Multiferroic Properties of BiSubstituted Co2MnO4

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Multiferroic Properties of Bi-Substituted Co_2MnO_4

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Abstract. Single phase polycrystalline samples of BixCo2-xMnO4 (x = 0.0, 0.1 and 0.3) were synthesized by conventional solid state reaction. The crystallographic structure of all samples is found to be cubic spinel (space group Fd3m). Partial substitution of Bi3+ in place of Co3+ varies the ferroelectric and ferrimagnetic transition temperatures. The magnetocapacitive effect exhibited in the temperature range 150 – 300 K suggests that the material can be envisaged as promising multiferroic.

Keywords: Multiferroic, ferroelectricity and ferrimagnetism
PACS: 78.20.Ci, 77.22.Gm, 75.50.Gg, 77.80.–e

INTRODUCTION

Ternary spinels are widely recognized as versatile systems from both technological and fundamental point of view. The physical properties of the spinel compounds can be tailored by changing cation distribution [1]. Recently, it has been reported that the spinel compounds with nonlinear magnetic spins may lead to multiferroic behaviour [2, 3]. Stereochemically active lone pair of electrons is supposed to introduce off centering in the structure of oxides containing magnetic transition metal ions that leads to a spontaneous polarization, and super exchange interaction between magnetic ions is responsible for magnetic ordering [4]. Although the existence and applications of many mixed transition metal spinels are known, only a few investigations hitherto, on bismuth incorporated cobalt-based spinels. In this work, we report the multiferroic properties of $Bi_xCo_{2-x}MnO_4$ (x = 0.0, 0.1 and 0.3) and report on the preparation, crystal structure, ferroelectric and ferrimagnetic behaviour of Bi-substituted cobalt manganite.

EXPERIMENTAL

The compositions of the cobalt based manganite spinel $Bi_xCo_{2-x}MnO_4$ (BCMO) with varying Bi content were synthesized by solid state reaction. Temperature and frequency dependent dielectric measurements of the samples were performed using a

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HP4192 precision LCR meter. The magnetization measurements were carried out using the VSM option of a Quantum Design PPMS set up in a temperature range 5 - 300 K. The magnetocapacitive effect has been investigated using a cryogen free low temperature high magnetic field facility.

RESULTS AND DISCUSSION

The analysis of XRD patterns of the BCMO samples exhibits the single-phase nature as shown in Fig.1 (a). The samples correspond to a disordered cubic spinel structure with Fd3m space group (SG) in which cations occupy two non-equivalent sites; tetrahedral 8a (A-sites) and octahedral 16d (B-sites). The substitution of Co^{3+} by Bi^{3+}(at B-sites) leads to the increase of lattice constant 'a' (Table 1), probably due to the changes in the cation distribution and the greater ionic radius of Bi^{3+} (1.17A°) than that of Co^{3+} (0.65A°). It is found that the solid solution synthesized retains the normal cubic spinel structure of the parent compound only up to x = 0.3.

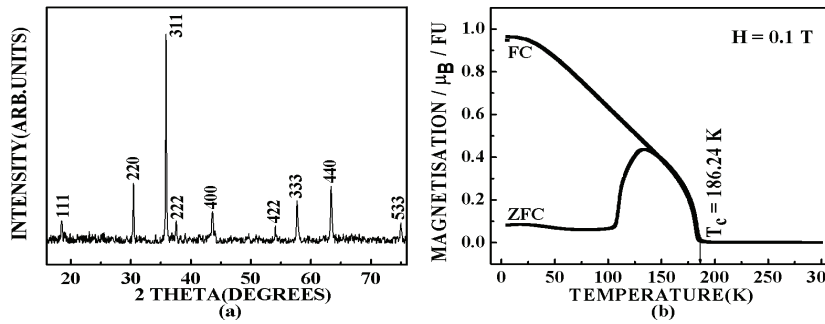

FIGURE 1. (a) XRD pattern and **(b)** Temperature dependence of magnetization of BCMO with x = 0.3

Fig.1 (b) shows the variation of magnetization vs. temperature for the selected nominal composition, $Bi_{0.3}Co_{1.7}MnO_4$ (BCMO with x = 0.3). Both the temperature dependent magnetization and inverse susceptibility ($1/\chi$) reveal that the ferrimagnetic transition temperature (FM T_c) is slightly varied depending on the Bi concentration (Table 1). At all measured temperatures, saturation magnetization (M_S) is found to be increasing by increasing Bi content, with low remnant magnetization. The appearance of ferrimagnetism in this compound may be attributed to both the canting of the antiferromagnetically ordered spins by the structural distortion [5] and a breakdown of the balance between the antiparallel sublattice magnetization of Co^{2+} due to the substitution Mn and Bi ions of different valence states [6]. The super exchange interaction, Co^{2+} - O^{2-} - Co^{3+} - O^{2-}- Co^{2+} that keeps the antiferromagnetism in the cobalt spinel oxide is strongly influenced by the presence of Mn^{3+} and Bi^{3+}. This distorts the oxygen octahedron, resulting in incommensurate magnetic ordering in the system that leads to ferrimagnetism even at low temperature.

The temperature dependence of the dielectric constant (ε') at different frequencies is shown in Fig.2 (a) for the composition ($Bi_{0.3}Co_{1.7}MnO_4$). The dielectric constant and the ferroelectric Curie temperature (FE T_c) are found to vary with Bi^{3+} substitution, but

the ferroelectric transition is not observed for the parent compound, Co_2MnO_4 up to 450 K (Table.1). This can be attributed to the polarization associated with the $6s^2$ lone pair electrons of Bi^{3+}, accommodated at octahedral sites. The studies on magnetocapacitive (ε′-H) coupling vs. Temperature show variation in dielectric constant above 150 K, as in Fig.2 (b). This can be correlated with the spin fluctuations at the cation sites along with the hopping of charges in spinel oxides, influenced by both the magnetic field and the presence of non-magnetic Bi^{3+} ions.

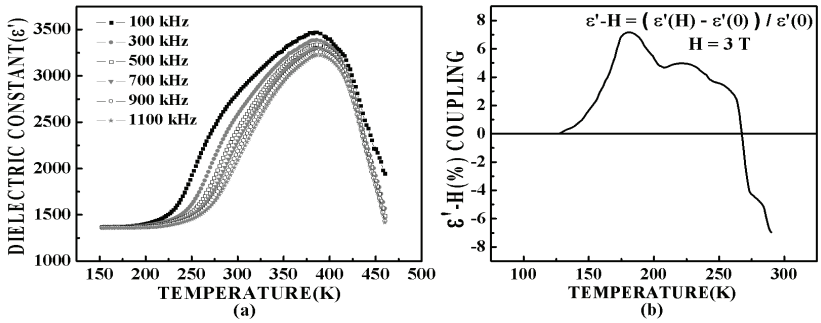

FIGURE 2. (a) Dielectric constant vs. Temperature at selected frequencies and **(b)** Temperature dependent magnetocapacitive coupling(%) for BCMO with x = 0.3

TABLE 1. Comparison of ferroelectric and ferrimagnetic properties

$Bi_xCo_{2-x}MnO_4$	Lattice constant 'a'	FE T_c (100 kHz)	FM T_c
x = 0.0	8.283A°	>450 K	180 K
x = 0.1	8.296A°	350 K	182 K
x = 0.3	8.301A°	380 K	186 K

CONCLUSION

To summarize, we have synthesized Bi-substituted cobalt manganite spinel, which exhibit ferrimagnetic ordering along with ferroelectricity. We have also demonstrated the magnetocapacitive coupling, persisting close to room temperature which makes these materials to be a promising candidate for future multiferroic applications.

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