

Evidence of morphotropic phase boundary displacement in lead-free $(\text{Bi}_{0.5}\text{Na}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ polycrystalline thin films

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Lead-free $(\text{Bi}_{0.5}\text{Na}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ (BNBT) thin films with compositions at $x = 0.055$, 0.100 , and 0.150 were prepared by chemical solution deposition on $\text{Pt}/\text{TiO}_2/\text{SiO}_2/(100)\text{Si}$ substrates. The dielectric behavior of the films was studied, and the ferroelectric-antiferroelectric phase transition observed was used to situate the morphotropic phase boundary (MPB) for compositions with $x \sim 0.100$ (BNBT-10), a value that differs from that reported for bulk materials (BNBT-5.5). Extrinsic effects derived from the thin-film configuration (e.g., microstrains, residual stresses) may be responsible for the shift of the MPB. Consequently, the dielectric permittivity is significantly improved for this composition, showing the best ferroelectric response obtained up to now for films of the BNBT system ($P_r = 13.0 \mu\text{C}/\text{cm}^2$, $E_c = 70 \text{ kV}/\text{cm}$).

Keywords: Dielectrics; Ferroelectrics; Perovskites; Thin films

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1. Introduction

Lead-free electronic materials based on multioxide ceramics have experienced renewed interest in the last decade mainly motivated by the strict environmental regulations that are being enforced worldwide [1]. Among them, the $(\text{Bi}_{0.5}\text{Na}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ (BNBT) solid solution is attracting considerable attention owing to the morphotropic phase boundary (MPB) formed between its respective end members; the rhombohedral $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ and the tetragonal BaTiO_3 perovskites [2]. Similar to other lead-based compositions such as $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) or $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$, the electromechanical properties of BNBT ceramics are maximized at the MPB. Thus, a piezoelectric coefficient of $d_{33} \sim 450$ pC/N and an electric-field-induced strain up to 0.25% are obtained in BNBT single crystals at the MPB composition with $x = 0.06$ [3]. Bulk ceramics of MPB-BNBT display still high piezoelectric coefficients ($d_{33} \sim 125$ pC/N; ~ 200 pC/N for textured samples), with a strong ferroelectric polarization at room temperature ($P_r \sim 40$ $\mu\text{C}/\text{cm}$) [2,3]. This actuator performance is at present among the highest ones observed in ceramic materials, very close to commercial PZT and to the most investigated lead-free system, $(\text{K,Na})\text{NbO}_3$ (KNN) [4]. The integration of this material in thin-film form is therefore of large interest due to its potential use in microelectronic devices with optimum electrostrictive or piezoelectric actuation [5,6]. Recent publications have therefore been devoted to BNT-BT films [7-10], although most of them focused on processing issues. In a previous work [10] we reported on the synthesis of BNBT solutions by a novel sol-gel method, where the film properties related to system composition were not investigated in detail. It is expected that due to the different constraints of thin films, important extrinsic effects appear in these materials, which may produce variations in the phase diagram with respect to the bulk values [11]. Structural studies by XRD and Raman spectroscopy on

BNBT films prepared by pulsed laser deposition (PLD) have suggested the shift of the MPB toward higher BaTiO₃ concentrations with respect to bulk ceramics, although support by electrical data was not provided [7,8]. Therefore, the determination of the composition at which the best properties of the films are obtained is still an open issue.

In this letter, we report on (Bi_{0.5}Na_{0.5})_{1-x}Ba_xTiO₃ films with compositions close to the reported MPB of this system for bulk materials ($x = 0.055, 0.100, 0.150$), and prepared by chemical solution deposition (CSD) on Pt/TiO₂/SiO₂/(100)Si substrates. The MPB nature of the films was investigated in relation to their dielectric and ferroelectric characteristics.

2. Experimental

Details of solution synthesis and processing conditions for the fabrication of the films can be found elsewhere [10]. The crystalline phases developed in the films were studied by X-Ray Diffraction (XRD) using a Bruker D8 Advance diffractometer with Cu anode ($\lambda_{\text{Cu}} = 1.54 \text{ \AA}$). Supporting analysis by XRD was also carried out in solution-derived powders calcinated at 900 °C for 1 h. Top platinum electrodes were sputtered on the films using a shadow mask. The variation of the dielectric constant and loss tangent with temperature was measured using a HP 4284A precision LCR meter. Ferroelectric hysteresis loops were obtained by means of a virtual ground set up circuit, using a HP 8116A pulse generator to produce sinusoidal electrical excitation with 1 kHz frequency and maximum amplitude of 10 V.

3. Results and discussion

Figure 1 shows the X-ray diffraction diagrams of the films of this work, denoted as *BNBT-5.5*, *BNBT-10*, and *BNBT-15* ($x = 0.055$, 0.100 , and 0.150 , respectively). All of them present the characteristic reflections of a randomly-oriented perovskite structure, without any trace of secondary phases. The strong peak observed at $2\theta \sim 38.1^\circ$ could be attributed to an intermetallic Bi_xPt phase, formed between the BNBT film and the platinum bottom electrode of the substrate [12]. On the other hand, the clear shift in the peak maxima of the (200) reflection (see inset *i*) when x increases provides evidence for the structural changes derived from the incorporation of Ba^{2+} into the $(\text{Bi}_{0.5}\text{Na}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ system. Unlike XRD analysis of bulk materials, the broadening of the peaks, consequence of the small grain size and large microstrains usually found in polycrystalline thin films, prevents a more detailed study on the structural coexistence of both rhombohedral and tetragonal phases at the MPB. Instead, a pseudocubic structure can only be inferred from these results for all the films of this work. The deformation of the unit cell in the film due to the clamping of the substrate can be clearly observed in the inset *ii* of this figure, which compares the respective 100 peaks of the film and the bulk powder obtained for the BNBT-15 composition. In the last one, the reflection corresponding to the 100 peak is accompanied by a shoulder associated with the 001 peak of the perovskite, indicative of the larger tetragonal symmetry expected for this composition. Although tetragonality is not detected in the equivalent film for the aforementioned reasons, the displacement of the (100) reflection toward higher 2θ angles demonstrates the deformation in the lattice parameters produced in the BNBT films, which is relaxed when the constraints of the substrate disappears, as previously reported [13].

The variations of the dielectric constant (K') and loss tangent ($\tan\delta$) with temperature are shown in Figure 2. A broad anomaly around 290°C is observed for all the films which corresponds to a diffuse antiferroelectric-paraelectric (AF-P) phase transition

originally reported by Takenaka et al. [2] for bulk ceramics. The exact temperature values for this transition, calculated from the derivative of the respective dielectric curves (not shown), are 292, 288, and 298 °C for the corresponding BNBT-5.5, BNBT-10, and BNBT-15 films. In the aforementioned work, the authors made use of a maximum observed in the $\tan\delta$ curve to define the position of a second anomaly produced at lower temperatures, which they ascribed to a ferroelectric-antiferroelectric (F-AF) phase transition. Based on this interpretation, the F-AF transitions in our films occur at ~200, ~150, and ~225 °C for BNBT-5.5, BNBT-10, and BNBT-15, respectively. In this last film, the F-AF transition is accompanied by a second maximum in the dielectric permittivity curve (marked at 228 °C) not detected in the other two. Figure 3 shows the phase diagram originally proposed for the $(\text{Bi}_{0.5}\text{Na}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ system [2], where the phase transitions measured for the BNBT films of this work have been included for the sake of comparison. It can be seen that the transition temperatures follow similar tendencies for bulk ceramics and thin films, but shifted in composition. To illustrate this shift, the expected area for the AF region in the films has been shaded. By analogy, we can say that the MPB in these films is close to compositions with $x = 0.100$, in contrast to $x = 0.06-0.07$ for the corresponding bulk ceramic. This compositional displacement may be explained on the basis of extrinsic effects arisen from the thin-film configuration. The different nature of the films with a high surface to volume ratio (i.e., low thickness) and fine-grained microstructures is usually relevant, due to the important size effects derived in MPB ferroelectrics. Additionally, the stresses induced by the substrate produce lattice distortions in the crystal [13-15] that must be considered, as they define the position of the MPB. In our case, the different thermal expansion coefficients of film and substrate, and the subsequent stress generated in the film, may explain that the lattice parameters of the BNBT films do not correspond to those

of the corresponding bulk materials with the same composition, where the clamping to a substrate is not present [13]. The residual stress in the films would therefore account for their reduced lattice parameters with respect to the bulk ceramics (see peak displacement to higher 2θ angles at inset *ii* of Fig. 1), denoting a larger rhombohedral symmetry in the BNBT cell responsible for the shift of the MPB observed.

To corroborate the shift of the MPB in the films, we can consider that the dielectric and ferro-piezoelectric properties of these materials are expected to significantly improve in the vicinity of the MPB. The BNBT-10 film of this work shows maximum K' values of ~ 1560 , while those corresponding to the BNBT-5.5 and BNBT-15 films are between 900-1030. Figure 4 displays the compensated ferroelectric hysteresis loops of the films, i.e., without any non-switching contributions [16]. The BNBT-10 film shows a remanent polarization of $13.0 \mu\text{C}/\text{cm}^2$, in contrast to the lower values obtained for the BNBT-5.5 ($6.4 \mu\text{C}/\text{cm}^2$) and BNBT-15 ($3.8 \mu\text{C}/\text{cm}^2$) films, in all cases with a coercive field relatively low, around $70 \text{ kV}/\text{cm}$. All these results point that the MPB in these films is situated closer to $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.9}\text{Ba}_{0.1}\text{TiO}_3$ ($x = 0.100$), where the highest polarization values in thin-film form reported to date are obtained. The large dielectric and ferroelectric properties measured at this MPB composition makes it promising for their potential use in microelectronic devices.

4. Conclusions

The ferroelectric-antiferroelectric phase transition temperature found out in the BNBT-10 ($x \sim 0.100$) film together with its superior dielectric and ferroelectric properties, in comparison with the results of the other compositions studied in this work, allowed us to situate the morphotropic phase boundary (MPB) of this system, in the vicinity of this composition. This result implies a displacement of the boundary to BT rich compositions in

comparison with bulk ceramics in this solid solution. The existence of a composition displacement in the MPB must be taken into account in the design of lead-free piezoelectric or electrostrictive thin-film devices.

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Figure Legends

Fig.1. XRD patterns of the BNBT films of this work. Inset *i* shows magnification of the (200) reflection. Inset *ii* compares the respective (100) reflections of the film and the bulk powder obtained for the BNBT-15 composition.

Fig.2. Variation of dielectric constant (K') and loss tangent ($\tan\delta$) with temperature of the BNBT films of this work, measured at several frequencies.

Fig.3. Phase diagram of the BNBT system (after [2]) where the phase transitions of the films of this work are included (F: ferroelectric, AF: antiferroelectric, P: paraelectric). Shaded area illustrates the shift of the expected AF region for the films with respect to bulk materials.

Fig.4. Compensated ferroelectric hysteresis loops of the BNBT films of this work. Insets show (left upper) experimental loops measured at room temperature and 1 kHz, and (right lower) non-switching contribution coming from capacity and conductivity of the sample.

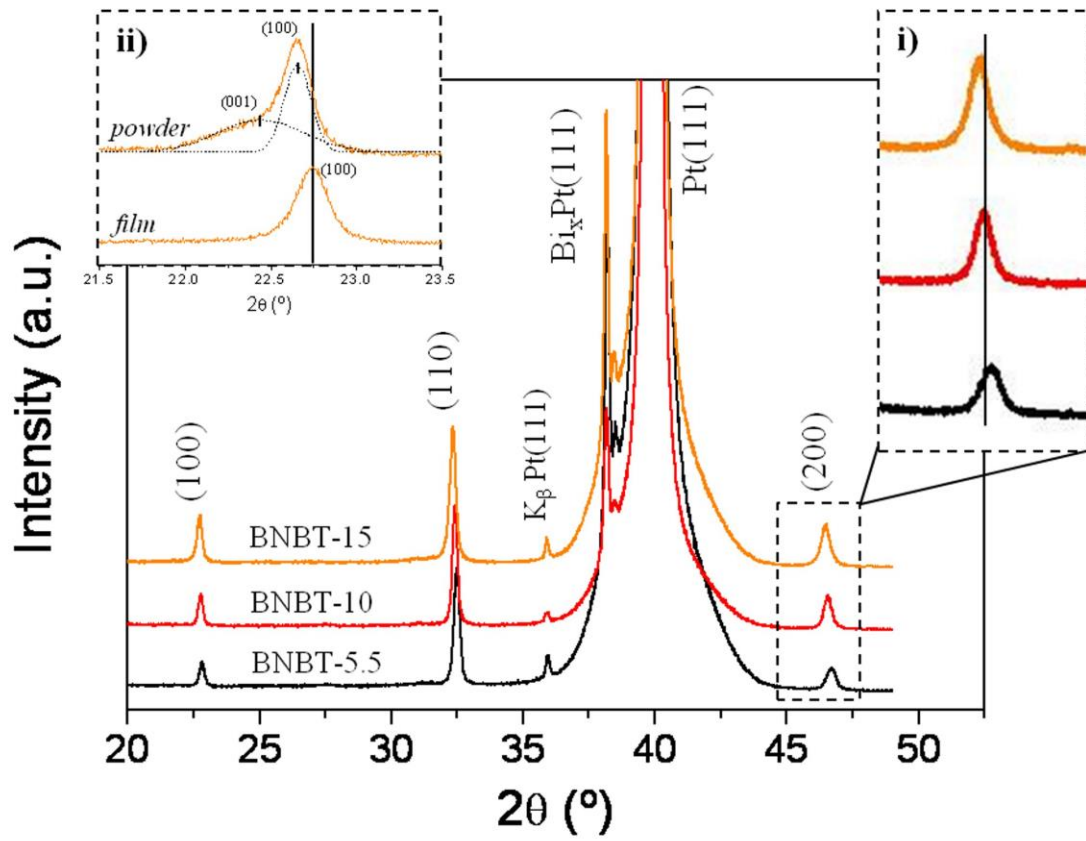


Figure 1

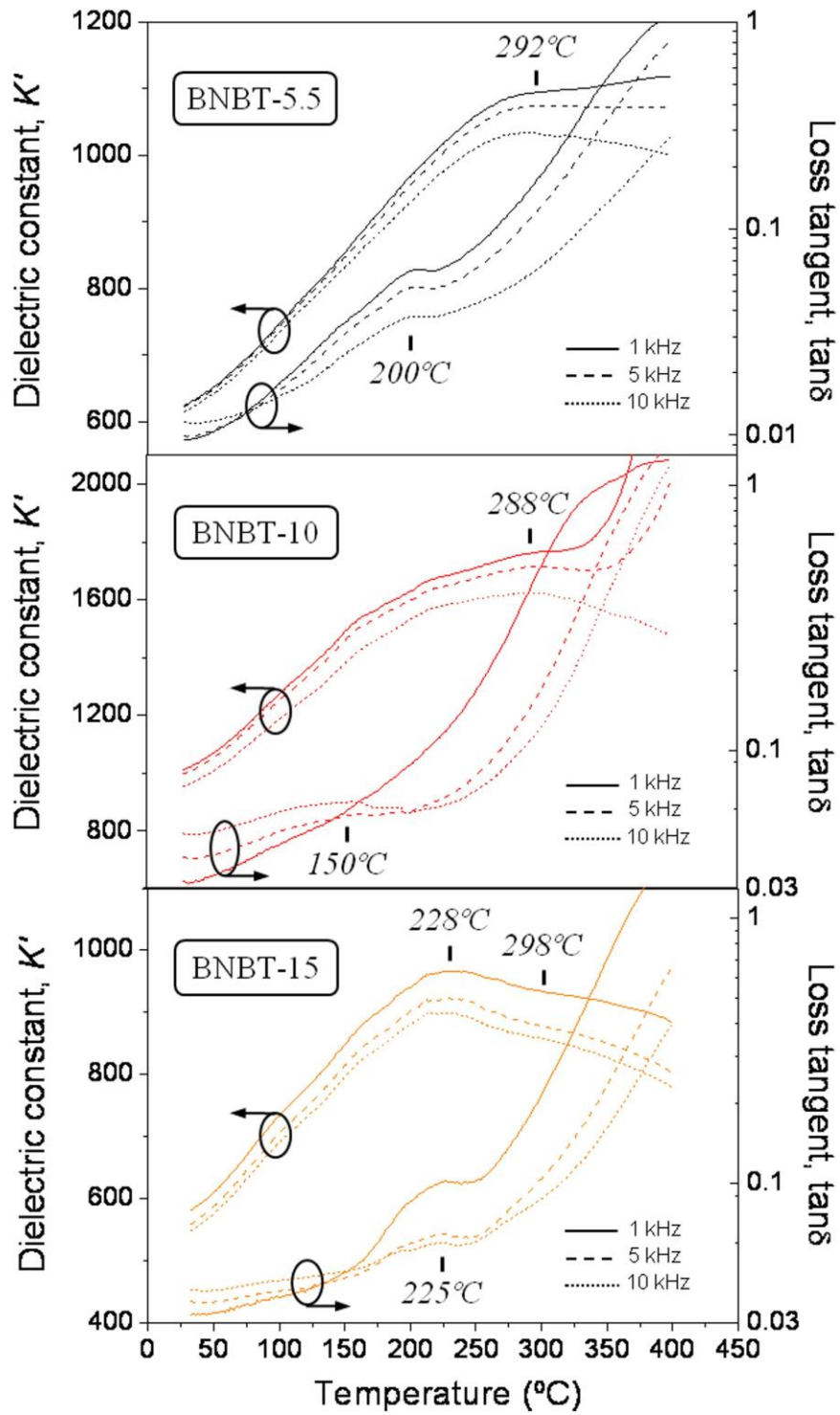


Figure 2

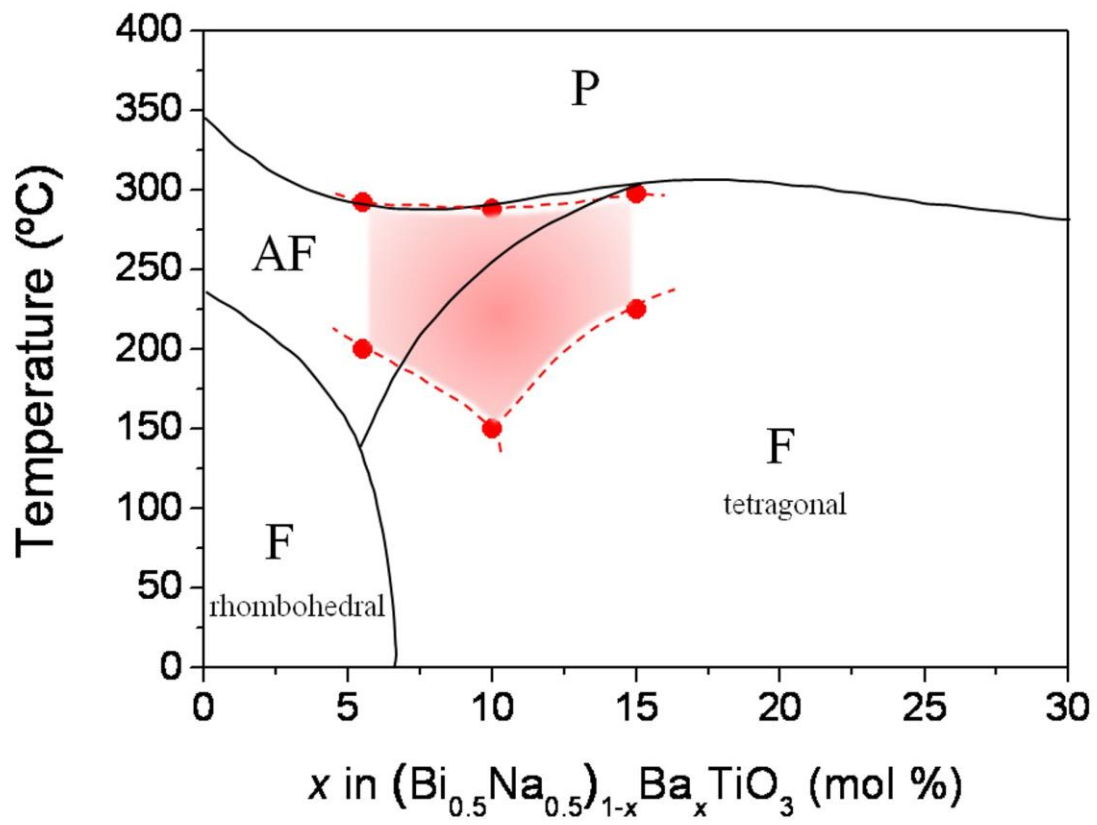


Figure 3

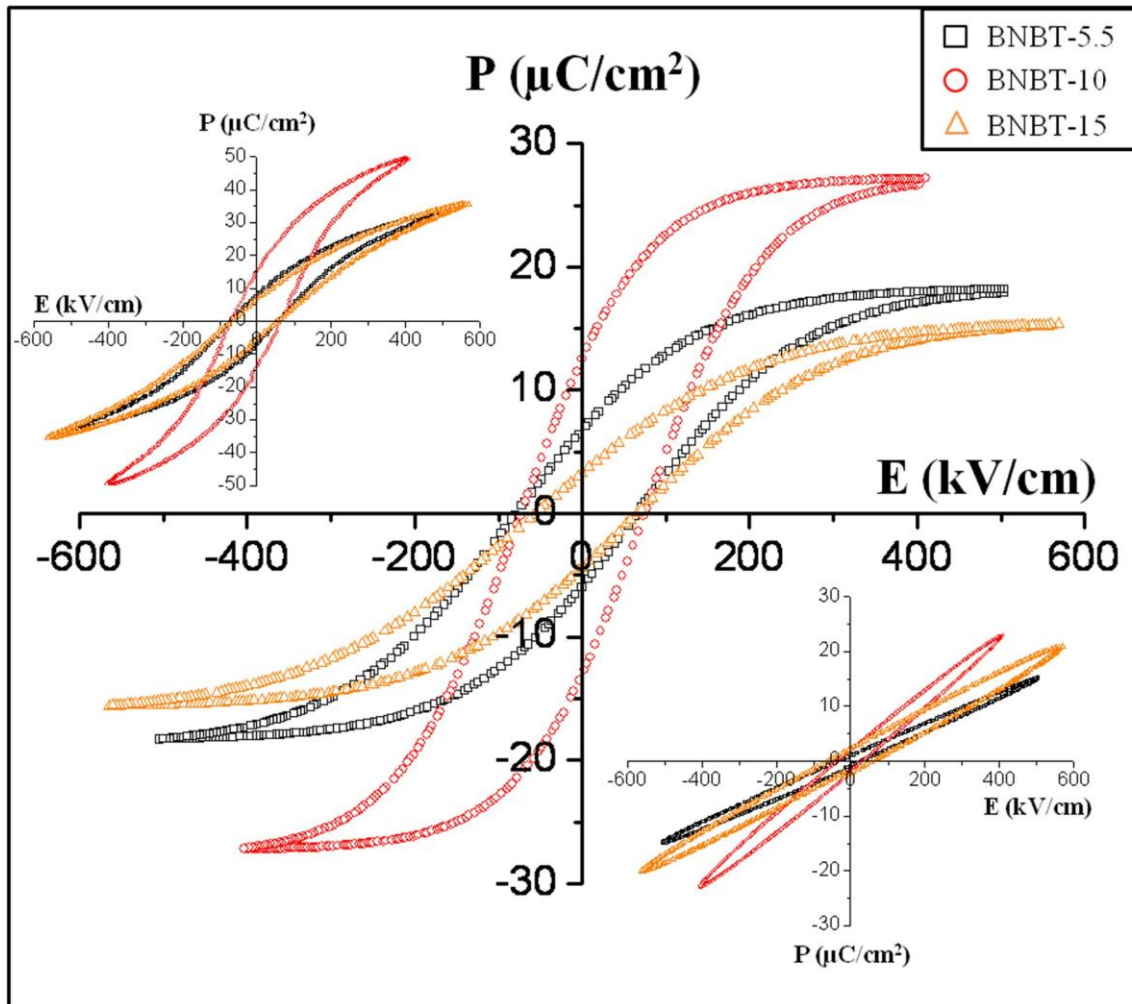


Figure 4