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Weiwei Li, Junxing Gu, Qian He, Kelvin H. L. Zhang, Chunchang Wang, Kuijuan Jin, Yongqiang Wang, Matias Acosta, Haiyan Wang, Albina Y. Borisevich, Judith L. MacManus-Driscoll, and Hao Yang

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Oxygen-vacancy-mediated dielectric property in perovskite Eu$_{0.5}$Ba$_{0.5}$TiO$_{3-\delta}$ epitaxial thin films

Weimei Li,1,2,a) Junxing Gu,3 Qian He,4 Kelvin H. L. Zhang,5 Chunchang Wang,6 Kuijuan Jin,3 Yongqiang Wang,7 Matias Acosta,2 Haiyan Wang,8,9 Albina Y. Borsievich,4 Judith L. MacManus-Driscoll,9 and Hao Yang1,b)

1College of Science, Nanjing University of Aeronautics and Astronautics, Nanjing 211106, China
2Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge CB3 0FS, United Kingdom
3Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Science, Beijing 100190, China
4Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA
5Department of Chemical and Biochemical Engineering, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China
6Laboratory of Dielectric Functional Materials, School of Physics and Material Science, Anhui University, Hefei 230039, China
7Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA
8Department of Electrical and Computer Engineering, Texas A&M University, College Station, Texas 77843-3128, USA
9School of Materials Engineering, Electrical and Computer Engineering, Purdue University, West Lafayette, Indiana 47907, USA

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Dielectric relaxation in ABO$_3$ perovskite oxides can result from many different charge carrier-related phenomena. Despite a strong understanding of dielectric relaxations, a detailed investigation of the relationship between the content of oxygen vacancies (V$_O$) and dielectric relaxation has not been performed in perovskite oxide films. In this work, we report a systematic investigation of the influence of the V$_O$ concentration on the dielectric relaxation of Eu$_{0.5}$Ba$_{0.5}$TiO$_{3-\delta}$ epitaxial thin films. Nuclear resonance backscattering spectrometry was used to directly measure the oxygen concentration in Eu$_{0.5}$Ba$_{0.5}$TiO$_{3-\delta}$ films. We found that dipolar defects created by V$_O$ interact with the off-centered Ti ions, which results in the dielectric relaxation in Eu$_{0.5}$Ba$_{0.5}$TiO$_{3-\delta}$ films. Activation energy gradually increases with the increasing content of V$_O$. The present work significantly extends our understanding of relaxation properties in oxide films. Published by AIP Publishing. https://doi.org/10.1063/1.5025607

Complex ABO$_3$ perovskite oxides exhibit a broad spectrum of physical properties due to their highly tunable ground states that make them indispensable in oxide electronic devices. The functional properties of perovskite oxides are strongly influenced by composition, defects, and BO$_6$ octahedral distortions. Among them, oxygen vacancies (V$_O$) are one of the fundamental and intrinsic defects that affect crucial functionalities such as optical properties, superconductivity, magnetism, ferroelectricity, multiferroicity, resistive switching, and ionic conductivity. The low-frequency relaxation properties of perovskite oxides, which are critical for applications in sensors, actuators, transducers, and dynamic random access memories, are known to be closely related to V$_O$. The dielectric properties in the low-frequency regime offer rich information about impurities, defects, and space charge effects. For example, in the ATiO$_3$ (A = Ba, Ca, and Pb) system, V$_O$ create space charge regions at the dielectric/electrode interfaces, inducing dielectric relaxation. Dielectric relaxation phenomena have been reported in La- and Ti-co-doped or La- and Mg-co-doped BiFeO$_3$ and Bi-doped SrTiO$_3$ with the effect attributed to the ionization and movement of V$_O$. Furthermore, the movement of V$_O$ confined at the vertical interfaces and hampered by the misfit dislocations is responsible for the relaxation behavior in nanocomposite (BaTiO$_3$)$_{1-x}$(Sm$_2$O$_3$)$_x$ films. It clearly shows that the role of V$_O$ as a complex defect on the relaxation phenomena is very complicated. More detailed work is needed to fully understand the role of V$_O$ on the dielectric relaxation of ABO$_3$ perovskite oxides, which is both fundamentally interesting and technologically important. Tuning the content of V$_O$ is an ideal way to reveal the relationship between V$_O$ and dielectric relaxation and is also critical for practical applications. However, a systematical investigation of this correlation has not been reported to date, largely due to the difficulties in controlling and determining V$_O$ precisely.

Eu$_{0.5}$Ba$_{0.5}$TiO$_3$ (EBTO), an antiferromagnetic-ferroelectric multiferroic material with ferroelectric Curie temperature of 213 K in bulk, is an interesting system for probing dielectric relaxation effects. In Eu$_{0.5}$Ba$_{0.5}$TiO$_{3-\delta}$ (EBTO$_{3-\delta}$) films, it has been demonstrated that the introduction of V$_O$ creates Ti$^{3+}$ 3d$^1$ defect states, which mediates the ferromagnetic coupling between the localized Eu 4f$^7$ spins. Also the introduction of

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a)Email: w337@cam.ac.uk
b)Email: yanghao@nuaa.edu.cn

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$V_O$ increases the off-center displacement of Ti ions. This enhances the ferroelectric Curie temperature above room temperature, which makes EBTO$_{3,5}$ films a promising candidate for memory device applications.8,11

In this letter, dielectric permittivity, modulus, and impedance of EBTO$_{3,5}$ films were studied as a function of temperature and frequency. Epitaxial EBTO$_{3,5}$ films were grown on (001) oriented SrTiO$_3$ (STO) and Nb-doped SrTiO$_3$ (Nb-STO, Nb: 0.5 wt. %) substrates. Details on sample synthesis can be found elsewhere.8,11 The EBTO$_{3,5}$ films, grown at oxygen partial pressure ($P_{O2}$) of 1 × 10$^{-1}$, 1 × 10$^{-2}$, 1 × 10$^{-3}$, and 1 × 10$^{-4}$Pa, were named as Samples A, B, C, and D, respectively. The crystal structure was investigated by X-ray diffraction (XRD) and scanning transmission electron microscopy (STEM, Nion UltraSTEM 200). Nuclear resonance backscattering spectrometry (NRBS) was performed on 3 MV Pelletron Tandem Accelerator. A sandwich capacitor structure of Pt/EBTO$_{3,5}$/Nb-STO with a thickness of 4 nm was used for electrical measurements. Top Pt electrodes with an area of 8 × 10$^{-4}$ cm$^2$ were fabricated by sputtering. The dielectric properties were measured using an Agilent 4294A Impedance Analyzer as a function of temperature from 120 to 350 K and frequency between 1 and 100 kHz. Current-voltage characteristics were measured using a Keithley 6517 analyzer.

Sample D, grown under the lowest $P_{O2}$ and presumed to have the maximum content of $V_O$, was chosen for the detailed analysis. Figure S1 shows a typical XRD rocking curves, $\omega$-scan, and reciprocal space maps (RSMs). The EBTO$_{3,5}$ film peaks have the same position as those of Nb-STO substrate, indicative of cubic-on-cubic epitaxy [Fig. S1(d)]. RSMs clearly demonstrate that the EBTO$_{3,5}$ film is free from strain [Fig. S1(e)]. Moreover, there is no difference on the $q_x$ and $q_y$ of the EBTO$_{3,5}$ peaks and the c/a (c/a: out-of-plane/in-plane lattice constant) ratio is above 1, meaning the structure of the EBTO$_{3,5}$ film is tetragonal.

The stoichiometry and oxygen concentration in EBTO$_{3,5}$ films were analyzed by Rutherford Backscattering Spectrometry (RBS) and NRBS. A 3.043 MeV $^4$He$^+$ was used in the measurement. At such beam energy, there is a strong and narrow resonant scattering from oxygen in the EBTO$_{3,5}$ films (not in the substrate). Figure 1(a) shows the RBS spectrum measured from Sample D. With the uncertainty of the measurements (~5%), a SIMNRA simulated spectrum overlapped with the measured spectrum determined that the cation ratio in EBTO$_{3,5}$ films (Eu: Ba: Ti) is 1:1.2.26,27 Figure 1(b) shows the measured oxygen scattering spectrum in Sample D along with a SIMNRA fitted oxygen spectrum. A bare STO substrate was also measured to use it as a standard reference and to minimize uncertainties. The concentration of O was estimated to be 2.98, 2.96, 2.91, and 2.85 for Samples A, B, C, and D, respectively. Thus, the content of $V_O$ is inferred to be 0.02, 0.04, 0.09, and 0.15 for Samples A, B, C, and D (Table S1), respectively.

To investigate the microstructure, aberration-corrected STEM imaging under the high-angle annular dark-field (HAADF) mode was conducted on Sample A (Fig. S2) and Sample D (Fig. 2). HAADF imaging in STEM, also known as Z-contrast imaging,28 can provide the relative cation displacements of the B-site atoms in the ABO$_3$ perovskite oxides.29 Figure 2 shows a high resolution STEM image at the interface between the thin film and the substrate, confirming the heteroepitaxial growth of the EBTO$_{3,5}$ thin film on the STO substrate. The inset provides a schematic representation of the quantification method used to determine the cation column positions and relative displacements. The in-plane ($d_y$) and out-of-plane ($d_z$) displacements of Ti ions for the EBTO$_{3,5}$ thin film and the STO substrate are plotted. The line profiles show that the EBTO$_{3,5}$ film features displacement of the Ti ions along in-plane ($d_y$) and the out-of-plane ($d_z$) directions. The Ti ions displacement renders a non-centrosymmetric structure, which is a sufficient condition for a material to exhibit piezoelectricity (discarding the point group 432). As shown in the previous study, the domain switching was found in Sample D, indicating that it is indeed a ferroelectric state above room temperature.11 In contrast, the average of $d_y$ and $d_z$ for Sample A (Fig. S2) is very close to zero, indicating the ferroelectric Curie temperature is below room temperature. Comparing Sample A with Sample D, we find that the off-center displacement of Ti ions is increased with the increasing content of $V_O$. It can also be seen that the average of $d_y$ and $d_z$ for the STO substrate is around zero, confirming its room temperature paraelectricity.

FIG. 1. Stoichiometry and oxygen concentration of Sample D: (a) RBS spectrum and (b) oxygen resonance peak with the simulated curve (red line).

FIG. 2. Top panel: higher magnification HAADF-STEM image of EBTO$_{3,5}$ on STO for Sample D. Bottom panel: line profiles of out-of-plane and in-plane displacement of B-site cation (Ti) in the EBTO$_{3,5}$ thin film. The inset shows atomic model to illustrate the displacement of B-site cation (Ti) from the center position.
The temperature dependent real part of dielectric permittivity ($\varepsilon'$) and dielectric loss ($\tan \theta$) for Samples B and D is shown in Fig. 3. Figure S3 shows the results measured from Samples A and C. The temperature profiles of dielectric permittivity, displayed in Figs. 3(a) and 3(c), indicate the presence of frequency-dependent dielectric relaxation peaks for Samples B and D, respectively. The peaks move to higher temperature and their intensity decreases with the increasing frequency. The peaks observed in the $\tan \theta$ curves [Figs. 3(b) and 3(d)] also shift towards higher temperature with increasing frequency. To probe the physical mechanism, the relaxation parameters were calculated by fitting the loss-peak using the Arrhenius law

$$f = f_0 \exp \left( -\frac{E_a}{k_B T_p} \right),$$

(1)

where $f_0$ is the pre-exponential factor, $E_a$ is the activation energy required for the relaxation process, $k_B$ is the Boltzmann constant, and $T_p$ is the temperature where the maximum loss tangent occurs. The Arrhenius plots are presented as insets in Figs. 3(b) and 3(d). The values of $E_a$ and $f_0$ (Table SI) obtained after the fitting were (0.32 ± 0.02) eV and (1.89 ± 0.1) × 10^{10} Hz for Sample A, (0.35 ± 0.02) eV and (2.13 ± 0.1) × 10^{10} Hz for Sample B, (0.40 ± 0.02) eV and (1.96 ± 0.1) × 10^{11} Hz for Sample C, and (0.44 ± 0.02) eV and (2.18 ± 0.1) × 10^{11} Hz for Sample D, respectively. Clearly, $E_a$ is increased with the increasing content of $V_O$ (i.e., from Samples A to D).

To further confirm the dielectric relaxation of the EBTO$_{3.\delta}$ films, the electrical modulus ($M^*$) was introduced. $M^*$ is defined as

$$M^* = M' + jM'' = \frac{\varepsilon'}{|\varepsilon'|^2} + j\frac{\varepsilon''}{|\varepsilon'|^2}.$$

(2)

The modulus is the reciprocal of complex dielectric permittivity. Thus, the more conductivity loss contributes to the dielectric permittivity, and the less conductivity loss affects the modulus. Moreover, the modulus also aids in suppressing the electrode polarization effect. The imaginary ($M''$) part of electrical modulus ($M^*$) given by $M'' = \varepsilon''/[(\varepsilon')^2 + (\varepsilon'')^2]$ was plotted as a function of temperature, and the results of the fitting were made using the Arrhenius law [Eq. (1)]. The results are presented in Fig. S4 for Samples B and D. As expected, similar to the dielectric permittivity, well-defined frequency-dependent relaxation peaks were found. The relaxation parameters of $E_a$ and $f_0$ (Table SI) were calculated to be (0.34 ± 0.02) eV and (8.33 ± 0.1) × 10^{10} Hz for Sample B, (0.42 ± 0.02) eV and (1.54 ± 0.1) × 10^{11} Hz for Sample D. The $E_a$ obtained from $M''(T)$ is the same as the calculated values from $\tan \theta(T)$, re-affirming the existence of the dielectric relaxation in EBTO$_{3.\delta}$ films.

It is noteworthy that the value of $E_a$ gradually increases with the increasing content of $V_O$. This means that the dielectric relaxation observed in EBTO$_{3.\delta}$ films is closely related to $V_O$. Now, we turn to explore the origin of dielectric relaxation in EBTO$_{3.\delta}$ films. Because a sandwich capacitor structure of Pt/EBTO$_{3.\delta}$/Nb-STO was used for dielectric measurements, the dielectric relaxation should be derived from either the EBTO$_{3.\delta}$ films or interfaces between the electrodes and the EBTO$_{3.\delta}$ films. It was reported that $V_O$ gradients at the film/electrode interface affect the fatigue and dielectric loss in ferroelectric oxides. In order to distinguish whether the film/electrode interfaces or thin films dominate the relaxation process, the impedance spectra of EBTO$_{3.\delta}$ films were studied. By definition, $Z^\prime$ is defined as

$$Z^\prime = Z' - jZ'' = \frac{1}{j\omega C_0 \varepsilon^*},$$

(3)

FIG. 3. Temperature dependent dielectric permittivity spectra for Samples B (a) and D (c), dielectric loss ($\tan \theta$) spectra for Samples B (b) and D (d) measured at various frequencies. The insets show the Arrhenius plots of the relaxation. The straight line is the linear fitting result based on the Arrhenius law.
Dipolar defects and concomitant local random fields may be a preponderant factor in determining the development of a glassy state or a ferroelectric state, as well as the order of a phase transition in metal oxides. Typical examples of materials in which ferroelectricity can be promoted due to dipolar defects include the $\text{K}_1\text{Li}_x\text{TaO}_3$, $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$, and $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ systems with the high doping content. It was also reported that dipolar defects induced by $\text{V}_\text{O}$ can result in ferroelectricity in either $\text{CaTiO}_3$ or $\text{BaZrO}_3$. In previous work, we demonstrated via first principle calculations that $\text{V}_\text{O}$ are located nearer to the Ti ions, thereby forming a dipolar defect that generates a local polar distortion.

The strong correlation between the dielectric permittivity and the second harmonic generation signal clearly suggests that the development of a ferroelectric non-centrosymmetric structure is associated with the dielectric relaxation. The idea that the development of a ferroelectric state with a concomitant dielectric relaxation is possible in materials with dipolar defects is well established. It was demonstrated both with an experimental and a phenomenological approach that the ferroelectric Curie temperature is enhanced with the increasing dipolar defect concentration. This is in good agreement with our experimental observations. Therefore, the development of a dielectric relaxation near the ferroelectric Curie temperature observed in $\text{EBTO}_3.5$ films is a direct consequence of polar clusters originating from the dipolar defects. The percolation of the polar cluster results in the long range ferroelectric order below the Curie temperature.

In summary, epitaxial $\text{EBTO}_3.5$ films with different contents of $\text{V}_\text{O}$ were studied as a model system to investigate the relationship between the content of $\text{V}_\text{O}$, microstructure, and dielectric relaxation behavior in $\text{ABO}_3$ perovskite oxide films. It was determined that the off-center displacement of Ti ions in $\text{EBTO}_3.5$ films is enhanced by the introduction of $\text{V}_\text{O}$. When an electric field is applied, dipolar defects created by $\text{V}_\text{O}$ are coupled with the off-centered Ti ions, resulting in the dielectric relaxation behavior. Also, the activation energy was determined to increase with an increasing content of $\text{V}_\text{O}$.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Frequency dependent real part impedance $Z'$ spectra for Samples B (a) and D (c) measured at various temperatures. The dc conductivity is defined from the plateau of real part impedance $Z'$, as indicated by the triangle. Arrhenius plots of the dc conductivities for Samples B (b) and D (d).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{(a) Schematic diagram of dipolar defects interacting with the off-center Ti ions. (b) The activation energy obtained by fitting dielectric loss-peak as a function of the content of $\text{V}_\text{O}$ ($\delta$).}
\end{figure}
See supplementary material for the complete crystal structure, dielectric permittivity, modulus, impedance, and leakage behavior of EBTO$_{3.4}$ films.

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