Study of electric and magnetic properties of $(Bi_{0.9}Pb_{0.1})$ $(Fe_{0.9}Ti_{0.1})O_3$ nanomultiferroic system

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Multiferroic compound $(Bi_{0.9}Pb_{0.1})(Fe_{0.9}Ti_{0.1})O_3$ (BPFTO), having particle size of 15–25 nm, was synthesized by solution combustion method. BPFTO shows the coexistence of ferroelectricity and magnetism at room temperature. Significant enhancement in magnetic moment with moderate value of the electrical polarization is observed for nano-BPFTO. Remanent polarization and maximum polarizations were 1.056 and 1.866 $\mu C/cm^2$, respectively (at 20 kV/cm), with remanent magnetization of 285 memu/g. Such materials, possessing good value of dielectric constant and showing ferroelectric and ferromagnetism in same phase, are of great importance from technical point of view. © *2008 American Institute of Physics.* [DOI: 10.1063/1.3030989]

In recent years, there has been an increasing interest in multiferroic materials, which have simultaneously two or more order parameters such as ferromagnetic, ferroelectric, and/or ferroelastic ordering.[1,2] Coupling between magnetic and electric ordering leads to electromagnetic (EM) effect. The EM effect provides an additional degree of freedom in designing of functional sensor, current devices, transducers, and multistate memory devices.[3,4] However there is a scarcity of materials exhibiting magnetoelectric behavior at room temperature, which is possibly due to the fact that the transition metal d electron, essential in the presence of magnetic moment, also reduces lattice distortion. Lattice distortion is essential in the presence of the ferroelectric behavior. The perovskite $BiFeO_3$ (BFO) is one of the few known magnetoelectric multiferroics in which ferroelectric ($T_c \sim 830$ °C) and antiferromagnetic (AF) ($T_N \sim 370$ °C) order parameters coexist up to quite high temperature.[5,6] In BFO, Bi–O orbital hybridization due to Bi $6s^2$ lone pair is responsible for ferroelectric instability while Fe–O–Fe Dzyaloshinski Moriya-antisymmetric interaction (DMI) gives rise to complicated magnetic structure.[7] The structural properties of bulk BFO single crystal have been extensively studied and have been shown to possess rhombohedral distorted perovskite structure and space group $R3C$ at room temperature.[8] The spontaneous polarization of bulk BFO was expected to be $90-110$ $\mu C/cm^2$ (Ref. 9) because of large atomic displacement and a high Curie temperature. However, a small polarization has been observed in bulk BFO single crystal[10] and BFO bulk ceramics,[11] and their hysteresis loops were not saturated, which were attributed to the high level of leakage due to charge defects and nonstoichiometry.[12] To overcome these leakage problems ion substitution[13,14] or solid solution with other perovskite materials[15,16] has been tried, and well-saturated hysteresis loop with remanent polarization has recently been reported in single phase $BiFeO_3$ ceramics.[17,18]

Stoichiometric BFO has a G type AF structure[19] and has residual magnetic moment due to the canting of magnetic moments arising from oxygen vacancies.[20]

In the present work we report the synthesis and study of electric and magnetic properties of the $(Bi_{0.9}Pb_{0.1})$ $\times(Fe_{0.9}Ti_{0.1})O_3$ (BPFTO) nanocrystalline multiferroic system.

The BPFTO samples were prepared by solution combustion synthesis (SCS) method from α-alanine containing precursor.[21] The precursor was prepared in 2-methoxy ethanol by taking known the amount of $Fe(NO_3)_3 9H_2O$, $Bi(NO_3)_3 5H_2O$ $Ti(C_4H_9O)_4$, $Pb(CH_3COO)_2 3H_2O$, and α-alanine. Bismuth nitrate and lead acetate were taken in 5 and 10 mol % excess to compensate bismuth and lead loss during sintering process. Powder obtained was calcined at 500 °C for 2 h and 650 °C for 3 h. The calcined powder was milled and then pressed into 1-mm-thick pellets of 10 mm in diameter. The pellets were sintered rapidly at 800 °C for 20 min. For electric and dielectric measurements both surfaces of pellet were coated with silver paste to make electrodes. X-ray diffraction (XRD) data were collected using an XPERT-PRO diffractometer with Cu $K\alpha$ radiation at a step of 0.02 in the range $2\theta = 20$ and 60°. Dielectric constant and dielectric loss were studied by Precision LCR meter 4285A in frequency range of 75 KHz and 15 MHz. Particle size has been determined by transmission electron microscopy (TEM).

Figure 1 shows the diffraction patterns of BPFTO nanoparticles calcined at 650 °C for 3 h. All the diffraction peaks
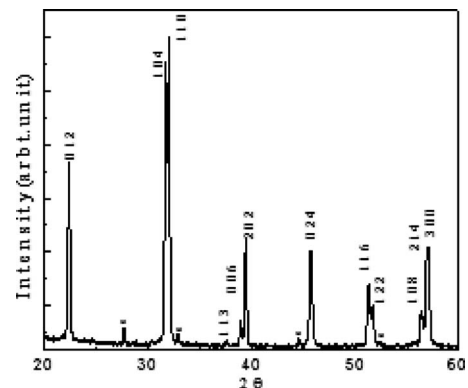

FIG. 1. XRD pattern of BPFTO powder calcined at 650 °C for 3 h.

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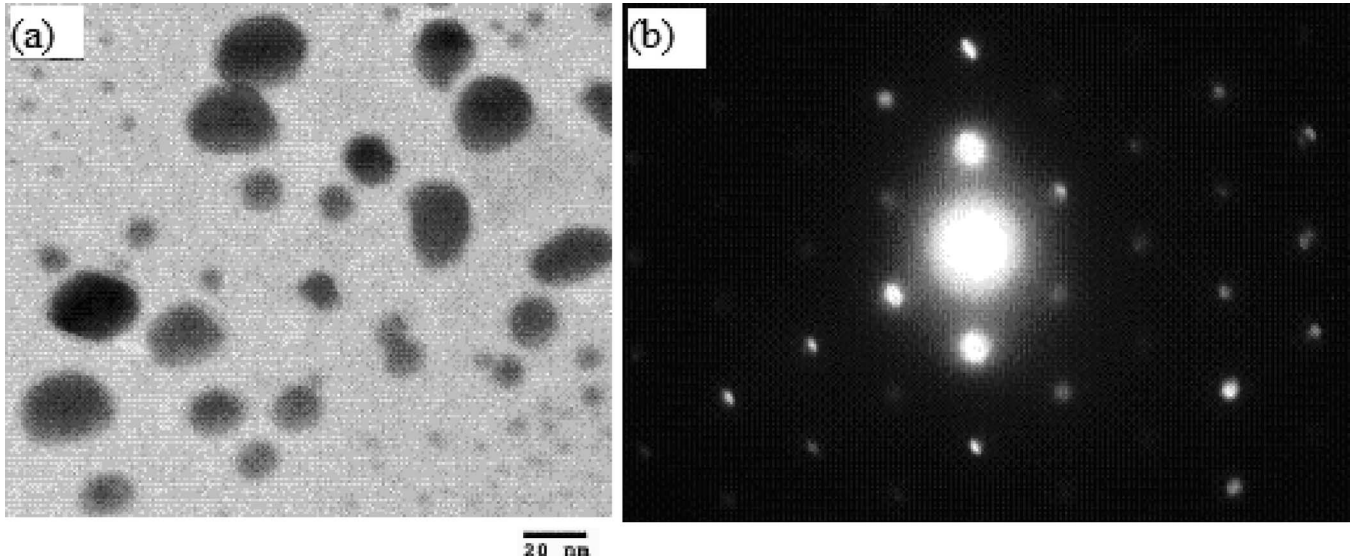
FIG. 2. (a) TEM of powder calcined at 650 °C for 3 h. (b) Selected area electron diffraction of BPFTO.

can be indexed according to standard powder diffraction data of BFO,[22] indicating the single perovskite phase of the ceramics. Minor impurities such as $Bi_{24}Fe_2O_{39}$, $Bi_2Fe_4O_9$, and $Bi_{46}Fe_2O_{12}$ phases were also present. However, none of these impurities is ferromagnetic at room temperature. Therefore the room temperature ferromagnetic property observed here cannot result from any of these impurities.

Figure 2(a) is the transmission electron micrograph showing spherical particles with a narrow particle size distribution in the range of 15–25 nm. Figure 2(b) shows the selected area electron diffraction pattern of BPFTO pattern which confirms the rhombohedral structure.

The variations in dielectric constant and dielectric loss in BPFTO ceramics with frequency (75 kHz–12 MHz) measured at room temperature are shown in Fig. 3(a). Initially dielectric constant decreases slowly with frequency up to 1 MHz and becomes almost constant up to 12 MHz. Initial decrease in dielectric constant with frequency (up to 1 MHz) can be explained by the phenomenon of dipole relaxation[23,24] and justifies the depression in dielectric constant at low frequency. Similarly the dielectric loss decreases rapidly at low frequency and then becomes frequency independent at higher frequency.

Dielectric measurements as a function of temperature at frequency of 75 kHz are shown in Fig. 3(b). Anomaly has also been observed in dielectric constant and dielectric loss near 310 °C which may be due to magnetic transition. Landau–Devonshire theory of phase transition predicted this type of anomaly in magnetoelectrically ordered system as a consequence of vanishing magnetic order on electric order.[25] Dielectric measurement showed broad peak around 600 °C, which can be assigned to ferroelectric phase transition.

Symmetric magnetic hysteresis loop for solid solution of BPFTO nanoparticles is shown in Fig. 4(a), which indicates that BPFTO nanoparticles exhibit the magnetic order in materials at room temperature. Remanent magnetization, saturation magnetization, and coercivity are found to be 285 memu/g, 750 memu/g, and 296 Oe, respectively, and are comparatively higher than those observed for modified bulk BFO ceramic.[26,16] The improvement in magnetization in nanoscale particle may be due to the suppression of helical
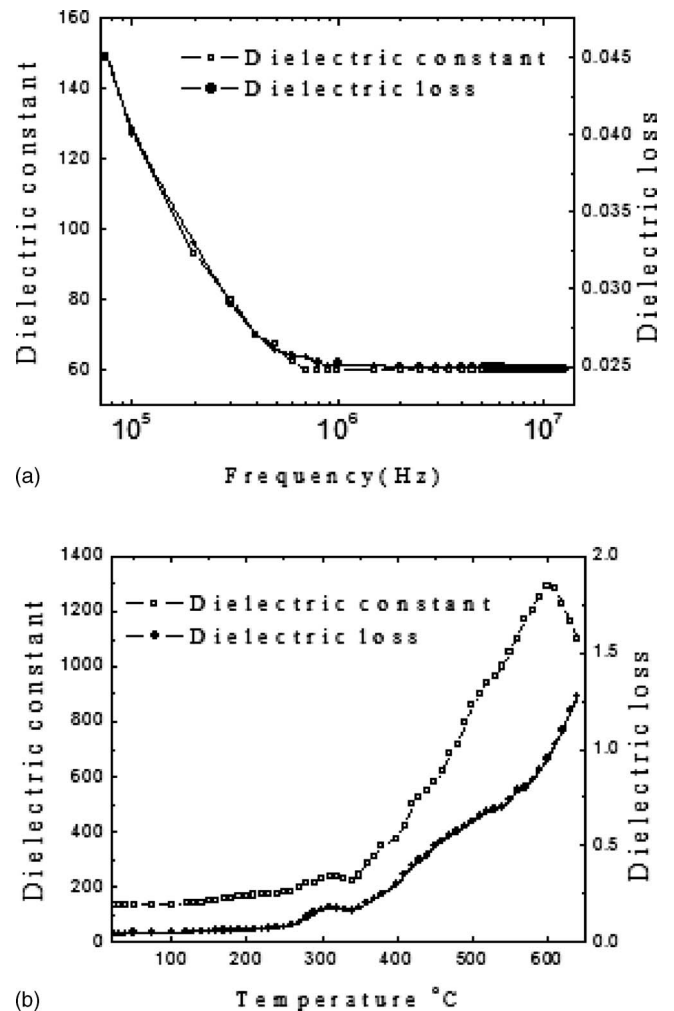

(a)

(b)

FIG. 3. (a) The variation in dielectric constant and dielectric loss in BPFTO as a function of frequency. (b) The variation in dielectric constant and dielectric loss in BPFTO as a function of temperature.
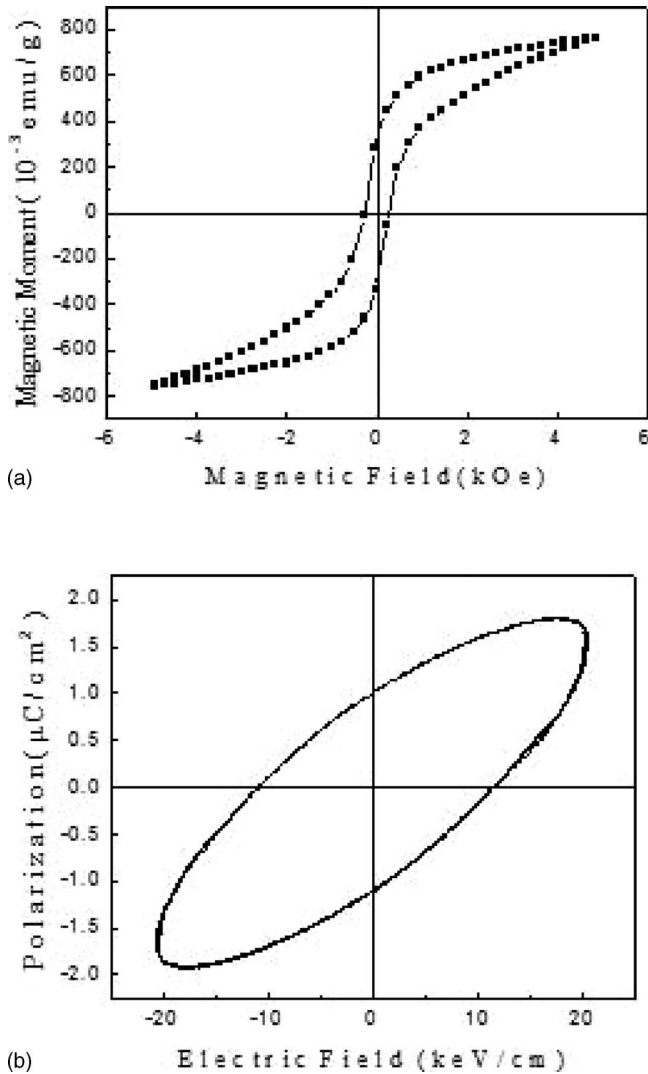
FIG. 4. (a) *M-H* curve of BPFTO multiferroic system. (b) *P-E* loop of BPFTO multiferroic system.

order and increase in spin canting due to the lattice strain, which gives rise to weak ferromagnetism.[27] The observed weak ferromagnetism may also be attributed to the structural distortions of BFO by incorporation of PbTiO$_3$. Incorporation of Pb^{2+} cation at Bi^{3+} sites and Ti^{4+} at Fe^{3+} site causes the canted spin arrangement of unpaired electron on Fe^{3+} ions according to the DMI.[28]

The presence of ferroelectricity in BPFTO is indicated by ferroelectric hysteresis loop measured (at 50 Hz) by ferroelectric loop tracer at room temperature [Fig. 4(b)]. The remnant polarization (Pr) and the coercive field are ~1.05 μC/cm^2 and 10 kV/cm, respectively. The measured Pr is comparable to that of doped BFO ceramic prepared by Benfang *et al.*,[29] Sahu and Rao,[30] and Zhu and Ye.[15] But the observed Pr value is much less than the theoretically predicted value.[9] This may be due to high leakage current, which prevents *P-E* loop measurement at higher fields.

In conclusion, solid solution of nano-BPFTO multiferroics having good value of magnetization and moderate value of polarization can be prepared by SCS. Dielectric studies of BPFTO confirm its multiferroic nature with magnetic transition temperature of ~310 °C and ferroelectric transition temperature of ~600 °C.

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