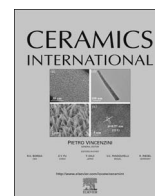




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Natural-superlattice structured $\text{CaBi}_2\text{Nb}_2\text{O}_9\text{-Bi}_4\text{Ti}_3\text{O}_{12}$ ferroelectric thin films

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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 $[\text{Bi}_2\text{O}_2\text{-}(\text{CaNb}_2\text{O}_7)\text{-Bi}_2\text{O}_2\text{-}(\text{Bi}_2\text{Ti}_3\text{O}_{10})]_n$ 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).

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].

$\text{CaBi}_2\text{Nb}_2\text{O}_9$ (CBNO), with lattice parameters of $a=5.544 \text{ \AA}$,

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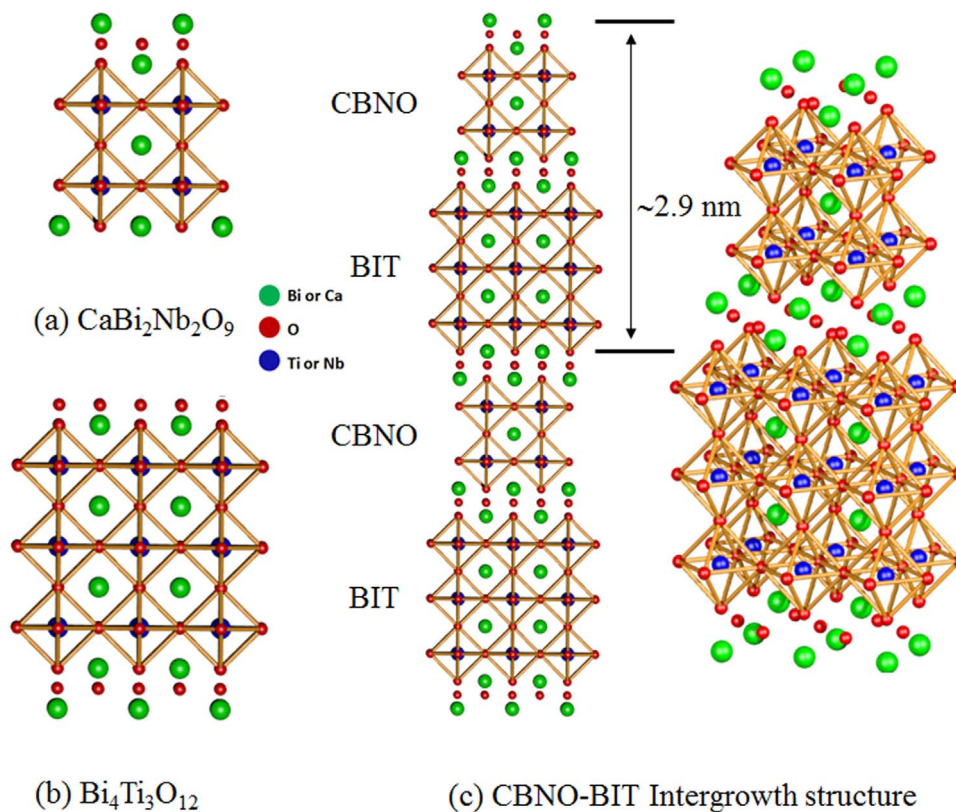


Fig. 1. Illustrations of (a) $\text{CaBi}_2\text{Nb}_2\text{O}_9$, (b) $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, and (c) the $\text{CaBi}_2\text{Nb}_2\text{O}_9$ (CBNO) – $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT) intergrowth ferroelectrics (left: 2-D projection, right: 3-D structure).

$b=5.466 \text{ \AA}$, $c=24.970 \text{ \AA}$ [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 $\sim 3.6 \mu\text{C}/\text{cm}^2$ 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 $\sim 14 \mu\text{C}/\text{cm}^2$ 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, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (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 $4 \mu\text{C}/\text{cm}^2$ and $3.5 \text{ kV}/\text{cm}$ along the c -axis, while they are $50 \mu\text{C}/\text{cm}^2$ and $50 \text{ kV}/\text{cm}$ 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 ($\sim 90 \text{ pm/V}$) 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 ($\Phi=50 \text{ mm}$, $t=5 \text{ mm}$) $\text{CaBi}_2\text{Nb}_2\text{O}_9$ - $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramic target was calcined at $1120 \text{ }^\circ\text{C}$ for 10 h using a reactive sintering method and annealed at $700 \text{ }^\circ\text{C}$ in air for 6 h 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 200–300 nm were deposited on single crystalline (100) MgO substrates via a rf magnetron sputtering process. Prior to the film deposition, a base pressure of $2.0 \times 10^{-4} \text{ Pa}$ was achieved and then the substrate was heated to $600 \text{ }^\circ\text{C}$ at a ramping rate of $6\text{--}7 \text{ }^\circ\text{C}/\text{min}$. 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/ O_2 flow ratio of 4:1 and a moderate sputtering power of 70 W [22]. The deposition pressure was fixed at 1.2 Pa, and the target-substrate distance was set to 55 mm. Before deposition of the ferroelectric film, a bottom electrode layer of SrRuO_3 was sputtered on the substrate under the same conditions. The multi-layer structure was cooled down in the same Ar/ O_2 atmosphere post processing, at a cooling rate of $6\text{--}7 \text{ }^\circ\text{C}/\text{min}$.

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, 200 mA). 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

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