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Frequency and Compositional Variation of Dielectric Parameters for La substituted M-Hexaferrite

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Abstract : *In the present investigation Polycrystalline compounds with chemical formula* $\mathbf{Ca_xSr_yBa_{1-x-y}Fe_{12-z}La_zO_{19}}$ *with (x = 0.1, 0.25, 0.4; z = 0.1, 0.2, 0.3 & y = 0.2) were synthesized by high temperature solid state diffusion reactions. The dielectric constant (ε') dielectric loss tangent (tanδ) and complex dielectric constant* (ε^*) *of the compounds were studied in the frequency range of 10Hz –2MHz. The dielectric parameters for the compound shows normal dielectric behavior as observed in hexaferrites. The study of frequency dependence dielectric loss tangent (tanδ) was found to be giving a peak around certain frequency range (16 to 35Hz) for present compounds. The dielectric constant for these mixed ferrites was found approximately inversely proportional to the square root of their respective resistivity. The frequency variation of ε' and tanδ is explained by Koop's phenomenological theory and hopping frequency of electrons between* Fe^{2+} *and* Fe^{3+} *on octahedral sites.*

Keywords: *Dielectric Constant, La M- hexaferrite; Loss tangent, Maxwell-Wagner theory*

I. Introduction

The reduction of military platform radar cross-sections has been a major challenge since the Second World War. Possible solutions for reducing the radar signatures of targets include the design of objects with small cross sections or the use of radar absorbing materials (RAMs) for covering the metallic surface. The main problem in designing a magnetic absorber is related to the choice of the material, preferentially with control over some magnetic and dielectric properties, such as permeability (μ), permittivity (ε) and the dissipation factor (tanδ) [1-5]. The use of hexaferrites as RAMs has been widely cited in literature during the last two decades. In the same way, individual or simultaneous substitution of Ba^{2+} ions by La^{3+} can also change the magnetic and dielectric behavior of these materials, allowing their application as RAMs at various frequencies [3][4].

Ferrimagnetic oxides or Ferrites as they are usually called, are ceramic ferromagnetic materials which are dark brown or gray in appearance and very hard and brittle in character. In 1952, a new class of ferrites having permanent magnetic properties was discovered. They are called hexagonal ferrites with the formula MFe12O19 where M is usually barium Ba, strontium Sr, Calcium Ca or Lead Pb. The crystal structure is complex but it can be described as hexagonal with a unique c axis. The M type hexaferrites are very good dielectric materials and very useful for microwave applications. The effect of frequency, temperature and composition on the dielectric behavior offers much valuable information about the localized electric charge carriers which in turn helps to elucidate the mechanisms responsible for charge transport phenomena and dielectric behavior. Various researchers have studied the dielectric and electrical properties of different hexaferrites[6][7]. However, investigations of the substitution effect on the dielectric properties of combined substitution of Ca, Sr, & Ba (CSB) hexaferrite are rare. We selected La^{3+} ion as partial substitution of Fe^{3+} because among the lanthenoids La^{3+} has the largest solubility limit in Ba and Sr hexagonal ferrite as observed by C doroftet & E Rezelscue et al. [8]. In the same way, individual or simultaneous substitution of Ba^{2+} ions by La^{3+} can also change the magnetic and dielectric behavior of these materials, allowing their application as RAMs at various frequencies [3][4]. Moreover, hexaferrites are of interest not only for their magnetic behavior but also for the dielectric polarization inherent in their structure.

In the process of preparation of ferrites in M type hexaferrites, when the ferrite powder is sintered, the divalent iron ions formed in the bulk lead to high-conductivity grains separated by low conductivity layers, so that they behave as inhomogeneous dielectric materials. The dielectric behavior observed in ferrites is attributed to Maxwell–Wagner polarization [9][10].

As Ca belongs to same group & has same electronic configurations that of Sr and Ba but substitution of trivalent La is associated with a valence change of one Fe^{3+} per formula unit to Fe^{2+}. By taking the footprints of above authors, we devoted present work to improve the dielectric properties M-type hexaferrite, Therefore study of electric and dielectric parameter of Ca-Sr-La doped hexaferrite is focus of the present work.

II. Experimental Detail

The synthesis of polycrystalline compounds with chemical formula $\mathbf{Ca_xSr_yBa_{1-x-y}Fe_{12-z}La_zO_{19}}$ (CSBFLO) (with x = 0.1, 0.25, 0.4; z = 0.1,0.2,0.3 & y = 0.2) was done by high temperature solid state diffusion reactions. The stoichiometric mixtures of AR grade oxides Fe_2O_3, La_2O_3, CaO, SrO, and BaO were grounded together in agate mortar in an acetone medium. The synthesis was divided into two steps:

(i) calcinations at 500 K for 8 h in air followed by mixing and rigorous grinding, and preparation of pellets, and
(ii) thermal treatment at 1157 K for 72 hr.

The XRD patterns [FIG.1a, 1b, 1c] were taken using CuKα-radiation with Ni as a filter to confirm the formation of compound. The patterns were indexed to predominant hexagonal magnetoplumbite structure [4], which belongs to the space group P63/mmc (No.194). The lattice parameters and X-ray densities of the compounds were computed from XRD analysis. The bulk densities were determined by measuring the mass and bulk volume of compounds from its physical dimensions from these the porosities for compounds were calculated.

Dielectric parameters were measured from 10 Hz–2 MHz using a digital LCR-Q meter. The value of the dielectric constant (ε') of the compounds is calculated using the formula:

$\varepsilon' = c.t / \varepsilon_0 A$

where,

ε_0 = Permittivity of free space equal to 8.854×10^{-12} F/m;
C = capacitance of the specimen in cm,
t = thickness of the specimen in cm; and
A= area of the specimen in cm^2.

The loss tangent (tan δ) is calculated using the relation:

$\tan \delta = Df$,

where,

D= the observed dissipation factor,
f = frequency of the applied electric field.

The complex dielectric constant (ε^*) of the samples is given by

$\varepsilon^* = \varepsilon' + j\,\varepsilon''$

The dc electrical conductivity and Seeback-coefficent of the compounds over a range of temperature were measured by the standard two-probe method.

III. Result and Discussion

3.1 Structural Analysis

The lattice parameters of the mixed ferrites were calculated are given in Table 1. It is observed that the values of lattice parameter *a* varies from 5.8959 to 5.8278Å, where as lattice parameter *c* values varies from 22.7442 to 23.0741Å. No specific trend in the variation of lattice parameters was observed even though the ratio of *a/c* has remained fairly constant, Similar behavior has been reported in La^{3+} substituted M-type strontium ferrites [11]. Hence this behavior may be attributed to the presence of secondary phase (α-Fe_2O_3) along with the main phase due to lower solubility and incomplete replacement between Ba and Ca ions.

3.2 Variation of Dielectric constant (ε')

The composition wise explanation to observed values of dielectric constant of the compounds at room temperature is explained with the concept of dielectric polarization. It was observed that ε' increases with increase in the concentration Ca and La in the compounds [Table2]. It was also observed that the composition $Ca_{0.4}Sr_{0.2}Ba_{0.4}Fe_{11.7}La_{0.3}O_{19}$ has the dielectric constant with an average value of 15,000 over the entire frequency range. This high value can be explained on the basis of the fact that it could have maximum number of ferrous ions whose exchange $Fe^{2+} \leftrightarrow Fe^{3+}$ gives rise to a maximum dielectric polarization. As the amount of La^{3+} increases in the CSBFLO hexaferrite, it affects the solubility factor highly, which associates with valancy change of Fe^{3+} to Fe^{2+} on 2a or $4f_2$ octahedral site [7][12].

The activation energy and the average resistivity were determined from the DC electrical studies. The values of resistivity for the compounds decrease with increasing Ca and La concentration. It reveals that the variation of resistivity and dielectric constant of CSBFLO hexaferrites runs parallel to the variation of available ferrous ions on octahedral sites. Thus, it is the number of ferrous ions on the octahedral sites that plays a dominant role in the processes of conduction as well as dielectric polarization [11]. The low values of activation energy for the present compounds which are in the range 0.2 to 0.3 eV also supports to high conduction phenomenon [Table2].

The mechanism of dielectric polarization also depends on the concept of interfacial polarizations at interfaces of grains and grain boundaries caused by a non-uniform distribution of oxygen ions during sintering [13]. An oxygen ion possesses two extra loosely bound electrons. Therefore, polarization can be produced even by a small applied electric field. and hence the observed high values of dielectric constant which are in the range 10^3 to 10^4 [Table 2] can be explained on the basis of this explanation. This is dually supported by high conductivity and negative value of Seeback coefficient [FIG.3].

To explain the polarization in dielectric constant in ferrites, Koops [14] has proposed a general model for heterogeneous dielectrics consisting of well-conducting grains separated by poorly conducting grain boundaries as found in polycrystalline ferrites. Based on this model, certain relations have been derived which depict that an increase in frequency causes a decrease in dielectric constant as it is observed in the present compounds of CSBFLO hexaferrites [FIG.4]. A physical interpretation of polarization can be done on the basis of hopping of electrons between Fe^{3+} to Fe^{2+} ions. The electrons are displaced slightly by the applied electric field and polarization is produced. But the electrons can respond to the changes in applied electric field as long as the time required for hopping is less than half the period of the alternating field [15].

3.3 Variation of the dielectric loss tangent (tanδ)

The plot of dielectric loss tangent (tanδ) and frequency, with separately for lower frequency range and higher frequency range is shown in fig. 2a & 2b. it can be seen that ‘tanδ’ show maximum peak for frequency range 16 to 35 Hz for respective compounds. The corresponding peak point in the graph is explained by resonance phenomenon between hopping frequency and external frequency [12][16]. Which explain the high value of dielectric loss tangent at lower frequency region but remains independent to higher frequency region. And as explained above the conduction mechanism in n-type ferrite is considered as due to hopping of electrons between Fe^{2+} and Fe^{3+} situated at octahedral sites. A similar variation of tanδ vs. frequency was also observed by Murthy et.al [11].

3.4. Relationship between the dielectric constant (ε') and the resistivity (ρ)

The analysis of dielectric constant for the compounds reveals that value of dielectric constant is approximately inversely proportional to square root of resistivity [17]. The values of ε' and resistivity ρ for mixed CSBLF mixed hexaferrites are given in Table 2. This reflects that the product $(\varepsilon' \times \sqrt{\rho})$ remains fairly constant. Hudson [18] showed that the dielectric measurements in ferrites are generally reflected in the resistivity measurements, where materials with low resistivity exhibiting higher value dielectric constant and vice versa. It is found that the result holds good in the case of CSBLF mixed hexaferrites prepared in present work [9][14].

IV. Conclusions

This study reveals, on substitution of ions like Sr^{2+} and La^{3+} within M-type hexaferrites measured dielectric parameters shows higher value of dielectric constant with good support to Maxwell–Wagner’s Bi-layer model. According to this model, in lower frequency region dielectric polarization is high and becomes fairly independent in higher frequency region. Also results showed a strong correlation between the conduction mechanism and the dielectric behavior as reported by Iwauchi et.al [17]. As the present compounds are having high value of dielectric constant (10^3 to 10^4), it can be used as one of the possible material for RAM’s.

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Table -1 Lattice Parameters "a", "c", X-ray Density (D_X), Mass (bulk) Density (D_M), Porosity (P) Molecular weight and volume of CaxSryBa1$_{-x-y}$Fe$_{12-z}$La$_z$O$_{19}$

$Ca_xSr_yBa_{1-x-y}Fe_{12-z}La_zO19$			a(Å)	c (Å)	a / c	$D_x \times 10^3$ (kg/m³)	$D_M \times 10^3$ (kg/m³)	P	Volume	Mol.wt.(gm)
x	y	z								
0.1	0.2	0.1	5.8569	23.107	0.25347	5.32241	4.13344	0.22339	686.45111	1100.0903
0.25	0.2	0.2	5.8278	22.7442	0.25623	5.43026	3.96327	0.27015	668.97575	1093.809
0.4	0.2	0.3	5.8959	23.0741	0.25552	5.19965	3.97363	0.23579	694.63301	1087.5277

Table 2 Variation of dielectric constant ε', tanδ , ε^* and resistivity ρ with composition (x, y & z)

$Ca_xSr_yBa_{1-x-y}Fe_{12-z}La_zO19$			$\varepsilon' \times 10^3$	ρ(Ω m)	$\rho^{1/2}$ ($\Omega^{1/2}.m^{1/2}$)	ε' x $\rho^{1/2}$ x 10^3($\Omega^{1/2}.m^{1/2}$)	(tanδ) x10^4	ε^* x10^3	E_A (eV)
X	y	Z							
0.1	0.2	0.1	7.00	54.41	7.37	51.59	14.6	10.26	0.34
0.25	0.2	0.2	8.56	5.881	2.42	20.71	18.4	15.82	0.279
0.4	0.2	0.3	15.32	3.153	1.77	27.20	15.9	48.303	0.31

FiG. 2(a) & 2(b) representing tangent loss (tanδ) Vs Frequency for lower range (0-400 Hz) and higher (0-2 MHz)

FIG. 2(a)

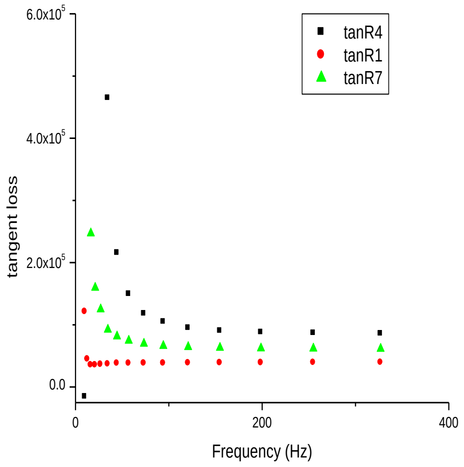
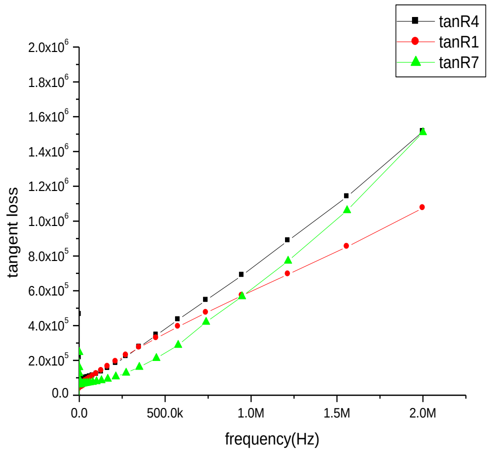
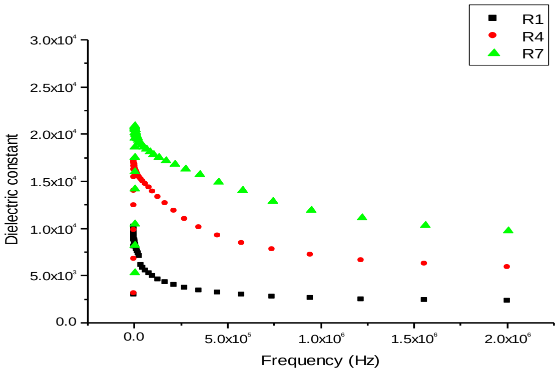


FIG. 2(b)





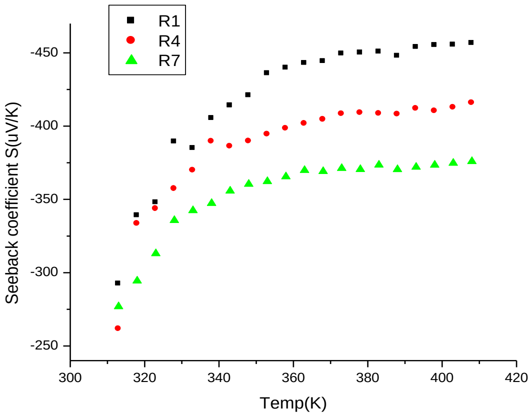


FIG.4 Dielectric constant (ε') Vs Frequency **FIG. 3 Seeback coefficient Vs Temperature**

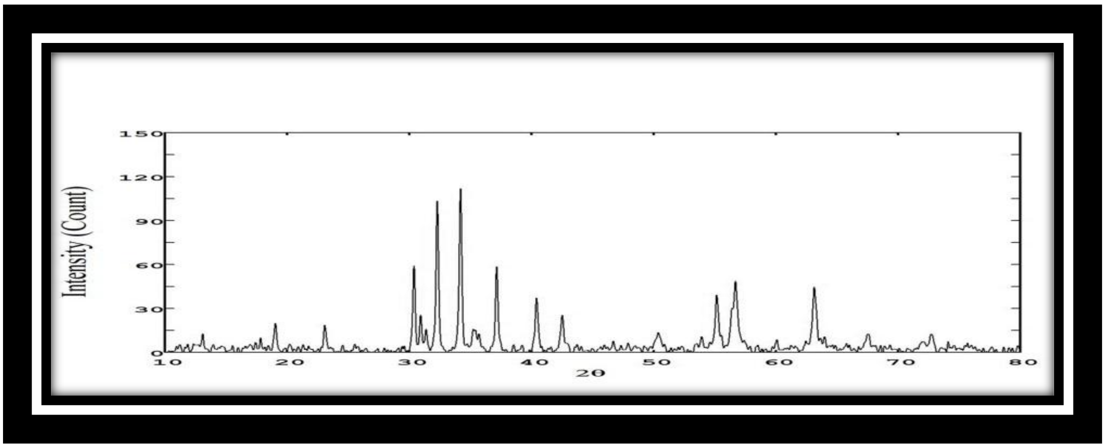


Fig.1 (a) XRD pattern for Sample R1

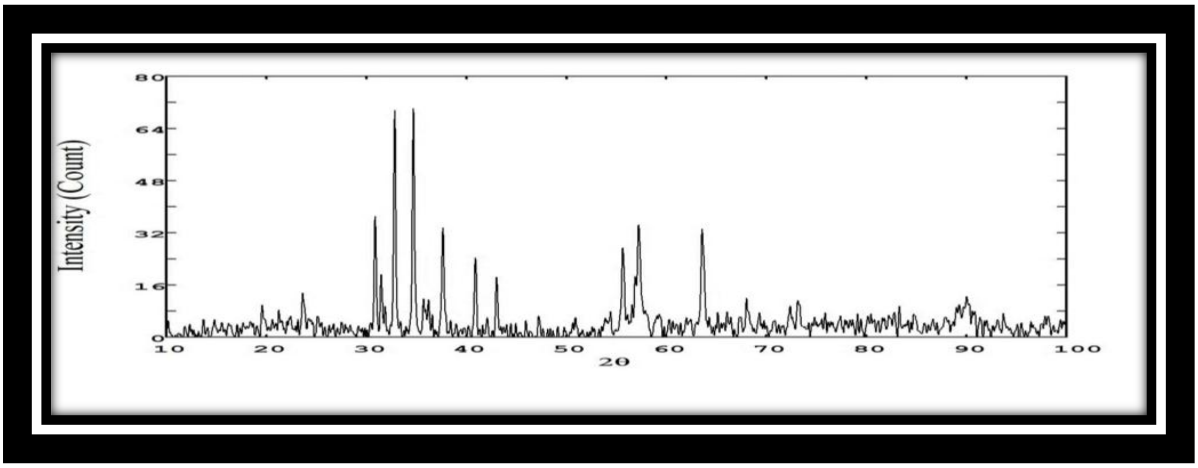


Fig.1 (b) XRD pattern for Sample R5

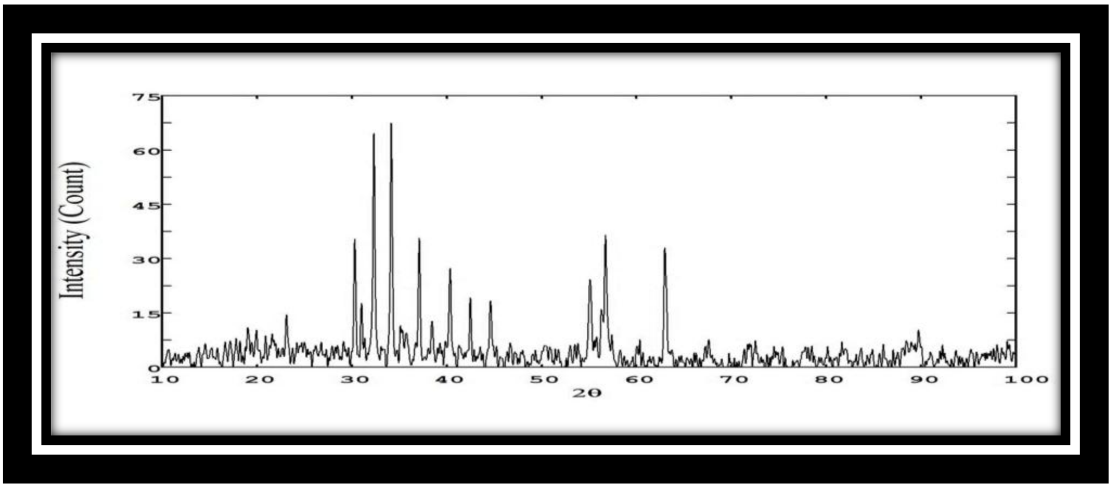


Fig.1 (C) XRD pattern for Sample R7