Natural-superlattice structured $\text{CaBi}_2\text{Nb}_2\text{O}_9\text{-Bi}_4\text{Ti}_3\text{O}_{12}$ ferroelectric thin films

Caihong Xue^{a,b}, Xin Sun^{c,†}, Yunxiang Zhang^{a,b,‡}, Yuyao Zhao^{a,b}, Hanfei Zhu^{a,b},
Qian Yang^{a,b}, Menglin Liu^{a,b}, Chunming Wang^d, Jun Ouyang^{a,b,e*}

^a Key Laboratory for Liquid-Solid Structure Evolution and Processing of Materials (Ministry of Education), School of Materials Science and Engineering, Shandong University, Jinan 250061, China

^b Suzhou Institute of Shandong University, Suzhou 215123, China

^c Center for Materials, Devices and Integrated Systems, Rensselaer Polytechnic Institute, Troy, NY 12180, USA

^d State Key Laboratory of Crystal Materials, School of Physics, Shandong University, Jinan 250010, China

^e National Institute of Standards and Technology, Gaithersburg, Maryland, 20899, USA

^{†,‡}: These two authors contributed equally to this work.

* Corresponding Author: E-mail address: ouyangjun@sdu.edu.cn

Abstract: Natural-superlattice-structured/Intergrowth $\text{CaBi}_2\text{Nb}_2\text{O}_9\text{-Bi}_4\text{Ti}_3\text{O}_{12}$ (CBNO-BIT) ferroelectric thin films were successfully prepared via a magnetron sputtering process. XRD and TEM analysis revealed the $[\text{Bi}_2\text{O}_2\text{-(CaNb}_2\text{O}_7)\text{-Bi}_2\text{O}_2\text{-(Bi}_2\text{Ti}_3\text{O}_{10})]_n$ intergrowth structure of the film, as well as a

(200)/(020) texture. XPS and EDS results confirmed that the film composition is close to the chemical stoichiometry. With its microstructure being successfully tailored at the nanoscale, the CBNO-BIT film exhibits good electrical properties, including a large dielectric constant ($\epsilon_r \sim 390$), a high piezoelectric coefficient ($d_{33} \sim 90$ pm/V) as well as a high energy storage density ($W_E \sim 76$ J/cm³). Finally, the intergrowth nature of the film was verified by the measured temperature-dependent dielectric response (C-T).

Keywords: intergrowth bismuth layer-structured ferroelectrics (iBLSFs); magnetron sputtering; strain engineering; electrical property

1. Introduction

Since the discovery by Aurivillius in 1949 [1, 2], bismuth layer-structured ferroelectrics (BLSFs) have attracted widespread interests for their applications in non-volatile ferroelectric random access memories (FRAM) [3] and high temperature piezoelectrics [4], because they are fatigue-free and have high Curie temperatures (T_c). These materials have a general formula of $[\text{Bi}_2\text{O}_2][\text{A}_{m-1}\text{B}_m\text{O}_{3m+1}]$, where A can be mono-, di- or tri-valent ions at the 12-coordinated sites, B can be tetra-, penta- or hexa-valent ions at the 6-coordinated sites, and m represents the number of BO_6 octahedrons in the pseudo-perovskite blocks [5, 6]. The most noticeable feature in the crystalline structure of a BLSF is an alternative stacking of the $[\text{Bi}_2\text{O}_2]$ layer and the pseudo-perovskite layer along its long axis (the c -axis). Different from a perovskite

ferroelectric, the spontaneous polarization (P_s) of a BLSF is mainly aligned along its short axes (a - or b -axis).

Among the BLSFs, $\text{CaBi}_2\text{Nb}_2\text{O}_9$ (CBNO, $m = 2$) and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT, $m = 3$) have good overall electrical properties and very high T_c values (Fig. 1 a, b) [7, 8]. Nevertheless, the remnant polarizations (P_r) of these materials remain relatively low as compared with those of typical perovskite ferroelectrics (PZT, BiFeO_3 , BaTiO_3 , etc.), and therefore have hindered their further applications. Recently, several experimental methods have been explored in an attempt to enlarge the P_r values of BLSFs, including substitution [3], doping [9, 10] and formation of intergrowth ferroelectrics [11].

The intergrowth BLSFs (iBLSFs) were first discovered by Kikuchi et al. [12] in bismuth titanate niobate ($\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$). The crystalline structure of this compound was analyzed by Horiuchi et al. [13] via high-resolution transmission electron microscopy. It was revealed that the perovskite blocks of $[\text{Bi}_2\text{Ti}_3\text{O}_{10}]$ and $[\text{BiTiNbO}_7]$ are alternatively sandwiched between the $[\text{Bi}_2\text{O}_2]$ layers, forming a natural superlattice structure. This self-assembled nanostructure provides tremendous opportunities in tailoring the properties and expanding the class and applications of BLSFs. For instance, similar to that in an artificial superlattice, polarization enhancement is expected in an intergrowth BLSF due to the effect of the periodic structural alternation [11, 14-16]. A good example is the above-mentioned $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ (BTN), which exhibited a larger spontaneous polarization than those of its parent compounds of $\text{Bi}_3\text{TiNbO}_9$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ [17, 18].

CaBi₂Nb₂O₉ (CBNO), with lattice parameters of $a = 5.544 \text{ \AA}$, $b = 5.466 \text{ \AA}$, $c = 24.970 \text{ \AA}$ [19], has the highest curie temperature ($T_c \approx 943 \text{ }^\circ\text{C}$) [7] among BLSFs. CBNO shows a large anisotropy in its properties along different crystalline directions. Cho et al. fabricated highly c -axis oriented CBNO films with a remnant polarization of $\sim 3.6 \text{ }\mu\text{C}/\text{cm}^2$ on (100) Si substrates via pulsed laser deposition [20, 21]. Zhang et al. fabricated highly a -axis oriented CBNO films with a remnant polarization of $\sim 14 \text{ }\mu\text{C}/\text{cm}^2$ on (100) MgO substrates via a rf magnetron sputtering process [22]. As for the piezoelectric property, the d_{33} piezoelectric coefficients for CBNO ceramics are $\sim 7.5 \text{ pm/V}$ and $\sim 20 \text{ pm/V}$ for randomly-oriented and textured ceramics, respectively [7]. For CBNO films, the reported highest d_{33} values are in the range of $\sim 30\text{-}60 \text{ pm/V}$ for a -axis oriented CBNO films [23-25]. On the other hand, Bi₄Ti₃O₁₂ (BIT) is another typical BLSF with lattice parameters of $a = 5.41 \text{ \AA}$, $b = 5.45 \text{ \AA}$, $c = 32.80 \text{ \AA}$ [26], and a relatively high curie temperature ($T_c \approx 675 \text{ }^\circ\text{C}$) [8]. Its properties are highly anisotropic like CBNO. The spontaneous polarization (P_s) and coercive field (E_c) are $4 \text{ }\mu\text{C}/\text{cm}^2$ and 3.5 kV/cm along the c -axis, while they are $50 \text{ }\mu\text{C}/\text{cm}^2$ and 50 kV/cm along the a -axis [27]. As for the piezoelectric property, the d_{33} piezoelectric coefficient for BIT ceramics is $\sim 20 \text{ pC/N}$ [8], and the reported highest d_{33} in thin films is $\sim 60 \text{ pm/V}$ in Pr doped BIT films with a preferred a -axis orientation [28]. The above results indicated that the ferroelectric and piezoelectric properties of CBNO and BIT materials can be improved by increasing the amount of a -grains.

In this paper, intergrowth CBNO–BIT thin films were prepared on (100) MgO substrates via a rf magnetron sputtering process. A (200)/(020) film texture was

revealed by X-ray Diffraction analysis, while results of the TEM investigations supported the natural-superlattice microstructure (Fig. 1c). Electrical properties including P - E , C - f and ε_3 - E characteristics, as well as the temperature dependent dielectric response (C - T) of the films, were measured and correlated with the microstructure. A large d_{33} piezoelectric coefficient (~ 90 pm/V) and a slim P - E hysteresis loop observed in these films indicate their good potentials for applications in lead-free piezoelectric and dielectric devices.

2. Experimental

A cylinder shape ($\Phi = 50$ mm, $t = 5$ mm) $\text{CaBi}_2\text{Nb}_2\text{O}_9\text{-Bi}_4\text{Ti}_3\text{O}_{12}$ ceramic target was calcined at 1120°C for 10 hours using a reactive sintering method and annealed at 700°C in air for 6 hours to stabilize its structure. The starting materials were CaCO_3 (99.0% purity), Bi_2O_3 (99.8%), Nb_2O_5 (99.5%) and TiO_2 (99.8%), with molar ratios determined by the stoichiometric ratios of metal ions in the intergrowth ferroelectric $\text{CaBi}_6\text{Nb}_2\text{Ti}_3\text{O}_{21}$, except that 5 mol% excessive bismuth oxide was added to compensate its evaporation loss.

CBNO-BIT thin films with a thickness of 200-300nm were deposited on single crystalline (100) MgO substrates via a rf magnetron sputtering process. Prior to the film deposition, a base pressure of 2.0×10^{-4} Pa was achieved and then the substrate was heated to 600°C at a ramping rate of $6\text{-}7^\circ\text{C}/\text{min}$. In order to minimize the deviation of the film's composition from the chemical stoichiometry of $\text{CaBi}_6\text{Nb}_2\text{Ti}_3\text{O}_{21}$ due to surface decomposition (i.e., reduction of oxides) or a strong

bulk diffusion of the sputtering target, we chose a sputtering atmosphere with an Ar/O₂ flow ratio of 4:1 and a moderate sputtering power of 70 W [22]. The deposition pressure was fixed at 1.2Pa, and the target-substrate distance was set to 55 mm. Before deposition of the ferroelectric film, a bottom electrode layer of SrRuO₃ was sputtered on the substrate under the same conditions. The multilayer structure was cooled down in the same Ar/O₂ atmosphere post processing, at a cooling rate of 6-7 °C/min.

Phase structure and crystallographic orientations of the films were analyzed by using X-ray θ - 2θ scans (Rigaku Dmax-rc diffractometer equipped with a Ni-filtered Cu-K α radiation source) and pole figures (via a Rigaku SmartLab XRD, R-Axis Spider, 40 kV, 200mA). Surface scans of the films were performed by using a commercial MicroNano® Scanning Probe Microscope (SPM) in its atomic force microscopy (AFM) mode. Nanostructures of the films were investigated via transmission electron microscopy (TEM, JEOL JEM-2100HR). Chemical composition and valence states of the elements were analyzed via energy-dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS), respectively.

The room temperature ferroelectric hysteresis loops (P - E) of the films were measured by using a ferroelectric test system (RT-Precision LC, Radiant Technology). The out-of-plane piezoelectric strain-electric field curves (ϵ_3 - E) were measured by using a SPA-300HV Scanning Probe Microscope (controlled by SPI, Seiko Instruments, Inc.) in the quantitative piezoelectric force microscopy mode. Dielectric constant as a function of temperature was measured by using a

high-precision digital bridge (LCR meter, QuadTech 7600plus) with an attached temperature-controlled probe station (Linkam-HFS600E-PB2). Prior to the electrical characterizations, circular Au top electrodes ($\Phi=200\text{ }\mu\text{m}$) were sputtered at room temperature via a shadow mask.

3. Results and discussion

Fig. 2 (a) shows the XRD 2θ scan pattern of the CBNO-BIT film. All diffraction peaks correspond well to those of the standard diffraction pattern of intergrowth ferroelectric $\text{Bi}_3\text{TiNbO}_9$ - $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (ICSD #51801, $a=0.5442\text{ nm}$, $b=0.5404\text{ nm}$ $c=5.799\text{ nm}$), showing no signs of a second phase. The film is polycrystalline and has a (200)/(020) texture, which can be ascribed to an improved lattice matching between (200)/(020) CBNO-BIT and the underlying (100) MgO substrate [22]. To further investigate the film's crystalline orientations, X-ray pole figure analysis was performed by using the (200)/(020) reflection as shown in Fig. 2 (b). During the measurement, the sample's tilt angle ψ was varied between 0° and 70° , and its azimuthal angle ϕ was rotated from 0° to 360° . As can be seen, the (200)/(020) pole figure consists of four sets of peaks: the strong central diffraction spot coming from the preferential {200} grains, i.e., the a -grains; while the diffraction peaks with a four-fold symmetry at $\psi \approx 14^\circ$, 26° and 65° correspond to the {013}, {015} and {217} crystalline planes, respectively. The X-ray diffraction signals concentrated in the ψ angle range between 0° and 30° , suggesting that the film consists mostly of a -grains and grains slightly tilting away from the a -axis.

Fig. 3 (a) is the AFM surface scan image of the CBNO-BIT film (over an area of $5\mu\text{m}\times 5\mu\text{m}$), which yielded a root-mean-square (RMS) surface roughness of ~ 1.35 nm. Such a smooth surface allows the fabrication and integration of thin-film based microelectronic devices. Fig. 3 (b) is the cross-sectional TEM image of the film, which revealed a typical columnar grain structure with an average grain width ~ 40 nm. Except for a preferentially thinned interface layer (the “white” layer between the CBNO-BIT film and the SRO electrode) during the TEM sample preparation [29, 30], no other structural defects (voids, cracks, etc...) with a size of ~ 10 nm or above can be observed in the TEM image. Fig. 3 (c) (d) are the high-resolution transmission electron microscopy (HRTEM) images of the film taken along the $[1\ -2\ 0]$ and $[1\ 0\ 0]$ zone axes, while the insets of Fig. 3(c) (d) are the selected area electron diffraction (SAED) patterns. First of all, the lattice parameters computed from the SAED patterns ($a=b=0.5202$ nm, $c=5.859$ nm) are consistent with the XRD data interpreted by using the intergrowth model. Secondly, the c -axis lattice parameter (5.859 nm) can be directly measured on both HRTEM images and is the sum of those of the CBNO and BIT materials, revealing a natural-superlattice structure at the nanoscale. These results support the proposed unit cell model of $[\text{Bi}_2\text{O}_2-(\text{CaNb}_2\text{O}_7)-\text{Bi}_2\text{O}_2-(\text{Bi}_2\text{Ti}_3\text{O}_{10})]$ (Fig. 1c), i.e., a superlattice consisting of iterations of one unit cell of CBNO and another unit cell of BIT along their shared c -axis.

XPS and EDS analysis were performed to investigate valence states of the elements and chemical composition of the film. Fig. 4 (a) is the XPS spectrum of the film in the electron energy range between 0 and 600 eV. It clearly shows the

existence of Ca, Bi, Ti, Nb, and O elements in the film. Furthermore, except for C 1s (284.8 eV) coming from adventitious carbon which is used for calibration of the binding energies, there is no clear signature of other impurity elements. Fig. 4 (b)-(e) are the photoemission spectra of Ca 2p, Bi 4f, Ti 2p and Nb 3d core levels, respectively. In Fig. 4 (b), the binding energies of Ca 2p_{3/2} and Ca 2p_{1/2} are revealed to be 346.6 eV and 350.2 eV, respectively, matching those of the Ca-O bond in CaO. This indicates that the Ca element exists in the form of Ca²⁺ in the film. Similarly, the binding energies of Bi 4f_{7/2} and Bi 4f_{5/2} (158.9 eV and 164.2 eV, respectively, Fig. 4c), Ti 2p_{3/2} and Ti2p_{1/2} (458.2 eV and 466.1 eV, respectively, Fig. 4 d) and Nb 3d_{5/2} and Nb 3d_{3/2} (206.4 eV and 209.4 eV, respectively, Fig. 4e) suggest that the elements of Bi, Ti and Nb exist in the form of Bi³⁺, Ti⁴⁺ and Nb⁵⁺, respectively. Lastly, the film's composition was estimated to be $n_{Ca}:n_{Nb}:n_{Ti}=1:2.2:2.8$ via quantitative EDS analysis, which is close to the stoichiometric ratio of the elements. The EDS spectrum of the film is shown in Fig. 4 (f). It is noted that the Bi concentration of the film could not be properly estimated from EDS since the characteristic peaks of Bi and Au (coated for SEM analysis of the film) overlapped near the energy level $E\sim 2.45\text{eV}$. However, our previous studies of Bi-based ferroelectric films revealed that by using the 4:1 mixed Ar:O₂ sputtering atmosphere, the decomposition of Bi₂O₃ can be minimized in a sputtering process [22, 31]. Therefore, we concluded that the composition of the film did not deviate significantly from the chemical stoichiometry.

Fig. 5 (a) shows a polarization hysteresis loop (P - E) together with the corresponding switching current loop (I_{sw} - E) of the CBNO-BIT film, both measured

at room temperature and a frequency of 1 kHz. The P - E loop is slim and exhibits a ferroelectric switching, as evidenced by the peaks of switching current near the coercive fields ($\pm E_c$). Under an applied maximum field (E_{max}) of 2500 kV/cm, a saturated polarization (P_s) of $\sim 88 \mu\text{C}/\text{cm}^2$, a remnant polarization (P_r) of $\sim 13 \mu\text{C}/\text{cm}^2$ and a coercive field (E_c) of 199 kV/cm were obtained. While the improvement in P_r can be explained by a number of factors, including the increased amount of a -axis oriented grains (or grains slightly tilting away from the a -axis), a residual misfit stress [22], as well as the formation of a natural-superlattice [17, 18], the large enhancement in P_s is mostly due to an improved dielectric constant in the intergrowth ferroelectric film. In a dielectric material, $P_s = D_s = P + \epsilon_0 \epsilon_r E$, where E is the applied electric field, P is the spontaneous polarization ($P \approx P_r$ for ferroelectrics and $P=0$ for linear dielectrics), ϵ_0 and ϵ_r are the vacuum permittivity and relative dielectric constant of the material, respectively. For the CBNO-BIT film, its dielectric constant ϵ_r (measured ~ 390 @ 1kHz as shown in Fig. 6a) is significantly improved as compared with single component CBNO (~ 283) [22] or BIT (~ 180) [32] films, which can be attributed to the periodic interlayer stress in the $[\text{Bi}_2\text{O}_2-(\text{CaNb}_2\text{O}_7)-\text{Bi}_2\text{O}_2-(\text{Bi}_2\text{Ti}_3\text{O}_{10})]_n$ superlattice. This is a “misfit stress” induced by the lattice mismatch between the CBNO and BIT blocks in the intergrowth structure. Moreover, from the P - E loop, the energy storage density (W_E) and efficiency (η) are calculated to be $\sim 76 \text{ J}/\text{cm}^3$ and 66.3%, respectively, under an applied field of 2500 kV/cm. Both parameters for capacitive energy storage were substantially improved when compared with those for our previously reported CBNO films prepared under similar conditions ($W_E=43 \text{ J}/\text{cm}^3$ and $\eta\sim 50\%$

under $E=2600$ kV/cm) [22]. The enhanced energy storage capability in the CBNO-BIT film comes from its improved dielectric constant (ϵ_r) and saturated polarization (P_s).

Fig. 5 (b) shows the leakage current density-electric field (J - E) characteristic of the CBNO-BIT film at room temperature. The leakage current density was lower than $2.0 \times 10^{-6} \text{ A/cm}^2$ up to an applied field of 290 kV/cm, indicating a good insulating film. On the other hand, Fig. 5 (c) shows the piezoelectric strain loop (ϵ_3 - E) and the computed piezoelectric d_{33} loop (d_{33} - E) of the CBNO-BIT film. The average piezoelectric d_{33} coefficient (calculated by $d_{33}=\epsilon_3/E$) was ~ 90 pm/V, which is comparable to those of the lead zirconate titanate (PZT) films, and is much higher than those reported for single-phase CBNO (up to 58 pm/V [24, 25]) and BIT (up to 60 pm/V [28]) films. Considering the phenomenological equation governing the intrinsic piezoelectric d_{33} coefficient, i.e., $d_{33}=2Q\epsilon_0\epsilon_rPE$, where Q , ϵ_0 , ϵ_r , P and E are the electrostrictive coefficient, vacuum permittivity, relative dielectric constant, spontaneous polarization, and electric field, respectively, the enhancement in piezoelectric d_{33} coefficient can be mostly attributed to the improved dielectric constant (ϵ_r) and enhanced spontaneous polarization (P).

Fig. 6 (a) shows the frequency-dependent dielectric constant (ϵ_r) and dielectric loss ($\tan\delta$) of the film measured at room temperature. It can be seen that in the broad frequency range between 1kHz and ~ 100 kHz, ϵ_r only slightly decreases while $\tan\delta$ slightly increases from $\sim 2\%$ to 5% . This weak-frequency dependence can be attributed to the high resistance (Fig. 5 (b)) of the film. In the frequency range of

100 kHz-2 MHz where the relaxation process of bulk charge carriers dominates, ϵ_r decreases and $\tan\delta$ increases rapidly with frequency, typical of sputtered ferroelectric films. Overall, the CBNO-BIT film exhibits an enhanced dielectric property as compared with the single component CBNO [22] and BIT [32] films.

Lastly, Fig. 6 (b) shows the temperature dependent relative dielectric constant (ϵ_r) of the CBNO-BIT film. Dual dielectric peaks exist with the first one near $T_1=330^\circ\text{C}$ and the second one near $T_2=480^\circ\text{C}$, which is qualitatively consistent with those reported for the intergrowth ferroelectric ceramics [33-36]. However, the temperatures of the ϵ_r peaks are somewhat lower than those observed in the bulk ceramics by Pedro Durán et al. [37] ($T_1=655^\circ\text{C}$ and $T_2=855^\circ\text{C}$), and by Chu et al. [33] ($T_1=677^\circ\text{C}$ and $T_2=856^\circ\text{C}$). The decreased phase transition temperatures may be attributed to effect of the film-substrate misfit strain.

4. Conclusions

Intergrowth ferroelectric CBNO-BIT thin films have been successfully fabricated via a magnetron sputtering process. Formation of the natural-superlattice structure of $[\text{Bi}_2\text{O}_2\text{-(CaNb}_2\text{O}_7)\text{-Bi}_2\text{O}_2\text{-(Bi}_2\text{Ti}_3\text{O}_{10})]_n$ was confirmed by XRD and TEM analysis. The films showed good electrical properties including a sizable remnant polarization ($\sim 13 \mu\text{C}/\text{cm}^2$), a large dielectric constant ($\epsilon_r \sim 390$), and a high energy storage density ($W_E \sim 76 \text{ J}/\text{cm}^3$). Moreover, with a good thermal stability (up to $\sim 330^\circ\text{C}$), the piezoelectric d_{33} coefficient of the film reached $\sim 90 \text{ pm}/\text{V}$, which is comparable to those of the PZT films. Our results indicate that this thin film material is a

promising substitute of lead-based perovskite ferroelectrics in high performance dielectric capacitors and piezoelectric MEMS devices.

Acknowledgements

The authors acknowledge the financial support of the NSFC of China (Project Grant No. 91122024 and No. 50902087), the NSFC of Shandong Province of China (Project Grant No. ZR2012EMQ005 and ZR2014EMM012), the Program for New Century Excellent Talents in University (State Education Ministry), Nano Projects of Soochow City (Grant No. ZXG201445), the Fundamental Research Funds of Shandong University (Grant No. 2015JC034, 2015YQ009 and 2016JC036), and a foundation under the Grant No. 2015JMRH0103. J. O. would also like to thank the “Qi-Lu Young Scholar Fund” of Shandong University and the support from the Material Measurement Laboratory of NIST, Gaithersburg, MD (USA).

References

- [1] B. Aurivillius, Mixed bismuth oxides with layer lattices. 1. The structure type of $\text{CaNb}_2\text{Bi}_2\text{O}_9$, Arkiv for kemi, 1 (1950) 463-480.
- [2] B. Aurivillius, Mixed bismuth oxides with layer lattices. 2. Structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, Arkiv for kemi, 1 (1950) 499-512.
- [3] B.H. Park, B.S. Kang, S.D. Bu, T.W. Noh, J. Lee, W. Jo, Lanthanum-substituted bismuth titanate for use in non-volatile memories, Nature, 401 (1999) 682-684.
- [4] H. Yan, H. Zhang, M.J. Reece, X. Dong, Thermal depoling of high Curie point

- Aurivillius phase ferroelectric ceramics, *Applied Physics Letters*, 87 (2005) 2911.
- [5] P. Boullay, G. Trolliard, D. Mercurio, J. Perez-Mato, L. Elcoro, Toward a Unified Approach to the Crystal Chemistry of Aurivillius-Type Compounds: II. $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$, a Case Study, *Journal of Solid State Chemistry*, 164 (2002) 261-271.
- [6] C. Shao, Y. Lu, D. Wang, Y. Li, Effect of Nd substitution on the microstructure and electrical properties of $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ piezoceramics, *Journal of the European Ceramic Society*, 32 (2012) 3781-3789.
- [7] H. Yan, H. Zhang, R. Ubic, M.J. Reece, J. Liu, Z. Shen, Z. Zhang, A Lead-Free High-Curie-Point Ferroelectric Ceramic, $\text{CaBi}_2\text{Nb}_2\text{O}_9$, *Advanced Materials*, 17 (2005) 1261-1265.
- [8] E. Subbarao, A family of ferroelectric bismuth compounds with high Curie temperatures, *IRE Transactions on Electron Devices*, 8 (1961) 422-422.
- [9] K. Kawada, A. Kan, Y. Ueda, T. Moriyama, H. Ogawa, Influence of Ag-doping on ferroelectric properties of $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ ceramics, *Ferroelectrics*, 427 (2012) 105-113.
- [10] Y. Noguchi, M. Miyayama, Large remanent polarization of vanadium-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, *Applied Physics Letters*, 78 (2001) 1903.
- [11] Y. Noguchi, M. Miyayama, T. Kudo, Ferroelectric properties of intergrowth $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ - $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ ceramics, *Applied Physics Letters*, 77 (2000).
- [12] T. Kikuchi, Synthesis of New, Layered Bismuth Titanates, $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ and $\text{Bi}_6\text{Ti}_3\text{WO}_{18}$, *Journal of the Less Common Metals*, 48 (1976) 319-323.
- [13] S. Horiuchi, T. Kikuchi, M. Goto, Structure determination of a mixed-layer

- bismuth titanate, $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$, by super-high-resolution electron microscopy, *Acta Crystallographica Section A*, 33 (1977) 701-703.
- [14] W. Sakamoto, K. Imada, T. Shimura, T. Yogo, Synthesis and Properties of Intergrown $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ - $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ Ferroelectric Thin Films by Chemical Solution Deposition, *Japanese journal of applied physics*, 44 (2005) 6952.
- [15] A. Shibuya, M. Noda, M. Okuyama, H. Fujisawa, M. Shimizu, Natural-superlattice-structured $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ - $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ ferroelectric thin films, *Applied physics letters*, 82 (2003) 784.
- [16] H. Wang, J. Li, J. Xu, L. Yang, M. Ren, Fabrication and ferroelectric properties of sol-gel derived 1-1 intergrowth-superlattice-structured $\text{Bi}_3\text{TiNbO}_9$ - $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films, *Journal of Materials Science: Materials in Electronics*, 22 (2011) 654-658.
- [17] A. Shibuya, S. Ikemori, W. Wu, M. Noda, M. Okuyama, Preparation and basic properties of ferroelectric thin films having a superlattice structure of 2 $\text{Bi}_3\text{TiNbO}_9$ units-1 $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ unit, *Applied physics letters*, 83 (2003) 1411-1413.
- [18] Z. Yi, Y. Wang, Y. Li, Q. Yin, Ferroelectricity in intergrowth $\text{Bi}_3\text{TiNbO}_9$ - $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics, *Journal of applied physics*, 99 (2006).
- [19] G. Smolenskii, *Ferroelectrics and related materials*, Taylor & Francis US1984.
- [20] H. Cho, S. Desu, Structural and Electrical Properties of Oriented Ferroelectric $\text{CaBi}_2\text{Nb}_2\text{O}_9$ Thin Films Deposited on n+-Si (100) by Pulsed Laser Deposition, *physica status solidi (a)*, 161 (1997) 371-378.
- [21] S. Desu, H. Cho, P. Joshi, Highly oriented ferroelectric $\text{CaBi}_2\text{Nb}_2\text{O}_9$ thin films

- deposited on Si (100) by pulsed laser deposition, *Applied physics letters*, 70 (1997) 1393-1395.
- [22] Y. Zhang, J. Ouyang, J. Zhang, Y. Li, H. Cheng, H. Xu, M. Liu, Z.-P. Cao, C.-M. Wang, Strain engineered $\text{CaBi}_2\text{Nb}_2\text{O}_9$ thin films with enhanced electrical properties, *ACS applied materials & interfaces*, 8 (2016) 16744-16751.
- [23] Y. Zhang, C.-M. Wang, Y. Li, H. Cheng, M. Liu, C. Xue, H. Xu, J. Ouyang, Enhancing electromechanical properties of $\text{CaBi}_2\text{Nb}_2\text{O}_9$ thin films grown on Si, *Ceramics International*, 42 (2016) 17928-17931.
- [24] A. Simões, C. Riccardi, L. Cavalcante, E. Longo, J.A. Varela, B. Mizaikoff, Impact of oxygen atmosphere on piezoelectric properties of $\text{CaBi}_2\text{Nb}_2\text{O}_9$ thin films, *Acta materialia*, 55 (2007) 4707-4712.
- [25] A. Simoes, A. Ries, C. Riccardi, A. Gonzalez, E. Longo, J.A. Varela, High Curie point $\text{CaBi}_2\text{Nb}_2\text{O}_9$ thin films: A potential candidate for lead-free thin-film piezoelectrics, *Journal of applied physics*, 100 (2006) 074110.
- [26] E. Subbarao, Crystal Chemistry of Mixed Bismuth Oxides with Layer-Type Structure, *Journal of the American Ceramic Society*, 45 (1962) 166-169.
- [27] S. Cummins, L. Cross, Crystal symmetry, optical properties, and ferroelectric polarization of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ single crystals, *Applied Physics Letters*, 10 (1967) 14-16.
- [28] H. Matsuda, S. Ito, T. Iijima, Uniform field-induced strain in a/b-axes-oriented $\text{Bi}_{3.9}\text{Pr}_{0.1}\text{Ti}_3\text{O}_{12}$ thick films on IrO_2/Si substrates for lead-free piezoelectric microdevice applications, *Applied physics letters*, 85 (2004) 1220.

- [29] A. Barna, B. Pécz, M. Menyhard, TEM sample preparation by ion milling/amorphization, *Micron*, 30 (1999) 267-276.
- [30] J. McCaffrey, M. Phaneuf, L. Madsen, Surface damage formation during ion-beam thinning of samples for transmission electron microscopy, *Ultramicroscopy*, 87 (2001) 97-104.
- [31] H. Zhu, X. Sun, L. Kang, M. Hong, M. Liu, Z. Yu, J. Ouyang, Charge transport behaviors in epitaxial BiFeO_3 thick films sputtered with different Ar/O_2 flow ratios, *Scripta Materialia*, 115 (2016) 62-65.
- [32] T. Nakamura, R. Muhammet, M. Shimizu, T. Shiosaki, Preparation of C-axis-oriented $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films by metalorganic chemical vapor deposition, *Japanese journal of applied physics*, 32 (1993) 4086.
- [33] F. Chu, D. Damjanovic, O. Steiner, N. Setter, Piezoelectricity and Phase Transitions of the Mixed-Layer Bismuth Titanate Niobate $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$, *Journal of the American Ceramic Society*, 78 (1995) 3142-3144.
- [34] Z. Hongtao, Y. Haixue, M.J. Reece, High temperature lead-free relaxor ferroelectric: Intergrowth Aurivillius phase $\text{BaBi}_2\text{Nb}_2\text{O}_9\text{-Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics, *Journal of Applied Physics*, 107 (2010).
- [35] H. Miyabayashi, Y. Hiruma, H. Nagata, T. Takenaka, Temperature Dependences of Piezoelectric Properties of Grain-Oriented $\text{SrBi}_2\text{Nb}_2\text{O}_9\text{-Bi}_4\text{Ti}_3\text{O}_{12}$ Ceramics, *Ferroelectrics*, 404 (2010) 147-151.
- [36] E. Kharitonova, V. Voronkova, Synthesis and electrical properties of mixed-layer Aurivillius phases, *Inorganic Materials*, 43 (2007) 1340-1344.

- [37] P. Duran, F. Capel, C. Moure, M. Villegas, J.F. Fernandez, J. Tartaj, A.C. Caballero, Processing and dielectric properties of the mixed-layer bismuth titanate niobate $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ by the metal-organic precursor synthesis method, *Journal of the European Ceramic Society*, 21 (2001) 1-8.

Figure Captions

Fig. 1 Illustrations of (a) $\text{CaBi}_2\text{Nb}_2\text{O}_9$, (b) $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, and (c) the $\text{CaBi}_2\text{Nb}_2\text{O}_9$ (CBNO) - $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT) intergrowth ferroelectrics (left: 2-D projection, right: 3-D structure).

Fig. 2 (a) X-ray diffraction 2θ scan pattern, (b) X-ray pole figure analysis (using the (200)/(020) reflection).

Fig. 3 (a) AFM surface scan ($5\mu\text{m}\times 5\mu\text{m}$) image, (b) cross-sectional bright field TEM image of the CBNO-BIT thin film grown on $\text{SrRuO}_3/(100)\text{MgO}$; the “whiteness” of a thin interface layer between CBNO-BIT and SRO can be attributed to the preferential thinning along the cross-section direction, which has created the color contrast. (c) (d) high-resolution TEM images of the CBNO-BIT thin film taken along the $[1\ -2\ 0]$ and $[1\ 0\ 0]$ zone axes (insets are the SAED patterns).

Fig. 4 (a) XPS spectrum of the CBNO-BIT thin film in the energy range of 0-600eV; (b)-(e) are the XPS spectra of Ca 2p core level, Bi 4f core level, Ti 2p core level and Nb 3d core level, respectively, (f) EDS pattern of the CBNO-BIT thin film.

Fig. 5 (a) Ferroelectric polarization hysteresis (P - E) loop and its corresponding switching current-electric field (I_{sw} - E) loop (@ 1kHz), (b) leakage current density-electric field (J - E) curve, and (c) piezoelectric strain-electric field (ε_3 - E) and piezoelectric d_{33} coefficient-electric field (d_{33} - E) curves of the CBNO-BIT thin film, all measured at room temperature.

Fig. 6 (a) Dielectric constant and dielectric loss as functions of the measuring frequency, and (b) temperature dependent dielectric constant of the CBNO-BIT film.

Fig. 1

Fig. 2

Fig. 3

(d)

Fig. 4

Fig. 5

Fig. 6