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LANTHANUM (La^{3+}) SUBSTITUTION FOR Fe^{3+} IN Ba–Sr-Ca M-TYPE HEXAFERRITES AND THEIR SYNTHESIS AND CHARACTERIZATION

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Abstract

We have synthesized three different hexagonal Magnetoplumbite (M) types of ferrites by standard ceramic method at a high temperature of 1403 K. These ferrites are namely Lanthanum La substituted for Fe in Barium ($BaLa_{0.2}Fe_{11.8}O_{19}$), Strontium ($SrLaFe_{11}O_{19}$), Calcium ($CaLa_{0.5}Fe_{11.5}O_{19}$) ferrites. Their characterization is performed by using X-ray diffraction studies (XRD), Scanning electron microscopy (SEM) and Magnetic Studies By Quincks method. The XRD studies of te sample are very interesting. Lanthanum substitution Sr and Ca ferrites the 2θ and d values are nearly same for the maximum intense planes of 1 and 2 order diffraction peaks at (107) and (114) planes, however lanthanum substitution for Ba gets reversed for the same intense planes. These three ferrites crystallize into hexagonal magnetoplumbite structure with lattice parameters, for Ba: a = 5.87 Å, c = 22.17 Å for Sr; a= 5.82 Å, c= 22.10 Å, Ca: a= 5.81 Å, c= 21.87 Å. The SEM studies for Ba and Sr indicate the morphology of the samples to be regular equal in size and are hexagonal in shape, however the SEM micrographs of Ca ferrite are irregular in shape. The EDX studies shows the exact presence of pure elements Sr, La, Fe and O present in the sample.

Keywords*: Magnetoplumbites, Oxides, XRD, SEM and magnetic studies.*

Introduction

The worlds permanent magnets were based on hexagonal Barium and Strontium Magnetoplumbite (M) (Ferroxdure BaM, SrM) ferrites $BaFe_{12}O_{19}$, $Sr Fe_{12}O_{19}$ appeared in 1938 [1] and in 1951 [2] which paved the way for large spin-orbit coupling. The systematic study and application of magnetic properties of hexaferrites began in 1955 [3,4]. The hexagonal are very attractive materials for high frequency circuits and operative devices. Barium and strontium ferrites are suitable high density, over coat free contact and semi contact recording [5] media. These ferrites have superior chemical stability, mechanical hardness, low level noise media, high Curie temperature and have potential for applications in both perpendicular and longitudinal magnetic recording media [6-7].

Magnetoplumbites also known as magnetic Oxide has a hexagonal structure which it has from the mineral. It has a major preferred axis called as the *c*-axis and a minor axis called as *a*-axis. The oxygen ions are closely packed as they are spinel in structure but there are Oxygen layers which include the Ba, Sr or La ions of the same ionic radio as Oxygen ions and can replace them in the lattice. The other ferromagnetic oxides all of which can be derived from ferroxdure ($Ba_{o.6}Fe_2O_3$) [8-9]. There are five crystallographic sites in the M-type structure namely 2a, 2b,

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$4f_1$, $4f_2$, and 12k. The sites 2a,$4f_2$ and 12k are octahedral $4f_1$ the tetrahedral and 2b the trigonal bipyramidal site.

The ferrites are often doppped with metal ions to alter their electrical, magnetic and morphological properties. Metals are usually rea usually choosen that have the desired effect at a low level to avoid reducing the magnetic strength of the product [10-11-12] A literature survey shows that a lot of work on various combinations of Ba, Sr, Ca and La have been carried out /which revealed the uniaxial anisotropy in M hexaferrites [13-14]. Furthermore, a combination of Sr-La is found to affect positively the magnetic properties of the M-type hexaferrites in comparison to Ba-La and Ca-La combinations [15-16].

Substitution of Lanthanum La for iron Fe has been reported by Lotgering [17] in SrM and found an increase in the magnetocrystalline anisotropy, similar substation is also observed with general formula $Sr_{1-x}La_xFe_{12-x}O_{19}$[18-19]. The literature survey shows that very meager work is carried out on Lanthanum La substitution for Fe in B, Sr, Ca magnetoplumbites type of compounds. We have substituted the proper proportions of La in Ba, Sr, Ca ferrites so that the lattice parameters and *d* values are nearly same for all the three samples of Ba/Sr/Ca for the highest intensity reflections for planes (107) and (114) planes in these ferrite and reporting the synthesis by standard ceramic method structural studies by X-ray diffraction, morphological studies by Scanning electron microscope and magnetic behavior in the Se compounds.

Experimental

Synthesis

The three samples were synthesized by standard ceramic method. The Oxides of the powdered Ar grade materials of BaO, SrO, CaO, La_2O_3, Fe_2O_3 were taken in proper molar ratios. Stoichiometric amount of the material along with pure grade acetone were mixed in an agate mortar for about three days. Pellets of these samples 1 cm in diameter were made in a hydraulic press machine with a pressure of about 6 tons. The samples were then kept in three Silica crucibles separately and heated and in a electronically controlled muffle furnace in steps by increasing the temperature of 50 ^oC up to a temperature of 1403 K. The samples were heated continuously at this temperature for 70 hours. The temperature was slowly cooled down in steps of 50 ^oC up to the room temperature. Some of the pallets were fine powdered for use in XRD, SEM, EDX and magnetic studies.

XRD, SEM and EDX Analysis

The X-Ray diffraction studies of the three powdered samples were performed on the machine Model BRUKER, AXSDS ADVANCE. The XRD machine is operated at 35 mA, 40 kV with scanning range from 10 to 90. The target used is Cu and Cu K radiation of 1.45 A was used. The samples were further characterized by scanning electronic machine JEOL model JMS-6390 LV, to determine the morphology of the samples. The EDX studies were also performed on the same machine to know the elemental composition. The intense diffraction peaks of the samples are at (110) (107) (114) Planes. The magnetic susceptibility of the samples was performed by Quincks method.

Result and Discussion

X-ray Structural Analysis

The contents of La substitution for Fe is done in such a way that for $BaLa_{0.2}Fe_{11.8}O_{19}$: $SrLaFe_{11}O_{19}$: $CaLa_{0.5}Fe_{11.5}O_{19}$ the structural values of 2, d and (hkl) for the highest intense peaks of (107) first order diffraction and (114) second order diffraction remains the same Fig 1. However, the intense peaks gets reversed in $BaLa_{0.2}$ $Fe_{11.8}O_{19}$. Though the contents of La substation for iron Fe changed in Sr and Ca ferrites from > 5 to 1 the highest maximum peaks

(107) and (114) remains same at 2 values, however the intensity of peaks gets reversed I Ba ferrite for contents of 0.2 Lanthanum also.

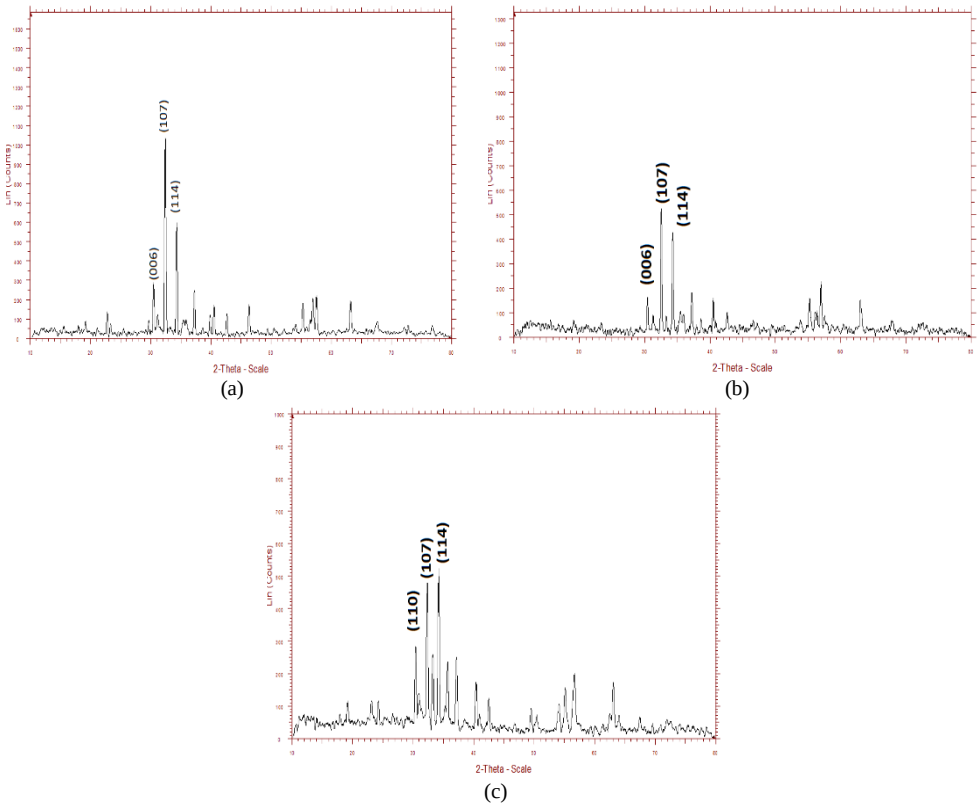

Fig. 1. (a) XRD of $SrLaFe_{11}O_{19}$ Fig. (b) XRD of $CaLa_{0.5}Fe_{11.5}O_{19}$ Fig. (c) $BaLa_{0.2}Fe_{11.8}O_{19}$

Table 1. XRD of $CaLa_{0.5}Fe_{11.5}O_{19}$

Sl. No	Angle, (2θ)	dvalue, (Å)	Intensity Count	Intensity %	(hkl)
1.	30.399	2.93804	161	30.7	(110)
2.	32.499	2.75285	524	100	(107)
3.	34.267	2.61474	426	81.2	(114)
4.	37.183	2.41611	178	33.9	(203)
5.	38.592	2.3311	70.7	13.5	(204)
6.	40.487	2.22624	155	29.7	(205)
7.	42.621	2.11956	99.1	18.9	(117)
8.	55.28	1.66044	157	30	(303)
9.	57.003	1.61428	225	42.9	(217)
10.	63.043	1.47336	148	28.3	(221)

The values of 2θ, d and (hkl) for the sample of intense planes (107) for Sr ferrite are 32.356, 2.764: for Ca ferrite are 32.499, 2.752: for Ba ferrite 34.190, 2.740. Similarly, for second order diffraction at (114) for Sr ferrite are 34.261, 2.615: for Ca ferrite 34.267, 2.614 and for Ba ferrite are 32.309, 2.769 (Table 2,3,4). The unwanted peaks of Fe_2O_3 and Fe_3O_4 (JCPDS file No

19-6290) disappeared at the higher temperature of 1403 K. The width of the ferrite peaks decreased as the temperature increased suggesting growth of the particle [21-22].

Table 2. XRD Pattern of$SrLaFe_{11}O_{19}$

Sl. No	Angle, (2θ)	dvalue, (Å)	Intensity count	Intensity %	(hkl)
1.	22.703	3.91365	131	12.3	(103)
2.	23.247	3.82325	69.5	6.5	(104)
3.	29.603	3.01524	88.8	8.3	(105)
4.	30.420	2.93612	285	26.7	(00 6)
5.	32.356	2.76465	1066	100	(107)
6.	34.261	2.61517	595	55.9	(114)
7.	37.213	2.41423	244	22.9	(201)
8.	39.807	2.26267	117	11	(114)
9.	40.475	2.22686	166	15.6	(202)
10.	42.604	2.12038	124	11.6	(204)

Table 3. XRD Pattern of $BaLa_{0.2}Fe_{11.8}O_{19}$

Sl. No	Angle, (2θ)	dvalue, (Å)	Intensity (I)	Intensity %	(hkl)
1.	32.299	2.76942	485	92.9	(112)
2.	33.218	2.69488	256	49.1	(111)
3.	34.190	2.62048	522	100	(107)
4.	35.666	2.51533	234	44.9	(112)
5.	37.147	2.41834	249	47.8	(113)
6.	40.381	2.23185	171	32.8	(201)
7.	42.485	2.12602	121	23.2	(204)
8.	55.134	1.66448	155	29.7	(301)
9.	56.660	1.62322	199	38.1	(122)
10.	63.098	1.47221	171	32.8	(036)

The XRD powder diffraction of the three samples, the diffraction peak position, the (hkl) values and the relative intensities showed good making with the standard powder diffraction file ICDD card number (33-1433) belonging to hexagonal Magnetoplumbite M-type structure with space group P6/mmc. The slight variation of Lanthanum in sample contents increased from Ba, Ca, Sr the lattice parameters *c* decreases slightly whereas *a* remains the same. This observation accounts for contraction of crystal structure of Lanthanum substituted samples [23-24-25]. The possible explanation of gradual reduction in one of the Strontium sale is smaller ionic radius of La compared to Sr.

The lattice constants *a* and *c* of the hexagonal ferrite were calculated using equation 1:

$$\frac{1}{d^2} = \frac{4(h^2 + k^2 + hk)}{c^2} + \frac{l^2}{c^2} \tag{1}$$

Where: (hkl) are the Miller indices, d is the interplanar distances.

The lattice parameters of the samples are given in Table 4. The crystallite size measurements are carried out the XRD and Debye-Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{2}$$

where β is the width of the observed diffraction peaks at its half maximum intensities, K is the space factor which takes a value of about 0.9 and λ is the wavelength (Cu-K_α radiation

equal to 1.5 Å). The average particle size for the three samples is found to be 46.79, 50.48, and 64.74 *nm* respectively for Ba, Sr, Ca doped ferrites.

Table 4. Lattice parameters

Sr. No.	Sample	a Å	c Å	Particle Size
1.	$BaLa_{0.2}Fe_{11.8}O_{19}$	5.87	22.17	46
2.	$SrLaFe_{11}O_{19}$	5.82	22.10	51
3.	$CaLa_{0.5}Fe_{11.5}O_{19}$	5.81	21,87	64

Morphological Analysis

The Scanning electron microscope studies (SEM), shows the morphological information of the hexagonal ferrites $BaLa_{0.2}Fe_{11.8}O_{19}$, $SrLaFe_{11}O_{19}$ and $CaLa_{0.5}$ $Fe_{11.5}O_{19}$, Figures 2, 3, 4 respectively. The microstructural study by SEM revealed that the samples $BaLa_{0.2}Fe_{11.8}O_{19}$ and $SrLaFe_{11}O_{19}$ have very regular grains and are hexagonal in shape about 1 μm in range. $SrLaFe_{11}O_{19}$ sample $CaLa_{0.5}$ $Fe_{11.5}O_{19}$ have irregular type of grains but they are also hexagonal in shape. This may be attributed to the insertion of La in lattice which results in lattice distortion and internal stress induced by lattice distortion resulting in increase in grain growth [23-30-32]. The average crystallite size determined is smaller than the average particle size obtained by SEM.

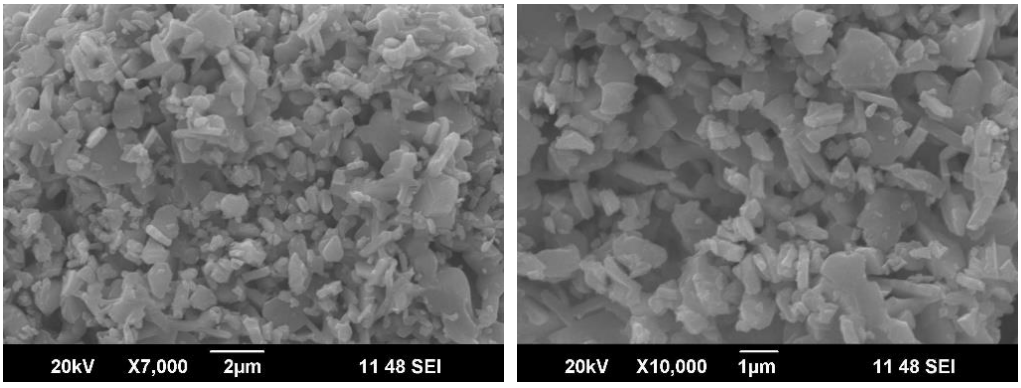

Fig. 2. SEM of $BaLa_{0.2}Fe_{11.8}O_{19}$

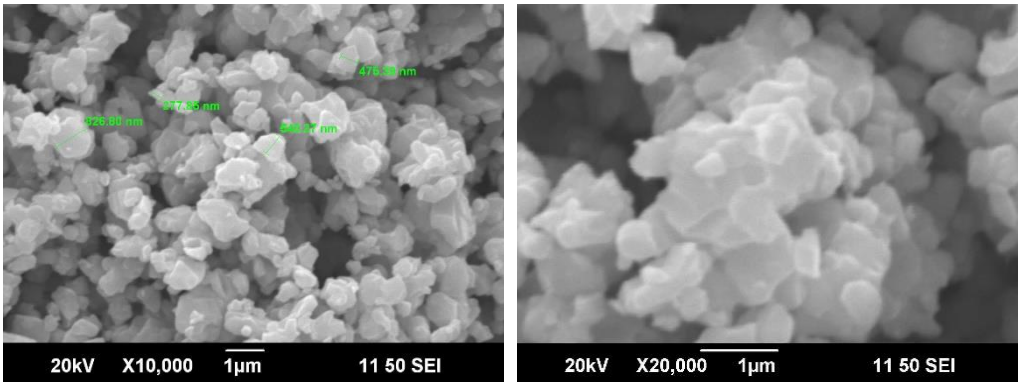

Fig. 3. SEM of $SrLaFe_{11}O_{19}$

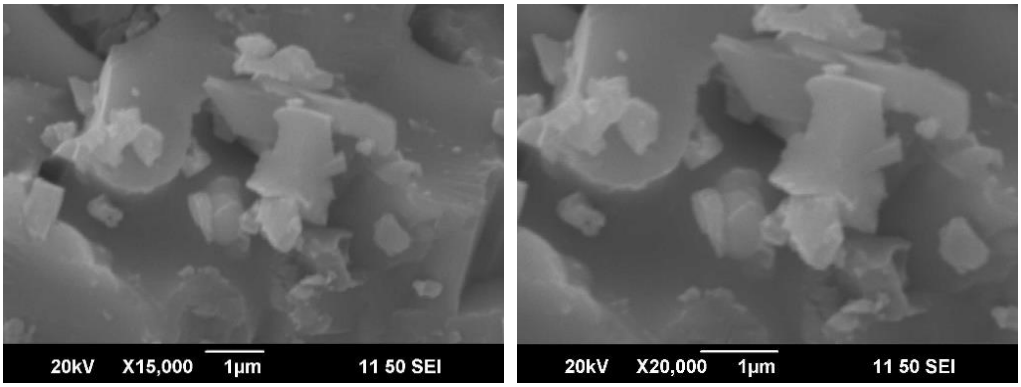

Fig. 4. SEM of $CaLa_{0.5}Fe_{11.5}O_{19}$

Therefore, we conclude that each particle is formed by the aggregation of several crystallites. The crystallite index (I_{cr}) were calculated from the following relation.

$$I_{\text{cry}} = \frac{D_{\text{SEM}}}{r_{\text{XRD}}} \tag{2}$$

where D_{SEM} is average particle size obtained from micrograph and r_{XRD} is average crystalline size as obtained from Scherrer equation. The samples were also subjected to EDX analysis which show that all the elements are present perfectly in the sample. Fig. Shows the typical EDX spectra of our samples.

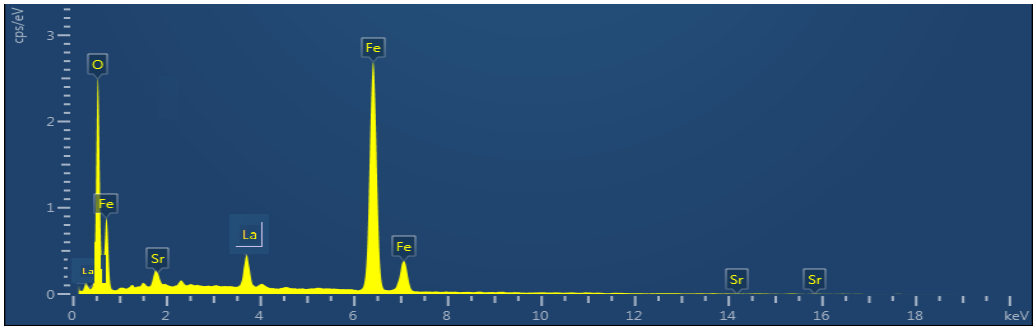

Fig. 5. EDX of SrLaFe11O19

Conclusion

In this study three types of hexagonal magnetoplumbites type of compounds of Ba, Sr, and Ca doped by Lanthanum (La) composition have been synthesized by standard ceramic method. The substitution of Fe by La in these compounds is achieved in such a way that the values of 2θ, d and (hkl) which are highest reflections of (107) and (114) planes for the three samples are displaced at the nearly same places. Similarly, the intensities of reflections for (107) and (114) for Sr and Ca Ferrites are also coming at the same place. However, for Ba ferrite the intensities get reversed. The XRD confirms that Ba, Sr, Ca ferrites on substitution of Fe by La gets crystallized into hexagonal magnetoplumbite structure. The crystallite size is reduced due to less ionic radius of lanthanum. The scanning electron microscopy gives us the clear morphology of the samples to be regular in size and are hexagonal in structure for Barium and Strontium ferrites,

however for Calcium ferrite the morphology of the sample is hexagonal but crystallite is not regular. This may be due to insertion of lanthanum in the Calcium ferrite sample which distorts the lattice structure.

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