Anomalous Magnetic Behavior of BaTiO$_3$ and La$_{0.7}$Ca$_{0.3}$MnO$_3$ Composite System

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Abstract. We report dc magnetization study of a composite made of well known ferroelectric material BaTiO$_3$ (BTO) and a colossal magnetoresistance material (CMR) La$_{0.7}$Ca$_{0.3}$MnO$_3$ (LCMO). The phase purity of the parent compounds and the composite are confirmed from Rietveld refinement of the XRD pattern. The insignificant change of the spin state of the composite with respect to parent ingredient has been confirmed from same values of Curie constant (C) and Curie Weiss temperature ($\theta_C$). A significant reduction of the magnetic moment of the composite below Curie temperature is explained in terms of magnetoelectric coupling induced magnetic anisotropy inside LCMO present in the composite and this magnetic anisotropy is observed to be wakened at lower temperature.

1. INTRODUCTION

Multiferroicity has simulated larger interest over many decades because of its foreseen application in spintronics where the magnetic property can be controlled by applying electric fields and the electric property by magnetic field [1, 2, 3, 4]. The multiferroic property help to control several magnetic properties like magnetocrystalline anisotropy [5,6], exchange bias [7,8] by applying electric field and many more. The origin of multiferroicity or magnetoelectric coupling in a material is intimately linked to temporal and spatial symmetry breaking associated with spin and charge respectively [9,10,11]. The major issue with single phase multiferroic material is that none of them shows a robust magnetoelectric coupling at room temperature [12]. So to enhance the multiferroic property at room temperature the artificial heterostructure of different materials are developed where the temporal and spatial inversion symmetry breaks naturally across the interface and coupled with each other at the interface [1,12]. Usually there are several origin has been found for this kind of interfacial coupling, like magnetic exchange bias field[7,8], elastic strain[13,14], charge mediated coupling[15,16,17] etc. In case of the strain mediated coupling the atomic displacement of the ferroelectric material at the interface causes instability in the atomic bonding of the ferromagnetic material across the interface, which causes a change in the magnetic property [18]. The changes of ferromagnetic property in case of interface between ferroelectric and Colossal magnetoresistance (CMR) materials is very nicely explained by charge based mechanism [17], because of the typical electronic band structure of the CMR materials [19]. In most of the above studies on ferroelectric and CMR material interfaces L0.7Sr0.3MnO3 (LSMO) is used as a CMR material. LSMO is having larger electronic band width than LCMO (having intermediate electronic band width) [19], so a different type of change in the magnetic property is expected in case of BTO and LCMO interface. With this intent in this paper we have prepared a composite made of BTO and LCMO to study the change of static magnetic properties of LCMO due to close proximity with BTO by using dc magnetization measurement.
EXPERIMENTAL DETAILS

LCMO is prepared by pyrophoric technique then it is annealed at 1150 °C for 36 hrs. BTO is prepared by solid state reaction route and final heat treatment is given at 1350 °C for 36 hrs. Oxygen stoichiometry of LCMO is determined from standard Iodometric titration method and the obtained chemical formula can be written as $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3.05}$. Then both LCMO and BTO powder is mixed thoroughly in proper weight ratio and annealed at 1000 °C for 6 hrs. The composite consisting of 90% BTO and 10% LCMO is nomenclature as A1( BTO (90) + LCMO (10)). X-ray diffraction (XRD) measurements are performed in Bruker X-ray diffractometer from 10°-80° at an interval of 0.02°. All the magnetization measurements are performed in Vibrating sample magnetometer (M/S. Quantum Design, USA).

RESULTS AND DISCUSSIONS

Structural Characterization

Figure 1(a) shows high resolution powder X-ray diffraction Pattern of LCMO, BTO along with the composite BTO(90)+LCMO(10)(A1). Fig1b shows the refined pattern of the A1. Initially the Rietveld refinement of the parent ingredients are performed then all the refined parameters of the parent compounds are taken as the initial parameter for the refinement of the XRD pattern of the composites and then by changing the parameter gradually we have fitted the XRD pattern of the composites. The phase fractions are obtained from the two phase Rietveld refinement of the composite, which is used to normalize the magnetization data of the composite. The refinement shows no considerable change in the lattice parameter of LCMO and BTO with respect to parent ingredient. It confirms that there is no significant strain is developed in LCMO or BTO lattice in the composite.

<table>
<thead>
<tr>
<th>Compounds/(Ingredient)</th>
<th>space group</th>
<th>a (Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>Phase fraction</th>
<th>$R_{wp}/R_{exp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{BaTiO}_3$ (NA)</td>
<td>P 4 m m</td>
<td>3.991(4)</td>
<td>3.991(4)</td>
<td>4.028(5)</td>
<td>NA</td>
<td>1.35</td>
</tr>
<tr>
<td>$\text{La}<em>{0.7}\text{Ca}</em>{0.3}\text{MnO}_{3.05}$ (NA)</td>
<td>P n m a</td>
<td>5.456(4)</td>
<td>7.714(9)</td>
<td>5.475(8)</td>
<td>NA</td>
<td>1.44</td>
</tr>
<tr>
<td>A1/(BTO)</td>
<td>P 4 m m</td>
<td>3.997(3)</td>
<td>3.997(3)</td>
<td>4.025(1)</td>
<td>91</td>
<td>1.47</td>
</tr>
<tr>
<td>A1/(LCMO)</td>
<td>P n m a</td>
<td>5.457(1)</td>
<td>7.712(6)</td>
<td>5.475(7)</td>
<td>9</td>
<td>1.47</td>
</tr>
</tbody>
</table>
Magnetization study

Fig-2a shows the plot of the normalized magnetic moment of LCMO and the composite A1 against temperature. The normalization is performed with respect to mass of LCMO present inside the composite [20] used for magnetization measurement. The measurements are performed in field cool warming (FCW) mode at 500 Oe. Inset shows the zoomed view of the paramagnetic region of the temperature dependent normalize magnetization graph. It shows that the normalized value of paramagnetic moment of LCMO and A1 are well matched along with that the Curie Weiss temperature ($\theta_{cw} = 270$K) of the composite (obtained from Curie Weiss fitting of the paramagnetic region) is found to remain same with respect to parent LCMO (As BTO is a d0 system). It indicates that there is no change of the spin state of LCMO or BTO in the composite (A1) with respect to its parent ingredient [20]. However, magnetization is significantly less for the composite compared to LCMO below the ferromagnetic $T_C$.

**FIGURE 2:** (Color Online) (a) The temperature dependent normalized magnetization graph of LCMO and the composite BTO (90) +LCMO (10). Inset shows the zoomed view Normalized paramagnetic region of the parent LCMO and the composite. The comparative magnetic isotherm of LCMO and A1 at 10K, 150K, 200 K and 250 K shown in Fig 2b, Fig 2c, Fig 2d and Fig 2e respectively.
This anomalous difference between the normalized magnetization value of A1 and parent LCMO is quite surprising because the spin state and the crystal structure of LCMO remain invariant in the composite with respect to parent LCMO, so this difference in magnetization value is not expected. To get more insight of this problem isothermal magnetization measurements are performed against dc field at different temperature like 10K, 150K, 200K and 250 K as shown in Fig2b, Fig2c, Fig2d, and Fig2e respectively. All the mass normalized magnetic isotherms are showing technical saturation below 1 T of magnetic field. However the isotherm of A1 at 10 K (shown in Fig 2b) shows the continuously upward increase in magnetization value with increase in field and it appears to match the magnetization value of LCMO. Linear extrapolation indicates that the isotherms will converge at ~ 10T. All other isotherms of A1 at higher temperature (shown in Fig 2c-Fig 2e) do not show any tendency to reach the magnetization value of parent LCMO, they almost become parallel with respect to the isotherm of LCMO and shows lesser value at all fields. So the isotherms at high temperature (shown in Fig 2c - Fig 2e) are depicting that there may be an extra magnetic anisotropy affecting LCMO due to magnetoelectric coupling across the interface of BTO and LCMO in A1. Due to this reason the spins of LCMO in A1 are not able to align completely in the direction of the applied magnetic field, whereas the isotherm at 10 K is depicting that this magnetoelectric coupling energy or the induced anisotropy inside LCMO reduces at lower temperature, as a result of it the magnetization value of the composite A1 matches with the magnetization value of the parent LCMO at higher values of magnetic field. This anomalous decrease of magnetocrystalline anisotropy at lower temperature is inconsistent with the previous mechanism discussed in case of a ferroelectric and CMR ferromagnet interfaces [12, 13, 14, 15, 16]. So, further detailed magnetization measurements of BTO/LCMO heterostructurers are required to obtain the nature of magnetoelectric coupling and its thermal evolution across the interface.

CONCLUSIONS

The composite of polycrystalline BTO and LCMO has been prepared through solid state route and their phase purity has been confirmed from XRD measurements. The same value of the normalized paramagnetic moment and Curie temperature of A1 with respect to parent LCMO is depicting the spin state of both the compounds (BTO and LCMO) remain invariant with respect to the parent ingredient. The magnetic isotherms at high temperature and low temperature are depicting there developed an extra anisotropy inside LCMO due to magnetoelectric coupling across the interface of BTO and LCMO. This anisotropy energy is found to diminish at lower temperature. So detailed magnetization measurements are required to find out the temperature dependent magnetoelectric coupling between BTO and LCMO across the interface.

ACKNOWLEDGMENTS

Dr. Mukul Gupta is acknowledged for XRD measurements.

REFERENCES