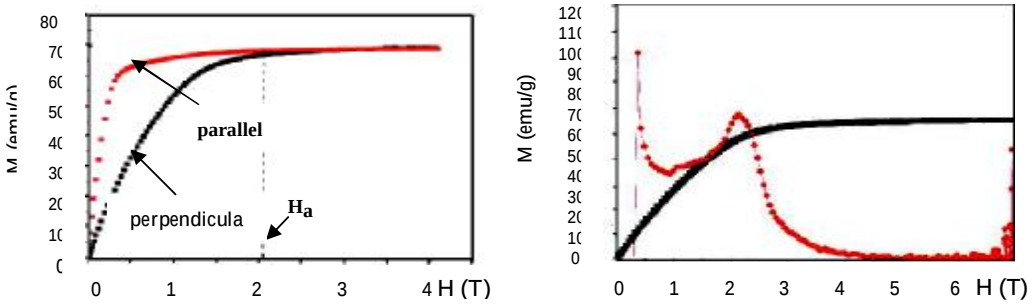

Fig. 2. M (H) curve (left) and $\frac{d^2M(H)}{dH^2}$ curve (right) of sample M4 sintered at 1260°C/2h.

Table 2. Constant K_1 of samples M1 and M4 derive from SPD measurement

Sample	K_1x10^5 [J/m^3]
M1	3.60
M4	3.93

Table 3. Lattice parameters of studied SrLaCo-M ferrites

Sample	a [Å]	c [Å]
M1	5.8868	23.0370
M3	5.8775	23.1034
M4	5.8740	23.1091

Measured results from Tab.2 showed the value $K_1 = 3.6.10^5$ J/m^3 for pure SrM ferrite which is completely agreement with the results given by other authors, for example [5, 10, 11]. Note that ferrite $LaFe_{12}O_{19}$ has K_1= (10-13) $.10^5$ J/m^3 at 0K [12], whereas ferrite $CoFe_2O_4$ has $K_1 = 3.9.10^5$ J/m^3 at room temperature [13]. H. Zijlstra [14] pointed out that in La-Co ferrite anisotropic field H_a could reach the value of 10^5A/m and $K_1 = 5.10^6$J/m^3.

Thus with the simultaneous substitution of La for Sr and Co for Fe in the SrM-ferrite hard magnetic properties of hexagonal ferrite significantly improved.

The crystallographic structure of samples has been examined by diffractometer and the XRD patterns of samples M_1, M_3 and M_4 are presented in Fig.3. The results indicated that the structure of studied ferrite corresponding to magnetoplumbite structure with c-axis is a little longer but a-axis is shrinked a little in comparison with pure SrM-ferrite as shown in Tab.3

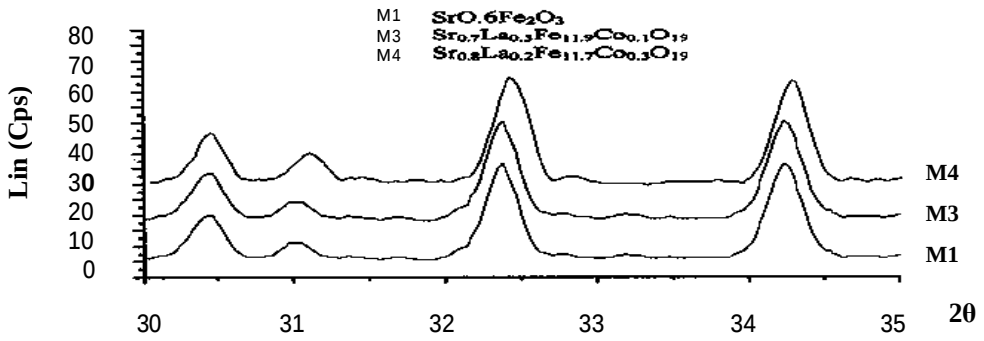

Fig. 3. X-ray diffraction patterns of the samples M1, M3 and M4 sintered at 1260°C/2h.

From Tab.3 we can conclude that by substitution in our study the unit lattice has more shape anisotropy with longer needle form.

To understand about particle size of fine milled SrLaCo-ferrite, the powder was measured by Microtrac machine S3000 and the results are indicated in Tab.4. It is clearly seen that in samples M_1-M_3 almost the particles have small size and especially by optimal substitution in sample M_4, 100% of particles has single domain structure with high shape anisotropy (Tabs. 3 and 4).

Table 4. Crystal grain size of SrLaCo- ferrite, which was presintered and fine milled

Sample	M1	M2	M3	M4
Crystal grain size	33.69 (5%)	30.93 (3%)	26.33 (7%)	
[μm] (ratio)	1.55 (54%)	1.62 (54%)	1.69 (58%)	1.59 (46%)
	0.39 (41%)	0.39 (43%)	0.41 (35%)	0.37 (54%)

A further demonstration on the role of La and Co substitution is the microstructure observation Figs. 4 and 5 show the SEM pictures of the samples. From both figures we can see the influence of substitution to make finer and more homogeneity of particles which are correspond to single domain structure. It is also obviously seen from Fig. 5 that the appropriate substitution (and small doping of SiO_2) not only restricting the grain growth but making the more shape anisotropy of them and both these factors leading to enhance the hard magnetic properties of studied samples.

Our purpose is not only to achieve high H_C but also to reach high value of magnetization. To find the solution for this problem, almost the authors focusing on the way to make increase up-spin of positions 2a and 2b. About the role of La to improve hard magnetic properties of hexagonal ferrite, the Vietnamese researchers have published a large number of publications among them several has been occured on the International Journals [15 -18].

In order to understand and discuss on the advance of La and La-Co as well as applied technology of authors inside and outside Vietnam we derive here some main related results:

- In previous our work [14], the structure and magnetic properties of ferrite $(SrO)_{1-x}(La_2O_3)_{x/2}$. $5,3(Fe_2O_3)$ + 0.5% weight SiO_2 (x = 0.00 to 0.12) have been detailly investigated. The new technology was applied there, namely the wet isostatic pressing was performed in a rubber die pressing. By that tool we have succeded to prepare anisotropic samples with very high density ($d>99\%d_X$) and very high orientation degree of particles along magnetizing field applied in pressing process and we have

received ferrite sample with record quality for quite long time: B_r = 4.3 kG; ${}_BH_C$ = 3.2 kOe, $(BH)_{max}$ = 5.5 MG.Oe).

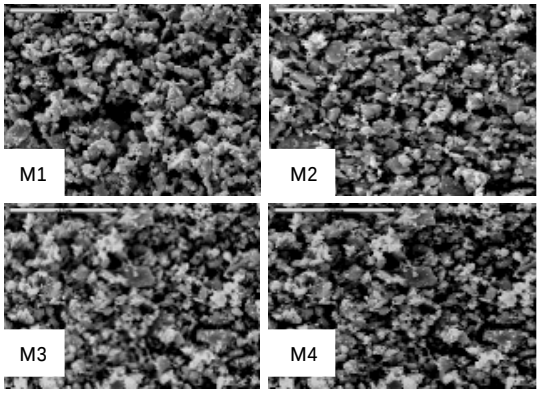

Fig. 4. SEM Images of isotropic bulk samples M1-M4 sintered at 1260°C/2h (bright line is10 μm).

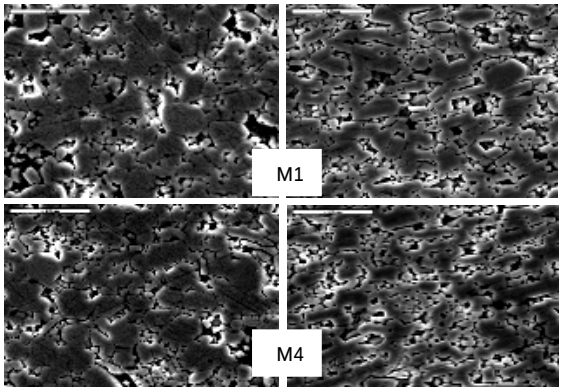

Fig. 5. SEM Images of anisotropic bulk samples M1, M4 perpendicular (left) and parallen (rigth) to the preferred magnetizing direction (bright line is 10 μm).

It is well known that the Fe^{3+} ions which are origine of magnetic moment of hexagonal ferrite normally located at 2a, 2b and 12k positions (up-spin) and $4f_1$ and $4f_2$ positions (down-spin) in the crystallographic lattice. Therefore magnetic moment of a molecule $SrO.6Fe_2O_3$ is equal to $20\mu_B$.

The substitution of La for Sr leads to the following change:

$$Sr^{2+} + Fe^{3+} \xrightarrow[Sr]{La} La^{3+} + Fe^{2+} \qquad (2)$$

The performed ions Fe^{3+} possibly are located at $4f_1$ and $4f_2$ positions (down-spin) and because ion Fe^{2+} has smaller magnetic moment than of ion Fe^{3+}, this valency conversion led to the increase of total magnetization of ferrite.

- Se-Dong Yang et al. [19] studied two compositions $SrFe_{11.7}Co_{0.3}O_{19}$ and $Sr_{0.7}La_{0.3}Fe_{11.7}$ $Co_{0.3}O_{19}$ and showed that Co alone enhanced B_r but both La and Co improved H_C.

- R. Grössinger et al. [20] indicated that the simultaneous replacement of La and Co in SrM - ferrite notably increased H_C due to increasing of anisotropic field H_a and especially they also helped stabilize H_C on temperature but one necessary thing is the replacement fractions are not exceeded 0.25 mol.

- K. Masuzawa et al. [21] have studied ferrites $Sr_{1-x}La_xFe_{11.7}Co_{0.3}O_{19}$ and showed that with x = 0.3-0.4 ferrites have phase M. When x <0.3 H_C becomes lower due to spinel phase (Co-ferrite) existed and while x> 0.4 magnetic properties of ferrite strongly decreased, particularly for the remanent induction B_r because of occurring hematite phase.

- Y. Kubota et al. [2] examined ferrite system $(Sr^{2+}_{1-x}La^{3+}_{x})O .n\{(Fe^{3+}_{1-y}Co^{2+}_{y})_2O_3\}$ where x = 2ny and n = 5.4-6.0 and showed that by substitutions of La for Sr and Co for Fe, respectively, ${}_JH_C$ of ferrite is significantly increased while B_r only slightly enhanced (${}_JH_C$ = 4.5kOe; B_r = 4.4kG). The

authors explained that the residual orbital magnetic moment of ion Co^{2+} plays the main role to make high value of H_C.

- F. Kools et al. [22] studied ferrite system $Sr_{1-x}La_xFe_{12-x}Co_xO_{19}$ ($x < 0.25$) and indicated that Co plays the important role for notably improvement of H_a (i.e H_C) and ions Co^{2+} possible located 12k and $4f_2$ positions. They also showed that remanent induction could be determined by expression:

$$B_r = s\,(d / d^o)\,fJ^o_S \qquad (3)$$

where s is ferrite fraction in the solid body, f is alignment factor, d and d^o are experiment and theoretical density, respectively, J^o_S is saturation magnetization. Beside J^o_S is intrinsic parameter, the others are extrinsic ones and strongly depend on the technological processes.

According to our knowledge, recently maximum energy product obtained in this report belongs to the highest value and very closed to the theoretical prediction.

4. Conclusion

By optimal substitution of La for Sr and Co for Fe in SrM hexagonal ferrite and used appropriate technology, the studied anisotropic sample $Sr_{1-X}\,La_X\,Fe_{12-y}\,Co_y\,O_{19}$ ($x = 0,2$; $y = 0.3$) + 0.5% weight of SiO_2 gives $B_r = 4.66$ kG; ${}_BH_C = 3.46$ kOe and (BH) max = 5.70 MG.Oe.

In our study, La and Co (together with small amount of SiO_2) played the role to reduce the sintering temperature, restricted the grain growth, created the single domain particles with needle shape, changed the valency of iron ions from Fe^{3+} to Fe^{2+} which located at down-spin positions and as the results leading to desirably increase of anisotropy (both magnetocrystalline and shape anisotropy of particles) as well as magnetization.

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