Effect of La/Mn substitution on electrical properties of BiFeO$_3$ multiferroics

Dillip K Pradhan, R N P Choudhary*, C M Tirado & R S Katiyar
Department of Physics, University of Puerto Rico, San Juan, PR00931, USA

Received 30 November 2006; accepted 28 February 2008

The polycrystalline fine powder (~60 nm) of Bi$_{0.90}$La$_{0.10}$(Fe$_{1-x}$Mn$_x$)$_3$O$_9$ (x= 0, 0.05, 0.10 and 0.20) have been synthesized by mechanical activation and mixed oxide methods. Preliminary structural analysis using X-ray diffraction exhibits formation of the single-phase compound in a hexagonal (distorted perovskites system). Detailed dielectric studies as a function of temperature show that dielectric constant of BFO (BiFeO$_3$), and also tanδ increase significantly on increasing Mn content in BiLa(FeMn)O$_3$ system. Impedance analysis of the system provides many interesting results.

Keywords: Multiferroics, X-ray diffraction, Complex impedance spectroscopy

Multiferroics, where ferroelectricity and ferromagnetism coexist in a single phase, have potential application for multifunctional devices taking the advantages of two coupled degrees of freedom based on local off centered distortion and electron spin$^1$. Magnetoelectric (ME) materials are studied not only for the technological applications but also for understanding of fundamental physics behind ME coupling. Hence, it is fascinating and interesting$^2$. After the discovery of magnetoelectric effect in some Pb-based perovskites (i.e., Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ (PFN), Pb(Fe$_{1/2}$Ta$_{1/2}$)O$_3$ (PFT)) in 1950’s$^3$-$^4$, a considerable number of materials, not only of perovskites but also of many other structural families have been examined to find out this effect in them with large ME coefficient required for multifunctional devices. Unfortunately, in most of the Pb-based materials ME effect was found in the low temperature region, and hence they are not very useful. Recent discovery of ME effect in the high temperature region of rhombohedrally distorted perovskite BiFeO$_3$ (BFO)$^5$-$^6$ with small polarization in a wide temperature region ($T_c=1100$ K and $T_N=650$ K) has attracted much attention of researchers with a great hope to use this material in future for devices. In recent past various attempts have been made to solve the inherent problem and enhance spontaneous polarization, magnetization and coupling co-efficient of BFO by (i) suitable substitution at the Bi/Fe sites, (ii) making composites, and (iii) using suitable processing techniques. In this paper, detailed studies of Mn effect on structural and electrical properties (impedance studies) of La/Mn modified BFO (i.e., Bi$_{0.90}$La$_{0.10}$(Fe$_{1-x}$,Mn$_x$)$_3$O$_3$ for x= 0 (BLFO), 0.05 (BLFMO05), 0.10 (BLFMO10) and 0.20 (BLFMO20) have been reported.

Experimental Procedure

The polycrystalline samples of Bi$_{0.90}$La$_{0.10}$(Fe$_{1-x}$,Mn$_x$)$_3$O$_3$ (BLFMO) with 0≤x≤0.20 were prepared using high purity (>99.9%) oxides; Bi$_2$O$_3$, La$_2$O$_3$, Fe$_2$O$_3$, Mn$_2$O$_3$ (all from M/s Alpha Aesar Co.) by mecanosynthesis (high energy ball mill) and solid state reaction techniques at room temperature and atmospheric pressure. The calcination of the mechanical/ball-milled powder was carried out at 800°C for 2 h. The sintering of the compacted (at 6 × 10$^7$ kg/cm$^2$) pellets was completed at 850 °C for 2h. The formation of the compound was checked by X-ray diffraction technique. For X-ray structural analysis, XRD data were collected at slow scan in a wide range of Bragg angles (20≤2θ≤80) with CuK$_\alpha$ radiation (λ=1.5405Å) at room temperature. The microstructure of the samples was recorded with scanning electron microscope (SEM) at different magnification at room temperature. The electrical measurements (capacitance, dissipation factor, impedance, phase angles) were carried out from 200 K to 630 K in a wide frequency range (100 Hz – 1 MHz) using impedance analyzer (HP4294A) with a sample holder (M/s MMR Technologies K-20).

Result and Discussion

Figure 1 compares X-ray diffraction (XRD) of Bi$_{0.90}$La$_{0.10}$(Fe$_{1-x}$,Mn$_x$)$_3$O$_3$ (x= 0, 0.05, 0.10, 0.15, and

*For correspondence (E-mail: crnpfl@phy.iitkgp.ernet.in)
0.20) pellets. It exhibits the formation of single-phase material.

All the peaks of \((\text{Bi}_{0.90}\text{La}_{0.10}\text{Fe}_{1-x}\text{Mn}_x)\text{O}_3\) have tetragonal splitting. It is clearly seen that the splitted peaks slowly converted into a single peak on increasing Mn doping in BLFO. All the peaks were indexed using 20 value of peak in different crystal system and cell configurations. Finally a unit cell of hexagonal system was selected and cell parameters are refined using a standard computer software POWD. The least-squares refined cell parameters are compared in Table 1.

The interplaner spacings \(d\) (calculated with refined cell parameters) of \((h k l)\) planes was calculated, and compared with those of observed/experimental values. The best agreement between (i.e., \(\Sigma \Delta d = (d_{\text{obs}} - d_{\text{cal}}) = \text{minimum}\)) was found between them. The crystallite size of the samples was determined using peak broadening \((\beta/2)\), Bragg angles (20) and wavelength (\(\lambda\)) using Scherrer equation, \(P = K\lambda/(\beta_{1/2}\cos \theta)\) and was found to be in the range of 40-60 nm. Figure 2 exhibits SEM micrographs of the pellet samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.

The uniform grain distribution of the sample surfaces was observed for BLFO. On increasing Mn content, the size of grains decreases as well as the voids increases. As the voids are uniformly distributed through out the sample, the density of the pellet sample of BLFMO is found low compared to BLFO. Agglomeration of fine particles on substitution of Mn is seen in the micrographs of BLFMO samples.
It has been observed that there is a decrease in $\varepsilon$ on increasing frequency for all the compositions. The dielectric constant of BLFO is small in the low frequency region whereas it increases fast on increasing Mn concentration. A monotonous decrease of $\varepsilon$ on increasing frequency is observed for all Mn concentration. Due to the presence of interface, atomic/ionic, dipolar and electronic polarization, $\varepsilon$ has higher value at lower frequencies (valid for any temperature), which decreases with rise in frequency. At higher frequencies, except electronic polarisation, other polarizations are reduced to minimum (or zero). It is seen that tan$\delta$ increases with rise in frequency for BLFO, whereas it decreases with rise in frequency for all Mn modified BLFO. It is observed that tan$\delta$ drastically increases on increasing Mn content in the samples.

Figure 4 exhibits the temperature dependence of relative dielectric constant ($\varepsilon_r$) and loss tangent (tan$\delta$) of BLFM at 100 kHz.

For BLFO dielectric constant increases slowly with rise in temperature. On increasing the value of Mn (up to 10%), $\varepsilon_r$ was found almost temperature independent up to 450 K, and there after it increases very fast with rise in temperature. The values of $\varepsilon_r$ are very much dependent on concentration of Mn. The temperature variation of tangent loss (tan$\delta$) shows that it decreases upto 400 K and after that it increases for BLFO. There is a similar trend of variation of tan$\delta$ for Mn doped samples (i.e., it increases with rise in temperature).

Figure 5 shows the variation of $\sigma_{ac}$ with inverse of absolute temperature (K$^{-1}$) of BLFMO for different concentrations ($x$) at frequency 100 kHz.

The $\sigma_{ac}$ was calculated using dielectric data in the empirical relation $\sigma_{ac} = \omega\varepsilon_0\varepsilon_r\tan\delta$ ($\omega$ = angular frequency, $\varepsilon_0$ is vacuum permittivity). For BLFO the variation of $\sigma_{ac}$ is almost independent of temperature (in low temperature region). On increasing Mn concentration in BLFMO at the B-site, $\sigma_{ac}$ decreases on decreasing temperature, and follow a normal behaviour of ferroelectrics/dielectrics. It is clearly seen that each plot has two slopes; one of high temperature and other is of low temperature range. This behaviour satisfies the relation $\sigma = \sigma_0\exp(-E_a/kT)$ ($k$ = Boltzman constant, $\sigma_0$ = pre-exponential factor) in the high temperature regions. The activation energy of the compounds was calculated from the slope of the $\ln\sigma_{ac}$ versus $1/T$ plot. The calculated value of $E_a$ in the high temperature range for $x$=0, 0.05, 0.10 and 0.20 was found to be as 0.18, 0.46, 0.48 and 0.42 eV respectively.

Figure 6 shows the complex impedance plots (symbols), and compared with fitted data (solid line) (by a commercially available software ZSimp Win Version 2) for different Mn-composition at a particular temperature. The complex impedance plots for all composition comprises of two overlapping semicircular arcs with center below the real axis.
suggesting the departure from ideal Debye behaviour. The two semicircular arcs can be assigned due to bulk (high frequency) and grain boundary (low frequency) phase element connected in series with parallel capacitance (bulk capacitance) along with a constant phase element representing the departure from Debye-like ideality (not shown in figure). It has been found from the plots that the $Z''$ spectra are broadened in the low frequency side of the peak (maxima) where as the $M''$ spectra broadened in the high frequency side. In addition to this, the two peak maxima, which are not frequency-coincident, suggest the departure from ideal Debye behaviour. For ideal Debye-like response the equivalent circuit comprises of a parallel combination of a resistor and capacitor. The imaginary component of complex impedance and modulus graphs ($Z''$ and $M''$ versus frequency) were plotted in a log-log scale in order to emphasize the departure from the ideality (not shown in figure). It has been found from the plots that the $Z''$ spectra are broadened in the low frequency side of the peak (maxima) where as the $M''$ spectra broadened in the high frequency side. In addition to this, the two peak maxima, which are not frequency-coincident, suggest the departure from ideal Debye behaviour. For ideal Debye-like response the equivalent circuit comprises of a parallel combination of a resistor and capacitor.

**Fig. 6—Comparison of complex impedance plot, fitted data of Bi$_{0.90}$La$_{0.10}$(Fe$_1$-xMnx)O$_3$ for different value of x at a particular temperature. The equivalent circuit is shown as inset for each figure**

usually depend on temperature, $A_0$ determines the magnitude of the dispersion and $0 \leq n \leq 1$. The CPE describes an ideal capacitor for $n=1$ and an ideal resistor for $n=0$. In the present work, two overlapping semicircular arcs of the impedance spectrum can be modeled to an equivalent circuit of parallel combination of a resistance (bulk resistance), capacitance (bulk capacitance) along with a constant phase element connected in series with parallel combination of a resistance (grain boundary resistance), capacitance (grain boundary capacitance) (shown as inset of Fig. 6.). Similar equivalent circuits are also reported in literature.

**Conclusions**

The polycrystalline samples of Bi$_{0.90}$La$_{0.10}$(Fe$_1$-xMnx)O$_3$ (x= 0, 0.05, 0.10 and 0.20) were fabricated using a novel mechanical activation followed by a conventional solid-state reaction techniques. The formation of single-phase material was confirmed using an X-ray diffraction technique. The dielectric constant and loss tangent increase with increase of Mn content. Complex impedance spectroscopy enables us to separate the grain and grain boundary contribution of the materials.

**References**

7. “POWD” an interactive powder diffraction data interpretation and indexing programme Ver. 2.1, Wu E, School of Physical Sciences, Flinder University of South Australia, Bedford Park, SA-5402, Australia.