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Unconventional crystal field splitting in non-centrosymmetric BaTiO$_3$ thin films

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Understanding the crystal field splitting and orbital polarization in non-centrosymmetric systems such as ferroelectric materials is fundamentally important. In this study, taking BaTiO$_3$ as a representative material we investigate titanium crystal field splitting and orbital polarization in non-centrosymmetric TiO$_6$ octahedra with resonant X-ray linear dichroism at Ti L$_2$3-edge. The high-quality BaTiO$_3$ thin films were deposited on DyScO$_3$ (110) single crystal substrates in a layer-by-layer way by pulsed laser deposition. The reflection high-energy electron diffraction and element specific X-ray absorption spectroscopy were performed to characterize the structural and electronic properties of the films. In sharp contrast to conventional crystal field splitting and orbital configuration ($d_{xz}/d_{yz} < d_{xy} < d_{3z^2−r^2} < d_{2x^2−y^2}$ or $d_{xy} < d_{xz}/d_{yz} < d_{2x^2−y^2} < d_{3z^2−r^2}$) expected from compressive or tensile epitaxial strain, respectively, it is revealed that $d_{xz}$, $d_{yz}$, and $d_{xy}$ orbitals are nearly degenerate, whereas $d_{3z^2−r^2}$ and $d_{2x^2−y^2}$ orbitals are split with an energy gap $\sim$ 100 meV in the epitaxial BaTiO$_3$ films. We find that the unexpected degenerate orbitals $d_{xz}/d_{yz}$ result from the competition between the orbital splitting induced by epitaxial strain and that induced by polar distortions of BaTiO$_3$ films. Our results provide a route to manipulate orbital degree of freedom by switching electric polarization in ferroelectric materials.

I. INTRODUCTION

Ferroelectric materials (oxide films in particular) exhibiting robust spontaneous electric polarization that can be reoriented with an external electric field, have attracted increasing attention, due to their extensive applications such as transistors, memories, and high frequency devices realized in various systems [1–10]. For conventional ferroelectrics, the polarization emerges from a inversion-symmetry breaking lattice distortion. In BaTiO$_3$ (BTO), for example, the displacement of the Ti$^{4+}$ cation from the center of surrounding O$_6$ octahedral cage gives major contribution to the induced polarization. The underlying mechanism that drives the off-centering of Ti$^{4+}$ cation is attributed to pseudo Jahn-Teller effect (PJTE) [11–13] in which a symmetry-lowering distortion can lower the energy of system by mixing the ground state and excited states by vibronic coupling ($\partial H/\partial Q$, $Q$: normal displacements). The off-centering of Ti$^{4+}$ cation is a typical PJTE case (usually identified in literatures as a “$d^0$-ness” [14]) when the mixing of empty Ti 3$d$ with filled O 2$p$ orbitals results in a host of electronic configurations allowing to decrease the total energy by the distortion induced change in the bonding between Ti 3$d$ and O 2$p$ orbitals [15–18]. Studies of modified crystal fields by inversion-symmetry breaking distortions and associated orbital splitting are fundamentally important for understanding the properties of ferroelectric materials and non-centrosymmetric superconductors (e.g., the coexistence of superconducting and ferroelectric states in doped perovskite oxides [19, 20]). However, crystal field splittings in these systems have not been extensively studied yet [21, 22].

To address the above concern, we take BTO thin films as a representative material to investigate crystal field splitting and orbital polarization in the presence of polar distortions induced by ordering of ferroelectric dipoles. Bulk BaTi$^{4+}$O$_3$ with 3$d^0$ electron configuration undergoes complex structural and ferroelectric phase transitions upon cooling, e.g., from high temperature cubic to tetragonal (393 K), tetragonal to orthorhombic (278 K), and orthorhombic to rhombohedral (183 K), where ferroelectric properties are present below 393 K [23–25]. Moreover, under biaxial compressive
strain (such as epitaxial tetragonal BTO films on DyScO$_3$ substrates) the transition temperature can be enhanced to nearly 500 K and the remnant polarization is at least 2.5 times higher than bulk BTO single crystals [26]. Due to strong B-site ferroelectricity at room temperature [27–31], the BTO single crystals are widely used as ferroelectric substrates for epitaxial thin film synthesis [32–34], where its epitaxial films can be employed to manipulate interfacial electric field for controlling order parameters and achieving novel functionalities [35, 36].

In this work, high-quality BTO thin films were grown on DyScO$_3$ (DSO) (110) single crystal substrates in a layer-by-layer way by pulsed laser deposition (PLD). The structural and electronic properties were characterized by reflection high-energy electron diffraction (RHEED) and element-specific X-ray absorption spectroscopy (XAS). In sharp contrast to conventional crystal field splitting expected with the compressive strain from DSO substrate, an anomalous orbital structure, nearly degenerate $t_{2g}$ ($d_{x^2}$,$d_{y^2}$,$d_{z^2}$) and split $e_g$ ($d_{3z^2-r^2}$ < $d_{x^2-y^2}$ about 100 meV) orbitals, was revealed in the epitaxial BTO films resulting from the competition between orbital splitting induced by compressive strain and that by spontaneous polar distortion from PJTE resulting in non-centrosymmetric TiO$_6$ octahedra of polar BTO films.

II. EXPERIMENTS AND FIRST-PRINCIPLES CALCULATIONS

As shown in Fig. 1, the BTO films (20 unit cells, $\sim$ 8.2 nm) had been grown along [110] (orthorhombic notation, corresponding to [001] orientation in a pseudo-cubic notation) DSO substrates ($5 \times 5 \times 0.5$ mm$^3$) by PLD, using a KrF excimer laser operating at $\lambda = 248$ nm and 2 Hz pulse rate with 2 J/cm$^2$ fluence. The BTO films were epitaxially grown on DSO substrates with pseudo-cubic in-plane lattice constants of $a = 3.946$ Å and $b = 3.952$ Å with 0.15% difference. During the growth, the oxygen pressure was kept at $\sim 10^{-6}$ Torr, the temperature of the substrates was $\sim 850^\circ$C (from reader of infrared pyrometers). At room temperature, the bulk lattice parameters are $a = 3.99$ Å and $c = 4.04$ Å for tetragonal BTO, and $a = 3.95$ Å for DSO (pseudo cubic). Due to the lattice mismatch, the epitaxial BTO films on DSO are under biaxial compressive strain, indicated by a pair of arrows in Fig. 1(a). In order to monitor the growth of the BTO thin film, an in-situ RHEED was performed during the deposition. The sharp
FIG. 2. (a) Schematic of experimental setup. $E \parallel c$ and $E \parallel ab$ ($E$ is the polarization vector of the photon) indicate out-of-plane (red solid line, $I_c$) and in-plane (blue dash line, $I_{ab}$) linearly polarized incident X-ray, respectively. The grazing angle $\theta = 20^\circ$. The yellow arrows at the bottom of DSO substrate indicates the bulk-sensitive luminescence yield detection mode. The arrow along [001] direction (pseudo-cubic notation) indicates the growth direction of BTO films. (b) XAS of BTO films at Ti $L_{2,3}$-edge at room temperature. All collected spectra are repetitively measured more than six times. Enlarged XAS spectra at (c) Ti $L_3 (t_{2g})$ and (d) Ti $L_3 (e_g)$ absorption peaks. $\Delta_1$ and $\Delta_2$ are defined as the splitting between $d_{xy}$ and $d_{xz}/d_{yz}$ orbitals, and between $d_{x^2−y^2}$ and $d_{3z^2−r^2}$ orbitals, respectively.

III. RESULTS AND DISCUSSIONS

Figure 2(b) shows the XAS spectra of BTO films at Ti $L_{2,3}$-edge. There are four well split characteristic peaks, arising from the excitation from Ti $2p$ to Ti $3d$ states (the electronic...
configuration changes from Ti $2p^63d^9$ to $2p^53d^1$). Generally, in octahedral symmetry, the transition-metal $d$ bands split into $t_{2g}$ ($d_{xy}$, $d_{xz}$, $d_{yz}$) and $e_g$ ($d_{3z^2-r^2}$, $d_{x^2-y^2}$) [47–53]. The degenerate $t_{2g}$ and $e_g$ bands further split when the octahedron experiences uniaxial elongation or compression along the $c$-axis [54], leading to the orbital structure of $d_{xz}/d_{yz} < d_{xy} < d_{3z^2-r^2} < d_{x^2-y^2}$ or $d_{xy} < d_{xz}/d_{yz} < d_{x^2-y^2} < d_{3z^2-r^2}$, respectively. Using that intensity of linearly polarized XAS carries the information of crystal field splitting and orbital polarization [47–53]. Figure 2(c) and (d) show the differences between out-of-plane ($I_c$) and in-plane ($I_{ab}$) polarized XAS. As seen, the $t_{2g}$ orbitals are nearly degenerate ($\Delta_1 \sim 0$, see Fig. 2(c)), whereas the splitting $\Delta_2$ between $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals in $e_g$ state is about 100 meV, shown in Fig. 2(d). The same orbital splitting is observed at Ti $L_2$ edge as well. This kind of orbital structure in BTO films ($d_{xz}/d_{yz}/d_{xy} < d_{3z^2-r^2} < d_{x^2-y^2}$) is unexpected and in sharp contrast to conventional crystal field splitting ($d_{xz}/d_{yz} < d_{xy} < d_{3z^2-r^2} < d_{x^2-y^2}$) in elongated TiO$_6$ octahedra along the $c$-axis [55].

To further understand this anomalous orbital structure in the BTO films, we obtain the spectra of X-ray linear dichroism (XLD), which is defined as XLD = $I_c - I_{ab}$ in this work. Fig. 3 shows the XLD spectra of the strained BTO with out-of-plane polar distortion at room temperature at Ti $L_{2,3}$ edge and the XLD spectra of tetragonal BTO without polar distortion simulated by atomic multiplet scattering calculations using CTM4MAX code [56]. As highlighted area in Fig. 3, the XLD of the BTO films shows nearly degenerate ($d_{xz} \simeq d_{yz} \simeq d_{xy}$) $t_{2g}$ orbitals, whereas $e_g$ orbitals show clear dichroism with $d_{3z^2-r^2} < d_{x^2-y^2}$.

The discrepancy between the degenerate $t_{2g}$ orbitals and the expected crystal field splitting from the compressive strain strongly suggest an additional mechanism behind unusual orbital splitting. Since the bulk BTO is ferroelectric at room temperature [23], it is natural to include the polar distortion in BTO and investigate its contribution to the orbital splitting. From epitaxial growth, the BTO thin film is under a compressive strain about 1.25% relative to the cubic phase (4.00 Å). This leads to the orbital splitting having $d_{xz}/d_{yz}$ orbitals lower than $d_{xy}$ [37]. Using the first-principles DFT method, we first calculate the effect of epitaxial strain on orbital splitting from the change in the $c/a$ ratio without considering the polar distortion. With 1.25% compressive strain based on the lattice mismatch between BTO and DSO, the $c/a$ ratio obtained by strained-bulk calculation increases to 1.02. Next, we allow a polarization along the $c$-axis, experimentally observed under the compressive strain [57, 58]. The relaxed atomic structure with 1.25% compressive epitaxial strain lowers the total energy by 19 meV per formula unit from a polar distortion, mainly contributed by Ti displacement from the center of the octahedron with Ti-O-Ti angle of 172°. The calculated polarization is 33 μC/cm$^2$ along the $c$-axis with further increase in the $c/a$ ratio to 1.04.

In order to investigate the effect of the strain and polar distortion to orbital polarization, we consider two atomic configurations: one with compressive strain with $c/a = 1.04$ with zero polar distortion and the other with cubic lattice constant with 1.25% compressive strain applied for all three lattice constants and with the polar distortion of the strained bulk calculation. The projected density of states (PDOS) and Wannier tight-binding parameters are presented in Fig. 4 and Table I, respectively. In Fig. 4(a), we find that the effect of the compressive strain is straightforwardly shown in the PDOS with $d_{xz}/d_{yz} < d_{xy}$ and $d_{3z^2-r^2} < d_{x^2-y^2}$ orbital splitting, consistent with on-site energy difference $E_{xz/yz} - E_{xy} = -0.13$ eV for $t_{2g}$ orbitals and $E_{3z^2-r^2} - E_{x^2-y^2} = -0.45$ eV for $e_g$ orbitals (Table I). We note that the splitting between $t_{2g}$ orbitals is smaller than that of $e_g$ orbitals due to the relatively weaker $\pi$ bonding of $t_{2g}$ orbitals compared to the $\sigma$ bonding of $e_g$. In contrast, the inclusion of the polar distortion without strain (cubic lattice constants) results in the opposite trend in the PDOS as shown in Fig. 4(b): $d_{xz}/d_{yz} > d_{xy}$ and $d_{3z^2-r^2} > d_{x^2-y^2}$ orbital splitting, consistent with the on-site energy difference of $E_{xz/yz} - E_{xy} = 0.15$ eV for $t_{2g}$ orbitals and of $E_{3z^2-r^2} - E_{x^2-y^2} = 0.13$ eV for $e_g$ orbitals (Table I). We note that the splitting between the $t_{2g}$ orbitals from the polar distortion is larger than that between $e_g$ orbitals, consistent
TABLE I. On-site energies and major hopping parameters of Ti d orbitals for BTO (in eV) obtained from Wannier functions of Ti d band. For hopping parameter t, \( || \) and \( \perp \) represent the in-plane and out-of-plane hopping, respectively.

|                | On-site energy difference | Intra orbital hopping |
|----------------|--------------------------|-----------------------|
|                | \( E_{xz/yz} - E_{xy} \) | \( t_{xy}^|| \) \( t_{xz/yz}^|| \) \( t_{x2-y2}^|| \) \( t_{x2-y2}^\perp \) \( t_{x2-r2}^\perp \) |
| Cubic          | 0                        | -0.31                | -0.31               | -0.50              | -0.66 |
| Tetragonal \((P = 0)\) | -0.13                    | -0.30               | -0.33               | -0.25              | -0.50 | -0.64 |
| Cubic \((P \neq 0)\) | 0.15                     | -0.30               | -0.26               | -0.28              | -0.48 | -0.66 |

FIG. 4. PDOS of the strained bulk calculations with 1.25% biaxial compressive strain. PDOS of (a) tetragonal BTO with zero polarizations \((c/a = 1.04)\), (b) cubic BTO with Ti polar distortion, and (c) fully relaxed tetragonal BTO with Ti polar distortion along the c direction \((c/a = 1.01)\).

FIG. 5. PDOS of the atomic structures linear interpolated between non-polar strained bulk BTO structure with \( c/a = 1.02 \) and polar strained bulk BTO structure with \( P = 33 \mu C/cm^2 \). The symbol \( \lambda \) is defined as the parameter of the linear interpolation \((\lambda = 0 \text{ and } 1 \text{ for non-polar and polar structures})\). PDOS for (a) \( \lambda = 0 \), (b) \( \lambda = 0.4 \) \((P = 13.9 \mu C/cm^2)\) and (c) \( \lambda = 0.8 \) \((P = 27 \mu C/cm^2)\).

with relatively larger reduction in the in-plane hopping \( t_{xz/yz}^|| \) about 50 meV than that of \( t_{x2-y2}^|| \) about 20 meV compared with the hopping parameters of cubic BTO. This suggests that the bonding between the \( t_{2g} \) orbitals is more sensitive to the Ti-O-Ti angle than that between the \( e_g \) orbitals. In the case without epitaxial constraints (fully relaxed), the spontaneous polarization in the c-direction by PJTE increases \( c/a \) ratio to 1.01 with a-lattice constant decrease about 0.35%. Due to the \( t_{2g} \) orbital splitting being more sensitive to the polar distortion than to the increased \( c/a \) ratio, we find \( d_{xy} < d_{xz}/d_{yz} \) orbital splitting (Fig. 4(c)), which is consistent with transport measurement of BTO thin films \([59]\). In contrast, we find \( d_{3z^2-r2} < d_{x2-y2} \), due to the \( e_g \) orbital being more sensitive to the increased \( c/a \) ratio than to the polar distortion.

The degeneracy of the \( t_{2g} \) orbitals observed in XLD can be understood by combined effects from the compressive strain and from polar distortion. The degeneracy of the \( t_{2g} \) orbitals is induced by the cancellation between orbital splitting from the compressive strain and polar distortion which are similar in
amount (−0.13 eV vs 0.15 meV), while the degeneracy of $e_g$ orbitals is lifted due to larger difference of the orbital splitting from the strain and polar distortion (−0.45 eV vs 0.13 eV). To confirm this idea, we calculate the PDOS of the structures obtained by linear interpolation between the strained bulk atomic structure without polarization ($c/a = 1.02$) parameterized by $\lambda = 0$ and strained bulk atomic structure with out-of-plane polarization ($c/a = 1.04$) parameterized by $\lambda = 1$. Figure 5 shows the PDOS with $\lambda = 0, 0.4,$ and 0.8. For the all values of the $\lambda$, the splitting of the $e_g$ orbital ($d_{3z^2-r^2} < d_{x^2-y^2}$) is maintained due to the splitting from the elongated $c$-axis ($c/a > 1.02$) dominating the $e_g$ orbital splitting. In contrast, the sign change in the $t_{2g}$ orbital splitting is clearly seen for $\lambda = 0$ and $\lambda = 0.8$. In particular, for $\lambda = 0.4$, the $t_{2g}$ orbitals are closely degenerate while $e_g$ orbitals split about 0.3 eV, consistent with the experimental data. For the $\lambda = 0.4$, the polarization value reduced to about 42% of the $\lambda = 1$ structure, which may come from the finite thickness of BTO, suppressing the polarization.

Here, we compare the crystal-field splitting between the strained BTO without and with the polar distortion, illustrated in Fig. 6. The unusual orbital structures we have observed in this work may provide a clue to understand the peculiar band splitting of BTO investigated by angle-resolved photoemission spectroscopy (ARPES) [60], by including the crystal field splitting from polar distortions. Our finding here provides an effective way to manipulate orbital degree of freedom by manipulating ferroelectric polarization which could be used to design exotic quantum states, such as metal-insulator transitions, superconductivity, and colossal magnetoresistance.

**IV. CONCLUSION**

In summary, we have synthesized high-quality BTO thin films on DSO substrates with a layer-by-layer growth by PLD and characterized the structural and electronic properties by RHEED, element-specific XAS/XLD, and first-principles calculations. In sharp contrast to conventional crystal field splitting and orbital configuration ($d_{xz}/d_{yz} < d_{xy} < d_{3z^2-r^2} < d_{x^2-y^2}$) in elongated TiO$_6$ octahedra, the XLD spectra reveals that the orbital structure in BTO films is unconventional: nearly degenerate $t_{2g}$ ($d_{xz}/d_{yz}/d_{xy}$) with split $e_g$ ($d_{3z^2-r^2} < d_{x^2-y^2}$ with a gap $\sim 100$ meV) orbitals. The first-principles DFT calculations show that this unexpected degenerate $t_{2g}$ orbitals are from the competition between the orbital splitting from the compressive strain and polar distortion. Our work could pave a way to design exotic quantum states (such as tunable multiferroic properties) by manipulating the orbital degree of freedom using the switchable ferroelectric polarizations.

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Tetragonal

Orthorhombic

Energy (eV)

PDOS (eV⁻¹)

(b)

(a)

Tetragonal

Orthorhombic

FIG. A.1. PDOS of (a) tetragonal (a = 3.9005 Å) and (b) orthorhombic (a = 3.9034 Å, b = 3.8976 Å) BTO, both with P = 0.

Appendix A

Fig. A1 shows calculated PDOS of tetragonal (a = 3.9005 Å, c = 3.9856 Å) and orthorhombic (a = 3.9034 Å, b = 3.8976 Å, c = 3.9856 Å) BTO with strained a (±0.76 %) and b (−0.76 %) lattice constants relative to the tetragonal structure. The PDOS shows almost identical PDOS between the two structures due to the small difference in the in-plane lattice constants.

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