J Mater Sci (2006) 41:7190–7196
DOI 10.1007/s10853-006-0921-y

Dielectric constant, magnetic permeability and microwave absorption studies of hot-pressed Ba-CoTi hexaferrite composites in X-band

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Received: 13 October 2005 / Accepted: 6 December 2005 / Published online: 18 October 2006

Abstract The microwave absorption, complex permittivity and complex permeability studies of hot-pressed hexaferrite composites prepared with $Ba(CoTi)_xFe_{12-2x}O_{19}$ (x = 0.0, 0.2, 0.4, 0.8, and 1.0) were made in the frequency range from 8.0 to 12.4 GHz. The hexaferrite composites with $x > 0.0$ exhibit significant dispersion in the complex permittivity (ε_r'-jε_r''). However the dispersion in complex permeability (μ_r'-jμ_r'') is not significant and is attributed to the shielding effect of polymer matrix over the ferrite crystallites. The reflection loss has been studied as function of frequency, composition and thickness of absorber. A comparison of reflection loss of hot-pressed ferrite composites with that of normal sintered ferrite composites was made and analyzed. A minimum reflection loss of—24.0 dB is obtained at 9.9 GHz for 2.8 mm thick sample of $BaCo_{0.4}Ti_{0.4}Fe_{11.2}O_{19}$ hot-pressed hexaferrite composite.

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Introduction

An electromagnetic wave absorber for suppression of reflection loss must be composed of material capable of providing the attenuation of incident signal over broad frequency range. The magnetoplumbite–type hexagonal ferrites have played an important role in producing absorbers for higher frequency region of the X-band [1, 2]. These ferrites absorb microwaves due to various interactive loss mechanisms related to magnetization and electric polarization of the material. The complex permeability and permittivity determine the reflection and attenuation characteristics of such materials. The permeability and permittivity of ferrite-polymer composites may depend on the composition of ferrite, nature of the polymer and fill factor, besides microstructure, temperature and frequency of operation. The effect of composition on the microwave absorption characteristics of ferrite-epoxy composites has been reported [3–5] by many researchers. The influence of the fill factor on microwave loss characteristics of ferrite-epoxy composites has been reported [6, 7]. In the present work, we report the variation of reflection loss with substitution of $Co^{2+}Ti^{4+}$ ions in place Fe^{3+}

ions in selected hot-pressed $BaFe_{12}O_{19}$ hexaferrites. It also attempts to compare the reflection loss of normal sintered ferrite composite with those of hot-pressed samples. The results have been discussed on the basis of intrinsic properties and various possible mechanisms of losses in the materials.

Experimental details

A series of samples was prepared by the uniaxial hot pressing method with composition $Ba(CoTi)_xFe_{12-2x}O_{19}$ wherein $x = 0.0, 0.2, 0.4, 0.8$, and 1.0. The samples were synthesized from stoichiometric mixtures of Fe_2O_3, $BaCO_3$, $CoCO_3$, TiO_2 of 99.9% purity by pulverizing each sample and heating in air at 1000 °C for 2 h. The presintered powder was compressed in a die under a pressure of about 780 kg/cm^2 to produce pellets of diameter slightly less than the inner of the silicon carbide die. The pellets were annealed at 400 °C for 1 h to remove binder, which helps to reduce porosity since the sintering parameters like temperature, pressure and time play an important role in controlling the microstructure and magnetic properties of hot-pressed ferrites, an optimum sintering profile was judiciously selected [8–9]. Figure 1 shows the sintering profile used for hot–pressing of various ferrites.

The ferrites–epoxy composites were prepared by homogeneously mixing the ferrite powder with 90% epoxy resin (EPG 280, commercial grade) and 10% hardener (NO 10, commercial grade). The hexaferrite composites of thickness 2.0 and approximately 3.0 mm were prepared by Perspex dies of rectangular shape and size that fit exactly into the rectangular cavity of the X-band microwave bench. The typical rectangular size of samples was ~1.0 cm × 2.54 cm with varying thickness. These samples were cured at 80 °C for 2 h and coated on this aluminum substrate. The variations of reflection loss versus frequency were studied by measuring voltage standing wave ratio in the X-band of microwave bench. X-ray diffraction analyses for few typical samples were made by Philips diffractometer model PW 1730/10, by using Cu-Kα (λ = 1.54056 A°, 40 KV, 30 mA) and Ni filter in wide range of Braggs angles $20° < 2\theta < 70°$ at step size 0.02° 2θ, scan rate 2°/min under controlled room temperature (22° C ± 1), which confirmed the magnetoplumbite type crystal structure for these samples.

To measure the complex relative permeability (μ_r'-jμ_r'') and complex relative permittivity (ε_r'-jε_r'') of these ferrite composites, toroidal shaped samples of 3.5 mm outer diameter and 1.5 mm inner diameter were prepared. The samples were prepared with 50%(weight%) ferrite loading in epoxy resin. The measurement of μ_r', μ_r'', ε_r' and ε_r'' versus frequency were made by reflection/transmission technique [10, 11] using a calibrated Hewlett Packard Network Analyzer Model HP 8510 B. The test samples of toroidal shape were tightly inserted into the standard coaxial line of 15 cm air length. The measured scattering parameters (S_{11}, S_{21}) were used to calculate the values of ε_r', ε_r'', μ_r', and μ_r''. SEM micrographs of fractured surfaces of the ferrite samples were recorded on a Cambridge Stereo Scan 360 Scanning Electron Microscope. The samples for SEM were obtained from broken pellets of sintered hexaferrites and sputter coated with gold on Jeol sputter coater at 12 kV, 7 mA current for 3 min and then viewed directly on scanning electron microscope.

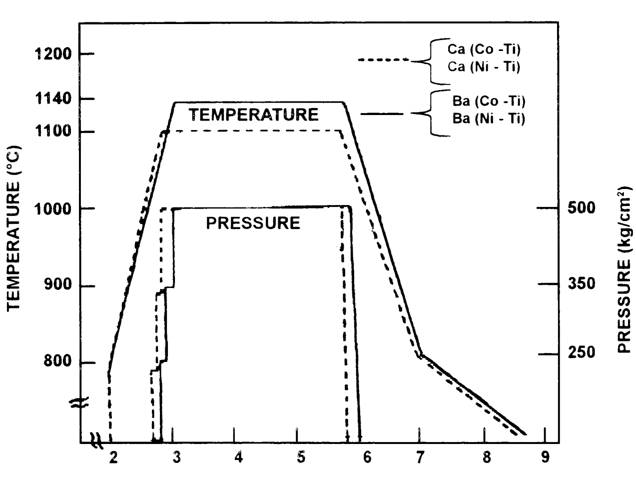

Fig. 1 Sintering profile used for making various hot-pressed hexagonal ferrites

Results and discussion

Dielectric and magnetic parameters

The frequency dependence of ε_r' and ε_r'' for hot-pressed Ba-CoTi hexaferrites-epoxy composites with $Co^{2+}Ti^{4+}$ content $x = 0.0, 0.2, 0.4, 0.8$, and 1.0 are shown in Fig. 2a–e respectively. The unsubstituted hot-pressed hexaferrite composite exhibits slightly higher values of dielectric constant ε_r' than that of unsubstituted normal hexaferite composite in the frequency range from 2.0 to 7.0 GHz. However for other substituted hot-pressed hexaferrite composites with x equal to 0.2, 0.4, 0.8, and 1.0, the value of ε_r' is smaller than that for the corresponding normal hexaferrite composites as reported by us [12]. The normal

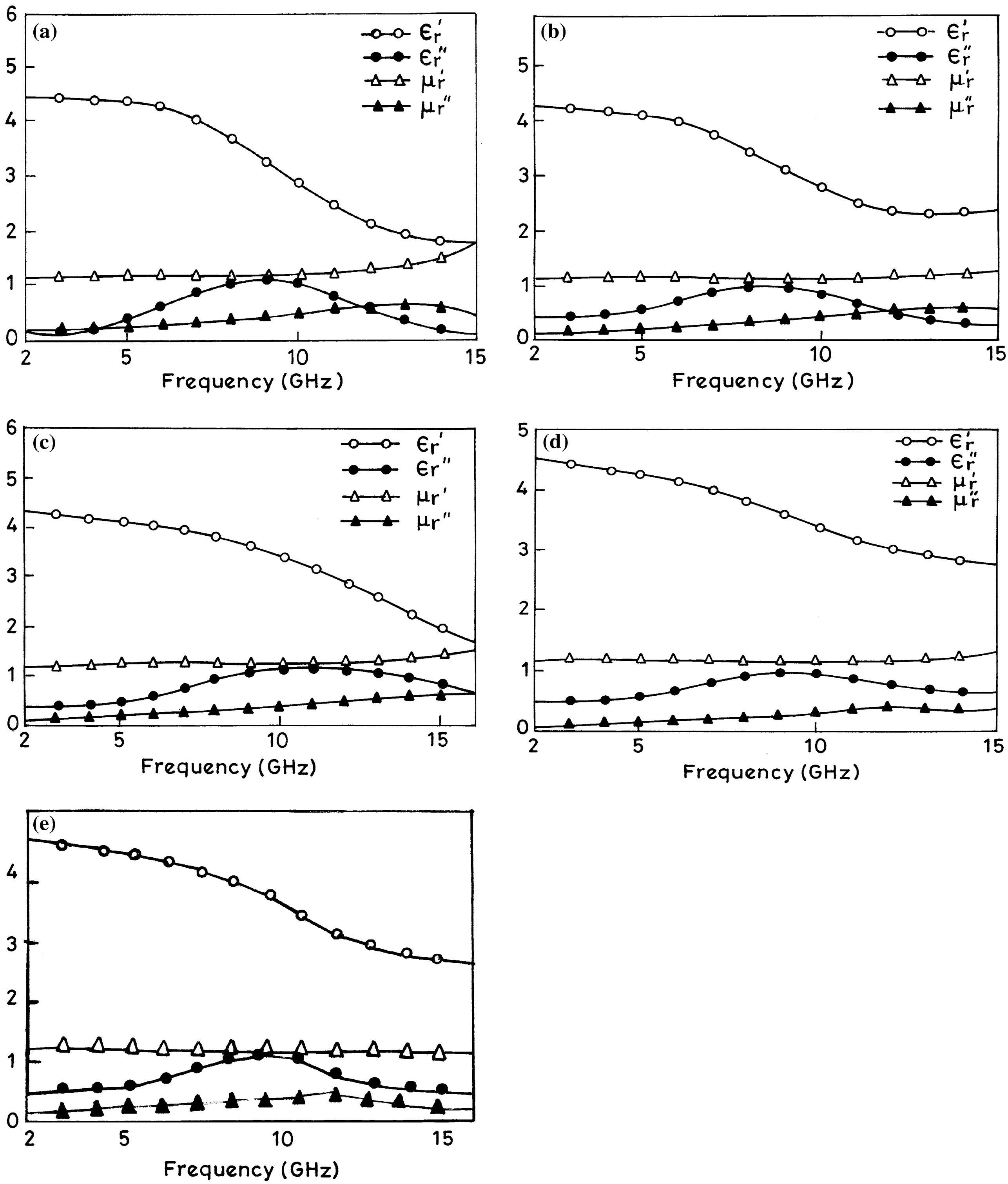

Fig. 2 Variations of ε_r', ε_r'', μ_r' and μ_r'' with frequency for hot-pressed $BaCo_xTi_xFe_{12-2x}O_{19}$ hexaferrite composites (a) x = 0.0; (b) x = 0.2; (c) x = 0.4; (d) x = 0.8; and (e) x = 1.0 respectively

hexaferrite samples show a little higher values for dielectric constant, ε_r', for x = 0.2, 0.4, 0.6, 0.8, and 1.0 as compared with hot-pressed hexaferrites composites in X-band. The dielectric loss component, ε_r'', for normal hexaferrite samples shows higher values at slightly higher frequencies as compared to hot-pressed hexaferrites composites. Dielectric loss component, ε_r'', shows a somewhat higher peak value of 1.0 between 8.0

and 10.0 GHz for hot-pressed ferrite composites as compared to a value of 0.7 for normal hexaferrite composites [12] in the same frequency region as shown in Fig. 2a–e. Thus, hot-pressed composites show higher dielectric loss between 7.0 and 12.0 GHz, in X-band region of microwave frequencies. The values of real component of permeability, μ_r', remain nearly constant from 1.0 to 1.2 up to 10.0 GHz for hot-pressed hexaferrite with $x = 0.0$, 0.2, 0.4, 0.8, and 1.0. The values for the magnetic loss component, μ_r'', are 0.2, 0.1, 0.2, 0.1, and 0.2 at 4.0 GHz for hot-pressed hexaferrite composites with $x = 0.0$, 0.2, 0.4, 0.8, and 1.0 respectively, which increase to the range (0.4–0.5) in the frequency range of 10.0–12.0 GHz for these composites.

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 [13]. 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 [13] 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, ε_r', caused by oxygen ions [14]. The epoxy resin has also got larger degree of electronic conductivity due to large number of polar groups in its polymer chain. The dielectric loss, ε_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 ε_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^{2+} and Fe^{3+} ions on equivalent lattice sites, which remain f_{VI} and 2b sites present in the R-block of M-type barium ferrite [15, 16]. The exact loss mechanism is however, yet to be ascertained. The electrons can hop between Fe^{2+} and Fe^{3+} ions on the neighbouring equivalent sites and cause conduction. As Co^{2+} and Ti^{4+} ions have site preference for $4f_{VI}$ and 2b sites, the substitution of these ions in barium ferrite forces some of the 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 ferrites with high dielectric constant. The dielectric loss which is expressed as $\varepsilon_r'' = k\sigma/\omega$, k is constant, ω is angular frequency and σ is conductivity. Brockman [17] et al. has 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:

$$\varepsilon = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)/(1 + (\omega\tau)^2) \quad (1)$$

where ε_0 and ε_∞ respectively represent permittivity for angular frequency $\omega \to 0$ and $\omega \to \infty$ and τ is the relaxation time for polarization of ferrite-epoxy composite system.

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 [18]. The relations expressing the resonance-relaxation phenomena near the characteristics frequency of spin rotation or domain wall displacement are available in literature [19]. Polycrystalline specimen of a hexagonal ferrite, when c-axis is preferred direction of magnetization, initial permeability due to rotation is generally small and is given by $(\mu_0–1)\,4\pi = 2/3\ M_s/H_a$. For $BaFe_{12}O_{19}$, $(\mu_0–1) = 0.17$, $H_a = 2K_1/M_s$, an additional component to permeability is added by reversible domain wall displacement due to some large grain in specimen. M_s is saturation magnetization, 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 domain wall, a second dispersion arises out of relaxation phenomena at higher frequency, where both μ_r' and μ_r'' increase with frequency as has been witnessed in these sample in X-band of microwave region. As we know that natural resonance frequency, f_o, can be expressed as $f_o = \gamma H_a$ and $f_o = \gamma(H_\theta H_\phi)^{1/2}$ for c-axis and easy c-plane anisotropies respectively, $\gamma = 2.8$ MHz/Oe is the gyro-magnetic ratio. Moreover, the effective magnetic spectra of composite have been described in a model [20], 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 [21, 22].

Reflection loss versus frequency

Figure 3 shows the variation of reflection loss as a function of frequency for the hot-pressed hexaferrite composites with $x = 0.0$, 0.2, 0.4, 0.8, and 1.0 and of 2.0 mm thickness. A minimum reflection loss –10.0 dB for hot-pressed composites with $x = 0.2$ and 2.0 mm thickness was observed at 9.9 GHz. Another sample of 2.0 mm thickness with $x = 1.0$ showed a minimum reflection of –9.0 dB at 10.0 GHz. All other hot-pressed hexaferrite composites of 2.0 mm thickness showed an absorption loss of less than 8.0 dB in the X-band.

A maximum reflection loss of –12.0 dB was obtained for $Ba(CoTi)_{1.0}Fe_{10.0}O_{19}$ hot-pressed hexaferrite composite of 2.5 mm thickness at 9.9 GHz as shown in Fig. 4. Figure 5 shows the comparison of reflection loss as a function of frequency for $BaCo_{0.4}Ti_{0.4}$ $Fe_{11.2}O_{19}$ ferrite composites of 2.8 mm thickness prepared by the normal ceramic and hot-pressing technique. The hot-pressed sample showed an improvement of absorption to –24.0 dB at 9.9 GHz as to that of –16.0 dB at 9.2 GHz observed by normal sintered composite sample of same 2.8 mm thickness and with same composition of ferrite. This is primarily because of higher dielectric losses in lower region of frequencies and slightly reduced values of dielectric constant, ε_r' obtained for hot-pressed ferrites.

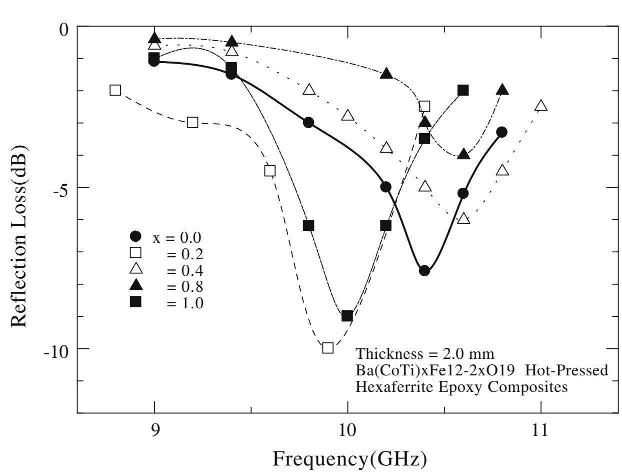

Fig. 3 Reflection loss (dB) versus composition for hot-pressed $BaCo_xTi_xFe_{12\text{-}2x}O_{19}$ hexaferrite epoxy composites of 2.0 mm thickness

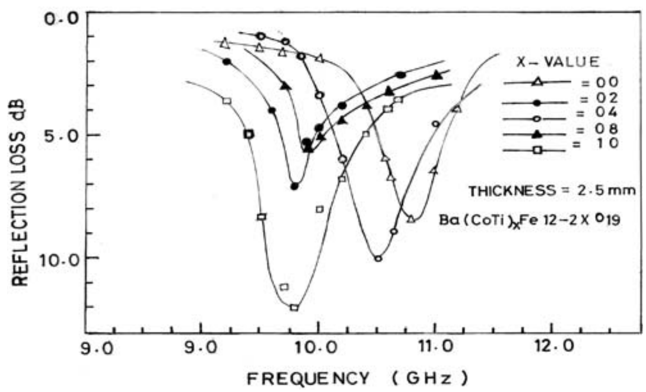

Fig. 4 Reflection loss (dB) versus composition (x) for hot-pressed $BaCo_xTi_xFe_{12\text{-}2x}O_{19}$ hexaferrite epoxy composites of 2.5 mm thickness

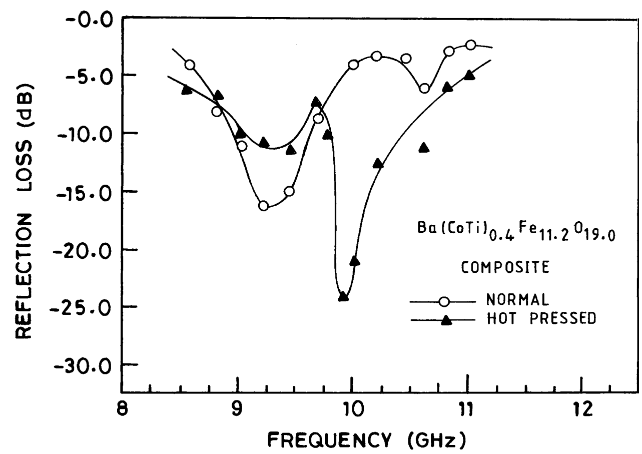

Fig. 5 Comparison of reflection loss (dB) achieved for $BaCo_{0.4}$-$Ti_{0.4}Fe_{11.2}O_{19}$ hexaferrite epoxy composites of 2.80 mm thickness prepared by normal ceramic and hot-pressed methods

Microwave absorbing properties

Reflection loss is related to reflection coefficient (Γ) & VSWR as given below:

$$\text{Reflection loss (dB)} = 20\log_{10}\Gamma = 20\log_{10} (\text{VSWR}-1)/(\text{VSWR}+1) \tag{2}$$

where VSWR is voltage standing wave ratio, this reflection loss can be expressed as a function of normalized input impedance of metal backed absorber. The normalized input impedance (Z_{in}) of a microwave absorbing layer backed by reflector at rear surface is given by:

$$Z_{in} = Z_i/Z_0 = (\mu_r/\varepsilon_r)^{1/2}\tanh[j2\pi(\mu_r\varepsilon_r)^{1/2}fd/c] \tag{3}$$

Z_{in} is the normalized input impedance at the absorber surface, Z_i is the input impedance and Z_0 is the free space impedance, μ_r and ε_r are relative permeability and permittivity of medium, f is the frequency of microwave in free space, c is the velocity of electromagnetic wave and d is the thickness of absorber.

Reflection loss, a ratio of reflected power to that of incident power, is related to Z_{in} as:

$$\text{Reflection loss (dB)} = 20\log_{10}[|(Z_{in}-1)/(Z_{in}+1)|] \tag{4}$$

Thus surface reflectance of an absorber is a function of six characteristic parameters, viz, f, d, μ_r', μ_r'', ε_r', and ε_r''. It is possible to evaluate the numerical values of the parameters f and d corresponding to the zero reflection condition (Z_{in} = 1.0) by substituting the measured values of μ_r', μ_r'', ε_r', and ε_r'' into the Eqs. (1) and (2). The values of reflection loss calculated using Eqs. (2) and (3) for various measured values of μ_r', μ_r'', ε_r', and ε_r'' for $BaCo_{0.4}Ti_{0.4}\ Fe_{11.2}O_{19}$ hot-pressed hexaferrite composite are shown in Fig. 6. The comparison of reflection loss measured and calculated for $BaCo_{0.4}Ti_{0.4}\ Fe_{11.2}O_{19}$ hot-pressed hexaferrite composite can be made from Figs. 5 and 6. The peak of experimental curve falls almost at the same frequency as that of theoretical curve. However, half bandwidth of experimental reflection loss does not match with theoretical curve. This is because of various errors at experimental measurement level due to spurious reflections caused by various components of waveguide in measurement of reflection on microwave bench, and also due to surface irregularity of absorbing sample. The gap

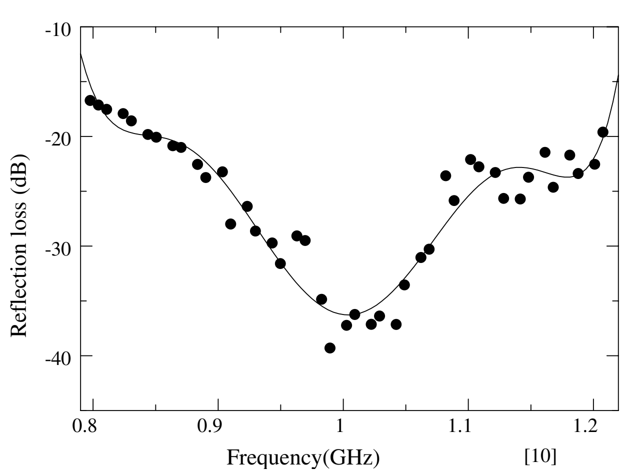

Fig. 6 Reflection loss (dB) theoretically obtained by substituting the experimentally measured values of ε_r', ε_r'', μ_r' and μ_r'' in numerical equations for hot-pressed $BaCo_{0.4}Ti_{0.4x}Fe_{11.2}O_{19}$ hexaferrite epoxy composites at 2.80 mm thickness

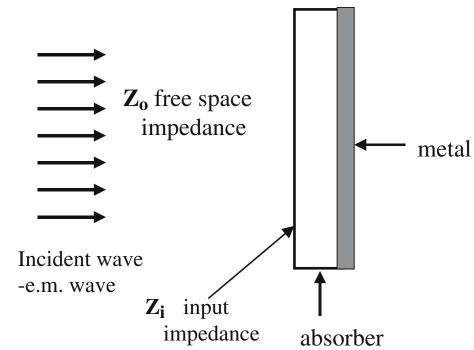

Fig. 7 Schematic diagram of microwave absorber

between the waveguide dimensions and sample size and instability in the frequency source of microwave bench cause errors in the measured values of voltage standing wave ratio. If we assume that $\mu_r.\varepsilon_r$ is a constant for short region of frequency, reflection loss varies sensitively on the product $f{\cdot}d$, d is the thickness of absorber. High negative values of reflection loss (Fig. 6) correspond to larger absorption of microwaves in the samples. There are two basic requirements for thin layer isotropic absorbers, first its thickness should be of quarter of wavelength in region of frequencies of interest and second materials must show higher dielectric and magnetic loss in the same region of interest. This is the way; we obtain low reflection loss in desired frequency band. (Fig. 7)

Morphology and microstructure

Microstructure plays a key role in obtaining the desired dielectric and magnetic properties of these materials for their microwave absorption applications. Few typical samples of hot-pressed Ba-CoTi hexaferrites with x = 0.4 and 1.0 were studied with scanning electron microscopy. The micrographs were obtained on specimen without giving any magnetic orientation to particles. SEM micrograph (Fig. 8) of sample x = 0.4 shows small grains of varying sizes. The sample with x = 1.0 shows bigger grains of up to 10 μm size also (Fig. 9). Domain wall exists when the grain size in the sintered ferrite and the particle size of the magnetic powder in the composite matrix become larger than critical grain size such as Dc = 18 $\mu_0\sigma_w/M_s^2$, where σ_w is domain wall energy, M_s is saturation magnetization for given sample. So loss due to displacement of domain wall is added to magnetic losses.

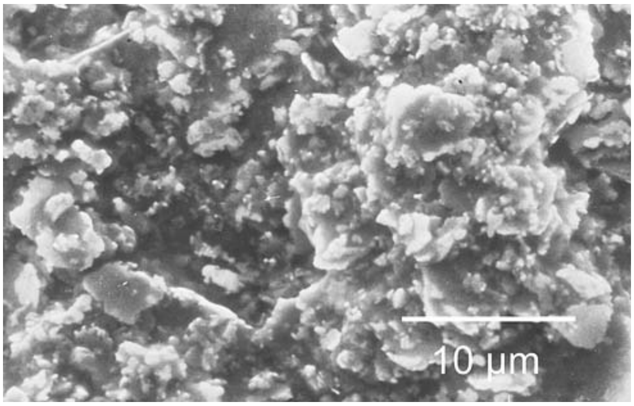

Fig. 8 SEM micrograph shows smaller grains of various sizes for $BaCo_{0.4}Ti_{0.4}Fe_{11.2}O_{19}$ sintered hexaferrite

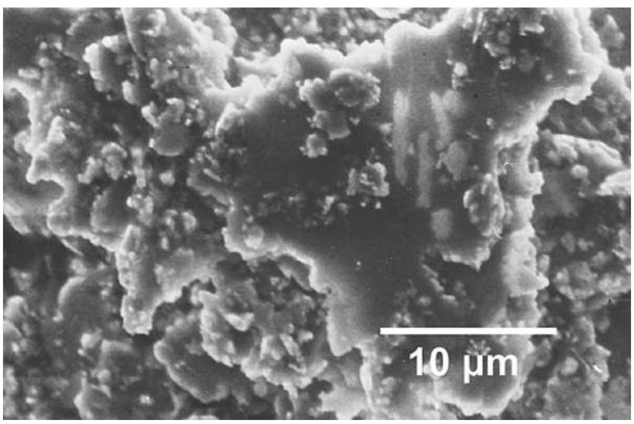

Fig. 9 SEM micrograph shows the larger plate shaped grains (>10 μm) along with smaller grains for $Ba(CoTi)_{1.0}Fe_{10.0}O_{19}$ sintered hexaferrite

Conclusions

1. The dielectric constant (ε_r', ε_r'') for hot-pressed hexaferrite composites $Ba(CoTi)_xFe_{12-2x}O_{19}$ with x = 0.0, 0.2, 0.4, 0.8, and 1.0 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. Variation of complex permeability is not significant; μ_r' varies from 1.1 to 1.3 for all hot-pressed hexaferrite composites, whereas μ_r'' shows no peaks in X-band. Absence of significant dispersion in magnetic permeability is attributed to the shielding effect of polymer matrix over the ferrite's crystallites.
3. A partial substitution of $Co^{2+}Ti^{4+}$ ions for Fe^{3+} in hot-pressed $Ba(CoTi)_{0.4}Fe_{11.2}O_{19}$ hexaferrite has produced an improved microwave absorber which exhibits a reflection loss (–24.0 dB) at 9.9 GHz as compared to normal sintered hexaferrite (maximum absorption –16.3 dB) at 9.2 GHz. Thus hot-pressed $Ba(CoTi)_{0.4}Fe_{11.2}O_{19}$ hexaferrite composite is a superior microwave absorber at 9.9 GHz region of microwave frequency.
4. The theoretically calculated values of reflection loss for 2.8 mm thick hot-pressed $Ba(CoTi)_{0.4}Fe_{11.2}O_{19}$ hexaferrite composite absorber obtained by putting the measured values of parameters f, μ_r', μ_r'', ε_r', and ε_r'' show similar graph (Fig. 6) as that of experimental curve (Fig. 5) for same thickness. Experimental curve differs due to several errors and assumptions made while making experimental measurements.

Acknowledgements The author (PS) would like to thank Dr. R. K. Puri, former professor, Department of physics, I.I.T. Delhi, New Delhi for his guidance and support in this work. Thanks are also due to Mr. Vipitya Katiyar, Department of physics, Allahabad University for his help at measurement stage on MNA Model HP 8510B.

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