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Strontium ferrite for magnetic recording prepared by self-combustion method

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In the last time, the M-type hexagonal ferrites ($BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$) have drawn a great interest for magnetic recording media because of their large coercivity which is derived from magnetocrystalline anisotropy and small particle size. Rare-earth substituted strontium ferrite nanopowders $SrFe_{12-x}R_xO_{19}$ (R = La, Gd and Er; x = 0.2, 0.5 and 1) were prepared by self-combustion method. In this method one realizes an optimum mixing of ions on the atomic level so that the crystallization of hexaferrite particles can occurs at relatively low temperatures. The combusted powders were annealed at different temperatures (800, 900 and 1000 °C) for various annealing times (5, 10, 20, 40, 80, 160 and 320 minutes). The results of X-ray diffraction measurements showed the M-type hexagonal structure formation by heat treatments. Magnetic properties as well as microstructure depend on heat treatment conditions. We believe that further investigations are necessary to explain why in the nanoparticles system the heat treatment time influence on the coercivity is much stronger compared to the heat treatment temperature.

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1. Introduction

The application of hexagonal ferrites in the magnetic media industry requires materials with strict control of homogeneity, morphology and magnetic properties resulting from preparation technology and heat treatments. Hexagonal ferrites show good chemical and thermal stability which would result in longer storage life of the media [1]. For magnetic recording media application it is important to study coercivity, saturation magnetization as well as particle size of the hexaferrite materials.

In this paper the strontium hexaferrite containing rare earth elements is investigated. Rare earth ions (La, Gd and Er) substitute Fe ions in $SrFe_{12}O_{19}$ ferrite in various concentrations. The rare earth substitution was employed to inhibit the growth of the grains [2] and to enhance the sintering power [3].

The preparation route of the samples was self-combustion method followed by heat treatments. The main advantages of selfcombusted method 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 [4].

The aim of the present work is to study the effect of the heat treatment conditions (temperature and time) on the structure and magnetic properties of the strontium hexaferrites doped with rare earth ions.

The obtained results show that the self-combustion method followed by an adequate heat treatment [5] offers the possibility for preparing the Sr-hexaferrite submicron powders having coercivity suitable for recording applications.

2. Experimental

Ferrite samples having the general formula $SrR_xFe_{12-x}O_{19}$ ($0.2 \le x \le 1.0$ and R = La, Gd and Er) were prepared by selfcombustion method followed by heat treatments, starting from metal nitrates as raw materials. Preparing method includes:

- solution of metal nitrates [$Fe(NO_3)_3 \cdot 9H_2O$, $Sr(NO_3)_2$, $R(NO_3)_3$] in deionized water,
- polivinyl alcohol addition to make colloidal solution,
- NH_4OH addition to adjust pH to about 8,
- stirring at 80 °C,
- drying at 120 °C of the gel,
- self-combustion,
- calcinations at 500 °C of combusted powders,
- pressing of the calcined powders into cylindrical shape ($p = 5 \cdot 10^6$ daN/m^2),
- heat treatment in air at 800, 900 and 1000 °C for various times, from 5 minutes to 320 minutes.

The nanometric structure and the phase composition was established by X-ray diffraction, using DRON-2 diffractometer (Cu Kα radiation). The morphology was studied by a high resolution scanning electron microscope (SEM) TESLA-BS 340. The grain size was appreciated from SEM micrographs on the facture surface of the samples.

The magnetic measurements (specific saturation magnetization M_s, and coercivity H_c) were performed by a vibrating sample magnetometer operating up to a maximum field of 10 kOe, in air, at room temperature.

3. Results and discussion

By X-ray diffraction were detected the phases present in the as prepared powders by selfcombustion which consist of wustite (FeO), hematite (α-Fe_2O_3), orthoferrite ($RFeO_3$), magnetite (Fe_3O_4) and a small amount of Sr hexaferrite nanocrystallites, having the particle size below 40 nm. The inability of hexaferrite synthesis during autocombustion may be attributed to: too low a temperature, too short a reaction time and oxygen deficiency. After treatments at 800 and 900 °C, traces of α-Fe_2O_3 and foreign phases in small amounts were observed, but after treatment at 1000 °C only single phase hexaferrite could be obtained. In figure 1, XRD patterns for two samples $SrFe_{12}O_{19}$ (thin line) and $SrEr_{0.2}Fe_{11.8}O_{19}$ (dense line) heat treatedat 900 °C for 40 minutes are shown. We can observe peaks of α-Fe_2O_3 phase and traces of Er_2O_3. The lattice constants for $SrFe_{12-x}R_xO_{19}$ (x = 0 , 0.2, 1) samples heat treated at 900 °C for 40 minutes are given in table 1. One can see that the partial replacement of Fe^{3+} by R^{3+} resulted in a slight increase in the lattice constant.

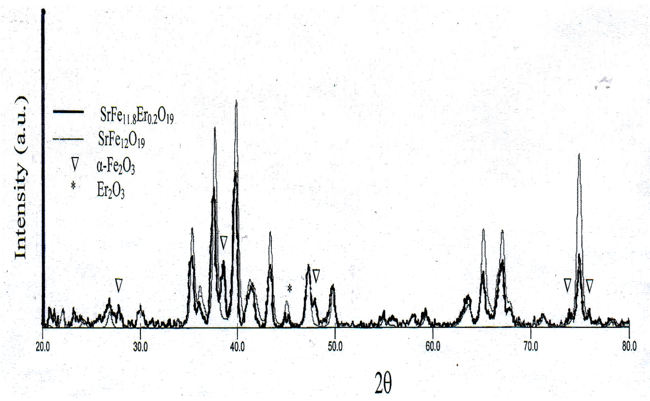

Fig.1. XRD pattern of $SrFe_{12}O_{19}$ (thin line) and $SrEr_{0.2}Fe_{11.8}O_{19}$ (dense line) heat treated at 900 °C for 40 minutes.

Table 1. The values of the hexagonal lattice parameters of the samples annealed at 900 °C for 40 minutes.

Sample composition	**Lattice parameters (Å)**	
$SrFe_{12}O_{19}$	a = 5.875	c = 23.042
$SrLa_{0.2}Fe_{11.8}O_{19}$	a = 5.881	c = 23.050
$SrLaFe_{11}O_{19}$	a = 5.889	c = 23.062
$SrGd_{0.2}Fe_{11.8}O_{19}$	a = 5.877	c = 23.047
$SrGdFe_{11}O_{19}$	a = 5.884	c = 23.070
$SrEr_{0.2}Fe_{11.8}O_{19}$	a = 5.876	c = 23.045
$SrErFe_{11}O_{19}$	a = 5.883	c = 23.068

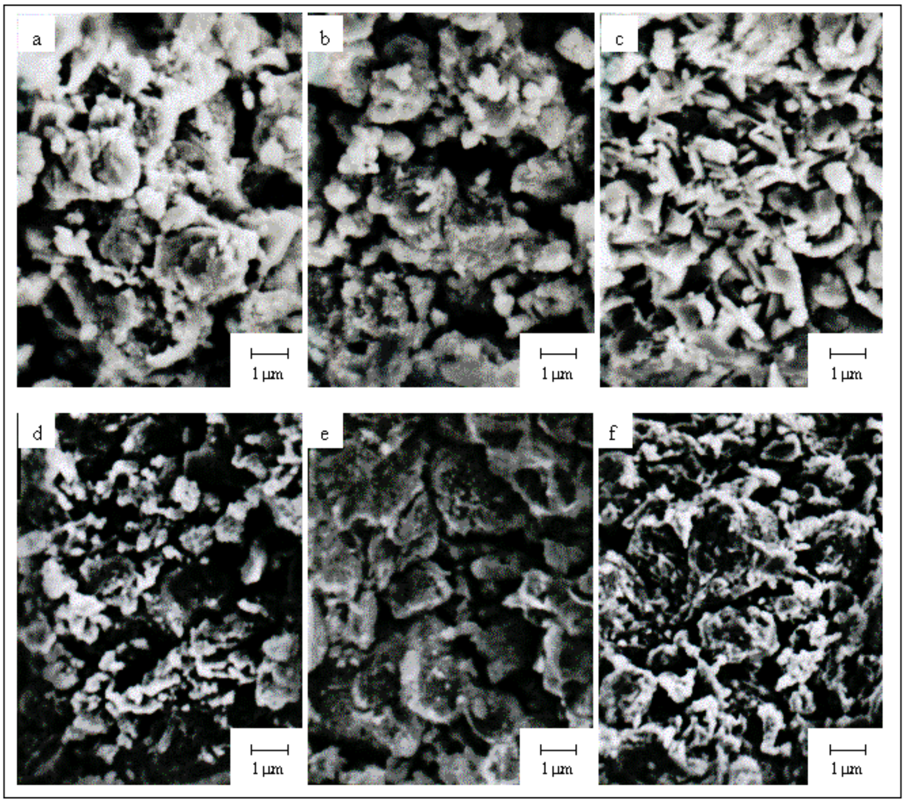

Fig. 2 . SEM micrographs of the $SrFe_{11.8}La_{0.2}O_{19}$ samples heat treated for 40 min at various temperatures: (a) 800 °C, (b) 900 °C, (c) 1000 °C, and for $SrFe_{11.8}Er_{0.2}O_{19}$ samples heat treated at 900 °C for various times: (d) 10 minutes, (e) 40 minutes and (f) 160 minutes.

The influence of the heat treatment conditions on the microstructure is shown in Fig. 2. A substantial porosity (closed and open pores) was evidenced which hinders the densification of the material. One can remark the presence of the large crystalline agglomerations composed of very small discrete crystallites in the samples treated at 800 or 900^{0}C (Fig.2 a and b). Within the agglomerations the particle sizes are of 0.1 to 0.2 µm at 800^{0}C and grow up to 0.4 – 0.5 µm at 900^{0}C. Larger particles as well as large pores were located at the agglomerated junctions. The individual particle size increased to about 0.8 µm (Fig.2c) when the treatment temperature increased at 1000 ^{o}C. Moreover, the shape of the crystallites changed from irregular spheres to lamellae (Fig.2c) that attest a better crystallinity of M phase. The important point is that the powders prepared by selfcombustion route and then heat-treated at 1000 ^{o}C have fine grains (submicron), being in the single-domain limit suitable for electronic applications. The microstructure of the sample heat treated for short time, of 10 minutes (Fig.2d), consists of fine, spherical particles, of about 0.1 – 0.2 µm. A radical change of the microstructure takes place when the heat treatment time increases from 10 to 40, or 160 minutes (Fig.2 e, f).

A longer treatment time favors the formation of an agglomerated state with a fine substructure. The agglomerates with diameters up 4 – 5 µm were observed. By prolonging the treatment time to 160 minutes, many closed pores appear in the agglomerations (Fig. 2f) which affect magnetic quality of the material. On the other hand, a reduced grain growth was observed, from 0.1 – 0.2 µm to about 0.4 – 0.6 µm, if the treatment period was extended to 160 minutes. The following two comments can be made from the above results:

- The presence of rare earth ions has a main contribution in the obtaining the submicron granular structure. The ionic radii of La^{3+}, Gd^{3+} and Er^{3+} ions being larger than that of Fe^{3+} ions (r_{La} = 1.17 Å, r_{Gd} = 1.08 Å, r_{Er} = 1.03 Å, r_{Fe}^{3+} = 0.69 Å) [6], their incorporation in hexaferrite structure can generate internal stress which will hinder the crystal growth [7,8]. Also, it is possible that some R^{3+} ions reside on the grain boundaries, limiting mobility of the grain boundaries and thus, further growth of the crystals is stemmed [9,10];
- The microstructure of the $SrR_xFe_{12-x}O_{19}$ hexaferrite powder obtained by selfcombustion can be controlled favorably by selecting correctly both time and temperature of the heat treatment.

Figs. 3 and 4 show the effect of the annealing time on the static magnetic properties (H_c and M_s) of the samples heat treated at 800 and 900 ^{o}C, respectively. One can distinguish two regions of H_c behavior. In the first region, from heat treatment time of 5 minutes up to a critical treatment time, H_c remains small (300-700 Oe) and almost constant, although it slightly depends on composition. In the second region, over the critical heat treatment time, there is a sharp hardening transition in coercivity indicating that the heat treatment time was sufficient to crystallize the hexaferrite. This sharp increase of H_c shifts towards higher treatment times by lowering the treatment temperature. Thus after heat treatment for 80 minutes at 800 ^{o}C, H_c increased from 300-700 Oe to about 3200-3500 Oe, but the same increase was obtained after shorter heat treatment time, of 20 minutes only, by heating at 900 ^{o}C (Fig. 3).

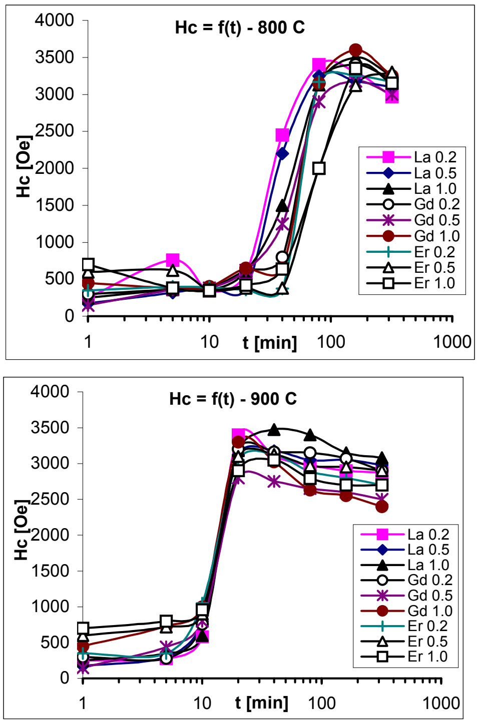

Fig. 3. Influence of heat treatment time on the coercivity H_c of $SrFe_{12-x}R_xO_{19}$ samples (R=La, Gd, Er; x=0.2, 0.5, 1.0) heat treated in air at 800 ^{o}C and 900 ^{o}C.

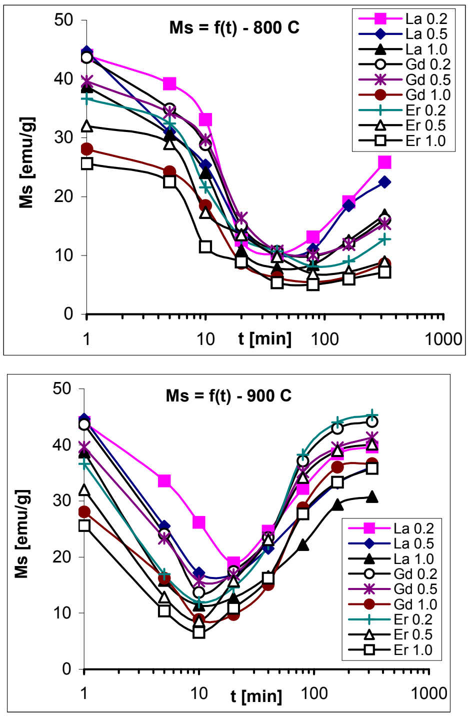

Fig. 4. Influence of heat treatment time on the specific magnetization M_s of $SrFe_{12-x}R_xO_{19}$ samples (R=La, Gd, Er; x=0.2, 0.5, 1.0) heat treated in air at 800 ^{o}C and 900 ^{o}C.

The heat treatment time evolution of the H_c clearly shows a strong dependence of H_c on the microstructure. Such anomalous increase of H_c can be explained by an increase of particle size and the transition from the superparamagnetic behavior to the normal state of the single domain nanoparticles when heat treatment time exceeds a certain value [11].

It was also evidenced a heat treatment time dependence of M_s (Fig. 4).

The gradual decrease of M_s, followed by an increase with increasing the treatment time, is certainly an indication that some processes such as crystallization of hexaferrite and the formation of the agglomerations are taking place. For longer heat treatment times (over 80 minutes), the M_s curves are slightly dispersed. This influence depends on both content and type of R^{3+} substitution for Fe^{3+}. The difference in ionic radius (between R^{3+} and Fe^{3+}) introduces local strains which may cause the disorder and modifications of local electronic states. Various R^{3+} concentrations which substitute for Fe^{3+} in the spinel block of the hexagonal structure have different influences on the superexchange interactions between magnetic cations, on the total magnetic moment and hence on the saturation magnetization [10].

Table 2. The magnetic characteristics of $SrFe_{12-x}R_xO_{19}$ samples heat treated at 800 ^{o}C, 900 ^{o}C and 1000 ^{o}C for 80 min.

	Untreated		Treated at 800^{o}C, 80 min.		Treated at 900^{o}C, 80 min.		Treated at 1000^{o}C, 80 min.	
Sample	M_s (emu/g)	H_c (Oe)	M_s (emu/g)	H_c (Oe)	M_s (emu/g)	H_c (Oe)	M_s (emu/g)	H_c (Oe)
La 0.2	44.00	250	13.12	3400	32.23	2975	47.45	2800
La 0.5	44.62	175	11.07	3250	27.71	3050	44.70	3075
La 1.0	38.73	250	8.47	3130	22.21	3400	39.56	3300
Ga 0.2	43.66	300	9.84	3150	37.11	3150	48.10	3100
Ga 0.5	39.61	150	10.06	2900	35.18	2650	42.73	2700
Ga 1.0	28.07	450	5.48	3150	28.77	2630	38.90	2700
Er 0.2	36.63	350	8.17	3170	38.25	2890	47.21	2850
Er 0.5	32.01	600	6.88	2000	34.16	2970	44.70	3000
Er 1.0	25.62	700	5.06	2000	27.70	2790	39.30	2850

The magnetic characteristics (M_s and H_c) of the investigated samples are summarized in Table 2.The highest M_s values of about 45-48 emu/g were obtained by heat treatment at 1000 ^{o}C. The best coercivities, of 3400 Oe, were achieved for the samples containing La.

4. Conclusions

We have studied the effects of the annealing conditions (time, temperature) and rare earth content on the structural and magnetic properties (M_s and H_c) in $SrFe_{12-x}R_xO_{19}$ (R = La, Gd and Er; x = 0.2, 0.5 and 1) powder samples obtained by self-combustion method folowed by heat treatments in air at three temperatures, 800, 900 and 1000 ^{o}C, for different times: 5, 10, 20, 40, 80, 160 and 320 minutes.

X-ray diffraction investigations show that the heat treated powders crystallize in a hexagonal structure. The partial replacement of Fe^{3+} by R^{3+} resulted in a slight increase in the lattice parameters with rare earth content. This result is a prove of limited solubility of R ions in the spinel block of the M-type hexagonal structure.

Remarkable changes in microstructure and magnetic properties (M_s and H_c) were obtained by the modification of the heat treatment conditions (time and temperature). A longer treatment time favors the formation of the particle agglomerations with a fine submicron substructure. The heat treatment determines a reduced grain growth due to internal stress generated by R ions.

After heat treatment for 80 minutes at 800^{0}C, H_c increased from 300-700 Oe to about 3200-3500 Oe. The same increase was obtained after shorter heat treatment time, of 20 minutes only, by heating at 900 ^{o}C.

The obtained M_s values are not very high (47 – 48 emu/g) due to the dissolution of R ions into the hexaferrite lattice. The highest M_s value was obtained by heat treatment at 1000 ^{o}C of the samples containing small R amount (x = 0.2) and the highest coercivity was achieved for La substituted Sr hexaferrite.

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