

High Frequency Dielectric Behavior of Rare Earth Substituted Sr-M Hexaferrite

S. Bindra Narang^a, Anterpreet Singh^b and Kulwant Singh^b

^aDepartment of Electronics Technology, Guru Nanak Dev University, Amritsar, India

^bDepartment of Physics, Guru Nanak Dev University, Amritsar, India

Strontium hexaferrites of a structural formula $Sr_{1-x}RE_xFe_{12}O_{19}$, where $RE=La^{3+}$, Nd^{3+} and Sm^{3+} with ($x=0$ to 0.30) were prepared by a standard ceramic technique. The lattice constants, density, porosity, dielectric constant and dielectric loss tangent were studied on a series of rare earth substituted strontium hexaferrites. The dielectric constant and dielectric loss tangent were measured in the frequency range of 0.3 GHz to 3.0 GHz at room temperature. The dielectric constant decreased with increasing frequency for all the three series. This behavior of dielectric properties with frequency has been explained with the Maxwell-Wagner type interfacial polarization in agreement with the Koops phenomenological theory. The substitution of rare earth ions into $SrFe_{12}O_{19}$ increases the value of the dielectric constant. This increase in dielectric constant could be due to the electronic exchange between $Fe^{2+} \leftrightarrow Fe^{3+}$ and results in a local displacement determining the polarization of the ferrites. For these ferrite samples the Curie temperature decreases as rare earth ions substitution increases.

Key words: Hexagonal ferrites, Lattice constants, Dielectric constant, Dielectric loss tangent, Curie temperature.

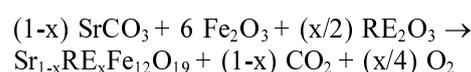
Introduction

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. They are prepared by various techniques. These include a chemical coprecipitation method [1], glass crystallization [2], an organic resin method [3], a sol-gel method [4] and a ceramic process [5]. In 1952, a new class of ferrites having permanent magnetic properties was discovered. They are called hexagonal ferrites with the formula $MFe_{12}O_{19}$ 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, which is the easy axis of magnetization in the basic structure. Several studies of the magnetic properties for hexagonal ferrites have been reported [6-9]. Apart from magnetic properties, electrical properties of these ferrites are very sensitive to the processing conditions and type of substitution. Also we know, the electrical properties of ferrite are derived from many physical and chemical characteristics, and the effect of frequency, temperature and composition on the dielectric behavior offer 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 [10-13]. However, investigations of the substitutional effect on the dielectric properties of strontium ferrite are rare. Moreover, hexaferrites are of interest not only for their dielectric behavior but also for the electrical polarization inherent in their structure. In this study, a systematic investigation of the dielectric behavior and possible polarization mechanisms of rare earth substituted Sr-M hexaferrites have been carried out and results are presented here.

Experimental

A series of $Sr_{1-x}RE_xFe_{12}O_{19}$ samples with different substitution molar ratios were prepared by a standard ceramic processing technique. High purity materials $SrCO_3$, RE_2O_3 and Fe_2O_3 were used as starting raw materials and were mixed together in the appropriate molar ratios, calculated from the following chemical reaction:



where, x varies from 0 to 0.30 with an increment of 0.10. Details of the method of preparation have been given in an earlier publication [14]. The dielectric measurements were made using a Network Analyzer from Agilent Technologies, 8714ET and were carried out as a function of frequency in the range 0.3 GHz to 3.0 GHz at room temperature. The magnetic properties of the samples were determined by a Vibrating Sample Magnetometer. The Curie temperature T_c (K) of all the samples was determined by the gravity method [15].

*Corresponding author:
Tel : +91-183-2256203
Fax: +91-183-2258820
E-mail: sukhleen2@yahoo.com

Results and Discussion

Lattice Constants

X-ray diffraction patterns of $\text{Sr}_{1-x}\text{RE}_x\text{Fe}_{12}\text{O}_{19}$ hexagonal ferrites of three series under investigation have been obtained using Cu-K α radiation. The lattice constants 'a' and 'c' were calculated from the following equation:

$$d_{(hkl)} = \left(\frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \right)^{-\frac{1}{2}} \quad (1)$$

The variation of lattice constant 'a' and 'c' with composition (x) for three series prepared with RE=La³⁺, Nd³⁺ and Sm³⁺ are shown in the Figs. 1 and 2 respectively. It was observed that 'a' and 'c' both decrease regularly with increasing substituted amount of rare earth ions for the three series. The observed variation in the lattice constants can be explained on the basis of the relative ionic radii of Sr²⁺ ions and RE³⁺ ions, which are (1.27 Å) and (1.22 Å, 1.16 Å and 1.13 Å) for La³⁺, Nd³⁺ and Sm³⁺ respectively [16]. Since RE³⁺ ions have ionic radii less than the ionic radii of Sr²⁺ ions, the replacement of Sr²⁺ ion by RE³⁺ ions results in the decrease of the unit cell dimensions of the hexagonal lattice. The larger decrease in lattice constants 'a' and 'c' for Sm³⁺ ions substituted hexaferrites as compared to those for Nd³⁺ ions and La³⁺ ions substituted ones is attributed to the smaller ionic radii of Sm³⁺ ions than those of Nd³⁺ ions and La³⁺ ions.

Density and Porosity

The X-ray density D_x was calculated by using the known formula:

$$D_x = \frac{2nM}{\sqrt{3}N_a a^2 c} \quad (2)$$

Here n is the number of molecules per unit cell, N_a is Avogadro's number per gram mole, 'a' and 'c' are the lattice constants obtained from X-ray diffraction analysis and M is the molecular weight of the sample.

The porosity of the samples was calculated using the relation:

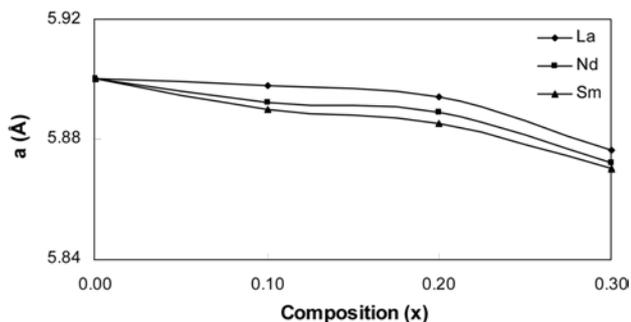


Fig. 1. Variation of the lattice constant 'a' with composition (x) for the three series.

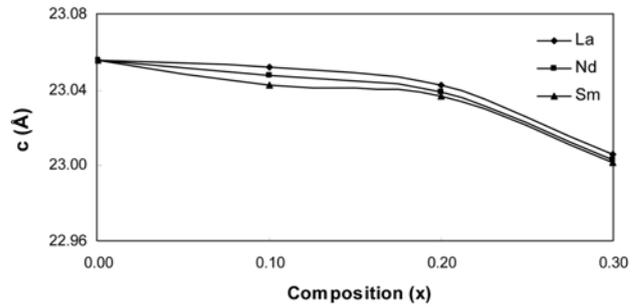


Fig. 2. Variation of the lattice constant 'c' with composition (x) for the three series.

Table 1. X-ray density D_x , Observed density D and Porosity P (%) of $\text{Sr}_{1-x}\text{RE}_x\text{Fe}_{12}\text{O}_{19}$ where RE=La³⁺, Nd³⁺ and Sm³⁺ with (x=0 to 0.30)

RE ³⁺	Composition (x)	D (g/cm ³)	D_x (g/cm ³)	P (%)
La	0	4.20	5.07	17.03
	0.10	4.27	5.10	16.20
	0.20	4.31	5.13	16.02
	0.30	4.37	5.20	15.80
Nd	0.10	4.28	5.11	16.26
	0.20	4.32	5.15	16.03
	0.30	4.39	5.21	15.81
Sm	0.10	4.28	5.12	16.31
	0.20	4.33	5.16	16.07
	0.30	4.39	5.22	15.97

$$P = \left(\frac{D_x - D}{D_x} \right) \times 100\% \quad (3)$$

The compositional dependence of the apparent density D, X-ray density D_x and porosity P is shown in Table 1 for the three series. The increase in density with rare earth content can be attributed to the atomic weight and density of the rare earths (138.9, 6.15 g/cm³; 144.2, 7.01 g/cm³ and 150.3, 7.52 g/cm³) for La³⁺, Nd³⁺ and Sm³⁺ respectively, which are higher than those of Sr (87.6, 2.54 g/cm³). The replacement of Sr²⁺ by RE³⁺ ions in the hexagonal structure leads to a variation in the bonding and consequently interatomic distance and density. The oxygen ions which diffuse through the material during sintering also accelerate the densification of the material. The apparent density of the same sample reflects the same general behavior of the theoretical density D_x . The X-ray density is higher than the apparent density value due to the existence of pores which depends on the sintering condition. This was determined by the Archimedes principle-based method. The porosity decreases as the rare earth content increases reflecting the opposite behavior of density. The higher values of X-ray densities for Sm³⁺ ions substituted hexaferrites as compared to those for Nd³⁺ ions and La³⁺ ions substituted ones may be due to the lower value of lattice constants in the former type of substitution.

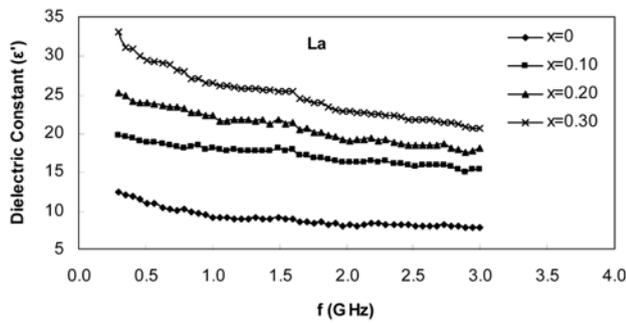


Fig. 3. Variation of the dielectric constant (ϵ') with frequency for the $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12}\text{O}_{19}$ series.

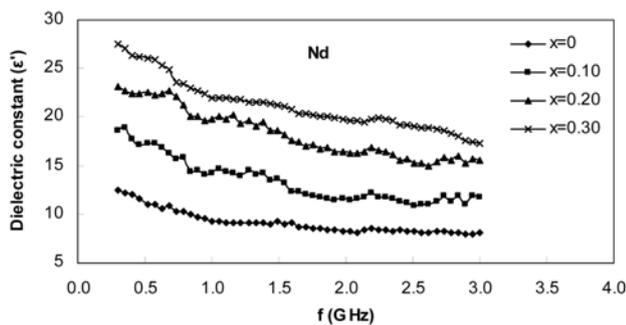


Fig. 4. Variation of the dielectric constant (ϵ') with frequency for the $\text{Sr}_{1-x}\text{Nd}_x\text{Fe}_{12}\text{O}_{19}$ series.

Frequency variation of dielectric constant

The variation of dielectric constant (ϵ') with frequency at room temperature for three series prepared with $\text{RE}=\text{La}^{3+}$, Nd^{3+} and Sm^{3+} are shown in the Figs. 3, 4 and 5 respectively. It is observed that the value of dielectric constant also decreases with increasing frequency in all the three series. This behavior is normal ferrimagnetic behavior and has also been observed by several investigators [17-20]. The variation of the dielectric constant with frequency reveals the dispersion due to Maxwell-Wagner type interfacial polarization in agreement with the Koops phenomenological theory [17, 21]. According to these models the dielectric structure is supposed to be composed of the fairly well conducting ferrite grains, separated by a second thin layer of grain boundaries of poorly conducting substances. These grain boundaries could be formed during the sintering process due to the superficial reduction or oxidation of crystallites in the porous materials as a result of their direct contact with the firing atmosphere [22].

Introduction of rare earth ions to a $\text{SrFe}_{12}\text{O}_{19}$ ferrite increases the value of the dielectric constant. The dielectric constant is increased due to the electronic exchange between $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ resulting in local displacement of charges to determine the polarization of the ferrites. It is evident from Figs. 3, 4 and 5 that the composition $x=0.30$ shows the maximum value of the dielectric constant for all the three series. Such a high value can be explained on the basis that it has the

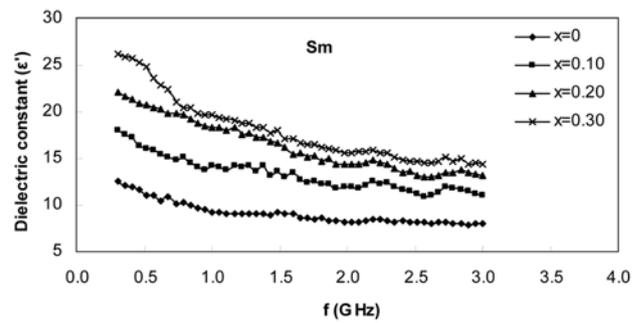


Fig. 5. Variation of the dielectric constant (ϵ') with frequency for the $\text{Sr}_{1-x}\text{Sm}_x\text{Fe}_{12}\text{O}_{19}$ series.

maximum number of ferrous ions which are involved in the phenomenon of exchange $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ giving rise to this maximum dielectric polarization. Both the dielectric constant and electrical conductivity are basically electrical properties and it has been recognized that the same mechanism viz. exchange of electrons between Fe^{2+} and Fe^{3+} is responsible for both the phenomena. A strong correlation between the conduction mechanism and the dielectric behavior of ferrites has been established by Iwauchi [23] and Rezlescu and Rezlescu [24]. It has been concluded that the electron exchange between $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ results in the local displacement of charges, which is responsible for polarization in ferrites. The magnitude of the exchange, which also controls the conduction in ferrites, depends upon the concentration of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ion pairs present on the B sites (octahedral sites). For the same substitutional content, the dielectric constant (ϵ') of La-substituted strontium hexaferrites is larger than those of Nd-doped and Sm-doped hexaferrites due to the larger concentration of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ion pairs present on the octahedral sites.

Frequency variation of dielectric loss tangent

The variation of dielectric loss tangent ($\tan \delta$) with frequency at room temperature for three series prepared with $\text{RE}=\text{La}^{3+}$, Nd^{3+} and Sm^{3+} are shown in the Figs. 6, 7 and 8 respectively. The value of dielectric loss tangent decreases monotonically with increasing frequency for all three series. Dielectric loss in ferrites is considered to originate from two mechanisms: electron hopping and charged defect dipoles. The former contributes to the dielectric loss mainly in the low frequency range. In the high frequency range, the dielectric loss mainly results from the response of defect dipoles to the field. These dipoles in ferrites are formed due to the change of the cation state, such as $\text{Fe}^{3+}/\text{Fe}^{2+}$, during the sintering process. The relaxation of dipoles under an electric field is decreased with increasing frequency ultimately resulting in a decrease in the dielectric loss in the high frequency range. The minimum loss has been observed in the $\text{RE}=\text{Sm}$ series. This may be attributed to the ionic radius size of the Sm ions substituted for the Sr sites. The ionic radius of Sm ions

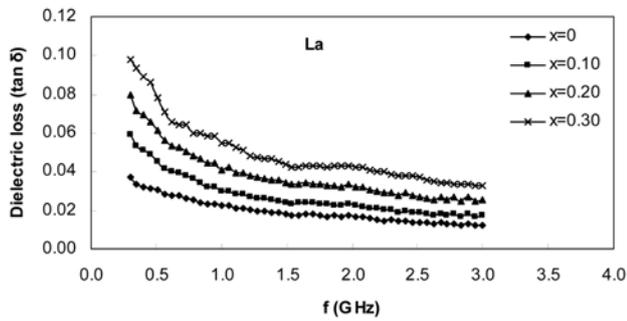


Fig. 6. Variation of the dielectric loss ($\tan \delta$) with frequency for the $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12}\text{O}_{19}$ series.

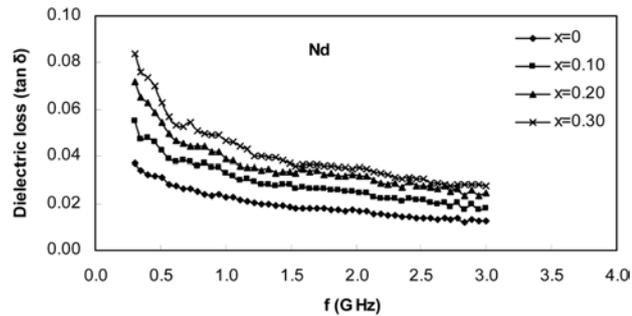


Fig. 7. Variation of the dielectric loss ($\tan \delta$) with frequency for the $\text{Sr}_{1-x}\text{Nd}_x\text{Fe}_{12}\text{O}_{19}$ series.

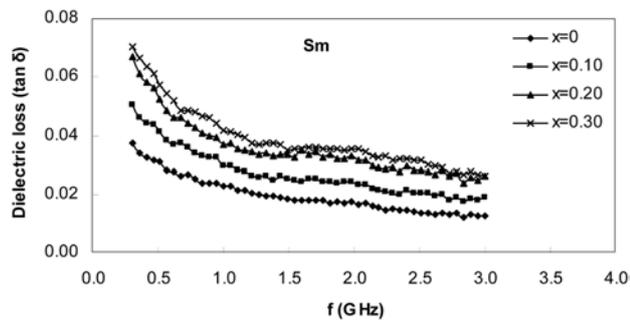


Fig. 8. Variation of the dielectric loss ($\tan \delta$) with frequency for the $\text{Sr}_{1-x}\text{Sm}_x\text{Fe}_{12}\text{O}_{19}$ series.

is the smallest of the three rare-earth ions used for substitution. Since the atomic size of the Lanthanides decreases with increasing atomic number, due to the smaller ionic radius of Sm ions, they will diffuse well into most of the Sr sites and vacancies leaving very few defects for the generation of an absorption current which results in the dielectric loss.

Magnetic Measurements

To ascertain the basic nature of strontium ferrite all the samples of the different series were characterized for their magnetic behaviour by a Vibrating Sample Magnetometer (VSM). For the samples M-H hysteresis curves were obtained from VSM and from them the saturation magnetic moment, retentivity & coercivity were determined. In the general magnetic moment ranges from 59 to 70 emu/g, retentivity in the range 23

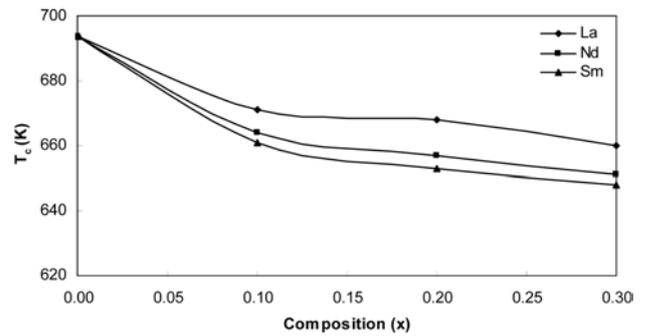


Fig. 9. Variation of the Curie temperature with composition (x) for the three series.

to 29 emu/g and the coercivity varied between 229 to 266 kA/m for all the samples confirming the good quality of samples.

Curie temperature

Figure 9 shows the variation of the Curie temperature T_c (K) with composition for all the series. It shows that the value of the Curie temperature T_c (K) decreases with increasing RE content in each case. This trend can be explained on the basis of the number of magnetic ions present in the two sub-lattices and their mutual contraction. As Fe^{3+} ions are gradually replaced by RE ions, the number of magnetic ions begins to decrease at both sites, thus leading to a decrease of AB exchange interaction of the type $\text{Fe}^{3+}\text{-O}^{2-}\text{-Fe}^{3+}$. As the Curie temperature T_c (K) is determined by the overall strength of the exchange interactions, the weakening of exchange interactions results in a decrease of the Curie temperature as the concentration of RE ions is increased [8]. Also the exchange interactions between different magnetic ions are dependent on the concentration of these ions and their magnetic moments. It is therefore expected that a greater amount of energy will be required to offset the effects of exchange interactions in the material having a larger number of magnetic ions. As the magnetic moment of La^{3+} , Nd^{3+} and Sm^{3+} ions are $2.78 \mu_B$, $1.06 \mu_B$ and $0.67 \mu_B$ respectively compared to the magnetic moment of $10 \mu_B$ for the two Fe^{3+} ions, the replacement of Fe^{3+} ions by La^{3+} , Nd^{3+} and Sm^{3+} ions is likely to decrease the Curie temperature. However due to the larger magnetic moment of La^{3+} ions, the values of the Curie temperature for Sr-La ferrites are expected to be more than those for Sr-Nd and Sr-Sm ferrites.

Conclusions

In M-type hexagonal ferrites $\text{Sr}_{1-x}\text{RE}_x\text{Fe}_{12}\text{O}_{19}$, where $\text{RE}=\text{La}^{3+}$, Nd^{3+} and Sm^{3+} with ($x=0$ to 0.30) prepared by a ceramic technique, the dielectric constant and loss tangent both decrease with increasing frequency, which agrees well with the Maxwell-Wagner double layer model. Out of the three series prepared, La-substituted

strontium hexaferrites had the greater dielectric constant (ϵ') and dielectric tangent loss ($\tan \delta$). The Curie temperature decreases as the RE-ions substitution increases.

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