INFLUENCE OF TEMPERATURE ON THE MICROSTRUCTURE AND MAGNETIC PROPERTIES OF $Sr_{0.85}(La\text{-}Sm)_{0.15}Fe_{12}O_{19}$ HEXAFERRITES

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***ABSTRACT*- The M-type $Sr_{0.85}(La\text{-}Sm)_{0.15}Fe_{12}O_{19}$ hexaferrite was prepared by sol–gel autocombustion method and was calcinated at 900 °C and 1200°C for 3 h respectively. The structural, morphological and magnetic properties of prepared material were characterized by X-raydiffraction (XRD), Scanning electron microscope (SEM) and vibrating sample magnetometer(VSM).XRD analysis confirms the magnetoplumbite structure and space group p63/mmc. The lattice parameter (a) and (c) shows slight variation with temperature . The unit cell volume and FWHM increases with temperature. However, the particle size shows the reverse trend. The SEM micrographs shows that the synthesized particles are homogenously distributed and have well defined platelets like morphology .EDX confirms the presence of strontium La, Sm, O and Fe. The value of squareness ratio in our prepared material is above 0.5 indicating that the material consists of single domain particles.The prepared samples show small coercive field and high saturation magnetization which is suitable for magnetic recording application.**

Key words: **Sol–gel autocombustion, XRD, SEM, Coercive field.**

1. INTRODUCTION

Since last few decades, researchers have widely studied M-type hexaferrites due to its excellent magnetic properties, high electrical resistivity, high Curie temperature and better chemical stability[1]. These hexaferrite have become important materials commercially and technologically for a number of applications, like computer memory chips, high density recording media, transformer, microwave devices, plastic and permanent magnetic materials [2].Several methods have been employed to prepare these hexaferrites like hydrothermalprocess[3], self-propagating high-temperature synthesis[4], the microwave-assisted calcination route[5], and the citrate precursor method [6]. It is well-known that preparation method, sintering temperature, chemical concentration and even particle size can modify the many properties of hexaferrites. Several investigators have focussed on cationic substitution like Cr^{3+},Al^{3+} , Zn^{2+}-Co^{2+}, La^{3+}- Co^{2+}, Ti^{4+}-Co^{2+},Al^{3+}- Ga^{3+} , Zr^{4+}- Ni^{2+} [7-10], were substituted for iron in order to improve the fundamental properties in strontium hexaferrites.

The aim of the present research is to report the influence of heat treatment (900 and 1200°C) on the structural and magnetic properties of Sm-La substituted M-type hexaferrites, the prepared materials. The preparation route of the samples was sol-gel combustion followed by heat treatment. The main advantage of sol-gel auto-combustion powders over solid state are molecular scale homogeneity, nanosized granulation, improved reactivity and controlled grain size by subsequent heat treatment. Sol–gel autocombustion method followed by a sample heat treatment offers the opportunity to make the hexaferrite submicron powders having coercively suitable for recording application.

2. EXPERIMENTAL DETAILS

M-type hexaferrite $Sr_{1-x}(La\text{-}Sm)_xFe_{12}O_{19}$ (x=0.15) was prepared by the method of sol–gel autocombustion method. Stoichiometric amounts of the starting materials Sr(NO3)2 (99%, Sigma–Aldrich), Fe(NO3)3.9H2O (98%, Applichem), La(NO3)3.4H2O (99%, Sigma– Aldrich), and Sm(NO3).4H2O (99.9%, Sigma– Aldrich) were

dissolved in 500 mL de-ionized water in a 1000-mL Pyrex beaker. Citric acid was added to the solution (metal-to-citric acid molar ratio 1:1). Then the pH was adjusted to 6.5 by addition of ammonia solution (Riedel–de Haen, 33%). This solution was evaporated at a constant temperature of approximately 90^{o}C with constant stirring on a hot plate magnetic stirrer until it turned into a viscous gel. The temperature of the hot plate magnetic stirrer was then increased to approximately 200^{o}C for ignition of the gel. The gel was burnt to a dendrite and brittle powder with citric acid as reductant and nitrate as oxidant. The as-prepared powders were reddish–brown and voluminous. The whole powder was then heated at 500^{o}C to remove the organic moiety. Finally the powder was calcinated at 900 ^{o}C and 1200^{o}Cfor 3 h respectively.

The structural phase of the synthesised samples were determined by D8 Advance Bruker X-ray diffractometer with CuKα (λ=1.5406 Å) radiation. The measurement was taken at the rate of 2^{0}/min and the step size was 0.0198. The surface morphology of the samples was characterized using scanning electron microscope (SEM, JEOL JSM-6490) equipped with energy dispersive X-ray spectroscopy (EDX).Magnetization measurements, major hysteresis loops, were obtained at room temperature using a vibrating sample magnetometer (MicroSense EZ9 VSM) with maximum field strength of 20 kOe.

3. RESULTS and DISCUSSIONS

3.1.XRD ANALYSIS

The X-ray powder diffraction patterns for the $Sr_{0.85}(La\text{-}Sm)_{0.15}Fe_{12}O_{19}$ hexaferrite at 900^{o}C and 1200^{o}C are shown in the Fig.1. The diffraction peaks corresponding to planes (110), (107), (114), (203), (205), (206) (217), (2011), (220) match well with the standard pattern for M-type strontium hexaferrites. This suggests that the prepared material belongs to hexagonal structure with the space group $P6_3/mmc$. The lattice parameters of the prepared samples were calculated and are shown in Table 1.The particle size 'D' is calculated using Scherer formula [11], i.e.

$$D=K\lambda/\beta\cos\theta$$

Where, λ is the X-ray wavelength and is equal to 1.54060 Å, β is the half peak width in radian, θ is the Bragg's angle and k is the shape factor that is equal to 1 for hexagonal system. It is observed that the lattice parameter (a) and (c) shows slight variation with temperature. The unit cell volume and FWHM increases with temperature. However, the particle size shows the reverse trend. The intensities of diffraction peaks are somewhat different but approximately appear at same positions.

Table I: Lattice parameters, unit cell volume, FWHM and particle size of $Sr_{0.85}(La\text{-}Sm)_{0.15}Fe_{12}O_{19}$ sample at different temperatures.

Composition $Sr_{0.85}(La\text{-}Sm)_{0.15}Fe_{12}O_{19}$	a (Å)	c (Å)	V_{cell} (Å^3)	2θ	FWHM	Particle size (nm)
900^{o}C	5.88	22.93	792.79	33.935	0.319	5.04
1200^{o}C	5.90	23.05	802.37	34.070	0.326	4.94

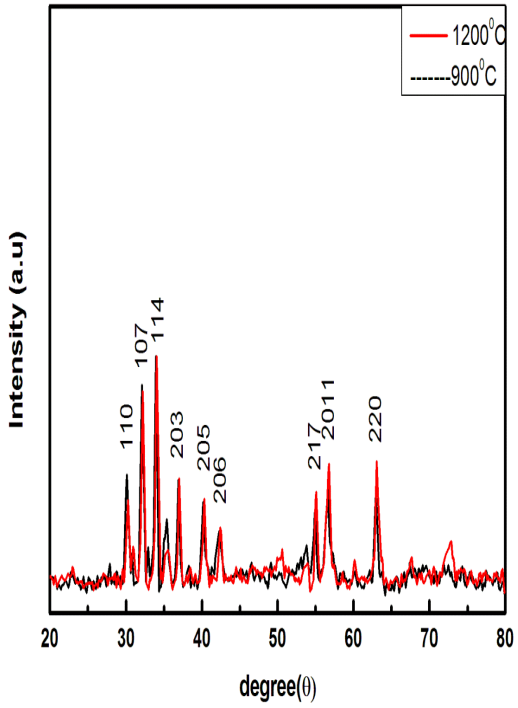

Fig 1.X-ray powder diffraction patterns for the $Sr_{0.85}(La\text{-}Sm)_{0.15}Fe_{12}O_{19}$ sample at different temperatures.

3.2.MICROSTRUCTURE ANALYSIS:

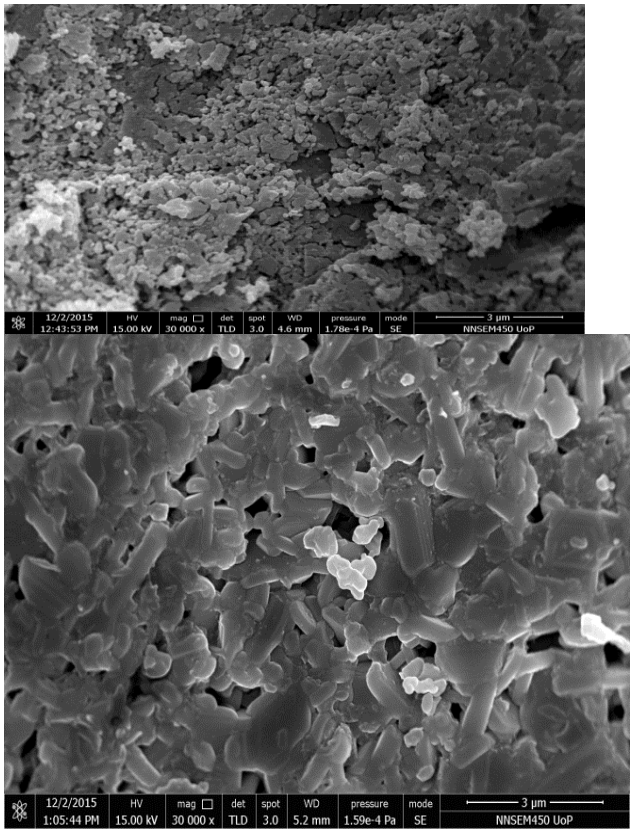

Fig 2.SEM images of $Sr_{0.85}(La\text{-}Sm)_{0.15}Fe_{12}O_{19}$ sample at different temperatures

SEM images and EDX spectra of $Sr_{0.85}(La\text{-}Sm)_{0.15}Fe_{12}O_{19}$ hexaferrite sintered at different temperature are shown in Fig.2 and Fig.3, respectively. The SEM micrographs shows that the synthesized particles are homogenously distributed and have well defined platelets like morphology [12].The platelet shaped hexaferrites are the most suitable for microwave absorbing purpose[13]. This agglomeration can be ascribed to a strong magnetic dipole dipole and Vander Waals interactions between the particles or due to the chemical reaction that occursamong the particles during the sintering process [14-15]

Fig.3. representative X-ray elemental maps of all the elements detected inenergy dispersive X-ray spectroscopy (EDX) i.e., strontium La, Sm, oxygen, Iron. The element Carbon is due to the carbon coating of the sample prior to the SEM analysis.

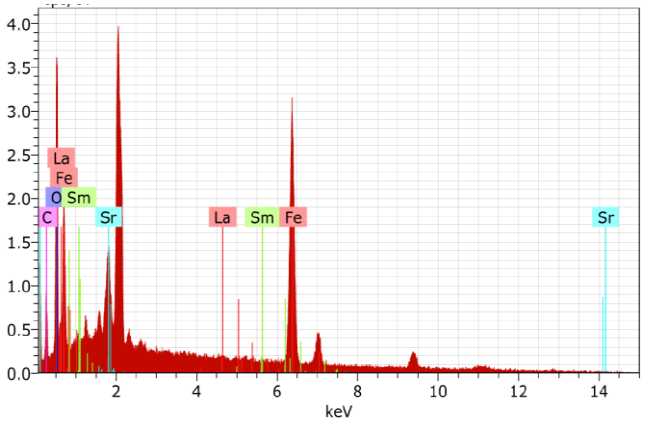

Fig 3.EDX-Spectra for the $Sr_{0.85}(La\text{-}Sm)_{0.15}Fe_{12}O_{19}$ sample at different temperatures

3.3.VSM ANALYSIS

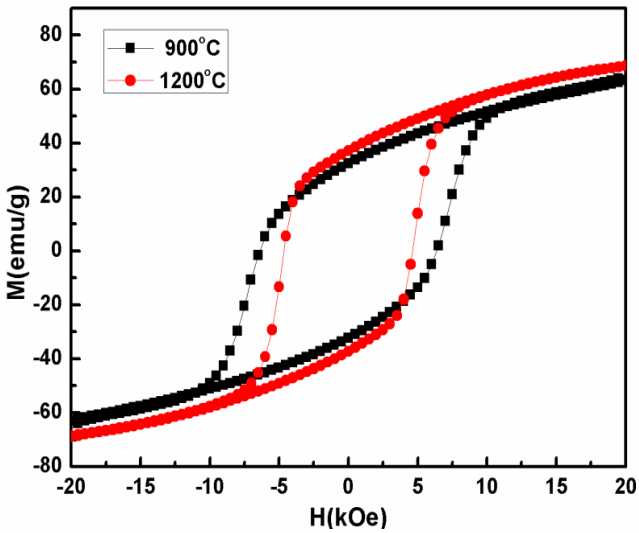

Fig 4.Hysteresis loops for the $Sr_{0.85}(La\text{-}Sm)_{0.15}Fe_{12}O_{19}$ sample at different temperatures

In order to obtain parameters like saturation magnetization and coercivity, the hysteresis loops were measured for $Sr_{0.85}(La\text{-}Sm)_{0.15}Fe_{12}O_{19}$ ferrite samples and are shown in Fig.4. The saturation magnetizations of the samples were found in the range 65emu/g - 69emu/g, respectively as the calcinations temperature increases (900^{o}C to 1200^{o}C). These values are smaller than the theoretically predicted values (72 emu/g), but agree well with other experimental values obtained from various preparation methods [16]. The enhancement in saturation magnetization may be attributed to the variation in particle size, since it is well known that the energy of the magnetic particle is proportional

to the particle size [17]. When this energy gets as good as to thermal energy, thermal fluctuations will appreciably decrease the total magnetic moment in a given field [18].Moreover, the spin canting phenomenon is also decreased with the growth of particle size at the elevated temperature. The observed values of saturation magnetization are found smaller than the theoretical values (74.3 emu/g) of the single crystal strontium hexaferrites[19-20].Small coercive field and high saturation magnetization are suitable for magnetic recording application[21].

From Fig.4. it is observed that coercive field decreases with the raise of the sintering temperature. This result can be described on the basis of the observed transformation of the single domain to multi-domain, when the particle size increases after sintering. In the case of the single domain, magnetization is caused by the rotation of magnetization which contributes to high coercive field, while as in the case of the multi-domain structure magnetization occurs through the displacement of the domain wall which results to a small coercive field [22]. The squareness ratio is basically determined of how square the hysteresis loop and is known by the ratio of (Mr/Ms). In the present investigation, the value of squareness ratio (Mr/Ms) is estimated from the magnetic data and is shown in theTable. 2. If the value of squareness ratio is equal to 0.5 or above it indicates that all the prepared material are in the single domain while as if the value is below 0.5 it may be attributed to the formation of multidomain structure. However, the value of squareness ratio in our prepared material is above 0.5 indicating that the material consists of single domain particles [23].

Table 2: Value of saturation magnetization, coercivity and squareness ratio of $Sr_{0.85}(La\text{-}Sm)_{0.15}Fe_{12}O_{19}$ heated at different temperature.

Sample	M_s (emu/g)	M_r (emu/g)	H_c(k Oe)	M_r/M_s
900^{o}C	65	33	57	0.50
1200^{o}C	69	36	66	0.52

4. CONCLUSION

The M-type $Sr_{0.85}(La\text{-}Sm)_{0.15}Fe_{12}O_{19}$ hexaferrite was successfully synthesized employing sol–gel autocombustion method and was calcinated at 900^{o}C and 1200^{o}C for 3 h respectively. Phase formation was confirmed by X-ray diffraction. XRD analysis confirms the magnetoplumbite structure and space group p63/mmc. The lattice parameter (a) and (c) shows slight variation with temperature . The unit cell volume and FWHM increases with temperature. However, the particle size shows the reverse trend.The SEM micrographs shows that the synthesized particles are homogenously distributed and have well defined platelets like morphology. EDX confirms the presence of strontium La, Sm, O and Fe. The materials consist of single domain particles as confirmed by squareness ratio. These materials show small coercive field and high saturation magnetization. . It is confirmed that the present materials can be useful for magnetic recording application.

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