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# Microwave and electrical properties of Co-Zr substituted Ba-Sr ferrite

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The electromagnetic parameters of synthesized M-type hexagonal ferrites,  $Ba_{0.5}Sr_{0.5}Co_xZr_xFe_{(12-2x)}O_{19}$  (x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0), were measured from 8.2-12.4 GHz. The dielectric loss in the ferrites is higher than the magnetic loss and increases with substitution, suggesting their use for lossy dielectric applications. The various mechanisms behind increased permittivity and dielectric loss are discussed in this paper.

Key words: A-Ceramics, D-Dielectric Properties, D-Magnetic Properties, D-Electrical Properties.

# Introduction

Electromagnetic interference (EMI) is a potential hazard in the form of environmental pollution due to the tremendous growth in technological applications. It can be controlled through shielding or absorption of microwave signals. Hexagonal ferrites are widely used as microwave absorbing materials [1]. A number of researchers have reported microwave attenuation in ferrites by increasing magnetic losses. Alternatively dielectric losses can also accompany attenuation in ferrites.

In this research, we have measured the complex permittivity, complex permeability and resistivity of Co-Zr substituted Ba-Sr hexagonal ferrites for the first time and the possibility of synthesized ferrite for high frequency applications is discussed.

## **Experimental**

M-type Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>x</sub>Zr<sub>x</sub>Fe<sub>(12-2x)</sub>O<sub>19</sub> hexagonal ferrite (x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) is synthesized by a standard ceramic method [2]. Complex permeability ( $\mu^*$ ) and complex permittivity ( $\epsilon^*$ ) were measured with a network analyzer (Agilent 8722ES) at 8.2-12.4 GHz using the Nicholson-Ross method [3]. Resistivity was measured by a two-probe method with a Keithley setup 6517A [4]. The analyzer was calibrated in air before final measurements and the X-band was divided into 201 points, readings were taken with successive frequency increments of 0.021 GHz.

The procedure proposed by the Nicholson-Ross method is deduced from the following equations:

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$$S_{11} = \frac{\Gamma(1-T^2)}{(1-\Gamma^2 T^2)} \quad and \quad S_{21} = \frac{T(1-\Gamma^2)}{1-\Gamma^2 T^2} \tag{1}$$

where  $\Gamma$  is the reflection coefficient and the T transmission coefficient in a two port network.

These parameters can be read from the network analyzer. The reflection coefficient can be obtained from following equation:

$$\Gamma = X \pm \sqrt{X^2 - 1} \tag{2}$$

The root of the above equation can be found out from the modulus of  $\Gamma$  (< 1).

Also 
$$X = \frac{S_{11}^2 - S_{21}^2 + 1}{2S_{11}}$$
 (3)

and 
$$T = \frac{S_{11} + S_{21} - \Gamma}{1 - (S_{11} + S_{21})\Gamma}$$
 (4)

The complex permeability is given as:

$$\mu^* = \frac{1+\Gamma}{\Lambda(1-\Gamma)\sqrt{\frac{1}{\lambda_0^2} - \frac{1}{\lambda_c^2}}}$$
(5)

where  $\lambda_0$  is the free space wavelength and  $\lambda_c$  is the cut-off wavelength and  $\Lambda$  is further

equal to 
$$\frac{1}{\Lambda^2} = \left[\frac{1}{2\pi L} ln \left(\frac{1}{T}\right)\right]^2$$
 (6)

The complex permittivity is given as:

$$\varepsilon^* = \frac{\lambda_0^2}{\mu} \left[ \frac{1}{\lambda_c^2} - \left[ \frac{1}{2\pi L} ln \left( \frac{1}{T} \right) \right]^2 \right]$$
<sup>(7)</sup>

where L is the thickness of the sample.

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# **Results and Discussion**

Structural characterization, using X-ray diffractograms and micrographs, has been explained in our previous investigation [5].

#### Complex permittivity and permeability

The dielectric constant Fig. 1(a), (b) of all samples exhibits non-linear variation with substitution of  $Co^{2+}$  and  $Zr^{4+}$  ions; this behavior is neither a resonance nor relaxation type. A large  $\epsilon'$  is observed in all samples. This is due to the formation of Fe<sup>2+</sup> ions from Fe<sup>3+</sup> ions at the sintering temperature of 1250 °C. This high temperature causes an increase in electron hopping between Fe<sup>2+</sup> ions and Fe<sup>3+</sup> ions. The dielectric constant in ferrites depends



**Fig. 1.** (a) Variation of  $\varepsilon'$  with frequency and substitution in Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>x</sub>Zr<sub>x</sub>Fe<sub>(12-2x)</sub>O<sub>19</sub> ferrites (x = 0.0, 0.2, 0.4), (b) Variation of  $\varepsilon'$  with frequency and substitution in Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>x</sub>Zr<sub>x</sub>Fe<sub>(12-2x)</sub>O<sub>19</sub> ferrites (x = 0.6, 0.8, 1.0).

on space charge polarization and charge formation at grain boundaries. The electron hopping between Fe<sup>2+</sup> ions and Fe<sup>3+</sup> ions leads to conductivity and dielectric polarization in ferrites [6]. Researchers have reported the formation of Fe<sup>2+</sup> ions from Fe<sup>3+</sup> ions in the high temperature synthesis of ferrites [7-11]. An undoped sample 0.0 possesses large  $\varepsilon'$ and  $\varepsilon''$  in spite of having the highest porosity [5]; pores offer hindrance to electron flow. Sample 0.0 has a larger number of Fe<sup>3+</sup> ions than doped samples, so a large number of Fe<sup>2+</sup> ions are produced from Fe<sup>3+</sup> ions. Thus polarization is enhanced resulting in an increase of both  $\varepsilon'$  and  $\varepsilon''$  in sample 0.0.

The loss factor Fig. 2(a), (b) of doped samples decreases (except 0.8) with substitution by  $Co^{2+}$  and  $Zr^{4+}$  ions. The dielectric loss mechanism in ferrites depends on DC and



**Fig. 2.** (a) Variation of  $\varepsilon$ " with frequency and substitution in Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>x</sub>Zr<sub>x</sub>Fe<sub>(12-2x)</sub>O<sub>19</sub> ferrites (x = 0.0, 0.2, 0.4), (b) Variation of  $\varepsilon$ " with frequency and substitution in Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>x</sub>Zr<sub>x</sub>Fe<sub>(12-2x)</sub>O<sub>19</sub> ferrites (x = 0.6, 0.8, 1.0).

X	Log(ρ) (Ω·cm)
0	4.5
0.2	6.4
0.4	4.1
0.6	3.5
0.8	3.9
1	5.1

Table 1. Resistivity of Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>x</sub>Zr<sub>x</sub>Fe<sub>(12-2x)</sub>O<sub>19</sub> ferrites

AC conductivity or ion jumping and dipole relaxation according to the expression,  $\varepsilon' = [(\sigma_{DC}/\omega\epsilon_o) + \varepsilon''_{AC}]$  [12, 13]. This implies the inverse nature of conductivity with respect to frequency; all samples (except 0.8) follow this equation. Thus  $\varepsilon''$  increases in the low frequency region.

The high value of  $\varepsilon$ " in the undoped sample 0.0 is related to an increased hopping mechanism between Fe<sup>2+</sup> and Fe<sup>3+</sup> ions as explained earlier, this sample has the maximum number of easily polarizable Fe<sup>2+</sup> ions.

We reported in our previous investigation that porosity decreases with substitution of  $Co^{2+}$  and  $Zr^{4+}$  ions [5], increasing polarization ( $\varepsilon'$  and  $\varepsilon''$ ) due to the ease of field flow. On the other side the resistivity varies nonlinearly (Table 1) with substitution; two maxima occur 6.4  $\Omega$ cm in sample 0.2 and 5.1  $\Omega$ cm in sample 1.0. A high resistivity discourages polarization and conductivity. The highest density in samples 1.0 [5] causes an increase in  $\varepsilon'$  and  $\varepsilon''$  while it has a high resistivity (141 kohm.cm) than sample 0.8 (8 kohm.cm), which will lower down  $\varepsilon'$  and  $\varepsilon''$ . The competition between the two factors results in a larger  $\varepsilon'$  in sample 0.8 than in sample 1.0. Thus the reciprocal nature of resistivity and polarization causes non-linear variation of  $\varepsilon'$  and  $\varepsilon''$ with substitution.

The octahedral site (B) in hexagonal ferrites is large in comparison to the tetrahedral site (A) [14] and their resistivity primarily depends on the former. Ligand theory describes the dependence of site occupancy on the d-configuration and the nature of partner cation [15]. Thus  $Co^{2+}$ ions (d<sup>7</sup> orbit) would go to B sites and  $Zr^{4+}$  ions (d<sup>0</sup> orbit) have no site preference. On the other side Zr<sup>4+</sup> ions carrying a  $4p^6$  configuration are less compressible than  $Co^{2+}$  ions with a 3d<sup>7</sup> configuration and can occupy B sites. The substitution of Co<sup>2+</sup> and Zr<sup>4+</sup> ions displaces Fe<sup>3+</sup> ions from B to A sites, increasing the resistivity at lower substitution. Further substitution increases the number of Fe<sup>3+</sup> ions displaced. This increases the electron hopping between  $Fe^{2+}$  and  $Fe^{3+}$  ions, hence the resistivity starts decreasing for x > 0.2. Another reason for this variation is the preference of Co<sup>2+</sup> ions for A-sites in addition to B-sites, Simsa et al. reported preferential occupancy for both A and B sites [16]. So further substitution of  $Co^{2+}$  ions may displace Fe<sup>3+</sup> ions from A to B sites. More specifically, substitution of both Ru<sup>4+</sup> ions and Co<sup>2+</sup> ions causes displacement of Fe<sup>3+</sup> ions from B to A sites and Co<sup>2+</sup> ions displace Fe<sup>3+</sup> ions from

A to B sites. Thus for x > 0.2, the net movement of Fe<sup>3+</sup> ions from B to A site is less than at a lower substitution and the resistivity increases. However Rane *et al.* reported a preference of Zr<sup>4+</sup> ions for B sites at higher substitution [14], this causes an increase in resistivity at higher substitution.

The mechanism of complex permittivity can be discussed in this way: Substitution of ions in ferrites with different valencies causes defects in the lattice either in the form of vacancies or in the form of interstitials. In this composition,  $Co^{2+}$  and  $Zr^{4+}$  ions are substituted to Ba-Sr ferrite containing  $Fe^{3+}$  ions. So some of the  $Fe^{3+}$  ions are replaced with lower valency ions ( $Co^{2+}$ ) creating anionic vacancies and higher valency  $Zr^{4+}$  ions will result in cationic vacancies. These vacancies created, along with the preferential site occupancy of  $Co^{2+}$  and  $Zr^{4+}$  ions, will change the resistivity of the material and modify the hopping conduction. The electron hopping in cationic and anionic vacancies will increase dielectric losses. The formation of defects and ionic vacancies results in bonding of the material becoming more ionic in nature, thereby increases permittivity.

The present synthesis of ferrite was carried out at a high sintering temperature of 1250 °C and Fe<sup>2+</sup> ions will be formed by the reduction of Fe<sup>3+</sup> ions at such high temperature. The additional d electrons in the Fe<sup>2+</sup> ions can move to the neighboring Fe<sup>3+</sup> ions with following equation:

$$Fe^{2+} + Fe^{3+} \leftrightarrow Fe^{3+} + Fe^{2+}$$
(8)

The electron hopping also results in an increase of the dielectric loss. As discussed before, these Fe<sup>2+</sup> ions are more easily polarized than Fe<sup>3+</sup> ions causing an increase in  $\varepsilon'$  and  $\varepsilon''$  in all the samples. Consequently all the samples possess a large dielectric constant and dielectric loss.

The permeability and magnetic loss dispersion of all the samples is weak in the low frequency region Fig. 3(a), (b) and 4(a), (b) and high in the high frequency region, it varies non-linearly with frequency. Sample 1.0 exhibits an unexpected increase in  $\mu'$  and  $\mu''$  with frequency which can not be attributed to a particular reason.  $\varepsilon'$  and  $\mu''$  in sample 0.8 does not vary much with frequency.

A low magnetic loss is present at a lower substitution and vice-versa. The increase in grain size at higher substitution [5] causes a low reluctance to applied field, thereby increasing in  $\mu$ " at higher substitution. In general complex permeability does not reflect any significant variation which can be discussed.

### Oscillatory behavior of $\mu^*$ and $\epsilon^*$

The hexagonal ferrites manifest an oscillatory behavior in their dielectric and magnetic properties. The dielectric properties of Ba-Co and Ba-Mn-Ti hexagonal ferrites were reported by Meshram *et al.* at the X-band [17]. These samples revealed the oscillatory behavior for both the dielectric and magnetic properties. Abbas *et al.* [18] also reported similar oscillatory behavior in the complex permeability and complex permittivity of substituted M-type Ba hexagonal ferrites. The oscillatory mechanism of dielectric properties was explained on the basis of a difference



Fig. 3. (a) Variation of  $\mu'$  with frequency and substitution in Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>x</sub>Zr<sub>x</sub>Fe<sub>(12-2x)</sub>O<sub>19</sub> ferrites (x = 0.0, 0.2, 0.4), (b) Variation of  $\mu'$  with frequency and substitution in Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>x</sub>Zr<sub>x</sub>Fe<sub>(12-2x)</sub>O<sub>19</sub> ferrites (x = 0.6, 0.8, 1.0).

in the relaxation frequencies of various dipoles and magnetic properties were dependent on interactions of the magnetic vector with the electromagnetic signal, and the change in the direction of the magnetic vector with substitution.

In our ferrite series, there are a variety of positive ions with different valencies which have different co-ordination with  $O^{2-}$  ions reported by Abbas *et al.* [18]. This causes the formation of dipoles of different strengths in the same material. These different dipoles have obviously different relaxation frequencies. The electron hopping between Fe<sup>2+</sup> and Fe<sup>3+</sup> ions will give rise to another relaxation. Therefore different relaxation mechanisms of the various dipoles formed, hopping of the electrons and the relaxation characteristics (space charge polarization) altogether could be the presumed factors behind the oscillatory behavior of the dielectric properties.



**Fig 4.** (a) Variation of  $\mu$ " with frequency and substitution in Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>x</sub>Zr<sub>x</sub>Fe<sub>(12-2x)</sub>O<sub>19</sub> ferrites (x = 0.0, 0.2, 0.4), (b) Variation of  $\mu$ " with frequency and substitution in Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>x</sub>Zr<sub>x</sub>Fe<sub>(12-2x)</sub>O<sub>19</sub> ferrites (x = 0.6, 0.8, 1.0).

The oscillatory behavior in the complex permeability can be explained in terms of the precision motion of the magnetization vector. In M-type hexagonal ferrites the 12 Fe<sup>3+</sup> ions are distributed in three different interstitial sites that is tetragonal, octahedral and bi-pyramidal. The seven octahedral ions and one bi-pyramidal ion are oppositely coupled with two octahedral ions and two tetrahedral ions giving a net magnetization of only 4 Fe<sup>3+</sup> ions. The magnetization vector should produce stable resonances on interaction with the electromagnetic signal. But with the substitution of Co<sup>2+</sup> and Zr<sup>4+</sup> ions, the magnetization vector will be inclined more towards the base line and its interaction with the electromagnetic signal results in a zig-zag or oscillatory behavior of the magnetic properties. Referring to Figs. 1-5, it could be stated that the sample responses vary with the frequency and substitution, other



Fig. 5. Anti-phase oscillations of  $\mu$ " and  $\epsilon$ " in Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>x</sub>Zr<sub>x</sub>Fe<sub>(12-2x)</sub>O<sub>19</sub> ferrites (x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0).

parameters such as sample thickness and measurement conditions are identical for all the samples.

Moreover, a slight oscillation in the measured data is possible from the measurement procedure. It is known that the Nicholson-Ross method, adopted to determine complex permittivity and permeability, shows a divergence at frequencies corresponding to integral multiples of half wavelengths in the sample. In this study, the complex transmission T and reflection coefficient  $\Gamma$  are calculated from the S-parameter measurements. Nicholson and Ross assumed an infinitely thick sample taking into consideration the behavior of the reflection coefficient. The reflection coefficient is an oscillatory function of sample layer thickness with periodic oscillations at every half wavelength [19]. In the case of absorbing materials, the amplitude of oscillation increases with the reduction in sample thickness. When the sample is infinitely thick, the refection coefficient becomes constant. In the present investigation, the Nicholson Ross method was used to calculate the T in terms of measured  $\Gamma$ , complex permittivity and complex permeability. This method cannot eliminate the effect of the oscillatory behavior of the complex reflection coefficient ( $\Gamma$ ) in the dielectric and magnetic properties until the sample is of finite thickness.

The Fig. 5 shows that the dielectric loss is in anti-phase

oscillations with the magnetic loss from 8.2 GHz to 12.4 GHz. Thus the total loss (dielectric + magnetic) does not oscillate with frequency, concluding that oscillations in  $\mu$ " and  $\epsilon$ " (also in  $\mu$ ' and  $\epsilon$ ') are due to measurement uncertainties and the apparent splitting is ascribed to the measurement error. Negative values in  $\mu$ ' (X-Band) and tan $\delta_{\epsilon}$  from 0-40 GHz have also been reported elsewhere [20-22].

Therefore, the oscillatory behavior in the electromagnetic parameters can be considered as the combined behavior of material properties and the measurement procedure itself.

Fig. 6(a),(b) shows the non-linear variation of  $tan\mu_{\epsilon}$ and  $tan\delta_{\mu}$  frequency. All samples exhibit large  $tan\mu_{\epsilon}$  than  $tan\delta_{\mu}$  over almost the entire frequency region.

#### Conclusions

1. This first ever investigation on Co-Zr substituted Ba-Sr ferrites concludes that microwave attenuation is possible by increasing dielectric losses through choosing an appropriate sintering temperature and substitution, while in previous reports magnetic properties are enhanced to achieve microwave attenuation. 2. The dielectric properties have a dominance over the magnetic properties over the entire frequency region.

3. An increased hopping mechanism at a high sintering 1250 °C, the resistivity and porosity variation are the key factors behind increased  $\varepsilon'$  and  $\varepsilon''$  in all the samples. The resistivity depends on the preferential site occupancy of  $Co^{2+}$  and  $Zr^{4+}$  ions substitution.

4. The high tand<sub>e</sub> in sample 1.0 suggests the possibility of using it for EMI shielding applications at the X-Band.

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