



Role of Cr Substitution at Iron Site on Structural and Electrical Properties of Sr-hexaferrites Nanomaterials Synthesized by the Sol-Gel Combustion Method

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Abstract:

The sol-gel auto-combustion technique has been employed to synthesize the M-type Sr-hexaferrites nano materials substituted with mixture of lanthanum and Chromium at the iron site. The phase purity of the samples is confirmed by X-ray diffraction analysis and the nano crystalline granules in the size range of 52 nm obtained. The transmission electron microscopic analysis also confirms that the particles are in nano size (25–50nm) The room temperature DC electrical resistivity is measured by the two point probe method and is found to increase with chromium substitution These materials can be used in microwave devices as these devices require highly resistive materials with low eddy current losses. The review literature leads to the facts that these nano-sized Hexa ferrites could be used in magnetic storage devices; micro waves satellite communications, digital data analysis etc. so that our prepared samples could be proposed to find their vital applications in demanding fields where data storage is of great concern.

Keywords: Strontium ferrite, X-ray density, porosity, electrical conductivity etc

1. Introduction :

Nanotechnology deals with the structures of sizes below 100 nm where unique phenomenon enables some vital applications [1]. The nano-scale materials are renowned for the interesting properties that are different from their bulk materials which are attributed to their extremely small size and very large surface area [2,3]. Ferrites nanomaterials are considered to be superior over other magnetic materials such as metals and alloys due to their high DC electrical resistivity and low eddy current losses [4]. Amongst different classes of these ferrites nanomaterials, M-type hexagonal ferrites i.e. $\text{Sr M}_y \text{Me}_x \text{Fe}_{12-x-y} \text{O}_{19}$ ($\text{Me} = \text{Al or Cr}$, $\text{M} = \text{La}$, $x = 0,2,4,6,8$ and $y = 1$) have been intensively investigated because of their potential applications in microwave devices, magnetic recording media and as permanent magnets [5]. Strontium hexaferrite nanomaterials have recently gained much attention for high density magnetic recording and magneto-optical recording media because of their distinctive magnetic characteristics, perfect chemical stability, excellent corrosion resistivity, good mechanical strength and good expected tribological performance, as well as weak temperature dependence of coercivity in the vicinity of room temperature [6–8]. The properties of these nanomaterials





strongly depend upon the composition and microstructure of the surface which are influenced by the method of their preparation. Strontium hexa ferrites have been synthesized by a variety of techniques such as the hydrothermal method [9], salt melt method [10], co-precipitation method [11] and sol-gel method [12]. In the present investigation, the citrate assisted sol-gel auto-combustion technique has been applied for the synthesis of strontium hexaferrites nanomaterials and its derivative. The main advantages of the sol-gel method over other conventional methods include the molecular scale homogeneity, nano-sized granulation and enhanced reactivity at lower annealing temperatures. Currently, the workers are interested to enhance the saturation magnetization, remanence and resistivity as high as possible and to decrease the coercivity to a reasonable value to make the materials useful for recording media, microwave devices and permanent magnets. For this purpose many attempts have been made to dope various cations at iron as well as at strontium sites but there are only few examples in which the saturation magnetization increases and at the same time the coercivity decreases [13–15]. The main purpose of the present work is to use a simple method for the synthesis of these materials in the nano-size range and to enhance the saturation magnetization, remanence while to decrease the coercivity simultaneously. The other purpose is to enhance the DC electrical resistivity of the synthesized samples

2. Synthesis :

Powders of $\text{SrLa}_y\text{Fe}_{12-x}\text{Cr}_x\text{O}_{19}$ with ($0 \leq x \leq 8$, $y = 1$) were synthesized using a sol-gel auto combustion process. All chemicals used for this synthesis were of analytical reagent grade. A yellow-brown transparent aqueous solution of $\text{Sr}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{CO}(\text{NH}_2)_2$ was prepared. The solution was heated under constant stirring at a temperature of about 140°C in a Pyrex beaker so that it concentrated slowly without producing any precipitation, but changed its viscosity and color, until it turned into a brown gel. When the temperature of the microwave oven was raised to about $250\text{--}300^\circ\text{C}$, the gel swelled into foam and underwent a self-propagating combustion reaction changing the brown gel into black powders. The entire combustion process was over after half an hour. The resulting black ashes were ground in an agate mortar, put into alumina crucibles, and then calcined at 800°C for 1h until complete decomposition of the carbonaceous residues and solid state reaction occurred. Calcined powders were ground and after adding polyvinyl alcohol as a binder mixtures were shaped into pallets using hydraulic press under uniaxial pressure of 75kNm^{-2} . These pallets of each composition were then sintered at 1200°C in electric furnace for 7-8 hours. During sintering process crystallization gave rise to a hexagonal polycrystalline phase. Fig.1 shows modified version of domestic microwave oven used in the present work having 2.45 GHz frequency.





Fig. 1. Modified domestic microwave oven used for synthesis of SrLa_yFe_{12-x-y}Cr_xO₁₉.

3. Characterization of samples:

The powder X-ray diffraction (XRD) analysis was performed by X-Ray Diffractometer (PW-1710 Philips Holland). to confirm M-type hexagonal phase of the synthesized samples. The TEM of the sample is carried out by the instrument of make PHILIPS, Model CM 200 operates in voltage 20-200 kV and resolution of 2.4 Å. As the electron diffraction shows ring pattern superimposed with spots, revealing the poly-crystallinity of individual crystallites. The DC electrical resistivity was measured by the two point probe method. Pellets of 13mm diameter and 2mm thickness were used for DC electrical resistivity measurements.

4. Results and Discussion :

4.1 Structural properties : The phase formation of the synthesized M-type hexaferrites is confirmed by XRD analysis and the patterns for all the samples are shown in Fig.2. It is clear from the figure that there is no extra peak which shows that there is no other phase except hexagonal

phase. This is due to relatively small ionic radius of Cr³⁺ (0.64 Å) comparing with that of Fe³⁺ (0.67 Å) for six-fold coordination by Rezsescu. As a result, the cell volume of Strontium Lanthanum ferrite decreases after being doped. The average crystallite size for all the synthesized samples is calculated by Scherer's formula and the values are given in

Table 1 The crystallite size of as-burnt annealed substance at 1000 °C was in the range of 7.23 to 36.19 of 31–45 nm which is smaller as compared to 70–100, 151–200, and 60–300 nm as reported earlier by various researchers [18–20]. The present crystallite size is small enough in obtaining the suitable signal-to-noise ratio in high density recording media. The as burnt powders were calcined at 1000°C for 2 hrs to get more crystalline homogeneous hexagonal phase. This observation revealed that the nano-crystalline SrLaCr ferrite powders with high surface area could be synthesized directly by the auto-combustion of urea gels. The lattice constants (a and c) and cell volume are calculated from XRD data using respective relations and their values are given in Table 2 The lattice parameter 'a' and 'c' are in the range of 5.5–6 Å and 22.15 to 23.55 Å pertaining to SG: P63/mmc (no. 194). Lattice constant 'a' shows less variation and lattice constant 'c' initially varies rapidly followed by slow variation with substitution. This is in agreement with the fact that all hexagonal ferrites exhibit constant lattice parameter 'a' and variable parameter 'c' by Deschamp which shows that 'c' is more susceptible to stoichiometric changes than 'a' Popa [17] The TEM images for the synthesized





materials are shown in Fig. 3. The particle size calculated from TEM is found in the range of nano scale (≈ 52 nm) (Fig. 3).

4.2. Electrical properties

The DC electrical resistivity of the synthesized materials was also measured at room temperature using two point probemethod. The variation of resistivity as a function of Cr. is shown in Fig. 2 and The conduction mechanism in ferrites is the hopping of electrons between ferrous and ferric ions at the octahedral sites.

5. Conclusions :

A simple and economic sol-gel auto-combustion method using urea as chelating agent has been used for the synthesis of strontium hexaferrites and its La-Cr doped derivatives. Fig 2 shows XRD pattern of high purity Cr doped strontium ferrites with different doping concentrations. All peaks belongs to M-structure ferrite phase and no intermediate phases are observed. The particle morphology was examined by Transmission Electron Microscope (TEM). The particle size was in nano scale (≈ 52 nm) (Fig. 3). The variation in the values of resistivity and hence conductivity and activation energies may be concluded that an electron hopping mechanism between Fe^{3+} ions might reasonably be assumed and so the conductivity is related to the presence of Fe^{2+} ions in sample

Fig. 5. shows Variation of DC electrical resistivity with the Cr concentration. M. NaeemAshiqetal./JournalofMagnetismandMagneticMaterials332(2013)93–97
96 resistivity enhanced by the substituents reveals that the materials can be used in microwave devices.

I J R B A T



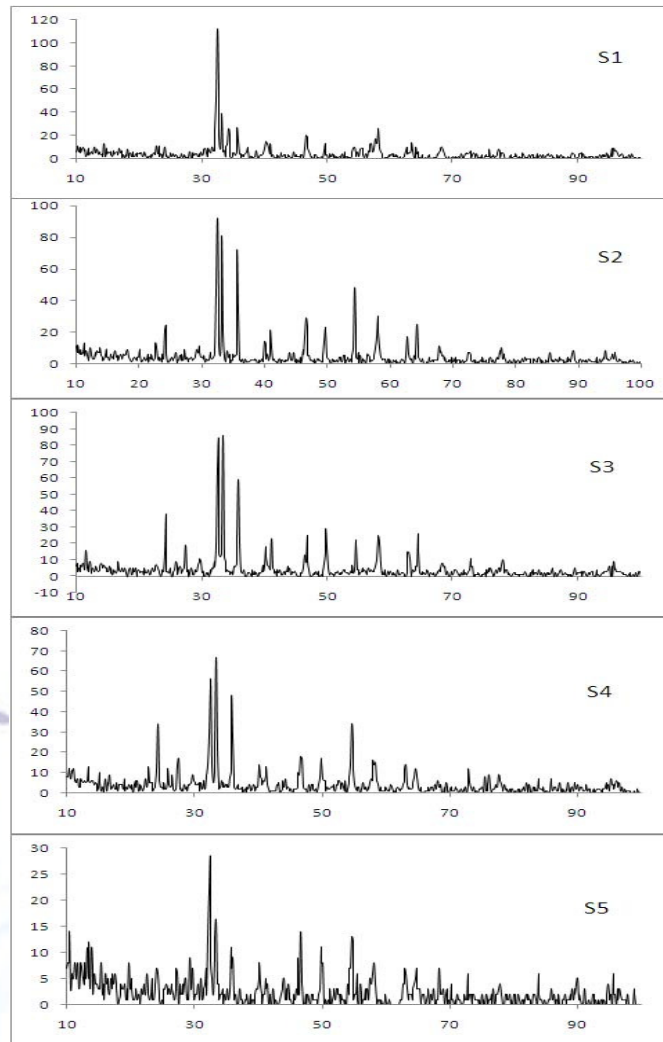


Fig. 2.XRD pattern at room temperature of $\text{SrLa}_y\text{Fe}_{12-x-y}\text{Cr}_x\text{O}_{19}$.

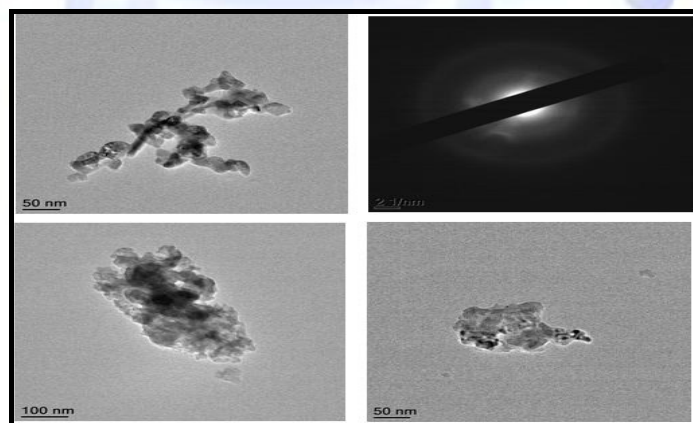


Fig. 3.TEM of $\text{SrLa}_y\text{Fe}_{12-x-y}\text{Cr}_x\text{O}_{19}$, where (a) S1, (b) S2, (c) S4, (d) S5.

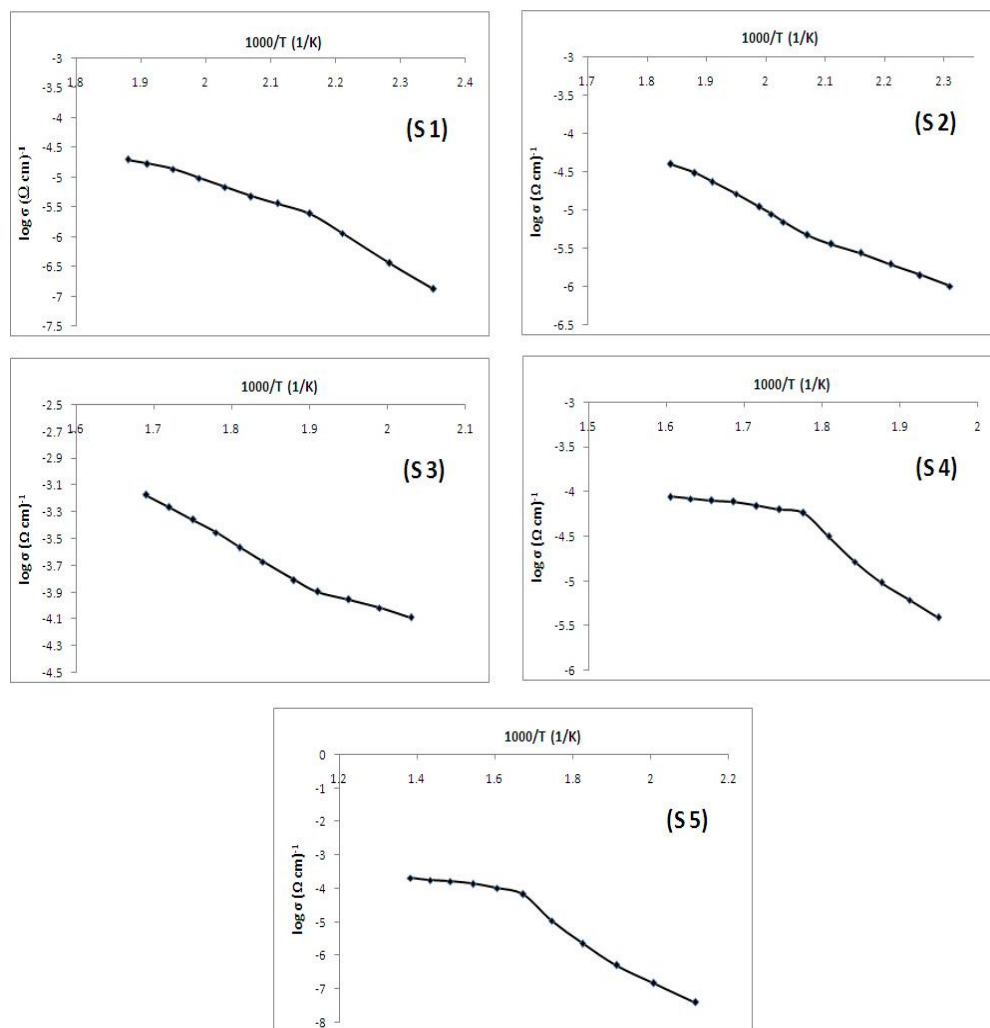


Fig.4. Arrhenius Plot: Effect of Temperature on Conductivity of Aluminium doped Lanthanum substituted Strontium Hexaferrit (S 1) $\text{SrLaFe}_{11}\text{O}_{19}$, (S 2) $\text{SrLaCr}_2\text{Fe}_9\text{O}_{19}$, (S 3) $\text{SrLaCr}_4\text{Fe}_7\text{O}_{19}$, (S 4) $\text{SrLaCr}_8\text{Fe}_3\text{O}_{19}$, (S 5) $\text{SrLaCr}_8\text{Fe}_3\text{O}_{19}$

Table 1. Lattice Parameters, X-Ray Density, Particle Size and Porosity $\text{SrLa}_y\text{Fe}_{12-x-y}\text{Cr}_x\text{O}_{19}$

Samples	x	Molecular Weight (gm/mol)	2θ	Lattice Parameters		c/a (Å)	X Ray Density (gm/cm ³)	Bulk Density (gm/cm ³)	Porosity (%)	Particle Size (Å)	Volume (Å ³)
				a (Å)	c (Å)						
S 1	0	1144.8091	32.42	5.826	23.527	4.038	5.496	2.777	49.4	7.237	691.65
S 2	2	1137.1111	32.47	5.819	23.481	4.035	5.462	2.619	52.7	36.19	691.27
S 3	4	1145.4137	32.52	5.812	23.435	4.030	5.549	2.428	54.5	12.065	688.68
S 4	6	1145.7157	10.95	5.805	23.356	4.035	5.546	2.399	56.3	34.908	685.98
S 5	8	1146.0179	32.37	5.794	22.206	3.832	5.894	2.377	59.4	7.617	645.66





Table 2. Electrical Conductivity Calculations for the samples SrLaCr_xFe_{11-x}O₁₉

Samples	x	Resistivity (ρ) at 300 K (Ω -cm)	Capacitan ce (F)	Dielectric Loss Factor(ϵ)	ΔE (eV)		Transition Temprature T_d (K)	Curie Temperature T_c (K)
					Para	Ferri		
S 1	0	1.23E+07	3.19E-11	4.28E-10	0.3026	0.6222	473	475
S 2	2	3.31E+05	2.46E-10	1.25E-08	0.5882	0.4483	513	518
S 3	4	1.22E+04	7.85E-09	1.02E-03	0.6588	0.3454	523	528
S 4	6	2.27E+05	1.26E-10	1.47E-10	0.732	0.3189	583	590
S 5	8	2.11E+07	3.19E-11	4.28E-10	1.0794	0.2641	598	604

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