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Magnetoelectric behavior of ferrimagnetic $Bi_xCo_{2-x}MnO_4$ (x=0, 0.1 and 0.3) thin films

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ABSTRACT

Thin films of $Bi_xCo_{2-x}MnO_4$ (x=0, 0.1 and 0.3) were grown on quartz, $LaAlO_3$ (LAO) and $YBa_2Cu_3O_7$ (YBCO) buffer layer coated LAO substrates by pulsed laser deposition (PLD). X-ray diffraction (XRD) and Raman scattering measurements showed that the thin films exhibit single phase polycrystalline cubic spinel structure on all the substrates. Near edge X-ray absorption fine structure (NEXAFS) studies confirmed the octahedral occupancy of the substituted Bi^{3+} ions. Temperature dependent zero-field cooled (ZFC) magnetization measurements show the ferrimagnetic (FM) behavior ($T_C \sim 186$ K) and magnetization undergoes a crossover from positive to negative, owing to the opposite contributions of magnetic moments from Co and Mn ions. A weak ferroelectric property exhibited by the films above room temperature was evidenced through the capacitance–voltage (C–V) and dielectric measurements. Magnetoelectric coupling was found to be maximum just below FM-T_C.

1. Introduction

Multiferroic magnetoelectric materials exhibit coexistence of ferro/ferrimagnetism (FM) and ferroelectricity (FE) in the same phase and coupling between these order parameters. Recent studies showed that coupled FM and FE properties offered multiple state memory and logic device applications [1–3]. However, because of the contrasting origins of FM and FE properties, very few multiferroic materials exist naturally with sufficient magnetoelectric coupling. For FE and FM to coexist in single phase, atoms that move off-center to induce electric dipole moment should be different from those that carry magnetic moment (atoms with partially filled d orbitals, responsible for FM). Among recently established magnetoelectric multiferroic materials [4], magnetic frustration and geometrical frustration of lattice degrees of freedom have been found to be the leading mechanisms for perovskite manganites and cubic spinel systems, respectively. Magnetoelectric behavior in these systems was shown to arise from spin–lattice coupling. In practice, coexistence of FE and FM is achieved through induction of non-magnetic ions having stereochemically active lone pair of electrons, which can introduce off centering in the structure containing magnetic transition metal oxides [5,6]. Recently, we have reported that incorporation of Bi has introduced noncentrosymmetric charge ordering and consequently polarization in the Co_2MnO_4 spinel structure along with non-collinear antiferromagnetic (AFM) ordering among the Co^{2+} sublattices, which lead to FM and magnetoelectric effect [7,8]. It is important to mention here that the above work was reported for the bulk material, whereas these properties in the thin film form are required for device realization. In general, it is seen that the physical properties of the thin films are highly dependent on the deposition technique and parameters like substrate orientation and temperature, oxygen partial pressure, etc. Among various deposition techniques PLD is the widely used deposition technique for thin film growth, by which the stoichiometry of the target can be retained in the films. Many researchers have utilized PLD to grow thin films of complex spinel oxide materials [9–14]. Multiferroic composite thin films of multilayered $Pb(Zr_{0.53}Ti_{0.47})O_3$ – $CoFe_2O_4$ prepared by PLD on platinized silicon substrate were found to have a high dielectric constant and showed reduction in ferroelectric polarization with the application of external magnetic field [15].

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In the present work, we have grown thin films of $Bi_xCo_{2-x}MnO_4$ (x=0, 0.1 and 0.3) on amorphous quartz, crystalline LAO and YBCO buffer layer coated LAO substrates by pulsed laser deposition (PLD). The main objective of this work is to establish the multiferroic magnetoelectric nature of the Bi-substituted Co_2MnO_4 thin films through structural, magnetic and magneto-electric studies for multiferroic device applications.

2. Experimental

Thin films (~350 nm thick) of the spinel $Bi_xCo_{2-x}MnO_4$ with variable Bi-content (x=0, 0.1 and 0.3) were deposited by PLD technique (KrF Excimer Laser source, λ=248 nm, repetition rate of 10 Hz and pulse laser energy of 220 mJ) using single phased targets on chemically cleaned amorphous quartz, LAO (0 0 1) and YBCO buffer layer (to provide bottom electrode for FE measurements) coated LAO substrates (YBCO/LAO). During deposition, oxygen partial pressure of 60 mTorr was maintained in deposition chamber and substrates were kept at 700 °C. After deposition, substrates were cooled at a rate of 5 °C per minute in the same oxygen environment as used during deposition. Room temperature powder X-ray diffraction (XRD) studies of the films were performed using Cu–K_α radiation (Rigaku, Japan). The Raman spectra were recorded at room temperature in backscattering configuration using a HR800 Jobin-Yvon spectrometer having a resolution of 1 cm^{-1}, and He–Ne laser (488 nm) was used as an excitation source at 9 mW power. During the measurements, an 1800 g mm^{-1} grating is used in high-resolution dispersive geometry. In order to achieve a very high positional accuracy, grating was kept unmoved during the entire temperature scan and a spectral window of ~325 cm^{-1} was covered with a high positional accuracy. The Local symmetry/valence state of Bi^{3+} ions was confirmed by performing the near edge X-ray absorption fine structure (NEXAFS) measurements at the Bi L_3-edge of the $Bi_xCo_{2-x}MnO_4$ thin films. These experiments were performed at the BL7C1 beamline of the Pohang Light Source (PLS), operating at 2.5 GeV with a maximum storage current of 200 mA. All the scans were made in fluorescence yield mode at room temperature. The beam was monochromatized by a double-crystal Si (1 1 1) monochromator having a resolution of ~1.5 eV in the studied energy range. Ferroelectric measurements of the thin film samples were performed using a HP4192 precision LCR meter. For ferroelectric measurements top electrodes were made using a good quality silver paste. Magnetization measurements were carried out using vibrating sample magnetometer (VSM) option of physical property measurement system (PPMS) within a temperature range of 20–300 K under a constant magnetic field (H=0.1 T). Isothermal DC magnetization hysteresis measurements using the same equipment were performed at 150 K. Magnetoelectric coupling studies of the films were investigated using a cryogen free low temperature high magnetic field facility.

3. Results and discussion

In Fig. 1, XRD patterns of thin films of $Bi_xCo_{2-x}MnO_4$ (x=0, 0.1 and 0.3) on amorphous quartz substrates are shown, which clearly support that the films grown are of single phase and preferentially oriented in (1 1 1) plane. Being amorphous, quartz substrate does not cause any substrate induced strain and the film grows completely relaxed with preferential (1 1 1) orientation. Lattice parameters of thin films on quartz are found very close to that of the bulk. In the spinel $Bi_xCo_{2-x}MnO_4$ thin films, oriented growth along (1 1 1) is most favoured, as it offers lower surface energy and greater oxygen packing density than other

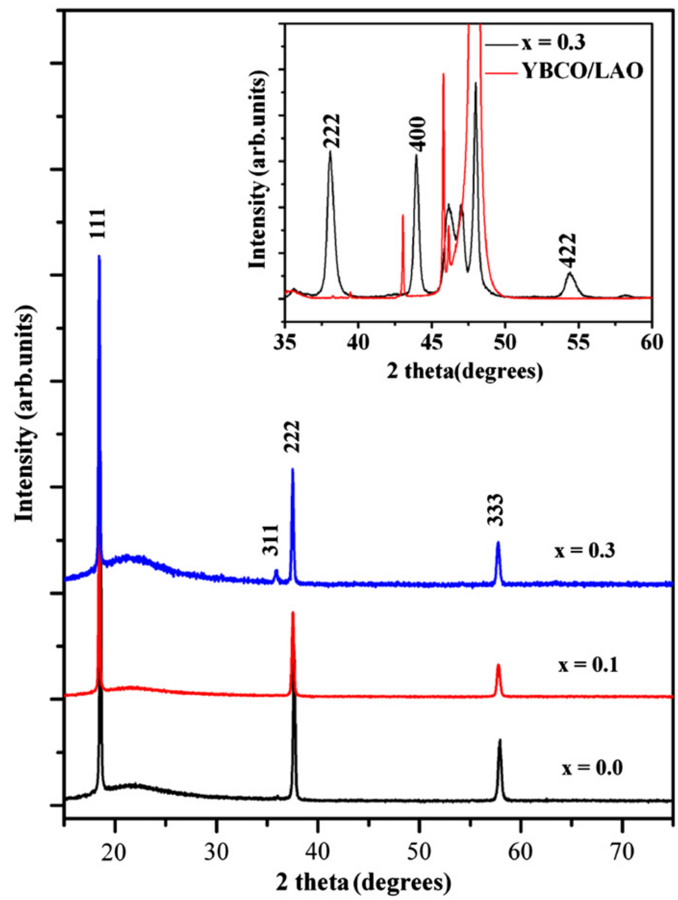

Fig. 1. XRD pattern for the thin films of $Bi_xCo_{2-x}MnO_4$ (x=0, 0.1 and 0.3) on quartz substrates. Inset shows the XRD pattern of film $Bi_xCo_{2-x}MnO_4$ (x=0.3) on YBCO/LAO substrate.

crystallographic planes, as evident for the films on quartz substrates. Also, for the films on both LAO and YBCO/LAO substrates, we observe the single phase polycrystalline growth. On YBCO/LAO substrates, films were preferentially grown in (2 2 2), (4 0 0) and (4 2 2) planes as shown in inset for x=0.3. On pure LAO (0 0 1) substrates, films were grown with preferential (2 2 0), (4 0 0) and (4 4 0) planes (*not shown here*). Appearance of a dominant (2 2 2) reflection from the film deposited on YBCO/LAO substrate reveals a slow texturing in the thin films on this substrate. Lattice parameters obtained from XRD patterns of the films on YBCO/LAO substrate (a=8.24 Å) were found slightly more deviated in comparison with the films on quartz (a=8.33 Å) and LAO (a=8.29 Å) substrates. This indicates lattice contraction of the representative composition (x=0.3) shown here. This may be due to greater strain induced by the YBCO electrode on the films owing to lattice mismatch (for YBCO, a=3.81 Å, b =3.88 Å, c=11.68 Å). XRD reflections from the films on all the three substrates revealed the oriented growth of cubic structured films (space group Fd3m). We would like to mention that the deposition of these thin films has been carried out on the amorphous and crystalline substrates as an investigation regarding the stability of this multiferroic material in thin film form. A stable and single phase growth of polycrystalline films on all the three substrates is observed.

Charge distribution in normal cubic spinel structure is represented by $[A^{2+}]_{8a}[B_2^{3+}]_{16d}[O_4^{2-}]_{32e}$, where Wyckoff positions 8a denote the tetrahedral sites and 16d the octahedral sites surrounded by O^{2-}ions at the 32e sites. In the present system, Bi-substitution leads to charge redistribution owing to its larger ionic