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Investigations of Lead free BLFO-BT Composite for Multiferroic Sensors

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Abstract—*The strong coupling between magnetization and polarization can be exploited in multiferroic materials to produce marvellous magnetoelectric switching devices and sensors. In this work, we have synthesized $Bi_{0.85}La_{0.15}FeO_3$ (BLFO) and $Bi_{0.85}La_{0.15}FeO_3$-15%$BaTiO_3$ (BLFO-15BT) composite ceramics by solid state reaction route. These composites were structurally characterized by analysis of X-ray diffraction patterns which confirmed the simultaneous existence of both BLFO and BT phases in composites due to the observed broadening and splitting in prominent peaks. The room temperature M-H studies display a decrease in the saturation magnetization in BLFO-BT composite. Significantly the coercivity of BLFO and BLFO-BT composite remain constant confirming separate existence of the constituent phases. A slim ferroelectric hysteresis loop of BLFO-BT composite is observed as compared to BLFO ceramic due to the lattice distortion. The increase in coercivity in BLFO-BT composite is attributed to the interfacial polarization at the grain boundaries. Thus the BLFO-BT composite display an enhanced multiferroic nature which is very promising for magnetic memory devices and sensors.*

Introduction

Multiferroics are the materials which have the simultaneous existence of two or more physical properties in a single material like ferroelectric, (ferro) magnetism and ferroelasticity. Bismuth ferrite is an excellent multiferroic material among the very rare present multiferroics in the nature [1] and used in various applications including sensors [2, 3]. The reason of rare existence of multiferroics is the different chemistry i.e. fully filled or d^o-ness is the nature for the electrical oxide materials and partial filled 'd' shell for magnetic oxide materials [4]. Although BFO is an excellent multiferroic but there are some processing issues and as a result of which there are some impurities like $Bi_2Fe_4O_9$, $Bi_{25}FeO_{39}$ etc. and unsaturated electrical hysteresis loop present in the material. The unsaturated hysteresis P-E loop shows the lossy nature of material which is not acceptable for the sensing as well as memory applications. Such type of problems in BFO comes from the volatile nature of Bi with respect to Fe. The processing temperature of Fe is very high comparative to Bi [5]. So there is a need of proper optimization and enhancement in the multiferroic properties of BFO either by doping or formation of composite with other suitable material or both. So in the light of it, the present study is focused to prepare optimized pure phase multiferroic composite for sensors. First the impurities of BFO are the issue and solved by the doping at the Bi site as reported in the literature like Gd^{3+}, La^{3+} and Sm^{3+} [6-8]. As per the literature the doping of La^{3+} at the Bi^{3+} site is more effective and the composite of La doped BFO with high piezoelectric as well as lead free ferroelectric BT has a number of important improvements in the physical properties like ant ferromagnetic to ferromagnetic change, low coercive and countable maximum polarization of electric hysteresis loops for loss analysis and removal of impurities due to the distortion in the structure of BFO after the doping of La at the Bi site.

Experimental

Polycrystalline $Bi_{0.85}La_{0.15}FeO_3$ and $Bi_{0.85}La_{0.15}FeO_3$-15%$BaTiO_3$ were synthesized by the standard solid-state route using very high purity powders of Bi_2O_3, La_2O_3, Fe_2O_3, $BaCO_3$ and TiO_2. Both BLFO and BT were prepared separately and then mechanical mixing was applied for the composite formation. These materials were meticulously weighed in appropriate stoichiometric proportion with 5% extra Bi_2O_3, which was needed as spacer for compensation of bismuth loss at the time of heat treatment. The ceramic powders were mixed properly in stoichiometric ratio and ground systematically. Subsequently, the ground powders of BLFO and BT were calcined 750 ^oC and 850^o C respectively for 10 hrs. The pelletized samples of BLFO and BLFO-BT composite were sintered for 8 hrs at 650 ^oC respectively.

The structural measurements of the samples were taken from X-ray diffractometer employing Cu-Ka radiations. The magnetization data were collected using vibrating sample magnetometer (VSM). Polarization vs electric field (PE-loop) measurements were done with the help of 'Marine India' instrument at 50 Hz under a field of 25 kV/cm. Before ferroelectric vs electric field (P-E loop) measurements, samples were heated at 100 ^oC for 1 hr in an oven for the removal of any moisture. Sintered pellets were polished and coated from both sides using silver paste to make good electrical contacts for measuring ferroelectric properties.

Results and discussion

Structural analysis is a tool for the confirmation of material phase formation and measured by powder X-ray diffraction. Fig. 1 shows the powder XRD spectra of BLFO and BLFO-15BT composite. The spectrum shows the polycrystalline nature of the samples. The indexing of the XRD spectra peaks have been done on the basis of distorted rhombohedral structure with space group R3c [9]. The impurities reported in the literature for pure bismuth ferrite ($Bi_2Fe_4O_9$ and $Bi_{25}FeO_{39}$) [4] are almost suppressed after the La doping on the Bi site and also in line with the reported literature [6-8]. Fig. 1 shows that BFO-15BT holds the peaks of both BLFO as well as BT (denoted by '*'). This is the confirmation of composite formation without any impurity.

Fig. 2 shows the expanded view of XRD data near to 32^o and the peaks are shifting with splitting towards higher 2 theta side. It is due to the different ionic radii of different ions present in the composite (Bi^{3+}, Ba^{3+}, La^{3+}, Fe^{2+} and Ti^{4+}). As per the literature, shifting in the peaks indicates the distortion in the lattice due to compression and it is related to the polarization switching [10].

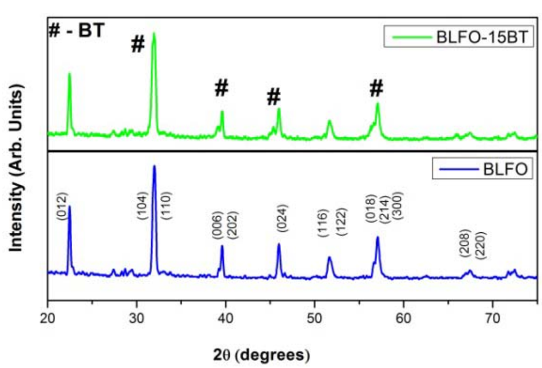

Fig. 1 X-ray diffraction patterns of BLFO and BLFO-15%BT composites

The room temperature magnetization (M-H) hysteresis loop measurements confirm the different magnetic parameters of the material like saturation magnetization, coercivity and remnant magnetization. Such type of measurements decide the role in device applications like data storage, magnetic read heads and sensors etc. Fig. 3 shows the room temperature saturated M-H hysteresis loops for both the samples viz BLFO and BLFO-15BT. As per the literature reported, BFO shows the antiferromagnetic nature [1] but the doping of La at

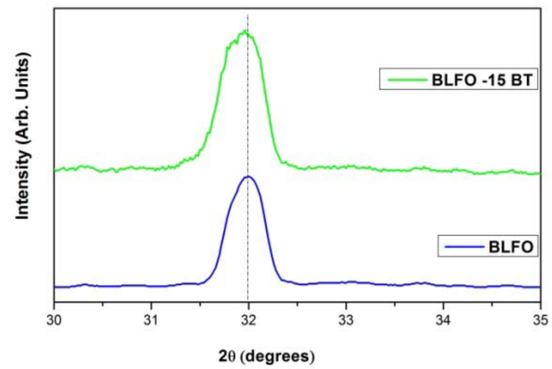

Fig. 2: Enlarged X-ray diffraction pattern of BLFO and BLFO-BT composites in the range of 30^o to 35^o

the Bi site of BFO greatly enhance its magnetization and the reasons behind such enhancement is (i) due to the increase of the spin canting angle (ii) pre-dominantly due to destroying of the spiral spin-modulated incommensurate structure. And as a result of both the reasons the net macroscopic magnetization is obtained [11-13]. The addition of 15%BT in to BFO reduces the saturation magnetization but the coercivity (intrinsic property of the material) does not change which confirms that the BT is on the interface or on the grain boundaries and not inside the grains of the BLFO. It is also the reason of the composite formation and both peaks present in XRD patterns (Fig. 1). The coercivity is very low and nearly 442 Oe which confirms the loss is minimum in the samples.

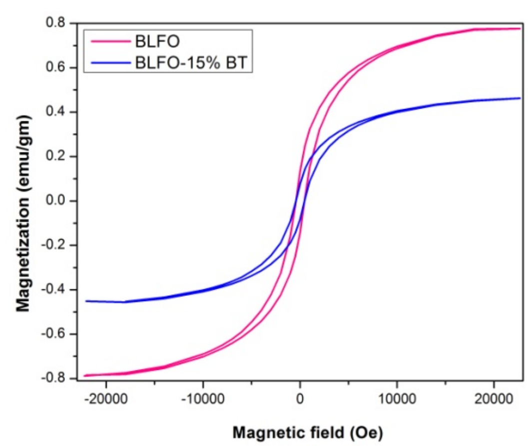

Fig. 3: Room temperature M-H hysteresis loop of BLFO and BLFO-BT composites

The room temperature electric hysteresis loops (P-E loop) measurement is an excellent technique to find the loss analysis and the maximum polarization in the samples. Fig. 4 shows the P-E loops of BLFO and BLFO-15BT composite, measured at a frequency of 50 kHz, 25 kV/cm and at room temperature. The maximum polarization of pure BFO is along the diagonals of the perovskite unit cell (111) pseudocubic / (001) hexagonal [1] but the incorporation of BT with La modified BFO changes ferroelectric hysteresis and the values of the maximum polarization obtained are 0.65 and 0.24 $\mu C/cm^2$ for BLFO and BLFO-15BT respectively. The BT substitution in to BLFO reduces the leakage current and improves the electrical properties. It is very interesting to note that the coercivity increased from 3.5 kV/cm for BLFO to 12.1 kV/cm BLFO-15BT composite. The increase in coercivity of BLFO-BT composite is attributed to the interfacial polarization at the grain boundaries.

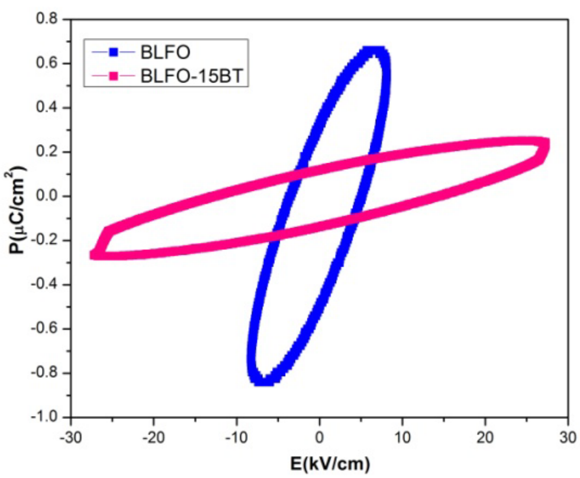

Fig. 4 P-E ferroelectric hysteresis loop of BLFO and BLFO-15%BT

The ferroelectric and ferromagnetic nature of both (BLFO and BLFO-15BT composite) enhance after the doping at Bi site and composite with BT of BLFO, which confirms the multiferroic nature of the pure BFO enhanced and such type of materials can be used in sensing application. The further analysis of the effect of magnetic field on ferroelectric properties and as a result of it magnetoelectric coupling is under investigation.

Conclusions

Multiferroic materials with pronounced magnetic and electronic properties have flooded everywhere in modern technology including electric field-controlled magnetic memory data storage. The solid state reaction route has been employed to prepare multiferroic BLFO and BLFO-BT composite. The co-existence of rhombohedral and tetragonal phases of BLFO and BT in BLFO-BT is confirmed from the splitting of marked peaks in the XRD pattern. The magnetic studies display a decreased coercivity due to addition of BT in BLFO. A dramatic change in the P-E loop of BLFO-BT composite is observed as compared to BLFO arising out of the interfacial polarization.

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