STRUCTURAL AND ELECTRICAL CONDUCTIVITY OF $CaLa_xFe_{12-x}O_{19}$

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Abstract

The aim of the present work is to synthesize calcium ferrite by standard ceramic method and to investigate its properties. The crystalline powder of La substituted calcium hexaferrite with chemical composition $CaLa_xFe_{12-x}O_{19}$, have been chosen for their studies on structural and electric properties. The prepared powder was characterized by using X-ray Diffraction (XRD), Scanning Electron Microscope (SEM). XRD shows hexagonal Magnetoplumbite (M) type structure having unit cell determination 'a' and 'b' varies between 5.80 $\dot{A}$ and 22.12 $\dot{A}$

Keyword: Hexagonal ferrite (Hexaferrite), X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), Magnetoplumbite (M-type), Calcium Oxide (CaO), Iron Oxide (Fe_2O_3) etc.

Introduction: Magnetoplumbite is hard ferromagnetic material. Ferrite continued to attract attention of many researchers over the years due to their various category of applications over wide frequency range, low cost and high performance [1]. In 1952, a new class of ferrites so called hexagonal ferrites with formula $MFe_{12}O_{19}$ having permanent magnetic properties were discovered. where, M is the divalent alkaline metal cations and can be replaced by a suitable cations or their combinations [2]. Alkaline metal likes barium, strontium, calcium or lead.

The calcium ferrite having general formula $CaFe_{12}O_{19}$ is one of the most important hard magnetic materials, widely used for above application. M-type are very useful for microwave application[3]. The magnetic and electric properties of the hexagonal ferrites can be altered by the doping of various cations at M (Ca, Sr, Ba, Pb). Several researchers have substituted many cations and their combinations in M-type hexagonal ferrites [4-6]. In this research work La doped calcium hexaferrite and from literature review, that worked is carried out on the simultaneous combinational effect of these cations , namely Ca^{2+} and La^{3+} on electric , magnetic properties of the M-hexaferrite, hence formed composition formula $CaLa_xFe_{12-x}O_{19}$ was synthesized by standard ceramic method[8].

Experimental Details:

Synthesis: The preparation of compounds with chemical formula $CaLa_xFe_{12-x}O_{19}$ (with x=0.7) by standard ceramic method. The molecular concentration x substituted cations in the chemical formula. The oxides Fe_2O_3, La_2O_3, CaO of Merck grade (with 99.90% purity) were used as starting material for the synthesis of present series of compounds. The stoichmetric proportion of weight oxides were mixed thoroughly by grinding for 6 hours in agate mortar with help of acetone to get ultra-fine homogeneous powder of sample. The resulting powder pre-sintered at 200℃ for half hours to moisture free, homogeneous, calcinations. The calcination powder were pressed into the pellet machine to form pellet at 75 kg/cm^2 and then sintered at 1130℃ in air atmosphere for about 68 hours and slowly cooled to room temperature at the rate of 200℃/half hours using a microprocessor controlled furnace. The synthesized pellet break with hydraulic pressure of pellet machine at 120 kg/cm^2. Then grinding in agate mortar to get ultra-fine powder of sample. The synthesized powder of

sample again heated at 300°C for 30 minute to remove impurity.

Characterization: X-ray diffraction pattern of $CaLa_{0.7}Fe_{11.3}O_{19}$ hexagonal ferrite under investigation were obtained using X-ray Diffractometer.

Result and Discussion:

Structural analysis: The XRD pattern of $CaLa_{0.7}Fe_{11.3}O_{19}$ powder (fig1) investigated ferrite sample synthesized by ceramic method correspond to M-type calcium hexaferrite structure fig(1). The hexagonal M-structure with space group (SG:$P6_3/mmc$) (No. 194), which confirms that phase belongs to magnetoplumbite, indicating that the crystal structure were single phase hexagonal magnetoplumbite after substitution with La^{3+} ions respectively. The lattice constant a and c of hexagonal calcium ferrite were calculated using equation(1)

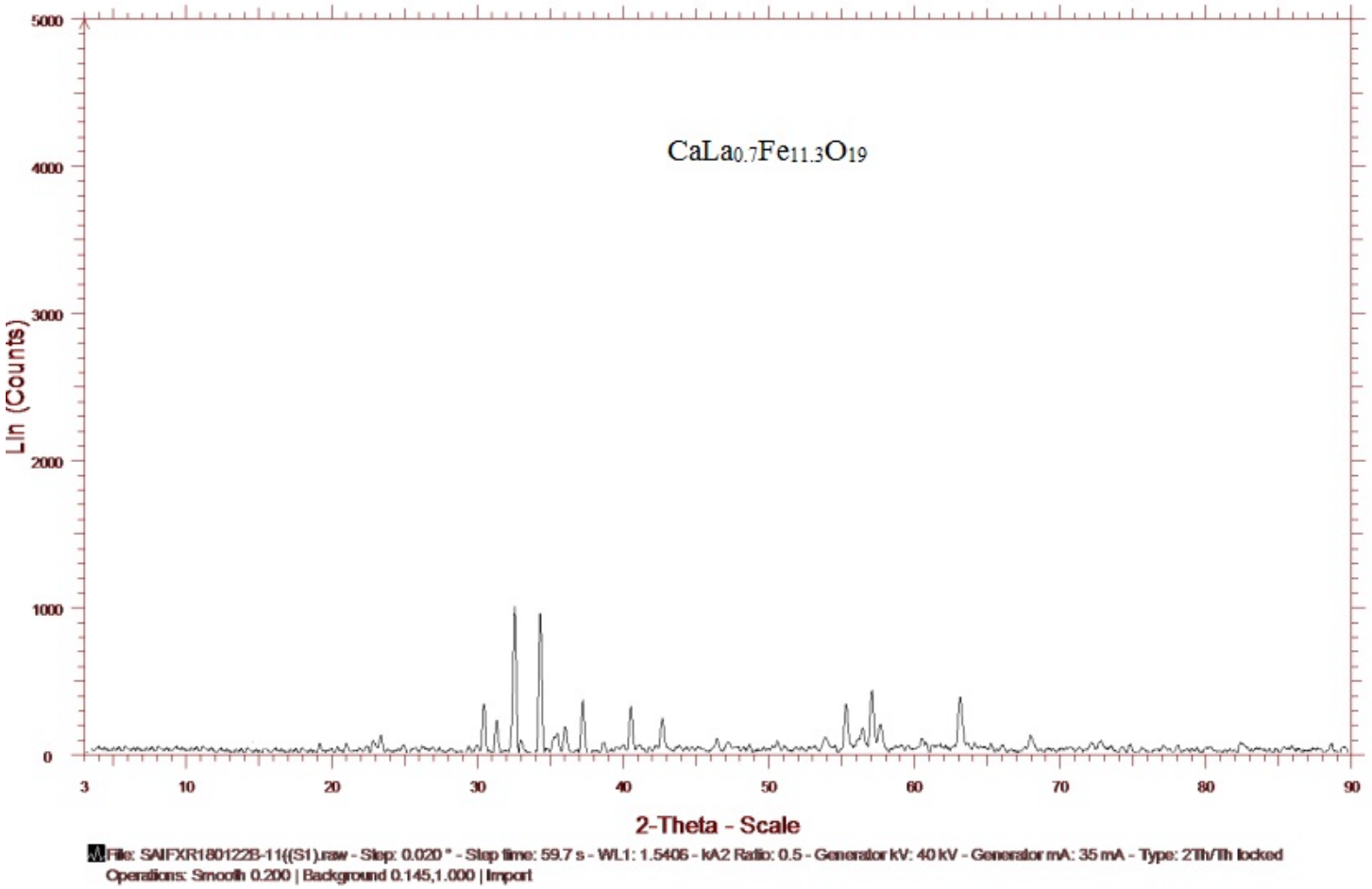
$$\frac{1}{d^2} = \frac{4(h^2+k^2+hk)}{3a^2} + \frac{l^2}{c^2} \quad \text{---------- (1)}$$

Where h ,k, l are miller indices, d is interplaner distance. The lattice parameter a and c found to be 5.80$\dot{A}$ and 22.12$\dot{A}$ respectively. The crystallite size measurements were also carried out using the XRD data and using scherrer equation

$$D = \frac{k\lambda}{\beta \cos\theta} \quad \text{---------- (2)}$$

Where β is width of the observed diffraction peak at its half maximum intensity ,K is the space factor which take value of about 0.9 & λ is the wavelength (Cuk_α radiation equal to 0.154 nm). And the average particle size was found to be about 56.17nm.

sample	a ($\dot{A}$)	c ($\dot{A}$)	Particle size (D)nm	Volume ($\dot{A}^3$)
$CaLa_{0.7}Fe_{11.3}O_{19}$	5.80	22.12	56.17	644.4240



Sr. No.	2θ	D value (Å)	Observe intensity count	Intensity in %
1	30.397	2.9382	337	35 %
2	31.259	2.8591	222	10 %
3	32.523	2.7508	996	100 %
4	34.277	2.6140	950	99 %
5	37.195	2.4153	360	40 %
6	40.509	2.2250	319	25%
7	42.669	2.1173	273	20 %
8	55.313	1.6595	332	30 %
9	57.087	1.6121	430	50 %
10	63.154	1.4710	383	45 %

Table I: Observation table for X-R-D results

Sr. No	Temp in (K)	Voltage (V)	$\log\rho$	$\frac{1}{T} * 10^3$
1	297	30	3.3670	1.3538
2	303	29	3.3003	1.3391
3	308	28	3.2460	1.3239
4	313	27	3.1940	1.3081
5	318	25	3.0953	1.2747
6	323	24	3.0487	1.2570
7	328	23	3.0030	1.2384
8	333	20	2.9158	1.2192
9	338	19	2.8735	1.1778
10	343	18	2.8328	1.1555
11	348	17	2.7932	1.1320
12	353	16	2.7932	1.1083
13	358	16	2.7548	1.0809
14	363	15	2.7173	1.0809
15	368	14	2.6809	1.0229
16	373	14	2.6455	1.0229
17	378	13	2.6109	0.99070
18	383	12	2.5773	0.95590
19	388	12	2.5445	0.91810
20	393	11	2.5125	0.91810
21	398	11	2.4813	0.91810
22	403	11	2.4509	0.87670
23	408	10	2.4213	0.87670
24	413	10	2.3923	0.83100

Table: 2. Observation table of $CaLa_{0.7}Fe_{11.3}O_{19}$

Energy band gap of $CaLa_{0.7}Fe_{11.7}O_{19}$ hexagonal ferrite under investigation were obtained using Energy band gap apparatus (INSIF ELECTRONICS) in VMV college Nagpur University.

The energy band gap of calcium ferrite were calculated using equation (3)

$$E_g = \frac{2k * 2.3026 * \log\rho}{\frac{1}{T}}$$

where K is Boltzmann constant equal to 8.6* 10^{-5} ev/deg and 'ρ' is the resistivity of the crystal sample given by

$\square = (\rho_\circ)/(f(w/s))$ where, $\square_\circ = V/I * 2\pi S$

for function f(w/s) refer to the data table given in the calculation S is the distance between the probes , w is the thickness of pallet and V & I are the voltage and current across and through the sample.

The slope of straight line graph between log of resistivity $\log_{10}\rho$ and reciprocal of temperature $1/T * 10^3$ is found by formula Slope = AB/BC

Eg = 2.3026×103×2K×slope

Sample	Energy band gap (ev)	Resistivity at room temp	Transition temp (k)
$CaLa_{0.7}Fe_{11.7}O_{19}$	0.230	$2.39 * 10^7$	413

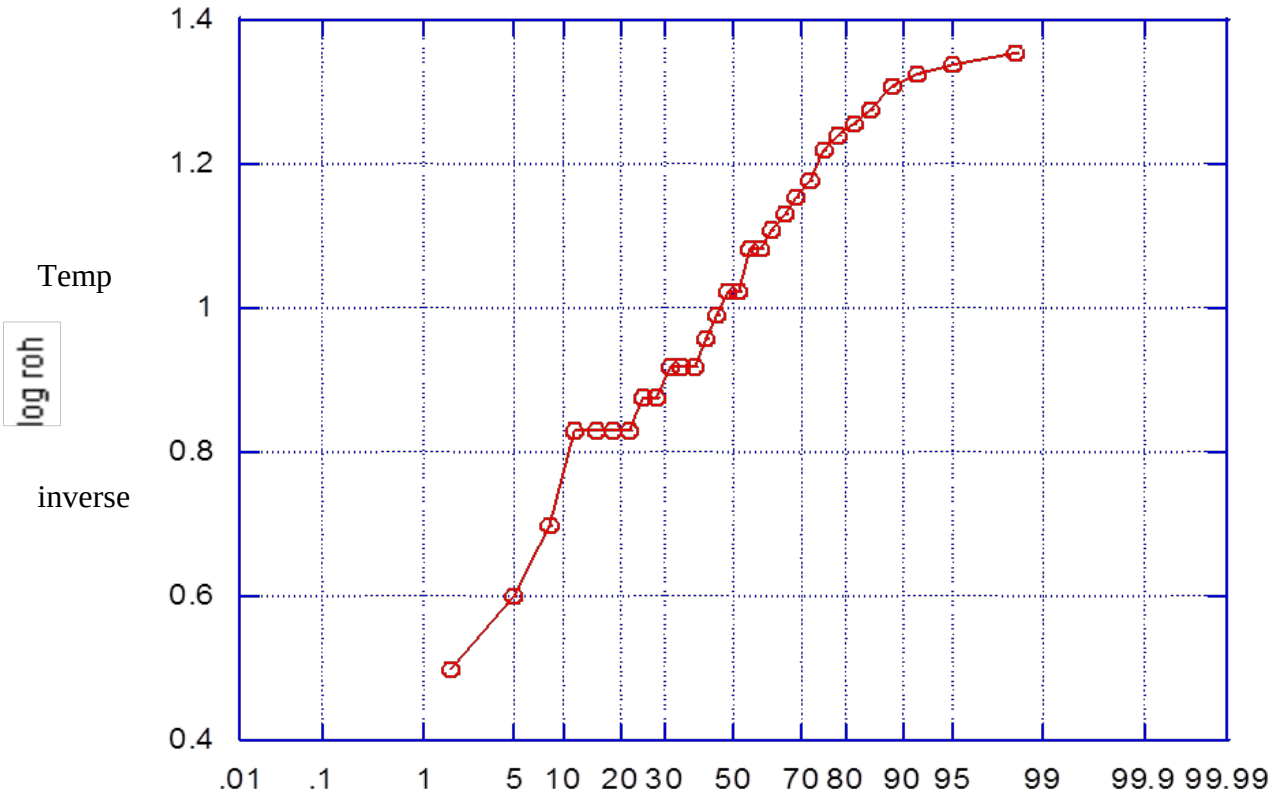


Fig 3 Electrical Resistivity plots of the sample.

Figure 4 shows the representative SEM micrographs of fractured surface of La-substituted sintered CaM The micrograph shows that La substitution reduces the particle size. La substituted calcium hexaferrite. Crystallinity index (Icry) were calculated from following relation

$$I = \frac{D(SEM)}{r(XRD)}$$

Where D is average particle size obtained from micrograph and r is average crystalline size as obtained from Scherrer equation.

There might be possibility that a small fraction of La_2O_3 Remained unsubstituted which cause pinning effect and inhibit the particle growth.

Sample	Particle size(μm)	$I_{Crystal}$ (A.U)
$CaLa_{0.7}Fe_{11.3}O_{19}$	5.62	24

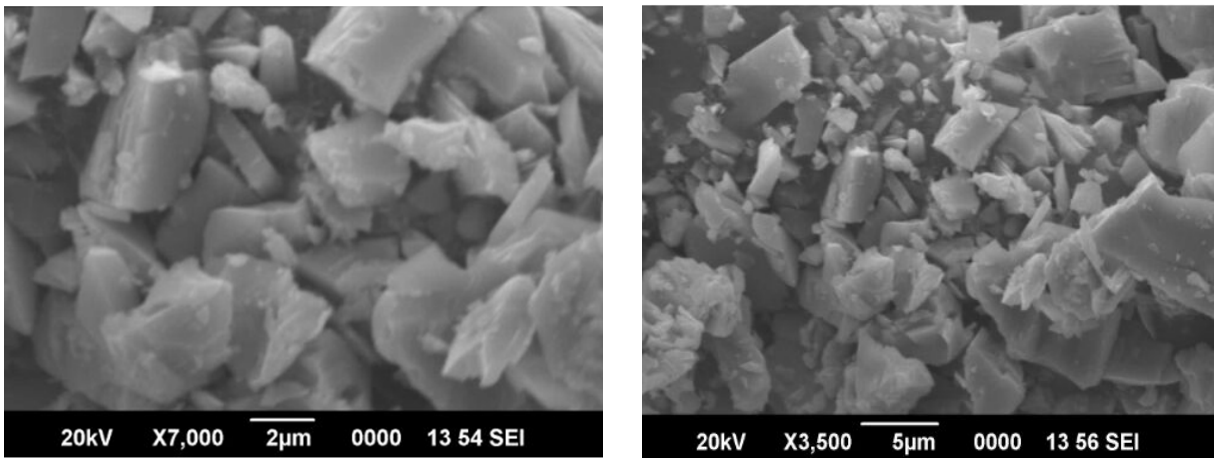


Fig 4 : SEM images of $CaLa_{0.7}Fe_{11.7}O_{19}$ (a) on 2 □m and (b) on 5 □m.

Conclusion:

Lanthanum substituted calcium M-type hexaferrite (CaM) were synthesized by standard ceramic method. The XRD confirms that calcium hexaferrite have hexagonal structure and single phase. The crystallite size is reduced due to less ionic radius of lanthanum. Lattice constant also found to decreases with substitution. The Energy band gap of La-substituted powders and sintered pellets are determined by four probe method, which shows that resistivity and energy band gap of sample decreases as the lanthanum substitution increases. particle size is determine by shcerrer formula. Substitution of lanthanum increase with increasing particle size.

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