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Crystallographic and magnetic investigations of textured bismuth ferrite lead titanate layers

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Abstract— In present work we demonstrate the synthesis of textured $60BiFeO_3$-$40PbTiO_3$ (60:40BFPT) by using the templated grain growth technique with platelets of $BaTiO_3$. Synthesised 60:40BFPT has been examined by High-energy X-ray diffraction utilizing a synchrotron X-ray source. The crystallographic structure refinement results revealed the co-existence of monoclinic and tetragonal phases. By employing an external electric field, the mixed monoclinic/tetragonal phases transformed to the predominantly tetragonal phase. In addition, a crystallographic texture refinement was completed on unpoled state of 60:40BFPT which showed the sample had 1.3 multiples of random distribution (MRD) {100} crystallographic textured in tetragonal phase. However, magnetic measurements showed isotropic ferromagnetism for the sample which is not in agreement with the crystallographic texture properties of the sample. Low temperature magnetic transition has been found in zero field cooled – field cooled (ZFC-FC) measurements. This could be due to the possible existence of a secondary magnetic phase, which dominated the magnetic result.

Keywords- Texture; Synchrotron; Phase transformation; ferromagnetic

1- Introduction

Ferroelectric materials with a morphotropic phase boundary (MPB) are of interest because the properties are maximized for compositions in proximity to the MPB. It has been suggested that mixed phase structures near the MPB are susceptible to electric field-induced phase transitions. For example, the large d_{33} reported by Park *et al.* was attributed to electric field-induced interphase boundary motion between the ferroelectric tetragonal and rhombohedral phases [1]. Consequently, an extrinsic strain arising from interphase boundary motion could be an important technique to improve the electromechanical properties [1,2].

The solid solution (1-x)$BiFeO_3$-x$PbTiO_3$ (BFPT) is a promising high-temperature multiferroic material system that exhibits an MPB between rhombohedral and tetragonal structures near 60 wt% $BiFeO_3$ [3,4]. Near the MPB a high Curie temperature (T_c) of 632 °C for BFPT was found. The high T_c has encouraged scientists to exploit the BFPT as a high temperature piezoelectric material. However, the high conductivity has prevented the use of BFPT in high-temperature applications [5,6]. BFPT has also received interest due to its extreme tetragonality (c/a≈ 1.187 at x=0.7)[5]. The spontaneous strain in tetragonal bismuth ferrite lead titanate (BFPT) (≈ 18%) could be used to induce a large strain response, resulting in an unprecedented electric field induced strain [7].

Zhu *et al.* showed the effect of chemical modification on the ferroelectric and antiferromagnetic properties of BFPT [8] and reported a new magnetic and nuclear phase diagram for BFPT generated using XRD and SQUID measurements on BFPT pellets [9]. The antiferromagnetic Néel temperature reduces approximately by 300 K by crossing the MPB from the rhombohedral to the tetragonal side.

A material with an entirely random dipole direction has a high potential energy to transform, which precludes a phase transition, therefore alignment of the dipoles is critical. Although phase transitions in polycrystalline materials have previously been reported [10], both single crystals and textured materials are points of interest in this regard[11-13]. The cost-prohibitive and complicated processing requirements limit the widespread availability of high quality ferroelectric single crystals. Alternatively, oriented dense bulk electroceramics can be prepared. Highly textured perovskite may, after poling, show similar piezoelectric properties compared to single crystals [14]. Preparation of textured piezoelectrics are of interest due to the high market demand for large strain actuators and high sensitivity piezoelectric sensors.

The objectives of the work reported here was not only to synthesis and measure the degree of textured 60:40 BFPT by using $BaTiO_3$ platelets as templates, but also to study the anisotropic crystal structure effect on the magnetic properties of synthesised BPFT. Structural analysis by synchrotron measurements suggested that the $BaTiO_3$ templates resulted in the formation of a weakly oriented 60:40 BFPT material.

2- Experimental

$0.6BiFeO_3$-$0.4PbTiO_3$ (60:40BFPT) was made using the templated grain growth method via tape casting process as detailed by Zhu *et al.* & Palizdar *et al.* [8,9,15-19]. Templates were aligned using tape casting. Stochiometric amount of oxides were used to synthesis 60:40BFPT plus 10% $BaTiO_3$ plate-like particles as templates by weight. The mixture was added to the slurry made from solvents and different additives such as binder, plasticizers and dispersant. After casting and drying, the tape was cut and stacked to make 1 mm thick layer. The obtained layer was sintered at 1100 °C for 1 hr.

High-energy X-rays from a synchrotron source were used in order to effectively probe the bulk of sintered materials. Diffraction was carried out at Beam I15 at the Diamond Light Source (Oxfordshire, UK) by using monochromatic beam X-rays of high energy while a voltage was applied across the 1 mm dimension, in 1 kV mm^{-1} steps [13,20-22]. Synchrotron data was measured using a 2D detector (MAR 3450). The Debye rings were caked into individual 2θ-intensity diffraction patterns, at +/- 5° about $0° < \alpha < 355°$. The azimuthal angle (α) was set as 0° in the vertical direction which is transverse to the normal of the casting direction (ND), and α =90° was the horizontal direction implying the tape casting direction (TCD).The crystallographic texture of template 60:40BFPT was determined by a Rietveld refinement for texture using the software package Materials Analysis Using Diffraction (MAUD)[23]. A 4^{th} order spherical harmonic orientation distribution function (ODF) with imposed fiber symmetry was used to model the crystallographic texture.

The magnetic measurement of the sample was carried out using MPMS XL 5 (Quantum Design) SQUID magnetometer from 5K to 300K under 5T magnetic field in two different directions: perpendicular (in-plane) and parallel (out-of-plane) to the preferred c-axis. The sample was demagnetized with a proper demagnetization protocol before each measurement [24].

3- Results

Fig. 1 shows measured diffraction data by high-energy X-ray diffraction for 60:40BFPT at α = 0° (ND) (applying no external electric field), revealing the as-processed ceramics is a phase mixture. Comparing the data at α = 0^o (ND) and 90^o (TCD) showed a degree of texture [15]. In our previous work it showed that the peak intensities for (100) and (200) peaks at different α angles i.e. between α = 0° and 355° were not identical [15]. For both (100) and (200) peaks the more intense ones had been observed at α = 0° (TCD), whereas less intense peaks had been obtained at α = 90° [15]. This reveals that the material could be textured. The existence of residual $BaTiO_3$ particles could contribute to additional peaks and influence the final intensities. The scanning electron microscopy results of the sample revealed the existence of both spherical and plate like regions [15]. However, in our previous work it was shown that the $BaTiO_3$ partially dissolved into the matrix material which represented Ba-dopped 60:40BFPT [15]. For more details on this see the references [15-18].

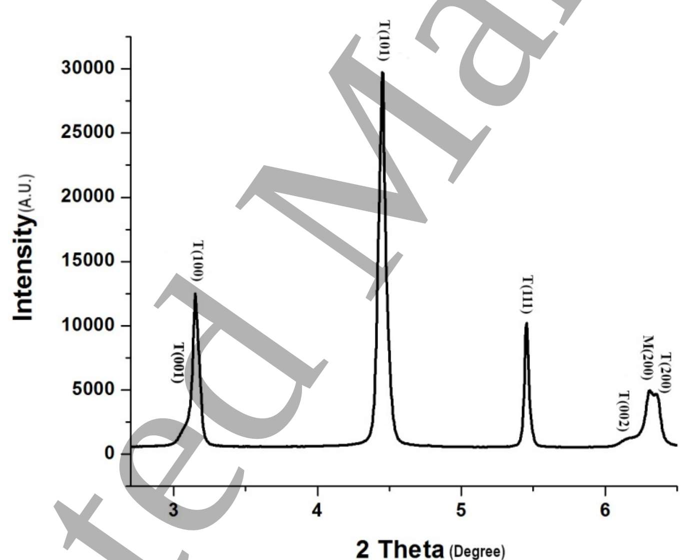

Figure 1. Diffraction data for 60:40 BFPT made from TGG method using 10% $BaTiO_3$ as templates.

The diffraction patterns of as-processed ceramics exhibited a (200) peak profile that is consistent with the presence of multiple phases. Zu *et al.* reported the existence of an orthorhombic phase together with the tetragonal and rhombohedral phases at MPB of BFPT [9], whereas other studies revealed the coexistence of rhombohedral and tetragonal phases at the MPB [19, 20]. In addition, in some relevant solid solutions such as PM-PT and PZT, the monoclinic phase as an intermediate state between tetragonal and rhombohedral structures has been reported [25,26]. Theoretical investigation on $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PZN-PT) and $Pb(Mg_{1/3}Nb_{2/3})O_3$- $PbTiO_3$ (PMN-PT) revealed the existence of monoclinic phase due to the lower free energy of the system in the MPB of mixed tetragonal-rhombohedral phases i.e. the tetragonal-monoclinic-rhombohedral pathway is preferred with the change of composition across the MPB region [27-29]. The obtained c/a ratio of ≈ 1.03 for Ba doped BFPT [15] is lower than that reported by Comyn *et al.* for 60:40BFPT pellets [30]. These different values of c/a ratio could be explained by reported chemical reaction between matrix and templates and could influence the crystallographic properties of the material [15,16]. The measured peak profiles were investigated in greater detail to gain insight into the phases present in templated BFPT. Asymmetry observed in {lll} reflections are not consistent with the reported phase mixture of tetragonal and rhombohedral phases [9,19-21]. To gain insight into the phases present the 111, 200, and 222 profiles were compared to the peak position for the tetragonal (*P*4*mm*), rhombohedral (*R*3*m*), and monoclinic (*Cm*) phases, as shown in Figure 2. From Figure 2, it can be seen that the combination of P*4mm*+C*m* correctly match the high 2θ peak asymmetry in the (111) reflection, high 2θ reflection near the (222) and also (200) reflection. However, the high 2θ asymmetry of the (111) as well as high 2θ shoulder of the (222) reflection could not be modeled using a P*4mm*+R*3m* structure model. This results suggests that the room phase structure of BFPT near the MPB is a phase mixture of tetragonal and monoclinic.

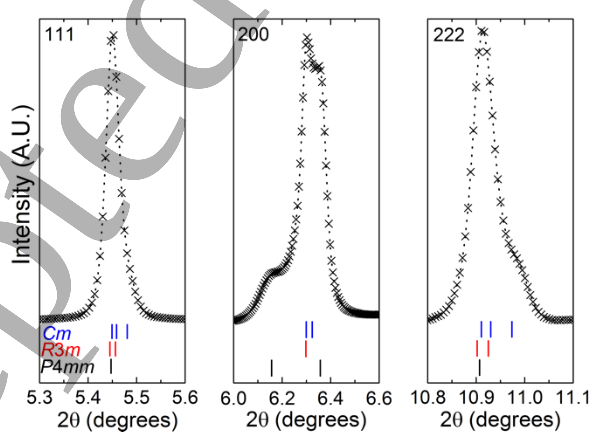

Figure 2. Measured diffraction profiles compared against peak marks for phased with a monoclinic (*Cm*), rhombohedral (*R*3*m*) tetragonal (*P*4*mm*).

The induced crystallographic texture in 60:40BFPT was quantified by Rietveld texture analysis using a P*4mm* and C*m* structure model. The equivalent texture coefficients of the harmonic texture model for the tetragonal and monoclinic phases were fixed. Figure 3 shows the angular dependence of the reconstructed crystallographic texture for the (00*l*) and (*lll*) poles for the tetragonal phase. A maximum of a 1.3 multiples of random distribution (MRD) {100} crystallographic texture was induced. Figure 3 shows that 60:40BFPT exhibits a slight {00*l*} crystallographic texture, as evidenced by an increase in f_{00l} at α = 0°. This obtained slight crystallographic texture could be the evidence of the reaction between $BaTiO_3$ templates and the matrix [15, 31].

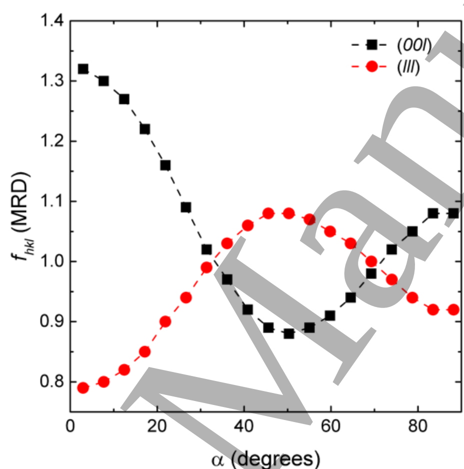

Figure 3. Reconstructed pole figure of the *lll* and 00*l* poles of the tetragonal phase.

The effect of an external applied electric field on the diffraction patterns of textured 60:40BFPT at low and high angles have been shown at figure 4. Increasing the applied field induces a phase transition that is changed from mixed monoclinic/tetragonal phases to predominately tetragonal phase. This phase transition initiates even at the low amount of applied field which could show evidence of crystallographic preferred orientation of the material. WinplotR software was used for profile fitting and also measuring the phases contributions. The phase fraction was identified by measuring the ratio of integrated areas of (002), (200) tetragonal and (200) monoclinic peaks. The data revealed that before applying the external electric field the proportion of tetragonal phase was ≈ 73.5% while at E= 6 kV/mm the proportion of tetragonal phase increased to ≈ 95%.

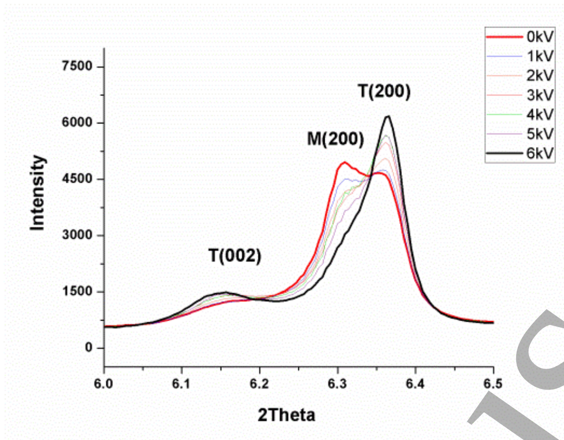

Figure 4. Evolution of the {200} diffraction profile during application of DC fields of various amplitudes evidencing an electric-field induced monoclinic to tetragonal phase transition

Zero Field Cooled (ZFC)–Field Cooled (FC) measurements [Figure 5] were performed to investigate the magnetization (M) behaviour of the sample as a function of temperature (T) in both directions. A relatively low field of 10 mT was applied for these measurements. The ZFC-FC curve followed different path throughout the temperature range which indicates ferromagnetic nature of the sample. A broad clear split between the ZFC–FC curves was observed below 100K, which could be due to the possible existence of secondary phase/inclusion [32-35]. It may be the size of secondary phase is very small (below single domain size) which behaves like super paramagnetic [24, 35].

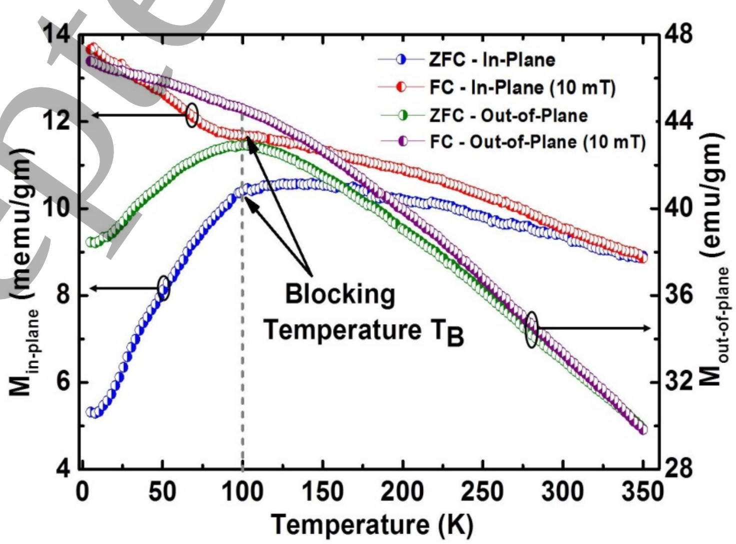

Figure 5. ZFC-FC plot and M vs H loops (inset) for both in-plane and out-of-plane directions for 60:40 BFPT made from TGG method using 10% $BaTiO_3$ as templates.

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Ferromagnetic behaviour of the sample can also be seen from the magnetization measurements as a function of applied magnetic field for both in-plane and out-of-plane directions [Figure 6]. Hysteresis loops (M-H) are measured in along the normal and tape-cast directions at different temperatures as shown in Figure 6(a) and (b). It is observed that the coercivity (H_C) and remanence (M_R) varies with temperature in a non-monotonic way where H_C remains same for both directions with temperature variation [Figure 6(c)], whereas value of M_R along out-of-plane direction being always slightly higher than that along in-plane direction [Figure 6(d)]. The coercivity (H_C) in both directions reduces as the temperature decreases from 300K to below 100K and then rises as the temperature is further reduced to 5K. This is contrary to the common behavior where H_C normally increases with reduction of temperature [36, 37]. Hence, such decrease in H_C and M_R above 100K and increase below 100K can only happen if two phases coexist. Since, the secondary phase is possibly super paramagnetic in nature with blocking temperature ~100K, the H_C and M_R increase at low temperature [24, 35]. At room temperature the coercivity is ~ 0.095 T along both the directions of measurement, whereas the remanent magnetizations (M_R) are ~0.08 emu/gm and ~0.07 emu/gm along out-of-plane and in-plane directions at room temperature (300K) respectively; the saturation magnetization (M_S) is ~0.17 emu/gm for both cases.

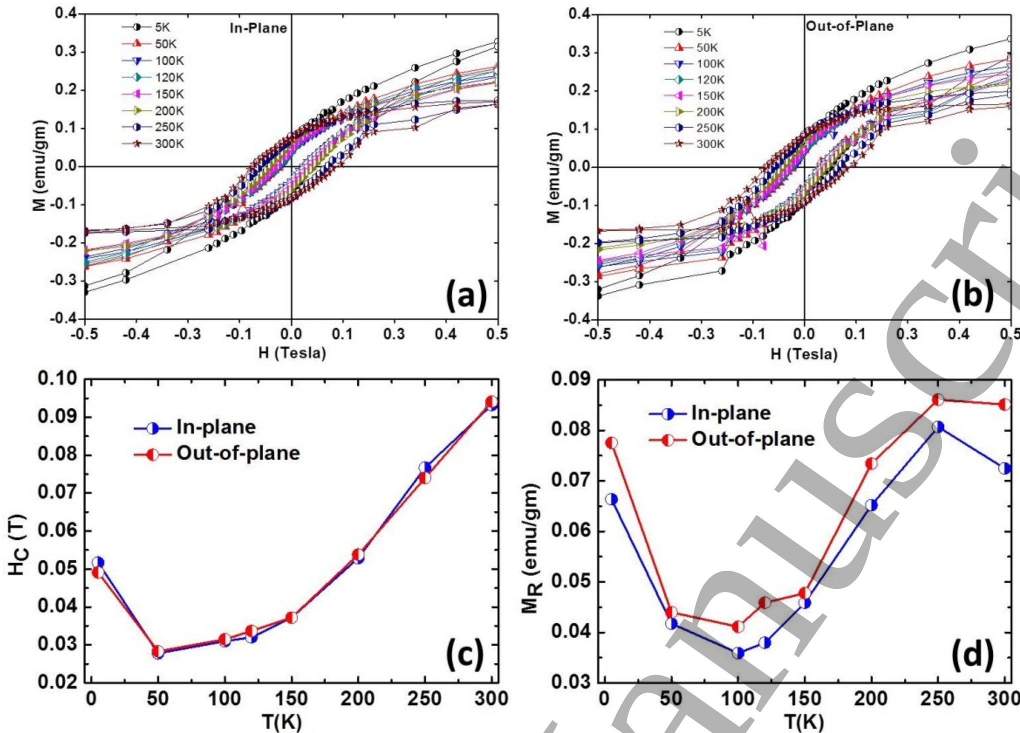

Figure 6. The M vs H loops at different temperatures for both (a) in-plane and (b) out-of-plane directions. Variation of (c) Coercivity and (d) Remanence with temperature for 60:40 BFPT made from TGG method using 10% $BaTiO_3$ as templates.

SQUID magnetometer data is in agreement with works who reported ferromagnetism in Ba-doped $BiFeO_3$ [38-42], that is, antiferromagnetic $BiFeO_3$ transforms to ferromagnetic ordering by doping with Ba^{2+}. Das *et al.* reported the magnetization of 1.2 emu/g for $Bi_{0.85}Ba_{0.15}FeO_3$ [38]. Change in spin canting or spiral spin modulation due to Ba doping could lead to the ferromagnetic response [38-40].

Since there is no such big difference between in-plane and out-of-plane magnetic measurements, it can be concluded that the sample is magnetically isotropic. However the synchrotron results of the 60:40BFPT sample, prepared by the templated grain growth method suggests a slight {00*l*} crystallographic texturing which might not be strong enough to induce a directional dependent magnetic response.

In addition, as shown elsewhere [32, 33] an existence of secondary phase could dominate the ferromagnetic behaviour. Thus, it can be inferred that the observed magnetization is entirely due to the magnetically isotropic Fe rich secondary phase e.g. $BaFe_2O_4$ or Fe_3O_4 [32, 33]. The existence of iron rich secondary phase can be only confirmed by detailed phase analysis such as high resolution transmission electron microscope (HRTEM) [32-34].

4- Conclusion

In conclusion, synchrotron radiation experiments highlight differences in crystallographic orientation between tape cast direction, and normal to the cast direction suggesting that textured mixed tetragonal/monoclinic BFPT has been synthesized. By applying the external electric field of 6kV, the obtained material transformed to predominately tetragonal phase. Although analysis show the synthesis of textured 60:40BFPT, the isotropic magnetic measurement is not in agreement with the anisotropic crystallography results of the material. This could reveal either the existence of slightly textured material or the significant influence of secondary magnetic phase which has dominated the magnetic properties of the main phase.

5- Aknowledgement

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