

Absence of morphotropic phase boundary effects in $\text{BiFeO}_3\text{--PbTiO}_3$ thin films grown via a chemical multilayer deposition method

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Abstract We report an unusual behavior observed in $(\text{BiFeO}_3)_{1-x}(\text{PbTiO}_3)_x$ (BF- x PT) thin films prepared using a multilayer chemical solution deposition method. Films of different compositions were grown by depositing several bilayers of BF and PT precursors of varying BF and PT layer thicknesses followed by heat treatment in air. X-ray diffraction showed that samples of all compositions show mixing of two compounds resulting in a single-phase mixture, also confirmed by transmission electron microscopy. In contrast to bulk compositions, samples show a monoclinic (M_A -type) structure suggesting disappearance of the morphotropic phase boundary (MPB) at $x = 0.30$ as observed in the bulk. This is accompanied by the lack of any enhancement of the remanent polarization at the MPB, as shown by the ferroelectric measurements. Magnetic measurements showed an increase in the magnetization of the samples with increasing BF content. Significant magnetization in the samples indicates melting of spin spirals in the BF- x PT films, arising from a random distribution of iron atoms. Absence of Fe^{2+} ions was corroborated by X-ray photoelectron spectroscopy measurements. The results illustrate that thin film processing methodology significantly changes the structural evolution, in contrast to predictions from the equilibrium

phase diagram, besides modifying the functional characteristics of the BP- x PT system dramatically.

1 Introduction

Recent years have witnessed tremendous research in multiferroic BiFeO_3 (BF), which shows co-existence of ferroelectric and magnetic ordering in the same phase [1]. BF makes a continuous solid solution with many insulating ABO_3 -structured perovskite oxides, such as PbTiO_3 (PT) [2] and BaTiO_3 [3]. In particular, the mixed $(1-x)\text{BiFeO}_3-x\text{PbTiO}_3$ (BF- x PT) system has generated significant interest because this system has been suggested to exhibit high piezoelectric coefficient and higher Curie temperature in comparison to the conventionally used $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ [2]. These two compounds form a continuous solid solution whose phase diagram exhibits a morphotropic phase boundary (MPB) [2]. The morphotropic phase region with composition width, Δx , is characterized by co-existence of both tetragonal and monoclinic phases as shown unambiguously by Bhattacharjee et al. [4], while, outside the MPB region, only either tetragonal or monoclinic phases are observed. Earlier, in another study, Zhu et al. reported the existence of an additional orthorhombic phase in the MPB region [5], but this is not supported by Rietveld refinement of the MPB compositions [6]. Moreover, although many reports have indicated a wide MPB region, a careful study by Bhattacharjee et al. has shown that Δx is as low as ~ 0.03 [7]. It should however be noted that precise determination of the width of the MPB region is subject to precise composition determination. BF- x PT also shows a high ferroelectric Curie temperature in the range of 763 to 1100 K [8], and displays an unusually large tetragonality [7, 9], three times more than that of PbTiO_3 . These unusual features in the bulk have led to

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a number of studies on BF- x PT solid solution thin films in the past few years [10, 11], typically reporting good quality hysteresis loops with high remanent polarization at temperatures below room temperature (RT) and at high frequencies (mostly above 1 kHz) [11].

Recently, we demonstrated excellent ferroelectric properties with high insulation resistance in BF-0.60PT films prepared using a multilayer chemical solution deposition method [12]. The films also showed a change in the crystal structure from equilibrium tetragonal structure to monoclinic M_A -type structure. In this paper, we show how compositional changes in multilayer processed BF- x PT thin films result in unusual characteristics where we do not observe a MPB-like behavior across $x = 0.30$ in either structure or properties, elucidating the significance of processing methodology resulting in a marked effect over the structure evolution and properties of the BF- x PT system.

2 Experimental details

The films were prepared by a chemical solution deposition method using a novel multilayer approach described in our previous work [12]. BF and PT solutions were spun coated alternately at a speed of 4000 rpm for 30 s on platinized Si substrates to grow the alternating PT and BF layers. Each coating step was followed by drying for 12 min at 360°C. Finally, after deposition of 16 bilayers of BF and PT, the whole stack was annealed at 700°C for 1 h in nitrogen atmosphere. Final samples were between 300- and 500-nm thick consisting of 16 bilayers of BF and PT of different thicknesses to yield overall compositions of $x = 0.27, 0.33, 0.60, 0.70$ and 0.80 . The thickness of each layer of each compound was varied by changing the solution concentration and thus the overall film compositions were estimated by converting the individual layer BF and PT thicknesses in the stack into the mole fraction. For all the film compositions, PT layers were deposited before BF layers.

A Thermoelectron ARL X'tra high-resolution X-ray diffractometer was used for collecting powder X-ray diffraction (XRD) data. The package Fullprof (J. Rodriguez-Carvajal, FULLPROF, Laboratory Leon Brillouin, CEA-CNRS, EA/Saclay, 91191 Gif sur Yvette Cedex, France, 2006) was used for Le-Bail refinements using the XRD data in the 2θ range of 20 to 100°. In the refinements, the data in the 2θ ranges of 36 to 43.3° and 85 to 88° were excluded due to strong texture effects and the substrate peaks. Further, co-existence of Pt substrate peaks was also taken into account in the refinements.

A transmission electron microscope (TEM, Jeol 1010) was used for cross-sectional imaging and compositional studies using energy dispersive spectroscopy (EDAX). Magnetic measurements were carried out using a vibrating sam-

ple magnetometer (ADE-DMS EV-7VSM). The ferroelectric and leakage properties of the films were measured by a Radiant Premier II ferroelectric tester. 200- μ m-diameter platinum electrodes were sputter deposited on the films to facilitate the electrical measurements. X-ray photoelectron spectroscopy (XPS) measurements on the films were carried out on a VG MicroTech ESCA 310F instrument at a vacuum better than 1×10^{-9} Torr. The general scan and core level spectra for Fe 2p, Bi 4f and Pb 4f were recorded with un-monochromatized Mg K α radiation (photon energy = 1253.6 eV) at a pass energy of 20 eV and an electron take-off angle of 90°. The core level binding energies (BEs) were aligned with the adventitious C 1s binding energy of 285 eV.

3 Results and discussion

3.1 Structural characterization

Crystal structure and phase analysis of the samples was carried out by XRD studies conducted at room temperature. Figure 1a shows the XRD patterns of all the samples. When the peak positions of our samples are compared with the standard ICDD XRD data for pure PT and BF, the structure does not fit either the rhombohedral BF or the tetragonal PT phase. This suggests the intermixing of the PT and BF precursor layers during post-deposition heat treatment and formation of a solid solution. No significant change in the peak profiles and their positions is observed even when the PT content of the BF- x PT thin film samples changes from $x = 0.27$ to $x = 0.80$, further affirming that the XRD peaks in Fig. 1a belong to a single solid-solution phase only, in agreement with our previous finding on BF-0.60PT films [12]. For the BF- x PT solid solutions in bulk, the structure is known to be tetragonal for more than 30 mol% PT and monoclinic for less than 28 mol% PT [7]. Interestingly and unexpectedly, the thin film multilayer samples do not show any obvious change of structure across the so-called bulk MPB composition [2].

To verify the compositional uniformity and mixing, we carried out TEM and EDAX analysis. Figure 1b shows a TEM image of a BF- x PT sample for $x = 0.27$ taken at a magnification of 300 000 \times . The image does not show any individual layer of BF or PT and the structure appears like a homogeneous film with the presence of nanocrystalline grains. This again confirms the mixing of the two types of layers. EDAX measurements on the cross-sectional TEM images of all samples verified the overall compositions of the samples within an error of ~ 5 –10% for various elements.

Upon a closer examination of the XRD patterns shown in Fig. 1a, we find that there is a change in the relative intensities of the peaks in the 2θ ranges of 45 to 48° and 55

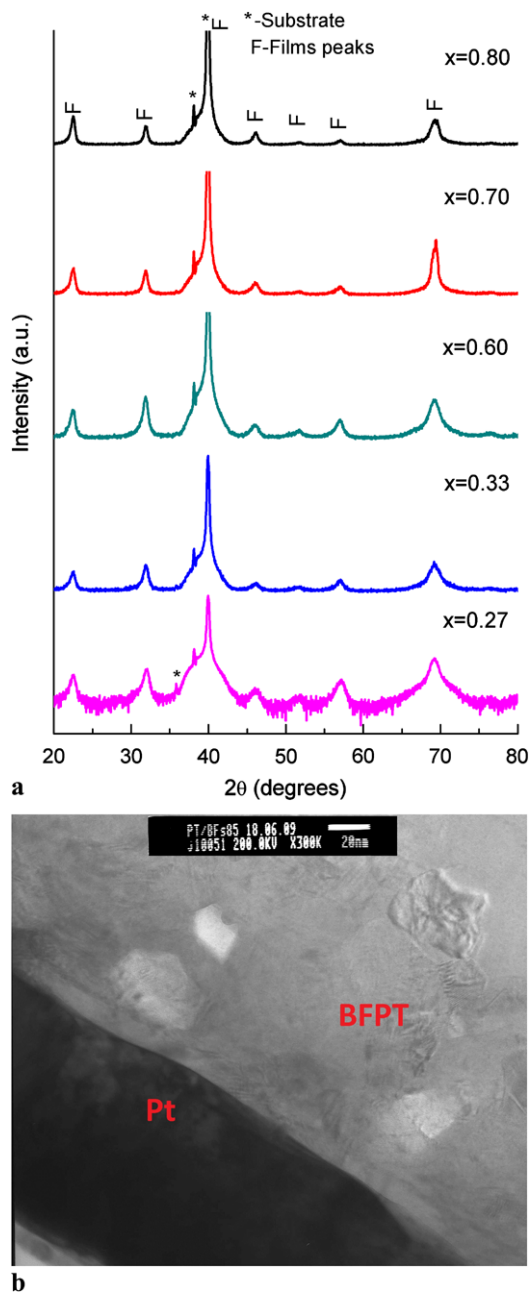


Fig. 1 (a) XRD patterns of BF- x PT thin films of varying compositions and (b) high resolution TEM images of a BF- x PT sample with $x = 0.27$

to 60° as the composition of the films changes. It is seen that as the PT content (x) increases, the peak in the range of 45 to 48° becomes stronger and the peak between 55 and 60° becomes weaker. The same is also true of the two peaks in the 2θ range of 25 to 35°. Although this change in the relative intensities of the two peaks is indicative of some structural change that may occur upon the change in the composition, it can also be associated with a slight change in grain orientation in the thin-film samples or due to thin film strain effects arising from the mismatch at the substrate-

sample interface. We then analyzed our XRD data using the Le Bail refinement technique to capture the significance of this change in the relative intensities, using a procedure similar to that described in our previous work [12] where we determined the crystal symmetry of the samples containing up to 60% PT to be M_A type (Vanderbilt and Cohen notation) [13] monoclinic structure with Cm space group symmetry. The refinements yield slightly lower χ^2 values, by only 0.21, for a tetragonal structure with space group $P4mm$ for compositions with PT higher than 60%, not sufficient enough to explicitly justify a structural change to a tetragonal structure after $x = 0.60$. Moreover, at the outset, it is tempting to associate the presence of monoclinic structure in samples with PT contents up to $\sim 60\%$ and possibly a subtle change to tetragonal beyond this composition to a shift in the MPB composition of BF- x PT thin films, prepared by the multilayer method, which otherwise occurs at $\sim 30\%$ PT in bulk solid solutions. However, again, notwithstanding the fact that the subtle structure change as predicted by the Le-Bail refinement after $x = 0.60$ itself is not conclusive, we do not associate this with the MPB due to reasons mentioned above. We also attempted fitting the patterns using the pseudo-cubic rhombohedral structure, but the fits resulted in much larger χ^2 values.

Further, the multilayer deposition technique may result in very fine compositional gradients across the sample thickness and may also cause strains in the films. Large full-width at half maximum (FWHM) of the film peaks, higher than 0.5°, is also indicative of the compositional variations across the film thickness. Such a behaviour is supported by previously observed strain-induced structural changes away from bulk structure in epitaxial BF films [1] as well as in PT films [14]. Previous studies have also shown the presence of monoclinic structure in BF thin films [15, 16] as well as solid solutions of BiFeO₃-BaTiO₃ [17]. These observations suggest that the observed structural change in our samples can be attributed to the strain resulting from a peculiar film synthesis process resulting in a single-phase yet chemically inhomogeneous structure.

3.2 Electrical measurements

We carried out ferroelectric measurements on our samples at 200 K. The measurements were made using a bipolar pulse at a frequency of 1 kHz. The measurement results, as shown in Fig. 2, confirm the ferroelectric nature of both BF-rich and PT-rich samples. The remanent polarization of the BF- x PT sample with $x = 0.33$ was $\sim 19.5 \mu\text{C}/\text{cm}^2$, which is only slightly larger than the values obtained for PT-rich samples but much smaller than the values reported for laser-ablated BF- x PT films of compositions close to the bulk MPB [11]. Importantly, the samples could withstand fields

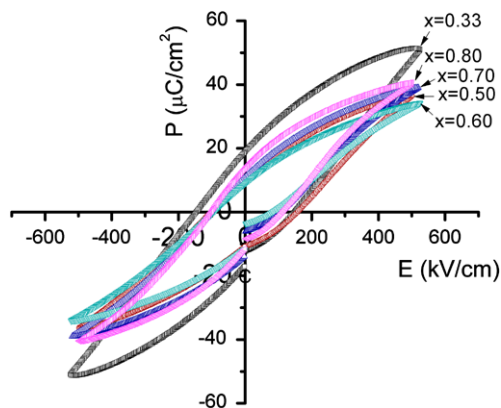


Fig. 2 Ferroelectric hysteresis measurements of BF- x PT thin films at 200 K (P : polarization, E : electric field)

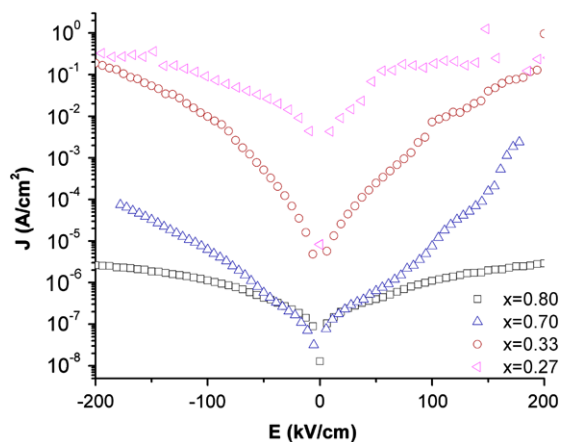


Fig. 3 Leakage characteristics of BF- x PT thin films at RT (J : current density, E : electric field)

at least up to ~ 600 kV/cm, high enough for device applications; this shows that the samples have good insulation resistance. Such high insulation resistance in these samples can be attributed to the alteration in the films' crystal structure to M_A -type monoclinic structure as compared to equilibrium (bulk) structure. Interestingly, as expected in bulk compositions at $x = 0.30$, i.e. MPB, any extraordinary enhancement in the ferroelectric polarization is not observed. This is a very interesting as well as important observation because on the one hand single-phase formation occurs as suggested by the XRD patterns and the TEM images, and on the other hand there appears to be incomplete mixing of atoms at the atomic level unexpectedly resulting in the disappearance of the MPB due to a peculiar processing technique.

Room-temperature leakage characteristics ($\log J$ (A/cm^2) vs E (kV/cm)) of the samples are shown in Fig. 3. The figure shows that the smallest leakage current of the order of 10^{-6} A/cm^2 at 100 kV/cm is shown by samples containing maximum PT content, i.e. $x = 0.80$, indicating a highly resistive nature of the samples, also supported by the ferroelectric hysteresis data. The leakage current increases

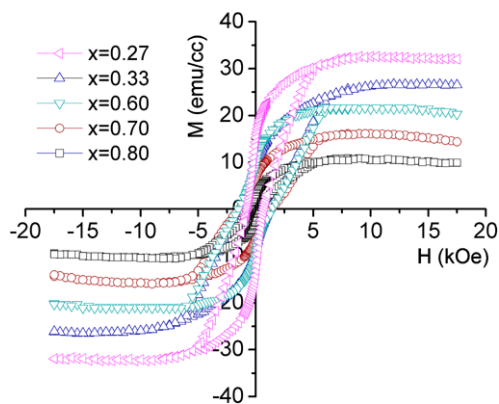


Fig. 4 Room-temperature magnetization (M) vs applied magnetic field (H) plots of BF- x PT thin films

as the BF content of the films increases and follows an expected trend because the leakage resistance of PT is far superior to BF.

From the above electrical data, one can observe that there is no obvious enhancement in the ferroelectric polarization near the usual (bulk) MPB composition range around $x = 0.30$. This is most likely due to the nature of film processing resulting in mixing of BF and PT to an extent that one observes single-phase XRD spectra and homogeneous TEM micrographs, but possibly not sufficient enough to exhibit the MPB effect which is observed in chemically homogeneous BF-PT solid-solution ceramics and thin films [7, 11]. The results illustrate that processing methods can lead to noticeable changes in the structure and properties of the BF-PT thin films to the extent that hitherto observed MPB effects are not noticed.

3.3 Magnetic studies

Magnetic measurements were conducted on all samples and the results are shown in Fig. 4. The figure shows that all the samples possess a saturated magnetic hysteresis loop along with finite remanent magnetization. The highest magnetization of ~ 15 emu/cc is exhibited by the BF- x PT sample with $x = 0.27$. We find that the saturation magnetization keeps increasing as the PT content of the films decreases until $x = 0.27$. This is in contrast to single-crystal BiFeO₃ [18], which does not exhibit a magnetic hysteresis loop. Although the magnetization values we observe are not very large and are of the order of $0.01 \mu_B$ (Bohr magneton), these are still significant when compared to the values shown by pure BFO films [19].

Previous studies suggest that a finite magnetization in BF can be achievable by various means such as by melting the spiral spin cycloid via application of large enough magnetic fields [20], by substrate-induced constraints in epitaxial BiFeO₃ thin films [1] or by means of chemical substitutions [2, 21]. In the present study, a high magnetic moment

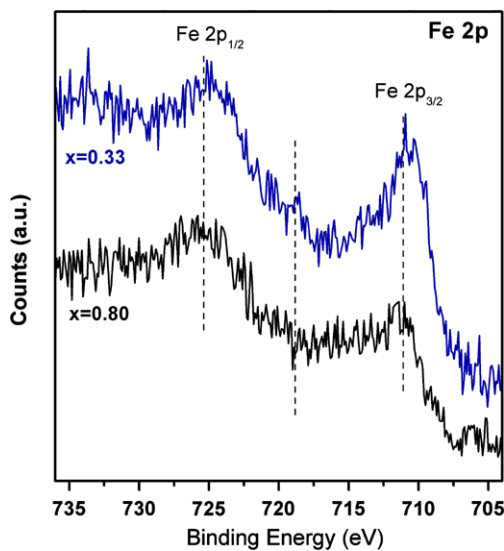


Fig. 5 XPS spectra for Fe in BF- x PT thin films

could result either due to the thin film clamping effect or due to the presence of PT in the solid solution destroying the spin cycloid or a structural change or a combination of these. Melting of the spin cycloid is expected since the thickness of each layer is less than the length of the spin cycloid of 62 nm. Moreover, any inhomogeneity in the composition would further enhance the breaking of such a spin cycloid, resulting in a finite magnetization.

In order to verify if the weak ferromagnetism is due to the presence of mixed valence of Fe ions, i.e. Fe³⁺ and Fe²⁺, we carried out X-ray photoelectron spectroscopic measurements on our samples. Figure 5 shows the XPS spectra of ions in two samples, $x = 0.33$ and 0.80 , of two extreme compositions. Figure 5 shows the Fe $2p$ peaks for both the samples. There are two peaks present at 711.1 and 725.3 eV, which correspond to Fe $2p_{3/2}$ and Fe $2p_{1/2}$, respectively, and are ascribed to Fe $2p_{3/2}$ -O and Fe $2p_{1/2}$ -O bonds for Fe³⁺. The satellite peak belonging to Fe³⁺ appears at 718.8 eV. The expected value of the major peak for Fe²⁺ is 709.5 eV, while its satellite peak is expected to occur at 716 eV [22]. The absence of these two peaks is indicative of the absence of Fe²⁺ in our films, as also shown previously [19]. One may also notice that in the sample with larger PT content, the peaks are slightly shifted towards higher binding energies, suggesting the influence of cation substitution and hence altered bond characteristics.

The presence of magnetism in BiFeO₃ thin films has been a subject of intense debate. For instance, while Wang et al. [1] reported large room-temperature saturation magnetization in epitaxial BiFeO₃ thin films and attributed this to thin film strain effects, subsequent reports suggested that this could be due to the presence of small amounts of Fe²⁺ ions [19] or impurities like γ -Fe₂O₃ or maghemite [23] which can remain undetected in the XRD pattern. It should

be noted that while the measurements showed by Eerenstein et al. were at room temperature [19], the measurements showed by Bea et al. were conducted at 10 K [23]. Reports on magnetic behaviour of nanocrystalline maghemite also suggest that nanocrystalline maghemite is ferromagnetic at very low temperatures and exhibits supraparamagnetism at RT, i.e. finite saturation magnetization but no remanent magnetization [24]. In the thin films of 300–400-nm thickness, any impurities that will be present in the samples are likely to be of nanocrystalline size, also corroborated by the representative TEM micrograph as shown in Fig. 1b showing the presence of nanocrystalline features. Hence, if there are any impurities like maghemite or magnetite present, these are likely to contribute only to the saturation magnetization at RT and not the remanent magnetization. This again supports our argument that the presence of finite remanent magnetization in the BF- x PT multilayer samples is likely to arise from the destruction of the spin cycloid in BF due to inhomogeneous mixing of atoms in the BF- x PT solid solution resulting in the distribution of Fe ions across the film in a manner leading to the formation of small pockets of magnetic regions of size smaller than the spin cycloid length of BF, melting the hitherto present spin spirals in homogeneous BF- x PT [5].

4 Conclusions

(BiFeO₃)_{1-x}-(PbTiO₃)_x films fabricated by chemical solution deposition of multilayers of BiFeO₃- and PbTiO₃-containing solutions showed a single-phase structure with a monoclinic structure (space group Cm) as confirmed by XRD patterns and TEM images. To our surprise, we did not observe any change in the structure at around $x = 0.30$, the MPB composition in the bulk, indicating the disappearance of the MPB, attributed to a peculiar processing technique. However, the broadness of the XRD peaks indicates the presence of a fine composition gradient across the films' cross section, resulting in unexpected as well as unusual observations in the structure evolution and the properties. Again, ferroelectric measurements do not show any particular enhancement at $x = 0.30$ and the polarization of the sample marginally increased at higher BF content, an observation consistent with higher ferroelectric polarization of pure BiFeO₃ reported in the literature. Magnetization measurements show that the magnetic moment of the samples increases with increasing BF content and this is attributed to the melting of the periodic spin structure. XPS measurements on the samples suggest the absence of any Fe²⁺ in the samples, ruling out any mixed-valence effect.

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