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Electrical and magnetic properties of barium hexaferrite nanoparticles prepared by citrate precursor method

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Abstract

Ferromagnetic nanomaterials are of particular interest, because at nanoscale a crystallite can exhibit a single magnetic domain. These nanomaterials therefore exhibit different magnetic properties as compared to bulk. Recently, barium ferrite has gained importance due to its potential use in magnetic recording and in microwave devices. Barium ferrite nanoparticles are prepared by the citrate precursor method by varying the pH of the solution and calcination temperature. The effect of particle size and capping reagent on the structural, dielectric and magnetic properties of the resulting barium hexaferrite particles has been studied, and reported in the present paper.

Keywords: C. Electrical properties; C. Magnetic properties; Barium hexaferrite

1. Introduction

Hexaferrites are classified into five types depending on chemical formulae and crystal structure. These include M-type ($BaFe_{12}O_{19}$), W-type ($BaMe_2Fe_{16}O_{27}$), X-type ($Ba_2Me_2Fe_{28}O_{46}$), Y-type ($Ba_2Me_2Fe_{12}O_{22}$), and Z-type ($Ba_3Me_2Fe_{24}O_{41}$). M-type barium hexaferrite $BaFe_{12}O_{19}$ has been intensively studied as a material for permanent magnets, high-density magnetic recording media and microwave devices [1–7]. Because of current interests in nanoparticles of M-type materials, the nanoparticles have been prepared by various groups employing different methods such as ceramic method, chemical coprecipitation, aerosol pyrolysis, sol–gel, crystal glass, and citrate precursor [8–13].

The present work investigates the effect of the pH on the microstructure, structure, Curie temperature, microwave permeability and permittivity of M-type barium hexaferrite nanoparticles prepared by citrate precursor method. The citrate precursor method is versatile for preparing nanoparticles, and does not violate the laws of green chemistry. In addition it is a low temperature method and results in homogeneously distributed particles because of the mixing of the constituents at atomic level.

2. Experimental procedure

2.1. Material preparation

$BaFe_{12}O_{19}$ nanoparticles were prepared by the citrate precursor method. The starting materials used were iron citrate (Merck, Germany), barium nitrate (Merck, Germany) and citric acid (Merck, India) of high purity. The chemicals were weighed according to their stoichiometric proportion. Iron citrate solution was prepared in DI water by heating at 40 °C with continuous stirring. Barium nitrate was added to citric acid and dissolved in DI water. The pH of the solution was controlled by adding NH_4OH. The solutions were mixed, and the solvent was vaporized at 40 °C. The precursor powder was calcined at 600 °C for 1 h for the ferrite phase formation. The resulting powder was sintered at 1100 °C for 3 h.

X-ray powder diffraction technique was used for the identification of phases and also for the estimation of the particle size formed at different pH values and calcinations temperatures in various specimens.

2.2. Microwave measurement

Measurements of the complex permeability and permittivity were carried out by a Microwave Network Analyzer (Hewlett Packard model 8719E) using cavity perturbation method [14]. The cavity was made up of a standard X-band brass wave-guide of length 13.5 cm (Fig. 1). The upper broad

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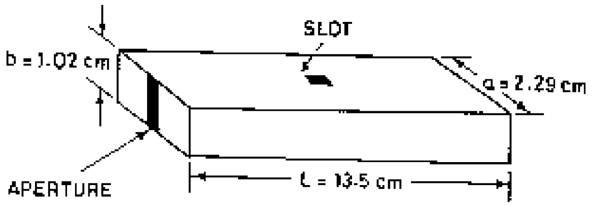

Fig. 1. Rectangular resonator cavity with dimensions $L = 13.5$ cm, $a = 2.29$ cm, $b = 1.02$ cm. Slot is 3 mm × 1.2 mm and the width of the aperture is 2.5 mm.

wall of the guide had a slot ~2.5–3 mm in length and 1.2 mm in width. Conducting plates with small aperture opening (2.5 mm wide) on either side of the guide provided inductive coupling to the cavity. The number of resonant peaks being dependent on the length of the cavity, the cavity was excited into five modes (TE_{105}–TE_{109}) utilizing the swept frequency option of the analyzer.

Accordingly five resonant peaks corresponding to frequencies 8.6, 9.36, 10.18, 11.06 and 11.97 GHz appeared on the screen of the analyzer. Looking at the field configuration in the cavity, when we consider symmetrical loading of the specimen in the cavity (i.e. specimen at the geometrical center of the cavity), the specimen will be in the maximum electric field for odd modes and it will be in the maximum magnetic field for even modes. Therefore odd resonant modes give the electrical parameter while even modes the magnetic one. Measurements of resonant frequency, quality factor and geometrical parameter of the cavity and the specimen enabled the calculation of the complex permittivity and permeability of a specimen.

The real and imaginary parts of the complex pemittivity and permeability were calculated using the following relations:

$$\varepsilon' = 1 + \left[\frac{V_c}{V_s}\right]\left[\frac{(f_2 - f_1)}{2f_1}\right], \tag{1}$$

$$\varepsilon'' = \left[\frac{V_c}{4V_s}\right]\left[\frac{1}{Q_2} - \frac{1}{Q_1}\right], \tag{2}$$

$$\mu' = 1 + \left[\frac{1}{k}\right]\left[\frac{V_c}{V_s}\right]\left[\frac{(f_2 - f_1)}{f_2}\right] \tag{3}$$

$$\mu'' = \frac{V_c}{2kV_s}\left[\frac{1}{Q_2} - \frac{1}{Q_1}\right] \tag{4}$$

where V_c and V_s are the volumes of the empty cavity and the sample, respectively, f_1 and Q_1 are resonance frequency and the quality factor of the empty cavity, and f_2 and Q_2 are corresponding qualities for the perturbed case. The geometrical parameter $k = 2a^2/(a^2 + l^2)$, where 'l' and 'a' are, the length and breadth of the cavity.

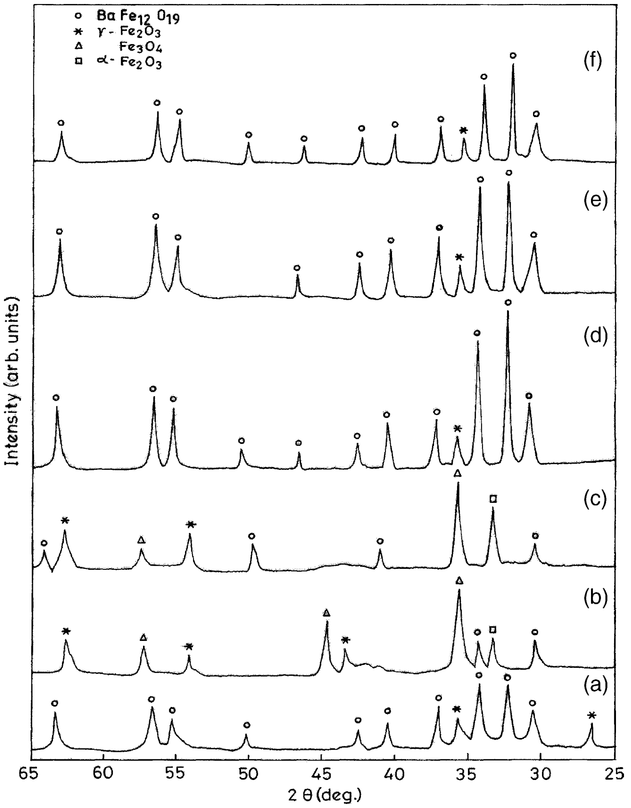

Fig. 2. X-ray diffraction patterns: (a–c) for the calcined (600 °C/1 h) powders obtained at pH = 1.88, 5.25 and 9; (d–f) for the sintered (1100 °C/3 h) samples of barium ferrite.

3. Results and discussion

The XRD patterns of the calcined powder obtained from solutions having pH = 1.88, 5.25 and 9.0 are shown in Fig. 2(a–c), and after sintering the powder at 1100 °C for 3 h are shown in Fig. 2(d–f). It is evident from the Fig. 2(a) that at pH = 1.88, powder M-type barium ferrite. But for the powder obtained from solutions with pH = 5.25 and pH = 9, exhibit in addition peaks of γ-Fe_2O_3, α-Fe_2O_3 and Fe_3O_4 as intermediate phases. These get converted into barium ferrite phase after sintering at higher temperature (Fig. 2(d–f)). Even at 1100 °C there is one peak for the Fe_2O_3 (Fig. 2(d–f), which can convert to purely M-type barium ferrite phase at 1200 °C or higher sintering temperatures [15]. The barium ferrite phase was formed at lower temperature 600 °C for the powder prepared from the precursor solution having pH = 1.88, which is strongly acidic. On increasing NH_4OH for increasing the pH value there is more number of OH^- ions in the solution, that disturbs the balance between the Fe^{3+} and Fe^{2+} ions and that may cause the formation of intermediate phases Fe_2O_3 and Fe_3O_4 in excess with the barium ferrite phase, which transforms into a M-type barium ferrite phase after sintering.

The particle size estimated from the Scherrer formula as given below. The average crystallite diameter (L) can be calculated by formula:

$$L = 0.9\frac{\lambda}{\Delta w \cos\theta} \tag{5}$$

where λ is the X-ray wavelength, θ the angle of Bragg diffraction and Δw is the difference between the full width at half-maximum (FWHM) and instrumental broadening. The particle size was estimated to be 14.5 nm for the powder obtained from the solution having pH = 5.25. For other samples prepared from solutions of pH = 1.88 and pH = 9.0, the particle sizes were found to be 21.1 and 21.7 nm, respectively. A pH value of 5.25 thus resulted in a powder having minimum particle size of 14.5 nm.

The Curie temperature for the barium ferrite nanoparticles was measured as 516 °C, which is higher in comparison to $BaFe_{12}O_{19}$ bulk value of 450 °C. The presence of γ-Fe_2O_3 and α-Fe_2O_3 phases affects the Curie temperature. This inference is drawn from the fact that for the powders obtained at pH = 5.25 and pH = 9.0, the Curie temperature is found to be very high (649 and 644 °C, respectively) in comparison to the first sample (pH = 1.88). This observed higher Curie temperature feature confirms the formation of Fe_2O_3 phase with the M-type barium ferrite phase in our sample.

The frequency dependence of dielectric and permeability parameters of these particles is shown in Figs. 3 and 4, respectively. For the powder prepared from the precursor solution having pH = 1.88, the value of dielectric constant (ε') decreases with the increase in frequency, which is a normal dielectric behavior of ferrites and can be explained on the basis of space charge polarization, which is a result of the presence of higher conductivity phases (grains) in the insulating matrix (grain boundaries) of a dielectric, causing localized accumulation of charge under the influence of an electric field. For the samples prepared from the precursor solution pH = 9.0, ε' is nearly constant. But dielectric constant increases about 2–3-folds for the sample prepared from

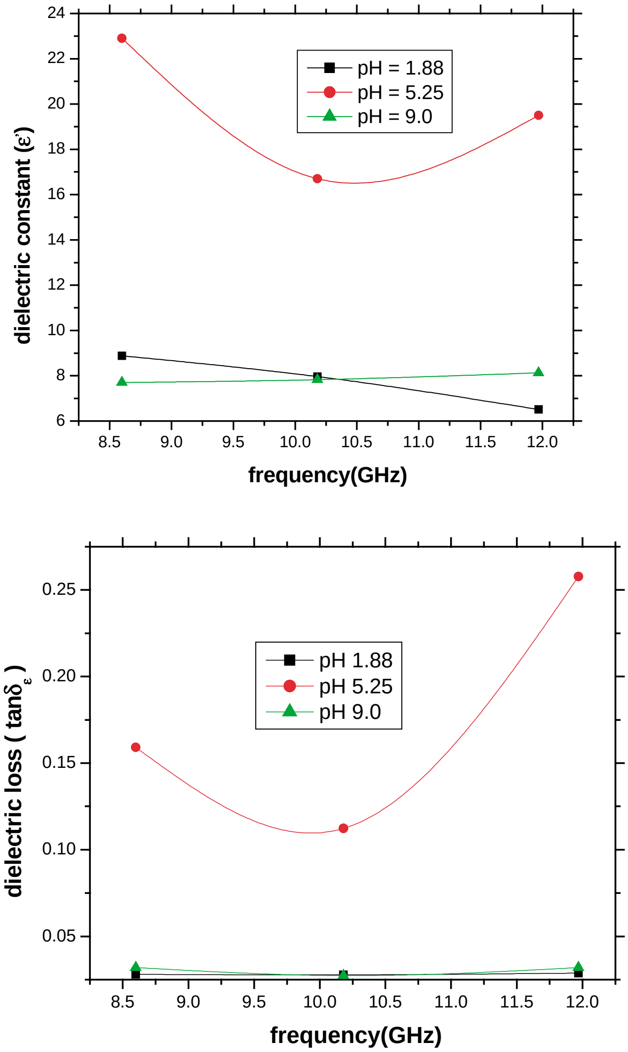

Fig. 3. Dielectric constant (ε') and dielectric loss ($\tan\delta$) of barium ferrite nanoparticles at microwave frequencies.

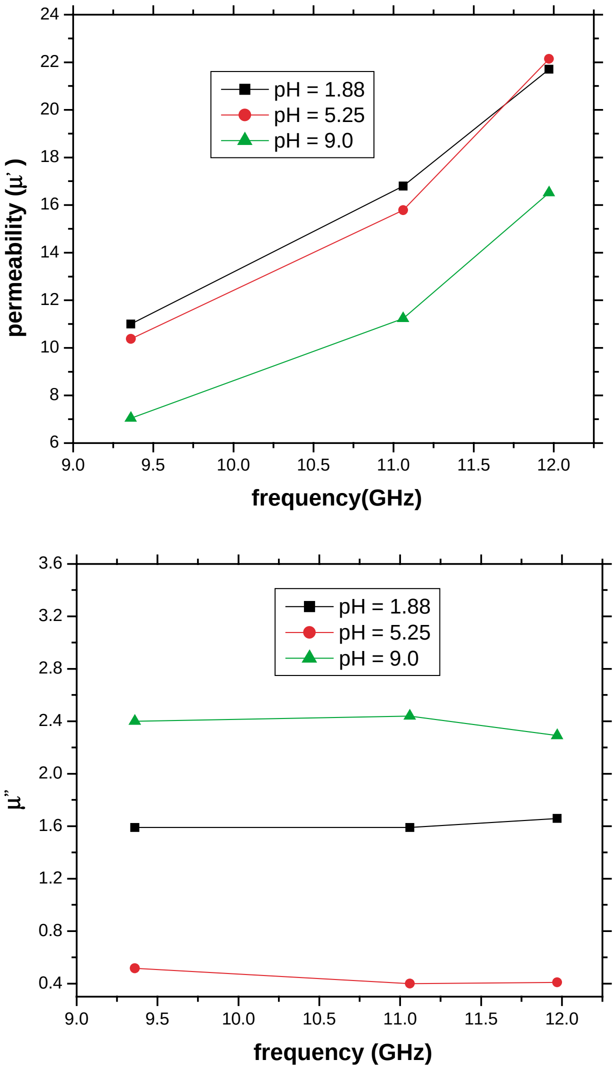

Fig. 4. Real and imaginary parts of permeability of barium ferrite nanoparticles at microwave frequencies.

precursor solution of pH = 5.25, in comparison to other two samples (pH = 1.88, pH = 9.0). This is because of the presence of more number of Fe^{2+} ions, which are easily polarizable. And larger the number of Fe^{2+}, higher will be both dielectric constant and losses, as indeed has been found in the present case. The losses ($\tan\delta$) are also 2–3-folds for the sample having pH = 5.25 (particle size = 14.5 nm) in comparison to other two samples (pH = 1.88, pH = 9.0). The high losses can also be due to hopping conduction between Fe^{2+} and Fe^{3+} ions.

The permeability (μ') of all the samples increases with frequency, and there is no dispersion in permeability till the 13 GHz. But μ'' is almost constant for the all samples. The value of the permeability is higher in comparison to bulk value. In these samples the main contribution is due to spin rotation, because domain wall contribution is negligible above 50 MHz [16]. This may be due to nanoparticle nature because there are more number of atoms at grain boundaries.

4. Conclusion

The particle size can be controlled by varying the pH of the precursor solution; the minimum size of the particles was 14.5 nm for the powders prepared from the solution having pH = 5.25. The Curie temperature for these nanoparticles were 516, 649 and 644 °C when prepared in solutions having pH = 1.88, 5.25 and 9.0, respectively, which are much higher than the Curie temperature of the bulk barium ferrite (450 °C). The dielectric constant, dielectric losses are about 2–3-folds higher for the sample prepared from the solution having pH = 5.25 in comparison to other two samples prepared from the precursor solution having pH = 1.88 and 9.0. The permeability also increases with frequency in X-band. However, no dispersion peak was found till 13 GHz. The magnetic losses were nearly constant though different for all the three samples.

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