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ENHANCEMENT OF MAGNETIC PROPERTIES OF La-SUBSTITUTED STRONTIUM HEXAFERRITE PARTICLES PREPARED BY SOL-GEL ROUTE

TRAN THI VIET NGA, NGUYEN PHUC DUONG, AND THAN DUC HIEN
International Training Institute for Materials Science (ITIMS),
Hanoi University of Technology, 01 Dai Co Viet Road, Hanoi, Vietnam

Abstract. *La-substituted strontium hexaferrite particles* $Sr_{1-x}La_xFe_{12}O_{19}$ $(x = 0 \div 0.2)$ *were prepared by using sol-gel method and subsequent calcination at temperatures ranging from 750°C to 1050°C for 2h in air. The effects of the initial La concentration and the calcination temperature on the structure, particle morphology and magnetic properties of the hexaferrite samples were investigated by using X-ray diffraction (XRD), scanning electron microscopy (SEM) and vibrating sample magnetometer (VSM). The high magnetic coercivity* ($_iH_c$) *of 6.6 - 6.7 kOe and magnetization in maximum applied magnetic field (13.5 kOe) of 68 - 72 emu/g were achieved with the particles of compositions* $x = 0.1 \div 0.2$ *and calcination temperatures between 850°C and 1000°C. The experimental data indicate that La replacement for Sr improves the crystallinity and inhibits the grain growth of the samples in a wide range of calcination temperature. These factors are important for production of high-coercivity hexaferrites by sol-gel technology.*

I. INTRODUCTION

Because of the relatively low cost, chemical stability and high uniaxial magnetocrystalline anisotropy, SrM hexaferrite plays an important role in various industrial applications such as permanent magnets, magnetic recording, microactuators and ferrofluids [1]. In order to achieve high coercivities in hexaferrites, fine structures with particle sizes significantly smaller than the single-domain particle size ($\sim 1\ \mu$m) are required [2]. Further improvements in magnetic properties were expected by substituting elements at various lattice sites. This has led to many attempts via different preparation routes including conventional ceramic [1], mechanical alloying [3], chemical coprecipitation [4], hydrothermal synthesis [5] and sol-gel [6]. In a pioneering work, Lotgering [7] reported a remarkable increase of anisotropy in La hexaferrite. The increase was explained by a change in valence of the Fe ions at the $2a$sublattice in the crystal structure from 3+ to 2+, which gives a positive contribution to the anisotropy constant K_1. The change is necessary in order to compensate additional charges caused by the 3+ valence of the La ions instead of 2+ like in Sr hexaferrite. In addition, it was shown that the addition of La ions is useful for stabilizing the magnetoplumbite structure [8]. Recently, partial substitution of La into SrM hexaferrite has been tried [5, 6, 9, 10] to improve the magnetic and structural properties. However, most of the magnetic parameters reported so far are still considerably lower than the theoretical limits for SrM and additional information about the influence of La substitution on the formation of the microstructure is necessary.

This paper emphasizes on the roles of La substitution in maintaining high degree of the crystallinity and inhibiting the particle growth which result in high magnetic coercivity and magnetization of the $Sr_{1-x}La_xFe_{12}O_{19}$ samples obtained by sol-gel route at calcination temperatures below 1050°C. Due to the low solubility of La in the SrM ferrite structure [11], the maximum La concentration x was kept at 0.2.

II. EXPERIMENTAL

Ultrafine $Sr_{1-x}La_xFe_{12}O_{19}$ particles with different La concentration were produced by the following process. The chemical precursors of purity 3N are $Fe(NO_3)_3.9H_2O$, $Sr(NO_3)_2$, $La(NO_3)_3.nH_2O$ and citric acid. The salt components were weighted according to different xLa^{3+}/(1-x)Sr^{2+} mole ratios, where $x = 0$, 0.05, 0.1, 0.15, 0.2, while the [Sr^{2+} + La^{3+}]/Fe^{3+} was fixed at 1/12. The aqueous solutions containing Sr^{2+}, Fe^{3+} and La^{3+} were poured into citric acid with [Sr^{2+} + La^{3+} + Fe^{3+}]/[citric acid] = 3. The mixture was stirred at 1000 rpm and slowly evaporated at 80°C. As the water evaporated, the remainder became highly viscous gels with brown color as result of chelation process. These gels were dried at 100°C for 2h and then heated at 450°C for 2h in order to eliminate the rest of residual water and other organic impurities. Finally they were calcined in air at 750°C, 850°C, 900°C, 950°C,1000°C and 1050°C for 2h. The resultant particles were carefully washed using deionized water and dried overnight at 80°C.

X-ray diffraction (XRD, Cu-Kα, Siemens D-5000) was employed to identify the crystal structure. A Scanning Electron Microscopy (SEM) was used to examine the particle size and morphology. The magnetic parameters and the temperature dependence of magnetization were measured using a Vibrating Sample Magnetometer (VSM) with maximum field H of 13.5 kOe and at temperatures from room temperature up to 800 K.

III. RESULTS AND DISCUSSION

X-ray diffraction analysis for selected La-substituted SrM powders fired at 750°C and 850°C are given in Fig. 1. Generally, for all the La substitution levels, the XRD patterns mainly correspond to the hexagonal M-type phase. Some low-intensity peaks which may be related to α-Fe_2O_3 phase are also observed. Thus, samples of desired structure are already formed at low heat-treatment temperatures.

The ${}_iH_C$, magnetization M at the magnetic field of 13.5 kOe and remanent magnetization M_r of the samples were determined from the hysteresis loops measured at room temperature on compact powders. The effect of the La^{3+}/Sr^{2+} ratio on the magnetic properties of the La substituted samples at different calcination temperatures are shown in Table 1.

The highest coercivity of 6.7 kOe was achieved for La-substituted SrM particles with $x = 0.05$ and 0.1 calcined at 850°C for 2h. As example, Fig. 2 shows the full magnetic loop of particles with $x = 0.1$ calcined at 850°C. The initial magnetization curve exhibits a marked change of slope, indicating single domain particle behavior.

The observed coercivity is one of the highest values so far reported for this material and approaches theoretical limit of SrM (7.5 kOe) based on Wohlfrath's model of a coherent rotational magnetization for an assembly of single-domain, randomly oriented

Table 1. The magnetic parameters at room temperature of the studied $Sr_{1-x}La_xFe_{12}O_{19}$ particles

$_iH_C$(kOe)

Heat treatment for 2h at	$x = 0$	$x = 0.05$	$x = 0.1$	$x = 0.15$	$x = 0.2$
750°C	5.5	3.7	5.2	4.2	3.9
800°C	6	6	5.8	4.9	5.2
850°C	6.6	6.7	6.7	6.6	6.6
900°C	6.4	6.3	6.4	6.6	6.6
950°C	6.2	5.7	5.8	6.6	6.6
1000°C	6	4.9	5.2	6.4	6.3
1050°C	5.4	4.2	4.6	5.8	6.0

M at 13.5 kOe (emu/g)

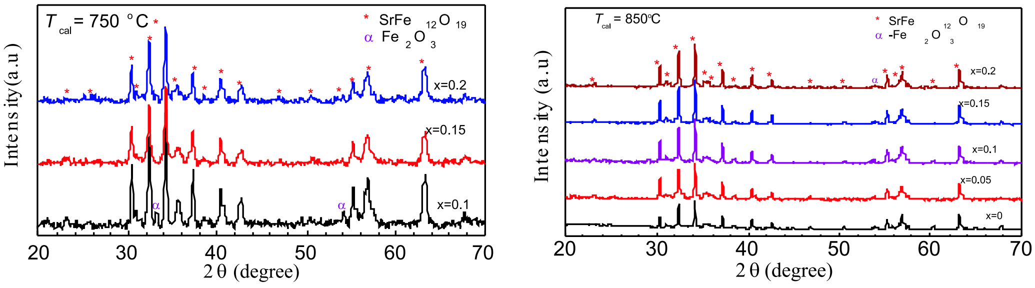
Heat treatment for 2h at	$x = 0$	$x = 0.05$	$x = 0.1$	$x = 0.15$	$x = 0.2$
750°C	57	60	61	60	60
800°C	56	61	65	60	63
850°C	59	63	68	62	66
900°C	60	63	68	62	66
950°C	61	65	72	72	72
1000°C	62	65	70	71	72
1050°C	67	72	72	67	65

M_r (emu/g)

Heat treatment for 2h at	$x = 0$	$x = 0.05$	$x = 0.1$	$x = 0.15$	$x = 0.2$
750°C	30	34	35	33	32
800°C	34	34	38.3	35.5	34
850°C	33	35.5	44	35.5	36
900°C	34	35	38	38	38
950°C	35.3	36	40	40	39
1000°C	33	35	37	39	44
1050°C	37.5	38.4	39	35	24

particles [12]. The $_iH_C$ of a sample depends on its magnetocrystalline anisotropy and on its microstructure. In this study, no obvious tendency of $_iH_C$ versus La concentration x at each calcination temperature can be derived (Table 1).

The effect of heat treatment temperature on the magnetic coercivity of La substituted samples is plotted in Fig. 3. The values of $_iH_C$ increase steeply with the increase of calcination temperature from 750°C to 850°C, reach the maximum values at 850°C and decrease strongly above 950°C. This can be understood via the development of grain size with increasing the calcination temperature. The grain size of the samples with fixed La



(a) (b)

Fig. 1. XRD patterns for the La substituted SrM particles with (a) $x = 0.1, 0.15, 0.2$ and calcination at 750°C for 2h; (b) $x = 0, 0.05, 0.1, 0.15, 0.2$ and calcination at 850°C.

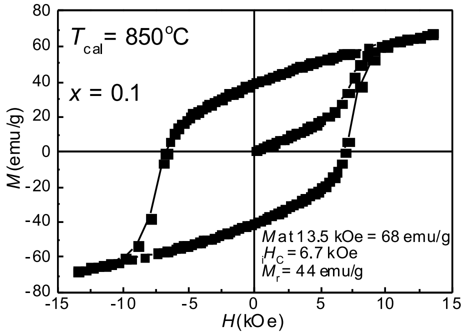


Fig. 2. A typical magnetic hysteresis curve of the La substituted SrM particles (x = 0.1, calcination at 850°C for 2h).

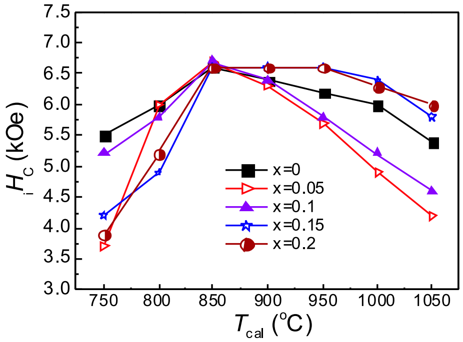


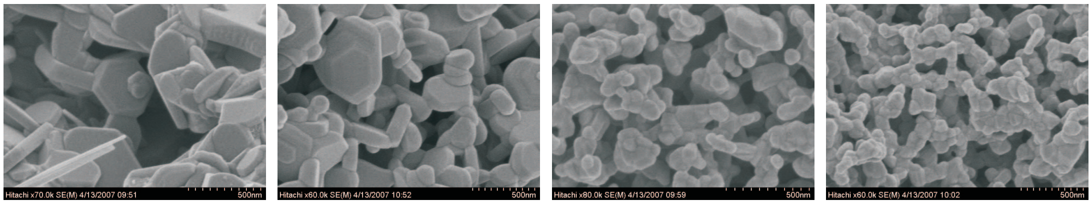
Fig. 3: **Fig. 3.** The intrinsic coercivity $_iH_C$ of the La substituted SrM particles (x= 0, 0.05, 0.1, 0.15, 0.2) as a function of the calcination temperature.

concentration $x = 0.1$ indicated in Table 2. All the samples mostly consist of hexagonal crystallites with rather narrow size distribution in the single – domain region.

Table 2. Average particle size of samples with fixed La concentration $x = 0.1$

Calcination temperature °C)	750	850	950	1000
Particle size (nm)	53	55	83	186

The average grain size d_{av} has increasing values 53 nm, 55 nm, 83 nm, 186 nm with increasing temperature 750°C, 800°C, 850°C, 950°C and 1000°C, respectively. On the other hand, SEM investigation on the samples with varied La concentration and fixed calcination temperature of 1000°C (Fig. 4) shows decreasing d_{av} values 259 nm, 186 nm, 105 nm, 91 nm with increasing x = 0.05, 0.1, 0.15 and 0.2, respectively. The later SEM study exhibits clear evidences for the inhibition of the grain growth by La substitutions and therefore explains the fact that different optimum calcination temperatures are observed for different La concentrations.



(a) (b) (c) (d)

Fig. 4. SEM images of the La substituted SrM particles calcined at 1000˚C and the derived average particle diameter d_{av}: (a) $x = 0.05$, (b) $x = 0.1$, (c) $x = 0.15$, (d) $x = 0.2$.

The dependence of the magnetization at 13.5 kOe for La-substituted SrM samples on the calcination temperature for various x values is plotted in Fig. 5. There is an increasing tendency of M(13.5 kOe) with calcination temperature for the samples with $x = 0$, 0.05 and 0.1. It is also seen that in general, the magnetization is significantly enhanced in the La-substituted samples at all investigated calination temperatures (Table 1). According to Lotgering's suggestion [7], the substitution of Sr^{2+} ions by La^{3+} results in the valence change of Fe^{3+} to Fe^{2+} in the $2a$-sublattice and hence the magnetization is expected to decrease because Fe^{2+} ions have smaller magnetic moment than that of Fe^{3+}. The enhancement of the M(13.5 kOe) values observed in this work can be assigned to the stabilization of the crystal structure with the presence of the La^{3+} ions which had been pointed out in other previous works [6,8]. The stable hexagonal structure ensures the Néel model for ferrimagnetic configuration in these materials. The maximum M(13.5 kOe) value of 72 emu/g was achieved in several samples calcined above 900˚C which attains ∼90 % of the saturation magnetization of the SrM single crystal [13]. The declination of magnetization of the samples with high La concentrations 0.15 and 0.2 observed at calcination temperature 1050˚C may be explained by the coexistence of impurity phases. It is noted that for these compact samples, the remanent magnetization M_r gains 53 % - 64 % of the M_S value, being dependent on their density and magnetic anisotropy.

The remark on the improvement of the crystallinity by La substitution is corroborated by the measurements of the DC susceptibility χ as a function of temperature T in low applied magnetic field (50 Oe). The χ versus T curves for the sample series calcined at 1000˚C shown in Fig. 6 indicate, in the vicinity of the Curie temperature, a Hopkinson peak for hard magnetic SrM hexaferrite phase. The Hopkinson peaks become stronger and sharper at higher La concentrations, revealing the crystallites of better quality and the enhancement of magnetic anisotropy. A detailed analysis on the Hopkinson phenomena observed for these materials in various applied magnetic fields will be discussed in a separate publication. The Curie temperatures of these samples are derived between 725 K and 739 K which are slightly lower than the value for SrM bulk (770 K) [13].

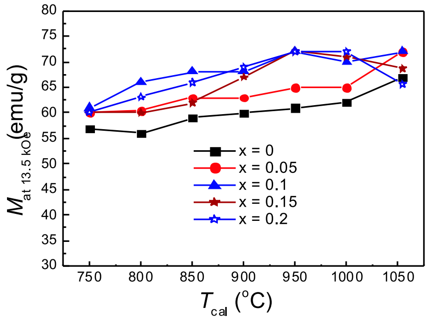


Fig. 5. The magnetization at 13.5 kOe of the La substituted SrM particles (x= 0, 0.05, 0.1, 0.15, 0.2) as a function of the calcination temperature.

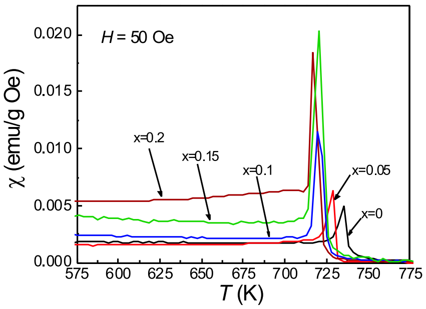


Fig. 6. DC susceptibility versus temperature curves measured in H = 50 Oe for the La substituted SrM particles (x = 0, 0.05, 0.1, 0.15, 0.2) calcined at 1000°C.

IV. CONCLUSIONS

Ultrafine $Sr_{1-x}La_xFe_{12}O_{19}$ ($x = 0 \div 0.2$) powders were synthesized by sol-gel method followed by heat treatments in air at 750°C, 850°C, 900°C, 950°C, 1000°C and 1050°C for 2h. The samples have average particle size ranging from 53 nm to 259 nm. The optimum calcination temperature was derived for each composition. The highest magnetic coercivity (6.7 kOe) and magnetization at 13.5 kOe (72 emu/g) are observed in the La-subsituted samples. The experiments show that La replacement for Sr facilitates the ferritization reaction as well as the formation of favorable microstructures and improves the quality of the hexagonal SrM crystallites.

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