Structural, dielectric and magnetic properties of nanocrystalline BaFe$_{12}$O$_{19}$ hexaferrite processed via sol-gel technique

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ABSTRACT

In the present work BaFe$_{12}$O$_{19}$ nano-hexaferrite had been synthesized by sol-gel method and then characterized for its structural, electric, dielectric and magnetic properties. X-ray diffraction studies confirmed the hexagonal structure of the prepared nanohexaferrite with no secondary phase and the particle size was found to be of the order of 49 nm. Further, the morphology of the sample has been studied by using transmission electron microscopy (TEM). A high value of the DC resistivity ($5.5 \times 10^{12}$ Ω cm), has been obtained at room temperature. The dielectric properties such as dielectric constant (ε'), dielectric loss tangent (tan δ) and ac electrical conductivity (σac) are investigated as a function of frequency. The dielectric constant and loss tangent are found to be decreasing with the increase in frequency while ac electrical conductivity is observed to be increasing with the increase in frequency. The dielectric properties have been explained on the basis of Maxwell-Wagner’s two-layer model and hopping of the charge. The magnetic properties such as initial permeability (μi) and relative loss factor (RLF) have been investigated as a function of frequency in the range 75 kHz to 30 MHz. Fairly constant value of initial permeability and low values of RLF of the order of $10^{-4}$ over a wide frequency range are the cardinal achievements of the present work. The room temperature M-H study shows that present nanohexaferrite has high value of coercivity (2151.3 Oe) and high saturation magnetization (32.5 emu/gm), which make present nanohexaferrite very suitable for magnetic applications. The M-T study shows that prepared nano-hexaferrite has high $T_c$ (746 K). Copyright © 2014 VBRI press.

Keywords: Nanoparticle; electrical properties; grain boundaries; initial permeability; sol-gel preparation.

Introduction

Ferrites are the ceramic compounds which much high electrical resistivity than the metallic ferromagnetic materials. Ferrites reduce the eddy current losses and also absorb the electromagnetic field penetration. Ferrites can be divided into three categories namely spinel, hexagonal and garnets according to their crystal lattice structure [1]. The
ferrites, having formula MFe₁₂O₁₉ (M = Ba, Sr, Pb), are those ferrites which have magnetoplumbite structure commonly called as hexagonal structure. The hexagonal ferrites containing Barium as divalent cations are the best ferrites [2]. The unit cell of BaFe₁₂O₁₉ is combination of two structural blocks which are aligned in the direction of c-axis: RSR*S* where * indicate the 180° rotation of the structural block with respect to c-axis, where S-block has a spinel structure with closed packed ‘O’ ions and Fe ions on its tetrahedral and octahedral sites. The R block is formed of hexagonally closed-packed ‘O’ ions and one ‘Ba’ ion and ‘Fe’ ions occupy the interstitial, tetrahedral, octahedral and bipyramidal sites, respectively. Now a day due to the changing nature of day to day technologies like RADAR, microwave, communication etc. there is a need of materials which must have a high saturation magnetization, high core activity, high magnetic anisotropy, excellent chemical stability, high natural resonant frequency and good capability of absorbing the unwanted electromagnetic signals. All these properties stated above are only possessed by BaFe₁₂O₁₉ hexaferrite so M-type ferrites has been investigated during the last few years intensively and become one of the most high-tech materials [3]. Due to larger intrinsic magnetocrystalline anisotropy M-type Barium hexaferrite can be used at much higher frequency than the ferrites with spinel and garnet structure [4]. It can be used as a permanent magnet, high density magnetic and magneto-optic recording media and filters for microwave devices. Since synthesizing technique plays a very vital role for the modifications of properties of BaFe₁₂O₁₉ hexaferrite thus many workers have synthesized the same by different methods [5-10]. M type Barium hexaferrites are quite heavy as in granular materials, which restrict their practical application in microwave absorbing and shielding materials. This can be reduced by producing these materials with low dimensional and large specific surface area, which will enhance the absorbing ability per unit mass [3]. Exploration of the nanosized ferrites is one of the most imperative and rapid growing areas of research in the field of nanotechnology. Nanomaterials are materials possessing one or more dimensional features having a length on the order of a nanometer. They manifest extremely fascinating and useful properties due to nano dimensions and which can be exploited for a variety of engineering technologies, nano photonics, solar energy conversion, opto-electronics, sensors, labeling, catalysis, and in medical applications [11]. The volume to surface area ratio is high in nanomaterials which efficiently enhance the physical, chemical and magnetic properties. Further, these properties are often differ from those of bulk materials [12]. It is a well known fact that the dielectric properties of ferrites strongly depend on frequency. As the quality of ferrite powder has a strong influence on the performance of the final device, hence, the study of dielectric properties and ac electrical conductivity at different frequencies will give valuable information about the conduction phenomenon in ferrites [13]. Since BaFe₁₂O₁₉ hexaferrite is quite versatile because of its practical applications and the dc resistivity of a ferrite is an important property, since it determines its performance at high frequencies, where eddy currents losses may be high, resulting in a significant loss of energy. Further, frequency dependent dielectric and magnetic properties is a very important factor to be considered in designing any component for practical applications, therefore we are reporting the synthesis and study of electric, dielectric and magnetic properties of same in this letter. The nanocrystalline BaFe₁₂O₁₉ hexaferrite has been synthesized by sol-gel technique. The dielectric properties such as dielectric constant (ε′), dielectric loss tangent (tan δ) and ac electrical conductivity (σac) as well as magnetic properties such as initial permeability (µi) and relative loss factor (RLF) are investigated as a function of frequency.

**Experimental**

**Materials**

Barium nitrate Ba(NO₃)₂.9H₂O (Merck Germany, purity >99.9%) and ferrie nitrate (Merck Germany, purity >99.9%) are purchased from Germany, whereas citric acid (Merck India, purity = 99%) is purchased from India.

**Material synthesis and methods**

BaFe₁₂O₁₉ nano-hexaferrite was prepared by using the Sol-gel method [5-6]. Stoichemetric amounts of Ba(NO₃)₂.9H₂O and Fe(NO₃)₃.9H₂O were dissolved in citric solution at 30°C with constant stirring. The different pH values were taken into account but finally the pH value 7 was chosen in the present work as it gave the optimum results. The system was then heated at 80°C with constant stirring until the wet gel was formed. The formed wet gel was then inflated resulting into black powder. The obtained powder was then sintered at 1100°C for 4 hours. The single-phase nature of the prepared samples is checked by x-ray diffraction (XRD) studies, which are made by Cu-Kα radiation of wavelength 1.54 Å using XPERT-PRO X-ray diffractometer and the microstructures of the fractured surfaces are studied using QUANTA 250 FFID 9393. The dc resistivity of the sample was studied with the help of Keithley instrument model 2611. The dielectric properties such as dielectric constant and dielectric loss tangent have been investigated as a function of frequency in the range of 20 Hz to 1 MHz by using WAYNER KERR 6500 B impedance analyzer. The value of dielectric constant was calculated by using the following relation [14].

\[
\varepsilon' = \frac{C_p d}{\varepsilon_0 A}
\]

where \(\varepsilon_0\) is the permittivity of free space, \(d\) is the thickness of the pellets, \(A\) is the area of cross-section of the pellets and \(C_p\) is the measured value of the capacitance of the pellet.

The ac electrical conductivity (\(\sigma_{ac}\)) is calculated from dielectric data using the following relation [15]

\[
\sigma_{ac} = \varepsilon' \varepsilon_0 \omega \tan \delta
\]

where \(\varepsilon'\) is dielectric constant, \(\varepsilon_0\) is permittivity of free space, \(\tan \delta\) is the loss tangent and \(\omega\) is the angular frequency. The M-H measurements at room temperature have been performed using Lake Shore’s Vibrating Sample Magnetometer by applying the field from - 5000 to 5000 Oe. The initial permeability and RLF (tanδ/µi) were
investigated as a function of frequency; 75 KHz to 30 MHz, using Precision LCR meter 4285 A. For measurement of initial permeability, the torroidal ring of the nano-hexaferrite was formed under a pressure of ~5 tons having thickness 2 mm and the ratio of outer diameter to inner diameter equal to 1.5. The torroid was wound with about 50 turns of 32 SWG enameled copper wire. The initial permeability is calculated by using the relation [16]

$$\mu_i = \frac{L}{L_0}$$  \hspace{1cm} (3)

where L is measured inductance of the sample and \(L_0\) is air core inductance and is expressed as \(L_0 = 4.6 N^2d \log (OD/ ID) \times 10^9\) henry, N being the number of turns, \(d\) is thickness of toroid in meters, OD and ID are outer and inner diameters of the toroid respectively.

$$\mu_i = \frac{L}{L_0}$$  \hspace{1cm} (3)

Table 1 shows the values of particle size, \(a, c\) and volume for the studied BaFe\(_{12}\)O\(_{19}\) nano-hexaferrite. The obtained values are nearly same as reported by other worker [9] which shows the perfection of crystal structure of the BaFe\(_{12}\)O\(_{19}\) nano-hexaferrite. The transmission electron micrograph for studied nanohexaferrite is shown in Fig. 1 which confirms the hexagonal phase of BaFe\(_{12}\)O\(_{19}\) nano-hexaferrite. Further, the dc resistivity obtained in the present work, \(5.5 \times 10^6\) \(\Omega\) cm, is increased by 3 orders of magnitude as compared to those reported earlier [17]. The improved value of dc resistivity makes present BaFe\(_{12}\)O\(_{19}\) nano-hexaferrite very suitable for microwave applications.

**Dielectric study**

Fig. 2a, 2b and Fig. 2c show the variations of dielectric constant, loss tangent and ac conductivity with frequency in the range 20 Hz to 1 MHz for BaFe\(_{12}\)O\(_{19}\) nano-hexaferrite respectively. It is evident from the results that dielectric constant and loss tangent are decreasing while ac conductivity is found to be increasing with the increase in frequency. This can be explained on the basis of Maxwell–Wagner model [18–19]. According to this model the dielectric structure was supposed to be composed of well conducting grains separated by the poorly conducting grain boundaries. The electrons reach the grain boundary through hopping and if the resistance of grain boundary is high enough then electrons pile up there and produce polarization. The decrease in dielectric constant with the increasing frequency can be explained on the basis of the fact that the space charge carriers require a finite time to line up their axes in the direction of an applied alternating field. Thus, if the frequency of the applied field increases, the electrons turn around their direction of motion more frequently. This reduces the possibility of electrons reaching the grain boundary and as a result polarization decreases resulting thereby in the decrease of dielectric constant with an increase in frequency. Further, the dielectric loss tangent arises, if the polarization lags behind the applied altering field and is caused due to the presence of impurities and structural inhomogeneities. The low dielectric loss tangent values obtained in the present work are therefore attributed to the more structurally perfect and homogeneous BaFe\(_{12}\)O\(_{19}\) nano-hexaferrite.

### Results and discussion

#### Structural and electric study

The X-ray diffraction pattern indexed with (hkl) values for each peak of BaFe\(_{12}\)O\(_{19}\) nano-hexaferrite is shown in Fig. 1. The observed diffraction lines were found to be corresponding to the standard pattern of the BaFe\(_{12}\)O\(_{19}\) ferrite with no extra lines, thereby, indicating that the sample has a single-phase hexagonal structure and no unreacted constituents are present in the sample. The particle size (\(D\)) and lattice parameters (\(a\) and \(c\)) were calculated by using the relations reported by Bsoul et al. [9].

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Obs. Values</th>
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</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>5.88</td>
</tr>
<tr>
<td>c (Å)</td>
<td>23.16</td>
</tr>
<tr>
<td>c/a</td>
<td>3.939</td>
</tr>
<tr>
<td>V (Å(^3))</td>
<td>693.57</td>
</tr>
<tr>
<td>D (nm)</td>
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</tr>
<tr>
<td>M(_s) (emu/gm)</td>
<td>32.5</td>
</tr>
<tr>
<td>H(_c) (Oe)</td>
<td>2151.3</td>
</tr>
<tr>
<td>M(_r) (emu/gm)</td>
<td>19.26</td>
</tr>
<tr>
<td>dc resistivity (Ωcm)</td>
<td>(5.5 \times 10^6)</td>
</tr>
<tr>
<td>(T_c) (K)</td>
<td>746</td>
</tr>
</tbody>
</table>

Fig. 1. (a) XRD pattern and (b) TEM of BaFe\(_{12}\)O\(_{19}\) nano-hexaferrite.
**ac conductivity study**

The plot for variations of ac electrical conductivity with frequency is shown in Fig. 2c and the same is observed to be almost linear confirming the polaron type conduction. In ionic solids, the electrical conduction is because of the migration of ions and depends on the angular frequency. Since ac conductivity is proportional to the angular frequency thus linear nature is then justified. In the present study, it has been observed that the ac conductivity gradually increases with an increase in frequency.

![Graph](image)

**Fig. 2.** Variation of (a) dielectric constant, (b) loss tangent and (c) ac conductivity with frequency for BaFe$_2$O$_9$ nano-hexaferrite.

The increase in ac conductivity with an applied field frequency can be explained on the basis of pumping force of the applied field which facilitates in transferring the charge carriers between different localized states as well as liberate the trapped charges from different trapping centers. These charge carriers will contribute in the conduction process simultaneously with the electrons produced from a valence exchange between different metal ions. In other words, an increase in frequency improves the electron hopping frequency between the charge carriers resulting thereby in an increase in conductivity. Further, the frequency dependence of ac conductivity can be explained with the help of Maxwell-Wagner heterogeneous model [18-19]. According to this model the dielectric structure is composed of two layers. The first layer consists of well conducting grains which are separated by a thin layer of poorly conducting grain boundaries. At lower frequencies these grain boundaries are much active hence the hopping frequency of electron between Fe$^{3+}$ and Fe$^{2+}$ is less at lower frequencies. As the frequency of an applied field increases, the conductive grains become much active in upholding the hopping of electron between Fe$^{3+}$ and Fe$^{2+}$ ions, thereby increasing the hopping frequency.

![Graph](image)

**Fig. 3.** Variation of (a) initial permeability and (b) relative loss factor with frequency for BaFe$_2$O$_9$ nano-hexaferrite.

**Initial permeability and RLF study**

Fig. 3a and Fig. 3b shows the variation of initial permeability and RLF as a function of frequency in the range 75 kHz to 30 MHz respectively. The initial permeability in ferrite is because of domain wall displacement and remains almost constant with frequency as long as there is no phase leg between the applied field and the domain wall displacement [20]. The variation of initial permeability with frequency shows that $\mu_i$ has fairly constant values of over a large frequency range which is a desirable characteristic for broadband pulse transformers and wide band read-write heads for video recording. It was not however possible to observe the complete resonance peak as it seems to appear at frequencies beyond 30 MHz, which is the upper limit of the frequency used in our studies. As the resonance frequency represents the high frequency limit up to which the material can be used in a device and in this study the resonance is occurring at higher frequencies this leads to the extended zone of utility for present nano-hexaferrite [16]. The variations in magnetic loss in the form of relative loss factor (tan$\delta/\mu_i$) as a function of frequency shows that RLF decrease initially with frequency, reaching a minimum value, and the starts to rise thereafter. The frequency at which RLF is minimum, called threshold frequency. The loss is due to the leg of domain
walls with respect to the applied alternating field and is attributed to imperfections in the lattice. The low value of RLF is required for high frequency magnetic applications. The RLF value observed in this work is of the order of $10^{-4}$ in a wide frequency range, 75 kHz to 30 MHz, which means that the investigated nanohexaferrite will be more useful in this regards.

Frequency dependence of dielectric constant showed normal dielectric behavior and is in good agreement with Koop’s phenomenological theory of dielectric dispersion. A very low value of RLF ($10^{-4}$) has been obtained in the present work. The improved M-H loop is obtained and the increment in $T_c$ is also observed.

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