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Co-existence of tetragonal and monoclinic phases and multiferroic properties for $x \leqslant 0.30$ in the $(1-x)Pb(Zr_{0.52}Ti_{0.48})O_3$–$(x)BiFeO_3$ system

Subhash Sharma [a], Vikash Singh [a], R.K. Kotnala [b], Rajeev Ranjan [c], R.K. Dwivedi [a,*]

[a] Department of Physics and Materials Science and Engineering, Jaypee Institute of Information Technology, A-10, Sector-62, Noida 201307, Uttar Pradesh, India
[b] National Physical Laboratory (CSIR), Dr. K.S. Krishnan Marg, New Delhi 110012, India
[c] Department of Materials Engineering, Indian Institute of Science, Bangalore 560012, India

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ABSTRACT

Compositions with $x \leqslant 0.30$ in the system $(1-x)Pb(Zr_{0.52}Ti_{0.48})O_3$–$(x)BiFeO_3$ were synthesized by sol–gel method. Rietveld analysis of X-ray diffraction data reveals tetragonal structure (P4mm) for $x \leqslant 0.05$ and monoclinic (Cm) phase along with the existence of tetragonal phase for $0.10 \leqslant x \leqslant 0.25$ and monoclinic phase for $x = 0.30$. Transformation of E(2TO) and E + B1 vibrational modes in the range 210–250 cm^{-1} (present for $x \leqslant 0.25$) into $A' + A''$ modes at ~236 cm^{-1} for $x = 0.30$, and occurrence of new vibrational modes A' and A'' in Raman spectra for $x \geqslant 0.10$ unambiguously support the presence of monoclinic phase. Occurrence of remnant polarisation and enhanced magnetization with concentration of $BiFeO_3$ indicates superior multiferroic properties. Variation of magneto-capacitance with applied magnetic field is a strong evidence of magneto-electric multiferroic coupling in these materials.

1. Introduction

$PbZr_xTi_{1-x}O_3$ (PZT) system exhibits solid solution formation between lead zirconate (orthorhombic, anti-ferroelectric) and lead titanate (tetragonal, ferroelectric) over a complete range of x [1]. This system has been extensively studied in virtue of its high electro-mechanical coupling coefficients [2,3]. It has a complex phase diagram near the morphotropic phase boundary (MPB) which shows excellent piezoelectric properties at around $x = 0.52$. The MPB is not well defined and has been a complex issue for last few years, however, since it appears to be associated with a phase coexistence region whose width depends on the compositional homogeneity and the processing conditions [4–6]. It has, therefore, become the subject of interest for several researchers who have illustrated the onset of room-temperature phase transitions and the width of phase in the MPB region. Jaffe et al. [1] proposed nearly a vertical phase boundary that separates the rhombohedral (R3m) and tetragonal (P4mm) phases; although the fact is that the symmetry of neither phase is a subgroup of the other. A recent study by M. Deluca et al. [25] explores the coexistence of tetragonal and monoclinic (T + M) phases for $x = 0.52$ at room temperature. On the other hand, $BiFeO_3$ (BFO) is one of the multiferroics that exhibits G-type anti-ferromagnetic order with $T_N \sim 643$ K [7] and ferroelectricity with Curie temperature (T_C) ~ 1103 K [8,9]. It is known to have a rhombohedrally distorted perovskite structure with R3c space group symmetry and reported to exhibit weak magnetism at room temperature due to the residual moment from the canted spin structure and also a weak linear magneto-electric (ME) effect in bulk samples [10,11]. The origin behind the concept of outstanding ferroelectric properties in PZT around MPB was recently confirmed with the discovery of a new ferroelectric phase with monoclinic symmetry [12], where the polarization vector is no longer constrained to lie along a symmetry axis, but instead, the polarization vector can rotate within monoclinic plane [13–16]. This property is now associated with a universal characteristic of ferroelectric systems with huge electro-mechanical coupling coefficient around MPB. This phenomenon has already been experimentally observed in PZT [1], PMN-PT [17] and (PZN-PT) [18]. Also, processing technique has been found to be effective to influence phase formation around MPB [19]. A few recent reports on solid solution formation between BFO and $PbTiO_3$ reveal occurrence of a morphotropic phase boundary (MPB) [20–22] similar to the well known system like PZT and PMN-PT ceramics [17,18]. In addition to the above, multiferroic properties of solid solution compositions between BFO and BT by Singh et al. [23] are found to be the centre of attraction in recent years. PZT system with ratio Zr/Ti equivalent to 52/48, is known to have excellent piezoelectric properties at room temperature [24–26]. The solid solution formation of PZT (52/48) with BFO may be an interesting functional

* Corresponding author.
E-mail address: rk.dwivedi@jiit.ac.in (R.K. Dwivedi).

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material system from the magneto-electric multiferroic point of view. Although, a long back, T.S. Robert et al. [26] have studied the similar system with PZT (50/50)–BFO solid solutions, prepared by solid state reaction method [26] as well as research on BFO/PZT multilayer thin films has also been reported [27–29]. Here, we have synthesized PZT (52/48)–BFO system by sol–gel method. In this paper, detailed investigations on the structural studies have been reported, where we have analyzed more precisely the evolution of monoclinic phase with increasing x along with tetragonal phase with the help of Rietveld analysis of XRD data and analysis of Raman spectra and experimental evidence of magneto-electric multiferroic coupling in these materials has also been demonstrated as well.

2. Experimental detail

Ferroelectric ceramics with composition $x = 0.0$, 0.05 0.10, 0.15, 0.20, 0.25 and 0.30 in the system $(1-x)PbZr_{0.52}Ti_{0.48}O_3$–$(x)BiFeO_3$ [i.e. $(1-x)PZT-(x)BFO$] were prepared by sol gel method. The raw materials of high purity reagents $Pb(CH_3CO_2)_2 3H_2O$, $Zr(OCH_2CH_2CH_3)_4$, $Ti[OCH(CH_3)_2]_4$, $Bi(NO_3)_2{\cdot}5H_2O$, $Fe(NO_3)_2{\cdot}9H_2O$ were used as the starting materials, and 2-methoxyethanol ($CH_3OCH_2CH_2OH$) and acetic acid as the solvents. The detail of synthesis process is described somewhere else [30]. The dried gels of these compositions were crushed into powders and calcined at 800 °C for 2 h to obtain crystalline powder. The calcined powders were mixed with 2% PVA binder and pressed into cylindrical pellets of 10 mm diameter using co-axial hydraulic press. These pellets were finally sintered at 950 °C for 2 h followed by polishing and subsequently coated with silver paste for electrical measurements. X-ray diffraction (XRD) patterns of sintered materials in the powder form were recorded by XRD (Shimadzu XRD-6000) with Cu Kα ($\lambda = 1.5418$ Å) radiation. Raman spectra of these samples were recorded by Nd-YAG laser, 1064 nm, 500 mW laser power. Ferroelectric and magnetic measurements were carried out using P–E Loop Tracer (Marine India) and VSM (Lakeshore – 7305) respectively.

3. Results and discussion

In this paper, we focus our investigations on the solid solution formation, structural analysis and magneto-electric multiferroic behaviour in the system $(1-x)$PZT–(x)BFO upto compositions with $x \leqslant 0.30$. Fig. 1 shows Rietveld fitted diffraction patterns of all these compositions. It has been observed that compositions with $x \leqslant 0.05$ show single phase formation with tetragonal (P4mm) structural symmetry. Rietveld refinement of diffraction data for these samples was carried out using FullProf software programme [31]. It has been observed that composition with $x = 0.00$ shows quite good fitting (the fitted data i.e. dotted lines exactly match with experimental data i.e. solid lines) with fitting parameters $R_{wp} \approx 13.3$, $R_{exp} \approx 14.5$ and $\chi^2 \approx 1.80$. Similarly, structural refinement for $x = 0.05$ has also shown tetragonal symmetry with agreement factor $\chi^2 \approx 1.74$ (see Table 1). The refined data for the composition with $x = 0.10$ do not fit well with the experimental data on the basis of considering only tetragonal symmetry (P4mm) as for $x = 0.05$, or only rhombohedral (R3c) symmetry. However, when fitted with mixed phase of tetragonal (T) and monoclinic (M) symmetry i.e. the coexistence of two structural phases with tetragonal and monoclinic symmetries, the refined data is found to be in quite good agreement with experimental data. Similar results are obtained for $0.10 \leqslant x \leqslant 0.25$. The refined parameters for all these compositions are given in Table 1. With increasing BFO concentration for $x = 0.30$, the refined data for the existence of two structural (T + M) phases was not found to be satisfactory. Further, when diffraction data was refined with monoclinic symmetry only, the fitting has been found to be much better with refined parameters $R_{wp} \approx 12.4$, $R_{exp} \approx 8.3$ and $\chi^2 \approx 2.29$ (Table 1). Further, in order to make the precise study of the existence of structural phases in these compositions, we have carefully analysed the powder X-ray diffraction profiles of the (111), (200) and (220) reflections for $0 \leqslant x \leqslant 0.30$ in Fig. 2. For the tetragonal phase, the (200) reflection shows a doublet (200, 002) while (111) reflection shows a singlet, whereas for the rhombohedral phase, (200) is reported to be singlet and (111) a doublet [24]. On the other hand, (220) reflection shows doublet for both the tetragonal as well as for rhombohedral structure. For the tetragonal phase, the stronger (202) peak occurs at lower 2θ side as compared to the weaker (220) reflection, whereas, for the rhombohedral phase the stronger (220) peak occurs at

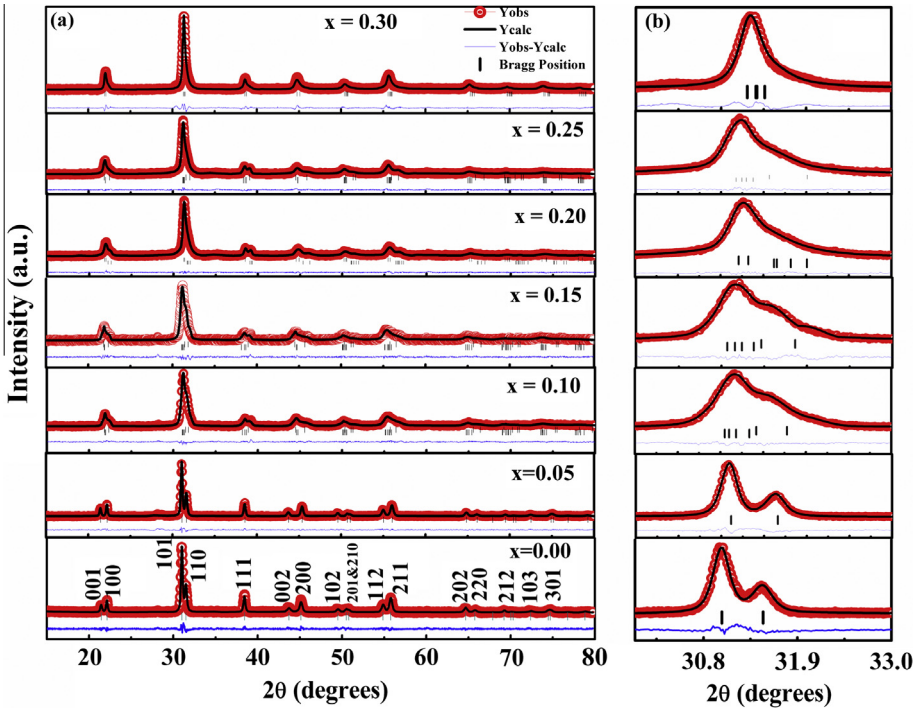

Fig. 1. Observed (dots), calculated (continuous line), and difference (bottom line) profiles obtained after the Rietveld refinement for $x \leqslant 0.30$ in $(1-x)$PZT–(x)BFO system (a) XRD patterns in the 2θ range 15–80° and (b) expanded profile of (110) plane.