JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 8, No. 3, June 2006, p. 1023 - 1027

The influence of the technological factors on strontium hexaferrites with lanthanum substitution prepared by self-combustion method

C. DOROFTEI*, E. REZLESCU, P. D. POPA, N. REZLESCU
Institute of Technical Physics, Bd. D. Mangeron 47, 700050 Iasi, Romania

La substituted Sr hexaferrites with compositions $SrLa_xFe_{12-x}O_{19}$ (x = 0; 0.2; 0.5; 1) were prepared by sol-gel selfcombustion. The combusted powders were annealed at different temperatures (800, 900 and 1000 °C) for various annealing times (10, 20, 40, 80, 160 and 320 minutes). Experiments show that M_s and M_r increase both the annealing time and annealing temperature, but coercivity H_c exhibits a spectacular variation with annealing time. H_c significantly increases after short annealing time. For longer annealing time H_c begins to decrease. This variation was explained by the transition from single domain to multidomain particles by increasing annealing time. Thus, by manipulating the annealing time, the crystal growth can be controlled to obtain SrLa hexaferrite having properties for special applications.

(Received March 15, 2006; accepted May 18, 2006)

Keywords: Strontium ferrite, Hard magnetic material, Sr-La-Fe-O, Magnetic properties

1. Introduction

M-type hexagonal ferrites ($BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$) are known for their high uniaxial magnetocrystalline anisotropy with the easy axis of magnetization along the hexagonal c-axis and their chemical stability [1]. These materials have been used in bulk form for many applications due to their hard magnetic properties, for example, as permanent magnets. In the last time these ferrites have drawn a great interest for magnetic recording media [2,4]. Hexagonal ferrites show good chemical and thermal stability which would result in longer storage life of the media. Various preparation methods for the synthesis of fine particles of hexagonal ferrites with good recording characteristics, have been developed. 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.

In this study strontium-lantanum hexaferrite fine powders were prepared by sol-gel self combustion method and subsequent heat treatments [5]. Lanthanum was substituted iron in $SrFe_{12}O_{19}$. The main feature of this method is the intimated mixing of ions on the atomic level, so that the crystallization of hexaferrite particles can occurs at relatively low temperatures. In this method, which is an improved variant of the coprecipitation, the reacting substances are metal nitrates and ammonium hydroxide. The coprecipitation of metal hydroxides takes place into a colloidal medium. By quick combustion of a dried gel one obtained a powder with nanogranular structure. Due to rapidly moving combustion fronts and extremely high heating rates, the combustion reaction avoids the growth of the hexaferrite crystallites. By subsequent heat treatments schedules the growth of the hexaferrite crystallites and magnetic properties can be controlled. Thus, the method offers the possibility for preparing the hexaferrite submicron powders with coercivity suitable for recording applications.

The effects of annealing time and temperature on the microstructure and static magnetic properties (saturation specific magnetization M_s, remanent specific magnetization M_r and coercivity H_c) of Sr-hexaferrite containing various La concentrations were investigated in this paper. We selected La^{3+} as partial substituent for Fe^{3+} because among the lanthanoids, La^{3+} ion has the largest solubility limit in Ba or Sr hexagonal ferrites [6]. Also, the experiments carried aut by Dung et al [7] evidenced that the substitution of La for Sr impoves hard magnetic properties of Sr-hexaferrite.

2. Experimental

The polycrystalline M-type hexaferrites having the following formula $SrLa_xFe_{12-x}O_{19}$, with x = 0; 0.2; 0.5 and 1.0, were prepared by sol-gel-selfcombustion starting from metal nitrates. The analytically pure materials: $Fe(NO_3)_3 \cdot 9H_2O$, $Sr(NO_3)_2$ and $La(NO_3)_3$,(La_2O_3 dissolved in diluted nitrate acid) were weighed in the desired proportions and dissolved with small amounts of water. Polyvinil alcohol was added to make a colloidal solution. The pH was adjusted (pH ~ 8) by droping NH_4OH solution and a sol of metal hydroxides was formed. The sol dried at 100 °C was ignited and a combustion wave spontaneously propagates through the whole gel. It results a fine magnetic powder. This powder was compacted in a disc shape and the compacted samples were subjected to three thermal treatments: 800, 900 and 1000 ^{o}C for various times: 10, 20, 40, 80, 160 and 320 minutes. After each treatment, the mass and dimensions of the disks were measured to determine the bulk density ($d = m/V$) and porosity ($p = 1 – d/d_x$), were d_x is the theoretical density (X-ray density).

By X- ray powder diffraction was determined the nanometer structure of the powder obtained by combustion and was evidenced the crystallization of M-hexagonal phase by thermal treatments. The microstructure was studied by a high resolution scanning electron microscopy (SEM). The grain size was determined from micrographs on the fracture surface. The magnetic measurements were performed by a vibrating sample magnetometer operating up to a maximum field of 10 kOe.

3. Results and discussion

The present investigation describes the effects of technological factors (time and temperature) on magnetostructural properties of La doped M-type Sr hexaferrite.

By X-ray powder diffraction was detected the phases present in the as prepared powders by sol-gel-autocombustion which consist of wustite (FeO), hematite (α-Fe_2O_3), orthoferrite ($LaFeO_3$), magnetite (Fe_3O_4) and few very small crystallites (below 50 nm) of Sr-La hexaferrite.

The inability of M-phase synthesis during selfcombustion may be attributed to: (i) too low temperature, (ii) too short reaction time and (iii) deficient in oxygen. Consequently, combusted powders were subjected to heat treatments at higher temperatures in order to finish the feritization reaction and to grow the Sr hexaferrite crystallites nucleated during the combustion process.

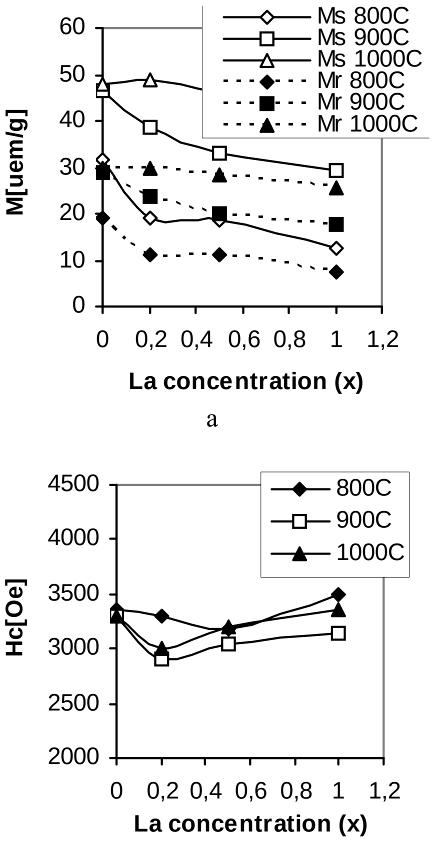
The as combusted powders were characterized by low coercivity and relatively large magnetization as can see in Table 1. The presence of the magnetite (Fe_3O_4) can justify the relatively large specific magnetization and low coercivity. One can see also the effect of lanthanum on the magnetic properties. As shown in Table 1, the lanthanum can raise the H_c value but decrease M_s and M_r. Taking into account that in $SrFe_{12}O_{19}$, the saturation magnetization is determined by magnetic Fe^{3+} ions only, the partial substitution of Fe^{3+} ions by nonmagnetic La^{3+} ions will lead to a magnetic dilution of the hexaferrite and a decrease of the saturation magnetization. The specific saturation magnetization M_s decreases with increasing La concentration.

Table 1. Magnetic parameters of the $SrLa_xFe_{12-x}O_{19}$ ($0 \leq x \leq 1$) powders prepared by sol-gel-selfcombustion.

Sample	Ms (uem/g)	Mr (uem/g)	Hc (Oe)
$SrFe_{12}O_{19}$	49.517	11.986	210
$SrLa_{0,2}Fe_{11,8}O_{19}$	44.006	11.803	250
$SrLa_{0,5}Fe_{11,5}O_{19}$	44.623	11.394	275
$SrLaFe_{11}O_{19}$	38.731	10.297	250

For recording media, high coercivity is necessary to stabilize small bits. The grain size is significant for achieving high coercivity H_c. The largest coercivity can be obtained for single domain particles as the magnetization process takes place by the spin rotation, and no by domain wall displacement. Thus, the control of the crystal growth is important to obtain hexaferrites with predetermined properties.

To obtain high coercivities, the combusted powders were subjected to heat treatments for various times and temperatures. XRD patterns of the samples treated at 800, 900 and 1000 ^{o}C showed only the peaks corresponding to the hexagonal solid solution and the absence of any intermediate phases. Moreover, the slight increase of the lattice parameters with increasing La concentration from a = 5.8787 Å and c = 23.0420 Å for x = 0.0 to a = 5.8891 Å and c = 23.0621 Å for x = 1.0 is a prove of the solubility of La^{3+} ions in the M-type hexagonal structure. It is known that La^{3+} ion has a large solubility limit in the magnetoplumbite structure [6] being the most suitable for substitution. Fang et al. [8] have evidenced the role of dissolved La_2O_3 in inducing the M-phase. The increase of the lattice parameters was attributed to the large ionic radius of La^{3+} ions (1.17 Å) as compared to the ionic radius of Fe^{3+} ions (0.69 Å) [9]. La^{3+} ions prefer to substitute the Fe^{3+} ions on the octahedral sites in the S block of the hexagonal structure of magnetoplumbite type.



a

b

Fig. 1. The effect of La concentration and annealing temperature on magnetic properties of $SrLa_xFe_{12-x}O_{19}$ hexaferrites ($0 \leq x \leq 1$) (annealing time is 40 minutes).

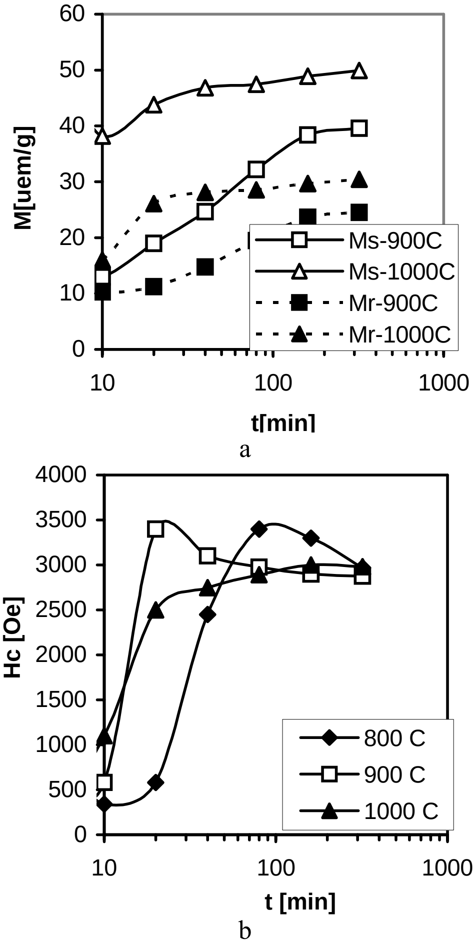
The effect of the annealing temperature on the static magnetic properties (M_s, M_r and H_c) is shown in Fig. 1 (a and b). One can see that M_s and M_r increase with increasing annealing temperature, but in the same time these parameters decrease with increasing La concentration (x).

This reveals that the partial incorporation of La^{3+} ions in the M-hexagonal structure can be possible leading to a magnetic dilution. However, it is possible that some La^{3+} ions reside on grain boundary [10] to form a weak magnetic compound, $LaFeO_3$, in a small amount, nondetectable by X-ray diffraction because of its low concentration.

Fig. 2 (a and b) shows the effect of annealing time on the quality of the ferrites. M_s and M_r increase with increasing annealing time from 10 minutes to 160 minutes. For longer annealing times, M_s and M_r are almost independent on both time and temperature of the thermal treatment. One can remark a significant increase of H_c from 500 Oe to 3400 Oe after short thermal treatment time, of about 20 minutes, for samples treated at 900 °C and of about 80 minutes for samples treated at 800 °C. For longer times a slightly lowering of the H_c was obtained.

The results regarding the influence of the thermal treatments (time and temperature) and La concentration (x) on the magnetic properties of samples prepared by sol-gel-combustion are summarized in Table 2.

One can see that the higest values of H_c, of 3500 Oe, were obtained for sample 3 annealing at 800 or 900 °C for 160 and 40 minutes respectively. M_s and M_r decrease with increasing La concentration, but increase with increasing annealing temperature. The strong dependence of H_c on the annealing time can be correlated with the structural changes induced by heat treatments.



a

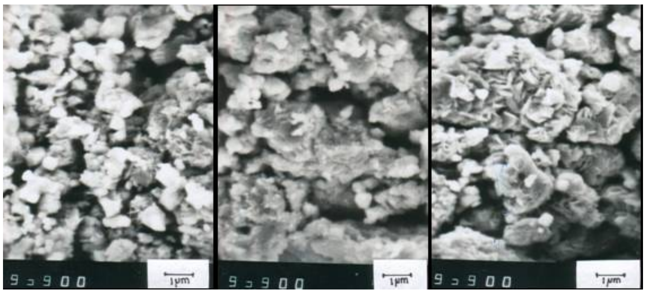
b

Fig. 2. The effect of annealing time on the magnetic parameters: magnetization (a) and coercivity (b) of $SrLa_{0.02}Fe_{11.8}O_{19}$ annealed at 800, 900 and 1000 °C.

Table 2. Magnetic parameters M_s, M_r, H_c) of the $SrLa_xFe_{12-x}O_{19}$ $(0 \leq x \leq 1)$ powders compacted in a disc shape and heat treated at various temperatures and times.

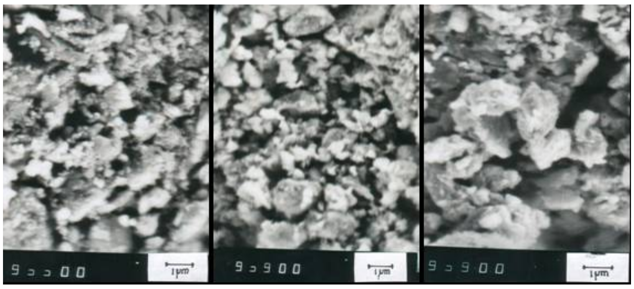
Annealing temperature (°C)	800 °C					900 °C					1000 °C				
Annealing time (min)	10	20	40	160	320	10	20	40	160	320	10	20	40	160	320
Pure sample,x=0															
Ms [uem/g]	36.4	20.4	16.4	31.7	40.6	33.8	28.7	36.3	46.5	47.8	45	48	48.4	48.1	48
Mr [uem/g]	8.9	6.7	9.3	19.2	24.8	10.1	17.4	22.2	28.8	29.9	23.6	29.3	28.8	29.7	29.8
Hc [Oe]	680	930	3100	3350	3100	350	3150	3375	3300	3200	2150	2950	3050	3300	3100
Sample 1, x =0.2															
Ms [uem/g]	34	12.6	10.2	19	25.8	41	19	24.6	38.3	39.6	38	43.7	46.8	48.8	49.8
Mr [uem/g]	8.8	4.3	5.4	11.3	15.5	10	11	14.7	23.6	24.5	16	26	28	29.7	30
Hc [Oe]	340	580	2450	3300	2970	580	3100	3400	2900	2875	1100	2500	2750	3000	3000
Sample 2, x =0.5															
Ms [uem/g]	25	11.5	10	18.5	22.5	17.2	17	21.5	33.1	36	37.4	42	44.8	46.2	47.4
Mr [uem/g]	7.3	5.2	5.4	11	13.4	6.2	10	13	20.2	22	22.1	25	27	28.3	29
Hc [Oe]	350	500	2200	3180	3100	800	3120	3175	3050	2980	2650	2850	3050	3200	3150
Sample 3, x = 1															
Ms [uem/g]	24	10.8	7.8	12.5	16.8	11.4	12.7	16.5	29.3	30.8	29.4	36	39	41.7	42.5
Mr [uem/g]	6.8	4	3.8	7.4	10	4.3	7.5	10	17.8	18.8	17.8	22	23.8	25.6	26.3
Hc [Oe]	350	610	1500	3500	3250	600	3180	3500	3150	3080	2900	3100	3250	3350	3350

In Fig. 3 are shown SEM images of $SrLa_{0.2}Fe_{11.8}O_{19}$ annealed at 900 °C for 10, 40 and 320 minutes and in Fig. 4 are given SEM images of the $SrFe_{12}O_{19}$ treated at 800, 900 and 1000 °C for 40 minutes. One can see that all the annealed samples exhibit a high porosity. Also, it is evidenced an agglomerated microstructure consisted of very small crystallites. Both the crystallite size and the size of the interacting particle agglomerations increase with increasing the annealing time and temperature. After long annealing time (320 minutes) large grains in the form of lamellae occur, which attest that the M hexagonality is marked improved for M-phase.



a b c

Fig. 3. SEM micrograph of $SrLa_{0.02}Fe_{11.8}O_{19}$ annealed at 900 ^{0}C for different annealing time: a) 10 minutes; b) 40 minutes; c) 320 minutes.



a b c

Fig. 4. SEM micrograph of $SrFe_{12}O_{19}$ for different annealing temperature: a) 800 ^{0}C; b) 900 ^{0}C; c) 1000 ^{0}C; annealing time is 40 minutes.

The influence of the annealing time on the grain size of the $SrLa_{0.2}Fe_{11.8}O_{19}$ annealed at 900 °C is shown in Fig. 5. and the annealing time dependence of the coercivity on the grain size is illustrated in Fig. 6.

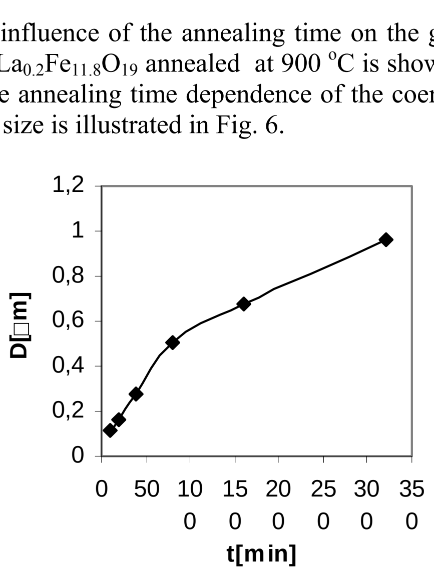


Fig. 5. The dependence of grain size D on annealing time t for $SrLa_{0.2}Fe_{11.8}O_{19}$ annealed at 900 °C.

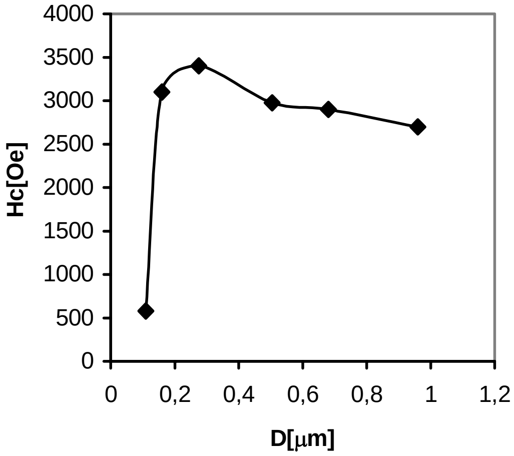


Fig. 6. The dependence of coercivity H_c on grain size D for $SrLa_{0.2}Fe_{11.8}O_{19}$ annealed at 900 °C.

Fig. 6 reveals the dependence of the coercivity H_c on the grain size D, for $SrLa_{0.2}Fe_{11.8}O_{19}$ treated at 900 °C. H_c increases with increasing D and then, for a further increase of the grains, it slightly decreases. Therefore, the control of grain size is significant for achieving high H_c. In this case,the transition from the single domain to multidomain state of the particles will lead to a decrease of H_c. It is easier to magnetize by the domain wall dispalcement than by spin rotation. The boundary between single and multidomain particle is given by the critical diameter of the particles, D_{crit}. The critical diameter of a spherical particle, below which a single domain is stable was estimated by us using the formula [1]:

$$D_{crit} = \frac{9\sigma_s}{2\pi M_s^2} , \tag{1}$$

where

$$\sigma_s = \left(\frac{2k_B T_c |K_1|}{a} \right)^{\frac{1}{2}} \tag{2}$$

is the specific wall energy, $[K_1]$ is the magnetocrystalline anisotropy constant, T_c is the Curie temperature, M_s is the saturation magnetization, k_B is the Boltzman constant and a is the lattice constant. For $D < D_{crit}$ the particle is a single domain particle. For the sizes $D > D_{crit}$, the particles are already multidomains and the magnetization proces requires smaller energy compared to the spin rotation.

For $Sr_{0.2}Fe_{11.8}O_{19}$ hexaferrite, using T_c= 720 K, $a = 5.88\times10^{-8}$ cm, $K_1 = 3.6\times10^{6}$ erg/cm^3 and M_s = 365 emu [11], was calculated D_{crit} = 320 nm which is in a reasonable agreement with D_{crit} appreciated from experimental results, of about 500 nm (Fig. 5). Below this critical size, the particles have a single domain behavior. If the single domain particle size is too small, below an inferior limit D_i, the thermal fluctuations become important, the anisotropy energy ($K_{ef}V$) becomes comparable or smaller than the thermal energy (k_BT), $k_BT \geq K_{ef}V$, and the particles show a superparamagnetic behavior [12], characterized by zero coercivity. However, the measured coercivities are different from zero because of magnetic coupling between the grains (each grain is not magnetically izolated from neighbouring grains). K_{ef} is the effective anisotropy constant including shape and magnetocrystalline anisotropies [13]. For hexaferrite, D_i was evaluated to be of 20 nm [14]. The abrupt increase of H_c (Fig. 6) can be due to the decrease of the number of superparamagnetic particles and the increase of the single-domain particle size. The dependence of the H_c on the grain size (Fig. 6) can be plotted qualitatively as in Fig. 7 [15]. One may distinguish four zones:

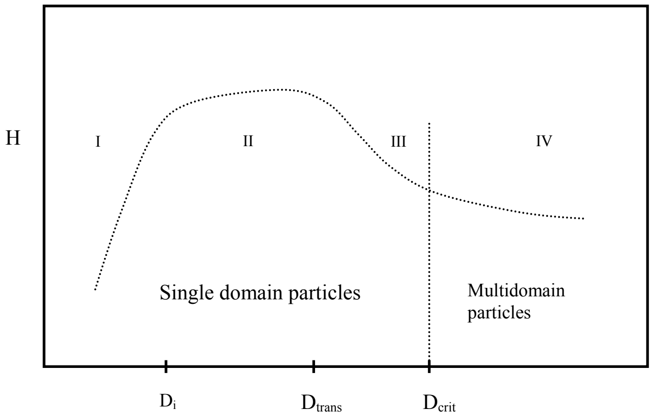


Fig. 7. Qualitative dependence of H_c on the average grain size D. The four zones are determined by the three diameters: for the thermal activation (D_i), transition to inhomogeneous rotation (D_{trans}) and the formation of multidomain particles (D_{crit}).

I - For very small so-called superparamagnetic particles with $D < D_i \approx 30$ nm; the reversion of M_s takes place by a thermally activated process.

II - For single domain particles with $D_i < D < D_{trans}$; the reversion of M_s is independent of the grain size and takes place by a uniform rotation process.

III - For larger single domain particle sizes, $D_{trans} < D < D_{crit}$; an inhomogeneous magnetisation process with decreasing coercive field takes place.

IV - For large particles, $D > D_{crit}$; the single domain particles become multidomain particles, in which the reversion of the magnetisation takes place by domain wall displacements.

It is interesting that in the large particles, $D > D_{crit}$, coercivity H_c is increased. This can be ascribed to the microstructural defects which act as possible pinning centres for domain walls in the multidomain particles.

4. Conclusions

In this paper, the effects of annealing time at three annealing temperatures of 800, 900 and 1000 °C on the magnetostructural properties of the M-type hexagonal ferrite $SrLa_xFe_{12-x}O_{19}$ ($x = 0$; 0.2; 0.5; 1.0) obtained by sol-gel-self-combustion method have been studied. One can suppose that La^{3+} ions substitute Fe^{3+} ions on the octahedral sites in the S block of the M-hexagonal structure and favors the formation of the magnetoplumbite-type ferrite.

The magnetic properties are closely linked to the crystal size developed by thermal treatments of the powders obtained by self-combustion. By manipulating the annealing temperature and time the crystal growth can be controlled to obtain LaSr hexaferrite materials with predetermined properties.

References

[1] J. Smit, H. P. J. Wijn, Les Ferrites, Dunod, Paris 1961.

[2] R. G. Simmons, IEEE Transactions on Magnetics **25**, 4051 (1989).

[3] D. E. Speliotis, IEEE Transactions on Magnetics **25**, 4048 (1989).

[4] P. D. Popa, E. Rezlescu, C. Doroftei, N. Rezlescu, J. Optoelectron. Adv. Mater. **7**(3), 1533 (2005).

[5] P. D. Popa, N. Rezlescu, Romanian Reports in Physics **52**, 769 (2000).

[6] A. Deschamp, E. Bortant, C. R. Acad. Sci. Paris **224**, 3069 (1957).

[7] N. K. Dung, D. I. Minh, B. T. Cong, N. Chau, N. X. Phue, Procceedings of the 7th International Conference on Ferrites, Bordeaux France, September 3-6, 1996; Journal de Physique IV (France) **7**, p.C1.313 (1997).

[8] T. T. Fang, B. H. Lin, K. T. Lee, J. Am. Ceram. Soc. **71**, 368 (1988).

[9] J. E. Huheey, E. A. Keiter, R. J. Keiter, Chemistry. Principles of structure and reactivity, Harper Collins, College Publiehers, 1993.

[10] A. A. Satar, A. M. Samy, R. S. El-ezza, A. E. Eatah, Phys. Stat. Sol. (a) **193**, 86 (2002).

[11] T. Fujii, H. Kato, Y. Miura, J. Takada, Growt and properties of multilayered Ba- and Sr-ferrites films, Procceedings of the 7th International Conference on Ferrites, Bordeaux France, September 3-6, 1996; Journal de Physique IV (France) **7**, p.C1.485 (1997).

[12] G. P. Bean, J. Appl. Phys. **26**, 13 (1955).

[13] J. L. Dormann, Rev. Phys. Appl. **16**, 275 (1981).

[14] A. Henis, V. V. Pankov, The modified aerosol pyrolisis as a preparation route of Hexaferrite particles for magnetic media, Procceedings of the 7th International Conference on Ferrites, Bordeaux France, September 3-6, 1996; Journal de Physique IV (France) **7**, p.C1.747 (1997).

[15] H. Kronmuller, Micromagnetism and Magnetization Process in Modern Magnetic Materials, in Science and Technology of Nanostructured Magnetic Materials (p.657), Edited by G. C. Hadjipanayis and G. A. Prinz, Plenum Press, New York and London 1990.

---

[*] Corresponding author: dcorneliu@yahoo.com