Structure, magnetic properties and magnetoelectric effect in Mn-ferrite-barium titanate composites

R P Mahajan, K K Patankar, N M Burange, S C Chaudhari, A N Patil & S A Patil

Physics Department, Shivaji University Kolhapur 416 004, India

Received 25 February 2000; accepted 25 July 2000

Polycrystalline samples of mixed composites of MnFe$_2$O$_4$+BaTiO$_3$ have been prepared by a standard ceramic method. The phase formations in the composites have been confirmed using XRD. The lattice parameter of ferrite phase increases with BaTiO$_3$ content. However, the lattice parameters of ferroelectric phase do not vary much. The magnetisation (M$_s$) decreases with decrease of ferrite content. The $\chi_{dc}$-T plots indicate that the present composites contain MD particles. The Curie temperature decreases with increase in BaTiO$_3$ content. The magnetoelectric effect has been studied as a function of dc magnetic field. The maximum value of magnetoelectric conversion factor ($dE/dH$) is observed as 180 $\mu$V/cmOe in the composition containing BaTiO$_3$ (50 mole%).

When a magnetic field is applied to a composite, the ferrite particles change their shape because of magnetostriction and the strain is passed along to the piezoelectric particles resulting in an electrical polarization. The magnetoelectric property of the ferroelectric-ferromagnetic composite is known as a product property of the composite and results from the interaction between different properties of its two phases. Neither ferroelectric nor the ferromagnetic phase has the magnetoelectric effect but composites of these two phases have magnetoelectric effect. ME conversion in ferrite-barium titanate composites was experimentally reported by Boomgaard et al. Manganese ferrite is magnetically used as magnetostrictive dopant in this composite, which is magnetically harder than other ferrites. Hence, the devices can operate in higher magnetic fields. The aim of present work is to study the magnetic properties, such as magnetization and ac susceptibility of MnFe$_2$O$_4$+BaTiO$_3$ composites.

Experimental

Polycrystalline samples of ferrite-ferroelectric MnFe$_2$O$_4$+BaTiO$_3$ composites (0, 25, 50, 75 mole%) were prepared by a standard ceramic technique using AR grade oxides. The samples were presintered at 700$^\circ$C for 10 h, separately, and then mixed in the required mole percent ratio and finally sintered at 1200$^\circ$C for 20 h. The samples were slowly cooled to room temperature at the rate of 100$^\circ$C h$^{-1}$. Torroides of the size (i.d. 2.5 cm and o.d. 3.5 cm) were prepared.

Confirmation of the phase formation and characterization of crystal structure were carried out on Philips X-ray diffractometer operated at 40 kV and 30 mA using Cu K$_\alpha$ radiation. Magnetic data for these samples were obtained with the help of high field loop tracer. The micrographs of the samples were obtained with the help of SEM Cambridge stereoscan S-250 MK II, and average grain diameter was estimated by intercept method. The density of samples was determined by liquid immersion method using Zylene. Low field ac susceptibility measurements of the powder samples were made in the temperature range 300-800 K at 263 Hz and in 7 Oe rms field. Further details of preparation and measurement are given elsewhere.

Results and Discussion

X-ray analysis

An X-ray diffraction pattern of 50% ferrite samples is shown in Fig. 1. Using ASTM data, it is confirmed that MnFe$_2$O$_4$ has formed cubic spinel structure where as BaTiO$_3$ formed perovskite structure. The $d$ spacing for the recorded peaks are calculated according to Bragg’s law. There is a close agreement between calculated and observed $d$ values. The lattice parameter(s) can be calculated directly using Eq. (1):

$$a_0 = d_{(h^2 + k^2 + l^2)^{1/2}}$$

... (1)
where $h$, $k$, $l$ are indices of crystal structure. The lattice parameter as a function of composition is tabulated in Table 1. From the table, it is seen that lattice parameter of individual phases remains nearly constant with composition. The absolute density of composite samples was determined by liquid immersion method.

The X-ray density $d_x$ and apparent density ($d_a$) are also given in Table 1. The porosity is about 12-14% and does not vary much with composition.

Magnetic moment ($\eta_B$)

The variation of saturation magnetisation in present composites is given in Table 2. The magnetic moment $\eta_B$ is observed to decrease with increasing BaTiO$_3$ content. The observed decrease in $\eta_B$ can be attributed to decrease in ferrite content. The observed $\eta_B$ can be explained on the basis of Neel’s two sublattice model. According to site preferences, Mn particles occupy A site. However, Mn ferrite is random spinel. The cation distribution for ferrite phase is described by Eq.(2):

$$\text{Table 1 — Physical constants of MnFe}_2O_4+$BaTiO$_3$ composites

<table>
<thead>
<tr>
<th>Ferrite content (%)</th>
<th>Lattice parameter (Å)</th>
<th>Apparent density (g/cm$^3$)</th>
<th>X-ray density (g/cm$^3$)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 (m$_1$)</td>
<td>8.444</td>
<td>4.4581</td>
<td>5.088</td>
<td>12.38</td>
</tr>
<tr>
<td>75 (m$_2$)</td>
<td>8.48</td>
<td>4.4927</td>
<td>5.2237</td>
<td>14.00</td>
</tr>
<tr>
<td>50 (m$_3$)</td>
<td>8.68</td>
<td>5.0336</td>
<td>5.7294</td>
<td>12.14</td>
</tr>
<tr>
<td>25 (m$_4$)</td>
<td>8.698</td>
<td>4.7847</td>
<td>5.4944</td>
<td>12.92</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ferrite content (%)</th>
<th>Saturation magnetisation $M_s$ (emu/g)</th>
<th>Magnetic moment from rule of mixture ($\eta_B \mu_B$)</th>
<th>Curie temperature $K$ from $\chi_m$</th>
<th>$dEdH$ (µV/cm * Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 (m$_1$)</td>
<td>189.23</td>
<td>2.84</td>
<td>595</td>
<td>—</td>
</tr>
<tr>
<td>75 (m$_2$)</td>
<td>151.19</td>
<td>2.13</td>
<td>528</td>
<td>110</td>
</tr>
<tr>
<td>50 (m$_3$)</td>
<td>35.775</td>
<td>1.42</td>
<td>483</td>
<td>180</td>
</tr>
<tr>
<td>25 (m$_4$)</td>
<td>17.479</td>
<td>0.71</td>
<td>470</td>
<td>120</td>
</tr>
</tbody>
</table>

Fig. 1—X-ray diffraction pattern of 50% MnFe$_2$O$_4+$50% Ba'TiO$_3$ composite
The values of $\eta_B$ are less than that reported in literature. This decrease in $\eta_B$ may be due to canting behavior of MnFe$_2$O$_4$. $\eta_B$ was calculated using rule of mixture as given in Table 1.

In the present system, the $M_s$ decreases with increasing BaTiO$_3$ content. By increasing BaTiO$_3$ content, the total value of the anisotropy constant decreases. Because of these variations, the permeability decreases with increase of BaTiO$_3$ content. However, polycrystalline ferrite-ferroelectric composite is a complex system consisting of crystallites, grain boundaries and pores. In such a case, any disturbance by inclusions, pores, inhomogenities or an excessively large grain boundary will decrease permeability.

**ac susceptibility**

Fig. 2 shows the variation of $\chi_{ac}-T$, near Curie temperature. $\chi_{ac}$ becomes zero for all compositions. The Curie temperature obtained from these plots is listed in Table 2. It was observed that the Curie temperature decreases with BaTiO$_3$ concentration. This behavior is related to the number of FeA-FeB interactions, their strength and the angle FeA-O-FeB and Fe$^{3+}$ on two sites and their inter sublattice distance. Also, at higher concentration of MnFe$_2$O$_4$, the tailing is observed which may be due to canting effect in MnFe$_2$O$_4$. $\chi_{ac}$ decreases continuously and near the Curie temperature; there is a tailing effect, which indicates that the present sample contains super paramagnetic (SP) particles.

**ME effect**

The variation of magnetoelectric coefficient with dc magnetic field is shown in Fig. 3. It is seen from the Fig. that all the composites show a decrease in (d$E$/d$H$) with increase in dc magnetic field beyond $H=600$ Oe. In the spinels, the magnetostRICTive coefficient reaches saturation at a certain value of magnetic field. The magnetoelectric coefficient (d$E$/d$H$) of the composites is a result of piezomagnetic strain in spinel phase which creates piezoelectric charge in ferroelectric phase with the intensity of magnetic field. MEC largely depends on the electrical resistivity of the samples and the mechanical coupling between the two phases. The value of dc (ME)$_H$ increases with increasing BaTiO$_3$ content up to 50%. Then, it decreases because the stiffness of the two phases is comparable in magnitude and the elastic interaction between the two phases is strongest near volume ratio $f=0.5$.

**Conclusions**

The phase formations in the composites MnFe$_2$O$_4$+BaTiO$_3$ have been confirmed using XRD. The lattice parameter of ferrite phase has been found
to increase with BaTiO$_3$ content while the lattice parameters of ferroelectric phase do not vary much. The magnetisation ($M_s$) decreases with decrease of ferrite content.

References