Dielectric and ferroelectric properties of (Bi$_{0.5}$Na$_{0.5}$)TiO$_3$ – (Bi$_{0.5}$K$_{0.5}$)TiO$_3$ – BaTiO$_3$ thin films deposited via chemical solution deposition

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Abstract

Polycrystalline ferroelectric lead-free 85 mol%(Bi$_{0.5}$Na$_{0.5}$)TiO$_3$ – 10 mol%(Bi$_{0.5}$K$_{0.5}$)TiO$_3$ – 5 mol% BaTiO$_3$ (85BNT – 10BKT – 5BT) thin films were fabricated via chemical solution deposition on platinized silicon substrates. The permittivity and dielectric loss at 1 kHz were 610 and ~3.5 %, respectively. The ferroelectric properties at room temperature and as a function of the temperature up to 125 °C were also investigated. The polarization hysteresis loop at room temperature showed a P$_{\text{MAX}}$ of 31 μC/cm$^2$ and P$_{r}$ of 6 μC/cm$^2$ at 200 Hz. The shapes of the hysteresis loops at room temperature and 125 °C were nearly identical, indicating good temperature stability. A dense surface morphology was observed and cross sectional microscopy revealed equiaxed grain growth. Based on these measurements, 85BNT – 10BKT – 5BT thin films may be a good candidate for lead-free piezoelectric-based microelectromechanical systems (MEMS).
1. Introduction

In the past few decades lead-based piezoelectric materials, represented by Pb(Zr,Ti)O$_3$ (PZT) and PZT-based solid solutions have been widely used in many electronic devices because they show the highest performing piezoelectric properties.[1-3] However, recent environmental legislation in the European Union, such as Waste from Electrical and Electronic Equipment (WEEE), Restriction of Hazardous Substances (RoHS), and End-of Life Vehicles (ELV), have sought to limit the usage of toxic elements.[4] The toxicity of lead oxide in PZT[5] and its high vapor pressure during processing have led researchers to develop new, environmentally benign piezoelectric materials as potential replacements for PZT-based materials.

Bismuth sodium titanate, (Bi$_{0.5}$Na$_{0.5}$)TiO$_3$ (BNT) was one of the earliest lead-free piezoelectric material candidates. In bulk form it exhibits good ferroelectric properties, with $P_r = 38 \mu$C/cm$^2$ and was long thought to have rhombohedral symmetry.[6, 7] Recent reports have shown that the structure of BNT is more complex; with Cc monoclinic symmetry and other structural features on different length scales.[8] However, BNT ceramics do not readily exhibit very strong piezoelectric properties because of the difficulty to pole the material due to the large coercive field, $E_c (=73$ kV/cm).[9] To improve the piezoelectric properties, BNT-based solid solutions formed with many other perovskite materials such as BaTiO$_3$ (BT), (Bi$_{0.5}$K$_{0.5}$)TiO$_3$ (BKT), NaNbO$_3$ (NN), Bi(Zn$_{0.5}$Ti$_{0.5}$)O$_3$ (BZT), and Bi(Mg$_{0.5}$Ti$_{0.5}$)O$_3$ (BMT) have been developed.[9-13] In particular, many researchers have investigated a ternary solution based on BNT – BKT – BT in the vicinity of a
morphotropic phase boundary (MPB). This system revealed good piezoelectric performance with a high $d_{33}$ of 181 pC/N and $k_p$ of 0.56.\cite{9, 14-16} Achieving this behavior in bulk materials is promising, however many of the ultimate applications of these systems will be in thin film form (i.e., MEMS devices). Thus, it is important to verify that this performance can also be achieved in thin film embodiments.

Due to the anisometric nature of thin films, and the difficulty in controlling the stoichiometry because of the inherently volatile A-site elements (Bi, Na, and K), an increased electrical conductivity is often observed in these materials. As a result, obtaining a large and reliable piezoelectric response is often challenging in thin films.\cite{17, 18} In previous work on BNT–BKT-based thin films\cite{19, 20}, high quality films on Pt/TiO$_x$/SiO$_2$/Si were fabricated by chemical solution deposition using an appropriate amount of excess cations (overdoping). These films showed good maximum polarization ($P_{\text{MAX}}$) and remanent polarization ($P_r$) values at low frequencies (200 Hz) with $P_{\text{MAX}} = 45 \mu\text{C}/\text{cm}^2$ and $P_r = 16 \mu\text{C}/\text{cm}^2$ for BNT–BKT films and $P_{\text{MAX}} = 52 \mu\text{C}/\text{cm}^2$ and $P_r = 12 \mu\text{C}/\text{cm}^2$ for BNT–BKT–BMgT films, respectively. For the closely related BNT-BKT-BT ternary system, Abazari et al. reported on 88BNT–8BKT–4BT epitaxial thin films synthesized by pulsed laser deposition on SrRuO$_3$ coated SrTiO$_3$ substrates.\cite{21} These showed a saturated polarization hysteresis loop with a large $P_r = 30 \mu\text{C}/\text{cm}^2$. Polycrystalline thin films of BNT–BKT–BT, however, have not yet been investigated. In this study, 85BNT–10BKT–5BT (near MPB composition) thin films were synthesized on Pt/TiO$_x$/SiO$_2$/Si substrates via chemical solution deposition and their structural and electrical properties were investigated.
2. Experimental Procedure

Bismuth acetate Bi(OOC$_2$H$_3$)$_3$, sodium acetate trihydrate Na(OOC$_2$H$_3$)•3H$_2$O, potassium acetate K(OOC$_2$H$_3$), barium acetate Ba(OOC$_2$H$_3$)$_2$, and titanium isopropoxide Ti[OCH(CH$_3$)$_2$]$_4$ were used as precursors. Acetic acid and propionic acid were chosen as solvents. First, titanium isopropoxide was chelated with acetylacetone in a molar ratio of 1:2 in a dry atmosphere to prevent hydrolysis, as shown in previous studies.[22, 23] Next, potassium acetate, sodium acetate trihydrate, and barium acetate were dissolved in acetic acid at 70 °C. Bismuth acetate was dissolved separately in propionic acid at room temperature. As previously reported [20], to compensate for the volatility of the A-site cations, 20 mol% excess potassium and sodium and 10 mol% excess bismuth were added to their corresponding solutions. The final mixture was achieved by pipetting an appropriate weight of the Bi, Na, K, and Ba solution into the Ti solution in order to achieve a final concentration of approximately 0.3 molarity.

The precursor solution was spin-cast on 100 nm Pt/33 nm TiO$_x$/500 nm SiO$_2$/Si substrates at 3000 rpm for 30 seconds. After each spin, the film was pyrolyzed at 300 °C for 5 min on a hot plate and annealed in air at 700 °C in a preheated furnace for varying times. The annealing and pyrolysis conditions were adopted from previous work on BNT – BKT thin films[19], with the first layer annealed for 30 min and subsequent layers annealed for 10 min each. The films were comprised of 6 total spin cast layers. The phase purity of the films was confirmed using X-ray diffraction (XRD, Bruker, AXS D8 Discover). Film thickness
was obtained via variable angle spectroscopic ellipsometry (J. A. Woollam, V-VASE).

Thermally evaporated silver electrodes (0.2mm diameter) were deposited through a shadow mask for electrical measurements. An impedance analyzer (HP 4192A) was used to obtain dielectric properties at a 50 mV oscillation level. Polarization hysteresis loops up to 125 °C were recorded using a ferroelectric tester (aixACCT Systems GmbH, TF Analyzer 2000HS system). The microstructure of the crystallized films was observed via scanning electron microscopy (SEM, FEI Quanta 600F).

3. Results and discussion

A representative XRD pattern of an 85BNT – 10BKT – 5BT film is shown in Figure 1. Perovskite phase with no second phase formation was observed, with the pattern indexed according to a pseudo-cubic perovskite structure. Similar to previous work on BNT – BKT thin films[19], the (110) peak showed the strongest intensity, with the films having an overall random orientation. The thickness of the crystallized film was approximately 240 nm.

Figure 2 shows the permittivity and dielectric loss as a function of frequency for a typical 85BNT – 10BKT – 5BT thin film at room temperature. As the frequency increased from 100 Hz to 100 kHz, the permittivity decreased from 640 to 550, as is very common for high permittivity materials. The dielectric loss remained relatively stable over this frequency range, with only a slight increase at lower frequencies. The permittivity and dielectric loss at 1 kHz were 610 and ~3.5%, respectively.

Compared to the work reported by Abazari, et al. the permittivity at 1 kHz is similar but the dielectric loss here is lower.[21] However, it is difficult to compare directly
with these previously reported BNT – BKT – BT films as those films were grown on different substrates with very different crystallographic orientation (epitaxial vs. polycrystalline). A lower dielectric loss (<6.5%) over the frequency range measured here is a strong indication of a lower defect concentration in these films.

Figure 3 shows polarization-electric field hysteresis loops (PE loops) at different measuring conditions. First, in Figure 3(a), PE loops at room temperature were measured at 200 Hz. The shape of the loop indicates good ferroelectric behavior, with maximum and remanent polarizations at 360 kV/cm of 31 µC/cm² and 6 µC/cm² respectively. Considering that the \( P_r \) of bulk BNT – BKT – BT is typically over 30 µC/cm², here the \( P_r \) is only 20% of that of the bulk ceramic value.[24, 25] This could be attributed to being slightly off the morphotropic phase boundary composition or to the very different morphology and stress states in thin films compared to bulk.[26, 27] Polarization hysteresis loops taken at +/-370 kV/cm and 500 Hz as a function of temperature up to 125 °C are displayed in Figure 3(b). The polarization values for these 85BNT – 10BKT – 5BT thin films were very stable as a function of temperature, and the shape of the loops changed very little. Both \( P_{MAX} \) and \( P_r \) at room temperature and 125 °C were nearly identical; approximately 32 µC/cm² and 6 µC/cm², respectively. Hysteresis loops above this temperature range (> 125°C) became highly rounded in shape, which is indicative of conduction and defect migration beginning to occur. For loops measured at lower frequencies (i.e., 200 Hz, not shown) this electrically lossy behavior was apparent at lower temperature, indicating some optimization of process conditions is still necessary.
Nevertheless, good polarization hysteresis loops at 200 Hz and room temperature were observed with temperature stability demonstrated at 500 Hz.

Figure 4(a and b) shows the surface morphology and cross-sectional image of a 85BNT – 10BKT – 5BT thin film by SEM. There are many “clusters” present on the film surface, which consist of small grains. Outside of these clusters, the grain size is approximately 80 - 100 nm. Pores or voids, which could result from solvent evaporation or carbon oxidation during heat treatment of the film, were not observed. Previous work on 80BNT – 20BKT showed some degree of columnar growth in cross-sectional SEM images, however this was not observed in these 85BNT – 10BKT – 5BT thin films (Fig. 4b). Instead, a significant degree of equiaxed growth was observed. Columnar grain growth can be achieved when a heterogeneous nucleation event at the substrate is favored over a homogenous nucleation events within the amorphous gel.[28] To be favored over a homogenous nucleation event, increased crystallization temperatures could lower the driving force for crystallization on the substrate surface. Using higher annealing temperatures to do this could cause two potential issues. First, increasing the crystallization temperature would likely have an adverse effect of the film stoichiometry due to increased volatilization of A-site cations (Bi, Na, and K).

Second, delamination and hillock formation from diffusion of the TiOx adhesion layer due to thermophysical instabilities of the platinized silicon are known to be issues at higher temperatures (>700 °C)[29] Additionally, this type of equiaxed microstructure has been observed in CSD BaTiO3 thin films[22, 28], indicating even 5% BaTiO3 can alter the nucleation and growth mechanism in the films shown here.
It has also been reported that BaTiO$_3$ thin films can show microstructures varying from columnar to fine-grained depending on the thickness of the individually crystallized layers.\[30\] In this study the dependence of the film microstructure on changing solution molarity (and hence thickness of each spin-cast layer) was not explored, but could potentially alter the film morphology from an equiaxed nature to a columnar nature.

### 4. Conclusions

Thin films of the composition 85BNT – 10BKT – 5BT were synthesized via chemical solution deposition. By adopting the processing conditions from previous work on the BNT-BKT-Bi(Mg$_{1/2}$Ti$_{1/2}$)O$_3$ system, phase pure perovskite films were achieved as confirmed by XRD. Excellent dielectric properties were obtained over the frequency range 100 Hz to 100 kHz. The observed permittivity and dielectric loss at 1 kHz were 610 and 3.5%, respectively. Polarization hysteresis loops were obtained at 350 kV/cm and 200 Hz with $P_r = 6 \ \mu$C/cm$^2$ and $P_{MAX} = 31 \ \mu$C/cm$^2$.

Analysis of the film microstructure using SEM revealed fine-grained homogenous film growth. Future investigations of this system should include using seed or buffer layers and the effects of varying solution molarity for different microstructure or nucleation mechanisms. The results of this current work suggest that BNT – BKT – BT thin films are promising candidates for thin film piezoelectric applications.
References


Figure Captions

Figure 1. XRD pattern for a 85BNT – 10BKT – 5BT thin film synthesized with excess cations (+10% Bi, +20% Na, and +20% K).

Figure 2. Permittivity and dielectric loss of a 85BNT – 10BKT – 5BT thin film as a function of frequency.

Figure 3. P-E loops of 85BNT – 10BKT – 5BT thin films (a) at room temperature and 200 Hz and (b) as a function of temperature up to 125 °C at 500 Hz.

Figure 4. Plan view (a) and cross-section (b) SEM images of a 85BNT – 10BKT – 5BT thin film.
Figure 1. XRD θ-2θ pattern for 85BNT–10BKT–5BT thin film synthesized with excess cation concentration in solution (+10% Bi, +20% Na, and +20% K). The Si peak at 33° is from λ/2 of the Si (400)
Figure 2. Permittivity and dielectric loss of a 85BNT – 10BKT – 5BT thin film as a function of frequency.
Figure 3. PE loops of 85BNT – 10BKT – 5BT thin films (a) at room temperature and 200 Hz (b) as a function of temperature up to 125 °C at 500 Hz.
Figure 4. Plan view (a) and cross-section (b) SEM images of a 85BNT – 10BKT – 5BT thin film.