Magnetic, dielectric and microwave absorption studies of Ba-CoTi hexaferrite — Epoxy composites


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The microwave absorption, complex permittivity and complex permeability studies of hexaferrite composites prepared with Ba(CoTi)xFe12-2xO19 wherein x varies from 0.0 to 1.0 in steps of 0.2 were made in frequency range from 8.0 to 12.4 GHz. The effect of Co2+Ti4+ substitution and of microstructural variation on complex permeability, permittivity and microwave absorption have been analysed. The hexaferrite-composites with x > 0.0 exhibit significant dispersion in the complex permittivity (εr′-jεr″) with maximum value of εr″ is observed for x equal to 1.0. The dispersion in complex permeability (μr′-jμr″) is not significant and is attributed to the shielding effect of polymer matrix over the ferrite crystallites and to the low alternating electromagnetic field applied to the sample. The variation of reflection loss has been studied as a function of frequency (f), Co2+Ti4+ content and thickness of the absorber. A maximum absorption of 16 dB (86%) is obtained for composites with x equal to 0.4 and of 2.8 mm thickness.

[Keywords: Microwave absorption, Complex permeability, Complex permittivity, Microwave ferrite composites]

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1 Introduction

Microwave ferrite composites, which absorb microwave over wide range of frequencies, are useful because of their multifarious applications and radar absorbing application in particular. The hexagonal ferrites with high anisotropy field, high saturation magnetization, high coercive field and host of other electromagnetic properties, have been found most suitable materials to yield a high loss microwave absorber over a broad band of frequencies. The magnetoplumbite-type hexagonal ferrites are of importance to extend the range of microwave absorbers to a higher frequency region of X-band. These ferrites absorb microwaves due to various interactive loss mechanisms related to magnetization and electric polarization of the material. The values of complex relative permeability (μr′-jμr″) and permittivity (εr′-jεr″) of constituent material of the microwave absorbers determine the reflection and attenuation characteristics of each such material. The permittivity and permeability of ferrite-epoxy composites may depend on the composition of ferrite, nature of polymers, and fill-factor, besides the temperature and frequency of operation.

The present work investigates the variations of reflection loss with substitution of Co2+Ti4+ ions in BaFe12O19 hexaferrites. It also attempts to find optimum amount of Co2+Ti4+ ions needed to yield the minimum reflection loss (maximum absorption) over broad region in X-band. The results have been discussed on the basis of various loss mechanisms in the materials.

2 Experimental Details

The magnetic ceramics Ba(CoTi)xFe12-2xO19 with compositions x = 0.0-1.0 in steps of 0.2 were synthesized by conventional ceramic method. The materials were ferric oxides (99.9% Merck, Germany), Barium carbonate (99%, BDH, India) TiO2 and CoCO3 of 99.9% purity. The mixture was crushed for 6 hr in agate mortar and pestle and pre-sintered at
1000.0 °C for 12 hr. The pre-sintered materials were crushed for 6 h, and then cold pressed into pellets, which were finally sintered 1300.0 °C for 12 hr. X-ray diffraction analyses for few typical samples were made in from Rigaku-Denki diffractometer, by using Cu-Kα (λ = 1.54056 Å) and Ni filter in wide range of Bragg's angles 20° < 2θ < 90° at room temperature, which confirmed the magnetoplumbite type crystal structure for these samples. The composite samples were prepared by mixing the fine powders of BaFe12-2x(CoTi)xO19 with epoxy resin; the ratio of the powders for resin is 50% by weight. The samples were cured at 80 °C for 2 h and were coated on thin aluminium substrate of dimension suitable for X-band microwave bench for reflection loss measurement. The variations of reflection loss versus frequency for different thickness and composition of ferrite were studied by measuring the voltage standing wave ratio (VSWR) on the X-band microwave bench. The real and imaginary part of permeability and permittivity in the frequency range of 2-15 GHz were measured using reflection/transmission technique based on the algorithms developed by Nicolson and Ross and by Weir. For this toroidal-shaped ferrite-epoxy composite samples of 1.51 mm inner diameter and 3.49 mm of outer diameter were inserted into a central conductor of coaxial line of 15 cm air length. The samples of length approximately equal to one quarter of the guide wavelength were chosen for accurate measurements. The sample length varied from 4 to 5 mm at low frequencies and from 2 to 3 mm at higher frequencies. The measured values of reflected and transmitted scattering parameters (S11 and S21) were used to determine ε′, ε″, μ′, μ″ and transmission coefficient (τ). The measurement fixture is a set of 15 cm coaxial airline. The microwave measurement is conducted on a calibrated HP 8510B Hewlett Packard Vector Network Analzyer. The SEM micrographs of fractured surfaces of the ferrite samples were recorded on a Cambridge Stereo Scan 360 Scanning Electron Microscope.

3. Results and Discussion

3.1 Dielectric and magnetic properties

The frequencies dependence of ε′, ε″, μ′, μ″ for Ba-CoTi ferrite-epoxy composites with x equal to 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0 are shown in Figs.1a-f, wherein the points represent the measured values and the lines are only guide to eye. The dielectric constant, ε′, for BaFe12O19 hexaferrite composite remains constant at 4.0 from 2.0 GHz to 7.0 GHz and decreases slowly thereafter to a value of 2.2 at 12.0 GHz. However, for a composite prepared by using Ba(CoTi)0.2Fe11.8O19 hexaferrite, a larger value of 5.0 at 2.0 GHz for ε′, is obtained, which decreases first slowly to 4.2 at 9.0 GHz followed by a sharp decrease
to a value of 2.3 at 14.0 GHz. The dielectric constant for the composite prepared with Ba(CoTi)$_{0.6}$Fe$_{10.4}$O$_{19}$ hexaferrite has a value of 4.7 at 2.0 GHz, which decreases very slowly to 4.0 at 9.5 GHz followed by a sharp decrease to a value of 2.2 at 14.0 GHz. Almost similar variations of $\varepsilon'_r$, with frequency are observed for the composites with $x$ equal to 0.6 and 0.8. For these composites, the value of $\varepsilon'_r$ is 4.8 at 2.0 GHz, which decreases slowly to 4.3 at 9.0 GHz followed by a faster decrease to a value of 2.2 at 15.0 GHz.

The dielectric loss component, $\varepsilon''_r$, is negligible up to a frequency of 4.0 GHz. The $\varepsilon''_r$ has a value of 0.4 at 6.0 GHz for composites with $x = 0.0$ and 0.2. It is negligible up to 6.0 GHz for composites with $x = 0.4$ and 0.6. However, the composites with $x = 1.0$ shows larger values of $\varepsilon''_r$, at lower frequencies from 2.0 to 6.0 GHz range. The dielectric loss, $\varepsilon''_r$, for composite with $x = 0.0$ shows a value of 0.7 from 8.0 to 10.0 GHz which further decreases to 0.4 at 13.0 GHz. The value of dielectric loss, $\varepsilon''_r$, for the composite with $x = 0.2$, is small at 4.0 GHz which starts increasing linearly with frequency to attain a value of 1.4 at 10.0 GHz and further up to 1.5 at 13.0 GHz. The dielectric loss, $\varepsilon''_r$, is negligible up to 6.0 GHz for composites with $x = 0.4$ and 0.6. It then increases sharply to 1.0 at 10 GHz followed by a slow increase to 1.2 at 12.5 GHz and it finally decreases slowly to 0.8 at 16.0 GHz. The variations for composites with $x = 0.4$ and 0.6 are similar. The variations of $\varepsilon''_r$ for Ba(CoTi)$_{0.8}$Fe$_{10.4}$O$_{19}$ ferrite composite are similar to other samples i.e. that it first increases to 1.05 at 9.5 GHz followed by a gradual rise to 1.6 at 14.0 GHz and subsequent marginal decrease to 1.4 up to 16.0 GHz. This data illustrates the shift of loss peak towards higher frequency. The dielectric loss constant, $\varepsilon''_r$, is higher in lower frequency region from 2.0 - 6.0 GHz, increases to 0.8 at 6.0 GHz and then increases rapidly to 1.5 at 9.5 GHz followed by a slow increase to 1.7 at 12.8 GHz before decreasing to 1.2 at 16.0 GHz for composite $x = 1.0$.

The dielectric properties of polycrystalline ferrite-polymer composites arise mainly due to the interfacial polarization and intrinsic electric dipole polarization. The interfacial polarization results from the heterogeneous structure of ferrites comprising low-conductivity grains separated by higher resistivity grain boundaries as proposed by Koops$^{12}$. These boundary layers can be attributed to the superficial reduction or oxidation of the crystals in the porous material as a result of their direct contact with the firing atmosphere. Koops$^{12}$ has assumed that the
intrinsic dielectric constant has approximately the same value as that of the boundary layer. This will be approximately equal to the dielectric constant, \( \varepsilon' \), caused by oxygen ions\(^{13} \). The epoxy resin has also got larger degree of electronic conductivity due to large number of polar groups in its polymer chain. The higher value, \( \varepsilon'_r \), for composites with \( x \) equal to 0.2 and 0.4 may be due to the significant contribution of Co\(^{2+}\)-Ti\(^{4+}\) ions in addition to Fe\(^{3+}\) and Fe\(^{2+}\) ions to interfacial polarization. The dielectric loss, \( \varepsilon''_r \), which represents the phase lag of the dipole oscillations with respect to the applied electric field, depends on the number and nature of ions present. The maximum value of \( \varepsilon''_r \) for composites with \( x \) equal to 1.0 from 8.0 to 9.8 GHz indicated that both Fe\(^{3+}\) and Co\(^{2+}\)-Ti\(^{4+}\) ions contribute significantly as far as dielectric loss is concerned. The conduction in ferrite is attributed to the simultaneous presence of Fe\(^{3+}\) and Fe\(^{2+}\) ions on equivalent lattice sites, which remain f VI and 2b sites present in the R-block of M-type barium ferrite\(^{14,15} \). The exact loss mechanism is however, yet to be ascertained. The electrons can hop between Fe\(^{2+}\) and Fe\(^{3+}\) ions to migrate to 12 K sites, Thus weakening the hopping mechanism and increasing the resistivity. A relatively low resistivity is found to be associated in these ferrite with high dielectric constant. The dielectric loss which is expressed as \( \varepsilon''_r = k\sigma/\omega \), \( k \) is constant, \( \omega \) is angular frequency and \( \sigma \) is conductivity. Brockman\(^{16} \) et al. have discovered that sintered ferrites with a high conductivity at low frequencies always have a high dielectric constant.

The permittivity originated from electronic, ion and intrinsic electronic and interfacial polarization can be described in terms of relaxation formula:

\[
\varepsilon = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)\left[1 + (i\omega\tau)^2\right] \quad \ldots[1]
\]

where \( \varepsilon_0 \) and \( \varepsilon_\infty \) respectively represent permittivity for angular frequency \( \omega \rightarrow 0 \) and \( \omega \rightarrow \infty \) and \( \tau \) is the relaxation time for polarization of ferrite-epoxy composite system.

The real part of permeability, \( \mu'_r \), increases very slowly to 1.1 at 14.0 GHz for hexaferrite composite with \( x = 0.0 \). Permeability, \( \mu''_r \), for the composite with \( x = 0.2 \) increases marginally to 1.3 at 13.0 GHz and increases further to 1.6 at 15.0 GHz. The permeability, \( \mu''_r \), is 1.2 at 13.0 GHz and it increases to 1.4 at 16.0 GHz for the composites with \( x = 0.4 \) and 0.6. The value of \( \mu''_r \) for composite with \( x = 0.8 \) is 1.3 at 10.5 GHz, which increases to 1.4 at 14.0 GHz. The ferrite composite with \( x = 1.0 \) shows a higher values of permeability, \( \mu''_r \), equal to 1.4 in the lower frequency region, which first decreases to 1.2 at 10.0 GHz and again rises to 1.4 at 14.0 GHz. Permeability loss, \( \mu''_r \), is 0.2 at 6.0 GHz which further increases slowly to 0.6 at 12.0 GHz. A small dispersion in \( \mu''_r \) is observed around 13.0 GHz for hexaferrite composite with \( x = 0.0 \). The permeability loss, \( \mu''_r \), for hexaferrite composites with \( x = 0.2, 0.4, 0.6, 0.8 \) and 1.0 is 0.4, 0.3, 0.4, 0.3 and 0.2 respectively at 6.0 GHz, which increases to 0.6, 0.7, 0.7, 0.5 and 0.6 respectively at 13.0 GHz. For Ba(CoTi)\(_x\)Fe\(_{12-2x}\)O\(_{19}\) hexaferrite composite with \( x = 0.8 \), the values of permeability loss, \( \mu''_r \), decreases beyond 12.0 GHz.

The value of relative permeability (\( \mu'_r - j\mu''_r \)) for these composites show only a small variation in the X-band as shown in Figs 1a-f. The real part of permeability, \( \mu'_r \), varies between 1.1 to 1.6 for these composites in the X-band whereas loss component of permeability, \( \mu''_r \), shows almost linear increase for composites with \( x \) equal to 0.2, 0.6, 0.8 and 1.0 except 0.0 and 0.4. The imaginary part of permeability, \( \mu''_r \), exhibits a small peaks at 13.0 GHz for composites equal to 0.0. The magnetic behaviour of composites primarily depends on the hexagonal ferrites used as magnetic filler. The observed magnetic spectra are in agreement with mechanism of natural magnetic resonance involving domain-wall displacement, domain rotation and relaxation of magnetization. These motions lag behind the applied magnetic field and cause magnetic losses in the material, thus, relaxation of magnetization is dominant process and mainly responsible for microwave losses\(^{17} \). The relations expressing the resonance-relaxation phenomena near the characteristics frequency of spin rotation or domain wall displacement are available in literature\(^{18} \). Polycrystalline specimen of a hexagonal ferrite, when c-axis is the preferred direction of magnetization, initial permeability due to rotation is generally small and is given by (\( \mu_0 \rightarrow 1/4\pi = 2/3 \ M_s/H_a \)).
For BaFe$_{12}$O$_{19}$, $\mu_0 - 1 = 0.17$, $H_a = 2K_1/M_s$ is 0.17, $H_a$ is crystalline anisotropy field and $K_1$ is a constant. This contribution is frequency dependent, dispersion at low frequency is presumably associated with resonance of the domain wall, a second dispersion arises out of relaxation phenomena at higher frequency, where both $\mu'$ and $\mu''$ increase with frequency as witnesses in Fig. 1b. As we knew that natural resonance frequencies, $f_0$, can be expressed as $f_0 = \gamma H_a$ and $f_0 = \gamma(H_0 H_0)^{1/2}$ for c-axis and easy c-plane anisotropies respectively, $\gamma = 2.8$ MHz/Oe is the gyromagnetic ratio. This $f_0$ is expected to decrease substantially with progressive substitution of Co$^{2+}$Ti$^{4+}$ content. The effective magnetic spectra of composite have been described in a model$^{19}$, which attempts to predict effective permeability, susceptibility of composites on the basis of grain size and matrix reluctance and their dimensional parameters. The lower values of permeability and weak dispersion effects observed in these samples may be attributed to the presence of non-magnetic epoxy resin between the neighbouring crystallites, which weakens the magnetic interactions$^{20,21}$.

### 3.2 Reflection loss versus frequency

The values of reflection loss and percentage absorption as a function of frequency, obtained from VSWR measurements using the microwave bench for samples of different compositions and a representative thickness of 2.8 mm are shown in Fig. 2. A minimum reflection loss of -16.3 dB (~86% absorption) was observed at 9.2 GHz for composite with $x$ equal to 0.4 and 2.8 mm thickness. Also, a minimum reflection loss of -10.0 dB is observed at 10.8 GHz for Ba(CoTi)$_{1.0}$Fe$_{10.0}$O$_{19}$ hexaferrite composite of 2.8 mm thickness. Other composites with $x = 0.0, 0.2, 0.6$ and 0.8 had not shown any significant absorption in X-band.

Reflection loss is a ratio of reflected power to the incident power and is expressed in terms of reflection coefficient ($\Gamma$) as given below:

$$\text{Reflection loss (dB)} = 20 \log_{10} \Gamma = 20 \log_{10} \left( \frac{\text{VSWR} - 1}{\text{VSWR} + 1} \right) \quad \ldots \ [2]$$

where VSWR is voltage standing wave ratio, this reflection loss can be expressed as a function of normalized input impedance of a metal backed absorber, as:

![Fig. 2 — Variations of reflection loss as a function of frequency for Ba(CoTi)$_x$Fe$_{12-2x}$O$_{19}$ hexaferrite composites prepared by normal sintering and of 2.8 mm thickness](image-url)
Reflection loss (dB) =
\[20 \log_{10} \left(\frac{|Z_{in} - l|}{|Z_{in} + l|}\right)\]  \[\text{[3]}\]

where
\[Z_{in} = \frac{Z_i}{Z_0} = (\frac{\varepsilon_r}{\mu_r})^{\frac{1}{2}} \text{tanh}[j2\pi(\varepsilon_r)\frac{1}{2}fd/c]\]  \[\text{[4]}\]

If we assume that \(\mu_r, \varepsilon_r\) is a constant for short region of frequency, reflection loss varies sensitively on the product \(fd\), \(d\) is the thickness of absorber. High negative values of reflection loss corresponds to larger absorption of microwaves in the samples. Fig. 2 shows the effects of dielectric dispersion and magnetic resonance to reflectivity. This can be understood from two aspects; first, for a single layer of isotropic material, its thickness should be equal to a quarter of wavelength in the frequency region of interest. The quarter wavelength requirement could be fulfilled in the frequency range around dielectric loss and magnetic resonance, that is the way, we can obtain low reflectivity over a broader frequency range. Second, substantial electromagnetic energy is dissipated due to dielectric loss processes and magnetic relaxation, as a result, lower reflectivity is achieved.

4 Morphology and Microstructure

The microstructure control of the Ba-CoTi hexaferrites plays a key role in obtaining desired dielectric and magnetic properties of these materials for their microwave absorbing applications. Morphological characterization of Ba-CoTi hexaferrite was undertaken to study effect of grain size, its orientation and porosity on dielectric and magnetic properties. Fig. 3a-f show the scanning electron micrographs of sintered specimens of Ba(CoTi)\(_x\)Fe\(_{12-2x}\)O\(_{19}\) hexaferrites with \(x = 0.0, 0.2, 0.4, 0.6, 0.8\) and 1.0. The micrographs were obtained on specimen without giving any magnetic orientation to the particles. Small pores are seen in the grains of ferrites with \(x = 0.0, 0.2, 0.4, 0.6, 0.8\) and 1.0 as shown in Figs. 3a-f respectively. The sample with \(x = 1.0\) shows less pores and closely packed large grains as shown in Fig. 4f. The dielectric constant \((\varepsilon_r' - j\varepsilon_r'')\) and magnetic permeability \((\mu_r' - j\mu_r'')\) show fewer variations with frequency for substituted hexaferrite composites, which is attributed to less heterogeneous microstructure for these hexaferrite samples. The hexaferrite with \(x = 0.2\) and 1.0 show higher values of \(\varepsilon_r'\) and \(\varepsilon_r''\), which is probably due to large and almost pore-free grain structure with sharp boundaries of these hexaferrite samples. The permeability \((\mu_r' - j\mu_r'')\) of the composites show small variations in the values of \(\mu_r'\) and \(\mu_r''\) in the X-band, which is attributed to the variations in grain size and less variations in porosity for all hexaferrite samples in addition to the effects of non-magnetic coating of epoxy resin on effective reluctance of the composites, resulting in the weak dispersion phenomena in the spectra of \(\mu_r''\). The average grain size of 5.0-7.0 microns is observed for hexaferrite with \(x = 0.2\) and 1.0. In small grains only domain rotation contributes to \(\mu_r\), in dense and large specimen, a contribution is also made by wall displacements, then for this last magnetization process, we should expect an additional dispersion region. It is as if \(\mu_r\) is less in porous specimens because the rotation of the magnetization is not easier. Lower porosity results in less shape anisotropy and hence in higher rotational permeability and a lower ferromagnetic resonance frequency. Ti\(^{4+}\) non-magnetic ion is used to increase resistivity. Co\(^{2+}\) is used to make grain size small and homogeneous. It is also used to make density high.

The critical grain size at which magnetic material can have a domain wall is expressed by the following equation when the domain wall energy is \(\sigma_w\) and the permeability of vacuum is \(\mu_0\).

\[D_c = 18 \mu_0\sigma_w/M_s^2\]  \[\text{[5]}\]

Domain wall exists when the grain size in the sintered ferrite and the particle size of the magnetic powder in the composite material become larger than this value \(D_c\). The losses due to displacement of domain wall are added to the magnetic losses.

A typical X-ray diffraction spectrum for Ba(CoTi)\(_{0.2}\)Fe\(_{11.6}\)O\(_{19}\) hexaferrite sample is shown in Fig. 4, which confirms single phase magnetoplumbite structure for these hexagonal ferrites.

5 Conclusions

1. The dielectric constant \((\varepsilon_r' - j\varepsilon_r'')\) for hexaferrite composites Ba(CoTi)\(_x\)Fe\(_{12-2x}\)O\(_{19}\) with \(x = 0.0\)-1.0 in steps of 0.2 shows a dispersion characteristics in X-band microwave region. This dielectric dispersion is attributed to interfacial polarization of
ferrite material and to the electric dipole polarization of matrix.

2. The variation of complex permeability is less significant in X-band, the real part of permeability, μ′, is slightly larger than 1, whereas imaginary part, μ″, shows some peaks in few samples. It increases with frequency for a particular composition.

3. A partial substitution of Co²⁺Ti⁴⁺ ions for Fe³⁺ ions in Ba-CoTi hexaferrite-epoxy composites has produced better microwave absorbers at 9.2 GHz region of X-band. Ba(CoTi)₀.₄Fe₁₁.₂O₁₉ hexaferrite composite exhibits the largest reflection loss (16.3
dB) at 2.8 mm thickness, which corresponds to about 87% absorption. Thus, Ba(CoTi)xFe12-2xO19 is a potentially good candidate as electromagnetic absorber in X-band microwave frequency.

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