



Structural and Electrical Characterization of La^{3+} Doped Calcium Ceramics Synthesized by Standard Ceramic Method

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Abstract:

Calcium hexaferrites substituted with lanthanum ions having general chemical formula $\text{CaLa}_x\text{Fe}_{12-x}\text{O}_{19}$ where $x = 0, 0.5, 1.0, 1.5$ and 2.0 were successfully synthesized by the standard ceramic method. The aim of the present work is to synthesize and to investigate its structural, electrical properties. The crystalline powder of substituted calcium hexaferrite with chemical composition $\text{CaLa}_x\text{Fe}_{12-x}\text{O}_{19}$, 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 'c' are 5.821 \AA and 22.212 \AA

Keyword: Magnetoplumbite, Hexaferrite, Scanning Electron Microscope, Calcium Oxide, ferric Oxide and Lanthanum oxide etc.

Introduction:

Magnetoplumbite ferrite attract more 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 $\text{MFe}_{12}\text{O}_{19}$ 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 $\text{CaFe}_{12}\text{O}_{19}$ 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 present work, literature review by many research workers with combination of La^{3+} in calcium hexaferrite and that worked is carried out on the simultaneous combinational effect of these cations, namely Ca^{2+} and La^{3+} on electric, magnetic and other related properties of the M-hexaferrite, hence formed composition chemical formula $\text{CaLa}_x\text{Fe}_{12-x}\text{O}_{19}$ was synthesized by standard ceramic method with different ions concentration [7-9].

Experimental Details:

A new series of sample are prepared with chemical formula $\text{Ca La}_x \text{Fe}_{12-x} \text{O}_{19}$ (with $x=0.5$) by standard ceramic method in proper stoichiometric proportional molar ratio. The molecular concentration x substituted cations in the chemical formula. The oxides Fe_2O_3 , La_2O_3 , CaO of AR grade were used as starting material for the synthesis of present series of compounds. The stoichiometric 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 400°C for half hours to moisture free, homogeneous, calcinations. The calcination powder were pressed into the pellet machine to form pellet at 60 kg/cm² and then sintered at 1200°C in air atmosphere for about 120 hours and slowly cooled to room temperature at the rate of 200/cm² half hours using a microprocessor controlled furnace. The synthesized pellet break with hydraulic pressure of pellet machine at 120 kg/cm². Then grinding in agate mortar to get ultra-fine powder of sample. The synthesized powder of sample again heated at 400 for 2 hours to remove impurity.

Result and Discussion:

In this present wor, an investigated ferrite sample CaLa_{0.5}Fe_{11.5}O₁₉ powder synthesized by ceramic method correspond to M-type calcium hexaferrite

structure as shown in fig(1). X-ray diffraction pattern of CaLa_{0.5}Fe_{11.5}O₁₉ hexagonal ferrite under investigation were obtained using X-ray diffractometer. The hexagonal M-structure with space group (P6₃/mmc) (No. 194), which confirms that phase belongs to magnetoplumbite(M type) indicating the crystal structure were single phase hexagonal magnetoplumbite after substitution with La³⁺ ions respectively. The lattice constant 'a' and 'c' of hexagonal calcium ferrite were calculated using equation (1)

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

Where h ,k, l are miller indices, d is interplaner distance. The lattice parameter 'a' and 'c' found to be 5.80 and 22.12 respectively.

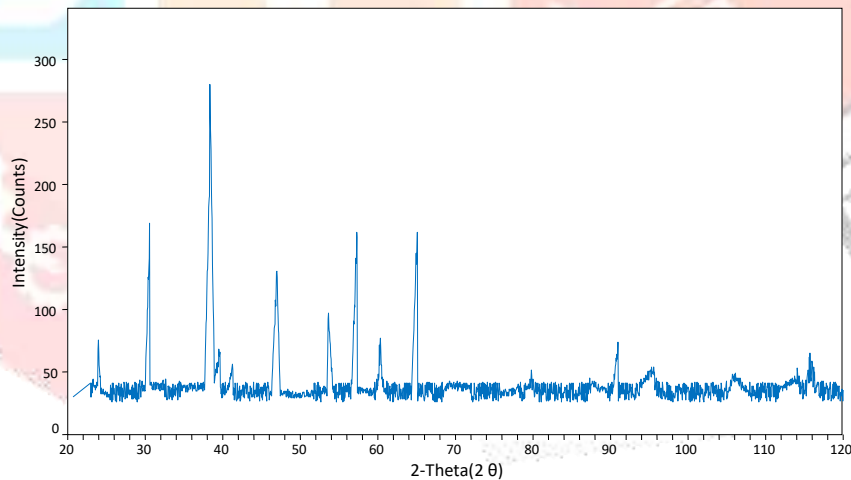


Fig 1: XRD pattern of sample Ca La_{0.5}Fe_{11.5}O₁₉

The crystallite size measurements were also carried out using the XRD data and using scherrer equation (2)

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

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 & is the wavelength (Cu α radiation equal to 0.154nm). The average particle size was found to be about 56.20 nm.

Table 1: X-ray diffraction data of compound

Lattice parameter a = 5.80 Å, c = 22.212 Å,

Particle size (D) = 56.20 nm and

Volume = 644.4240 Å³

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

6.	338	19	2.8735	1.1778
7.	343	18	2.8328	1.1555
8.	348	17	2.7932	1.1320
9.	353	16	2.7932	1.1083
10.	358	16	2.7548	1.0809
11.	363	15	2.7173	1.0229
12.	368	14	2.6455	1.0229
13.	373	14	2.6455	1.0229
14.	378	12	2.6109	0.9908
15.	383	12	2.5773	0.9559
16.	388	12	2.5445	0.9181
17.	393	11	2.5125	0.9181
18.	398	11	2.4813	0.9181
19.	403	11	2.4509	0.8767
20.	408	10	2.4213	0.8767

In electrical conductivity, the energy band gap of CaLa_{0.5}Fe_{11.5}O₁₉ hexagonal ferrite under investigation were obtained using fore prob energy band gap apparatus. The energy band gap of calcium ferrite were calculated using equation (3)

$$E_g = 2.3026 \times 10^3 \times 2K \times \text{slope} \quad \text{-----}(3)$$

where K is Boltzmann constant equal to 8.6 X 10⁻⁵ eV/deg and 'ρ' is the resistivity of the crystal sample given by $\rho = (\rho_s)/(f(w/s))$ where,

$$\rho_s = V/I \times 2 \pi S \quad \text{-----} (4)$$

for function f(w/s) refer to the data table given in the calculation of 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.[9]

Table 2. Electrical resistivity of CaLa_{0.5}Fe_{11.5}O₁₉

Sr. No	Temp (K)	Voltage (V)	Log ρ	$\frac{1}{T} \times 10^3$
1.	313	27	3.1940	1.3081
2.	318	25	3.0953	1.2747
3.	323	24	3.0487	1.5257
4.	328	23	3.0030	1.2384
5.	333	20	2.9158	1.2192

The slope of straight line graph between log of resistivity log₁₀ρ and reciprocal of temperature 1/T x 10³ is found by formula Slope = AB/BC

compound	Energy band gap (ev)	Resistivity at room temp	Transition temp (k)
CaLa _{0.5} Fe _{11.5} O ₁₉	0.230	2.39 x 10 ⁷	413

Figure 3 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 (I_{cry}) were calculated from following relation

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

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 La₂O₃ Remained unsubstituted which cause pinning effect and inhibit the particle growth.

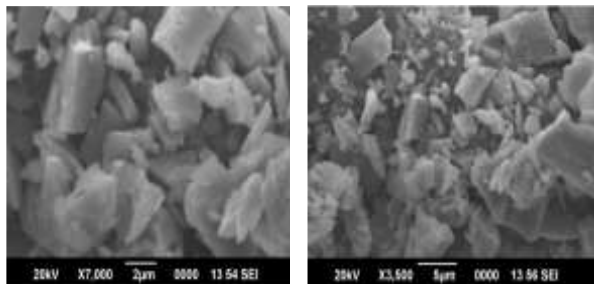


Fig.3: SEM of Sample $\text{CaLa}_{0.5}\text{Fe}_{11.5}\text{O}_{19}$

Particle size(nm) - 56.2 nm and

$I_{\text{Crystal}} = 24$ (A.U)

Conclusion:

In this present work, Lanthanum substituted calcium M-type hexaferrite (CaM) were synthesized by standard ceramic method was checked the formation of ferrite containing La^{+3} ions along with Fe^{+3} ions. The values of lattice parameters 'a' and 'c' confirms the formation of hexagonal unit cell.. 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 Lanthanum substitution. All these compounds have M-structure through the site distribution changes. No changes occur in the charge distribution, but the site distribution is change due to strichiometric changes in these compounds. By carried out the electrical study, the Energy band gap of La-substituted powder by four probe method, which shows that resistivity and energy band gap of compound are decreases as the lanthanum substitution increases. Particle size is determined by shcerrer formula which shows that the substitution of lanthanum increase with increasing particle size.

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