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Effect of substitution of Zn-Ti on magnetic and dielectric properties of BaFe$_{12}$O$_{19}$

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Abstract

The compounds with general chemical formula BaFe$_{12-2x}$Zn$_x$Ti$_x$O$_{19}$ ($x = 0.0, 1.0, 1.5, 2.0$), were synthesized by ceramic method. X-ray diffraction (XRD) confirmed the formation of single phase magnetoplumbite structure. The EDS spectra confirmed the presence of all the constituents. The lattice parameter $a$ decreased whereas $c$ increased with the increase in $x$. Magnetic parameters like coercivity, saturation magnetization decreased with increase in substitution. Superparamagnetism and canted antiferromagnetic ordering of magnetic moments was observed in the samples $x =1.5$ and $x = 2.0$ respectively. The effect of variation of composition, frequency and temperature on the dielectric constant ($\varepsilon'$), loss tangent (tan $\delta$) and conductivity ($\sigma$) has been carried out. The ac conductivity increased with temperature showing semiconductor like nature of the samples.

1. Introduction

Barium hexaferrite (BaFe$_{12}$O$_{19}$ or BaM) is a well studied ferrimagnetic material where the Fe$^{3+}$ ions occupy different sites and contribute to the magnetic properties in different ways. The non-magnetic ions, when replace Fe$^{3+}$ ions, occupy different sites and disturb the magnetic moment of Fe$^{3+}$ ions and therefore exhibit various kinds of magnetic structures. Ferrites have a wide range of applications from microwaves to radio frequencies and therefore the use of a ferrite for a certain application depends on its electrical and magnetic properties. In some earlier studies, Fe$^{3+}$ ion has been replaced by Zn$^{2+}$ and Ti$^{4+}$ ions. Such as, Wartewig et al. (1999) has studied the structural and magnetic properties of BaFe$_{12-2x}$Zn$_x$Ti$_x$O$_{19}$ ($0 \leq x \leq 2.0$), Dube et al. (2009) studied dielectric properties of BaFe$_{12-2x}$Zn$_x$Ti$_x$O$_{19}$ ($0.2 \leq x \leq 0.6$). In the present study therefore, the structural, magnetic and dielectric properties of BaFe$_{12-2x}$Zn$_x$Ti$_x$O$_{19}$ ($0 \leq x \leq 2.0$) have been carried out as a function of frequency and temperature.

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2. Experimental

2.1. Synthesis

BaFe_{12-2x}Zn_{x}Ti_{x}O_{19} (x = 0.0, 1.0, 1.5, 2.0) referred as BaM, Z1, Z1.5, Z2 respectively, were prepared through conventional ceramic method. The powders of BaO, ZnO and TiO_{2}, procured from Merck and Fe_{2}O_{3} from Sigma Aldrich were mixed together in proper stoichiometric ratio in agate mortar for about 6 h in acetone (Merck). They were presintered at 900 °C for 12 h and were finally sintered at 1300 °C for 24 h in an electronically controlled furnace as proposed by Dho et al.(2005) or Soman et al. (2013). Pellets of 10 mm diameter of these samples were sintered again.

2.2. Structural study with X-ray Diffraction and SEM with EDS

Phase identification and structural analysis of the samples using XRD was carried out for 20 = 20° to 80° with Cu Kα radiation of wavelength λ = 1.5456 Å, using PW1710 diffractometer. The lattice constants (a and c) and other structural parameters like interplanar spacing (d), crystallite size (D), miller indices (hkl), X-ray density (ρx), bulk density (ρ), porosity (P), were calculated. The morphology of the samples was studied using Scanning Electron Microscope (SEM) JEOL Model JSM - 6390LV and the elemental identification was carried out with Energy dispersive X-ray spectroscopy (EDS).

2.3. Magnetic Properties

The magnetization (M) versus magnetic field (H) measurements were carried out at room temperature (~ 30 °C) by model EV7(USA) and M versus temperature (T) measurements were carried out at constant magnetic field of 1.2 Tesla by EG and G Princeton Applied Research (USA) with model number 150 A vibrating sample magnetometer (VSM).

2.4. Dielectric Properties

The dielectric parameters such as ε', tanδ and σac were measured using Alpha-AN impedance analyzer from Novocontrol (Germany).

3. Results and discussion

3.1. X-Ray Diffraction

XRD pattern of BaM, Z1, Z1.5 and Z2 show sharp peaks of high intensity (Fig. 1) and match well with the standard data obtained from JCPDS file # 27-1029. The planes corresponding to the sharp peaks are indexed with (hkl) values as shown in the Fig. 1. The peaks of the host material as well as the substituted ferrites appear at the same positions but with different Full Width at Half Maximum (FWHM). This observation is attributed to the occupation of crystallographic sites of Fe^{3+} ions by the substituted ions. The XRD patterns of these ferrites indicate the formation of a single phase magnetoplumbite structure with the O^{2-} ions forming a hexagonal closed packed lattice. Therefore these peaks were indexed as a primitive hexagonal cell with space group P6_3/mmc using the Full Prof software. It is observed that the peak (006) has an appreciable intensity which may be due to higher atomic scattering factor of Zn. FWHM was found from the first three strongest peaks in the XRD pattern and its average was used to calculate D (average) using the well known Debye Scherer formula,

\[ D = \frac{k \lambda}{\beta \cos \theta} \]  

where, k = 0.9 is a constant dependent on values of reflection indices (hkl), λ = is the wavelength of X-rays used, β is FWHM and θ is Bragg’s angle.
Fig. 1. XRD of Zn-Ti substituted samples.

Fig. 2: SEM micrographs of (a) Z1, (b) Z1.5 (c) Z2

The lattice parameters $a$ and $c$ the interplanar spacing $d$ is calculated for a plane with Miller Indices (hkl) using formula:
The lattice parameter \(a\), for \(Z_1\) and \(Z_1.5\) is almost same as that of BaM \((a = 5.907 \text{ Å})\) and decreases abruptly in case of \(Z_2\) whereas the parameter \(c\) for \(Z_1\) and \(Z_1.5\) is slightly more than that of BaM \((c = 23.199 \text{ Å})\) whereas \(c\) of \(Z_2\) is the smallest of all. For BaM, these parameters are reported by Mallick et al. (2007). The changes in the lattice parameters due to substitution is attributed to different ionic radii of substituted ions \(\text{Zn}^{2+}\) (0.74 Å), \(\text{Ti}^{4+}\) (0.61Å) as compared to that of \(\text{Fe}^{3+}\) (0.67Å). The volume of unit cell \(V = a^2c\sin60^\circ\) increases with increase in \(x\). The variation of substitution parameter \(x\), can also cause changes in \(\rho_x\), \(\rho_x\), and \(P\). The values of \(\rho_x\) and \(P\) were calculated using the following relations:

\[
\rho_x = \frac{ZM}{N} \\
\rho = 1 - \left(\frac{x}{\rho_x}\right)
\]

where, \(Z = 2\) is the effective number of molecules per unit cell, \(M = \text{molecular weight}\) and \(N = 6.023 \times 10^{23} /\text{mole}\) is the Avogadro’s number.

It is further observed that \(\rho_x\) and \(P\) increase with the increase in \(x\). The bulk density \((\rho)\) values were observed to be lesser than the corresponding values of \(\rho_x\), which is attributed to the generation of unavoidable pores during sintering process. Similar observation has been reported by Ahmed et al. (2011). This observation can be correlated to the SEM micrographs given in Fig. 2. The values of the structural parameters are summarized in Table 1.

### Table 1: Consolidated data of crystallographic parameters of the modified ferrites

| Sample | \(a (\pm 0.006)\) (Å) | \(c (\pm 0.020)\) (Å) | \(V\) (Å\(^3\)) | \(\rho\) (kg/m\(^3\)) | \(\rho_x\) (kg/m\(^3\)) | \(P\)       |
|--------|-----------------|-----------------|---------|----------------|----------------|----------|
| \(Z_1\) | 5.964           | 23.310          | 718.11  | 4139.39        | 5146.65        | 0.195    |
| \(Z_{1.5}\) | 5.914           | 23.322          | 706.51  | 4079.86        | 5234.85        | 0.220    |
| \(Z_2\) | 5.283           | 22.682          | 548.42  | 2250.81        | 6748.60        | 0.666    |

### 3.2 SEM with EDS

As the bulk properties of these materials mainly depend on grain size, SEM was carried out along with EDS study. The sharp and well defined hexagonal grains have prominent grain boundaries. The grain size is found to be ranging from 2 \(\mu\)m to 5.5 \(\mu\)m. In \(Z_2\), it can be observed that small grains coalescing together to form a large grains. But some pores are also observed in the final structure because 100% theoretical density cannot be achieved during the sintering process and hence porosity increases. The XRD results indicate the formation of a single phase, and with the chemical composition identification of the constituents of the samples i.e. \(\text{Ba}^{2+}\), \(\text{Fe}^{3+}\), \(\text{Zn}^{2+}\), \(\text{Ti}^{4+}\) and \(\text{O}^{2-}\) in EDS diagrams, the replacement of \(\text{Fe}^{3+}\) ion by \(\text{Zn}^{2+}\)-\(\text{Ti}^{4+}\) can be concluded.

### Table 2: Elemental concentration of \(Z\) series ferrites obtained from EDS

| Element ↓ | \(Z_1\) atom % | \(Z_{1.5}\) atom % | \(Z_2\) atom % |
|-----------|----------------|------------------|---------------|
| \(\text{O}\) | 30.45          | 33.23            | 29.34         |
| \(\text{Ba} + \text{Ti}\) | 12.20          | 13.53            | 19.38         |
| \(\text{Fe}\) | 54.52          | 50.72            | 48.21         |
| \(\text{Zn}\) | 2.83           | 2.52             | 3.07          |
| Total     | 100.00         | 100.00           | 100.00        |

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\[
\frac{1}{d_{K\ell}} = \frac{4(h^2 + k^2)}{3a^2} \quad (2)
\]
3.3 Magnetic properties:

The $M-H$ loops at room temperature and $M-T$ curves for all the synthesised ferrites are shown in Figs. 3, 4 respectively and the magnetic parameters have been summarized in Table 3. For $x = 0$ these parameters agree well with those reported by Dho et al. (2005). It is observed that as the value of external field $H$ increases, the magnetization also increases till a constant value is reached. The magnetization shows a sharp increase at low fields and then continues to increase gradually at higher fields. This is a typical behavior for multi-domain structure which has also been reported by Topal et al. (2004). As compared to BaM, the value of $M_s$ and $M_r$ decrease with increase in substitution level. BaM has $H_C = 1.005$ kOe and is classified as a hard ferrite, but with the increase in $x$, the $H_C$ values decreased which indicate that the substituted ferrites are becoming soft. SEM micrographs show increase in grain size for Z1.5 and Z2 samples. The increase in grain size drops the value of $H_C$. As the hard ferrites require large coercive field to demagnetize, their $M_s$ is large and hysteresis loop shows a large area. Thus $SQR$ is more for hard ferrites. In the present study with increase in $x$, $M_s$ as well as area of hysteresis loop decrease which in turn reduces $SQR$ and the samples become soft ferrites. Z1 shows a nearly collapsed hysteresis loop whereas for the sample Z1.5, ‘S’ shaped hysteresis is observed showing their superparamagnetic behaviour. The superparamagnetic hexaferrites are of great interest due to their application where a switch between magnetic ‘on’ and ‘off’ state would be required. For Z2, magnetization goes on increasing continuously with the increase in the applied field with non zero coercivity. This suggests that with high substitution of $Zn^{2+}$ and $Ti^{4+}$ ions in $BaFe_{12}O_{19}$, the magnetic ordering may be changing to canted antiferromagnetic ordering. With the addition of $Zn$ and $Ti$ at high concentration (Z2), the ions occupying tetrahedral and octahedral positions respectively, spins may get oriented with some angle other than 0° or 180°. A spin wave may be considered to form which gives very small coercivity and remnant magnetization and this may be attributed to the occurrence of canted antiferromagnetic ordering in Z2. The observed decrease in $M_s$, $M_r$, and $SQR$, with increase in $x$, can be explained on the basis of the fact that in $BaFe_{12}O_{19}$, $Fe^{3+}$ ion occupies 12k, 2a (both with spin up) and 4f (spin down) in octahedral coordination, 2b (spin up) in bipyramidal coordination and 4f1 (spin down) in tetrahedral coordination. As $Zn$ and $Ti$ both are non magnetic ions, they cannot add to the magnetization of the samples. The external magnetic field is kept constant at 1.2 T and temperature is increased from room temperature (~ 25 °C). The decrease in Curie temperature ($T_C$), with increase in $x$ indicates that some intersublattice exchange interactions are strongly diminished with addition of the substituents. The lowering of $T_C$ may also be attributed to the presence of non magnetic ions in the tetrahedral and octahedral sites.

Table 3. Magnetic parameters of all the synthesized ferrites

| Sample | $M_s$ (emu/g) | $M_r$ (emu/g) | $H_C$ (Oe) | $SQR$ | $T_C$ (°C) |
|--------|---------------|---------------|-------------|-------|-------------|
| BaM    | 49.08         | 24.35         | 1005        | 0.49  | 523         |
| Z1     | 43.46         | 1.33          | 31          | 0.03  | 319         |
| Z1.5   | 33.45         | 0.9           | 16.5        | 0.02  | 261         |
| Z2     | 5.7           | $2\times10^{-3}$ | 4.75        | $4\times10^{-4}$ | 232 |

Fig.3 $M-H$ curves for BaM, Z1, Z1.5 and Z2.

Fig.4 $M-T$ curves for BaM, Z1, Z1.5 and Z2.
3.4. Electrical Properties:

3.4.1. Variation of $\varepsilon'$ with $f$, $T$ and $x$:

The variation of $\varepsilon'$ with $f$ for Z series is shown in Fig. 5. It is observed that at low frequencies, $\varepsilon'$ has high values and in general $\varepsilon'$ decreases with increase in frequency. The decrease in $\varepsilon'$ with frequency can be explained due to the existence of interfacial (intergranular) polarization and explained by Koops (1951) on the basis of Maxwell-Wagner (1913) two layer model. All of these ferrites have well conducting grains separated by poorly conducting thin layers of grain boundaries. In the polarization process exchange of electrons mainly takes place between Fe$^{3+}$ and Fe$^{2+}$ ions for which the electrons have to pass from one grain to another through poorly conducting grain boundaries which resist their flow causing accumulation of electrons near the boundaries. This increases the space charge polarization. At higher frequencies, hopping of electrons between Fe$^{3+}$ and Fe$^{2+}$ ions may not commensurate with the frequency of the applied ac electric field and therefore dispersion is observed. The variation of $\varepsilon'$ with temperature is shown in Fig. 6 where $\varepsilon'$ increases with temperature almost up to 200°C beyond, $\varepsilon'$ decreases gradually. The gradual increase in $\varepsilon'$ at low temperature, could be due to the enhanced drift velocity caused due to the thermal activation of hopping of the electrons between Fe$^{3+}$ and Fe$^{2+}$ ions present at the octahedral sites. This hopping causes local displacement in the direction of external electric field which increases the space charge polarization and hence $\varepsilon'$ also increases.

However, at high frequencies, significant change in $\varepsilon'$ with temperature is not observed as 'at the high frequencies, electronic and ionic polarizations are the main contributors and their temperature dependence is insignificant'. This can also be explained on the basis of the fact that at lower temperatures the hopping of electrons between Fe$^{2+}$ and Fe$^{3+}$ ions induces dielectric polarization in the ferrite which in turn increases the dielectric constant. The dielectric constant seems to be systematically increasing with the increase in temperature due to polarization and the decrease in dielectric constant at higher temperatures is due to significant increase in random vibrational motion of electrons and ions. Because of this random vibrational motion, dielectric constant becomes less susceptible to orientation in the direction of the external applied field. In case of Zn-Ti substituted samples, Z1.5 shows larger values of $\varepsilon'$ as compared to that for Z1 and Z2. 'The samples with a larger zinc concentration are likely to contain relatively greater amount of Fe$^{2+}$ ions as the probability of zinc evaporation would be more in these samples'. Similar observation has been made by Dube et al. (2009). Since Fe$^{2+}$ ions are easily polarizable, therefore, the samples with higher substitution level of Zn will have high dielectric constant. Hence $\varepsilon'$ for Z1.5 is higher than $\varepsilon'$ of Z1. Polarization also depends on factors like grain size and porosity. It is seen from Table 1 that with the increase in $x$, porosity increases. This reduces polarizing species per unit volume causing decrease in polarization and dielectric constant for Z2 is minimum.

3.4.2. Variation of dielectric loss ($\tan \delta$) with frequency and temperature:

The polarization produced due to hopping of electrons changes with the applied field. When this polarization lags behind the applied ac electric field, dielectric loss ($\tan \delta$) appears. This lagging is mainly due to the structural imperfections or defects in the solids. Fig. 7 shows variation of $\tan \delta$ with frequency for Z2. With increase in frequency, a rapid decrease in dielectric loss is observed. This decrease is due to the fact that the dipole oscillations cannot follow the changes of the external field at high frequencies. This is because, when the frequency is low, the conductivity through the grain boundary is low. Therefore, more energy is required for the exchange of electrons between Fe$^{3+}$ and Fe$^{2+}$ ions and hence the loss is high. With the increase in frequency, lesser energy is required for the exchange and therefore loss decreases rapidly. A peak is observed in the graphs between loss tangent ($\tan \delta$) and frequency for all the samples. The peak is obtained when the charge hopping frequency between Fe$^{3+}$ and Fe$^{2+}$ is in resonance with the frequency of the applied field. The peaks shift towards higher frequency with the increase in temperature. With the rise in temperature the electrons and ions get thermally activated which increases the conduction. Further, as the temperature increases, the degree of dipole orientation increases and therefore energy required to overcome the barrier of the medium is reduced and hence there is an increase in value of $\tan \delta$. 
3.4.3. Variation of ac conductivity (σ) with frequency, temperature

For all the samples it is observed that conductivity is small in the lower frequency region and increases for higher frequencies (Fig. 8). The electrical conductivity increases with temperature as shown in Fig. 9. Therefore, the iron oxides are generally termed as ‘magnetic semiconductors’. The lattice vibrations increase with temperature, giving rise to higher probability of the hopping of electrons at the octahedral sites, leading to enhanced mobility of charge carriers and hence the conductivity. Further, with addition of Zn, the conductivity decreases. Thus Z1 is more conducting than Z1.5 and Z2. It is further seen that with the increase in x the porosity increased. The pores are non-conducting and the increased number of pores caused hindrance to the motion of ions resulting in the decrease of conductivity. Thus in Z series samples porosity has pronounced effect in decreasing the conductivity as compared to the effect of increase in X-ray density. It was observed that there is a sudden decrease in ε' and an increase in σ in the frequency range 10^5-10^6 Hz. These variations have been shown in the Figs. 5 and 8 respectively. Representative curves of the variation conductivity of with temperature at 9.9 kHz for Z1, Z1.5 and Z2 are shown in Fig. 9.

Conclusions

All the compounds synthesized were found to have single phase M-type structure in the form of hexagonal platelets. This observation is supported by SEM micrographs. EDS spectra confirmed the presence of all the constituents. All the magnetic parameters of the substituted ferrites decreased with the increase in substitution. The hexaferrites which show superparamagnetic nature may be used as a switch where a magnetic ‘on’ and ‘off’ state would be required. Increase in conductivity with rise in temperature shows semiconducting nature of the samples.

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