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Manipulating multiple order parameters via oxygen vacancies: The case of Eu$_{0.3}$Ba$_{0.5}$TiO$_3$–δ

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Transition-metal oxides (TMOs) are attracting significant attention due to their astonishing variety of technologically important physical properties, such as two-dimensional electron gas, colossal magnetoresistance, multiferroic behavior, etc. [1–3]. Tuning the concentration and distribution of ions and vacancies in TMOs provides a route to create and control new functionalities [4]. For many applications, for better or worse, the functionality of TMOs and thin-film devices is strongly affected by the formation and distribution of oxygen vacancies (V$_0$). For instance, the introduction of V$_0$ causes a displacement of the Fe ions in (LaFeO$_3$)$_2$/SrFeO$_3$ superlattices, which induces the polar order [5]. V$_0$ also enable room-temperature ferroelectricity in SrTiO$_3$ thin films by manipulating the TiO$_6$ octahedral tilting around the vacancy site [6]. The electronic properties of these TMOs, especially $ABO_3$-perovskite structure, are extremely sensitive to structural distortions consisting of cation displacements, deformations, and rotations in an ideal three-dimensional framework of corner-connected BO$_6$ octahedra [7,8]. On the other hand, V$_0$ are well known to play a pivotal role in magnetic properties. Biskup et al. suggested that ordered V$_0$ are responsible for insulating ferromagnetism in strained epitaxial LaCoO$_3$–δ films [9]. Similarly, magnetic phenomena were observed at the SrTiO$_3$/LaAlO$_3$ interface [10,11] and oxygen-deficient bulk SrTiO$_3$–δ crystals [12].

Previous studies have shown that it is possible to manipulate the functionality of TMO materials by controlling one order parameter at a time through the concentration or spatial distribution of V$_0$. A natural question arises whether a single experimental parameter V$_0$ has the ability to simultaneously control multiple order parameters, such as both magnetism and ferroelectricity. In particular, multiferroics with ferromagnetic-ferroelectric (FM-FE) coupling are highly promising for fundamental research and practical applications [13–15]. They are scarce, however, due to the near-incompatibility of the formation of magnetic order (partial filled $d$ orbitals in 3$d$ TMOs) and the conventional off-centering mechanism of ferroelectricity (empty $d$ orbitals in 3$d$ TMOs) within a single phase [16]. Shimada et al. demonstrated theoretically that atomic-size multiferroics emerges in nonmagnetic ferroelectric PbTiO$_3$ through V$_0$ formed at surfaces [17], while, there are few experimental reports about V$_0$ manipulating magnetism and ferroelectricity in the thin films simultaneously. On the other
hand, one can engineer multiferroic properties in $ABO_3$ oxides by chemically controlling the functionality on a site-by-site basis, such as $A$-site cations providing ferroelectricity and $B$-site cations supplying magnetism or vice versa. It is well known that $BiFeO_3$ (BFO) is the case that ferroelectricity is originated from $Bi^{3+}6s^2$ lone-pair electrons hybridized with $O^{2-}2p^6$ at $A$ site and antiferromagnetism is derived from $Fe^{3+}3d^5$ at $B$ site $[18]$. Unfortunately, the calculations demonstrated that $V_0$ cannot significantly affect the electric polarization, but can slightly alter the value of the macroscopic magnetization of the BFO $[19]$. The ionic displacements are insensitive to $V_0$, which is responsible for the unaffected electric polarization.

In this paper, we report a pathway toward a realization of manipulating magnetism and ferroelectricity simultaneously by using $V_0$. Based on previous reports, the criteria that a material must satisfy for this proposed mechanism are as follows: (1) the magnetic and electric ordering should originate from different cations, and (2) the ionic displacement should be sensitive to $V_0$. In bulk, $Eu_{0.5}Ba_{0.5}TiO_3$ (EBTO) with a typical $ABO_3$-perovskite structure shows antiferromagnetic (AFM, $T_N \sim 1.9$ K) and ferroelectric (FE, $T_C \sim 213$ K) $[20,21]$. The AFM and FE stem from the $Eu^{2+}4f^7$ unpaired electrons at $A$ site and the off-center $Ti^{4+}3d^0$ at $B$ site, respectively. Moreover, EBTO is structurally similar to the archetypal TMOs, such as $BaTiO_3$ (BTO) and $SrTiO_3$ (STO), and the introduction of $V_0$ has been shown to enhance the ferroelectricity of STO $[6,22]$. Additionally, our previous results established that the doping of $V_0$ shows strong influence on the magnetic ordering of the $Eu_{0.5}Ba_{0.5}TiO_{3-\delta}$ (EBTO$_{3-\delta}$) thin films $[23]$. Our present work shows that careful manipulation of $V_0$ can improve both magnetic and FE properties in EBTO$_{3-\delta}$. We experimentally observed that the ferroic orders in EBTO$_{3-\delta}$ thin films are transformed from AFM-FE to FM-FE, and the FE Curie temperature is enhanced to be above room temperature. A small magnetodielectric response was also detected in the $V_0$-doped film, revealing the existence of magnetolectric coupling. First-principle calculations revealed that the introduction of $V_0$ induces defect-associated effects including spin-polarized $Ti^{3+}$ ions, mediating a FM coupling between the local $Eu^{2+}4f^7$ spins, and an enhanced off-center displacement of Ti ions, stabilizing the ferroelectric phase and thus increasing the Curie temperature. The tuning of magnetism and ferroelectricity is both through the medium of Ti sites, which is the origin of the magnetolectric coupling in EBTO$_{3-\delta}$.

Pulsed laser deposition was used to fabricate EBTO$_{3-\delta}$ films on (001) $SrTiO_3$ (STO) and (001) Nb-doped $SrTiO_3$ (Nb-STO, Nb: 0.5 wt.%) substrates. All of the EBTO$_{3-\delta}$ films were grown under identical deposition conditions, except

![FIG. 1. Magnetic hysteresis loops for samples (a) C and (b) D. Insets show temperature dependence of magnetization curves and the derivative of magnetization with respect to the temperature (obtained from FC curves). (c) Content of $V_0$ ($\delta$) dependences of coercivity and saturation magnetization.](115105-2)
for the oxygen pressure, which varied from $1 \times 10^{-1}$ to $1 \times 10^{-4}$ Pa (see Supplemental Material for more details [24]). Four kinds of EBTO$_{3-\delta}$ films with different content of $V_0$, grown at oxygen pressure of $1 \times 10^{-1}$, $1 \times 10^{-2}$, $1 \times 10^{-3}$, and $1 \times 10^{-4}$ Pa, were named as sample A, B, C, and D, respectively. Moreover, x-ray reciprocal space maps were measured to confirm that strain created by the lattice mismatch of EBTO$_{3-\delta}$ and Nb-STO is fully relaxed (not shown).

To quantitatively determine the stoichiometry and oxygen concentration of the EBTO$_{3-\delta}$ films, we used nuclear resonance backscattering spectrometry. The cation ratio in the EBTO$_{3-\delta}$ films (Eu:Ba:Ti) was revealed to be 1:1:2. According to the concentrations of the cations and O, the atomicity of O is estimated to be 2.98, 2.96, 2.91, and 2.85 for samples A, B, C, and D, respectively (see Fig. S1 of Supplemental Material [24]). By comparing the ideal and real atomicity of O, the content of $V_0(\delta)$ is calculated to be 0.02, 0.04, 0.09, and 0.15 in samples A, B, C, and D, respectively. X-ray photoemission spectroscopy (XPS) was used in consideration of very sensitive to variations in the valence state of transition-metal ions. The Eu 4d and Ba 3d spectra exhibit typical Eu$^{2+}$ and Ba$^{2+}$ features, while both Ti$^{3+}$ and Ti$^{4+}$ are observed in Ti 2p spectra (see Fig. S2 of Supplemental Material [24]). It is straightforward that Ti$^{3+}$ has one electron at 3d orbital (Ti$^{3+}$: 1$s^2$ 2$s^2$ 2$p^6$ 3$s^2$ 3$p^6$ 4$s^0$ 3$d^1$), indicating the appearance of Ti$^{3+}$ 3$d^1$ states in the EBTO$_{3-\delta}$ films. The presence of the Ti$^{3+}$ 3$d^1$ state is consistent with the density-functional theory (DFT) calculations and is believed to have contributed to the FM ordering in the EBTO$_{3-\delta}$ films (see below).

Figures 1(a) and 1(b) show the magnetization versus magnetic field for samples C and D, respectively. Similar results have also been obtained for samples A and B (see Fig. S3 of Supplemental Material [24]). Pronounced hysteretic loops are observed, consistent with ferromagnetism, having coercivity of 75.3 and 73.5 Oe for samples C and D, respectively. Note that the derivative of the magnetization shown as insets has a minimum at around 1.85 K, identified as the FM Curie temperature ($T_C$). In addition, the field-dependent magnetization curves are also measured at a higher magnetic field and temperature of 1, 1.5, and 5 K (see Fig. S3 of Supplemental Material [24]). The saturation magnetization, obtained at 1 K, is about 6.72 and 6.80 $\mu_B$/Eu for samples C and D, respectively, which is close to the ideal magnetic moment of Eu$^{2+}$ ions (7 $\mu_B$/Eu).

To further understand $V_0$ effects on magnetic properties, the $V_0$ dependence of coercivity and saturation magnetization are shown in Fig. 1(c). Assuming the local anisotropy energy of ferromagnetism does not change significantly with varying the concentration of $V_0$, and according to the Zeeman energy being equal to the anisotropy energy $E_a = H_c M_r$, the coercivity ($H_C$) gradually decreases with increasing saturation magnetization from samples A to D. These results demonstrate that the EBTO$_{3-\delta}$ films become ferromagnetism at low temperatures, in contrast to the antiferromagnetism of bulk EBTO. In addition, there is a possibility that the EBTO$_{3-\delta}$ films with even less $V_0$ are also showing ferromagnetism.

To investigate the $V_0$ effects on ferroelectric properties of EBTO$_{3-\delta}$ films, we performed the temperature-dependent optical second-harmonic generation (SHG). Optical SHG signals are plotted versus temperature for four samples in Fig. 2(a). Clearly, from samples A to D, the transition temperature increases from 260 to 395 K, which is significantly larger than that of bulk EBTO (∼213 K). To further confirm the huge enhancement of the FE $T_C$, we also attempted to measure temperature-dependent dielectric permittivity (see Fig. S4 of Supplemental Material [24]). The curves distinctly show a shift of the maximum in the permittivity (FE $T_C$) from around 255 K for sample A to 435 K for sample D. The trend is consistent with SHG results (see Fig. S5 of Supplemental Material [24]), reflecting that the increase in the content of $V_0$ enhances the FE $T_C$ of EBTO$_{3-\delta}$ films. Due to the introduction of $V_0$, the peak in permittivity clearly exhibits a frequency dispersion, which is probably a huge influence of Maxwell-Wagner relaxation derived from the leakage current.

Ferroelectric hysteresis loops were also recorded (see insets of Fig. S4 of Supplemental Material [24]), confirming the ferroelectricity of EBTO$_{3-\delta}$ films. The value of saturated polarization at 150 K is about 14 $\mu_C$ cm$^{-2}$, which is almost twice that of bulk EBTO (∼8 $\mu_C$ cm$^{-2}$ at 135 K) [20]. Additionally, the amplitude and phase images of the piezoelectric response measured at 300 K for sample D were acquired [Fig. 2(b)]. Stable ferroelectric domains with opposite polarization can be written by applying a dc bias to the AFM tip, suggesting room-temperature ferroelectricity and robust polarization. Similar results have also been observed in samples A to C (see Fig. S4 of Supplemental Material [24]). Moreover, room-temperature piezoelectric hysteresis loops (PHLs) were also obtained and shown in Fig. 2(c). Almost 180° phase contrast is
observed in the phase-voltage PHLs, indicating polarization switching. Associated with phase reversal, butterfly-shaped amplitude-voltage loops are also observed. The combination of these results proves that the oxygen-deficient $\text{EBTO}_{3-\delta}$ films preserve ferroelectricity. Remarkably, the FE $T_c$ was enhanced to be above room temperature, which makes $\text{EBTO}_{3-\delta}$ films attractive for the practical applications [25].

Considering the similarity of lattice structure between EBTO and BTO, the ferroelectricity in EBTO is believed to derive from the off-center displacement of Ti ions [20,21,26]. To further confirm the origin of room-temperature ferroelectricity in the $\text{EBTO}_{3-\delta}$ films, aberration-corrected scanning transmission electron microscopy (STEM) measurements were conducted to analyze the off-center displacement of Ti ions in the $\text{EBTO}_{3-\delta}$ films. High-angle annular dark-field (HAADF) imaging in STEM, also known as Z-contrast imaging [27], can be used to precisely measure cation column locations, from which local cation displacement (related to polarization) can be mapped out unit cell by unit cell [28]. The STEM results for sample D are shown as Fig. 3. An overview of the $\text{EBTO}_{3-\delta}$ film is shown in Fig. 3(a), indicating that the film has consistent thickness and uniform appearance on this scale. Close-up looks reveal that some defects have developed in the film. Figure 3(b) shows a medium-angle annular dark-field (MAADF) image of the region highlighted in Fig. 3(a), in which bright contrast can be seen in the film and at the interface. Since MAADF is sensitive to small lattice distortions [29], such contrast could be from grains in the specimen thickness direction along the electron beam, which are slightly misoriented with each other due to the presence of defects such as dislocations. In order to reliably measure displacements of Ti ions, HAADF images were taken in the areas away from those defective areas, where no MAADF contrast can be seen. The cation column positions, determined using a center-of-mass refinement method, were used to calculate the displacements [Fig. 3(c)]. The HAADF image and the resultant Ti ions displacement map for the $\text{EBTO}_{3-\delta}$ film and the STO substrate are shown in Figs. 3(d)–3(f) and 3(g)–3(i).
FIG. 4. (a) Differential charge upon the presence of $V_O$. (b) Differential charge between AFM order and FM order of EBTO$_{3-\delta}$. Type 1: $V_O$ at the EuO plane; type 2: $V_O$ at the BaO plane; type 3 and type 4: $V_O$ at the TiO$_2$ plane. In all cases, FM ordering is favored with the presence of $V_O$. (c) Sketch of the effects of $V_O$ on ferromagnetism and ferroelectricity in the oxygen-deficient EBTO$_{3-\delta}$. Left panel: Original AFM and FE orders in bulk EBTO. Right panel: FM and FE orders with $V_O$ at the EuO or BaO plane in the EBTO$_{3-\delta}$. (d) Band diagram of the oxygen-deficient EBTO$_{3-\delta}$.

respectively. From the displacement maps, it can be seen that the EBTO$_{3-\delta}$ film has nonzero Ti ions displacements in the in-plane ($d_x$) and the out-of-plane ($d_y$) directions. While the absolute value of the displacements is fairly small and approaches the detection limit for the technique, the histogram shown in Fig. 3(j) shows unambiguously that the average value of $d_x$ (blue) and $d_y$ (black) for the EBTO$_{3-\delta}$ film is distinct from zero, namely about 0.07 and 0.03 Å, respectively. This finding is consistent with the SHG and PFM results confirming that the FE $T_C$ of sample D is above room temperature. In contrast to that, the average value of $d_x$ (red) and $d_y$ (green) for the STO substrate (calculated the same way) is about zero, which is consistent with its room-temperature paraelectricity.

To understand the physical process underlying the manipulation of multiple order parameters in the EBTO$_{3-\delta}$ films, DFT calculations were performed. A-type atomic arrangement of Eu and Ba ions was used in the calculations due to the simultaneous lowest energy and AFM-FE (see Fig. S6 of Supplemental Material [24]). To further shed light on $V_O$ effects, electron distribution under different configurations of $V_O$ position (see Fig. S7 of Supplemental Material [24]) is investigated and shown in Fig. 4(a). The change of electron
distribution around Ti sites is clearly observed upon the presence of $V_O$, indicating the appearance of $Ti^{3+} \ 3d^1$ states, while the valence states of Eu and Ba ions remain divalent. Differential charge distribution between AFM and FM orders is also shown in Fig. 4(b). The electron around oxygen and Eu sites show spatially asymmetric variation. In particular, when $V_O$ is located at the TiO$_2$ plane, the electron distribution around Eu sites shows obvious differences between each other, implying a hybridization of Eu$^{2+}\ 4f^7$ and Ti$^{3+}\ 3d^3$. Note that the FM states of all $V_O$ configurations are energetically more favorable than their AFM states [Fig. 4(b)].

Based on the results given above, we now focus on understanding the effects of $V_O$ on FM and FE orders by presenting a model and a band diagram [Figs. 4(c) and 4(d), respectively]. Before taking into account $V_O$, superexchange coupling between Eu$^{2+}\ 4f^7$ spins via Ti$^{3+}\ 3d^0$ states and off-center displacement of Ti ions are responsible for AFM and FE orders observed in bulk EBTO [20,21,30], respectively [Fig. 4(c)]. Combined with XPS valence-band spectra [30,31], the existence of $V_O$ creates Ti$^{2+}\ 3d^1$ defect states, localizing within the band gap and overlapping with Eu$^{2+}\ 4f^7$ states [Fig. 4(d)]. In this case, the spin-polarized Ti$^{3+}$ will mediate FM coupling between the localized Eu$^{2+}\ 4f^7$ spins in EBTO$_{3-δ}$ [Fig. 4(c)]. Furthermore, in the presence of $V_O$, Ti ions with remaining oxygen form pyramid structure instead of oxygen octahedra (see Fig. S7 of Supplemental Material [24]) and increase the $d_{z^2-r^2}$ or $d_{xy}$ character of local orbitals of Ti$^{3+}$ ions adjacent to the $V_O$ sites [17,32]. When $V_O$ is situated in the EuO or BaO plane, Ti ions move naturally toward $V_O$ to avoid electrostatic interaction and the $d_{z^2-r^2}$ occupation can lead to a local polar distortion. On the other hand, when $V_O$ is placed in the TiO$_2$ plane, $d_{xy}$ orbital is preferred, resulting in an additional polar distortion in the TiO$_2$ plane. These local distortions should couple with globe polar distortion in pristine EBTO and will afford a totally new degree of freedom to tune the ferroelectricity in EBTO$_{3-δ}$. In other words, the off-center displacement of Ti ions will be enhanced by the introduction of $V_O$, thereby enhancing the FE Curie temperature in EBTO$_{3-δ}$ [Fig. 4(c)]. These results definitively confirm that tuning $V_O$ can effectively change magnetic and electric degrees of freedom in EBTO$_{3-δ}$ simultaneously. More than this, it should be emphasized that the manipulating of magnetism and ferroelectricity is both through the medium of Ti sites, revealing the existence of magnetoelectric coupling in EBTO$_{3-δ}$. The coupling between electric and magnetic orders was confirmed in the $V_O$-doped film by the magnetodielectric measurements (Fig. 5). Due to the spin-phonon coupling, as shown in Fig. 5(a), the dielectric constant shows a dependence on the external magnetic fields in the FM-FE state [33–35]. In contrast, as shown in Fig. 5(b), the influence of magnetic field is almost negligible in the PM-FE state.

In conclusion, a mechanism is proposed for controlling multiple order parameters simultaneously by using a single experimental parameter, $V_O$. EBTO$_{3-δ}$ was chosen to realize this strategy because magnetism and ferroelectricity are originated from different cations and the off-center displacements of Ti ions are sensitive to $V_O$. The emergence of ferromagnetism is the result of oxygen vacancy-created Ti$^{3+}\ 3d^1$ defect states, mediating ferromagnetic coupling between the localized Eu $4f^7$ spins. On the other hand, the introduction of $V_O$ increases an off-center displacement of Ti ions, enhancing the ferroelectric Curie temperature of EBTO$_{3-δ}$. The dual function of Ti sites induces magnetoelectric coupling, which reinforces the high potential of oxygen vacancies engineering as a tool for designing oxide thin films suitable for multifunctional device applications.

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