

# Dielectric and Pyroelectric Properties of Lead-Free Sodium Bismuth Titanate Thin Films Due to Excess Sodium and Bismuth Addition

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**Abstract:** Pb-free ferroelectric ( $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ ) (NBT) thin films were prepared by a modified sol-gel process. Their structural, dielectric and pyroelectric properties were investigated as a function of the excess Na/Bi ratio and the annealing temperature. In the case of thin films containing no excess Na and Bi, only partial amounts of the perovskite NBT were crystallized, where the films consisted mainly of the pyrochlore phase of  $\text{Bi}_2\text{Ti}_2\text{O}_7$  for annealing conditions of 600–800°C. With increasing excess Na/Bi ratio, the proportion of the perovskite phase effectively increased due to the compensation of the volatile Na and Bi components. For a Na/Bi ratio of 2.0, the thin film with single NBT perovskite phase was obtained within XRD detection limit after annealing at 700°C for 10 min and it showed the excellent dielectric properties,  $\epsilon_r$  of ~550 and  $\tan \delta$  of 0.03. While these properties were degraded for Na/Bi ratio of 2.5 despite the existence of pure perovskite phase. The NBT thin film with Na/Bi ratio of 2.0 are also promising candidates for applications requiring pyroelectric devices because it was found to have pyroelectric coefficients of 1.3~7 nC/cm<sup>2</sup>K in the temperature range of 30~100°C.

**Keywords:** Lead-Free Thin Films, ( $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ ), Sol-Gel Process, Dielectric and Pyroelectric Properties

## 1. Introduction

Pb(Zr,Ti)O<sub>3</sub>-based ceramics have been widely studied for use in various actuators and sensor applications due to their desirable ferroelectric and piezoelectric behaviors.<sup>1,2)</sup> However, Pb-free piezoelectric and pyroelectric ceramics have recently drawn significant attention because PbO is volatile, detrimental to the human health and not environment-friendly. Sodium bismuth titanate ( $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ , NBT) is well known as an excellent candidate for the lead-free piezoelectric materials because of its valuable ferroelectric properties.<sup>3,4)</sup> However, it has been reported that a stable single perovskite NBT phase is not easy to prepare due to the relatively low tolerance factor  $t \sim 0.799$  and volatility of Na and Bi.<sup>5,6)</sup> These problems result in the creation of secondary phases and the degradation of electrical performance. So until recently, various processes such as the compositional compensation and/or the ambient control have been widely reported with the aim of preparing pure perovskite NBT films.<sup>6-8)</sup> In the case of sputtered NBT films, various techniques such as NBT powder bedding process and oxygen atmospheric annealing have been

tested.<sup>8,11)</sup> In chemically wet processes, excessive Bi addition or excessive Na addition through control of the concentration of Na or Bi source have often been reported.<sup>6,7,10,12,13)</sup> A-site substitution has been employed with other materials with high tolerance factors such as BaTiO<sub>3</sub> and PbTiO<sub>3</sub> to improve their electrical properties by enhancing the purity of the perovskite phase.<sup>14,15)</sup> However, there are few studies regarding the relations between the amount of crystalline phases present in NBT thin films and their dielectric properties due to excessive addition of Na and Bi. In this study, ( $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ ) thin films with excessive A-site elements, Na and Bi, were prepared by a modified sol-gel process for various excess Na/Bi ratios and different annealing temperatures, and the dielectric and pyroelectric properties of the prepared films were investigated.

## 2. Experimental

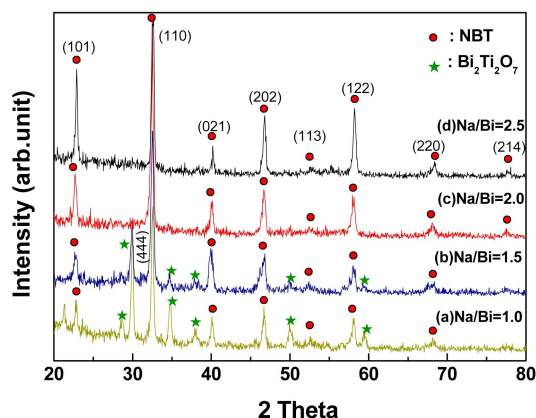
NBT thin films were prepared with a modified sol-gel technique and a spin-coating process.<sup>12)</sup> High-purity bismuth nitrate ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ), sodium acetate ( $\text{Na}(\text{CH}_3\text{COO})$ ),

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and titanium n-butoxide ( $\text{Ti}(\text{OC}_4\text{H}_9)_4$ ) were used as precursors. Acetic acid ( $\text{CH}_3\text{COOH}$ ), methanol ( $\text{CH}_3\text{OH}$ ) and acetyl acetone (AcAc) were selected as solvents and stabilizers. The Bi-Na precursor was prepared by dissolving bismuth nitrate and sodium acetate in an appropriate solvent and mixing at room temperature. In order to enhance the nucleation of the desired phase during the fabrication process, excess Na in the range of 10–25 mol% was added into the stoichiometric solution. Since the volatilization of Bi is expected due to its low melting point ( $\sim 271^\circ\text{C}$ ), 10 mol% of excess Bi was also added. Finally, solutions with excess molar ratios of 1, 1.5, 2.0, and 2.5 (excess Na/excess Bi) were prepared. Ti precursor was synthesized by dissolving the Ti source in 2-methoxy ethanol, where AcAc was used to suppress the gelation. By mixing the above precursors for 1 h, the stable complex Bi-Na-Ti solution was obtained without refluxing and high-temperature distillation to remove water. The concentration of the final solution was adjusted to 0.3 M, and a pH value of 2–4 was obtained by adding acetic acid and 2-methoxy ethanol. All the preparation of the precursor solution was carried out in the ambient atmosphere. The solution was spin-coated onto Pt(111)/Ti/SiO<sub>2</sub>/Si(100) substrates at a speed of 3000 rpm for 30 s. The coated films were dried at  $300^\circ\text{C}$  for 5 min and then heat treated for 1 min after each layer was coated. This process was repeated until a desired thickness of  $\sim 300$  nm was obtained. Finally, the NBT thin films were crystallized by heat treatment for 10 or 30 min. Various annealing temperatures in the range  $600^\circ\text{C} \sim 800^\circ\text{C}$  were tested with an RTA (MILA3000-P-N, Sinku-Riko) for both the hydrolysis and the crystallization processes. The crystal structure and surface morphology were investigated with an XRD (D/MAX-2500, Rigaku) and an AFM (SPM-9500J3, Shimadzu). The crystallinity of the perovskite NBT phase

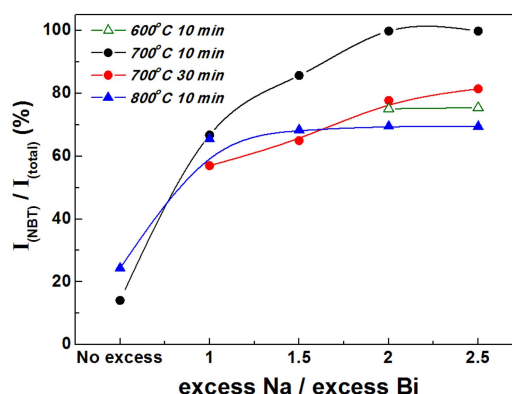


**Fig. 1.** XRD patterns of NBT thin films annealed at  $700^\circ\text{C}$  for 10 min for various ratios of excess Na content to excess Bi contents.

was estimated by using the equation of  $\% \text{NBT} = I_{\text{int(NBT)}} / (I_{\text{int(NBT)}} + I_{\text{int(BTO)}})$ .  $I_{\text{int(NBT)}}$  and  $I_{\text{int(BTO)}}$  are the integrated intensities of the highest peaks of the NBT and BTO ( $\text{Bi}_2\text{Ti}_2\text{O}_7$ ) phases, which correspond to the (110) plane of NBT and the (444) plane of BTO, respectively.<sup>10</sup> After deposition of Pt top electrodes, the dielectric properties of the films were measured by employing an impedance analyzer (HP4294A) and a precision materials analyzer (Precision Pro, Radiant Tech. Inc.). The pyroelectric properties were measured on an optical table equipped with a picoammeter (HP4140B) and an automatic climate control chamber (HCS600-STC200, Instec).<sup>16</sup>

### 3. Results and Discussions

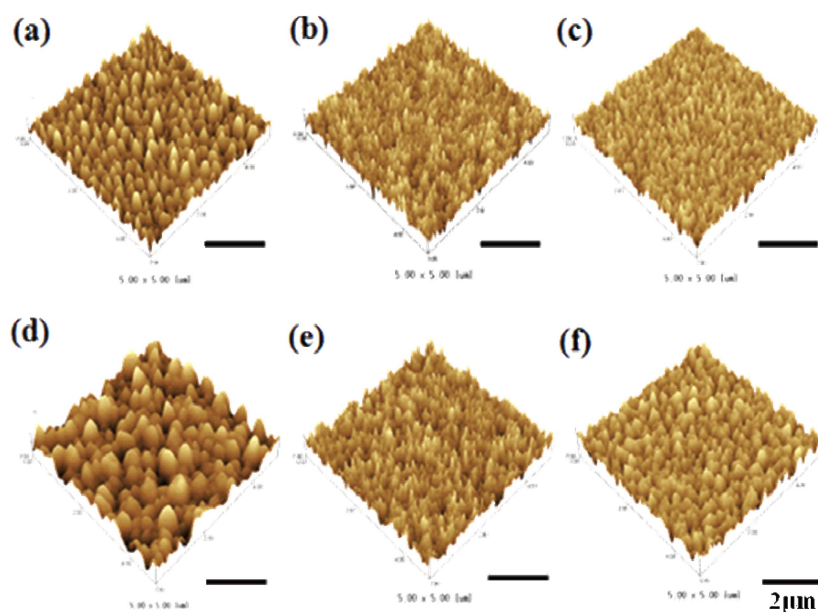
The XRD patterns of the NBT thin films annealed at  $700^\circ\text{C}$  for 10 min for various amounts of excess Na are shown in Fig. 1. The films contained mixed phases including the pyrochlore  $\text{Bi}_2\text{Ti}_2\text{O}_7$  (BTO) and the perovskite NBT. Many studies of the preparation of bulk ceramics<sup>10</sup> and thin films<sup>6</sup> have reported that the preferred pyrochlore BTO phases are often created. As shown in Fig. 1, the secondary BTO phase is dominant in NBT films for Na/Bi ratios of up to 1.5. This undesirable phase is successfully converted within the XRD detection limits into pure NBT phase at Na/Bi ratios of 2.0 or more. As can be seen from the XRD results, the NBT films have polycrystalline structures with no preferred orientation. It is also evident that the structure of crystallized NBT with  $a=3.83(\pm 0.04)\text{\AA}$  and  $\text{angle}=89.79(\pm 0.02)^\circ$  is rhombohedral (JCPDS 36-0340), as reported in other studies.<sup>12,14,15</sup> Figure 2 shows a plot of  $I_{\text{int(NBT)}} / I_{\text{int(total)}}$  versus the excess Na/Bi ratio for the NBT thin films annealed under various conditions. The proportion of NBT phase is initially around 20%, and



**Fig. 2.**  $I_{\text{int(NBT)}} / I_{\text{int(total)}}$  vs. ratio of excess Na content to excess Bi contents for the NBT thin films annealed at different conditions.

gradually increased with increasing amount of excess Na. The nucleation of pure NBT phase is completed at a Na/Bi ratio of 2.0 and an annealing temperature of 700°C for 10 min. However, the NBT films annealed at 800°C contained at most ~65% NBT perovskite phase even for excess content ratios of up to 2.5, implying the excessive annealing temperature. It can be concluded from the XRD analysis that the addition of excess Na contributes to the crystallization of the NBT films as a result of the compensation of the volatile components. Note that the relationship between the annealing temperature and the excess addition of Na and Bi is very important to the crystallization of the NBT thin films. The EDS analysis shows that the NBT thin films with a desirable composition of  $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$  can be manufactured at a Na/Bi ratio of 2.0, i.e. Bi and Na are still present at  $10 \pm 0.5$  at% after heat treatment, with a constitutional ratio of  $(\text{Na}+\text{Bi})/\text{Ti}$  of nearly 1. It was also confirmed with EDS analysis that the NBT films containing 10 mol% Bi without excess Na had non-stoichiometric compositions with sodium deficiencies of 28~30%. This result agrees with the report of J.R. Mercurio<sup>7)</sup> that compositional loss approaches 26% for Na and 4.6% for Bi when NBT films are prepared by sol-gel processing without any compensation of volatile elements. AFM images of NBT thin films for various excess Na and Bi contents and annealing temperatures are shown in Fig. 3. The surface morphologies of NBT films annealed at 700°C became uniform and smooth with increasing amount of excess Na. The rms (root mean square) value of the NBT

films was reduced from ~25 nm (Fig. 3(a)) to 8~10 nm for well-crystallized NBT films, as shown in Fig. 3(c). We conclude that the addition of excess Na is useful in maintaining the stoichiometric composition of the NBT films and improving their densification, as reported for Pb-based thin films.<sup>11,17)</sup> For NBT films with a Na/Bi ratio of 2.5, the surface was non-uniform and coarse, as shown in Fig. 3(d), which is possibly due to the presence of an excessive amount of Na. Although NBT films with a Na/Bi ratio of 2.0 have an excellent constitutional ratio, the surface morphology and roughness of the NBT films were poor when the films were annealed at the temperatures such as 600°C and 800°C, indicating that compositional compensation was not effective at this excess Na/Bi ratio. The AFM analysis shows that both compositional control and the annealing temperature had an influence on the morphology of NBT thin films. The variation of the dielectric properties as a function of frequency for the NBT thin films annealed at 700°C for 10 min is shown in Fig. 4. A typical frequency dependence was observed, in which  $\epsilon_r$  decreased and  $\tan \delta$  increased with frequency. The dielectric constants of the NBT thin films with various Na/Bi content ratios increased with frequency and the values of  $\tan \delta$  were below 3% for the NBT films with excess Na/Bi ratios less than 2.0. However, an extremely high value of  $\tan \delta$ , ~10%, accompanied by the highest  $\epsilon_r$  was found for the NBT films with Na/Bi = 2.5. Such inferior properties may be attributed to the non-uniform surface morphology as evidenced by the AFM analysis and probably some residual Na, not



**Fig. 3.** AFM images of NBT thin films with various ratios of excess Na and Bi (rms); (a) 1.0(25 nm), (b) 1.5(15 nm), (c) 2.0(9 nm), (d) 2.5(60 nm) at 700°C for 10 min, (e) 2.0 at 600°C for 10 min (18 nm), (f) 2.0 at 800°C for 10 min (40 nm). (bar = 2  $\mu\text{m}$ ).

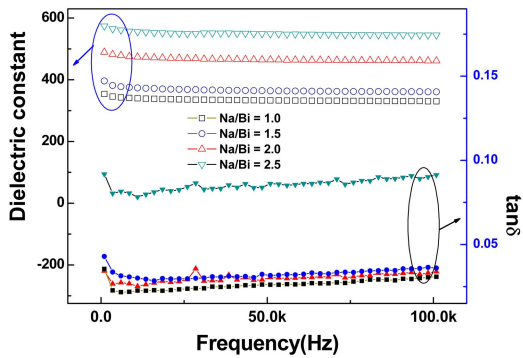


Fig. 4. Frequency dependence of the room temperature dielectric constant and  $\tan \delta$  for NBT thin films with various ratios of excess Na content to Bi content.

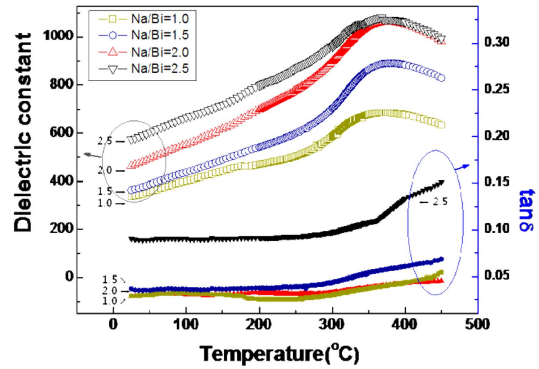


Fig. 5. Temperature dependences of the dielectric constant and  $\tan \delta$  for NBT thin films with various ratios of excess Na content to Bi content at 100 kHz.

detectable within XRD detection limit, despite the sole presence of perovskite phase as shown in Fig. 1(d). Thus, the NBT films with a Na/Bi ratio of 2.0 exhibited the optimal dielectric behavior. Considering the results of both the XRD analysis and dielectric properties, residual amounts of secondary BTO phase seem to affect the quality of the NBT thin films. Pyrochlore BTO is known to have a low dielectric constant that varies in the range 100~180, depending on the preparation methods.<sup>18)</sup> The increases in  $\epsilon_r$  with increasing ratio of excess Na/Bi arise because BTO phase with its lower  $\epsilon_r$  is gradually eliminated as sufficient excess Na is added. The dielectric properties ( $\epsilon_r \sim 550$  and  $\tan \delta \sim 0.03$  at 10~100 kHz) of the lead-free NBT films with the ratio of Na/Bi=2.0 are better than those reported elsewhere<sup>6,12,20)</sup> and furthermore that of PZT thin film prepared by sputtering<sup>21)</sup>, even though the properties of thin films are generally inferior to those of bulk ceramics due to their fine grain and low polar contributions.<sup>3,19)</sup> We conclude that the well-reacted and compensated composition that results from excess Na and Bi addition leads to an improvement in crystallinity. Watanabe and Ichinose<sup>11)</sup> have also reported that NBT films prepared by sputtering of an NBT target containing 50 mol% excess Na were found to have a  $\epsilon_r \sim 620$ . Figure 5 shows the temperature dependence of  $\epsilon_r$  as a function of the excess Na/Bi ratio. Variation in temperature was reported to affect crystal structure in NBT ceramic, resulting in its phase transition (ferroelectric-antiferroelectric-paraelectric) with peculiar variation of  $\epsilon_r$  with temperature.<sup>5,20)</sup> Although the changes in the dielectric constants of the thin films were weak and broad regardless of the excess content as shown in Fig. 5, the similar dielectric behavior to that of bulk ceramics was observed.<sup>5)</sup> The P-E hysteresis curves of the NBT thin films are shown in Fig. 6. Ferroelectric behavior was observed at 400 kV/cm and room temperature, although perfect saturation was not

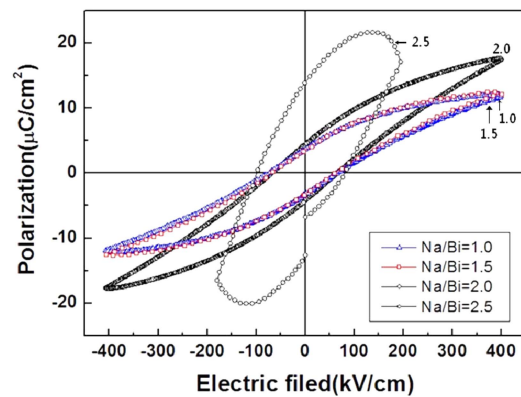


Fig. 6. P-E hysteresis loops of NBT thin films annealed at 700°C for 10 min with various ratios of excess Na content to Bi content.

achieved. Effective ferroelectric behavior with remanent polarization  $P_r \sim 4.6 \mu\text{C}/\text{cm}^2$  and coercive field  $E_c \sim 51 \text{ kV}/\text{cm}$  was found for the NBT film with a Na/Bi ratio of 2.0, which agrees with the results of the XRD analysis and the AFM imaging. On the other hand, the high lossy behavior for the thin film with Na/Bi ratio of 2.5 resulted in a bulging P-E hysteresis loop as shown in Fig. 6. The ferroelectric behavior of these thin films is inferior to that of bulk ceramics, for which  $P_r \sim 30 \mu\text{C}/\text{cm}^2$  and coercive field  $E_c \sim 70 \text{ kV}/\text{cm}$ , which might be associated with the fine grain and low densification of the thin film.<sup>8,14)</sup> It is also speculated that these properties of the thin films are affected by slow domain wall motion, which results in the opening of the hysteresis loop at zero field as has been observed for sputtered NBT films.<sup>22)</sup> In contrast to NBT ceramics,<sup>23)</sup> there are few reports of the pyroelectric properties of NBT thin films. In this study, the pyroelectric properties of NBT thin films with a Na/Bi ratio of 2.0 annealed at 700°C for 10 min were investigated for temperatures up to 400°C. The pyroelectric coefficient of the NBT films was calculated from



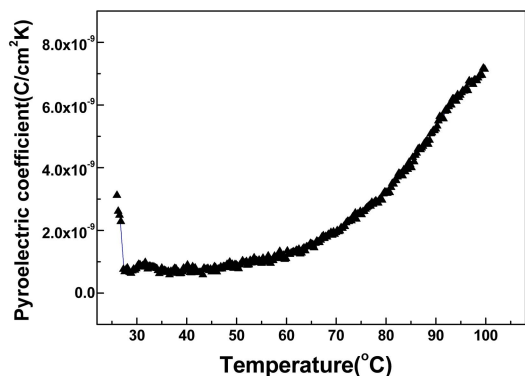


Fig. 7. Temperature dependence of the pyroelectric coefficient of NBT thin films with excess Na/excess Bi = 2.

the pyroelectric current and found to be  $3 \times 10^{-7} \text{ Ccm}^{-2}\text{K}$  at the phase transition temperature near  $350^\circ\text{C}$ , whereas that of bulk ceramics was reported to be  $9 \times 10^{-5} \text{ Ccm}^{-2} \text{ K}$ .<sup>23)</sup> The variation in the pyroelectric coefficient between room temperature and  $100^\circ\text{C}$ , which is the temperature range relevant to commercialization, is shown in Fig. 7; the pyroelectric coefficient at  $40\text{--}60^\circ\text{C}$  was found to be about  $1\text{--}1.3 \text{ nCcm}^{-2}\text{K}$ . This value is much lower than those of pyroelectric thin films based on PZT and  $\text{PbTiO}_3$ .<sup>16,24)</sup> However, this value seems to be meaningful in comparison with the lead-free pyroelectric thin film such as  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ , which has a pyroelectric coefficient of  $2\text{--}3 \text{ nCcm}^{-2}\text{K}$  at room temperature.<sup>25)</sup> Methods for improving preferred orientation of the thin films such as a modified film process and a poling process, and thus for improving their pyroelectric properties, are under investigation.

#### 4. Conclusions

Sol-gel derived NBT thin films have been prepared with various excess Na and Bi contents. It was found that increased amount of perovskite NBT phase and decreased amount of pyrochlore BTO phase resulted from increases in the excess Na/Bi ratio. The dielectric properties were improved with enhancing the perovskite phase. A pure perovskite phase NBT film was obtained for an excess Na/Bi ratio of 2.0, after annealing at  $700^\circ\text{C}$  for 10 min. Further increases in the excess amounts resulted in abrupt increases in dielectric loss, although no secondary phase was detected. In addition, the surface morphology became non-uniform and coarse. It is expected that the pyroelectric coefficient of  $1\text{--}1.3 \text{ nC/cm}^2\text{K}$  can be improved by enhancing the film orientation and carrying out an additional poling process.

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