Crystal Structure, Dielectric and Magnetic Properties of BaTiO$_3$-CoFe$_2$O$_4$ Multiferroic Composites

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Abstract. Multiferroics composites (BaTiO$_3$)$_x$-(CoFe$_2$O$_4$)$_{1-x}$ ($x=0.00$ and $0.10$) were synthesized via solid-state reaction. Structural properties of the samples were studied by using X-ray diffraction technique at room temperature. XRD patterns confirmed the existence of tetragonal phase with P4nm space group for BaTiO$_3$ and cubic phase with Fd3m space group for CoFe$_2$O$_4$, respectively. By using Rietveld refinement of XRD data verified that both phases are present without any secondary peak. The variation of tangent loss (tanδ) and dielectric constant (ε') was studied as a function of frequency in the range of 100Hz to 7MHz at room temperature. The dispersive behavior of both ε' and tanδ show at lower frequency region but at higher frequency region it remains constant. M-H loop was measured at room temperature that shows the magnetic behavior of composites.

INTRODUCTION

Multiferroics represent an interesting class of multifunctional materials that carry several ferroic orders simultaneously. Multiferroics composites are materials in which both ferroelectricity and ferromagnetism both exist and this result into a new phenomenon called “Magneto-electric Effect”. The first multiferroic composite of barium titanate (BaTiO$_3$) and cobalt ferrite (CoFe$_2$O$_4$) was studied by Boomgard et al. in 1974. Recently, these ME composite have become very interesting for their fundamental physics and attractive for various applications such as spintronics, multiple state memories, sensors etc. Above room temperature, single phase ME materials has limited applications because of weak ME effect. Alternatively, piezoelectric/ferrites composite have large ME effect because of their high magnetostriiction and piezoelectric coefficient in composites. [1-4]. Recently, multiferroics composite of barium titanate (BaTiO$_3$) and ferrite (like CoFe$_2$O$_4$, NiFe$_2$O$_4$) are found to exhibit large ME response. Barium titanate (BaTiO$_3$) is well known fundamental lead-free perovskite having ABO$_3$ structure. The first perovskite oxide found to exhibit ferroelectric behavior was BaTiO$_3$ in the early 1940’s. BaTiO$_3$ exist rhombohedral, orthorhombic, tetragonal and cubic phase transisitions. BaTiO$_3$ (BT) has relatively high Curie temperature $T_C=130$ C, the value of piezoelectric constant ($d_{33}= 260pC/N$) and the order of resistivity ($\sim 10^9\Omega cm$) [5]. On the other hand, cobalt ferrite (CoFe$_2$O$_4$) shows cubic spinlall structural having (AB$_2$O$_4$) perovskite structure. CoFe$_2$O$_4$(CFO) has good chemical stability, high coercivity and remanence, moderate saturation magnetization. In this paper, CFO chooses as a ferrite phase and BT as a ferroelectric phase to prepare magnetoelectric composites. To study crystal structure, dielectric and magnetic properties of xBaTiO$_3$-(1-x)CoFe$_2$O$_4$ ($x=0.00$, 0.10) composites systematically.

DETAILS OF EXPERIMENT

Polycrystalline composite xBaTiO$_3$-(1-x) CoFe$_2$O$_4$ ($x=0.00$, 0.10) were synthesized by solid state reaction method. Initially, an appropriate proportion of high purity Sigma Aldrich grade Ba$_2$Co$_3$TiO$_8$, Co$_3$O$_4$, and Fe$_2$O$_3$ (purity > 99%) as raw materials and all these raw materials were mixed properly and grinding for two hours in the agate pestle. Forx=0.00, these homogenous mixture of was calcination at 873K for four hours and reground for one hour for obtaining a more fine mixture and final heat treatment (quenching) of the sample was carried out at...
1273K for three hours and the xBaTiO₃ - (1-x)CoFe₂O₄ (x=0.10) was calcination at 1073K for six hours. The calcined sample was reground for 1 hour and final heat treatment (quenching) of the sample was done at 1403K for four hours at the rate of heating 5Kmin⁻¹. X-ray diffractometer Rigaku Miniflex-II with Cu Kα radiation (λ = 1.5405 Å) in the range of 2θ (20º-80º) is used to find the crystal structure of the prepared samples at room temperature with scanning rate of 2ºmin⁻¹. For further investigation, Rietveld refinement was used to detect the XRD pattern with the help of FullProof software. Dielectric properties were measured by impedance phase analyzer (Newton’s 4th Ltd) in range of frequency from 100Hz–7MHz at room temperature. The magnetic properties was done with the help of VSM (vibrating sample magnetometer) Lakeshore,7304 having maximum magnetic field upto6kOe at room temperature.

RESULTS AND DISCUSSION

Structure Analysis

Figure 1 signifies the X-ray diffraction pattern of the prepared samples of xBaTiO₃ - (1-x) CoFe₂O₄ (x=0.00 and 0.10). XRD patterns of the composites were found that peaks of both CFO and BT are present without any other impurity. XRD pattern confirms that BaTiO₃ has tetragonal with P4mm space group and CoFe₂O₄ has cubic symmetry with Fd3m space group. From Fig.1, XRD patterns of the prepared samples shows that for x=0.00 samples have CFO peaks are present but x=0.10 samples have both CFO and BT peaks that can be marked by C and B. Fig.2 displays the Rietveld refinement of the prepared samples. Further investigation the XRD data by Rietveld refinement using Full prof software for more accurate study of crystal structure. Initially, zero fit unit cell and backgrounds are used in the refinement. The index parameter Rwp(weighted residual factor)Rp(residual factor) and χ²(goodness of fit) and lattice parameter of the samples are given in Table 1. In these samples, the value of χ²is small which indicates the fitting is good. Rietveld analysis shows that the unit cell of the volume and the lattice parameter of the ferrite phase is similar that pure form of CFO and BT respectively, which indicates that no change in phase take place.

Tables

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<tr>
<th>Composites (x)</th>
<th>Lattice parameters</th>
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<tr>
<td></td>
<td>BT phase</td>
<td>Ferrite (CFO) phase</td>
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<tr>
<td>x=0.00</td>
<td>a=b=c= 8.382Å V= 588.963Å³</td>
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<tr>
<td>x=0.10</td>
<td>a=b=3.9855Å c= 4.0323Å V=64.050Å³</td>
<td>a=b=c= 8.359Å V= 584.128Å³</td>
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Dielectric Analysis

Fig.3 shows that the deviation of dielectric constant (εʹ) and tangent loss (tan δ) as a function of frequency at room temperature. Both εʹ and tanδ decreases continuously with increase in frequency and finally reached constant value at higher frequency. This dispersion behavior can be studied by Koop’s two-layer model and Maxwell Wagner interfacial polarization theory. At low frequency, the value εʹ is high due to space polarization which occurring inhomogeneous system. On the other hand, at higher frequency, the dielectric constant (εʹ) is the net resultant of ionic, electronic and orientation polarization whereas there is no contribution of space charge polarization. In these composites, as the concentration of CFO decrease then dielectric constant also increases [6-8].

Both εʹ and tanδ show similar dispersion behavior with frequency. The tanδ indicates the energy loss in the dielectric system which is equivalent to the imaginary part of the dielectric constant.
FIGURE 1. XRD patterns of $x$BaTiO$_3$ - (1-x) CoFe$_2$O$_4$ ($x=0.00$ and 0.10) composites at room temperature.

FIGURE 2. Rietveld refined XRD pattern of samples $x=0.00$ and $x=0.10$. 
**Magnetic Analysis**

Fig.4 illustrates that the M-H loops of the prepared samples at room temperature. It is observed that loops are thin which show ferromagnetic behavior at room temperature and get saturated beyond the applied magnetic field 3kOe. From the M-H loops, the values of saturation magnetization ($M_s$) for $x=0.00$ and $x=0.10$ samples is $M_s=67.130$emu/g and $M_s=57.302$emu/g and remnant magnetization are $M_r=19.96$emu/g and $M_r=15.64$emu/g respectively. The saturation magnetization ($M_s$) and remnant magnetization ($M_r$) increases with CFO content. The magnetization increases with increase of magnetic phase.

**CONCLUSIONS**

Polycrystalline composites $xBaTiO_3 - (1-x)CoFe_2O_4$ ($x=0.00$ and $0.10$) were prepared via solid state reaction method. Rietveld refinement verified that coexistence of phase ferrite as well as ferroelectric without any impurity
peaks. The value goodness of fit $\chi^2$ shows an excellent fitting of the samples. The dielectric constant and dielectric loss show dispersion behavior at lower frequency due to space polarization. The value of saturation magnetization ($M_s$) and remnant magnetization ($M_r$) is increase with ferrite (CFO) content.

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REFERENCES