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PII: S0304-8853(11)00050-3
DOI: doi:10.1016/j.jmmm.2011.01.032
Reference: MAGMA 56733

To appear in: *Journal of Magnetism and Magnetic Materials*

Received date: 11 August 2009
Revised date: 14 November 2010
Accepted date: 19 January 2011

Cite this article as: N.E. Rajeevan, Ravi Kumar, D.K. Shukla, R.J. Choudhary, P.P. Pradyumnan, P. Thakur, A.K. Singh, S. Patnaik, S.K. Arora and I.V. Shvets, Magnetoelectric behaviour of ferrimagnetic Bi$_x$Co$_{2-x}$MnO$_4$ ($x = 0$, 0.1 and 0.3) thin films, *Journal of Magnetism and Magnetic Materials*, doi:10.1016/j.jmmm.2011.01.032

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Magnetoelastic behaviour of ferrimagnetic Bi$_x$Co$_{2-x}$MnO$_4$ (x = 0, 0.1 and 0.3) thin films

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ABSTRACT

Thin films of Bi$_x$Co$_{2-x}$MnO$_4$ (x = 0, 0.1 and 0.3) were grown on quartz, LaAlO$_3$ (LAO) and YBa$_2$Cu$_3$O$_7$ (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 ($T_c$ ~ 186 K) and magnetization undergoes a cross-over 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. Magnetoelastic coupling was found maximum just below the FM-$T_c$.

Keywords: Magnetoelastic, ferroelectric, ferrimagnetic, Raman scattering, NEXAFS

PACS: 75.80.+q, 77.80.-e, 75.50.Gg, 78.30.-j, 61.05.cj

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I. 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, atom which moves off-centre 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], frustrated magnets and geometrical frustration of lattice degrees of freedom have been found to be the leading mechanisms for perovskite manganites and cubic spinel systems respectively. Magnetolectric behaviour in these systems was shown to be arising from spin-lattice coupling. In practice, coexistence of FE and FM are achieved through induction of nonmagnetic ions having stereochemically active lone pair of electrons that can introduce off centering in the structure containing magnetic transition metal oxides [5, 6]. Recently, we have reported that incorporation of the Bi has introduced noncentrosymmetric charge ordering and consequently polarization in the Co$_2$MnO$_4$ spinel structure along with non collinear antiferromagnetic (AFM) ordering among the Co$^{2+}$ sublattices that lead to FM, and magnetoelectric effect [7, 8]. It is important to mention here that 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 upon 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 the 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 was found to have high dielectric constant and showed reduction in ferroelectric polarization with the application of external magnetic field [15].

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). 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 magnetoelectric studies for multiferroic device applications.

II. EXPERIMENTAL

Thin films (~350 nm thick) of the spinel Bi_xCo_{2-x}MnO_4 with varying the 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 (001) 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 same oxygen environment, as used during deposition. Room temperature powder X-ray diffraction (XRD) studies of the films were performed using Cu-Kα radiation (Rigaku, Japan). The Raman spectra were recorded at room temperature in backscattering configuration using a HR800 Jobin-Yvon spectrometer having a resolution of 1cm⁻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 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$_x$Co$_{2-x}$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 (111) 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 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 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.

III. RESULTS AND DISCUSSION

In Fig. 1, XRD patterns of thin films of the Bi$_x$Co$_{2-x}$MnO$_4$ (x = 0, 0.1 & 0.3) on amorphous quartz substrates are shown which clearly support that films grown are single phase and preferentially oriented in (111) plane. Being amorphous, quartz substrate does not cause any substrate induced strain and the film grows completely relaxed with preferential (111) orientation. Lattice parameters of thin films on quartz are found very close to that of bulk. In the spinel Bi$_x$Co$_{2-x}$MnO$_4$ thin films, oriented growth along (111) is most favoured, as it offers lower surface energy and greater oxygen packing density than other 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 preferential grown in (222), (400) and (422) planes as shown in inset for x=0.3 on YBCO/LAO substrate. On pure LAO (001) substrates, films were grown with preferential (220), (400) and (440) planes (not shown here). Appearance of a dominant (222)
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 ($a = 8.24 \, \text{Å}$) were found slightly more deviated in comparison with the films on quartz ($a = 8.33 \, \text{Å}$) and LAO ($a = 8.29 \, \text{Å}$) 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 the YBCO, $a = 3.81 \, \text{Å}$, $b = 3.88 \, \text{Å}$, $c = 11.68 \, \text{Å}$). 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 $[\text{A}^{2+}]_{8a}[\text{B}^{3+}]_{16d}\text{O}_{4}^{2-}_{32e}$, where Wyckoff positions $8a$ denote the tetrahedral sites and $16d$ the octahedral sites surrounded by $\text{O}^{2-}$ ions at the $32e$ sites. In the present system, Bi-substitution leads to charge redistribution owing to its larger ionic radii and presence of non-bonded $6s^2$ lone pairs which substantially modifies the physical properties. Structural changes that are not revealed through the XRD technique may be probed using Raman scattering measurement, which is more prone to the vibrational modes that can give insight about site symmetries. The parent compound $\text{Co}_3\text{O}_4$ that crystallizes in normal spinel structure with $O_h$ spectroscopic symmetry, was shown to possess five Raman active modes, as $A_{1g} + E_g + 3F_{2g}$. Reported wave numbers (in cm$^{-1}$) corresponding to these Raman phonon modes [16] were 194.4 ($F_{1g}^1$), 482.4 ($E_g$), 521.6 ($F_{2g}^2$), 618.4 ($F_{3g}^1$), and 691 ($A_{1g}$). Substitution by the Mn into the $\text{Co}_3\text{O}_4$ lattice causes its Raman bands to become broader, shifted and even some bands get coalesced [17]. For the $\text{Co}_3\text{O}_4$ spinel, Raman mode at 691 cm$^{-1}$ ($A_{1g}$) is attributed to characteristics of the octahedral sites ($\text{CoO}_6$) and mode at $\sim 195 \, \text{cm}^{-1}$ ($F_{1g}^1$) is attributed to the tetrahedral sites.
(CoO₄) in the $O_h^7$ spectroscopic symmetry. Fig. 2 shows the Raman spectra of Bi-substituted Co₂MnO₄ thin films grown on quartz (for $x = 0$ & $x = 0.3$) and LAO (for $x = 0$ & $x = 0.3$). Raman modes of the same compositions in bulk and thin film forms do not exhibit considerable variation. Hence Raman scattering studies also confirms the single phase character of the BiₓCo₂₋ₓMnO₄ ($x = 0, 0.1$ and $0.3$) thin films. Greater shift in $A_{1g}$ mode (691 cm⁻¹ for Co₃O₄ is shifted to ~ 655 cm⁻¹ for Co₂MnO₄ as well as Bi₀.₃Co₁.₇MnO₄) is indicative of the fact that most of the substituted Mn and Bi cations are occupying the octahedral sites (Co/Mn/Bi-O₆). Nevertheless, effect of Bi substitution can be directly visualized in $F_{1g}$ mode, by comparing the Raman spectra for Co₂MnO₄ ($x=0$) and Bi₀.₃Co₁.₇MnO₄ ($x=0.3$). $F_{1g}$ mode which represents the tetrahedral sites, shows broadening due to Bi induced charge redistribution of Mn among octahedral and tetrahedral sites, as seen before [18]. In general, the Raman spectra with a flat background is indicative of only phonon structure present in the system, but increased background at higher wave numbers has been observed in large number of reports on superconductors [19] due to increased electronic scattering. Here, for the BiₓCo₂₋ₓMnO₄ films, considerable increase in background at higher wave numbers were observed, which confirms the strong electron-phonon coupling present in the system that leads to multiferroicity. We would like to mention that the similar trend of background in Raman data were observed for bulk samples too [18], which confirms the intrinsic nature of electron-coupling phenomenon in this system.

Figure 3 shows the normalized Bi L₃-edge NEXAFS spectra of the BiₓCo₂₋ₓMnO₄ thin films along with the reference compound of Bi₂O₃ (with formal valence 3+ having octahedral symmetry) for comparison, while inset in the Fig. 3 represents the extended view of the main region of the Bi L₃-edge spectra. It is well known that different threshold energy inflection points in the NEXAFS spectra provide the differences in the electronic configurations present in the ground state and on the formal oxidation states of the functioning ions in a system [20]. It is observed that the energy of the main peak ($E \sim 13432$ eV; $2p \rightarrow 6d$ transitions) does not
show any shifts for these samples and is equivalent to the Bi$_2$O$_3$ reference spectrum, indicating that Bi is in a trivalent state. These results are further supported by the absence of a pre-edge structure ($2p \rightarrow 6s$ transitions) in these samples, which was assigned to be an indicative of mixed valent states of Bi ions [21]. However, the secondary peaks occurring at a few 10 eV above the main peaks (corresponding to the multiple scattering effects from the neighboring atom shells) exhibits different spectral profile than that of Bi$_2$O$_3$. This can be attributed to the different nearest neighbors of Bi atom (Bi-O/Mn/Co) in the case of Bi$_x$Co$_{2-x}$MnO$_4$ thin films as compared to that of the Bi$_2$O$_3$ (Bi-O) reference sample. Therefore, it is worth to conclude from our Bi L$_3$-edge results that the average Bi valence for the entire Bi$_x$Co$_{2-x}$MnO$_4$ series is +3 and it is not affected by the progressive doping of the Bi ions at the octahedral site of the spinel structure.

Magnetization studies were carried out for the films deposited on LAO substrates. Figure 4 illustrates the temperature dependent magnetization for representative compositions $x = 0$ & 0.3, measured in the presence of an in-plane magnetic field, 0.1 T, which shows the ferrimagnetic (FM) transition shifting from temperature ($T_C$) ~ 182 to 186 K. Magnetization behaviour exhibited by the films is almost identical with that of the bulk samples of the respective compositions [8] and supports that thin films maintain an ion configuration similar to the bulk. Therefore, it is reasonable to attribute the appearance of FM in the thin films to the canting of antiferromagnetically ordered spins by the structural distortion [22] and a breakdown of the balance between the antiparallel magnetization at Co$^{2+}$ sublattices due to the substitution of Mn and Bi ions at Co$^{3+}$ sites, arising from the affect on the super exchange interaction, Co$^{2+}$-O$^{2-}$-Co$^{3+}$-O$^{2-}$-Co$^{2+}$, that primarily maintains the antiferromagnetism [23]. In other words, the overall FM behaviour of these spinel films with AB$_2$O$_4$ structure is found to be effected by the Bi-substitution induced competition among intrasite A-O-A ($J_{AA}$), B-O-B ($J_{BB}$) and intersite A-O-B ($J_{AB}$) superexchange interactions and consequent magnetic
frustration. The increase in FM-$T_C$ indicates the lowering of negative molecular field arising from the magnetic frustration due to Bi-substitution.

DC magnetization during zero field cooling (ZFC) for all the films is found to undergo a crossover from positive to negative values, which necessitates a magnetic compensation between the opposite contributions of magnetic moments from Co and Mn ions (see Fig. 4). This characteristic behaviour was not exhibited by the bulk samples. This may be the outcome of the oriented crystalline nature of the films formed on LAO, which hardens (pinning) one set of magnetic moments. The crossover temperature, $T_{CR}$, is found shifted from 157 K for $x = 0$ to 155 K for $x = 0.2$ and to 140 K for $x = 0.3$ (shown, only for $x = 0.0$ and 0.3 in Fig. 4). This further supports the influence of Bi-substitution in controlling the net magnetic moment of the presently probed thin films. The crossover to negative magnetization originates from the switching of the state with greater moment contribution of Mn ions to the state that provides greater moment contribution of Co ions. However this crossover is not visible in field cooled (FC) magnetization, as both the moments reorient towards the applied field. This kind of crossover of magnetization is already reported by Kulkarni et al [24], for Nd$_{0.75}$Gd$_{0.25}$Rh$_3$B$_2$ alloy at nominal zero fields. Thus, the observed crossover of ZFC magnetization to negative values can be correlated with the imbalance in the contributions spin moments of Co ions and Mn ions which are aligned antiparallel. The magnetization (M) vs. applied magnetic field (H) at 150 K showed clear hysteresis loops, depicting ferrimagnetic behaviour of the films (see Fig. 5). Saturation magnetization ($M_S$) is found to increase from 15 emu/cc for $x = 0.0$ film to 34 emu/cc for Bi-substituted ($x = 0.3$) film, along with drop in coercive field, $H_C$ (1016 Oe to 597 Oe). As a whole, M-H loop of the film having higher Bi-content depicted an increase in net magnetic moment which can be attributed to the Bi-substitution induced redistribution of cations at the octahedral and tetrahedral sites.

To investigate the ferroelectric behaviour of Bi-substituted films and the possible magnetoelectric coupling, the temperature dependent and magnetic field dependent dielectric
measurements were performed for the films on YBCO coated LAO substrate. YBCO was chosen as the bottom electrode, owing to the high temperature processing conditions required for the growth of stable Bi-substituted Co$_2$MnO$_4$ films, which makes conventional conducting Pt/Si electrode unsuitable. Also, YBCO is paramagnetic up to 80 K and diamagnetic below 80 K, which adds to its merit over many of the other conducting substrates commercially available for ferroelectric studies. The magnetoelectric coupling studies of the films on YBCO-LAO substrates have been carried out through dielectric constant ($\varepsilon'$) vs. temperature (T) measurement, with and without magnetic field. We measured $\varepsilon'$ without a magnetic field [$\varepsilon'(0T)$] and with a magnetic field of 3 Tesla [$\varepsilon'(3T)$] during warming cycle, after zero-field cooling. Distinct variation in $\varepsilon'(3T)$ was observed for Bi$_{0.3}$Co$_{1.7}$MnO$_4$ film, relative to $\varepsilon'(0T)$, during the entire range of the temperature of the measurement (100 - 300 K). Moreover, we could not detect any change for the undoped composition (x = 0) between $\varepsilon'(3T)$ and $\varepsilon'(0T)$ data. Inset of Fig. 4 shows the relative percentage variation in dielectric constant under an applied magnetic field (magnetoelectric coupling) and is determined as $\left[\frac{\varepsilon'(3T) - \varepsilon'(0T)}{\varepsilon'(0T)}\times100\right]$. Interestingly, the maximum magnetoelectric coupling was observed at 184 K, just below the FM-T$_C$ of the film material. Similar magnetoelectric effect was achieved in the bulk composition [7] and therefore it is reasonable to exclude extrinsic contribution like the strain effect induced by the substrates on the film prepared. The magnetoelectric response of the Bi-substituted Co$_2$MnO$_4$ films is originating from the non-collinear magnetic ordering occurring due to the geometrical frustration of the lattice by cation substitution (Mn$^{3+}$ and Bi$^{3+}$) that affect the collinear antiferromagnetic ordering of the parent composition Co$_3$O$_4$. This results in the magnetic origin of ferroelectricity as in the inversed Dzyaloshinskii-Moriya interaction occurring in complex magnetic structures such as non-collinearly canted antiferromagnets where the canted spins displaces the oxygen
sandwiched between them and leads to electric polarization through electron-phonon interaction [25, 26]. The diminution of the magnetoelectric effect at high temperature may be due to the order-disorder transition of magnetic ions in the complex magnetic structure of the Bi$_x$Co$_{2-x}$MnO$_4$ (x = 0.3) film which results in the flip of polarization against the normal FE polarization. The reduction in the magnetoelectric effect at lower temperature can be attributed to the collinear magnetic ordering.

Ferroelectric behaviour of Bi-substituted films is demonstrated through capacitance – voltage (C-V) characteristics along with temperature dependent dielectric measurements. C-V loop has been used to demonstrate the ferroelectric nature [27-29] for many of the multiferroic materials. The nearly butterfly nature of the C-V loop, as shown in Fig. 6, measured at 400 K (the film showed more pronounced FE characteristics at higher temperature than room temperature) and 100 kHz, indicates the weak FE nature of the film for x = 0.3. The asymmetric loop in the C-V plot may be attributed to the unlike electrodes (YBCO & Ag) on the two surfaces of the film. Inset (a) of Fig. 6 shows the temperature dependent variation in dielectric loss factor, tan $\delta$, at 100 kHz for x = 0.3. Dielectric constant ($\varepsilon'$) vs. Temperature (T) plot is shown as inset (b) of Fig. 6, which depicts a transition at temperature ~ 450 K for x = 0.3. The ferroelectric as well as magnetoelectric measurements of these films have been carried out at high frequency (100 kHz and above) to rule out the contribution of polarization arising from magnetoresistance combined with Maxwell-Wagner effect [30]. Although the thin film and bulk properties are qualitatively similar, the thin film samples show a usual reduction in FE polarization and dielectric response compared with the corresponding that of single crystal material [31] owing to the substrate-imposed pinning of the domains, which is known to suppress the ferroelectric response in thin films and reduce the dielectric constant. Similar behaviour is exhibited by the presently investigated Bi-substituted Co$_2$MnO$_4$ thin films also. However, our studies showed that the dielectric constant is very low compared to that of the bulk for the present series of films, which point to the
further investigation in ferroelectric properties with further optimization in electrode and film deposition conditions, which can really lead this material into multiferroic applications.

CONCLUSIONS

Polycrystalline films of the $\text{Bi}_x\text{Co}_{2-x}\text{MnO}_4$ ($x = 0, 0.1, \& 0.3$) with preferred orientation were grown by PLD technique on amorphous quartz, LAO and YBCO buffer layer coated on LAO substrates. Single phased growth of the films was confirmed by XRD and Raman spectrum. Bi-substitution at octahedral site is evidenced through NEXAFS study. Dielectric data of the $\text{Bi}_x\text{Co}_{2-x}\text{MnO}_4$ films reveals the weak ferroelectric behaviour in the Bi-substituted films. These films are found to possess lower dielectric constant compared to that of the bulk samples and exhibited better ferroelectric nature at higher temperature. Dc magnetization studies show that the thin films of $\text{Bi}_x\text{Co}_{2-x}\text{MnO}_4$ deposited on LAO exhibit well defined hysteresis loop at 150 K which reflects the FM behaviour. Both $M_S$ and $F-M-T_C$ increase as Bi-content increases in the films owing to the Bi-induced redistribution of cations among the octahedral and tetrahedral sites. In ZFC cycle, magnetization exhibited crossover from positive to negative values due to the compensation of oppositely oriented Mn and Co moments. The $\text{Bi}_x\text{Co}_{2-x}\text{MnO}_4$ films with higher Bi-content demonstrated magnetoelectric coupling, through the variation of dielectric constant in response to the applied magnetic field and exhibited maxima just below the $F-M-T_C$, similar to bulk samples, which confirms the magnetic origin of ferroelectricity. Magnetoelectric coupling present in these films is due to the interplay between structural distortion and magnetic exchange interaction. Finally, $\text{Bi}_x\text{Co}_{2-x}\text{MnO}_4$ ($x = 0, 0.1, \& 0.3$) thin films exhibit ferrimagnetic properties along with a weak ferroelectricity, and are suitable for multiferroic device applications.

ACKNOWLEDGEMENTS

N.E.R is thankful to the Inter-University Accelerator Centre (IUAC), New Delhi, India; UGC, India; DCE to State Govt. of Kerala and Z. G. College, Calicut, India for their
support to this work. Help and suggestions from Dr. V. Sathe and Dr. D. M. Phase of UGC-DAE consortium for scientific research, Indore, India is gratefully acknowledged. Also, authors are grateful to Dr K.H. Chae of KIST, Seoul, for the help during x-ray absorption experiments. This work was financially supported by DST, India under Project No. SR/S2/CMP-0051/2007.
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Rev. B 72, (2005) 220101-R.


FIGURE CAPTIONS:

FIG. 1. (Color online) XRD pattern for the thin films of Bi$_x$Co$_{2-x}$MnO$_4$ (x = 0, 0.1 and 0.3) on quartz substrates. Inset shows the XRD pattern of film Bi$_x$Co$_{2-x}$MnO$_4$ (x = 0, 0.1 and 0.3) on YBCO/LAO substrates.

FIG. 2. (Color online) Raman Spectra for the films of Bi$_x$Co$_{2-x}$MnO$_4$ (x = 0 and 0.3) on quartz and LAO substrates.

FIG. 3. (Color online) Bi L$_3$-edge absorption spectra of the Bi$_x$Co$_{2-x}$MnO$_4$ thin films and reference compound Bi$_2$O$_3$. Inset: Extended view of the main region of the Bi L$_3$-edge spectra.

FIG. 4. (Color online) Temperature dependent magnetization for Bi$_x$Co$_{2-x}$MnO$_4$ (x = 0 and 0.3) films. Inset shows magnetoelectric coupling $\left[ \frac{\varepsilon(3T)-\varepsilon(0T)}{\varepsilon(0T)} \times 100 \right]$ vs. temperature for Bi$_{0.3}$Co$_{1.7}$MnO$_4$ (x = 0.3) film.

FIG. 5. (Color online) M vs. H loops for the films with x = 0, 0.1 and 0.3 at 150 K.

FIG. 6. (Color online) C-V plot of Bi$_{0.3}$Co$_{1.7}$MnO$_4$ (x = 0.3) film. Inset (a) $\tan \delta$ vs. T and inset (b) $\varepsilon'$ vs. T, at 100 kHz, for the same film.
Fig. 1
Fig. 2
Fig. 3
Fig. 4
Fig. 5
Fig. 6
Research Highlights

In view of multiferroicity based practical device applications, for the first time synthesisization and magnetoelectric characterization of single phase Bi-substituted Co2MnO4 in thin film form is undertaken. Thin films are grown by pulsed laser deposition (PLD) as the stoichiometry of the target can be retained in the films. For ferroelectric measurements YBCO buffer layer is stabilized. Bi-substitution in the cobalt based manganite spinel was confirmed to improve the magnetoelectric behaviour. Basically, the modifications observed in the magnetoelectric prospects can be attributed to the frustration in the magnetic ordering, which is strongly influenced by the non-magnetic Bi ion, along with the enhanced electric polarization. So this spinel oxide material, Bi-substituted Co2MnO4, is supposed to assure its candidature in multiferroic applications.