The Influence of Heat-Treatment on Structural and Magnetic Properties of Rare-Earth Substituted Y-type Sr-Hexaferrites

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ABSTRACT

Rare-earth substituted strontium ferrite nanopowders $SrGa_2Fe_{12-x}R_xO_{22}$ (R = La, Gd and Er; x = 0.2, 0.5 and 1) were prepared by chemical co-precipitation method and subsequent heat treatments. The results of X-ray diffraction measurements showed the Y-type hexagonal structure. Magnetic properties, such as specific saturation magnetization Ms, specific remanent magnetization Mr and coercivity Hc, as well as microstructure depend on the heat-treatment conditions (temperature and time). The coercivity Hc exhibits a great increase after a critical heat-treatment time. This jump of Hc was explained by a transition from the superparamagnetic state to normal state of the single domain nanoparticles. The occurrence of an agglomerated structure composed of magnetically interacting ultrafine crystallites also contributes to the increase of Hc. With increasing R content both the Ms and Mr decrease due to the dissolution of R ions into the hexaferrite lattice.

Keywords: Hexafemites, Microstructure, Magnetic Properties, Rare-earth, Heat-treatment.

I. INTRODUCTION

Y-type hexagonal ferrites are perspective materials for developing of high-density data storage devices due to their high uniaxial magnetocrystalline anisotropy and chemical stability [1–4]. In comparison to Co-alloy films, the hexagonal ferrites have lower saturation magnetization but higher anisotropy field. In the present paper we investigate SrY ferrite containing three rare earth elements: La, Gd and Er. Rare earth ions substitute for Fe ion in $SrGa_2Fe_{12}O_{22}$ ferrite in various concentrations. The rare earth substitution was employed to inhibit the grains growth [5] and to promote the ferritization reaction [6]. The lanthanides also improve the mechanical materials hardness [7]. The experiments carried out by Dung [8] showed that the La substitutions improve the hard magnetic properties of Sr hexaferrite. The aim of the present work is to study the effect of different heat-treatment temperatures (800, 900 and 1000℃) and different heat-treatment times between 5 and 320 min on the structural and magnetic properties of rare earth doped strontium hexaferrites. The preparation route of the samples was chemical co-precipitation. The main advantages of co-precipitation powders over conventional powders (physical mixtures of oxides) are molecular scale homogeneity, nanosized granulation, enhanced reactivity (lower heat-treatment temperatures), and controlled grain size by subsequent heat treatments. Chemical co-precipitation method followed by an adequate heat treatment offers the possibility to prepare the hexaferrite submicron powders having coercivity suitable for recording applications.

II. EXPERIMENTAL

Table-1 shows the notation of the samples. The nanometric structure of the combusted powder and the phase composition were established by X-ray powder diffraction. The morphology was studied by scanning electron microscope. The grain size was appreciated from SEM micrographs on the fracture surface of the samples. The magnetic measurements (specific saturation magnetization Ms, specific remanent magnetization Mr and coercivity Hc) were performed by a vibrating sample magnetometer operating up to a maximum field of 10 kOe, in air, at room temperature.

III. RESULTS

3.1. Microstructural characterizations

The phases present in the as prepared powders consist of wustite FeO, hematite $\alpha\text{-}Fe_2O_3$, orthoferrite $RFeO_3$, magnetite Fe_3O_4 and a small amount of Sr hexaferrite nanocrystallites (particle size below 30 nm). The inability of hexaferrite synthesis during co-precipitation may be attributed to: (a) too low a

temperature, (b) too short a reaction time and (c) oxygen deficiency.

Table 1:

Symbol of Samples	Composition
SL1	$SrGa_2La_{0.2}Fe_{11.8}O_{22}$
SL2	$SrGa_2La_{0.5}Fe_{11.5}O_{22}$
SL3	$SrGa_2LaFe_{11}O_{22}$
SG1	$SrGa_2Gd_{0.2}Fe_{11.8}O_{22}$
SG2	$SrGa_2Gd_{0.5}Fe_{11.5}O_{22}$
SG3	$SrGa_2GdFe_{11}O_{22}$
SE1	$SrGa_2Er_{0.2}Fe_{11.8}O_{22}$
SE2	$SrGa_2Er_{0.5}Fe_{11.5}O_{22}$
SE3	$SrGa_2ErFe_{11}O_{22}$

For hexaferrite crystallization, the combusted powders were subsequently subjected to three heat treatments at 800, 900 and 1000°C. The room-temperature X-ray diffraction patterns for a thermal treated sample containing La ions show the peaks corresponding to the Y-type hexagonal phase, $SrGa_2Fe_{11.8}La_{0.2}O_{22}$ (Fig. 1). After treatments at 800 and 900°C, traces o f α-Fe_2O_3 and γ-$SrFe_2O_4$ were observed also, but only after treatment at 1000°C single phase $SrGa_2La$ hexaferrite was obtained. Hence, an increased treatment temperature was beneficial in order to eliminate the intermediate phases that can deteriorate the magnetic properties and to form single phase $SrGa_2Fe_{12-x}R_xO_{22}$.
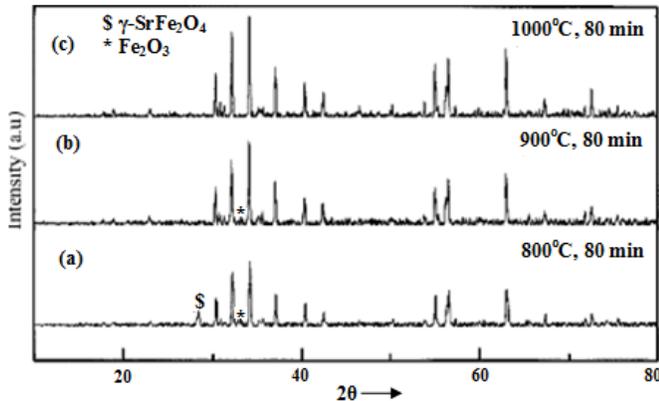

Fig. 1: The XRD patterns of the $SrGa_2Fe_{11.8}La_{0.2}O_{22}$ powders heat treated at temperatures of 800°C (a), 900°C (b) and 1000°C (c).

The scanning electron micrographs given in Fig. 2a–f revealed remarkable changes in the microstructure, regarding grain size, porosity and the particle distribution, by changing the heat-treatment conditions (time and temperature). The microstructure behavior as a function of heat-treatment temperature ranging from 800°C to 1000°C, for the $SrGa_2Fe_{11.8}La_{0.2}O_{22}$ compound is shown in Fig. 2a–c. A substantial porosity (closed and open pores) that hinders the densification of the material can be observed. One can also notice the presence of the large crystallite agglomerations composed of very small discrete crystallites in the samples treated at 800°C or 900°C (Fig. 2a and b). Within the agglomerations the particle sizes are of 0.1–0.2 µm at 800°C and grow to 0.3–0.4 µm at 900°C. Larger particles as well as large pores were located at the agglomerated junctions. When the treatment temperature increased at 1000°C, individual particle size increased to about 0.8 µm and the lamellae structure appears (Fig. 2c), attesting a better crystallinity of the Y phase.

SEM micrographs for the $SrGa_2Er_{0.2}Fe_{11.8}O_{22}$ compound treated at 900°C for three treatment times are given in Fig. 2d–f. The microstructure of the sample heat treated for 10 min (Fig. 2d), consists of fine particles, of about 0.1–0.2 µm. A radical change in the microstructure takes place when the heat-treatment time increases from 10 to 40, or 160 min (Fig. 2e and f). The agglomerates with diameters up 3–4 µm appear. But, the grain growth was reduced from 0.1–0.2 µm to 0.3–0.5 µm when the treatment period was extended to 160 min.
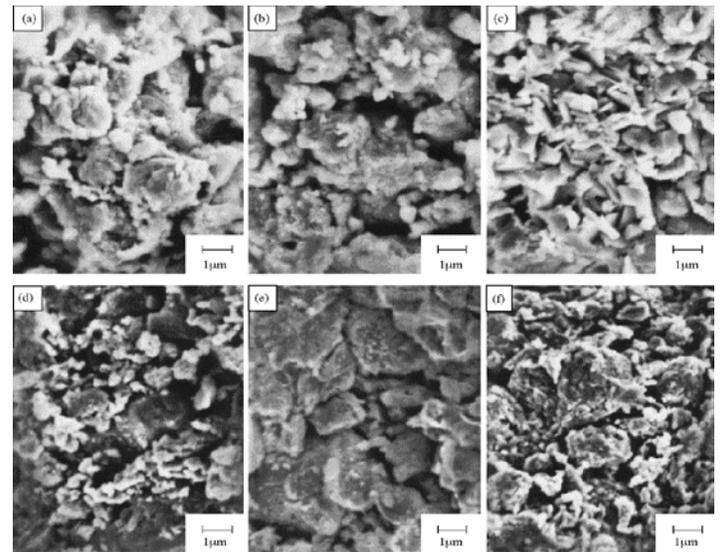

Fig. 2: SEM micrographs of the $SrGa_2Fe_{11.8}La_{0.2}O_{22}$ samples heat treated at various temperatures: (a) 800°C, (b) 900°C and (c) 1000°C for 40 min, and for $SrGa_2Fe_{11.8}Er_{0.2}O_{22}$ samples heat treated at 900°C for various times: (d) 10 min, (e) 40 min and (f) 160 min.

3.2 Magnetic properties

Figs. 3 and 4 shows the effect of the annealing time on the static magnetic properties (Ms, Mr and Hc) of the heat treated samples at 800 and 900°C, respectively. In

Figs. 3a and 4a one can distinguish two regions of Hc behavior. In the first region, from heat-treatment time of 5 min up to a critical treatment time, Hc remains small (350–750 Oe) and almost constant. In the second region, above the critical heat-treatment time, there is a sharp hardening transition in coercivity. This increase of Hc is explained by the increase of particle size and the transition from the superparamagnetic behavior to the normal state of the single domain nanoparticles when the heat-treatment time exceeds a certain value. For longer treatment

have a large contribution determining Hc. Fig. 2d and 2e shows the occurrence of multigrain agglomerations when the heat-treatment time is increased from 10 to 40 min. The applied field needed to reverse the magnetization of a particular grain depends on the magnetization of its neighboring grains [9]. Thus, one can say that the coercivity is a collective property of the system of interacting grains.
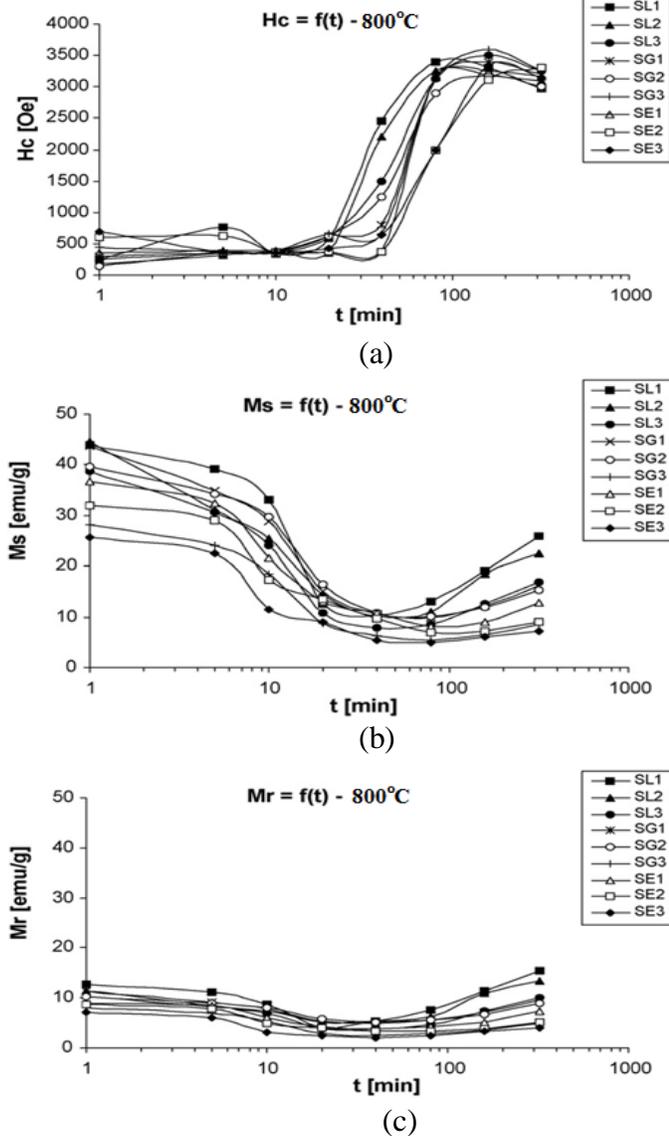

(a)

(b)

(c)

Fig. 3: Influence of heat-treatment time on the magnetic properties of $SrGa_2Fe_{12-x}R_xO_{22}$ samples heat treated in air at 800°C.

times (over 160 min), a slightly decrease in Hc was observed as a consequence of the increase of some grains and the appearance of domain walls. Certainly, the magnetic interactions between the agglomerated particles
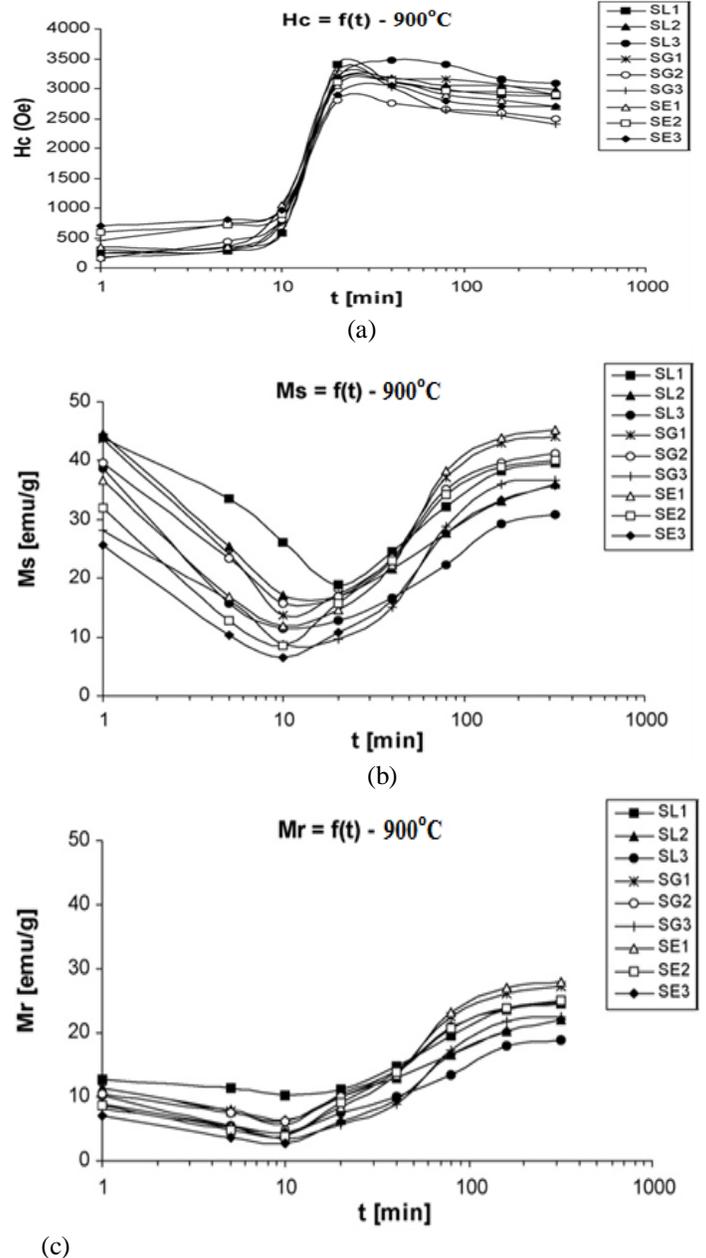

(a)

(b)

(c)

Fig. 4: Influence of heat-treatment time on the magnetic properties of $SrGa_2Fe_{12-x}R_xO_{22}$ samples heat treated in air at 900°C.

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The results also show a heat-treatment time dependence of Ms (Figs. 3b and 4b) and Mr (Figs. 3c and 4c). This pattern depends on both the content and the type of R^{3+} substitution for Fe^{3+}. The difference in ionic radius introduces local strain which may cause the disorder and modifications of local electronic states. Various R^{3+} concentrations have different influences on the superexchange interactions between magnetic cations and hence, on the saturation magnetization [10]. One might consider Fig. 4. Influence of heat-treatment time on the magnetic properties of $SrGa_2Fe_{12-x}R_xO_{22}$ samples heat treated in air at 900°C that the R substitutions weaken the superexchange interactions between Fe sites because of its strongly distorted environment. Also, R ions have low mobility and their slow diffusion requires a longer time which differs if the R ion is heavy or light (Er is heavy, but La and Gd are light lanthanides). On the other hand, by extending the heat-treatment time (over 160 min) it is possible to see the occurrence of a multidomain structure in some larger grains. In this case, the magnetization process can take place by domain wall displacement. This means an increase of Ms and a slight decrease of Hc, according to the results presented in Figs. 3 and 4. The effects of rare-earth concentration on the magnetic properties of $SrGa_2Fe_{12-x}R_xO_{22}$ ferrites heat-treated for 80 min at 800, 900 and 1000°C are summarized in Table 2.

For comparison, the magnetic parameters for untreated samples are also given. Regardless of the R type, Ms and Mr decrease with R concentration, following the decrease of the magnetic Fe^{3+} ion concentration. The dissolution of R ions into the hexagonal structure will result in a reduction of total magnetic moment.

treatment determines a reduced grain growth due to internal stress generated by R ions. A great increase of coercivity Hc was evidenced after a certain treatment time. The highest coercivity, of 3600 Oe was achieved for La substituted Sr hexaferrites. The highest Ms and Mr values were obtained by heat treatment at 1000°C of the samples containing small R amount (x = 0.2).

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Table 2:

The magnetic characteristics of the studied samples

Sample	Untreated			Treated at 800°C, 80 min			Treated at 900°C, 80 min			Treated at 1000°C, 80 min		
	Ms (emu/g)	Mr (emu/g)	Hc (Oe)	Ms (emu/g)	Mr (emu/g)	Hc (Oe)	Ms (emu/g)	Mr (emu/g)	H(Oe)	Ms (emu/g)	Mr (emu/g)	Hc (Oe)
SL1	44.70	13.60	270	16.14	8.72	3600	34.24	20.87	3025	49.74	30.10	2900
SL2	45.22	10.89	205	12.11	7.44	3370	29.83	18.52	3175	46.42	28.23	3150
SL3	37.53	09.96	265	9.45	5.86	3200	25.42	14.63	3480	42.57	26.74	3330
SG1	44.82	11.54	340	10.22	6.47	3280	38.53	23.74	3255	48.85	30.92	3200
SG2	40.11	10.21	170	9.26	5.36	3050	36.90	21.22	2775	44.56	28.62	2900
SG3	26.10	9.13	500	7.45	3.22	2990	29.44	18.42	2580	39.90	25.25	2910
SE1	38.61	8.44	420	8.10	5.45	3120	39.83	25.10	2990	47.28	30.70	2950
SE2	31.23	7.08	580	7.58	4.72	2700	35.92	23.72	2875	43.24	28.63	3110
SE3	24.72	6.07	730	6.12	3.33	2500	28.55	19.44	2720	40.10	25.68	2970

IV. CONCLUSION

Ultrafine $SrGa_2Fe_{12-x}R_xO_{22}$ ($0.2 \leq x \leq 1.0$ and R = La, Gd and Er) powders were synthesized by chemical co-precipitation method followed by heat treatments in air at three temperatures, 800, 900 and 1000°C, for different times: 5, 10, 20, 40, 80, 160 and 320 min. Remarkable changes in microstructure and magnetic properties (Ms, Mr and Hc) were obtained by the modification of the heat-treatment conditions (time and temperature). The heat