Defect-dipole defined nanoscale ferroelectric polar-orders induced in Barium Zirconate

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Keywords

Ferroelectric materials; Thin films; Vacancies; Scanning probe microscopy (SPM)

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4 In this emerging era of nanoscale ferroelectricity, the advances in precise control over
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6 fabrication process and characterization techniques have helped in realizing atomic-scale
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8 manipulation of polarization [1-3]. The miniaturization is leading towards improved device
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10 design and exploration of new physical phenomena. Though perovskites have proven to be one
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12 of the mostly studied areas of ferroelectricity, the origin of ferroelectricity in chemically different
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14 perovskites is yet to be understood in its entirety [4]. With the scaling down of technology to
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16 nanometre range and with recent breakthroughs in synthesis of complex oxides where
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18 ferroelectrics can be combined with various other functional oxides with atomic-level precision
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20 creating multifunctional materials and devices [5,6], study of ferroelectric domains in nanoscale -
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22 its origin and its outcome have attained considerable amount of attention. Studies have revealed
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24 that ferroelectricity need not to be essentially displacive in nature to exhibit its noble
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26 characteristic, those may be caused by other factors like charge ordering [7], oxygen vacancies
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28 [8], and so on.
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36 BaZrO₃ (BZO) has a cubic crystal structure (*Pm3m*) which retains its centrosymmetry
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38 over a wide range of temperature [9]. This stable perovskite, stable till it melts at 2920°C [10],
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40 find its role in various applications due to its distinguished dielectric behaviour, and mechanical
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42 and chemical stabilities [11-13]. As it adheres to paraelectric behaviour over a wide range of
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44 temperature, it never received much attention as a functional material. Recent investigations
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46 revealing ferroelectric distortions in BZO introduced by in-plane epitaxial strain [14], with the
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48 strain tunability further supported by the ref [15], have reinitiated the interest of analysing the
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50 potential of realizing this lead-free environment-friendly perovskite as a ferroelectric material.
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52 Moreover, recent work [16] indicating BZO to be a quantum paraelectric where the quantum
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54 fluctuations has been reported to shift the extrapolated Curie temperature of this incipient
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ferroelectric to a negative value, has made the investigation even more intriguing. In this study we provide, for the first time to our knowledge, experimental demonstration of oxygen vacancy driven nanoscale ferroelectric polarization switching in BZO thin films observed at ambient temperature. Different techniques of Scanning Probe Microscopy (SPM) have been employed for the purpose. Though there are studies substantiating the assistance of oxygen vacancies in switching behaviour of ferroelectric thin films, using it as a driving force for realizing polar orders in a structurally non-polar material like BZO has been explored for the first time. BZO films grown in oxygen deficient environment led to the inclusions of oxygen vacant sites which subsequently resulted in defect-dipole induced nanoscale ferroelectricity, reported in this work. Nanoscale ferroelectric behaviour along with polarization switching achieved by the application of opposite bias fields, was verified by responses acquired by piezoelectric force microscopy (PFM) with the oxygen vacancy distribution corroborated by electrostatic force microscopy (EFM).

The BZO thin films were epitaxially grown on $\text{SrRuO}_3(\text{SRO})/\text{Nb:SrTiO}_3(\text{STO})$ single crystal substrates by pulsed laser deposition (PLD). The multilayer thin film systems (as shown in Fig. 1(a)) were fabricated following the procedures established in references [17, 18]. A KrF excimer pulsed laser deposition system with a wavelength of 248 nm was employed, where a laser energy density of about 1.5 J/cm^2 and a repetition rate of 4 Hz was maintained under a temperature of 800°C to develop an optimal growing condition for the BZO films. The oxygen partial pressure was maintained at 10 mT to introduce considerable amount of oxygen vacancies into the BZO system. The thickness of the BZO films was measured to be $\sim 100 \text{ nm}$. The SRO bottom electrodes (of $\sim 100 \text{ nm}$ thick), implanted between BZO and STO, were deposited using

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4 an average laser energy density of $\sim 5 \text{ J/cm}^2$ per pulse, similar to that of ref [19]. Single-phase
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6 pure targets and 0.5 mm thick c-oriented STO substrates were used for the deposition.
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10 The crystallinity and epitaxial behaviour of the thin film system as characterized by X-
11 ray diffraction, indicates that the films possess good epitaxial quality with c-axis orientation. As
12 shown in Fig.1(b), the θ - 2θ spectrum, reveals prominent (00 l) peak of the BZO films epitaxially
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14 grown on c-oriented SRO/STO. As exhibited by the atomic force microscopy (AFM)
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16 topographical image (see Fig. 1d), the film surface bears a smooth morphology with root mean
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18 square roughness (R_q) of about 8.74 nm. The grains appear to possess triangular shape with a
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20 grain size of $\sim 200 \text{ nm}$.
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27 The nanoscopic polar behaviour and the ferroelectric polarization switching of the as
28 deposited BZO thin films were characterized by employing scanning probe approach. The
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30 capacitive layer of BZO formed between the bottom electrode of SRO and the conducting
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32 scanning probe on the top has been measured by piezoelectric force microscopy (PFM). The
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34 ferroelectric polarizations, ($P_{\uparrow}$) parallel and ($P_{\downarrow}$) antiparallel to the growth direction, are imaged
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36 by the PFM responses when the tip is scanned over the surface of the material. In this case, the
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38 SRO layer was grounded to the metal sample-mount using conducting tape and the BZO film
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40 was subjected to an *ac* driving voltage of 10 V applied through the conducting tip at ambient
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42 temperature. Fig 2(a) presents the surface morphology of the area used for the PFM
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44 measurements. As observed in Fig 2(b-e), substantial directionality of the polar vectors is
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46 detected when the out-of-plane (VPFM) and in-plane (LPFM) piezoresponse signals are
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48 compared; with the dark and bright phase contrasts conforming to the parallel and anti-parallel
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50 polarization states. To exemplify the polarization reversibility, opposite bias voltages $\pm 8 \text{ V}$ were
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52 used to pole the sample. Though a small amount of drift was noticed in the local morphology
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caused by the contact force, to guarantee a point-to-point correspondence of the polar scans, same location and frequency was maintained while acquiring all the PFM signals. Moreover, to ensure that the contrast in the PFM images are not contributed from any topographic feature, the original VPFM signals were subtracted from that obtained after poling the material. As can be seen in Fig 2(f)), well-defined switching contrasts are observed when oppositely poled (with the marked areas indicating the regions exhibiting switching). Therefore, it confirms that the polarization of the BZO grains is reversible under applied electric field - therefore signifying the existence of incipient ferroelectric polar domains. The ferroelectricity was further substantiated by measuring the localized piezoelectric hysteretic behaviour. It is worth noticing that, a distinct butterfly like amplitude-bias voltage response with corresponding phase-bias voltage hysteresis (as shown in Fig. 2(g-h)) have been successfully acquired while recording the response of domain dynamics with DC offset-bias ramping through -8 V to +8 V. Therefore, it corroborates the existence of ferroelectric polarization states which can be switched by applying suitable electric field.

To further study the scientific origin of this polarization reversibility, EFM has been performed with different scanning tip biases, -2.3 V to 2 V. The EFM responses of the film were captured, where the spatial distribution of trapped charges was imaged by the varying coulomb force on the conducting tip. As demonstrated in Fig. 3, the negative and positive trapped charges corresponded by increasing attractive and repulsive forces, corroborates inhomogeneous distribution of static charge over the film surface. While for positive tip bias the surface charges appear to get compensated at 1.8 V, for negative tip bias it persists till -2.15 V. Moreover, the topographical and EFM signal plots of the selected area confirms that the EFM responses do not possess any correspondence with the topological features, therefore eliminating the contribution

of cross-talk between the two in the detected EFM signals. Though surface-charge injected from SPM tip known to have influence on the surface potential measurements, here no EFM signal reversal is observed with time and the polar regions did not show any gradual growth in size - rather they get diminished with higher tip-voltage. Therefore, any parasitic contribution from tip injection can be ruled out attributing the EFM signals thus detected solely to the spatial potential dispersion, based on the study reported in ref [20].

Referring to the reversible phase signals acquired in the PFM responses, it can be inferred that the grains in the BZO layer have undergone some nanoscale polar switching under the influence of applied field. For centrosymmetric cubic structures like BZO, it is unlikely for these polar moments to be purely displacive in nature, rather indicate them to be originated from some other controlling factor. Moreover, the inhomogeneous charge distribution as exhibited in EFM responses, provide credible evidence for the role of local point defects in the polar orders observed. Barium Oxide and Zirconium oxide being chemically quite stable, the intriguing question that arises is what could be the driving factor for this nano-scale polar behaviour found in a system made up of two materials that are essentially non-polar in their bulk form. Though there could be various chemical, structural and electronic factors facilitating the polarity, pertaining to the experimental data acquired it is more logical to attribute the polar anisotropy thus developed to the oxygen vacancy accumulation, V_o (as shown in Fig.1(c)). Oxygen vacancies reported to assist in the switching behaviour of ferroelectric thin films [21,22] and complex oxides,[8] have been studied to possess highly anisotropic elastic dipole tensor which results in local strain effects that combine to form defect dipoles. These nanoscale polar orders almost vanish upon averaging over all possible defect orientations in a longer range. Thus it can be deduced that the nanoscale polar displacements have been induced by partial oxygen vacancy

ordering, predominantly found in oxygen deficit stoichiometry BaZrO_{3-x} . These nanoscale polar-orders however get shadowed by the intrinsic conductivity of the material, inhibiting the formation of long range domain structures.

Hence by controlling the oxygen partial pressure, vacant oxygen sites V_o have been incorporated in the deposited BZO films, which by altering the localized electrical conductivity have introduced defect dipole moments. These vacancy-induced defect dipoles resulted in the development of the observed nanoscale ferroelectric polarization states.

Therefore, we have experimentally demonstrated defect-dipole induced nanoscale ferroelectricity in a lead-free centrosymmetric perovskite, BZO. Polar behaviour triggered by ordered arrangement of the oxygen vacancies V_o , can open up a new approach of ferroelectric device design. Engineered-control over the oxygen vacancy concentration, preferentially leading to polar asymmetries, can be employed for polar state switching by introducing /annealing-out of V_o s as per the need of the application. Recent developments in achieving accurate control over oxygen vacancy ordering by regulating different fabrication process parameters like oxygen partial pressure, temperature, in-plane strain [23-26] strengthens the viability of this new approach.

In conclusion we have experimentally demonstrated oxygen vacancy driven polar behaviour in epitaxially grown Barium Zirconate thin films using different techniques of scanning probe microscopy. The simultaneous PFM and EFM measurements have suggested that the ferroelectric polar-states observed in centrosymmetric BZO are non-displacive in nature and they are induced by defect dipoles created by oxygen vacancies. Possibility of tuning the concentration and ordering of oxygen vacancies in a centrosymmetric oxide certainly add another degree-of-freedom in controlling the properties of a lead-free incipient ferroelectric

material. Therefore, by tuning the intrinsic defect formation by film deposition process-parameters, the paraelectric-ferroelectric transition has been achieved at ambient temperature; leading to the emergence of an eco-friendly potential ferroelectric material BZO.

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Figure 1

Figure 2

Figure 3

Fig.1. Thin film system and its crystal orientation: (a) Epitaxial thin film system studied. (b) XRD θ -2 θ diffractograms confirming the growth direction of BZO to be along (00 l), grown on c-oriented SRO/STO substrate. (c) Simulated crystal structure of BZO with V_0 denoting the oxygen vacancy sites, introduced during the film deposition, leading to induced polarization ($\vec{P}$). (d) 2d and 3d view of tapping mode surface topology (900X900 nm², 256X256 pixels) of the BZO film showing triangular shaped grains, with the roughness analysis depicting smooth surface morphology (root mean square roughness R_q = 8.74 nm and average roughness R_a = 6.81 nm).

Fig.2. Observation and analysis of ferroelectric polar states: (a) Topographic image of the surface area (1X1 μm^2 , 256X256 pixels) scanned for PFM measurements. Ambient-temperature amplitude (b & d) and phase (c & e) out-of-plane (VPFM) and in-plane (LPFM) piezoresponse signals. (f) Resultant VPFM phase contrasts (where the original PFM signals have been subtracted from that obtained after poling the thin film layer with opposite bias voltages ± 8 V) indicating polarization reversibility (switched regions are marked). (g) Butterfly shaped amplitude-bias and (h) hysteretic phase-bias PFM loops.

Fig.3. Height and EFM amplitude images (1.5X1.5 μm^2 , 256X256 pixels) with tip bias voltage varying from -2.3 V to +2 V indicating inhomogeneous distribution of trapped charges on BZO surface: Topographical and EFM signal plots of the selected area confirming that the EFM responses do not possess any correspondence with the morphological features, attribute them primarily to the measure of spatial potential dispersion.