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# Oxygen-Vacancy-Induced Antiferromagnetism to Ferromagnetism Transformation in $\text{Eu}_{0.5}\text{Ba}_{0.5}\text{TiO}_{3-\delta}$ Multiferroic Thin Films

Weiwei Li<sup>1</sup>, Run Zhao<sup>1</sup>, Le Wang<sup>2</sup>, Rujun Tang<sup>1</sup>, Yuanyuan Zhu<sup>3</sup>, Joo Hwan Lee<sup>3</sup>, Haixia Cao<sup>1</sup>, Tianyi Cai<sup>1</sup>, Haizhong Guo<sup>2</sup>, Can Wang<sup>2</sup>, Langsheng Ling<sup>4</sup>, Li Pi<sup>4</sup>, Kuijuan Jin<sup>2</sup>, Yuheng Zhang<sup>4</sup>, Haiyan Wang<sup>3</sup>, Yongqiang Wang<sup>5</sup>, Sheng Ju<sup>1</sup> & Hao Yang<sup>1</sup>

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Correspondence and requests for materials should be addressed to H.Y. (yanghao@suda.edu.cn) or S.J. (jusheng@suda.edu.cn)

<sup>1</sup>Jiangsu Key Laboratory of Thin Films, School of Physical Science and Technology, Soochow University, Suzhou 215006, China, <sup>2</sup>Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Science, Beijing 100190, China, <sup>3</sup>Materials Science and Engineering Program, Department of Electrical and Computer Engineering, Texas A&M University, College Station, Texas 77843-3128, USA, <sup>4</sup>High Magnetic Field Laboratory, Chinese Academy of Science, Hefei 230031, China, <sup>5</sup>Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA.

Oxygen vacancies ( $V_O$ ) effects on magnetic ordering in  $\text{Eu}_{0.5}\text{Ba}_{0.5}\text{TiO}_{3-\delta}$  (EBTO<sub>3- $\delta$</sub> ) thin films have been investigated using a combination of experimental measurements and first-principles density-functional calculations. Two kinds of EBTO<sub>3- $\delta$</sub>  thin films with different oxygen deficiency have been fabricated. A nuclear resonance backscattering spectrometry technique has been used to quantitatively measure contents of the  $V_O$ .  $\text{Eu}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$  ceramics have been known to exhibit ferroelectric (FE) and G-type antiferromagnetic (AFM) properties. While, a ferromagnetic (FM) behavior with a Curie temperature of 1.85 K has been found in the EBTO<sub>3- $\delta$</sub>  thin films. Spin-polarized  $\text{Ti}^{3+}$  ions, which originated from the  $V_O$ , has been proven to mediate a FM coupling between the local Eu 4f spins and were believed to be responsible for the great change of the magnetic ordering. Considering the easy formation of  $V_O$ , our work opens up a new avenue for achieving co-existence of FM and FE orders in oxide materials.

Multiferroics, or materials that simultaneously possess two or more ferroic orders [ferroelectric, (anti-)ferromagnetic, and ferroelastic], have recently returned to the forefront of materials research due to their rich physical properties and potential applications in data storage, sensors, and spintronics<sup>1,2</sup>. From an application point of view, multiferroics with ferromagnetic-ferroelectric (FM-FE) orders are more attractive and highly desired<sup>3</sup>. However, very few exist in nature due to the intrinsic contradiction in existence between the FM and FE ordering within a single phase<sup>4</sup>. On the other hand, antiferromagnetic-ferroelectric (AFM-FE) materials are more commonly found, such as rare-earth manganites (RMnO<sub>3</sub>) and the well known BiFeO<sub>3</sub><sup>5-11</sup>. It is fundamentally interesting and technologically important to develop FM-FE materials by changing magnetic ordering of the AFM-FE materials. An additional driving force and a deep understanding of physical phenomenon underlying the transformation are needed to realize this purpose.

In oxides, oxygen vacancies ( $V_O$ ) have been approved to be intrinsic defects and are believed to have a critical impact on their properties<sup>12</sup>. Coey *et al* reported that  $V_O$  play a key role in obtaining room temperature FM in HfO<sub>2</sub>, ZnO, TiO<sub>2</sub>, and other non-magnetic oxide systems<sup>13-16</sup>. It has also been proven that  $V_O$  are useful in increasing Curie temperature and enhancing magnetic moment of EuO thin films<sup>17-20</sup>. Furthermore,  $V_O$  are known to induce a room temperature ferroelectricity in SrTiO<sub>3</sub> thin films<sup>21-23</sup>. Despite the fact that the  $V_O$  are effective to manipulating the magnetic and ferroelectric properties of oxides, little attention has been focused upon the  $V_O$  effects on multiferroicity in single-phase materials. A natural question to ask is: are the  $V_O$  able to change the magnetic ordering from AFM to FM in multiferroic materials?

The beginning of the present work is to choose a suitable material to verify the above idea. In recent years, divalent europium oxidation materials showed attractive functionalities, rendering them subjects of intensive studies. Compared to the 0.05  $\mu_B/\text{Fe}$  in BiFeO<sub>3</sub><sup>24</sup>, rare-earth Eu<sup>2+</sup> ion has seven unpaired and localized 4f electrons, which resulted in a large magnetization of 7  $\mu_B/\text{Eu}$  and sometimes is coupled with electrical properties.

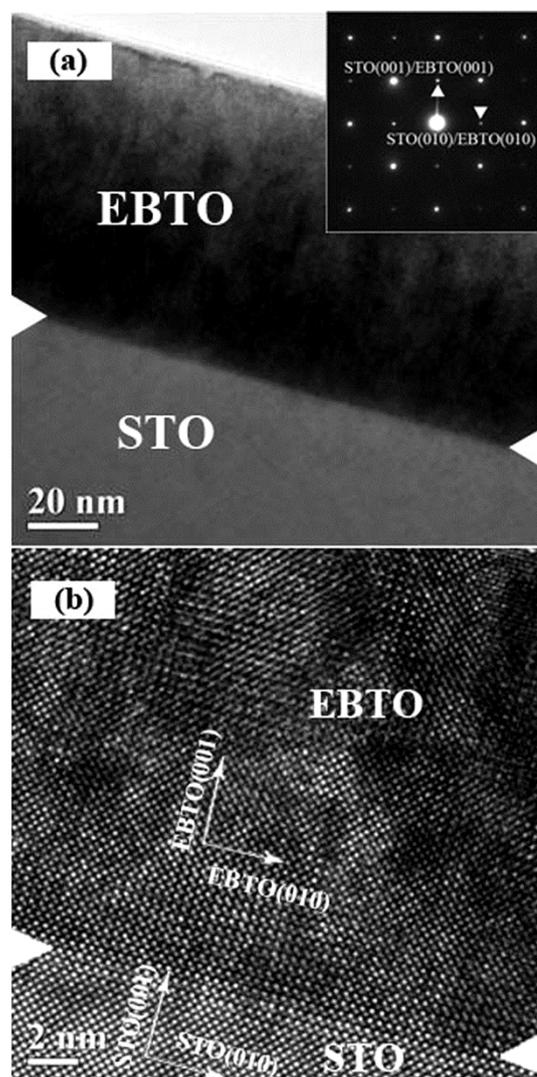


For example, Rushchanskii *et al* confirmed that  $\text{Eu}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$  (EBTO) ceramics exhibit FE (Curie temperature  $T_C \sim 213$  K) and G-type AFM (Néer temperature  $T_N \sim 1.9$  K) properties<sup>25</sup>. And coupling between magnetism and dielectric properties was predicted in  $\text{Eu}_{1-x}\text{Ba}_x\text{TiO}_3$  materials<sup>26</sup>. Furthermore, as we discussed earlier, the  $V_O$  have been proven to be useful in manipulating the magnetic orders of divalent Eu ions in EuO thin films. Therefore, EBTO is a potential material for the present study, based on the nature of a large magnetization of  $7 \mu_B/\text{Eu}$  and the AFM-FE orders. In addition, if we can alter magnetism of EBTO thin films by doping  $V_O$  and at the same time still preserve good ferroelectricity, it will certainly make EBTO itself appealing in fundamental research and practical applications. In the present work, we experimentally confirmed that the magnetic ordering in oxygen-deficient  $\text{Eu}_{0.5}\text{Ba}_{0.5}\text{TiO}_{3-\delta}$  (EBTO<sub>3- $\delta$</sub> ) thin films has been transformed from AFM to FM. First-principle calculations indicated that spin-polarized  $\text{Ti}^{3+}$  ions, which originated from the  $V_O$ , mediated a FM coupling between the local Eu  $4f$  spins. Considering the easy formation of  $V_O$ , our work presented an effective technique to achieve co-existence of FM and FE orders in oxide materials.

## Results

The EBTO<sub>3- $\delta$</sub>  thin films were fabricated on (001) oriented SrTiO<sub>3</sub> (STO) and Nb-doped SrTiO<sub>3</sub> (Nb-STO) substrates by pulsed laser deposition (PLD). Following the deposition, parts of the thin films were post-annealed under a reducing atmosphere to increase amount of the  $V_O$ . Typical X-ray diffraction (XRD)  $\theta$ - $2\theta$  scans confirmed that the EBTO<sub>3- $\delta$</sub>  is preferentially oriented along the  $c$  axis (not shown). In order to reveal the microstructure of the EBTO<sub>3- $\delta$</sub>  thin films, cross-sectional transmission electron microscopy (TEM) measurements were conducted. A low magnification bright-field TEM image (Fig. 1a) shows that the interface is clean without any obvious interface reaction or intermixing. In the view area, the film is continuous without any obvious grain boundaries, confirming the 2D growth of the film. The corresponding selected area diffraction (SAD) image taken from the interface area is shown as inset of Fig. 1a. The distinguished diffraction dots from the film and substrate indicate the high quality epitaxial growth. The out-of-plane and in-plane orientation relationships have been determined to be  $(001)_{\text{EBTO}} \parallel (001)_{\text{STO}}$  and  $[110]_{\text{EBTO}} \parallel [110]_{\text{STO}}$ , respectively. A high resolution TEM (HRTEM) image (Fig. 1b) confirmed the excellent heteroepitaxial relation with an atomically sharp interface. Similarly no obvious misfit dislocations have been found along the interface, which is consistent with the SAD observation.

To quantitatively analyze stoichiometry and oxygen concentration of the EBTO<sub>3- $\delta$</sub>  thin films, a nuclear resonance backscattering spectrometry (NRBS) technique was used. The advantage of NRBS over traditional Rutherford backscattering spectrometry (RBS) is its sensitivity to selectively measure oxygen in the EBTO<sub>3- $\delta$</sub>  film on an oxygen-rich substrate, such as STO in our experiment<sup>27,28</sup>. The NRBS was performed using a 3.043 MeV  $^4\text{He}^+$  analyzing beam and the backscattering particles were detected by a surface barrier silicon detector located at  $167^\circ$  from the beam direction. At such a beam energy, the He scattering from the heavier elements (Eu, Ba, and Ti) in the film is still Rutherford, therefore the Eu:Ba:Ti ratios



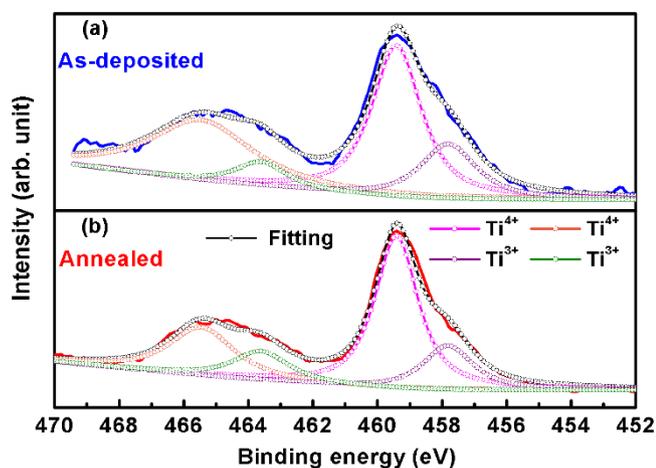
**Figure 1** | TEM images of the EBTO<sub>3- $\delta$</sub>  thin film on a STO substrate: (a) low magnification cross-sectional TEM; (b) high resolution TEM (HRTEM). The inset shows the corresponding selected-area diffraction (SAD) pattern.

can be determined reasonably well by fitting the experimental spectra data with the commercial Rutherford Universal Manipulation Program (RUMP) software<sup>29</sup>. Within the uncertainty of the measurements ( $\sim 5\%$ ), we determined that our EBTO<sub>3- $\delta$</sub>  thin films do have an Eu:Ba:Ti ratio of 1 : 1 : 2.

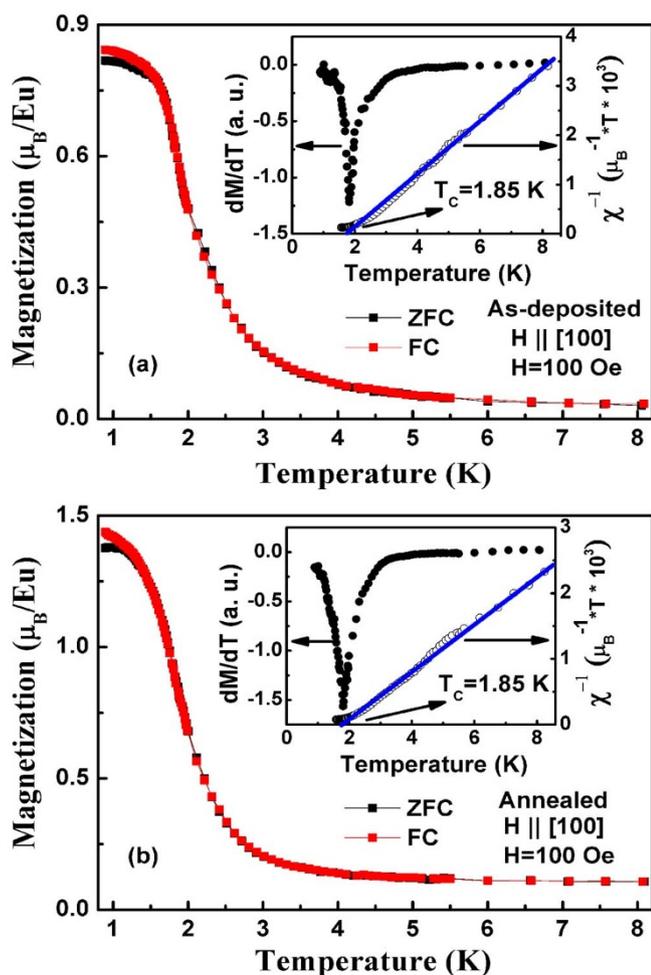
After the atomic ratios of cations were determined, a nuclear scattering and reaction simulation package (SIMNRA) was used to fit the nuclear resonant oxygen scattering spectra (not shown)<sup>30</sup>. To minimize uncertainties related to the nuclear scattering cross section and the incident beam energy, a bare STO substrate as a standard reference was measured and analyzed all together along with our

**Table 1** | The measured concentration of europium and oxygen from the NRBS. The content of  $V_O(x)$ , the value of  $\delta$  ( $\delta = 3x$ ), and the ideal and real content of  $\text{Ti}^{3+}$  are also shown. The ideal content of  $\text{Ti}^{3+}$  is estimated from  $\delta$  with a relationship of  $\text{Ti}^{3+}/\text{Ti} : \delta = 2 : 1$ . The real values are calculated by fitting peaks of XPS measurements

	Eu(at./cm <sup>2</sup> )	O(at./cm <sup>2</sup> )	Oxygen vacancies		Ideal $\text{Ti}^{3+}/\text{Ti}$	Real $\text{Ti}^{3+}/\text{Ti}$
			x	$\delta$		
As-deposited thin film	$8.7 \times 10^{16}$	$5.01 \times 10^{17}$	4.0%	0.120	24.0%	27.1%
Annealed thin film	$9.8 \times 10^{16}$	$5.58 \times 10^{17}$	5.1%	0.153	30.6%	33.4%



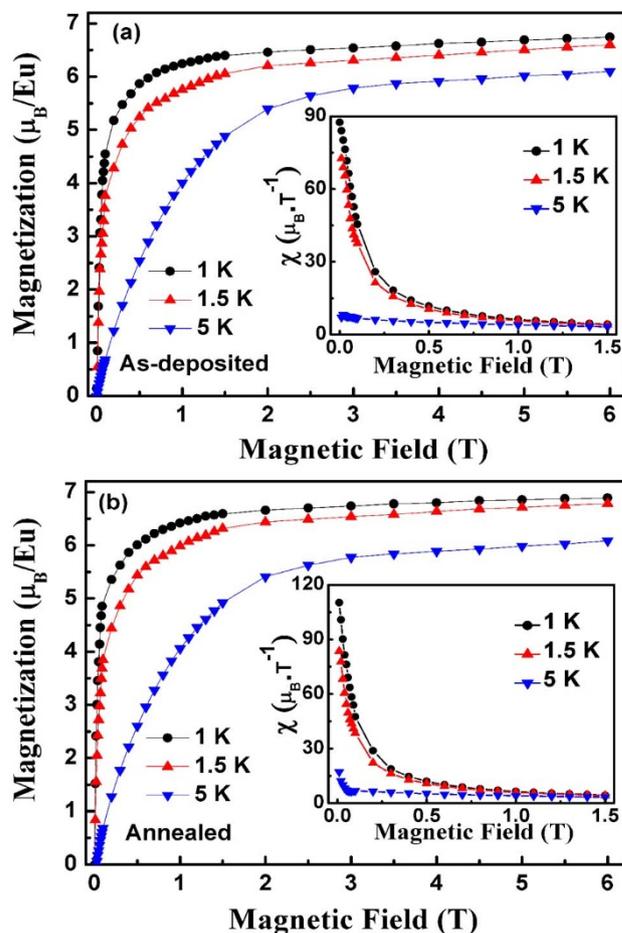
**Figure 2** | The open circles represent peak fittings on these graphs, which show the Ti 2*p* core-level photoemission spectra of (a) as-deposited and (b) annealed EBTO<sub>3- $\delta$</sub>  thin films.



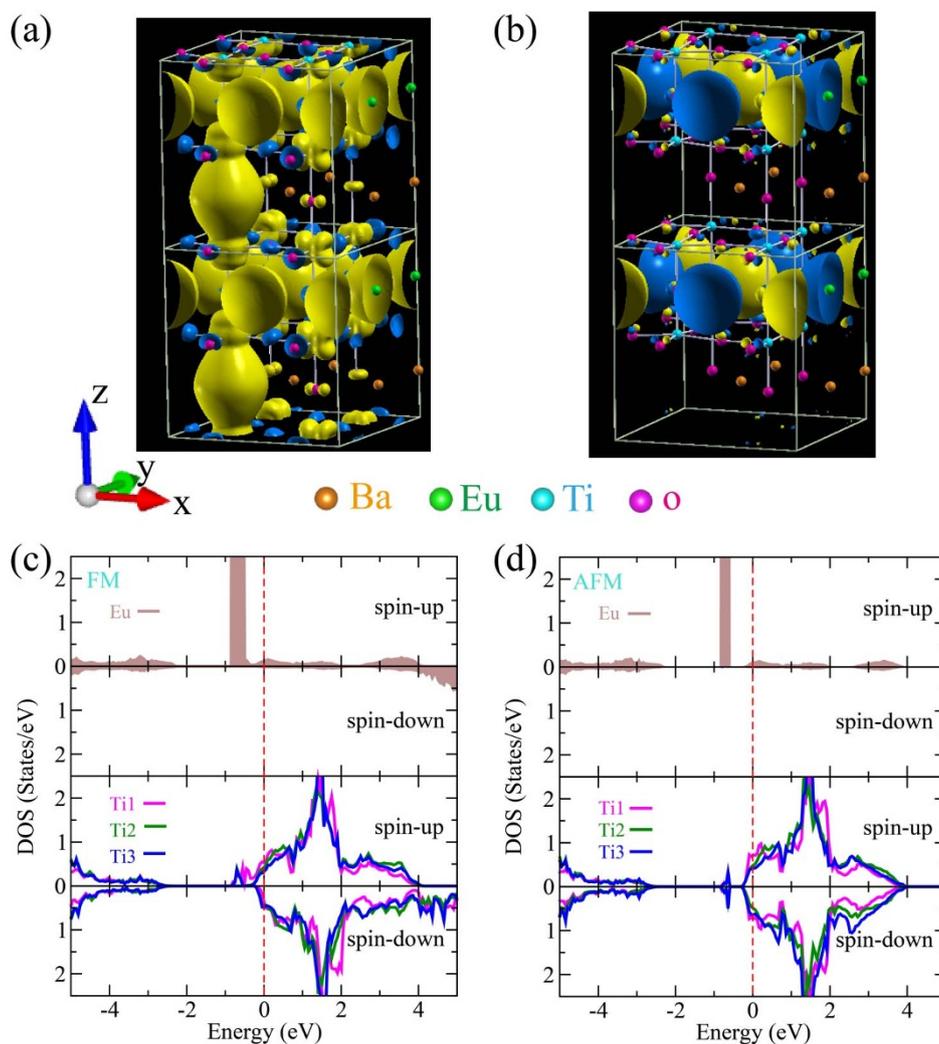
**Figure 3** | Temperature dependence of magnetization curves under ZFC and FC conditions for the (a) as-deposited and (b) annealed EBTO<sub>3- $\delta$</sub>  thin films. The insets show the derivative of the magnetization (the solid circles) and the reciprocal susceptibility (the open circles) with respect to the temperature (obtained from the FC curves). The blue lines in the insets are the Curie-Weiss law fittings of the reciprocal susceptibilities.

EBTO<sub>3- $\delta$</sub>  thin films. Table 1 shows the measured concentration of europium and oxygen in the as-deposited and annealed EBTO<sub>3- $\delta$</sub>  thin films. From the Eu concentration, the ideal oxygen concentration in the stoichiometric Eu<sub>0.5</sub>Ba<sub>0.5</sub>TiO<sub>3</sub> thin films is estimated to be  $5.22 \times 10^{17}$  and  $5.88 \times 10^{17}$  at./cm<sup>2</sup> for as-deposited and annealed thin films respectively. By comparing the measured and the ideal oxygen concentration, we have calculated that there are 4.0% oxygen deficiency ( $\delta \approx 0.120$ ) in the as-deposited film and 5.1% oxygen deficiency ( $\delta \approx 0.153$ ) in the annealed film. In other words, the  $V_O$  were introduced into the EBTO<sub>3- $\delta$</sub>  thin films and the content of the  $V_O$  were increased by post-annealing under a reducing atmosphere.

Because of the charge compensation, the existence of  $V_O$  should induce changes in the valance states of cations. To quantify these changes, we investigated the valance states of the EBTO<sub>3- $\delta$</sub>  thin films by using X-ray photoemission spectroscopy (XPS). We found that the valance states of Eu and Ba ions are remained in divalent (not shown), while those of Ti ions have been changed. Because  $V_O$  act as *n*-type dopants, the Ti<sup>3+</sup> and Ti<sup>4+</sup> formal valences should coexist in the EBTO<sub>3- $\delta$</sub>  thin films. Figure 2 shows Ti 2*p* core-level photoemission spectrum of (a) the as-deposited and (b) the annealed EBTO<sub>3- $\delta$</sub>  thin films with peak fittings. Compared with previous results, the peaks at a binding energy around 459.42 eV and 465.45 eV can be assigned as Ti<sup>4+</sup>, with peaks around 457.81 eV and 463.53 eV corresponding to Ti<sup>3+</sup><sup>31,32</sup>. By comparing the peak area, the content of Ti<sup>3+</sup> was calculated to be 27.1% and 33.4% in the as-deposited and annealed thin films respectively. On the other hand, by assuming two free carries for each  $V_O$ <sup>33</sup>, the ratio between the content of Ti<sup>3+</sup> and that of  $V_O$  ( $\delta$ ) will be 2 : 1. Therefore, the ideal content of Ti<sup>3+</sup> for the



**Figure 4** | Magnetic field dependent magnetization curves for (a) as-deposited and (b) annealed EBTO<sub>3- $\delta$</sub>  thin films at various temperature. The insets show magnetic susceptibility curves.



**Figure 5 | Spin-density and local density of states (DOS) in the  $\text{EBTO}_{3-1/8}$ :** (a) and (c) for FM ground state; (b) and (d) for AFM state. Here, yellow color is for up-spin and blue color for down-spin. The red vertical dash line is the Fermi level. Ti1, Ti2, and Ti3 are the nearest (just below the  $V_O$ ), next-nearest (at the same  $ab$ -plane of Ti1), and next-next-nearest (at the same  $ab$ -plane of Ti1) Ti ions with respect to the  $V_O$ . The Eu ions are almost similar to each other. The development of spin-polarized  $d_{z^2}$  orbital at  $\text{Ti}^{3+}$  is obvious in the FM ground state.

as-deposited and annealed thin films should be 24.0% and 30.6% respectively (see table 1). These results are well fitted with the calculated values and further confirmed that  $V_O$  were doped into the thin films. In addition, the fact that the change of the valence states only occurred in Ti cations has been verified by first-principles density-functional calculations and will be discussed in more details later.

To investigate  $V_O$  effects on magnetic properties of the  $\text{EBTO}_{3-\delta}$  thin films, temperature and magnetic-field dependences of magnetization were investigated using a superconducting quantum interface device magnetometer (SQUID). Figure 3 shows the temperature dependent magnetization curves. The measurements were performed under zero-field-cooled (ZFC) and field-cooled (FC) conditions with an external magnetic field of 100 Oe applied parallel to the films surface. The EBTO ceramics antiferromagnetically ordered at 1.9 K<sup>25</sup>. However, the magnetization on both ZFC and FC curves increased monotonically with decreasing temperature until 0.9 K and tend to be saturated at the lowest temperature, which is a typical FM behavior. The derivative of the magnetization and the reciprocal susceptibility as a function of temperature are shown as insets of Fig. 3a and 3b. It has been found that the derivative of the magnetization shows a sharp valley, in other words the magnetizations increase quickly, at around 1.85 K. In addition, the Curie-Weiss law fitting of the reciprocal susceptibilities at high temperatures

intersects the temperature axis at 1.85 K. Both of these results then confirmed the FM ordering in the  $\text{EBTO}_{3-\delta}$  thin films with a Curie temperature of 1.85 K<sup>34</sup>. Figure 4 shows the field dependent magnetization curves at 1, 1.5, and 5 K. It has been found that, at 1 and 1.5 K, the magnetization increased sharply at low fields and then approached saturation quickly. The large susceptibility at low fields (shown as insets of Fig. 4a and 4b) is also an evidence for the FM ordering below 1.85 K. The saturation magnetizations, measured for the as-deposited and annealed thin films at 1 K, are around  $6.75 \mu_B/\text{Eu}$  and  $6.85 \mu_B/\text{Eu}$  respectively. These values are close to the ideal magnetic moment of the  $\text{Eu}^{2+}$  ions ( $7 \mu_B/\text{Eu}$ ). It should be noticed that the susceptibility at low fields and the value of the magnetization in the annealed thin films are larger than those in the as-deposited thin films, which obviously originates from the enhanced content of  $V_O$ . In order to further prove the FM ordering of the  $\text{EBTO}_{3-\delta}$  thin films below 1.85 K, magnetic hysteresis loops were measured at 0.5 K (Supplementary Figure S1). Hysteretic behavior is observed with a coercivity of 30 Oe. The combination of these results proved that the  $\text{EBTO}_{3-\delta}$  thin films become a ferromagnet with a Curie temperature of 1.85 K, which is different from bulk EBTO – G-type antiferromagnet<sup>25</sup>.

Many theoretical studies of vacancy-induced magnetism in non-magnetic  $\text{SrTiO}_3$  have been performed using ab initio

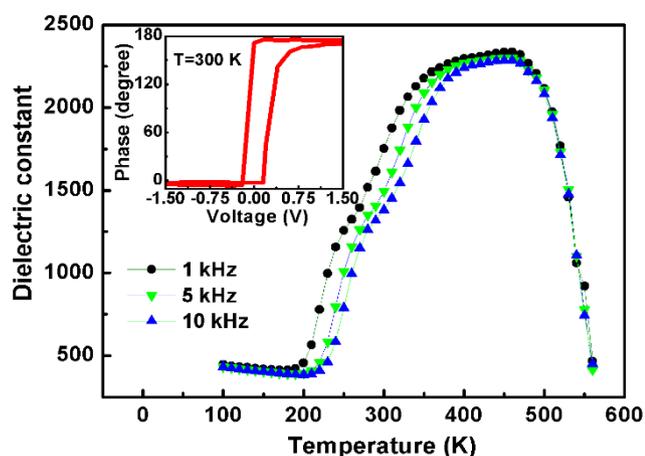


**Table 2 | Energy differences between AFM and FM states in  $\text{EBTO}_{3-1/4}$  with various atomic orderings of Eu and Ba ions. In all the cases, FM state is energetically favorable. In addition, A-type atomic arrangement of Eu and Ba ions is the ground state**

	A-type atomic ordering	C-type atomic ordering	G-type atomic ordering
$\Delta E = E(\text{AFM}) - E(\text{FM})$ (meV/Eu)	0.6	0.2	0.5

calculations<sup>35,36</sup>. To investigate the fundamental physics underlying the origin of the FM ordering in the  $\text{EBTO}_{3-\delta}$  thin films, we calculated total energies of  $\text{EBTO}_{3-1/8}$  with both FM and AFM orderings from first-principles density-functional theory. FM ordering is found to be 13.1 meV/Eu favorable. Figure 5 shows the spin-density and local density of states (DOS) in the  $\text{EBTO}_{3-1/8}$ : (a) and (c) for FM ground state; (b) and (d) for AFM state. As shown in DOS of local Ti ions, the occupancy of 3d orbital indicates the appearance of  $\text{Ti}^{3+}$ , in good agreement with the XPS measurements. Furthermore, the existence of  $V_O$  does not change the valence state of Eu, since almost fully occupied 4f<sup>7</sup> states are found, which is similar to the pristine  $\text{EuTiO}_3$  and confirmed by the SQUID and XPS measurements<sup>37</sup>. On the other hand, as shown in Fig. 5 (a) and (c), the development of large local spin moment at Ti sites makes the FM ground state differ significantly from the AFM state. The local magnetic moment at  $\text{Ti}^{3+}$  ions right above or under  $V_O$  is around 0.24  $\mu_B$  and the  $d_{z^2}$  dominates. While for other  $\text{Ti}^{3+}$  ions, the local orbital is either  $d_{xy}$  or  $d_{xz}/d_{yz}$ . Magnetic moment at Eu site does not change from the pristine case with a local magnetic moment of around 7  $\mu_B$ . Judging from Fig. 5, it is the appearance of spin-polarized  $\text{Ti}^{3+}$  that mediates the FM coupling between the localized Eu 4f spins. It should be noticed that with increase of the content of  $V_O$ , e.g.  $\text{Eu}_{0.5}\text{Ba}_{0.5}\text{TiO}_{3-1/4}$ , the FM ordering is still found to be energetically favorable than the AFM orderings (see Table 2). These results verified that the  $\text{EBTO}_{3-\delta}$  thin films do show FM ordering, which originated from the ordering of the spin of Eu 4f electrons mediated by the spin-polarized  $\text{Ti}^{3+}$  ions.

This article is mainly concerned about the magnetic ordering, but we also investigated the FE properties of the annealed  $\text{EBTO}_{3-\delta}$  thin films by measuring dielectric constant as a function of temperature and room-temperature hysteresis loop using piezoresponse force microscopy (PFM). It's surprised to find out that a peak in dielectric constant versus temperature curves (shown as Fig. 6) is clearly seen above room temperature. Moreover, a room-temperature hysteresis loop measured by PFM was shown as inset of Fig. 6. These results suggest that the FE Curie temperature of the annealed  $\text{EBTO}_{3-\delta}$  thin films is above room temperature, which is significantly higher than that of bulk EBTO (~213 K). The investigation on mechanism of the enhancement on the FE Curie temperature is presently in progress.



**Figure 6 | Temperature dependence of dielectric constant for the annealed  $\text{EBTO}_{3-\delta}$  thin film. The inset shows room-temperature hysteresis loop measured by PFM.**

## Discussion

In summary, two kinds of  $\text{EBTO}_{3-\delta}$  thin films with different content of  $V_O$  were fabricated. By using NRBS, SQUID, and first-principles calculations, we demonstrated that the magnetic ordering of oxygen-deficient  $\text{EBTO}_{3-\delta}$  thin films has been changed from AFM to FM. The transformation originated from the  $V_O$  induced Ti 3d electrons, which mediated the FM coupling between the local Eu 4f spins. The results are significant as they proved that  $V_O$  are effective to manipulating magnetic ordering in multiferroic materials. Considering the easy formation of  $V_O$ , the present work presents a methodology to enhance multiferroicity in the  $\text{EBTO}_{3-\delta}$  thin films and this method holds great promise for other oxide materials.

## Methods

The  $\text{EBTO}_{3-\delta}$  thin films were fabricated on (001) oriented  $\text{SrTiO}_3$  (STO) and Nb-doped  $\text{SrTiO}_3$  (Nb-STO) substrates by pulsed laser deposition (PLD) using a pulsed excimer laser (Lambda Physik, 248 nm, 3 Hz, 2 J/cm<sup>2</sup>). A high-density EBTO ceramic pellet was used as the target. The details of the preparation of EBTO ceramics can be found in elsewhere<sup>25</sup>. Deposition temperature was 700 °C and oxygen pressure was  $1 \times 10^{-4}$  Pa with the purpose of doping  $V_O$ . Following the deposition, parts of the thin films were annealed at 1000 °C under a flowing gas of 95 vol% Ar + 5 vol% H<sub>2</sub> for 10 hours to increase amount of the  $V_O$ . The film thickness, revealed by cross-sectional transmission electron microscopy (TEM), was 100–150 nm.

The crystal structures were characterized by X-ray diffraction (XRD, Rigaku K/Max) and TEM (FEI Tecnai F20 analytical microscope). Nuclear resonance backscattering spectrometry (NRBS) was performed on Los Alamos National Laboratory. A He<sup>+</sup> beam energy of 3.043 MeV was used to quantitatively analyze stoichiometry and oxygen concentration in the  $\text{EBTO}_{3-\delta}$  thin films. The valence states were investigated by X-ray photoemission spectroscopy (XPS) at PHI5000 VersaProbe.

Magnetic measurements were performed on  $\text{EBTO}_{3-\delta}$ /STO thin films using a superconducting quantum interface device magnetometer (SQUID) equipped with a He<sup>3</sup> insert (Quantum Design, MPMS-XL). The electrical properties were measured using a Pt/ $\text{EBTO}_{3-\delta}$ /Nb-STO heterostructure. The dielectric constants were investigated using an Agilent 4294A Impedance Analyzer. The measurements were performed at selected temperatures in a Linkam Scientific Instruments HFS600E-PB4 system. Room-temperature piezoresponse force microscopy (PFM) was measured using PFM mode of Asylum Research MFP-3D-SA atomic force microscopy.

Our ab initio calculations are performed using the accurate full-potential projector-augmented wave (PAW) method, as implemented in the Vienna ab initio simulation package (VASP)<sup>38,39</sup>. They are based on density-functional theory with the generalized gradient approximation (GGA) in the form proposed by Perdew, Burke, and Ernzerhof (PBE)<sup>40</sup>. The on-site Coulomb interaction is included in the GGA + U approach with effective U = 4 eV for Eu 4f orbitals<sup>41</sup>. A plane-wave cutoff of 600 eV is used throughout and the convergence criteria for energy is  $10^{-6}$  eV. PAW potentials are used to describe the electron-ion interaction with 17 valence electrons for Eu (4f<sup>7</sup>5s<sup>2</sup>5p<sup>6</sup>6s<sup>2</sup>), 10 for Ba (5s<sup>2</sup>5p<sup>6</sup>6s<sup>2</sup>), 10 for Ti (3p<sup>6</sup>3d<sup>4</sup>4s<sup>2</sup>), and 6 for O (2s<sup>2</sup>2p<sup>4</sup>). In our calculations, ions are relaxed toward equilibrium positions until the Hellman-Feynman forces are less than 1 meV/Å. In addition, lattice constants are optimized until the stress is less than 0.001 Pa. The fully optimized lattice constant of  $\text{Eu}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$  stems from an initial cubic lattice, from which the atoms shift a little from their high symmetric positions. Total energies are calculated and compared between different magnetic and A-site atomic arrangements.

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## Author contributions

H.Y. supervised the project. W.L., R.Z. and R.T. conducted the thin films fabrication and data analysis. W.L., L.W., H.G., C.W. and K.J. did the electrical properties measurements. Y.Z., J.H.L. and H.W. helped to collect and analyze the TEM images. L.L., L.P. and Y.Z. conducted the SQUID measurements. Y.W. performed the NRBS measurements. H.C., T.C. and S.J. did the first-principles calculations. W.L., H.Y. and S.J. co-wrote the manuscript. All authors reviewed the manuscript.

## Additional information

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