

Magnetoelectric properties of $\text{Bi}_x\text{Co}_{2-x}\text{MnO}_4$ ($0 \leq x \leq 0.3$)

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We present the structural, dielectric and magnetization study of single phase polycrystalline $\text{Bi}_x\text{Co}_{2-x}\text{MnO}_4$ ($0 \leq x \leq 0.3$), synthesized by a conventional solid state route. All the samples have the cubic spinel structure with $Fd3m$ space group. Bi-substitution in Co_2MnO_4 stabilizes the ferroelectric transition at a temperature of ~ 350 K and enhances the dielectric constant with a relaxor behavior. The capacitance-voltage (C - V) measurements confirm the ferroelectric nature at room temperature. Ferrimagnetic nature of the Co_2MnO_4 is preserved in the Bi-substituted samples. Magnetocapacitive coupling proves candidature of these materials from an application point of view. © 2008 American Institute of Physics. [DOI: [10.1063/1.2894518](https://doi.org/10.1063/1.2894518)]

In multiferroic materials, magnetism and ferroelectricity (FE) coexist. These materials have attracted considerable attention in recent years.¹⁻⁷ The simultaneous occurrence of ferromagnetism/ferrimagnetism (FM) and FE and the coupling between these two order parameters could lead to the emergence of new storage media, which enable electrically reading/writing of the magnetic memories and vice versa, yielding more degrees of freedom from device application point of view. Multiferroics with coupled electrical and magnetic properties are termed as magnetoelectric multiferroics. However, there are only very few multiferroic materials with a sufficient amount of magnetoelectric coupling because of the contrasting origins of these properties. Among recently established magnetoelectric multiferroic materials,⁸ 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. In this context, for FE and FM to coexist in single phase, the atom which moves off the center to induce the electric dipole moment should be different from those that carry the magnetic moment (atoms with partially filled d orbitals, responsible for FM). Recent *ab initio* calculations for existing ferroelectrics suggest that atoms with d^0 configuration create more off center distortion.^{2,4} In principle, coexistence of FE and FM can be achieved through either an alternative mechanism like a non- d electron for magnetism or through an alternative mechanism for FE. In practice, alternative mechanisms for FE are pursued.⁷ One such alternative followed is the induction of nonmagnetic ions having stereochemically active lone pair of electrons that may introduce off centering in the structure containing transition metal ions.⁹ Also, spin-phonon coupling that may lead to dielectric anomalies has been envisaged for geometrically frustrated ZnCr_2O_4 spinel.¹⁰

Multiferroicity in conventional spinel oxides has been predicted¹¹ and studied. However, the strength of magnetoelectric coupling was found to be weak.¹² One can think of a way to engineer a new class of materials, combining the

mechanisms discussed in previous paragraph to achieve multiferroicity in spinel materials. Incorporation of Bi is supposed to introduce noncentrosymmetric charge ordering and consequently polarization^{1,13} in the Co_2MnO_4 spinel structure containing magnetic transition metal ions. The incommensurate antiferromagnetic (AFM) ordering among the Co^{2+} sublattices ensures FM.¹⁴ Although the properties of many spinels are known, there appears to have been very little exploration hitherto on multiferroic properties of doped cobalt manganite spinels. In this letter, we present an investigation on multiferroic properties of $\text{Bi}_x\text{Co}_{2-x}\text{MnO}_4$ ($0 \leq x \leq 0.3$) and a study of magnetoelectric coupling parameter for the purpose of applications.

The compositions of the cobalt-based manganite spinel $\text{Bi}_x\text{Co}_{2-x}\text{MnO}_4$ ($0 \leq x \leq 0.3$) were synthesized by solid state reaction from the precalcined mixture of Bi_2O_3 , Co_3O_4 , and MnO_2 with purities of $>99.99\%$, as starting materials. The stoichiometric compositions were calcined at 820°C for 24 h. All the calcined samples were uniaxially dye pressed into pellets and sintered at 1000°C for 24 h, with intermediate grinding for better homogeneity. Room temperature powder x-ray diffraction (XRD) studies of these samples were performed using a Bruker D8 x-ray diffractometer with $\text{Cu } K_\alpha$ radiation. Temperature and frequency dependent dielectric measurements of the pellets were performed using a HP4192 precision LCR meter. The magnetization measurements were carried out using the vibrating sample magnetometer option of physical property measurement system set up within a temperature range of 5 – 300 K with zero field cooled (ZFC) and field cooled (FC) modes under a constant magnetic field ($H=0.1$ T). Isothermal dc magnetization hysteresis measurements were performed at different temperature values (5 , 120 , 130 , and 150 K). The data were recorded during warming up cycles. The magnetocapacitive effect of the samples has been investigated using a cryogen-free low temperature high magnetic field facility.

Figure 1 shows the XRD pattern for the samples $\text{Bi}_x\text{Co}_{2-x}\text{MnO}_4$ ($x=0, 0.1$, and 0.3). The XRD patterns are indexed in cubic spinel structure (space group $Fd3m$, with $Z=8$) which indicates single-phase formation of these mate-

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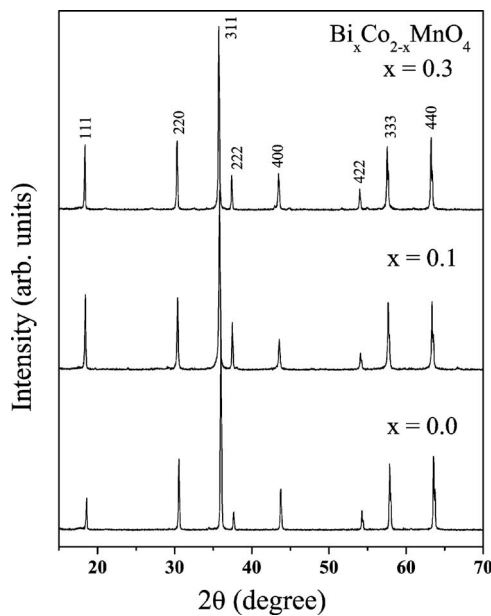


FIG. 1. XRD pattern for the samples $\text{Bi}_x\text{Co}_{2-x}\text{MnO}_4$ ($x=0, 0.1, \text{ and } 0.3$) measured at 300 K.

rials. It is clearly evident from the XRD analysis that there is no change in structural symmetry except the small change in lattice parameter a with Bi substitution. In this structure, cations (Co^{2+} , Co^{3+} , Mn^{3+} , and Bi^{3+}) occupy two non-equivalent sites: tetrahedral $8a$ (A Sites) and octahedral $16d$ (B sites). The substitution of Co^{3+} by Bi^{3+} leads to lattice expansion, i.e., lattice parameter a increases (8.283 \AA for $x=0.0$ to 8.301 \AA for $x=0.3$) due to the greater ionic radius of Bi^{3+} (1.17 \AA) than that of Co^{3+} (0.65 \AA) occupying the octahedral sites. It is found that the solid solution retains the normal cubic spinel structure of the parent compound only up to $x=0.3$. Beyond this concentration of Bi, the structure is no longer a cubic spinel (not shown here).

The temperature dependence of the dielectric constant at different selected frequencies illustrates that for $x=0$ there is no clear ferroelectric transition in the measured temperature range (150–450 K), whereas Bi doping stabilizes the ferroelectric transition at $\sim 350 \text{ K}$ (for $x=0.1$) and $\sim 380 \text{ K}$ (for $x=0.3$), as shown in Fig. 2. Moreover, Bi doping also leads to an increase in the dielectric constant (ϵ'). The loss factor for Bi-substituted system is found to be moderately high, which is in accordance with the relatively high conductivity of Bi-substituted spinel oxide (σ_{dc} at RT $\sim 5.56 \text{ m}\Omega^{-1} \text{ cm}^{-1}$). Within the range of frequencies investigated, both the dielectric constant (ϵ') and dielectric loss factor ($\tan \delta$) are found to decrease with increasing frequency. Maxima of dielectric constant (ϵ') shift toward high temperature with an increasing frequency indicating a relaxor behavior in Bi-substituted samples. The substantial variation in dielectric constant (ϵ') and transition temperature ($T_C \sim > 450 \text{ K}$, 350 K and 380 K for $x=0, 0.1$ and 0.3 respectively) can be attributed to the polarization of Bi $6s^2$ lone pair of electrons accommodated at octahedral sites. The insets in Fig. 2 show the capacitance versus voltage curves of the $\text{Bi}_x\text{Co}_{2-x}\text{MnO}_4$, (a) $x=0$, (b) $x=0.1$, and (c) $x=0.3$, using an applied voltage of 15 V. A typical butterfly-shaped loop, as seen in the C - V curves (very narrow for $x=0$), is again a signature of ferroelectric behavior in the doped samples. Similar to the dielectric constant (ϵ') measurement, the capacitance versus voltage curve

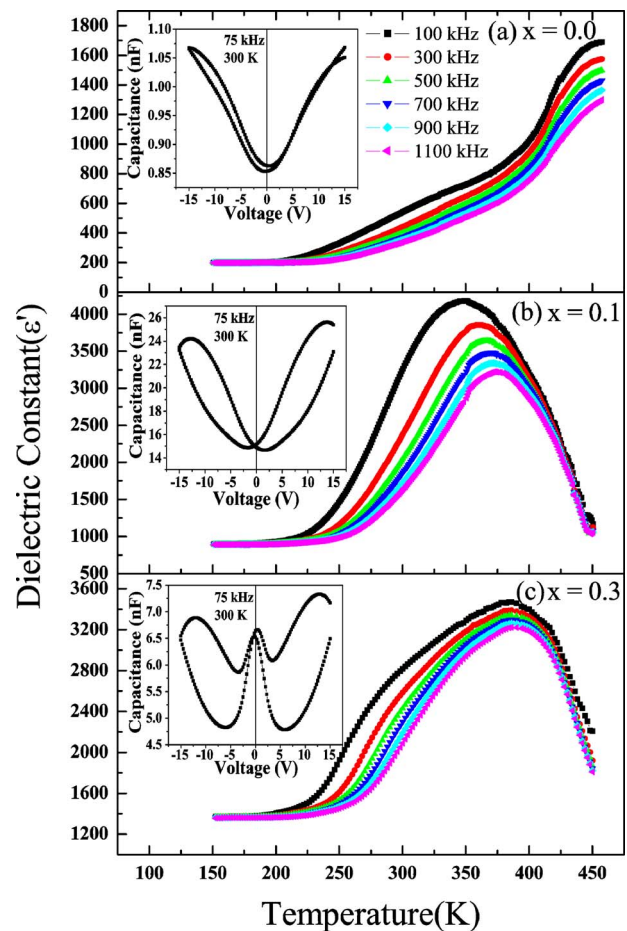


FIG. 2. (Color online) Dielectric constant (ϵ') vs temperature plot for $\text{Bi}_x\text{Co}_{2-x}\text{MnO}_4$ (a) $x=0$, (b) $x=0.1$, and (c) $x=0.3$. The insets show respective capacitance vs voltage behavior.

shows diffuseness, following Bi substitution. This can be attributed to the strain induced by Bi substitution.

The upper part of Fig. 3 shows the temperature dependent magnetization for $\text{Bi}_{0.3}\text{Co}_{1.7}\text{MnO}_4$ measured in ZFC and FC conditions in the presence of a 0.1 T magnetic field. It is observed that the magnetization under the FC process for all the samples increases (others are not shown) continuously after the ferrimagnetic transition temperature, with a decrease in temperature. The temperature dependent magnetization reveals that the ferrimagnetic transition occurs at a slightly varied temperature with Bi substitution ($T_C \sim 180 \text{ K}$, 182 K and 186 K for $x=0, 0.1$ and 0.3 respectively). Being a nonmagnetic ion, Bi substitution has only a marginal effect in AFM exchange interactions. Analysis of temperature dependence of the inverse susceptibility (not shown here) revealed that the Curie–Weiss temperature (θ) is negative, indicating that strong AFM interactions exist in the compound, besides the FM character, which sets at T_C . The magnetization (M) versus applied magnetic field (H) showed hysteresis loops, depicting ferrimagnetic behavior (top inset of Fig. 3). At all measured temperatures, saturation magnetization (M_S) is found to be increasing with increasing Bi content. Remnant magnetization observed in these compounds was not high. Interestingly, the coercive field (H_c) was found to decrease with Bi substitution. Regarding the magnetic behavior of spinel oxides, there are mainly three types of magnetic interactions, which are possible between the ions at A and B sites through the intermediate oxygen ions (O^{2-}) via

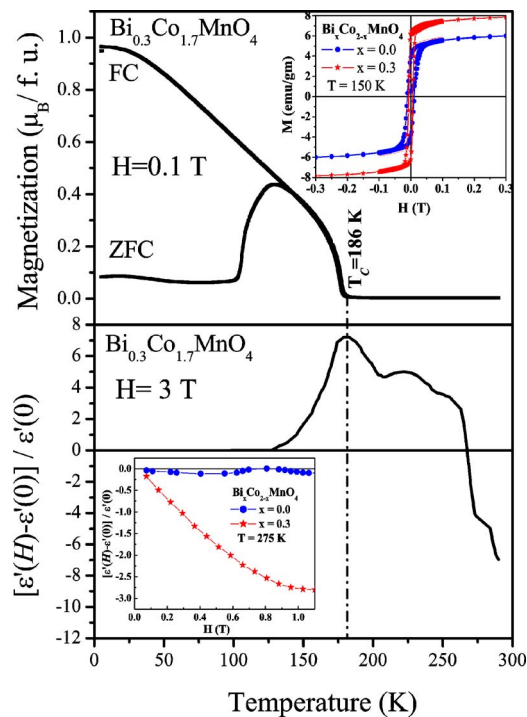


FIG. 3. (Color online) Upper part shows the temperature dependent magnetization for $\text{Bi}_{0.3}\text{Co}_{1.7}\text{MnO}_4$ measured during the warming (ZFC) and cooling (FC) cycles, whereas lower part shows magnetocapacitive coupling $[\varepsilon'(H) - \varepsilon'(0)]/\varepsilon'(0)$ vs temperature for $\text{Bi}_{0.3}\text{Co}_{1.7}\text{MnO}_4$. The top inset shows the M - H loops, whereas the bottom inset shows the field dependent magnetocapacitive coupling of $\text{Bi}_x\text{Co}_{2-x}\text{MnO}_4$ ($x=0$ and 0.3).

superexchange interaction. In the case of Co_3O_4 , the weak superexchange interaction, $\text{Co}^{2+}-\text{O}^{2-}-\text{Co}^{3+}-\text{O}^{2-}-\text{Co}^{2+}$, maintains the antiferromagnetism. In the present series, a sizable portion of Co^{3+} is replaced by Mn^{3+} and Bi^{3+} ions. As a result, the magnetic exchange interaction is strongly influenced by Mn^{3+} and the greater ionic radius of Bi^{3+} that distorts the oxygen octahedron and causes A -site frustration, resulting in an incommensurate magnetic ordering in the system. Therefore, the appearance of FM in $\text{Bi}_x\text{Co}_{2-x}\text{MnO}_4$ ($0 \leq x \leq 0.3$) may be attributed to the canting of the antiferromagnetically ordered spins by the structural distortion^{13,15} and a breakdown of the balance between the antiparallel magnetization at Co^{2+} sublattices due to the substitution of Mn and Bi ions.^{5,14}

In the scenario of measurements above, the studies on magnetocapacitive effect for $\text{Bi}_x\text{Co}_{2-x}\text{MnO}_4$ ($x=0.3$) are shown in Fig. 3. The percentage variation of dielectric constant $([\varepsilon'(H) - \varepsilon'(0)]/\varepsilon'(0)) \times 100$ versus temperature measured at 3 and 0 T shows maxima at FM transition temperature T_C (186 K) indicating magnetocapacitive coupling. This confirms the magnetic origin of FE and can be correlated to the inverse of the Dzyaloshinskii—Moriya type of interaction occurring in complex magnetic structures such as noncollinear canted antiferromagnets, where the canted spin polarizes the O $2p$ orbital through electron-lattice interaction.^{6,8,10} The decrease in magnetoelectric coupling, i.e., fall in dielectric constant at high temperature, may be due to

the flip of polarization that was originated from complex magnetic structure against the polarization related to the “proper” FE.⁶ This type of polarization flip is shown in TbMnO_3 on tuning by magnetic field.¹⁶ Magnetically tunable FE exhibited by the Bi-substituted Co_2MnO_4 at 275 K is depicted in the bottom inset of Fig. 3, where the parent compound shows almost zero response. This is attributed to non-linear magnetic ordering occurring due to the geometrical frustration with Bi substitution. The clear nonappearance of magnetoelectric coupling at lower temperature (below FM T_C) can be attributed to the collinear magnetic ordering, as in the case of hexaferrites.⁹

In this letter, the ferroelectric as well as magnetocapacitance measurements on these samples have been carried out in the high frequency range starting from 100 kHz, much more than the frequencies corresponding the time constants (RC) suggested by the Catalan¹⁷ and Scott.¹⁸ This rules out a possibility of magnetocapacitance due to magnetoresistance combined with the Maxwell–Wagner effect which has been the subject of debate on multiferroics showing magnetocapacitance.¹⁹

In conclusion, Bi substitution in cobalt manganite spinel brings in the balance of structural distortion and magnetic exchange interaction, which affects both ferroelectric and ferrimagnetic transitions and magnetocapacitance, making them promising candidates for the future multiferroic application.

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