Ferroelectric and magnetic properties of Aurivillius $Bim+1Ti3Fem−3O3m+3$ thin films

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Ferroelectric and magnetic properties of Aurivillius $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$ thin films

Abstract
Aurivillius $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$ ($m = 4, 5, 6$) thin films have been deposited by a pulsed laser deposition system. The x-ray diffraction patterns indicate the formation of orthorhombic phase. The remanent polarization ($2P_r$) of $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$ thin films is decreased with the $m$-number. Positive-up-negative-down measurements indicate the presence of ferroelectric (FE) polarization in as-obtained thin films. Piezoresponse force microscopy investigations confirm the existence of FE domains and the switchable polarization. Weak magnetic moment is detected in the Aurivillius films at room temperature. The present work suggests the possibility of Aurivillius $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$ ($m = 4, 5, 6$) materials as potential roomerature multiferroics.

Keywords
films, properties, ferroelectric, aurivillius, magnetic, 3, thin, 3o3m, 1ti3fem, bim

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I. INTRODUCTION

Multiferroic materials, which possess two or three ferric properties such as ferroelectric, ferromagnetism, and ferroelasticity, have received growing attention due to their novel physical phenomena and the prospect of multidimensional elastic phenomena such as electronic and magnetic order that would account for the magnetoelectric effect in multiferroic materials. Thin film multiferroics have been intensively studied because of their prospects for wide application. Numerous efforts have been made to investigate the coupling phenomena such as electronic and magnetic order that would account for the magnetoelastic effect in multiferroic materials. So far, BiFeO$_3$ (BFO) is the mostly studied compound when the $m$-number is increased because the thermal and chemical stabilities of the Aurivillius phases have been observed in the temperature ranges coinciding with structural phase transition from orthorhombic to tetragonal ($T_c$), fatigue free switching characteristics, and the propensity to form long period structures. The layered structure enables the incorporation of magnetic ions with $+3$ to $+5$ oxidation states in B sites of the perovskite units, which possibly allows both ferroelectricity and ferromagnetism through cations with unoccupied $d$ orbitals and partially filled $d$ orbitals occupying adjacent perovskite units.

Through this structure, BTFO compounds could potentially accommodate the normally conflicting electronic structure requirements for single phase multiferroics. In BTFO system, the structure and macroscopic electric (or magnetic) properties of Bi$_5$Ti$_3$FeO$_{15}$ (BTF, $m = 4$) have been the most investigated. Recently, it was reported that BTF is a competitive candidate for application as RT multiferroic material. The magnetoelastic coupling coefficient of BTF ceramic could be doubled by the initial poling and reached 20.7 mV/Oe cm. Until now, however, reports on the ferroelectric and magnetic properties of the BTFO system are still insufficient. It was found that significant changes in the physical properties of these materials occurred with increasing number of pseudoperovskite blocks in the Aurivillius BTFO materials. It is difficult to obtain single phase compounds when the $m$-number is increased because the thermal and chemical stabilities of the Aurivillius phases of the $(\text{Bi}_2\text{O}_2)^{2+}(\text{Bi}_{m-1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3})^{2-}$ system decreases with increasing number of pseudoperovskite blocks in the Aurivillius BTFO compounds. Moreover, during heating, a structural phase transition from orthorhombic to tetragonal has been observed in the temperature ranges coinciding with the temperatures of ferroelectric–paraelectric transitions.

So far, investigations on the magnetic properties of bilayer structured Aurivillius compounds still lack data. There is no agreement on the Néel temperature data in the literature for these compounds. Srinivas et al. reported that the anti-ferromagnetic Néel temperature of BTFO material increases with the $m$-number: 80 K for Bi$_5$Ti$_3$FeO$_{15}$ (BTF, $m = 4$), 160 K for Bi$_4$Ti$_3$Fe$_2$O$_{18}$ (BTF2, $m = 5$), and 195 K for Bi$_7$Ti$_3$Fe$_2$O$_{21}$ (BTF3, $m = 6$). Jartych et al. reported, however, that all the Aurivillius compounds showed

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Aurivillius Bi$_{m+1}$Ti$_3$Fe$_{m-3}$O$_{3m+3}$ ($m = 4, 5, 6$) thin films have been deposited by a pulsed laser deposition system. The x-ray diffraction patterns indicate the formation of orthorhombic phase. The remanent polarization ($2P_r$) of Bi$_{m+1}$Ti$_3$Fe$_{m-3}$O$_{3m+3}$ thin films is decreased with the $m$-number. Positive-up-negative-down measurements indicate the presence of ferroelectric (FE) polarization in as-obtained thin films. Piezoresponse force microscopy investigations confirm the existence of FE domains and the switchable polarization. Weak magnetic moment is detected in the Aurivillius films at room temperature. The present work suggests the possibility of Aurivillius Bi$_{m+1}$Ti$_3$Fe$_{m-3}$O$_{3m+3}$ ($m = 4, 5, 6$) materials as potential room-temperature multiferroics. © 2015 American Vacuum Society. [http://dx.doi.org/10.1116/1.4926982]
paramagnetic properties at room temperature, while the temperatures of magnetic transitions are completely different.

Since RT multiferroism is an essential issue for the realization of multiferroic devices, it is important to investigate both the ferroelectric and the ferromagnetic properties under ambient condition. In the present work, we reported the deposition of BTFO thin films by pulsed laser deposition (PLD). The potential room temperature multiferroic properties of BTF, BTF2, and BTF3 thin films have been investigated by studying their ferroelectric and magnetic properties.

II. EXPERIMENT

Ceramic targets were synthesized by a standard solid-state reaction method from the starting chemicals Bi$_2$O$_3$, Fe$_2$O$_3$, and TiO$_2$, with purity of 99.99%. Ten atomic percent excess Bi was used to maintain the stoichiometric content of volatile Bi. The Bim$_{m+1}$Ti$_3$Fe$_{m-3}$O$_{3m+3}$ ($m = 4, 5, 6$) thin films were deposited on Pt/TiO$_2$/SiO$_2$/Si substrates using a PLD system with the laser source at 355 nm and a repetition rate of 10 Hz. The thin films were deposited at various substrate temperatures ($T_s$) ranging from 460 to 500 °C with an oxygen pressure varied from 10 to 20 mTorr. The films were maintained under the same conditions for 30 min after deposition and then cooled to RT.

The structures of the targets and films were determined by x-ray diffraction (XRD) using Cu K$_\alpha$ radiation. The resultant thickness of the BTFO thin films was in the range of 250–300 nm, which was measured by secondary electronic microscopy (SEM JSM-6500F). For the electrical measurements, Pt top electrodes were coated on the surface of the Bim$_{m+1}$Ti$_3$Fe$_{m-3}$O$_{3m+3}$ ($m = 4, 5, 6$) thin films through a shadow mask with a diameter of 100 μm to form capacitors. The ferroelectric properties were measured at RT by an aixACCT TF-1000 ferroelectric tester. The local piezoelectric/ferroelectric properties were investigated by piezoresponse force microscopy (PFM) (Hitachi High-Tech Science Nanocute AFM system) with a conducting tip (Rh-coated Si cantilever). The piezoelectric/ferroelectric response was measured as a function of $V_{dc}$ with a small ac voltage applied to the bottom electrode in the contact mode. The magnetic properties of the as-deposited films were measured using a superconducting quantum interference device (quantum design magnetic property measurement system magnetometer). The field-cooled-zero-field-cooled (FC-ZFC) magnetization curves in a field of 200 Oe were measured in the temperature range from 5 K up to 300 K.

III. RESULTS AND DISCUSSION

A. Structural characterization

The crystal structures for the BTFO films determined by a typical θ-2θ XRD scan. Figure 1(a) compares the XRD patterns of BTF, BTF2, and BTF3 thin films deposited by PLD and of the Pt/TiO$_2$/SiO$_2$/Si substrate. The XRD profiles of the BTFO thin film is indexed according to an orthorhombic structure with a space group A21am(36), while BTF2 and BTF3 are indexed to F2mm(42) by powder diffraction file cards 01-089-8545, 01-075-8378, and 01-075-8067, respectively. The identification and assignments of the observed diffraction patterns were analyzed by xrdi software (Rigaku). For the BTF and BTF2 thin films, only diffraction peaks from the substrates and Aurivillius phase are observed. The polycrystalline samples show c-axis preferred growth habit. No impurity phases, such as might be indicated by BiFeO$_3$, Bi$_2$Fe$_6$O$_9$, or Fe$_2$O$_3$ diffraction peaks, are detected. In the XRD pattern for BTF3, however, there is a wide hump around 31° in addition to the Aurivillius peaks, indicating incomplete crystallization in the film.

Figure 1(b) shows the XRD patterns of all the targets. All visible diffraction peaks belong to the Aurivillius phase, and some additional peaks with weak intensity could be detected, indicating the existence of impurities in the ceramic targets. For PLD of thin films from a target, however, the target material does not need to be exactly the same compound as the film material, because the target material will experience a “plasma-ization” and following recrystallization process on the substrate. The PLD process is a strong nonequivalent crystallization process, which provides the possibility of forming certain unstable phases, which could not be easily obtained by conventional solid state reaction in the ambient environment.

B. Ferroelectric properties

Polarization-electrical field (P-E) hysteresis loops for Pt/BTFO/Pt, Pt/BTF2/Pt, and Pt/BTF3/Pt capacitors measured at 500 Hz under various electric fields at RT are shown in Figs. 2(a)–2(c). For each single capacitor, both the remanent polarization ($2P_r$) and the coercive field ($E_c$) are increased.
Fig. 2. (Color online) P-E hysteresis loops measured under various applying electric field of (a) BTF, (b) BTF2, and (c) BTF3 films; PUND switching polarization for (d) BTF, (e) BTF2, and (f) BTF3 films; inset of Fig. 2(d) is the PUND waveform with a pulse width of 2.5 ms and a rise time of 1 ms.

Fig. 3. (Color online) (a) Topographic image and (b) corresponding out-of-plane PFM images of BTF; (c) topographic image and (d) corresponding out-of-plane PFM images of BTF2; and (e) topographic image and (f) corresponding out-of-plane PFM images of BTF3 thin film.
with increasing applied electric field. An obvious decrease of $2P_r$ is observed, however, with increasing $m$-number in $\text{Bi}_{m+1}\text{Ti}_2\text{Fe}_{m-3}\text{O}_{3m+3}$ ($m = 4, 5, 6$). Note that since the applied electric field is higher than the coercivity of all the samples, artifacts associated with the incomplete saturation of polarization could be avoided. The unsaturated P-E loops for all the samples, due to decreasing field endurance in these capacitors, possibly originated from the leakage-related contribution. The leakage behavior is correlated with the valence transfer of multivalent Ti/Fe cations and/or the associated appearance of oxygen vacancies. The nature of the ion distribution over the nonequivalent sites determines many physical and chemical properties of compounds including their stability. Ferroelectricity in Aurivillius BTFO compounds originates from the rotation and tilting of Ti/Fe-O octahedra, lone pair electrons of Bi$^{3+}$ ions and distorted Bi$_2$O$_2^{2-}$ layers. When the number of pseudoperovskite blocks ($m$-number) increases, the chances for Fe ions to substitute on Ti sites would be increased and more defects such as oxygen vacancies would inevitably arise in BTFO thin films. Another possible reason for the leakage is grain boundary conduction in the film. According to the topographic images shown in Figs. 3(a), 3(c), and 3(e), the BTF thin film shows a uniform surface, with small grains present on the surface. With increasing the $m$-number, the grain size is increased. The grain size of the BTF3 thin film is the biggest. The grain boundaries become shorter and thicker with increasing grain size, so that it is easier to transport the leakage current.

Since the definition of ferroelectricity is strict, the so-called positive-up-negative-down (PUND) test is carried out with triangle pulses applied [inset of Fig. 2(d)] to manifest the ferroelectricity of the BTF, BTF2, and BTF3 thin films, as shown in Figs. 2(d), 2(e), and 2(f), respectively. In the PUND measurement, five sequential pulses were applied on the capacitors. In the beginning, a negative writing pulse is used to reset the polarization state. After that, a positive pulse $V_1$ is applied to record the switching polarization. Then, another positive pulse $V_2$ is applied to measure the nonswitching polarization, which contains only the nonremnant polarization. This also applies to the “negative-down” process. The $V_3$ pulse switches the ferroelectric domains to the opposite direction, and $V_4$ just measures the nonremnant polarization. A triangle waveform with a pulse width of 2.5 ms and a rise time of 1 ms was used in the measurement. PUND amplitude was $\pm 20 \text{V}$, and the frequency is 100 Hz. Obvious switching and nonswitching polarization were observed in the PUND results of all the samples, and the switching polarization values of these measurements match well with the $2P_r$ values obtained from the P-E loops, indicating the existence of ferroelectricity in the as-deposited BTFO thin films.

### C. Local piezoelectric and ferroelectric properties

Nowadays, PFM has emerged as a powerful technique for locally probing nanoscale phenomena in piezoelectric and ferroelectric materials on the nanometer scale. Electrical control of ferroelectric behavior in BTFO thin film relies on controlling the ferroelectric switching. To switch the films locally, a dc bias is applied to a conducting tip (Si cantilever coated with Rh) while scanning over the desired area. The tip deflection resulting from the expansion or contraction of the sample due to the applied bias is measured. Figure 3 shows topographic atomic force microscope (AFM) and out-of-plane PFM images of the as-deposited BTFO samples switched by electric field. The dark areas in Figs. 3(d)–3(f) are written with a positive voltage of $+10 \text{V}$, while bright contrast is written with a negative dc bias of $-10 \text{V}$ between the PFM tip and the bottom electrode due to the different phases of the PFM response for the up and down domains. Obvious switching of polarization confirms the ferroelectricity in the as-deposited films.

![Fig. 4. (Color online) Local piezoresponse vs applied voltage for (a) BTF, (b) BTF2, and (c) BTF3, respectively.](image-url)
The local piezoresponse hysteresis loops of the as-deposited thin films are shown in Figs. 4(a)–4(c). The butterfly loops in black represent the displacement as a function of applied voltage (V), and they exhibit asymmetric shape, which are due to the asymmetry between the top and bottom electrode. Piezoelectric hysteresis loops of piezoelectric coefficient as a function of applied voltage ($d_{33}$-V) were calculated from the displacement–voltage curve from $d_{33} = \Delta l/V$, where $\Delta l$ is the displacement, and are plotted in blue. The local $d_{33}$ value of BTF, BTF2, and BTF3 is 61.7, 7.8, and 11.7 pm/V, respectively. The $d_{33}$ value is drastically decreased with increasing the $m$-number, indicating that the piezoelectric property in BTFO thin films is largely dependent on the number of pseudoperovskite blocks.

D. Magnetic properties

People are still arguing on the magnetic properties about Aurivillius Bim$^{+1}$Ti$_3$Fe$_{m-3}$O$_{3m+3}$ compounds. Earlier literature claimed that Bim$^{+1}$Ti$_3$Fe$_{m-3}$O$_{3m+3}$ compounds for $m = 4–7$ are paramagnetic at RT. Jartych et al. studied the magnetic properties of these materials, however, and demonstrated the antiferromagnetic ordering in Bim$^{+1}$Ti$_3$Fe$_{m-3}$O$_{3m+3}$ compounds. To investigate the magnetic properties in our as-obtained thin films, magnetization (M)-applied magnetic field (H) hysteresis loops were measured at different temperatures. The magnetic hysteresis (M-H) loops of BTFO thin films measured at RT are presented in Fig. 5(a). The diamagnetic moment of the substrate is calculated from measurements on the bare substrate and subtracted from the raw data. All of the samples show a magnetic response at RT. The M-H loop of BTF thin film saturates at 6.2 emu/cm$^3$. As the $m$-number increases, however, the M-H loops of BTF2 and BTF3 show unsaturated behavior. The coercive field ($H_c$) and the remanent magnetization ($M_r$) of the samples are almost the same as shown in the inset of Fig. 5(a) (~100 Oe and 0.7 emu/cm$^3$). Figures 5(b) and 5(c) summarize the $H_c$ and the $M_r$ of all the samples measured at different temperatures. As the temperature increased from 5 to 300 K, $H_c$ and $M_r$ of all the samples decreased. What is more, the magnetization of these samples decreased with increasing $m$-number. The magnetization of BTF, BTF2, and BTF3 thin films are investigated as a function of temperature (M-T) at a magnetic field of 200 Oe. As shown in Fig. 5(d), it is found that both the field-cooling (FC) and the zero-field-cooling (ZFC) magnetization remain almost constant and almost the same when the temperature is cooled down from RT, but then the FC curves and ZFC curves split at 92 K for BTF, 155 K for BTF2, and 188 K for BTF3, respectively. When the $m$-number increases, the ZFC and FC curves separate from each other at higher temperature, suggesting that the temperature of the magnetic phase transition increases with the $m$-number in Aurivillius BTFO thin films. At temperatures below 25 K, the magnetization of the FC and ZFC curves increase sharply with decreasing temperature, which indicates the existence of a paramagnetic state at low temperature. The transition is assigned to spin reorientation from canted antiferromagnetic to the collinear antiferromagnetic state. In Aurivillius structure, Fe ions occupy two nonequivalent positions: one, inside the oxygen octahedron close to the (Bi$_2$O$_2$)$_2^{+}$ layer; the other, the octahedral site surrounded by O in the pseudoperovskite layer. Therefore, the Fe atoms have different magnetic moments due to the different chemical environments. It is possible that a net magnetic moment would be built from the different magnetic moments of two Fe atoms, even though the Fe atoms at the inner sites and the octahedral site should be coupled by antiferromagnetic superexchange interaction in...
according with the Goodenough–Kanamori rule.\textsuperscript{31} Taking these results together with M-H measurement result, we can propose the existence of short-range magnetic ordering starting from high temperature to above the splitting point of the BTFO films.\textsuperscript{14,32} All these features indicate the possible existence of Fe-rich nanoregions that have caused the inhomogeneity of magnetic ions and rich magnetism to coexist in the BTFO films. In addition, the saturation magnetization, $M_s$, observed in this study is relatively small. Therefore, we can conclude that the observed weak ferromagnetic hysteresis loops in the as-deposited thin films are due to canting of the spins. This is in accordance with the report of Zhao et al.\textsuperscript{14} that a canted AFM ordering exists in BTFO thin film.\textsuperscript{14}

Obviously, further investigations, especially neutron diffraction, are necessary to elucidate the magnetic structure in this system.

IV. SUMMARY AND CONCLUSIONS

We have deposited Aurivillius B$	ext{Bi}_{m+1/4}\text{Ti}_3\text{Fe}_m\cdot \text{O}_{3m+3}$ thin films by PLD. The XRD results indicate a preferred growth habit along the $c$-axis of the films. The ferroelectric properties were investigated at room temperature. Remanent polarization of the $P$-$E$ loops for the as-deposited films was decreased with increasing number of pseudoperovskite blocks ($m$-number). According to the PFM measurements, obvious switching of polarization indicates that the ferroelectric domain walls in these films are mainly $180^\circ$ domain walls. The local piezoelectric coefficient value is decreased when the $m$-number increases, indicating that the piezoelectric property in BTFO thin films is largely dependent on the number of pseudoperovskite blocks. All of the thin films show a magnetic response at room temperature. Although the magnetization of these samples decreases with increasing the $m$-number, the temperature of the magnetic phase transition increases with the $m$-number. The present work suggests the possibility of Aurivillius BTFO materials as potential room-temperature multiferroics. It is therefore feasible to consider a wide scope of potential applications in functional devices.

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