

# ELECTRIC PROPERTIES OF RARE EARTH DOPED STRONTIUM M-TYPE HEXAGONAL FERRITES

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## ABSTRACT

The Seebeck Coefficient for the strontium ferrites  $Sr_{1-x}RE_xFe_{12}O_{19}$  (where  $RE = Dy$ ,  $x = 0.0, 0.10, 0.20$  and  $0.30$ ), which have been prepared by employing the ceramic technique, were studied in the temperature range 313-473K. The value of thermoelectric power seems to increase with increasing temperature where as the AC conductivity has been observed to be independent of frequency at high temperatures for all values of  $x$ . In the relatively low temperature region, thermoelectric power value has been found to be negative confirming that the majority of carriers are electrons thereby indicating the rare earth substituted strontium ferrites to be classified as n-type semiconductors. The X-ray diffraction patterns show that the prepared samples have a single phase. The lattice parameters 'c' and 'a' were found to decrease whereas the X-ray density increases with increasing RE content. It has been found that the value of electrical conductivity also increases with an increase in RE content. The dispersion of dielectric constant has been discussed in the light of Koops model and hopping conduction mechanism.

Keywords: Hexagonal Ferrites, X-ray Diffraction, Scanning Electron Microscope, Thermoelectric Power, AC Conductivity.

## INTRODUCTION

The hexagonal ferrites,  $MFe_{12}O_{19}$  ( $M = Ba, Sr$  and  $Pb$ ) are well known as permanent magnetic material which have magnetoplumbite structure and exhibit large spontaneous magnetization with strong anisotropy [1]. M-type hexaferrite have widely been used in telecommunication, magnetic recording media, magneto-optics and microwave devices [2-5]. Strontium hexaferrite  $SrFe_{12}O_{19}$  is a hard magnetic material due to its high coercivity (6.64 kOe) which originates from its high magnetocrystalline anisotropy and is strongly dependent on the size and the shape of the particles. The Curie temperature of  $SrFe_{12}O_{19}$  is around 470°C and the saturation magnetization between 74.3 and 92.6 emu/g [6-11]. Hexagonal strontium ferrites have been intensively investigated during the last few decades due to their considerable importance in the electronic material industry. The hexagonal Barium (BaM) and Strontium ferrite (SrM) are considered to be excellent candidates for magnetic recording media and characterized with high magnetocrystalline anisotropy, moderate hard magnetic properties and high chemical stability, compared with other magnetic materials. The

thermoelectric power of hexagonal ferrites has rarely been studied. The thermoelectric properties of hexagonal ferrites depend on the preparation conditions such as sintering temperature, sintering atmosphere and the soaking time as well as the type of the substituted ions. The common processing methods of hexagonal ferrites are conventional ceramic processes of solid-state reaction, co-precipitation method, sol-gel process and molten salt method [12-14] etc. The conventional ceramic processes includes mixing the raw materials, calculation, milling, pressing and sintering at 1150- 1200°C. In a fine particle form, Strontium ferrite is suitable for high density recording media. Ultra fine strontium ferrite powder with narrow particle size distribution is desirable to increase the capacity of information storage as well as to reduce the medium noise [15].

In the present work, the temperature and composition dependence of thermoelectric properties of rare earth doped strontium M-type hexagonal ferrites  $Sr_{1-x}RE_xFe_{12}O_{19}$  (where  $RE = Dy$ ) has been studied at different frequencies and temperatures. Structural properties and particle size of hexaferrite have also been investigated by employing XRD technique.

## 1. Experimental Details

Strontium hexaferrites ( $\text{SrFe}_{12}\text{O}_{19}$ ) of nominal composition ( $x = 0.0, 0.10, 0.20$  and  $0.30$ ) were synthesized starting from ball-milling mixtures of  $\text{SrCO}_3$ ,  $\text{Fe}_2\text{O}_3$  and Dy-rare earth ion for 12hrs. After drying at  $60^\circ\text{C}$  for 6hrs, the powder mixture was heated at temperature of  $800\text{-}1150^\circ\text{C}$  for 4hrs in a lid covered alumina crucible with a heating rate of  $5^\circ\text{C}/\text{min}$  in air and was cooled to room temperature in furnace. In order to make the sintered magnet, the strontium ferrite powder were wet mixed in acetone medium with addition of 4% polyvinyl alcohol (PVA) binder solution by using a ball mill. The mixture were reground again for 5hrs and the final fine powder were pressed in disk-shaped pellets with thickness ranging from 2- 4mm and with diameter from 7- 9mm. Subsequently. The pellets were sintered in a resistance heated furnace for 3hrs at beach specified level of sintering temperature ranging from  $950$  to  $1250^\circ\text{C}$ . The samples were then slowly cooled to room temperature.

The structural characterization was carried out by employing X-ray diffraction (XRD) technique using a X-ray Diffractometer (XPERT-PRO) with  $\text{CuK}_\alpha$  ( $\lambda = 1.5406\text{\AA}$ ) radiations. The electric properties of the samples were measured by HP4284A precision LCR meter having frequency range from 20 Hz-1MHz. All the measurements have been carried by using a cell having platinum electrodes.

## 2. Results and Discussion

The XRD pattern obtained for different molar concentration in the prepared samples of  $\text{Sr}_{1-x}\text{RE}_x\text{Fe}_{12}\text{O}_{19}$  (where  $\text{RE}=\text{Dy}$ ) ferrite sintered at  $1250^\circ\text{C}$  for 6hrs have been shown in Figure 1. The analysis reveals that the prepared samples have single hexagonal M-type phase. All peaks correspond to hexaferrite but for the substitution  $x = 0.30$ , where extra peaks of hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) and tetragonal  $\text{Sr}_3\text{Fe}_2\text{O}_7$  have been observed, indicating that Dy for  $x = 0.30$  did not substitute totally into the Sr M-type structure resulting in incomplete reactions between  $\text{Fe}^{3+}$  and  $\text{Sr}^{2+}$ . This is further indicated by tracing of secondary phases in these samples and is attributed to the preparation process. The respective peaks show that a magnetoplumbite structure has been formed. The variation in relative intensities of peaks may be related to the occupation of lattice sites by substituted ions.

It is observed that both 'a' and 'c' decrease continuously with increasing substituted amount of rare earth ions in the ferrites. The observed variation in the lattice constants can be explained on the basis of relative ionic radii of Sr and Dy which are  $1.12\text{\AA}$  for Sr and  $0.912\text{\AA}$  for Dy respectively. Since  $\text{Dy}^{3+}$  ions have ionic radii less than that of the ionic radii of  $\text{Sr}^{2+}$  ions, the replacement of  $\text{Sr}^{2+}$  ions by  $\text{Dy}^{3+}$  ions results in the decrease of unit cell dimensions of hexagonal lattice. The peak for the doped strontium ferrites appears at the same position as for undoped ferrite, with different intensities [16].

$$T.D. = \frac{2nM}{\sqrt{3}.N_a a^2 c} \quad (1)$$

where 'n' is number of atoms, 'M' is molecular weight, ' $N_a$ ' is Avogadro's number per gram mole and 'a' and 'c' are lattice constants. The bulk X-ray density (B.D.) is measured using Archimedes' Principle. The porosity of all samples was calculated from the measured values of X-ray density and experimental density by using

$$P = (T.D - B.D.) / T.D \times 100\% \quad (2)$$

The values of observed density and porosity are listed in Table 1. It has been observed that density increases continuously with increasing substituted amount of rare earth ions for the series. This can be attributed to the atomic weight and density of rare earth ions ( $162.5\text{amu}$  and  $8.53\text{g}/\text{cm}^3$ ) for  $\text{Dy}^{3+}$  which are higher than those of  $\text{Sr}^{2+}$  ( $87.6\text{amu}$

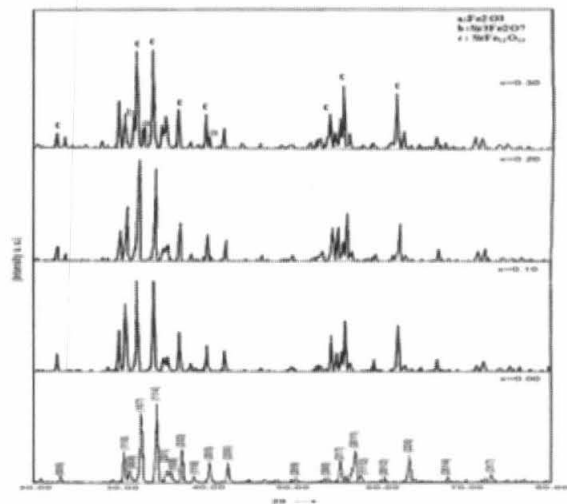


Figure 1. XRD Patterns of  $\text{Sr}_{1-x}\text{Dy}_x\text{Fe}_{12}\text{O}_{19}$  for compositions (a)  $x=0$ , (b)  $x=0.10$ , (c)  $x=0.20$  and (d)  $x=0.30$

and 2.54 g/cm<sup>3</sup>). The replacement of Dy<sup>3+</sup> by Sr<sup>2+</sup> 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 [16]. The apparent density of the sample reflects the same general behavior as the theoretical density. The X-ray density is higher than the apparent value due to the existence of pores which depend on the sintering condition. The porosity decreases as the rare earth content increases which reflects the opposite behavior of density.

Figure 2 shows plot of log  $\sigma_{AC}$  against frequency. It has been observed that  $\sigma_{AC}$  exhibits a semi-conductive behavior with the temperature and increases with increasing temperature. The conductivity also increases with increase in x. The results of AC conductivity could be explained on the basis of Koops Model [17], which assumes that ferrite samples act as a multilayer capacitor in which the ferrite grain and grain boundaries have different properties. According to this model, the bulk material of the ferrite could be considered as consisting of two layers, one representing the grains (a conducting layer) and the other representing the grain boundaries (a poor conducting layer). The grains having high conductivity are effective at high frequencies. However the grain boundaries with low

Composition (x)	D(g/cm <sup>3</sup> )	D <sub>x</sub> (g/cm <sup>3</sup> )	P(%)
0	4.20	5.07	17.03
0.10	4.28	5.12	16.31
0.20	4.33	5.16	16.07
0.30	4.39	5.22	15.97

Table 1. X-ray density  $D_x$ , Observed density, D and Porosity P (%) of  $Sr_{1-x}Dy_xFe_{12}O_{19}$  with (x = 0 to 0.30)

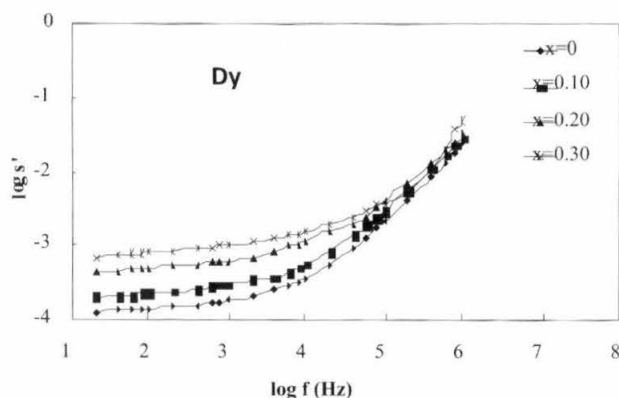


Figure 2. Variation of AC conductivity with frequency for  $Sr_{1-x}Dy_xFe_{12}O_{19}$  series at different compositions

conductivity are effective at lower frequencies.

The carrier concentration for these ferrite samples was calculated using the formula given by Morin and Gebella [18]

$$n = N \exp\left(\frac{-Se}{k}\right) \quad (3)$$

where S = Seebeck coefficient, e = charge of electron, k = Boltzman constant and N = density of states or concentration of electronic levels involved in the conduction process. In this case  $N = 2.8 \times 10^{22}$ , the number of octahedral cation sites/cm<sup>3</sup> of ferrite. The variation of Seebeck coefficient(S) and carrier concentration (n) with temperature are shown in Figures 3 and 4. It is observed that the value of charge carrier concentration increases with increase of temperature. Similar variation of 'n' with temperature has also been observed in Ba-Zn hexaferrites [19].

The computed values of carrier concentration are included in Table 2. It has been observed from the table

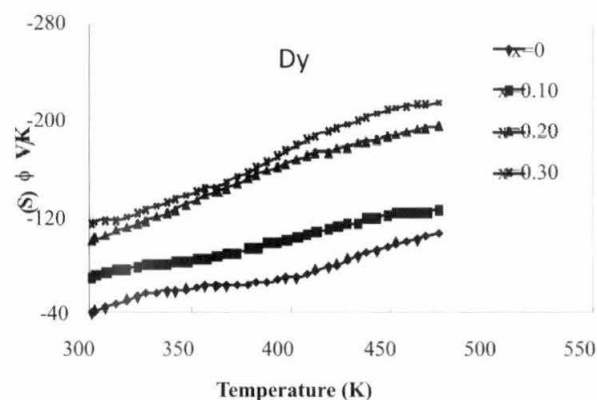


Figure 3. Variation of Seebeck coefficient with temperature for  $Sr_{1-x}Dy_xFe_{12}O_{19}$  series for different compositions

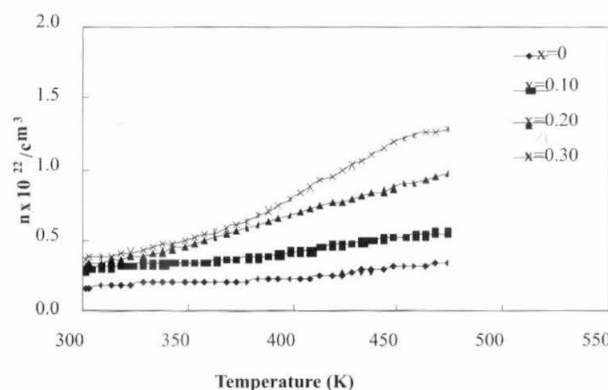


Figure 4. Variation of carrier concentration with temperature for  $Sr_{1-x}Dy_xFe_{12}O_{19}$  series for different compositions

Composition 'x'	Seebeck Coefficient 'S' ( $\mu\text{V/K}$ )	Carrier Concentration 'n' ( $10^{22}/\text{cm}^3$ )	Carrier Mobility ' $\mu$ ' ( $\text{cm}^2/\text{Vs}$ )
0	-45	0.15	$8.5 \times 10^{12}$
0.10	-73	0.28	$6.42 \times 10^{11}$
0.20	-104	0.32	$2.5 \times 10^{10}$
0.30	-115	0.36	$8.03 \times 10^{10}$

**Table 2.** Room temperature electrical conductivity and thermoelectric power data of  $\text{Sr}_{1-x}\text{Dy}_x\text{Fe}_{12}\text{O}_{19}$  for different compositions

that the value of charge carrier concentration also increases with an increase in Dy content.

Table 2 also gives the experimental values of Seebeck coefficient and electrical conductivity values at room temperature for the series prepared with  $\text{RE} = \text{Dy}^{3+}$ . The values of Seebeck coefficient vary from  $-45 \mu\text{V/K}$  to  $115 \mu\text{V/K}$  for different values of x. The values of charge carrier concentration have also been found to increase with an increase in RE content. Similar behavior of the electrical conductivity has been reported [19].

## Conclusions

The aim of the present work is to investigate the thermoelectric properties due to rare earth substitution in place of  $\text{Sr}^{2+}$  ion in hexagonal ferrites and to understand the various physical phenomena and mechanisms that lead to modifications in their properties. It has been observed that the replacement of  $\text{Sr}^{2+}$  ions by  $\text{RE} = \text{Dy}^{3+}$  ions in  $\text{Sr}_{1-x}\text{RE}_x\text{Fe}_{12}\text{O}_{19}$  hexaferrite yields hexagonal ferrites to a certain extent of unreacted oxides with an additional phases.

The observed variation in the lattice constants can be explained on the basis of relative ionic radii of Sr and Dy, which are  $1.12 \text{ \AA}$  for Sr and  $0.912 \text{ \AA}$  for Dy respectively. Since  $\text{Dy}^{3+}$  ions have ionic radii less than that of the ionic radii of  $\text{Sr}^{2+}$  ions, the replacement of  $\text{Sr}^{2+}$  ions by  $\text{Dy}^{3+}$  ions results in the decrease of unit cell dimensions of hexagonal lattice. The increase in bulk density with rare earth substitution may be attributed to the atomic weight and density of these ions, which are higher than those of strontium ions. The replacement of  $\text{Sr}^{2+}$  by  $\text{Dy}^{3+}$  ions in the hexagonal structure leads to a variation in the bonding and consequently interatomic distance and density. The bulk density of the sample reflects the same general behavior as of the X-ray density. The X-ray density is higher than the bulk density

value due to the presence of pores which depends on the sintering conditions. The porosity decreases as rare earth content increases thereby reflecting the opposite behavior of density. The negative values of the thermoelectric power found over the entire temperature range confirm that the majority of the charge carriers are electrons. On the basis of its negative sign, the rare earth substituted strontium ferrites have been classified as n-type semiconductors.

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