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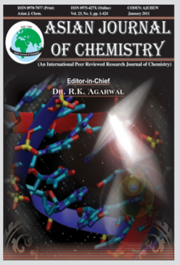

Enhancement of Ferromagnetic and Ferroelectric Properties in Codoped $BiFeO_3$†

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Co-doped insulating $Bi_{0.8}La_{0.2}Fe_{1-x}Mn_xO_3$, (x = 0, 0.1) ceramics were prepared by conventional solid state reaction method. The XRD study shows that 20 % substitution of La ions changes the structure from rhombohedral (space group R3c) that of $BaFeO_3$ to the orthorhombic (C222) for $Bi_{0.8}La_{0.2}FeO_3$ (BLFO). For further substitution of Mn-ions in Fe-site no structural change occurs. From DTA and TGA study, it is observed that magnetic transition temperature (T_m) decreases appreciably whereas ferroelectric transition temperature (T_C) does not affect much with the increase of Mn-concentration. The magnetization-magnetic field measurements show that increase of magnetization for co-doping of La and Mn in $Bi_{0.8}FeO_3$ is due to the destruction of the spin cycloid structure in it and the introduction of the mixed valance state. P-E measurement shows the ferroelectric nature of the sample.

Key Words: Multiferroics, Thermal property, Magnetism, Ferroelectricity.

INTRODUCTION

Multiferroics[1-10] is a special class of multifunctional materials with coupled electric, magnetic and structural order parameters that yield simultaneous effects of antiferroelectricity, antiferromagnetism and ferroelasticity in the same material. Such materials with a strong magneto-electric (ME) effect at room temperature could enable spintronics, data storage and many other device applications. But multiferroic materials are scarce and almost all of them are antiferromagnet (AFM) or weak ferromagnets (FM) with low transition temperatures[2-4]. This apparent incompatibility can be overcome in $BiFeO_3$ (BFO) which is still the only established multiferroic above room temperature. The crystal structure of the polar phase of $BiFeO_3$ is described within the rhombohedral space group R3c. The dipole order occurs owing to the stereochemical activity of the $6s^2$ lone pair of Bi^{3+} ions, whereas the Fe ions order antiferromagnetically (AFM). Though the R3c symmetry permits the existence of a weak ferromagnetic moment[11], originating from the Dzyaloshinsky-Moryia interaction[12,13] a cycloid-type spatial spin modulation prevents the observation of any net magnetization and the linear magnetoelectric effect[14]. This antiferromagnet structure of $BiFeO_3$ limits its potential for applications[15]. However, when this cycloidal modulation is destroyed/suppressed, for instance by applying high magnetic field, chemical substitutions or epitaxial strain *etc.*, a linear magnetoelectric effect occurs. Recently, considerable effort has been made to get both strong ferroelectric and ferromagnetic polarization and/or a large magneto-electric effect at room temperature through A-site and/or B-site doping in $BiFeO_3$[16-19]. In spite of the numerous investigations performed for $Bi_{1-x}La_xFeO_3$ multiferroic compounds in recent years, a clear understanding of what is going on with the crystal structure, ferroelectric and magnetic properties of the solid solutions upon A-site substitution is not yet achieved because the existing data are very much contradictory[20-22]. Moreover, a number of papers clearly confirm the fact that increasing the concentration of the substituting element tends to weaken the stereochemical activity of the Bi^{3+} lone pair electron, leading to a ferroelectric-paraelectric transition at x ~ 0.25 (in the case of La substitution). Hence, when taking into account the conclusions related to the concentrational range in which spontaneous ferroelectricity coexists with weak ferromagnetism might be very narrow. Again, manganese is a particularly interesting element for substitution, because it readily adopts the mixed-valence oxidation states of Mn^{3+} and Mn^{4+} in perovskites and for the reports[22-26] of enhanced multiferroic properties in $BiFe_{1-x}Mn_xO_3$ for $x \leq 0.3$. Moreover, it does not alter the crystallographic structure. Thus, the multiferroic properties can be tailored by the manganese content $x \leq 0.3$ in the ambient condition.

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Thus, with the motivation to enhance the ferromagnetic property (due to the destruction of the spin cycloid structure and the introduction of the mixed valance state) and by keeping the ferroelectric property undisturbed at the ambient temperature, we study $Bi_{0.8}La_{0.2}Fe_{1-x}Mn_xO_3$, (x = 0, 0.1) system.

EXPERIMENTAL

$Bi_{0.8}La_{0.2}Fe_{1-x}Mn_xO_3$ (x = 0, BLFO, x = 0.1 BLFMO) samples were prepared by solid state reaction. Stoichiometric amounts of Bi_2O_3, Fe_2O_3, La_2O_3 and MnO_2 were mixed with a mortar pestle for about 1 h and were calcined in a programmable furnace at 860 ºC for 2 h. Sintering of the pellets (*ca.* 1 mm thick) was done at 860 ºC for 2 h.

X-ray powder diffraction measurements were carried out with CuK_α radiation using a Rigaku (MiniFlex II DEXTOP) powder diffractometer for phase identification. Differential thermal analysis and thermogravimetric analysis were carried out with Mateller differential thermal analysis-thermogravimetric analysis to determine magnetic and ferroelectric transition temperatures T_m and T_c respectively. Magnetic measurements were done using MPMS SQUIDS magnetometer. Variation of polarization with applied electric field (P-E) measurements was carried out with ferroelectric loop tracer (Radiant Technology Inc, USA).

RESULTS AND DISCUSSION

It is known that $BiFeO_3$ crystallizes in a rhombohedrally distorted perovskite structure at room temperature with impurity phases in most of the cases[19,27]. XRD study (Fig. 1) shows that in 20 % La-substituted sample ($Bi_{0.8}La_{0.2}FeO_3$) impurity peaks are reduced appreciably except an impurity peak at $2\theta = 28º$. Moreover, it under goes a change from rhombohedrally distorted perovskite structure with the space group R3c to C222 orthorhombic symmetry, as evidenced by the merging into one peak of the splited diffraction peaks around $2\theta = 32º$ and $2\theta = 51º$. This observation for the compound $Bi_{0.8}La_{0.2}FeO_3$ (BLFO) supports the same results in the literatures[19,28], where it is evident that the compounds under goes a structural phase transition from rhombohedral to orthorhombic above La = 15 %. Furthermore, Mn substitution at Fe-site ($Bi_{0.8}La_{0.2}Fe_{0.9}Mn_{0.1}O_3$), does not affect the crystalline structure of that of the $Bi_{0.8}La_{0.2}FeO_3$. Thermogravimetric analysis-differential thermal analysis study (Fig. 2) shows no appreciable weight loss in the temperature range 150 to 850 ºC and two phase transitions. The transition at the lower temperature range correspond the magnetic (T_m) and at the higher temperature one corresponds ferroelectric transition (T_c) respectively. Table-1 shows the values of T_m and T_c for $Bi_{0.8}La_{0.2}FeO_3$ and $Bi_{0.8}La_{0.2}Fe_{0.9}Mn_{0.1}O_3$ samples. For the sample $Bi_{0.8}La_{0.2}FeO_3$, T_m decreases to 330 ºC from 370 ºC that of $BiFeO_3$ due to La-doping. This result is consistent with that the value of T_m decreases with the increase of La concentration in $BiFeO_3$[16,19,27]. T_m decreases further to 258 ºC for $Bi_{0.8}La_{0.2}Fe_{0.9}Mn_{0.1}O_3$. T_c decreases to 744 ºC for $Bi_{0.8}La_{0.2}FeO_3$ from 830 ºC of $BiFeO_3$ due to La doping. Further, T_c decreases slightly to 730 ºC for $Bi_{0.8}La_{0.2}Fe_{0.9}Mn_{0.1}O_3$ (Table-1).

The spatially modulated spin cycloidal structure of pure $BiFeO_3$ prevents the observation of any net magnetization resulting to antiferromagnetism[14]. The room temperature magnetization-magnetic field (M-H) curves of the $Bi_{0.8}La_{0.2}Fe_{0.9}Mn_{0.1}O_3$ ceramics is measured with a maximum magnetic field of 5 T, as shown in Fig. 3. The partly enlarged curve is shown in the corresponding inset. It is clearly evident that the curves are not collinear indicating the presence of weak ferromagnetic moment at room temperature. This result is quite similar to that of Cheng *et al.*[19] for La = 20 % doping in $BiFeO_3$. It is found that the magnetic moment of this sample is greatly improved *i.e.* ~ 0.048 emu/g for 100 Oe at room temperature in comparison to that of $BiFeO_3$ measured at 2000 Oe is 0.01 emu/g and ~0.042 emu/g for $Bi_{0.8}La_{0.2}FeO_3$[19]. Net magnetization in $Bi_{1-x}Ln_xFeO_3$ (Ln is a lanthanide) is related to an antisymmetric exchange mechanism[12,13] and appearance of magnetization

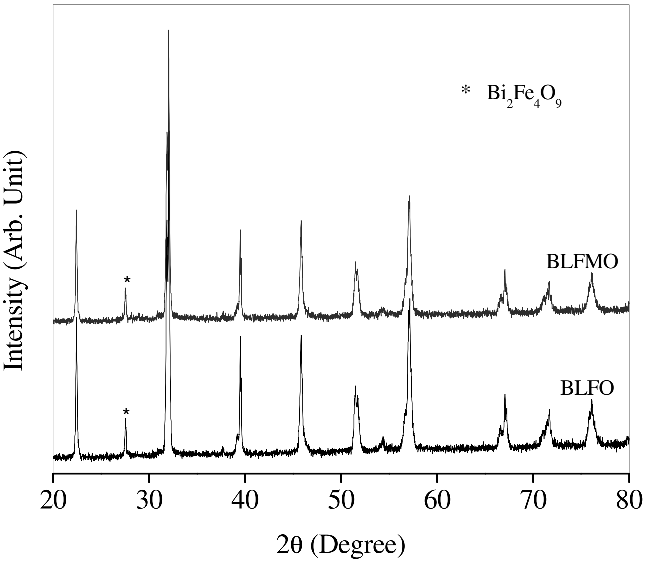

Fig. 1. X-ray diffraction pattern of $Bi_{0.8}La_{0.2}Fe_{1-x}Mn_xO_3$ (x = 0, 0.1) samples

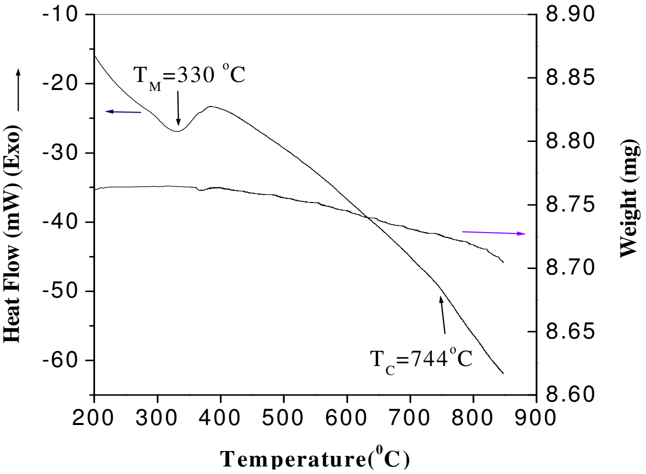

Fig. 2. Differential thermal analysis and thermo gravimetric analysis for a typical sample $Bi_{0.8}La_{0.2}FeO_3$

TABLE-1
VARIATION OF MAGNETIC (T_m) AND FERROELECTRIC (T_c) TRANSITION TEMPERATURES FOR $Bi_{0.8}La_{0.2}Fe_{1-x}Mn_xO_3$ (x = 0, 0.1)

Concentration of Mn(x)	T_m (ºC)	T_c (ºC)
0	330	744
0.1	258	730

should be due to the substitution-induced suppression of the cycloidal spin modulation[28]. Thus, increase of magnetization for $Bi_{0.8}La_{0.2}Fe_{0.9}Mn_{0.1}O_3$ can be attributed to the fact that La doping in $BiFeO_3$ destroys the cycloid spin structure (the structure which hinders the observation of any linear magneto-electric effect in pure $BiFeO_3$), releases the latent magnetization locked within this structure and enhances the magnetic moment. Mn-doping introduces mixed valence state (Mn^{3+} and Mn^{4+}) in the system. Room temperature P-E loop of $Bi_{0.8}La_{0.2}Fe_{0.9}Mn_{0.1}O_3$ sample was measured at different frequencies, as shown in Fig. 4. The P-E hysteresis loop confirms the ferroelectric nature of the samples. It is found (Fig. 4) that with increasing frequency, width of the P-E loops decreases, which supports the ferroelectric behaviour[29] of this composition.

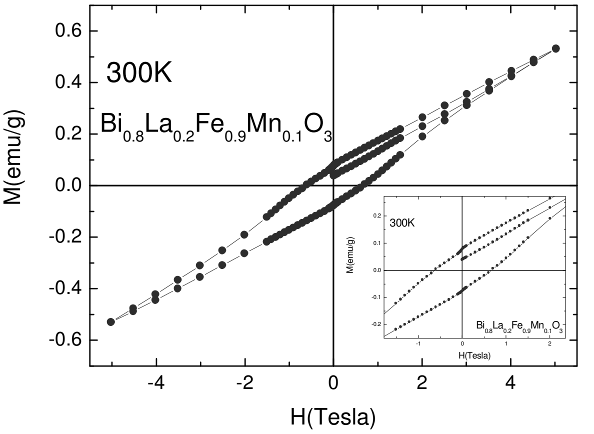

Fig. 3. Variation of magnetization (M) with magnetic field (H) (-5 T to +5 T) of $Bi_{0.8}La_{0.2}Fe_{0.9}Mn_{0.1}O_3$ shows weak ferromagnetism. Inset displays the M(H) behaviour in extended scale

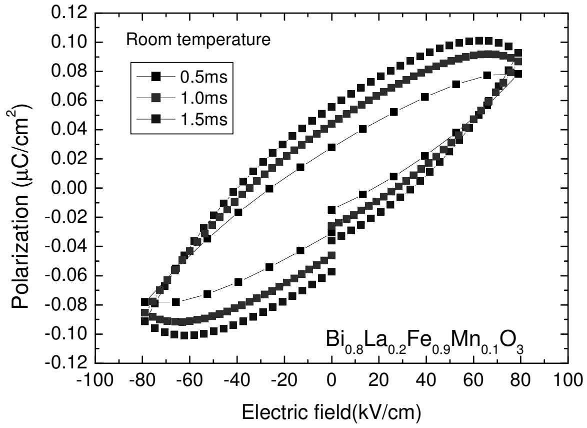

Fig. 4. Variation of electric polarization (P) with applied electric field (E) for the samples $Bi_{0.8}La_{0.2}Fe_{0.9}Mn_{0.1}O_3$

Conclusion

The room-temperature crystal structure, magnetic and ferroelectric properties of polycrystalline $Bi_{0.8}La_{0.2}Fe_{1-x}Mn_xO_3$ ($x = 0, 0.1$) samples were investigated by XRD, MPMS-SQUID magnetometer and ferroelectric P-E loop tracer. Transition temperatures and weight loss were measured by differential thermal analysis-thermogravimetric analysis. It was found that lanthanum and manganese substitution resulted in decrease of the magnetic transition temperature (T_m) and ferroelectric transition temperature (T_c). Moreover, the substitutions resulted in appearance of a weak ferromagnetic ordering at room temperature and gave rise to a significant increase in magnetization. The results were discussed in the context of destruction of the cycloid spin structure as well as introduction of mixed valence state (Mn^{3+} and Mn^{4+}). Samples also show the ferroelectric nature improving the multiferroic properties of doped $BiFeO_3$.

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