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Nanosized barium hexaferrite in novolac phenolic resin as microwave absorber for X-band application

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ABSTRACT

Nanosized barium ferrite ($BaFe_{12}O_{19}$) with Novolac phenolic resin (NPR) is developed as a magnetic absorber for application in the frequency range 8.2–12.4 GHz. The absorption is studied by modifying the microstructural properties of the ferrite inclusion with annealing temperature and its content in the composite. Transmission electron microscopy and X-ray diffraction pattern confirms the formation of hexagonal structure of barium ferrite. The crystallite size of the barium ferrite particles is in nano-range and increases with annealing temperature. The $BaFe_{12}O_{19}$/NPR composite is prepared with different weight percentage of ferrite inclusions. The complex permittivity and complex permeability is measured at X-band and found to increase with annealing temperature and contents of ferrite inclusion. Theoretical study of reflection loss gives that 2 mm absorber samples are showing the best results for X-band application. Reflection loss measurement of the samples shows absorption peak of −24.61 dB at 10.26 GHz for 30 wt%, −28.39 dB at 9.98 GHz for 40 wt% and −37.06 dB at 9.5 GHz for 50 wt% of $BaFe_{12}O_{19}$ in NPR matrix.

1. Introduction

Leakages of electromagnetic wave in various communication systems lead to electromagnetic interference (EMI). Shielding materials minimize the external electromagnetic waves from interfering in functioning of electronic devices as well as camouflaging materials in defence application. In the past few decades a lot of works on development on EMI shielding material has been carried out and some of the references are reported [1–5]. For maximum absorption of electromagnetic (em) wave, both the electric and magnetic components should be sufficiently attenuated within the absorber thickness. In dielectric absorbers, the magnetic loss component is zero, hence to get good absorption the thickness of the absorber has to be increased [5]. Presence of both the magnetic and dielectric losses in magnetic absorber helps to attenuate electromagnetic wave within a smaller thickness [6–8].

The extent of absorption depends on electromagnetic wave interactions with the material properties viz. complex permittivity and complex permeability, on size and shape of the filler particles and thickness of the absorber [9]. Nanosized particles have high interfacial area, which creates a large interaction zone and hence increases interfacial polarizations and magnetic interactive loss mechanism, leading to enhanced dielectric and magnetic properties and hence increases microwave absorption [9–12].

In the present work, the microwave absorption is studied with different size and shape of the filler particles for which the precursor powders are annealed at three different temperatures. The temperature is controlled to assure that only one phase of the barium ferrite is formed. M-type nano-barium hexagonal ferrite ($BaFe_{12}O_{19}$) is used for development of X-band absorbers as it has high saturation magnetization, high crystalline anisotropy, low density as compared to bulk barium ferrite and is chemically stable. The complex permeability of spinel type ferrites drops at high frequency range as given by Snoek's limit, which limits its use at gigahertz frequency range. Moreover, high crystalline anisotropy of barium ferrite leads to more electromagnetic energy dissipation, specially in the gigahertz frequency range [13–16].

In the present investigation, nanosized barium ferrite particles are synthesized and used as the magnetic inclusions in the novolac phenolic resin (NPR) matrix. The hydroxyl and methylene linkages present in NPR chemical structure, facilitates bonding for composite formation [17]. NPR has good heat resistance, electrical insulation, dimensional stability and chemical inertness and is also cost effective [18,19]. Microstructural properties of the synthesized M-type barium ferrite particles and thermal and electric properties of the $BaFe_{12}O_{19}$/NPR nanocomposites are studied. Microwave characterisations are conducted on the $BaFe_{12}O_{19}$/NPR nanocomposite to investigate its performance as microwave absorber. The thickness of the absorber is optimized using the transmission line method (TLM) [20], and

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reflection loss is measured using the transmission/reflection method [21].

2. Synthesis of magnetodielectric material

2.1. Preparation of M-type barium ferrite ($BaFe_{12}O_{19}$)

M-type barium ferrite ($BaFe_{12}O_{19}$) particles are prepared using nitrate precursors. Barium nitrate (≥98%) and iron (III) nitrate nonahydrate (≥98%) precursors are used as the base materials to which sodium hydroxide is added dropwise to control the size of the particles. Oleic acid is used as surfactants in order to reduce interparticle interaction and distribution. Aqueous solutions of barium and iron salts are prepared separately by dissolving the salts in RO (reverse osmosis) deionized water maintaining the molar ratio of barium to ferric nitrate as 1:12 with constant magnetic stirring condition. Then the iron and barium salt solutions are mixed together and heated at 70 °C with continuous magnetic stirring for 1 h. 4 M (25 ml) solution of sodium hydroxide is prepared separately and slowly added to the salt solution drop wise. The pH of the solution is maintained to a level of 11–12. A few drops (~0.1 ml) of oleic acid ($C_{17}H_{33}COOH$) is added to the solution as a surfactant and coating material [22]. The product is then cooled to room temperature. Subsequently, the precipitate is washed twice with distilled water and ethanol to get the precipitate free from sodium and nitrate compounds. Finally, the precipitate is dried at 100° C in order to remove the water. The dried powder is crumbled and annealed at three different temperatures, 700 °C (*T*7), 800 °C (*T*8) and 900 °C (*T*9) for 2 h to get barium ferrite particles of reduced size.

2.2. Fabrication of $BaFe_{12}O_{19}$/NPR composite:

Novolac type phenolic resin with 10% hexamethylene tetramine as harderner (supplied by Pheno Organic Limited, New Dehli) is used as matrix for the composite in the present investigation. The $BaFe_{12}O_{19}$ and NPR powders are mechanically blended to obtain uniform mixture with varying weight ratios of $BaFe_{12}O_{19}$ to NPR as 30:70, 40:60 and 50:50. The mixture is then placed in a specially designed three-piece die-mould and initially heated up to 95–100 °C. A pressure up to 1.5–2 t is slowly applied and the sample holder with the sample is isothermally heated at 150° C for 2 h and then allowed to cool at room temperature. Pellets of dimensions, 10.38 mm × 22.94 mm × 2 mm are prepared for microwave characterization.

2.3. Analysis and characterization techniques

Microstructural characterization: X-ray diffraction patterns (Rigaku, Miniflex 200 X-ray diffractometer) of the prepared materials are obtained using Cu Kα radiation (wavelength, $\lambda = 1.541841$ Å) at room temperature. Shape and size of the ferrite is determined by transmission electron micrograph using JEOL-TEM-100 CXII (Collidion Coated Copper Grids). Thermal gravimetric analysis (TGA) of the materials is performed on Thermal Analyzer, (Model STA 6000, Perkin Elmer). Electrical conductivity is measured by two probe method using Keithley 2400C—source metre. The resistivity is calculated using the measured value of resistance and the physical dimension of the samples.

Microwave characterization: Complex permittivity and complex permeability over the X-band is computed from S_{11} and S_{21} values using the Nicolson–Ross method [23]. Reflection loss parameter is measured using the transmission/reflection method, using Agilent WR-90 × 11644 A rectangular waveguide line compatible with Agilent 8722ES vector network analyzer [21].

3. Results and discussion

3.1. Microstructural, thermal and electrical studies of M-type barium hexaferrite

3.1.1. X-ray diffraction

X-ray diffraction (XRD) patterns of the barium ferrite particles are recorded at 2θ values from 20° to 80°. Diffraction pattern of $BaFe_{12}O_{19}$ particles annealed at $T = 700$ °C, 800° and 900° C is shown in Fig. 1a–c. The reflection planes: (1 0 2), (1 1 0), (1 0 7), (1 1 4), (2 0 0), (2 0 3), (0 0 10), (2 0 5), (10 12), (3 0 0), (2 1 7), (2 0 11), (2 2 0), (2 0 14), (3 1 6) and (4 0 4) indicate the presence of a hexagonal structure. Crystallinity and size of the particles are calculated from the XRD patterns using Debye–Scherrer formula [24]. The lattice parameters for the hexagonal magnetoplumbite phases are computed (Table 1) using the d-spacings value and the respective (*h k l*) parameters. Interplanar distance, *d* is given by

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + k^2 + l^2}{a^2}\right) + \frac{l^2}{c^2} \tag{1}$$

The lattice constants, $a = 5.88$ Å and $c = 23.22$ Å agree with those reported in JCPDS card number 43–0002. The average crystalline size is in nanometre range and is found to increase with annealing temperatures (Table 1). The size variation and control can be achieved by the annealing conditions.

3.1.2. Transmission electron micrographs

Transmission electron micrograph is taken to see the microstructural properties like shape and size using JEOL-TEM-100 CXII (Collidion Coated Copper Grids). Most of the particles appear hexagonal in shape for all the three annealing temperatures as seen in TEM images, Fig. 2a–c. The particle shape is hexagonal and its size is ~50 nm and ~60 nm for the samples annealed at temperature, $T = 700$° C and 800° C. Extended rod like shape in one direction is observed for the particles annealed at 900° C with crystal lattice plane anisotropy with particle size of ~70 nm (Fig. 2c) and explain in terms of surface energy. The surface energy of barium ferrite is different along different directions of the unit cell. The growth of the nanoparticles along [0001] direction is preferential i.e. the *c*-axis, as it is energetically favourable due to minimum surface energy at higher temperature and hence, the elongated rod shaped nanostructure formation is observed [25].

3.1.3. Thermal gravimetric analysis (TGA)

The thermal stability of the prepared samples of $BaFe_{12}O_{19}$/NPR composite is measured in the air atmosphere as shown in Fig. 3 (a) and (b). The TG analysis gives the weight loss of the samples in the temperature range of 50–685° C. TGA curve of NPR shows that there is small weight loss up to 160 °C. The major weight loss occurs due to growth of volatiles in between the temperatures 390–685° C [26]. The $BaFe_{12}O_{19}$ particles show thermal stability throughout the temperature range with a very small weight loss after 550° C. The TGA graph of all the three samples with varying weight percentage of ferrite inclusions (30 wt%, 40 wt% and 50 wt%) shows thermal stability up to 400° C. Thereafter, 30 wt% and 40 wt% show continuous weight loss of 28% and 31% respectively up to 685° C. With increase in the $BaFe_{12}O_{19}$ contents in the NPR matrix, thermal stability of the absorber samples increases. The thermal stability of the $BaFe_{12}O_{19}$/NPR composite does not change with the annealing temperature of the ferrite particles as can be seen from Fig. 3a.

3.1.4. DC conductivity study

Fig. 4a and b shows the variation of in-plane electrical conductivity of the $BaFe_{12}O_{19}$/NPR composite with increasing annealing temperature of the $BaFe_{12}O_{19}$ particles and with increasing