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Saurabh Raghuvanshi, Rulan Verma, Priyanka Tiwari, Arindam Ghosh, Frédéric Mazaleyrat, et al.. On the structural and magnetic investigation of CoF₂O₄/SrFe₁₂O₁₉ nano-composite via one pot synthesis. *Advances in basic Science (ICABS 2019)*, Feb 2009, Bahal, India. pp.070010, 10.1063/1.5122402 . hal-04453121

HAL Id: hal-04453121

<https://hal.science/hal-04453121>

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RESEARCH ARTICLE | AUGUST 29 2019

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AIP Conf. Proc. 2142, 070010 (2019)

<https://doi.org/10.1063/1.5122402>



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On the Structural And Magnetic Investigation Of CoFe₂O₄/SrFe₁₂O₁₉ Nano-composite via One Pot Synthesis

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Abstract. Soft-hard (CoFe₂O₄)_x(SrFe₁₂O₁₉)_{1-x} (0.0 ≤ x ≤ 1.0) nano-composite(s) were prepared by novel one pot reaction sol-gel auto-combustion route and annealed at 800 °C for 4 hours. X-ray diffraction (XRD), and vibration sample magnetometer (VSM) were utilized to monitor the effect of substitution on structural, and magnetic properties. XRD confirms the existence of soft (CoFe₂O₄), and hard (SrFe₁₂O₁₉) phase with average grain size (*D*) ranging between 57.7 nm to 59.4 nm for hexagonal and 34.6 to 64.5 nm for cubic phase. The magnetization of nano-composites demonstrates hysteresis loop that is characteristic of the exchange coupled system showing structurally two phases, but magnetically single phase. As a result of exchange coupling, between Co, and Sr ferrite enhanced saturation magnetization (70.65 Am²/kg), and remanence (26.29 Am²/kg) were observed as compared to pure SrFe₁₂O₁₉. Observed enhancement in energy product (BH)_{max} (0.83 – 28.96 kJ/m³) of nano composite also favors good exchange coupling between hard and soft phase.

INTRODUCTION

In recent years soft hard nano-composites have been a subject of systematic studies due to an attractive combination of good hard magnetic properties, and low manufacturing cost [1]. Soft hard nano-composite materials constitute fine combination of hard, soft magnetic phase, demonstrating enhanced properties which makes them suitable for various applications e. g.- as permanent magnets, magneto-optical magnetic materials, magnetic recording media, microwave, and millimeter wave low temperature cofired ceramics etc.[2-5]. Among various systems, the combinations of M type hexaferrite (BaFe₁₂O₁₉, SrFe₁₂O₁₉) with inverse spinel ferrite (CoFe₂O₄, NiFe₂O₄, Ni-ZnFe₂O₄, Fe₃O₄) [6, 7] have notable interest by researchers. Strontium hexaferrite (SrFe₁₂O₁₉) is important magnetic materials due to its remarkable properties e. g.- high Curie temperature (*T_c*), large magneto-crystalline anisotropy (*H_k*), excellent chemical stability and significant applications in variety of fields [8]. Pure strontium hexaferrite displays high coercivity (*H_c*) but low value of saturation magnetization (*M_s*), hence exhibiting a poor energy product (*(BH)_{max}*). (*BH)_{max}* can be tuned by tuning coercivity and saturation magnetization. CoFe₂O₄ is one of the suitable system which can be used with SrFe₁₂O₁₉ to enhance magnetization, and minimize the size of device for different microwave, and millimeter wave ferrite devices. Variation of composition, a specific synthesis process (e. g.- conventional solid phase, sol gel auto-combustion method, ball milling, Pulsed Laser Deposition, electrospinning etc.) [9-11] and, post preparation thermal treatments can be very efficiently used to control structural parameters (e. g. - lattice parameter, average grain diameter, density, etc.), as well as exchange coupling of soft-hard composite(s). For getting better exchange coupling in nano-composite, there is a requirement of structural homogeneity of soft-hard phase, which can be better achieved when both of the phases are grown together via single reaction mixture. Among many different approaches to synthesize nano-composite powder, sol-gel auto combustion

is one of the most efficient methods, as here one can synthesize nano-composite in one pot under moderate conditions e. g. – their preparation at relatively lower temperature ~ 110 °C. This allows one to tune magnetic properties by selectively controlling the structural properties via choosing appropriate sintering temperature [12]. Here sintering can be performed at relatively low temperatures resulting in the formation of nano-grains with increased surface area, which in turn will decrease the free energy during sintering, that remains the key driving force for lowering the sintering temperature [13].

Thus, goal of the present work is to develop hard soft nano-composite to enhance coercivity and saturation magnetization through one pot sol-gel auto-combustion technique. To achieve this purpose, different ratios of CoFe_2O_4 and $\text{SrFe}_{12}\text{O}_{19}$ for $(\text{CoFe}_2\text{O}_4)_x(\text{SrFe}_{12}\text{O}_{19})_{1-x}$ ($0.0 \leq x \leq 1.0$) were chosen to achieve the paramagnetic properties.

EXPERIMENTAL DETAILS AND DATA ANALYSIS

The soft, hard nano-composite having composition $(\text{CoFe}_2\text{O}_4)_x(\text{SrFe}_{12}\text{O}_{19})_{1-x}$ ($0.0 \leq x \leq 1.0$) was prepared by one pot sol-gel auto combustion method, utilizing nitrate-citrate precursor. In this process precursors of strontium nitrate, cobalt nitrate and ferric nitrate were dissolved in de-ionized water in the appropriate ratio with citric acid (salt-fuel mass ratio = 1:1) as fuel. The pH was maintained at 7 by using ammonia solution (NH_4OH), finally solution was heated at ~ 110 °C to obtain fluffy powder, which was annealed at 800 °C for 4 hours. X-ray diffraction (XRD) measurements were done at room temperature by using Bruker D8 advance diffractometer with CuK_α radiation ($\lambda = 0.15406$ nm). The XRD patterns were recorded in the angular range $10^\circ \leq 2\theta \leq 90^\circ$ with a step size of 0.02° . XRD data was analyzed to obtain structural information in the studied samples. Hysteresis measurements were done by means of Lakeshore Model 7410 vibration sample magnetometer (VSM) by applying maximum field – $H_{\text{max}} \approx \pm 1.8$ Tesla, to obtain coercivity (H_c), remanence (M_r), saturation magnetization (M_s) and squareness ratio or reduced remanent magnetization (M_r/M_s). Experimental lattice parameter (a , c), and cell volume (V) for hexagonal phase ($\text{SrFe}_{12}\text{O}_{19}$) were calculated by analyzing XRD data using following equations as described in [14]:

$$d_{hkl} = \left(\frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \right)^{-1/2} \quad (1)$$

$$V = 0.8666 \times a^2 \times c \quad (2)$$

Where h , k , l – Miller indices and d – interplanar spacing.

Figure of merit $(BH)_{\text{Max}}$ was evaluated from the obtained M_s values using the equation given in [15]:

$$(BH)_{\text{max}} = 0.25 \times \mu_0 \times M_s^2 \quad (3)$$

Where μ_0 = absolute permeability, and M_s = saturation magnetization.

Hopping length for site A and B of the cubic phase were also calculated as given below [16]:

$$\left. \begin{aligned} L_A &= \frac{a\sqrt{3}}{4} \\ L_B &= \frac{a\sqrt{2}}{4} \end{aligned} \right\} \quad (4)$$

Where L_A , L_B are respectively hopping length for site A, B, a – lattice parameter of cubic phase.

RESULTS AND DISCUSSION

Figure 1a depicts the XRD patterns of $\text{SrFe}_{12}\text{O}_{19}/\text{CoFe}_2\text{O}_4$ nano-composite with different value of x , heated at 800 °C for 4hrs whereas Fig. 1b, its inset illustrates variation of grain size (D) for cubic, hexagonal phases. Perusal of XRD patterns (Fig. 1a) shows presence of both hexagonal $\text{SrFe}_{12}\text{O}_{19}$ (*), cubic CoFe_2O_4 (\$) phase, without presence of any secondary phase. Observed patterns were identified according to standard JCPDS 81-1197.

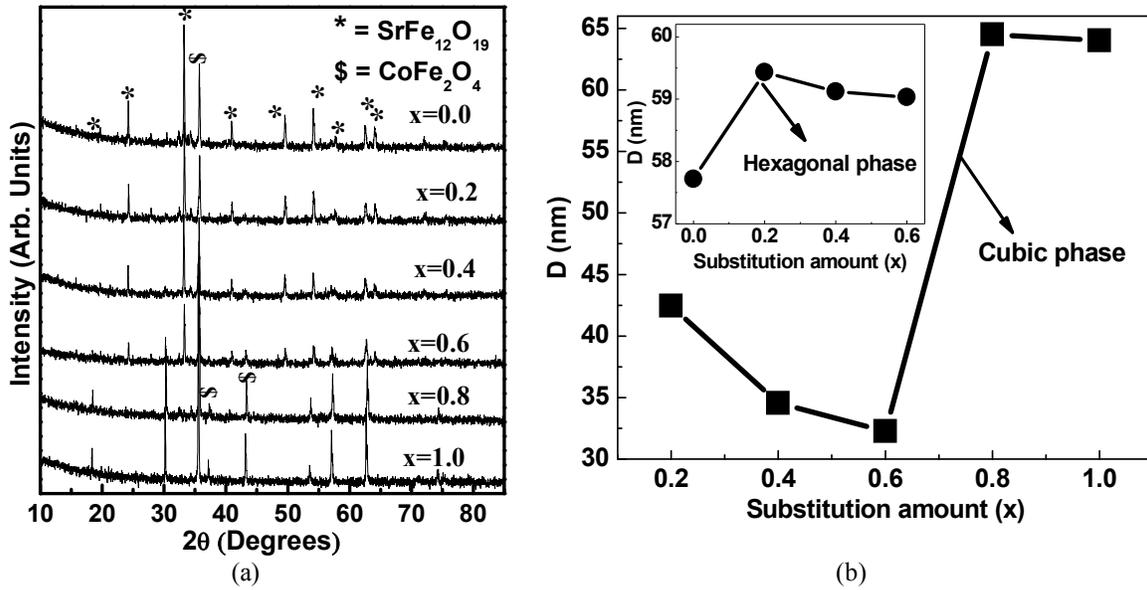


FIGURE 1. (a) X-ray diffraction patterns of $\text{CoFe}_2\text{O}_4/\text{SrFe}_{12}\text{O}_{19}$ nano-composite. (b) Variation of grain size of cubic phase, Inset: grain size for hexagonal phase with substitution amount. Line connecting points is guide to the eye

Table 1 depicts the variation of lattice parameter (a , c), unit cell volume (V), Scherrer's grain diameter (D), hopping length for tetrahedral and octahedral sites (L_A , L_B) for hexagonal and cubic phases of the prepared nano-composites. Perusal of table 1 shows that the lattice parameter (a , c) increases with increasing substitution amount upto $x = 0.4$ for hexagonal phase with a , c ranging respectively between 0.5567 nm to 0.5565 nm and 2.3392 nm to 2.3686 nm , and thereafter decreases for $x = 0.6$. Obtained values of lattice parameter for cubic phase range between $0.8324 \text{ nm} - 0.8371 \text{ nm}$, validates the formation of cubic spinel phase. Average grain size of the synthesized nano-composite was estimated from full width at half maximum (FWHM) values using Scherrer's formula: ($D = 0.9 \times \lambda / \beta \times \cos \theta$), Where λ – wavelength of the x-ray used, β – line width, θ – peak position (in 2θ scale), for both hexagonal, cubic phases. Grain size of studied composite for hexagonal, cubic phase varies from $57.7 - 59.4 \text{ nm}$, and $34.6 - 64.5 \text{ nm}$ respectively, shows nano-crystalline nature of composite. Observed increment in grain size for both hexagonal and cubic phases is attributed to crystal growth. The distance between the magnetic ions for tetrahedral (L_A) and octahedral (L_B) site (known as hopping length/jump length) and cell volume follows same trend as the variation of lattice parameter of cubic phase illustrates with increasing substitution amount.

Figure 2a shows hysteresis loop of the studied hard soft nano-composite, inset illustrates magnified view of the hysteresis loop to see changes in coercivity, whereas the Fig. 2b depicts the variation of saturation magnetization

TABLE 1. Lattice parameter (a , c), unit cell volume (V), Scherrer's grain size (D), hopping length for tetrahedral and octahedral sites (L_A , L_B) of $\text{CoFe}_2\text{O}_4/\text{SrFe}_{12}\text{O}_{19}$ nano-composite.

x	Phase		Lattice Parameter (nm)	V (nm ³)	D (nm)	L _A (nm)	L _B (nm)
0.0	Hexagonal	($\text{SrFe}_{12}\text{O}_{19}$) _{1.0}	a=0.5567, c=2.3392	0.6282	57.7	–	–
0.2	Hexagonal	($\text{SrFe}_{12}\text{O}_{19}$) _{0.8}	a=0.5602, c=2.2623	0.6153	59.4	–	–
	Cubic	(CoFe_2O_4) _{0.2}	a=0.8324	0.5768	42.5	0.3604	0.2947
0.4	Hexagonal	($\text{SrFe}_{12}\text{O}_{19}$) _{0.6}	a=0.5565, c=2.3686	0.6357	59.2	–	–
	Cubic	(CoFe_2O_4) _{0.4}	a=0.8348	0.5818	34.6	0.3615	0.2955
0.6	Hexagonal	($\text{SrFe}_{12}\text{O}_{19}$) _{0.4}	a=0.5620, c=2.2605	0.6187	59.0	–	–
	Cubic	(CoFe_2O_4) _{0.6}	a=0.8342	0.5805	32.3	0.3612	0.2953
0.8	Hexagonal	($\text{SrFe}_{12}\text{O}_{19}$) _{0.2}	–	–	–	–	–
	Cubic	(CoFe_2O_4) _{0.8}	a=0.8342	0.5805	64.5	0.3612	0.2953
1.0	Hexagonal	(CoFe_2O_4) _{1.0}	a=0.8371	0.5866	64.0	0.3625	0.2963

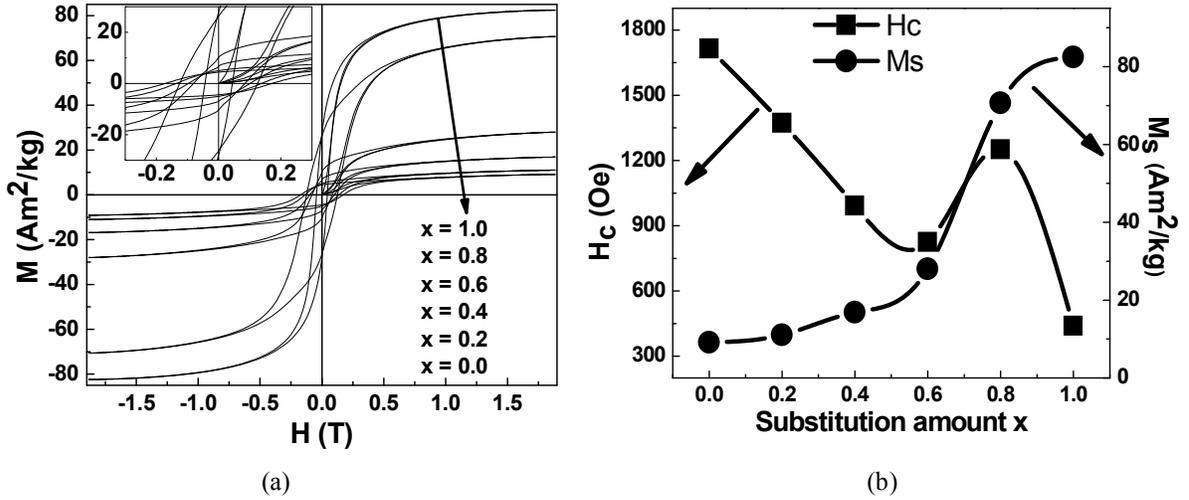


FIGURE 2. (a) Hysteresis loops (Inset: magnified view of hysteresis loops of CoFe₂O₄/SrFe₁₂O₁₉ nano-composite) (b) Variation of saturation magnetization (M_s) at 300K and coercivity (H_c) with substitution amount. Line connecting points is guide to the eye

(M_s) and coercivity (H_c) with varying substitution amount (x). Observed changes reveal a good single-phase magnetic behavior, and the magnetization changes smoothly with the applied field displaying a single magnetic phase, suggesting that the hexagonal (hard), cubic (soft) magnetic phases are strongly exchange coupled [17]. Substitution amount induced changes in hysteresis loops are evidenced by increase of M_s and decrease of H_c .

Substitution amount (x) dependent of magnetic parameters: Coercivity, saturation magnetization, remanence (M_r), squareness ratio (M_r/M_s), figure of merit $(BH)_{max}$ are listed in table 2. Perusal of table 2, pure SrFe₁₂O₁₉ shows very low value of magnetization, remanence, and higher coercivity, but with increasing substitution amount (CoFe₂O₄) M_s , M_r increases where as H_c decreases upto $x = 0.6$. The saturation magnetization, remanence and coercivity of the CoFe₂O₄ substituted SrFe₁₂O₁₉ ferrite reaches its high value 70.65 Am²kg⁻¹, 26.29 Am²kg⁻¹ and 1250.6 Oe respectively (see table 2) at $x = 0.8$, which is ascribed to better enhanced magnetic coupling between hexagonal and cubic phase, while the pure SrFe₁₂O₁₉ exhibits very low magnetization (9.13 Am²kg⁻¹) [18].

The magnetization values increases as the substitution amount increases, due to the rearrangement of cations among tetrahedral and octahedral sites at soft phase. Observed continuous linear increase of energy product $(BH)_{max}$ with M_s^2 (see Fig. 3) is ascribed to better enhanced magnetic coupling of hard-soft phases in the studied nano-composites. Obtained value of $(BH)_{max}$ for the studied samples range between 0.83 kJ/m³ – 60.32 kJ/m³. Observed results of the present work very clearly demonstrate the importance of single reaction vessel approach for preparing soft-hard nano composite, and can be effectively used to have single magnetic phase which enhanced exchange coupling between soft-hard phases.

TABLE 2. Variation of coercivity (H_c), saturation magnetization (M_s), remanence (M_r), squareness ratio (M_r/M_s) and figure of merit $(BH)_{max}$ of CoFe₂O₄/ SrFe₁₂O₁₉ nano-composite.

x	H_c (Oe)	M_s (Am ² /kg)	M_r (Am ² /kg)	M_r / M_s	$(BH)_{Max}$ (kJ/m ³)
0.0	1714.3	9.13	4.43	0.49	0.83
0.2	1372.5	11.03	5.03	0.46	1.23
0.4	992.1	16.87	6.83	0.41	2.68
0.6	824.6	28.01	10.29	0.37	7.47
0.8	1250.6	70.65	26.29	0.37	28.96
1.0	440.0	82.44	27.82	0.34	60.32

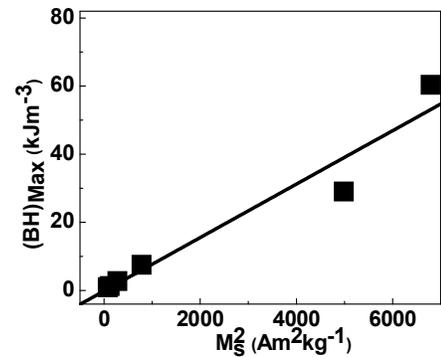


FIGURE 3. Variation of $(BH)_{Max}$ with M_s^2 . Continues line is linear fit to the data

SUMMARY

Hard soft SrFe₁₂O₁₉/CoFe₂O₄ nano-composite samples have been synthesized by one pot synthesis utilizing sol-gel auto-combustion technique. XRD confirms the formation of hard, soft phases (without any secondary phase) of the studied nano-composite with better exchange coupling having average grain size well within nano range. As a result of better exchange coupling between soft-hard phases, enhancement in saturation magnetization, remanence and energy product were observed than the pure SrFe₁₂O₁₉. The studied CoFe₂O₄/SrFe₁₂O₁₉ nano-composite sintered at relatively low temperature can provide enhanced magnetic properties for use in variety of applications (microwave low temperature co-fired ceramics ferrite devices, high density recording and millimetre wave applications etc.). The present work clearly demonstrate the importance of one pot sol gel auto combustion technique as a novel approach for tuning magnetic properties of exchange coupled nano-composites via controlling magnetic parameters of soft-hard phase.

ACKNOWLEDGMENTS

Authors thank Dr. M. Gupta, Mr. L. Behra, UGC-DAE CSR, Indore for XRD measurements. This work is financially supported by UGC-DAE CSR Projects: CSR-IC/CRS-149/2015-16/06. Research fellowship to SR from UGC-DAE CSR Project No. CSR-IC/CRS-74/2014-15/2104 is gratefully acknowledged.

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