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Low temperature magnetocaloric effect in polycrystalline $BiFeO_3$ ceramics

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We report on the structural, thermal, and magnetic properties of polycrystalline $BiFeO_3$ synthesized by sol-gel route. Powder x-ray diffraction data of the $BiFeO_3$ sample was refined with rhombohedral structure with space group $R3c$. Magnetization and coercive field measurements showed weak ferromagnetic nature below 10 K. We also investigated the low temperature magnetocaloric effect in polycrystalline $BiFeO_3$ ceramics. The anomalies observed in the magnetic entropy change of the $BiFeO_3$ ceramics were close to that of low temperature phase transitions. The combined relative errors in the magnetic entropy change are found to vary from 4% to 15% with increase in temperature. © *2009 American Institute of Physics*. [doi:10.1063/1.3242411]

Magnetoelectric (ME) multiferroics[1] are technologically and scientifically promising because of their potential applications in data storage, spin valves, spintronics, and microelectronic devices.[2–4] $BiFeO_3$ (BFO) is a single phase multiferroic, among the few reported so far, and it has great potential for practical applications exhibiting ferroelectricity with high Curie temperature[5,6] ($T_C \approx 1083-1103$ K), and antiferromagnetic properties below $T_N \approx 625-643$ K.[5–7] At the same time, BFO is a model ME perovskite because it presents a number of attractive distinct features compared to other MEs: simple chemical formula, exchange interactions in the Fe^{3+} sublattice, and the stereo-chemically active $6s^2$ lone pair of Bi^{3+}, which is the origin of ferroelectricity.[8]

Recent work aimed at studying the rare earth elements doped in to multiferroic manganite compounds[9–13] and many interesting effects have been shown on the magnetic properties, some focusing on the magnetocaloric effect (MCE). The MCE is intrinsic to magnetic solids and is induced via the coupling of the magnetic sublattice with the magnetic field, which alters the magnetic part of the entropy due to a corresponding change in the magnetic field.[14] Thus one of the main goals of the recent studies on MCE is to find useful magnetic materials, which have a large entropy change at low applied magnetic fields for magnetic refrigeration applications.[13] In this work, we report on the structural, thermal, and magnetic properties of the polycrystalline BFO sample. Particularly, we are interested in studying the nature of the magnetic interactions and the magnetic entropy change, $\Delta S_M(T)_{\Delta H}$, in this sample.

We have synthesized $BiFeO_3$ by ethanol mediated sol-gel process. Bismuth nitrate and iron nitrate (1.05:1 ratio) were dissolved in 100 ml ethanol. 5 ml HNO_3 and H_2O_2 were subsequently added to the above solution with stirring. The solution was then refluxed for about 2 h after stirring the solution for 30 min. The precursor powders thus obtained were heated at different temperatures (550–650 °C) for different durations (1–5 h). The powder x-ray diffraction (XRD) data of the samples were collected using a PANalytical X'Pert Pro x-ray diffractometer with Cu $K\alpha$ radiation. Phase pure BFO powders were obtained at a calcination temperature of 600 °C for 1 h. Finally, BFO powder was made in to 12 mm diameter pellets with 2 mm thickness and then sintered at 850 °C for 6 h. Crystal structure refinements were carried out using general structure analysis system.[15] Morphology and composition analysis of the sample were studied using field emission scanning electron microscope (FESEM) and energy dispersive x-ray analysis (EDX). Thermal properties of the sample were carried out using commercial differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The magnetization data of the samples were measured using physical property measurement system (PPMS, Quantum Design, USA).

The phase formation of $BiFeO_3$ was confirmed by XRD. XRD patterns revealed that the calcined sample was polycrystalline in nature and the peak positions were in good agreement with those of $BiFeO_3$ diffraction peaks.[16] BFO sample sintered at 850 °C was found to be phase pure and polycrystalline in nature. Figure 1 shows the results of the Rietveld refinements of the XRD data of BFO sintered at 850 °C for 6 h. The refinement was carried out using the rhombohedral crystal system with $R3c$ space group. The difference profile (Diff.) between the observed (Obs.) and calculated (Calc.) diffraction patterns is shown at the bottom of the plot. A good fit was obtained with R factors, $Rwp = 7.1\%$, $Rp = 5.3\%$, and $\chi^2 = 1.951$. The refined lattice constants and volume of the unit cell are $a = b = 5.581$ Å, c

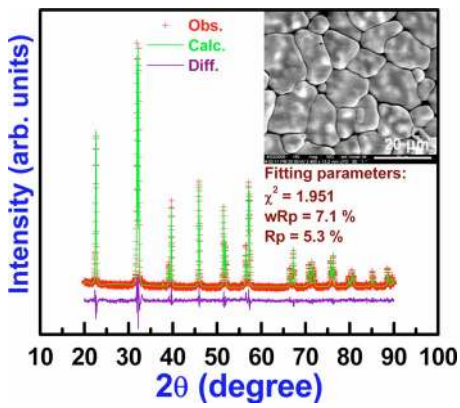

FIG. 1. (Color online) The Rietveld analysis of the XRD pattern of $BiFeO_3$ sample. The difference between observed (Obs.) and calculated (Calc.) pattern is shown in the below these Obs. and Calc patterns. Inset shows FESEM image of BFO ceramics.

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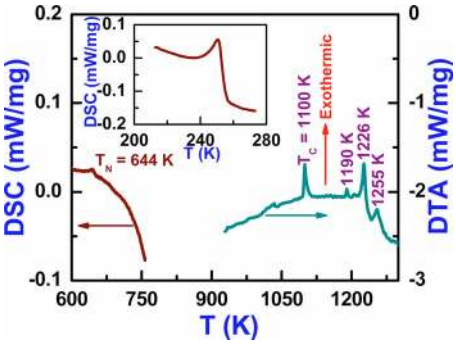

FIG. 2. (Color online) DSC and DTA analysis of polycrystalline BFO sample. Inset shows low temperature DSC analysis of BFO.

=13.879 Å, and V=432.3 Å^3, respectively. The sintering density of BFO pellet was found to be ~90% of its theoretical density. FESEM image (inset of Fig. 1) of the BFO pellet shows the presence of micro grains with sizes ~10 to 30 μm. EDX analysis of $BiFeO_3$ sample showed a Bi: Fe ratio of approximately 1:1.

High temperature DSC of BFO (Fig. 2) shows phase transition at 644 K, which corresponds to the Néel temperature. DTA measurement on BFO sample reveals four sharp peaks exist at 1100, 1190, 1226, and 1255 K. The first peak corresponds to the well known ferroelectric to paraelectric transition temperature (or α to β phase transition). The second transition is related to β to γ phase transition (ferroelastic transition), which happens at low temperature, 1190 K. The other two transitions correspond to decomposition temperatures of BFO, which occur at higher temperatures, 1226 and 1255 K. A similar behavior was reported by Palai *et al.*[17] We also observed the expected antiferromagnetic to spin glass transition from strong specific heat anomaly at around 251 K in low temperature DSC measurement, which is shown in the inset of Fig. 2.

Zero field cooled (ZFC) and field cooled (FC) magnetization measurements of polycrystalline BFO sample were measured at a magnetic field of 50 Oe in temperature range of 2–300 K (Fig. 3). In the measured temperature range of 300–250 K, ZFC and FC magnetization values decrease with the decrease in the temperature, which shows conventional antiferromagnetic nature. The ZFC and FC curves show small anomaly at around 250 K, which reveals the spin glass transition in polycrystalline BFO sample and which is also seen in the low temperature DSC measurement (inset of Fig. 2). At 150 K, a small anomaly is seen, which may be due to

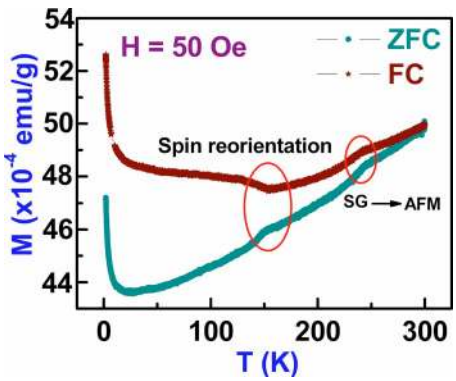

FIG. 3. (Color online) ZFC and FC magnetization measurement of BFO sample in a magnetic field of 50 Oe.

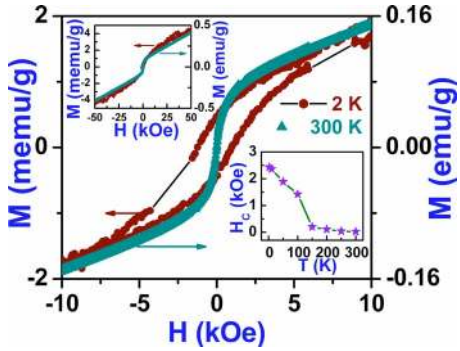

FIG. 4. (Color online) Magnetization vs magnetic field curves of BFO sample in a magnetic field of 1 T at 2 and 300 K. Top inset shows high magnetic field (5 T) M-H plots of BFO sample at 2 and 300 K, and bottom inset shows coercive field (H_c) vs temperature of BFO sample.

spin reorientation as seen in BFO single crystal[18] and orthoferrites.[19,20] Both ZFC and FC curves show sudden jump in magnetization below 10 K, indicating a weak ferromagnetic nature in polycrystalline BFO. Figure 4 shows magnetization (M) versus magnetic field (H) of BFO sample measured at 2 and 300 K. At room temperature, the magnetization curve shows antiferromagnetic nature. At 2 K, the magnetization curve exhibits weak ferromagnetism with a coercive field of 2433 Oe and it does not saturate even at a field of 5 T (top inset of Fig. 4). We also observed that the coercive field increases gradually below 150 K, which reaches the high value of 2433 Oe at 2 K (bottom inset of Fig. 4). Similar behavior was earlier observed in single crystal BFO by Singh *et al.*[18] However the observed coercive fields in this polycrystalline BFO sample are higher than that of BFO single crystal.

The magnetic entropy change, $\Delta S_M(T=T_{\mathrm{av}})_{\Delta H}$ for an average temperature $T_{\mathrm{av}}=(T_u+T_l)/2$ from the two magnetization isotherms measured at T_u and T_l in a magnetic field changing by $\Delta H=H_F$-H_I at a constant step δH is given by the following equation:[14]

$$\Delta S_M(T_{\mathrm{av}})_{\Delta H}=\frac{\delta H}{2\delta T}\left(\delta M_1+2\sum_{k=2}^{n-1}\delta M_k+\delta M_n\right),$$

where $\delta M_k=[M(T_u)_k$-$M(T_l)_k]$ is the difference in the magnetization at T_u and T_l, $\delta T=T_u$-T_l is the temperature difference between the two isotherms and n is number of points.

Magnetic entropy change $\Delta S_M(T=T_{\mathrm{av}})_{\Delta H}$ was evaluated from the magnetization data of BFO sample for the magnetic field change ($\Delta H=8T$) in the temperature range of 15–280 K in the step in δT=5 K using constant δH=402 Oe and n =200 (inset of Fig. 5). Both the magnetic entropy change $\Delta S_M(T_{\mathrm{av}})_{\Delta H}$ and the combined error in the magnetic entropy change of polycrystalline BFO sample are presented in Fig. 5. We observed five peaks in the magnetic entropy change $\Delta S_M(T_{\mathrm{av}})_{\Delta H}$ and each of them corresponds to low temperature transitions, which can be identified from elastic and electrical anomalies in BFO single crystal and ceramics reported by Redfern *et al.*[21] The observed peaks at 250 and 150 K correspond to antiferromagnetic to spin glass transition and spin reorientation as mentioned earlier. The other three peaks at 223, 178, and 38 K are identified as phase transitions, which are (i) magnetic, glassy, and also weakly coupled with polarization, (ii) magnetoelastic with small coupling with polarization, and (iii) magnetic, but glassy and

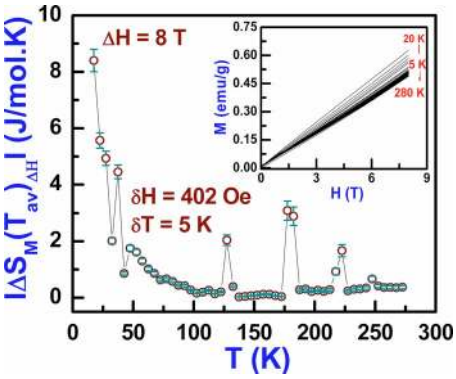

FIG. 5. (Color online) The magnetic entropy change, $\Delta S_M(T_{av})_{\Delta H}$ vs temperature of polycrystalline BFO sample. Inset shows magnetization vs magnetic field of BFO at high magnetic field (8 T) from 15 to 280 K in steps of 5 K.

with ME coupling, respectively. These peak temperatures are not the exact values but are close to that of low temperature phase transitions observed by Redfern *et al.*[21] The magnetic entropy change, $\Delta S_M(T_{av})_{\Delta H}$, in BFO at 223 K is about 1.7 J/mol K, which is much less than that of conventional magnetocaloric materials like Gd single crystal[14] ($\Delta S_M(T_{av})_{\Delta H}$=9 J/mol K at 300 K). However, magnetic entropy change in polycrystalline BFO is 8.4 J/mol K at 18 K comparable to that of Gd single crystal. The errors in the temperature give a constant contribution with constant δT =5 K, which is significant and cannot be neglected. However, the errors in the magnetic field (0.1%) and magnetic moment (0.5%) are very small and hence can be neglected. The combined relative errors in the magnetic entropy change calculated from the magnetization data are found to be temperature dependant and found to vary from 4% to 15% with increase in temperature keeping δH, δT, and ΔH as constant.

In conclusion, we synthesized single phase polycrystalline $BiFeO_3$ by ethanol mediated sol-gel process. The structural refinement of BFO sample reveals that the sample has crystallized in rhombohedral structure with noncentrosymmetric space group $R3c$. Thermal property studies of BFO showed high temperature phase transitions at 1100 K (α-β phase transition) and 1190 K (β-γ phase transition). The decomposition occurs at much higher temperatures, 1226 and 1256 K, compared to that of BFO single crystal. ZFC and FC magnetization measurements showed expected spin glass behavior below 150 K, and magnetization (M-H) measurements and the observed coercive field showed weak ferromagnetic nature below 10 K. We also investigated MCE in polycrystalline BFO ceramics. The observed anomalies in magnetic entropy change are close to that of low temperature phase transitions. This study can open a modern area of research in a model ME BFO because it presents a number of attractive features compared to other single phase ME multiferroics.

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