**Proceedings Paper:**

Palizdar, M, Mallick, D, Maity, T et al. (11 more authors) (2014) Texture analysis of thick bismuth ferrite lead titanate layers. In: Applications of Ferroelectric, International Workshop on Acoustic Transduction Materials and Devices and Workshop on Piezoresponse Force Microscopy, ISAF/IWATMD/PFM 2014. 2014 Joint IEEE International Symposium on the Applications of Ferroelectric, International Workshop on Acoustic Transduction Materials & Devices & Workshop on Piezoresponse Force Microscopy, 12-16 May 2014, State College, Pennsylvania. Institute of Electrical and Electronics Engineers , 1 - 3. ISBN 9781479938605

https://doi.org/10.1109/ISAF.2014.6922999

# *Texture analysis of thick bismuth ferrite lead titanate layers*

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***Abstract*— The template grain growth technique was used to synthesis textured 60BiFeO3-PbTiO3 (60:40BFPT) by using platelets of BaTiO3 as template. Synchrotron measurement clearly showed textured 60:40BFPT. Moreover, in situ high energy synchrotron radiation was employed to investigate the influence of an external electric filed on crystallographic structure of mixed phase 60:40BFPT. Application of an electric field ≥ 1 kV/mm resulted in phase transformation from mixed rhombohedral/tetragonal phases (≈ 73.5% tetragonal / 26.5% rhombohedral) to predominately tetragonal phase (≈ 95%) at applied field of 6 kV/mm. A crystallographic texture refinement was done by using software package materials analysis using diffraction (MAUD) with a $4^{th}$order spherical harmonic orientation distribution function (ODF). This refinement was completed using a P*4mm*+*Cm* structure model. Texture coefficients were constrained such that the equivalent texture coefficients of each phase are the same. The resulting texture refinement determined that sample has a 1.3 multiples of random distribution (MRD) {100} crystallographic texture.**

***Keywords- Texture; Synchrotron; Phase transformatio;Refinment***

## I. INTRODUCTION

In the past few decades lots of investigations have been done on materials with a morphotropic phase boundary to understand their possible phase transition behavior around the morphotropic phase boundary (MPB). The induced phase transition between the ferroelectric tetragonal and rhombohedral phases was highlighted first by Park in piezoelectric materials by applying external electric fields [1, 2]. The phase transition which was reported by Park resulted in a large $d_{33}$. Concequently, this encouraged different scientific groups in order to induce strain via phase transition inside the materials. To do so, alignment of the dipoles is critical. A material with an entirely random dipole direction has a high potential energy to transform, which precludes a phase transition. Hence, both single crystals and textured materials are points of interest in this regard. However, phase transition in polycrystalline materials have been reported before, for example in $PbZr_xTi_{(1-x)}O_3$ (PZT) as well as $K_{1/2}Bi_{1/2}TiO_3$-$Na_{1/2}Bi_{1/2}TiO_3$ (KNBT) during the poling [3].

It is complicated to synthesis single crystals either process wise or price wise. Consequently, there is more intendancy to deal with textured structures.

Bismuth ferrite and lead titanate (BFPT) possesses a morphotropic phase boundary (MPB) between the rhombohedral and tetragonal, with a spontaneous strain of 18% on the tetragonal side of the boundary. This considerable amount of strain is a good motivation in order to study about the possibility of employing phase transition in order to create high distortion inside the material.[4]. It is possible that this crystallographic distortion could be harnessed during transformation, generating unprecedented electric field induced strains. In addition, in BFPT the antiferromagnetic Néel temperature drops by approximately 300K on crossing the MPB from the rhombohedral to the tetragonal side [5]. It is of interest to investigate the influence of field-driven rhombohedral-tetragonal phase transitions across the MPB, to determine whether correctly oriented BFPT can provide both giant piezoelectric properties and significant magnetoelectric coupling, ultimately, turning antiferromagnetic ordering off and on.

In the current investigation the textured 60:40BFPT has been studied to evaluate the influence of applied external electric field. Furthermore, the synchrotron analysis was employed for texture investigation. Moreover, the magnetic properties of the specimen were studied.

## II. EXPERIMENTAL

60:40BFPT which was made by using template grain growth method as detailed in [6,7]. Platelets of $BaTiO_3$ were supplied by Penn State and Anadolu Universities which were synthesized via the molten salt method [8].

Synchrotron diffraction was carried out at Beam I15 at the Diamond Light Source facility (Oxfordshire, UK). Sample bars were placed in a thin polypropylene oil bath and submerged in silicone oil, to avoid any electrical breakdown which would be

**978-1-4799-3860-5/14/$31.00 ©2014 IEEE**

caused through air. A monochromatic beam X-rays of high energy was incident on the 1 x 6 $mm^2$ bar surface, while a voltage was applied across the 1 mm dimension, in 1 kV $mm^{-1}$ steps. Synchrotron data was collected using a 2D detector (MAR 3450). The Debye rings were "caked" into individual 2θ-intensity diffraction patterns, at +/- 5° between ψ = 0° and 355° as reported by Royles and Jonnes [3, 9].

Room temperature magnetic measurements were carried out using a SQUID magnetometer (superconducting quantum interference device, Quantum Design USA; Model MPMS XL5) over an applied magnetic field range of ±2 Tesla.

## III. RESULTS

The effect of external applied electric field on the diffraction patterns of 60:40BFPT has been shown at figure 1. It shows that upon the application of an electric field a significant change to the phase-contributions occurs, as indicated by disappearing of splitted 200 peak at approximately 6.35 Å, showing a transition from mixed phase to single phase. Moreover, 002 tetragonal peak appears by increasing the external field, indicating the gradual formation of a tetragonal single phase. Sample experienced breakdown at field more than 6 kV/mm. Starting the phase transition even after applying low electric field at E=1 kV/mm could suggest the existence of textured structure. This is in agreement with what observed earlier by using synchrotron diffraction for texture analysis of 60:40BFPT [6].

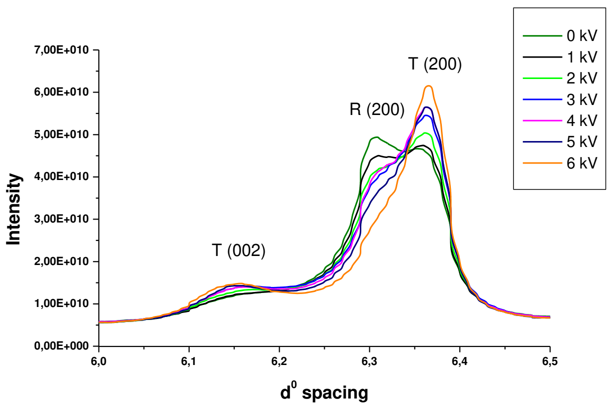


Figure 1. Diffraction patterns for 60:40 BFPT, after the application of electric field.

WinplotR software was used for profile fitting and also calculating the proportion of rhombohedral and tetragonal phases. 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 changed to ≈ 95%. A tetragonal *c/a* ratio of ≈ 1.04 was calculated, somewhat lower than that reported by Comyn *et al.* for 60:40BFPT pellets [9]. This could suggest reaction of the $BaTiO_3$ template with the matrix.

In order to have crystallographic texture refinement which could complete the texture investigation, the software package of materials analysis using diffraction (MAUD) was employed with a 4thorder spherical harmonic orientation distribution function (ODF). It is important to notice that this refinement was completed using a P*4mm*+C*m* structure model. Moreover, the refinement was applied for the sample which had not experiences external electric field.

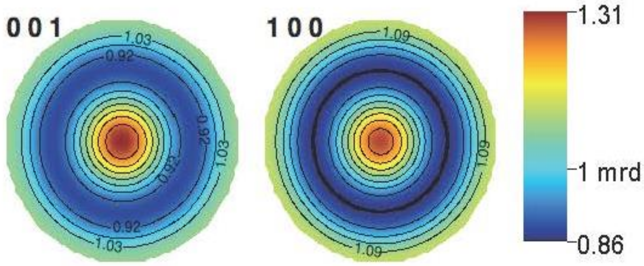


Figure 2. MAUD results for (001) and (100) tetragonal peaks for 60:40 BFPT, at application of zero electric field.

Texture coefficients were constrained such that the equivalent texture coefficients of each phase are the same. The resulting texture refinement determined that sample has a 1.3 multiples of random distribution (MRD) {100} crystallographic texture (Figure 2.). The final refinement error was high because MAUD is not capable of modeling the complex peak shapes observed in observed patterns. In addition, a crystallographic structure refinement using GSAS with two different starting structure models, P*4mm*+R*3m* and P*4mm*+C*m* was used (Figure 3.). The resulting refinements suggested that the diffraction pattern was not representative of randomly oriented samples.

Refinements that used a P*4mm*+C*m* starting model were able to correctly model the high 2theta peak asymmetry in the (111) reflection and capture a high 2theta reflection near the (222). The high 2theta asymmetry of the (111) and high 2theta peak of the (222) could not be modeled using a P*4mm*+R*3m* structure model. These features can be fit to a monoclinic structure. The resulting monoclinic structure that models the (111) and (222) reflections also models the (200) reflection. This leads to this suggestion that the room temperature crystallographic structure of obtained sample is a phase mixture of P*4mm*+C*m*.

The sample was measured in MPMS XL 5 (Quantum Design) SQUID magnetometer to compare the M-H (magnetization vs. applied magnetic field) loops at room temperature (300K) in two different directions perpendicular (in-plane) and parallel (out-of-plane) to the preferred *c*-axis of the oriented BFPT bar sample; the data are shown in Figure 3. The coercivity is ~940 Oe, with a remanent magnetization ($M_R$) of 80 m emu/gm and saturation magnetization ($M_S$) ~170 m emu/gm. The values are nearly same for both out-of-plane and in-plane measurements. The M-H loops confirm the existence of a ferromagnetic phase within the material. 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, which is in contrast into the synchrotron results of the 60:40BFPT sample prepared by the template grain growth method, where it is obvious that there is a considerable degree of texturing.

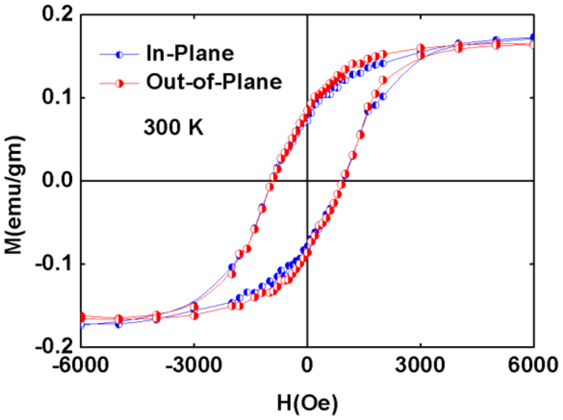


Figure 3. Comparison of M vs H loops for 60:40BFPT at room temperature (300K) with magnetic field perpendicular (in-plane), blue, and parallel (out-of-plane), red, to the preferred c-axis.

The similar in-plane and out-of-plane magnetic data can suggest that the sample is magnetically isotropic, but structurally anisotropic. We can infer from this that the observed magnetization is due entirely to the magnetically isotropic Fe rich secondary phase. We would anticipate that if the textured Aurivillius structure were indeed magnetic, then the resultant magnetic data would be heavily influenced by orientation. However, SQUID magnetometer data is in agreement with work by Das *et al*, who reported ferromagnetism in Ba-doped $BiFeO_3$ [10], that is, antiferromagnetic $BiFeO_3$ transforms to ferromagnetic ordering by doping with $Ba^{2+}$. They reported the magnetization of 1.2 emu/g for $Bi_{0.85}Ba_{0.15}FeO_3$. Hence, rigorous chemical analysis is essential to find out whether there is any magnetic secondary phase in the sample.

## IV. CONCLUSION

In conclusion, synchrotron radiation experiments highlight significant differences in crystallographic orientation between perpendicular and parallel to the cast directions which suggests the existence of the textured structure in BFPT. We show that an electric field induced phase transition occurs for textured 60:40BFPT in the system from mixed phase rhombohedral and tetragonal to predominately tetragonal phase.

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