EFFECT ON HIGH FREQUENCY DIELECTRIC AND MAGNETIC BEHAVIOR OF Co-Zr SUBSTITUTED ALUMINUM Sr-M HEXAFERRITE

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Abstract

Strontium hexaferrite of a structural formula $SrAl_2Fe_{10-2x}(CoZr)_xO_{19}$, where (x=0.6,1) have been synthesized by microwave induced sol gel autocombustion technique. The dielectric constant, dielectric loss tangent and magnetic properties were studied. The dielectric constant and dielectric loss tangent were measured in the frequency range of 1KHz to 99KHz at room temperature. The dielectric constant decreased with increasing frequency for all the samples. 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 Co and Zr ions in $SrAl_2Fe_{10-2x}(CoZr)_xO_{19}$ 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 increases as Co and Zr ions substitution increases.

Key words: Hexagonal ferrites, 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, strontium, Calcium or Lead. 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. In this study, a systematic investigation of the dielectric behavior and possible polarization mechanisms of Co and Zr substituted Aluminum Sr-M hexaferrites have been carried out.

Experimental

The samples of M-type substituted hexaferrites with formula $SrAl_2Fe_{10-2x}(ZrCo)_xO_{19}$ are synthesized for x=0.6 and 1. The reac-tive oxidants such as $Sr(NO_3)_2$, $Fe(NO_3)_2.9H_2O$, $Co(NO_3)_2.6H_2O$, $ZrO(NO_3)_2.H_2O$ were dissolved into an unionized distilled water at the temperature of 90°C for 15-20 min .Citric acid is used as fuel which gives requisite energy to initiate exothermic reaction. The gel produced is then kept for an hour in the room temperature and then it is heated in the digitally controlled microwave oven of 2.54GHz for 15-20 min, The gel get burnt and finally gets converted in homogeneous powder. The sample is then sintered by giving sporadic moderate heat treatments for further few minutes with further grinding.

The microstructure was verified by using transmission electron microscopy (TEM). The particle size was determined by using formula (D

= $0.9\lambda/\beta\cos\theta$), where β is the percentage intensity of FWHM of XRD. The magnetic measurements were carried out by a vibrating sample magnetometer operating up to a maximum field of 15 kOe. The dielectric measurements were made using a Impedance Analyzer were carried out as a function of frequency in the range 1KHz to 99KHz at room temperature. The magnetic properties of the samples were determined by a Vibrating Sample Magnetometer. The Curie temperature Tc (K) of all the samples was determined by the Gouy's method .
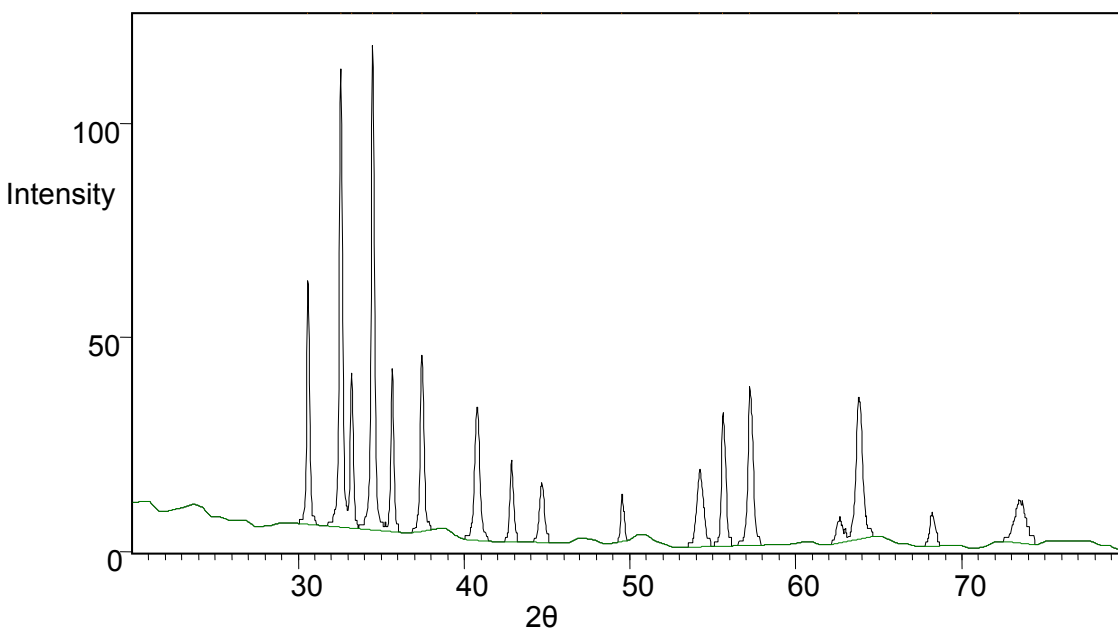
Results and Discussion: XRD

Fig1. X-ray diffractograms of SrAl$_2$Fe$_{8.8}$(ZrCo)$_{0.6}$O$_{19}$ferrite

X-ray diffraction pattern of sample x=0.6 (Fig.1) shows that magnetoplumbite structure has been formed. The change in relative intensities may be related to occupation of crystallographic sites by substituted ions. This is in agreement with the fact that all hexagonal ferrites exhibit constant lattice parameter 'a' and variable parameter 'c'. It also indicates that change of easy magnetized c-axis is larger than a-axis

with Co^{2+} and Zr^{4+} ions substitution. This is attributed to large ionic radii of Zr^{4+} ion (0.72 Å) and Co^{2+} ion (0.72 Å) than Fe^{3+} ion (0.64 Å).

TEM

Fig 2 shows TEM micrograph of Co-Zr substituted strontium ferrite. It is observed from TEM micrograph that the average particle size Co-Zr substituted strontium ferrite are varying from 44 to 89 nm TEM(Fig. 2) shows grains of different size attributing to large ionic radii of substituted Co^{2+} and Zr^{4+} ions in comparison to Fe^{3+} ions, thus grain size can be controlled with substitution.
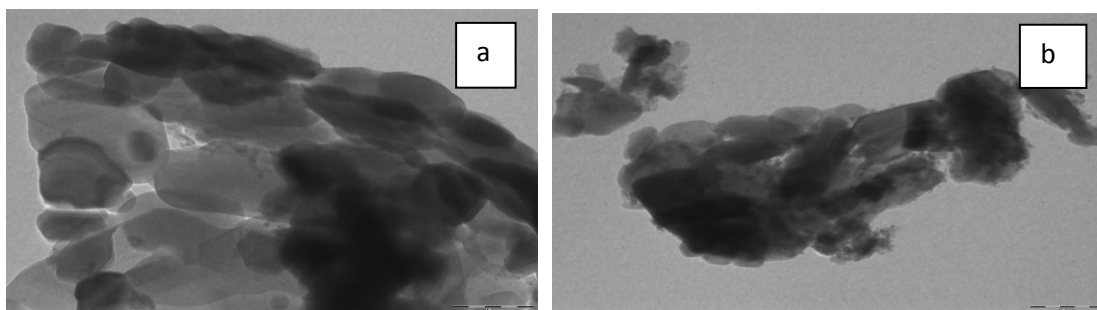

Fig2 TEM micrograph $SrAl_2Fe_{10-2x}(ZrCo)_xO_{19}$ (a) x=0.6   (b) x=1

Frequency variation of dielectric constant

The variation of dielectric constant (ε) with frequency at room temperature for the prepared samples $SrAl_2Fe_{10-2x}(ZrCo)_xO_{19}$ with x= 0.2,0.6,0.8 and 1 are shown in the Fig3. It is observed that the value of dielectric constant also decreases with increasing frequency in all the samples. This behavior is normal ferrimagnetic behavior and has also been observed by several investigators [14-17]. 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[14, 18]. 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 [19]. Concentration of Co, Zr ions to a $SrAl_2Fe_{12}O_{19}$ ferrite increases the value of the dielectric constant. The dielectric constant is increased due to the electronic exchange between $Fe^{2+} \leftrightarrow Fe^{3+}$ resulting in local displacement of charges to determine the polarization of the ferrites. It is clear from Fig3 that the concentration x=0.8 shows the maximum value of the dielectric constant. Such a high value can be explained on the basis that it has the maximum number of ferrous ions which are involved in the phenomenon of exchange $Fe^{2+} \leftrightarrow Fe^{3+}$ 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 . The strong correlation between the conduction mechanism and the dielectric behavior of ferrites has been established by Iwauchi
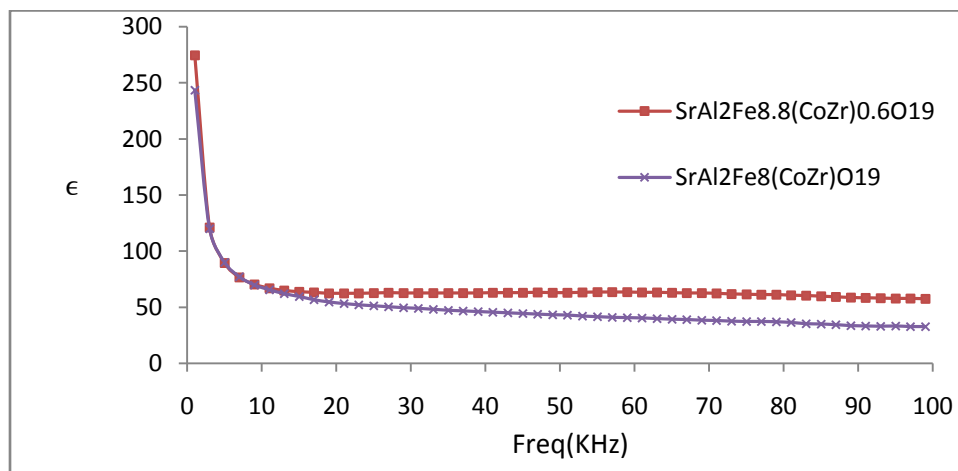

Fig.3. Variation of the dielectric constant (ε) with frequency for $SrAl_2Fe_{10-2x}(CoZr)_xO_{19}$

[20] and Rezlescu [21]. It has been concluded that the electron exchange between $Fe^{2+} \leftrightarrow Fe^{3+}$ 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 Fe^{3+}/Fe^{2+} ion pairs present on the B sites (octahedral sites).

Frequency variation of dielectric loss tangent

The variation of dielectric loss tangent (tan δ) with frequency at room temperature for the prepared samples $SrAl_2Fe_{10-2x}(ZrCo)_xO_{19}$ with x= 0.6 and 1 are shown in Fig4. The value of dielectric loss tangent decreases monotonically with increasing frequency for the samples. 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.
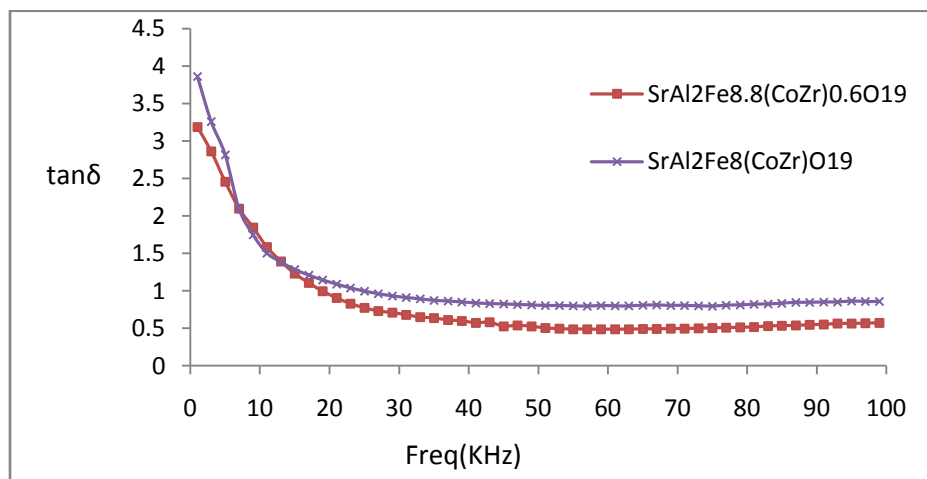

Fig.4. Variation of the dielectric loss (tan δ) with frequency for $SrAl_2Fe_{10-2x}(CoZr)_xO_{19}$

These dipoles in ferrites are formed due to the change of the cation state, such as Fe^{3+}/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.

Magnetic Measurements

To determine the basic nature of strontium ferrite all the samples were characterized for their magnetic behavior 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 and curie temperature by Gouy's method were determined.

Table1 Measurement of magnetic Parameters

Compound	Magnetization M_s (emu/g)	Retentivity M_r(emu/g)	Coercivity H_c **(KG)**	Curie temp. T_c (K)
$SrFe_{8.8}Al_2(CoZr)_{0.6}O_{19}$	22.765	11.529	4.38	600
$SrFe_8Al_2(CoZr)O_{19}$	41.336	18.118	2.63	628

In M-type hexagonal ferrite, Fe^{3+} ions occupy seven octahedral sites 12k and 2a,one trigonal site 2b with spins in one direction, two octahedral sites $4f_2$ and two tetrahedral sites $4f_1$ with spins in opposite direction. The variation of magnetic properties with substitution x is shown in Fig.3. Coercivity rapidly falls with substitution of Co^{2+} and Zr^{4+} ions at x = 1. This fast reduction in anisotropy is primarily related to intrinsic effect associated with replacement of Fe^{3+} ions at $4f_2$ and 2b sites. These two sites contribute towards large anisotropic field [22]. Furthermore, microstructure shows more intergranular pores in sample. These pores offer hindrance to the flow of applied field across the grains. The grain size increment with substitution reduces intergranular pores. Therefore, ferrite can be demagnetized at low applied field, which decreases coercivity. However, *M*s increases with the substitution attributing to the fact that the magnetic moments of both ions are not able to cancel out with spin-down moments of Fe^{3+} ions ($5\mu B$) owing to weak magnetic moment of Co^{2+} ions ($3\mu B$) and diamagnetic Zr^{4+} ions (0). More specifically strong superexchange interaction ($Fe_A^{3+}-O-Fe_B^{3+}$) will not

collapse with substitution of Zr^{4+} and Co^{2+} ions. This is confirmed from measured values of Curie temperature which varies from 600 K to 628K with substitution.

Conclusions

In M-type hexagonal ferrites $SrAl_2Fe_{10-2x}(CoZr)_xO_{19}$, with x=0.6 and 1 prepared by the microwave induced sol gel autocombustion technique. The dielectric constant and loss tangent both decrease with increasing frequency, which agrees well with the Maxwell-Wagner double layer model.The prepared sample with x=1, Co-Zr substituted strontium hexaferrites had the greater dielectric constant(ε) and dielectric tangent loss (tan δ). The Curie temperature increases with Co-Zr ions substitution.

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