Impact of process conditions on chemical solution deposited BNKT thin film electromechanical properties

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Received: 12 March 2021 / Accepted: 7 June 2021

Published online: 14 September 2021

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Abstract

Phase pure perovskite $(1-x)\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3 - x\text{Bi}_{1/2}\text{K}_{1/2}\text{TiO}_3$ (BNKT) thin films were successfully prepared via an inverse mixing order chemical solution deposition method and the impact of process conditions on film properties were observed. Process conditions evaluated included crystallization temperature and time, ramp rate, pyrolysis temperature, and cation excess. Properties measured included crystal structure, dielectric constant, dielectric loss, piezoelectric response, and ferroelectric response. A few notable trends were observed. A subtle impact on piezoelectric response was observed in films prepared using different ramp rates: 100 °C per second films ($d_{33,f} = 60 \pm 5$ pm/V at 1 kHz), 75 °C per second films ($d_{33,f} = 55 \pm 5$ pm/V) and 150 °C per second films ($d_{33,f} = 50 \pm 5$ pm/V). Films prepared using a 75 °C per second ramp rate displayed slightly higher dielectric loss ($\tan \delta = 0.09$ at 1 kHz) than films prepared using a 100 °C per second ramp rate ($\tan \delta = 0.07$ at 1 kHz) or 150 °C per second ramp rate ($\tan \delta = 0.05$ at 1 kHz). Pyrolysis temperatures greater than 350 °C are necessary to burn off organics and maximize film dielectric constant. Dielectric constant increased from 450 ± 50 at 1 kHz to 600 ± 50 at 1 kHz by increasing pyrolysis temperature from 300 to 400 °C. Excess cation amounts (for compositional control) were also evaluated and it was found films with higher amounts of Na and K excess compared to bismuth excess displayed an increase in $d_{33,f}$ of about 10 pm/V compared to films prepared with equivalent Bi and Na and K excess amounts.

Article highlights

- Impact of processing conditions on inverse mixing order chemical solution deposited bismuth based thin films.

- Dielectric, piezoelectric, and ferroelectric properties of thin film bismuth sodium titanate-bismuth potassium titanate thin films.
- Developing lead-free piezoelectric actuator materials.

Keywords Thin Films · BNKT · Process Optimization · Piezoelectric · Ferroelectric · Dielectric · Lead-Free

MSC 74K35 · 74C05 · 82D45

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s42452-021-04692-4>) contains supplementary material, which is available to authorized users.

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1 Introduction

Piezoelectric materials are those with the innate ability to convert mechanical energy to electrical energy and vice versa. They are used in a variety of applications including actuators, sensors, filters, resonators, and microelectromechanical systems (MEMS). The current industry standard piezoelectric materials, such as lead zirconate titanate (PZT), contain lead. Legislative restrictions on lead content in waste streams, including the Restriction of Hazardous Substances (RoHS) in the European Union are inspiring development of alternative lead-free piezoelectric materials [1–4]. A commonly used method for discovering new lead-free piezoelectric materials is to search for perovskite systems that display a morphotropic phase boundary (MPB) like that found in PZT at 52% lead zirconate and 48% lead titanate. One candidate material identified using this method is $(1-x)\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3\text{-}x\text{Bi}_{1/2}\text{K}_{1/2}\text{TiO}_{1/2}$ (BNKT) which displays a relatively large piezoelectric response making it a material of interest for piezoelectric actuator applications. The BNKT system displays a MPB between $x = 0.16$ and $x = 0.20$ [2, 3, 5].

A considerable number of bulk ceramic studies have optimized the piezoelectric properties of BNKT by introducing disorder via the inclusion of a third endmember such as $\text{BiZn}_{1/2}\text{Ti}_{1/2}\text{O}_3$ (BZT), $\text{BiMg}_{1/2}\text{Ti}_{1/2}\text{O}_3$ (BMGT), or $\text{K}_{1/2}\text{Na}_{1/2}\text{NbO}_3$ (KNN) [5–9]. The increase in piezoelectric properties caused by the addition of a third endmember is often associated with an increase in structural disorder and a transition from non-ergodic to ergodic relaxor behavior. There are considerably fewer studies on thin film embodiments compared to bulk embodiments of BNKT. The exact compositions and process techniques in these existing studies vary considerably. The primary deposition methods explored are chemical solution deposition and pulsed laser deposition [10–14]. Many BNKT based thin film studies do not report piezoelectric properties and most that do use quantitative piezoelectric force microscopy (PFM) which, unlike dual beam laser interferometry (DBLI), are susceptible to error from substrate bowing and electrostatic interactions between the PFM tip and the film [15–18]. Ternary BNKT based thin films have not displayed the same increase in piezoelectric response or the change in relaxor behavior that is characteristic of bulk BNKT based ternary systems [12, 18, 19]. Jeon et al. suggests the difference between thin film and bulk behavior could be caused by large substrate clamping stresses or chemical inhomogeneity through the thickness of the film [12]. In chemical solution deposited thin films, processing conditions are known to have considerable impact on film

stoichiometry, defect concentration, phase purity, stress state, and microstructure all of which can have an impact on key properties including dielectric constant, dielectric loss, ferroelectric response, and piezoelectric strain [12, 13, 20–26]. Inverse mixing order chemical solution deposition techniques are of particular interest since they can be easily scaled into industrial applications. This study focuses on improving understanding of process-property relationships for BNKT chemical solution deposition processes by observing how various process conditions can impact thin film crystallinity, dielectric properties, ferroelectric response, and piezoelectric response.

2 Experimental

Solutions were synthesized using an inverse mixing order (IMO) solution processing route [11, 13, 27]. The precursors used in the process were bismuth (III) acetate (99.9999%, Alfa Aesar), sodium acetate trihydrate (99%, Macron), potassium acetate (99%, Macron), and titanium (IV) isopropoxide (97%, TCI). Precursors and solvents are weighed in amounts to generate a 0.5 M solution. Bismuth acetate is first dissolved in propionic acid at room temperature by stirring for approximately one hour. Sodium acetate trihydrate and potassium acetate are weighed in a dry nitrogen atmosphere and dissolved in methanol by stirring at room temperature for approximately one hour. The titanium isopropoxide is weighed and chelated in a dry nitrogen atmosphere using a mixture of acetic acid and a small amount of propionic acid. After each solution was stirred for approximately one hour an appropriate amount of the bismuth precursor solution is weighed into the chelated titanium solution. This solution is mixed for one hour before the sodium and potassium precursor solution is weighed into the titanium/bismuth solution mixture. After the addition of the sodium and potassium precursor the final solution is mixed for ten to fifteen hours to ensure complete homogeneity before usage. Solution compositions and excess amounts are controlled by adjusting measured amounts of precursors during the solution synthesis process. All solutions used in this study were 80% BNT and 20% BKT.

The films were deposited on platinized silicon substrates ($\text{Pt}(110\text{ nm})/\text{TiO}_x(30\text{ nm})/\text{SiO}_2(500\text{ nm})/\text{Si}$, MEMS Exchange). The substrates were cleaned through a three-step sonication process in acetone, methanol, and isopropyl alcohol for five minutes each. Afterwards, the substrates are dried with a dry nitrogen gun and heated to 350 °C for two minutes on a hotplate in air to burn off any residual organic contaminants. The films were then wetted with the precursor solution and spin cast at 3000 rpm for 30 s. The pre-crystallization heat treatment process

includes a one-minute dry at 100 °C and a four-minute pyrolysis at 350 °C on separate hotplates. Finally, a rapid thermal annealing/crystallization (RTA) step is performed at 700 °C for five minutes with a 100 °C per second ramp rate and two standard liters per minute (SLPM) of UHP oxygen flow. Note that times and temperatures listed in this section describe the general synthesis process. For samples prepared using modifications to the standard process the differences will be clearly stated. For a 0.5 M solution deposited using the above standard conditions the typical per layer thickness is approximately 70 nm, confirmed using cross sectional scanning electron microscopy (SEM) and spectroscopic ellipsometry. All films in this study were 3 layers (210 nm) thick. For samples measured on the aix-ACCT DBLI a polishing process was completed on the back of the substrate to create a smooth reflective surface. The polishing process used 15, 5, 1 and 0.3 µm lapping paper. Films were protected using a layer of Kapton tape. Before deposition of electrodes a 15-min 400 °C heat cleaning was performed to remove any residue remaining from the tape. To prepare samples for electrical characterization, Pt top electrodes were DC sputtered through a shadow mask. The diameter of the electrode holes on the shadow mask was 0.675 mm which is approximately equivalent to overall film/substrate thickness [28, 29]. It should be noted that the actual diameter of the sputtered platinum electrodes may be slightly larger/smaller than the size of the holes on the shadow mask. To expose the bottom electrode, a corner of the film was etched with 10% hydrofluoric acid using a cotton tipped applicator. Crystallinity and phase purity were verified using a Bruker D8 Discover with CuK α radiation. An HP 4192A impedance analyzer was used to measure dielectric constant and $\tan \delta$ over a frequency range of 0.1 to 10 kHz with an oscillation voltage of 50 mV. Polarization–electric field (P-E) and strain loops were taken concurrently using an aixACCT DBLI system. Strain and P-E loops were taken at 1 kHz with fields up to 600 kV/cm. For most films prepared in this work, multiple measurements were performed using different top electrodes. In general, there was very little variation between measurements and the data presented in this paper are representative of the trends identified for each process condition. The supplementary data includes a summary table with ranges of observed experimental values.

3 Results and discussion

3.1 Deposition of perovskite BNKT thin films.

Depositing BNKT based perovskite thin films on platinumized silicon wafers poses numerous challenges. Sodium, potassium, and bismuth are all highly volatile cations, so

steps need to be taken to control stoichiometry during high temperature processing. Cations also diffuse into the platinum on the Pt/TiO $_2$ /SiO $_2$ substrate which can impact film stoichiometry. Volatilization and diffusion occur at different rates and could cause a chemical inhomogeneity through the thickness of the films. Additionally, BNT based thin films have complex thermal expansion properties [28] which do not match those of the platinumized silicon wafers on which they are deposited. This can cause mechanical issues during high temperature processing including high residual stress states that can impact piezoelectric and ferroelectric properties and/or cause cracking in thicker films.

In this work several processing strategies were employed to determine their impact on the issues described above. Excess cations were included to compensate for volatilization and diffusion. In general films were prepared with greater amounts of Na and K excess compared to Bi excess since Na and K are more volatile than Bi [30]. Crystallization conditions including temperature, time, and ramp rate were adjusted and their impact on film properties observed. In general crystallization temperature and time were kept as low and short as possible without causing a detriment to film properties to minimize the effects of diffusion, volatilization, and thermal expansion mismatch. Several ramp rates were tested since thin films nucleation and growth mechanisms have been shown to be impacted by ramp rate in lead based material systems [31, 32]. Finally, pyrolysis conditions were also evaluated since the gradual volatilization of organics is vital to ensure dense films are formed. It was found that films formed largely phase pure perovskites over a large range of process conditions and with additional process optimization completely phase pure films were also synthesized.

Phase pure perovskite films were successfully formed at crystallization temperatures of 650 °C and 700 °C using a five minute crystallization hold time with a 100 °C per second ramp rate and four minute pyrolysis at 350 °C. Figure 1 displays XRD patterns for films crystallized at 650, 700, and 800 °C.

From the XRD pattern, films crystallized at 650 and 700 °C were phase pure perovskites. The XRD curves display no tetragonal or rhombohedral peak splitting potentially indicating a pseudo-cubic phase is stabilized by residual stresses in the film. It is also possible the lab XRD scans do not have sufficient resolution to detect peak splitting in the tetragonal (200) or rhombohedral (211), (111) peaks in thin films. Ultimately, 700 °C was chosen as the optimal annealing temperature to minimize the thermal budget and to promote complete crystallization and densification. Once a process for depositing phase pure BNKT perovskites was determined, process optimization experiments were performed. During process optimization only one condition was

Fig. 1 Reference XRD scan of a substrate with no film deposited and scans of 210 nm films annealed at 650, 700 and 800 °C with present BNKT peaks labeled (Substrate peaks are marked by a * symbol)

varied at a time and all films were synthesized using the following general conditions: drying at 100 °C for one minute, pyrolysis at 350 °C for four minute and crystallization at 700 °C for 5 min with 100 °C per second ramp rate and 2 SLPM oxygen flow. Each optimization experiment was repeated two to three times to ensure repeatability and the data presented here are characteristic of the trends observed. Films were deposited on 1 cm by 1 cm coupons cut from an 8" wafer, for each set of conditions during each optimization experiment and at least 5 measurable electrodes were tested on each wafer. Each film had three spin cast layers for a total film thickness of 210 nm. Piezoelectric response, measured as $d_{33,f}$, typically varied by no more than ± 5 pm/V between electrodes on the same wafer, dielectric constant also remained relatively stable, varying no more than ± 50 between measurable electrodes without excessively high dielectric loss. The dielectric loss values varied considerably with measurements taken between different electrodes and, in some films, a number of electrodes were shorted. In some cases, the $d_{33,f}$ values varied between batches even when process conditions were kept constant. The electromechanical data show there is no clear and simple relationship between process conditions and electromechanical properties. The $d_{33,f}$ value, similar to the dielectric constant, is sensitive to many film characteristics (microstructure, point defects, etc.) and thus the relationship between process conditions and $d_{33,f}$ is complex. As a typical example of the variation of the measured properties, $d_{33,f}$ values ranged from 50 pm/V to 80 pm/V in 0.8BNT-0.2BKT films processed

Fig. 2 XRD data for 210 nm 0.8BNT-0.2BKT films annealed at 1 min, 5 min, and 10 min at 700 °C with present BNKT peaks labeled (Substrate peaks are marked by a * symbol)

with 6% Bi excess and 12% Na and K excess and annealed using the general process conditions described above.

3.2 Crystallization conditions

The hold time during crystallization can impact film properties by providing additional time for cation diffusion, volatilization, and crystallization. Three 210 nm films were prepared by annealing at 700 °C for 1, 5, and 10 min with a 100 °C per second ramp rate. Figure 2 shows XRD scans for all three samples.

No obvious trend in film crystallinity appeared with time, all three films developed phase pure randomly oriented perovskite structures. In thin film perovskite materials, crystallization typically happens very fast so the kinetics of crystallization is impacted more by ramp rate and maximum temperature than hold time [31, 33].

Figure 3 displays dielectric constant and loss vs. frequency data for films prepared at all three hold times. An increase in dielectric constant with increasing crystallization time was observed and the film held for one minute displayed a considerably higher dielectric loss than films prepared with longer hold times ($\tan \delta = 0.032$ for 1 min hold compared to 0.019 and 0.024 respectively for 5 and 10 min holds). This could be explained by an anticipated surplus of cations left in the films due to the short annealing time. This in turn leads to an increase in leakage current as surplus cations gather in disordered regions of the film, such as grain boundaries, which have been shown to be significant conductive pathways in piezoelectric materials such as BNKT, KNN, and PZT [34–36]. Due to the considerable advantages in terms of thermal budget and only a

Fig. 3 Dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) vs. frequency for 210 nm films annealed for 1 min, 5 min, and 10 min at 700 °C with a ramp rate of 100 °C per second

small difference in dielectric constant between the films prepared with 5 and 10 min crystallization steps, the 5 min step was identified as optimal for further experiments.

The impact of ramp rate on film properties was also observed. Ramp rate is an important factor in processing thin film perovskites due to the potential impact on film defect state and nucleation and growth mechanisms. While the impact of ramp rate on BNT based thin films has not been studied in detail, some studies on other material systems have shown an impact of ramp rate on film nucleation, grain growth and in turn grain size and density. For example Bastani et al. found higher ramp rates in thick PMN-PT films caused them to develop a denser microstructure with larger grains [31] while Velu et al. found that PZT crystallographic orientation was changed from (110) to (100) and grain size was decreased with the use of higher ramp rates compared to conventional thermal annealing [32]. In some material systems faster ramp rates can cause perovskite phases to form at lower temperatures compared to conventional furnace annealing techniques [33, 37]. Films were crystallized for 5 min at 700 °C with ramp rates of 75 °C per second, 100 °C per second, 125 °C per second and 150 °C per second. Figure 4 shows dielectric constant and loss data for films crystallized using all four ramp rates. Note that no trend in phase purity was observed with ramp rate (all films from the ramp rate had a small amount of second phase via XRD with a low intensity peak observed at a 2θ of 15°).

A considerably higher dielectric loss ($\tan \delta = 0.089$ at 1 kHz) was observed in the 75 °C per second film compared to films prepared with faster ramp rates ($\tan \delta = 0.07, 0.06$, and 0.05 at 1 kHz for 100 °C per second, 125 °C per second and 150 °C per second respectively). A slight increase in dielectric constant was observed in the 150 °C per second film and a slightly higher dielectric loss was observed in the 100 °C per second film. While the exact reason for the

Fig. 4 Dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) vs. frequency for 210 nm films annealed at 700 °C for 5 min with 75 °C per second, 100 °C per second, 125 °C per second, and 150 °C per second ramp rates

overall higher losses at slower ramp rates is not entirely clear, it could be related to a change in defect concentration, volatilization behavior, temperature of phase formation, and/or rate of cation volatilization brought about by a change in nucleation and growth mechanisms [31–33].

Strain and P-E loops for films prepared using all ramp rates are shown in Fig. 5.

No obvious trend in polarization behavior was observed with ramp rate. Piezoelectric response was maximized in the 100 °C per second sample ($d_{33,f} = 65 \pm 5$ pm/V), however, this is only slightly higher than the other ramp rates. More detailed studies are required to determine the exact crystallization mechanisms occurring here and their impact on piezoelectric response.

3.3 Pyrolysis temperature

The first heat treatments after spin casting, drying and pyrolysis, can have a major impact on film orientation, density, microstructure, and dielectric constant [38, 39]. During the pyrolysis step organics from the acid/alcohol-based solutions are burned off. If the majority of organics are not removed during the lower temperature pyrolysis step, they can violently volatilize during the high temperature RTA step leaving defects and voids in the films [36]. Figure 6 shows dielectric constant and loss data for films crystallized at 700 °C for 5 min with a 100 °C per second ramp rate and pyrolyzed for 4 min at 300, 350, and 400 °C. Note that hotplate surface temperatures were confirmed with an external thermocouple for these experiments.

Dielectric loss was largely unaffected by pyrolysis temperature. It was observed that dielectric constant increases in the 350 and 400 °C samples. Dielectric constant at 1 kHz was 450 ± 50 at 300 °C, 550 ± 50 at 350 °C,

Fig. 5 Strain and P-E response at 1 kHz with 600 kV/cm maximum applied field for 210 nm thick films crystallized for 5 min at 700 °C for **a** 75 °C per second **b** 100 °C per second **c** 125 °C per second and **d** 150 °C per second. Note P_{rrel} represents the relaxed remanent polarization

Fig. 6 Dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) vs. frequency for 210 nm thick films annealed at 700 °C for 5 min pyrolyzed for 4 min at 300, 350 and 400 °C

and 600 ± 50 at 400 °C. This indicates that not all organics burn off at 300 °C causing a likely increase in film porosity and ultimately a decrease in dielectric constant which is also shown to occur in both PZT and KNN thin films [38, 39].

3.4 Cation excess

Cation volatility can lead to generation of defects and changes in film composition during high temperature processing, which can ultimately lead to reduced piezoelectric response. One simple but effective method used to counter cation volatility is the inclusion of excess cations within the precursor solution. Typically too little excess gives rise to defects in the form of Na/K vacancies as well as oxygen vacancies, while too much excess often leads to a buildup of surplus cations in grain boundaries or the formation of an unwanted second phase [34, 35, 40]. For thin films in general, cation volatility is particularly difficult to control due to very high surface to volume ratio. Here this is exacerbated by the presence of three highly volatile cations; Bi, Na, and K. Films were prepared with a range of excess Bi, Na, and K included during solution preparation. Bi excess was varied from 6 to 10 mol% while Na and K excess amounts were varied from 8 to 16 mol%. In this work, chemical analysis was not performed, however, in previous work, Jeon, et al. performed X-ray photoelectron spectroscopy (XPS) in $(1-x)\text{BNKT-xBiMgTiO}_3$ films confirming proper relative cation ratios existed in films prepared via chemical solution deposition and crystallized at 700 °C

for 10 min in a conventional box furnace including 10% excess Bi and 20% excess Na and K, however, some fluctuation in cation amounts was found through the thickness of the films [41].

First the impact of cation excess values on dielectric properties was observed. Figure 7 shows dielectric constant and dielectric loss data for samples prepared with the following excess amounts: 6% Bi excess and 8% Na and K excess (6Bi-8Na-8 K), 6% Bi excess and 12% Na and K excess (6Bi-12Na-12 K), 8% Bi excess and 8% Na and K excess (8Bi-8Na-8 K), and 8% Bi excess and 12% Na and K excess (8Bi-12Na-12 K). All samples were 210 nm thick films annealed for 5 min at 700 °C with a 100 °C per second ramp rate.

Some impact was observed between excess amounts in the dielectric data. A slight increase in dielectric constant and loss was observed in the 8Bi-12Na-12 K film ($\tan \delta = 0.02$ and $\epsilon_r = 500 \pm 50$ at 1 kHz). This could be attributed to a surplus of Bi and Na/K carriers stacking at grain boundaries under field. Note dielectric constant was lowest in the 8Bi-8Na-8 K film ($\tan \delta = 0.017$ and $\epsilon_r = 450 \pm 50$ at 1 kHz) which could be due to a change in film stoichiometry brought about by loss of Na and K at a faster rate than Bi during high temperature crystallization. Further work on compositional analysis of these films is necessary to confirm this is the origin of the observed impact on film dielectric properties.

The impact of cation excess on polarization and piezoelectric response was also measured. Figure 8 shows polarization and piezoelectric response vs. electric field for 210 nm films with varying excess.

The largest measured $d_{33, f}$ value was for the 8Bi-12Na-12 K film ($d_{33, f} = 65 \pm 5$ pm/V), however, this sample

Fig. 7 Dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) vs. frequency for 210 nm thin films crystallized at 700 °C for 5 min with varying excess amounts: 6% Bi excess and 8% Na and K excess (**6Bi-8Na-8 K**), 6% Bi excess and 12% Na and K excess (**6Bi-12Na-12 K**), 8% Bi excess and 8% Na and K excess (**8Bi-8Na-8 K**), and 8% Bi excess and 12% Na and K excess (**8Bi-12Na-12 K**)

could not be measured above a field of 300 kV/cm due to a significant decrease in breakdown strength likely caused by a considerable surplus of cations in film grain boundaries. The piezoelectric constant was maximized without a decrease in breakdown field in the 6Bi-12Na-12 K film ($d_{33, f} = 60 \pm 5$ pm/V). Films with greater amounts of Na and K excess (6Bi-12Na-12 K and 8Bi-12Na-12 K) generally displayed an increase in piezoelectric response of about 10 pm/V which falls within the general fluctuation in piezoelectric response between sample sets (± 10 pm/V for 0.8BNT-0.2BKT), however, the increase was observed repeatedly when the experiments were replicated. This increase may be caused by a modification of film stoichiometry during the high temperature crystallization step changing the ultimately realized stoichiometry [34, 35]. Na and K are more volatile than Bi and thus a greater amount of Na and K excess must be included in order to control film composition [30]. Slight changes in excess can cause the final film composition to land further from the morphotropic phase boundary, thus leading to reduced structural disorder and in turn reduced strain response. Controlling cation excess is a complicated effort which must be optimized for each particular film synthesis process. Changes in crystallization atmosphere, temperature, time, and changing contamination levels over time in the RTA itself can all impact the optimal excess amounts needed to control film stoichiometry and minimize defect concentration. While the 6Bi-12Na-12 K excess was optimal for initial films in a new uncontaminated RTA, after approximately one year of consistent use the chamber was contaminated sufficiently that the annealing atmosphere changed, and a new optimal excess amount was necessary. Evidence of this was observed in XRD scans when a second phase began to appear in 6Bi-12Na-12 K films after 14 months of use. Figure 9 shows data from an excess study performed after the initial appearance of this phase impurity.

Films made with lower excess amounts (6Bi-8Na-8 K and 6Bi-10Na-10 K) were phase pure while the previously optimal 6Bi-12Na-12 K film displayed a second phase (circled in the figure). As such, it is important when designing a CSD process for BNKT thin films that excess amounts not just be initially optimized but tested and adjusted over time.

4 Conclusion

Inverse mixing order chemical solution deposition methods for lead-free thin films are of particular interest to industry due to scalability and use of non-toxic precursors. This study presents experimental data on process optimization for BNKT thin films focusing on actuator properties. Phase pure perovskite BNKT (0.8BNT-0.2BKT) thin films

Fig. 8 Strain and P-E response at 1 kHz for 210 nm thin films crystallized at 700 °C for 5 min with **a** 6% Bi excess and 8% Na and K excess (**6Bi-8Na-8 K**), **b** 8% Bi excess and 8% Na and K excess (**8Bi-8Na-8 K**) **c** 6% Bi excess and 12% Na and K excess (**6Bi-12Na-12 K**), and **d** 8% Bi excess and 12% Na and K excess (**8Bi-12Na-12 K**). Note P_{rrel} represents the remanent polarization

Fig. 9 XRD data from an excess study performed after contamination of RTA chamber for films crystallized at 700 °C for 5 min with varying excess amounts: 6% Bi excess and 8% Na and K excess (**6Bi-8Na-8 K**), 6% Bi excess and 10% Na and K excess (**6Bi-10Na-10 K**), and 6% Bi excess and 12% Na and K excess (**6Bi-12Na-12 K**) with present BNKT peaks labeled (* was used to mark substrate peaks)

were successfully prepared via an inverse mixing order chemical solution deposition process. Experiments were performed to evaluate the impact of process conditions on key film properties including phase purity, dielectric constant and loss, ferroelectric response, and piezoelectric strain. Crystallization temperatures of 600, 700, and 800 °C all produced phase pure perovskites. Crystallization times of five minutes or greater are required to maximize dielectric constant (ϵ_r at 1 kHz = 600 ± 50 for a 10-min hold). Piezoelectric response was maximized in films prepared using a 100 °C per second ramp rate ($d_{33,f} = 65 \pm 5$ pm/V at 1 kHz). Pyrolysis temperatures greater than 350 °C showed an increase in dielectric constant from 450 ± 50 at 1 kHz for a 300 °C pyrolysis step to a maximum of 600 ± 50 at 1 kHz for a 400 °C pyrolysis step. Excess cations should be employed in order to maintain BNKT film stoichiometry during high temperature crystallization. An increase of about 10 pm/V was observed in $d_{33,f}$ for films prepared with greater amounts of sodium and potassium excess relative to Bi excess. The inclusion of too much total excess cations can lead to a considerable decrease in observed breakdown field from about 800 kV/cm to about 300 kV/cm. Excess amounts must be adjusted as annealing atmosphere and conditions change over time in order to synthesize BNKT films with desired final stoichiometry. These

results may prove useful to those developing inverse mixing order processes for the fabrication of bismuth based thin film materials.

Funding The authors wish to acknowledge Xaar plc (Cambridge, UK) for their support for this research project.

Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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References

- Shibata K, Wang R, Tou T, Koruza J (2018) Applications of lead-free piezoelectric materials. *MRS Bull* 43(8):612–616. <https://doi.org/10.1557/mrs.2018.180>
- Zhang S, Xia R, Shrout TR (2007) Lead-free piezoelectric ceramics vs. PZT. *Journal Electroceramics* 19(4):251–257. <https://doi.org/10.1007/s10832-007-9056-z>
- Safari A, Abazari M (2010) Lead-free piezoelectric ceramics and thin films. *IEEE Trans Ultrason Ferroelectr Freq Control* 57(10):2165–2176. <https://doi.org/10.1109/TUFFC.2010.1674>
- DIRECTIVE 2011/65/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 8 June 2011 on the restriction of the use of certain hazardous substances in electrical and electronic equipment. <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32011L0065>
- Sasaki A, Chiba T, Mamiya Y, Otsuki E (1999) Dielectric and piezoelectric properties of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ – $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ systems. *Jpn J Appl Phys* 38(9B):5564–5567. <https://doi.org/10.1143/JJAP.38.5564>
- Patterson EA, Cann DP, Pokorny J, Reaney IM (2012) Electromechanical strain in $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ – $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ solid solutions. *J Appl Phys* 111(9):094105. <https://doi.org/10.1063/1.4714346>
- Kumar N, Cann DP (2013) Electromechanical strain and bipolar fatigue in $\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$ – $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ – $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ ceramics. *J Appl Phys* 114(5):054102. <https://doi.org/10.1063/1.4817524>
- Seifert KTP, Jo W, Rödel J (2010) Temperature-insensitive large strain of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ – $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ lead-free piezoceramics. *J Am Ceram Soc*. <https://doi.org/10.1111/j.1551-2916.2009.03573.x>
- Zhang X et al (2018) Mn doping effects on electric properties of $0.93(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ – $0.07\text{Ba}(\text{Ti}_{0.945}\text{Zr}_{0.055})\text{O}_3$ ceramics. *J Am Ceram Soc* 101(7):2996–3004. <https://doi.org/10.1111/jace.15457>
- Wu Y, Or SW (2018) Thickness-dependent structural and electro-mechanical properties of $(\text{Na}_{0.85}\text{K}_{0.15})_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ multilayer thin film-based heterostructures. *Material Des* 149:153–164. <https://doi.org/10.1016/j.matdes.2018.04.012>
- Jeon YH, Patterson EA, Cann DP, Gibbons BJ (2013) Dielectric and ferroelectric properties of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ – $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ – BaTiO_3 thin films deposited via chemical solution deposition. *Mater Lett* 106:63–66. <https://doi.org/10.1016/j.matlet.2013.04.096>
- Jeon YH, Patterson EA, Cann DP, Mardilovich P, Stickel W, Gibbons BJ (2013) Large piezoresponse and ferroelectric properties of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ – $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ – $\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ thin films prepared by chemical solution deposition. *J Am Ceram Soc* 96(7):2172–2178. <https://doi.org/10.1111/jace.12279>
- Walenza-Slabe J, Gibbons BJ (2017) Effect of annealing atmosphere pO₂ on leakage current in $80(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ – $20(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ piezoelectric thin films. *Appl Phys Lett* 110(16):162904. <https://doi.org/10.1063/1.4981771>
- Abazari M, Safari A, Bharadwaja SSN, Troler-McKinstry S (2010) Dielectric and piezoelectric properties of lead-free $(\text{Bi}, \text{Na})\text{TiO}_3$ -based thin films. *Appl Phys Lett* 96(8):082903. <https://doi.org/10.1063/1.3309706>
- Ahn CW, Won SS, Ullah A, Lee SY, Lee SD, Lee JH, Jo W, Kim IW (2012) Large piezoresponse of lead-free $\text{Bi}_{0.5}(\text{Na}_{0.85}\text{K}_{0.15})_{0.5}\text{TiO}_3$ thin film. *Curr Appl Phys* 12(3):903–907. <https://doi.org/10.1016/j.cap.2011.12.005>
- Cui W, Wang X, Li L (2015) Large piezoresponse of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ – $\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ thin films prepared via water-based sol–gel method. *Ceram Int* 41:S37–S40. <https://doi.org/10.1016/j.ceramint.2015.03.232>
- Acharya SK, Kim T-M, Hyung J-H, Ahn B-G, Lee S-K (2014) Ferroelectric and piezoelectric properties of lead-free $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ – $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ – BaTiO_3 thin films near the morphotropic phase boundary. *J Alloys Compd* 586:549–554. <https://doi.org/10.1016/j.jallcom.2013.10.028>
- Li W, Zeng H, Zhao K, Hao J, Zhai J (2014) Structural, dielectric and piezoelectric properties of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ – $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ – $\text{Bi}(\text{Zn}_{0.5}\text{Ti}_{0.5})\text{O}_3$ thin films prepared by sol–gel method. *Ceram Int* 40(6):7947–7951. <https://doi.org/10.1016/j.ceramint.2013.12.143>
- Li W, Zeng H, Hao J, Zhai J (2013) Enhanced dielectric and piezoelectric properties of Mn doped $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ – $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ – SrTiO_3 thin films. *J Alloys Compd* 580:157–161. <https://doi.org/10.1016/j.jallcom.2013.05.127>
- Wenhan C, Xiaohui W, Yunyi W, Yun-Gang L, Longtu L (2016) Investigation of thickness dependence of electric properties of sol-gel BNT-BT thin films with stepwise crystallization. *J Ceram Soc Jpn* 124(4):464–468. <https://doi.org/10.2109/jcersj2.15315>
- Quan ND, Hung VN, Dung DD (2017) Influence of film thickness on ferroelectric properties and leakage current density in lead-free $\text{Bi}_{0.5}(\text{Na}_{0.80}\text{K}_{0.20})_{0.5}\text{TiO}_3$ films. *Mater Res Express* 4(8):086401. <https://doi.org/10.1088/2053-1591/aa7b43>
- Onishi R, Ogawa H, Iida D, Kan A (2017) Synthesis and piezoelectric properties of $(1-x)\text{Bi}_{0.5}(\text{Na}_{0.8}\text{K}_{0.2})_{0.5}\text{TiO}_3$ – $x\text{Sr}_2\text{ZrTiO}_6$ ceramics. *Jpn J Appl Phys* 56(10S):10PD04. <https://doi.org/10.7567/JJAP.56.10PD04>
- Zhou Z, Sun W, Li J-F (2016) Sol–gel synthesis of $0.94(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ – 0.06BaTiO_3 lead-free piezoelectric films: effect of pyrolysis temperature on phase evolution and electrical properties. *J Sol-Gel Sci Technol* 77(2):423–429. <https://doi.org/10.1007/s10971-015-3870-6>
- Yao Y, Wu X, Shi P, Ye Z-G (2016) Effects of heat-treatment temperature on the properties of $(1-x)(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ – $x\text{BiAlO}_3$ Lead-free piezoelectric thin films. *J Am Ceram Soc* 99(4):1340–1344. <https://doi.org/10.1111/jace.14116>

25. Yang CH, Yao Q, Qian J, Han YJ, Chen J (2018) Growth, micro-structure, energy-storage and dielectric performances of chemical-solution NBT-based thin films: effect of sodium nonstoichiometry. *Ceram Int* 44(8):9152–9158. <https://doi.org/10.1016/j.ceramint.2018.02.123>
26. Dargham SA, Ponchel F, Abboud N, Soueidan M, Ferri A, Desfeux R, Assad J, Remiens D, Zaouk D (2018) Synthesis and electrical properties of lead-free piezoelectric $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ thin films prepared by Sol-Gel method. *J Eur Ceram Soc* 38(4):1450–1455. <https://doi.org/10.1016/j.jeurceramsoc.2017.06.019>
27. Sivaramakrishnan S, Mardilovich P, Mason A, Roelofs A, Schmitz-Kempen T, Tiedke S (2013) Electrode size dependence of piezoelectric response of lead zirconate titanate thin films measured by double beam laser interferometry. *Appl Phys Lett* 103(13):132904. <https://doi.org/10.1063/1.4821948>
28. Reichmann K, Feteira A, Li M (2015) Bismuth sodium titanate based materials for piezoelectric actuators. *Materials* 8(12):8467–8495. <https://doi.org/10.3390/ma8125469>
29. Sivaramakrishnan S, Mardilovich P, Schmitz-Kempen T, Tiedke S (2018) Concurrent wafer-level measurement of longitudinal and transverse effective piezoelectric coefficients (d_{33} , f and e_{31} , f) by double beam laser interferometry. *J Appl Phys* 123(1):014103. <https://doi.org/10.1063/1.5019568>
30. Honig RE (1957) Vapor pressure data for the more common elements. *RCA Rev* 18:195–204
31. Bastani Y, Bassiri-Gharb N (2012) Processing optimization of lead magnesium niobate-lead titanate thin films for piezoelectric MEMS application. *J Am Ceram Soc* 95(4):1269–1275. <https://doi.org/10.1111/j.1551-2916.2011.05042.x>
32. Velu G, Remiens D, Thierry B (1997) Ferroelectric properties of PZT thin films prepared by sputtering with stoichiometric single oxide target: Comparison between conventional and rapid thermal annealing. *Journal Eur Ceram Soc* 17(14):1749–1755. [https://doi.org/10.1016/S0955-2219\(97\)00031-9](https://doi.org/10.1016/S0955-2219(97)00031-9)
33. Dang EKF, Gooding RJ (1995) Theory of the effects of rapid thermal annealing on thin-film crystallization. *Phys Rev Lett* 74(19):3848–3851. <https://doi.org/10.1103/PhysRevLett.74.3848>
34. Wu Y, Wang X, Zhong C, Li L (2011) Effect of Na/K excess on the electrical properties of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ – $\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ thin films prepared by sol-gel processing. *Thin Solid Films* 519(15):4798–4803. <https://doi.org/10.1016/j.tsf.2011.01.077>
35. Ahn CW, Lee SY, Lee HJ, Ullah A, Bae JS, Jeong ED, Choi JS, Park BH, Kim IW (2009) The effect of K and Na excess on the ferroelectric and piezoelectric properties of $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ thin films. *Journal of Applied Physics*. 42(21):215304. <https://doi.org/10.1088/0022-3727/42/21/215304>
36. Arai T, Ohno T, Matsuda T, Sakamoto N, Wakiya N, Suzuki H (2015) Effects of synthesis conditions on electrical properties of chemical solution deposition-derived $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – PbTiO_3 thin films. *Thin Solid Films* 585:86–90. <https://doi.org/10.1016/j.tsf.2014.11.014>
37. Li Y, Zhang S, Fei W, Wang H (2008) Crystallization behavior of Nd-doped $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films prepared by magnetron sputtering. *Thin Solid Films* 516(16):5252–5257. <https://doi.org/10.1016/j.tsf.2007.07.054>
38. Yu Q, Li J, Chen Y, Cheng L, Sun W, Zhou Z, Wang Z (2014) Effect of pyrolysis temperature on Sol-Gel synthesis of lead-free piezoelectric (K, Na) NbO_3 films on Nb:SrTiO_3 substrates. *J Am Ceram Soc* 97(1):107–113. <https://doi.org/10.1111/jace.12675>
39. Gong W, Li J-F, Chu X, Li L (2004) Effect of pyrolysis temperature on preferential orientation and electrical properties of sol-gel derived lead zirconate titanate films. *J Eur Ceram Soc* 24(10–11):2977–2982. <https://doi.org/10.1016/j.jeurceramsoc.2003.10.007>
40. Khokhar A, Goyal PK, Thakur OP, Sreenivas K (2015) Effect of excess of bismuth doping on dielectric and ferroelectric properties of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ ceramics. *Ceram Int* 41(3):4189–4198. <https://doi.org/10.1016/j.ceramint.2014.12.103>
41. Jeon YH (2012) Development of Bi-based lead-free piezoelectric materials: thin film piezoelectric materials via PVD and CSD routes, Dissertation, Oregon State University

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