

Defect-Induced Hedgehog Polarization States in MultiferroicsLinze Li,^{1,2} Xiaoxing Cheng,³ Jacob R. Jokisaari,² Peng Gao,² Jason Britson,³ Carolina Adamo,⁴ Colin Heikes,⁴ Darrell G. Schlom,^{4,5} Long-Qing Chen,³ and Xiaoqing Pan^{1,6,*}¹*Department of Chemical Engineering and Materials Science, University of California–Irvine, Irvine, California 92697, USA*²*Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109, USA*³*Department of Materials Science and Engineering, Penn State University, University Park, Pennsylvania 16802, USA*⁴*Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853, USA*⁵*Kavli Institute at Cornell for Nanoscale Science, Ithaca, New York 14853, USA*⁶*Department of Physics and Astronomy, University of California–Irvine, Irvine, California 92697, USA*

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Continuous developments in nanotechnology require new approaches to materials synthesis that can produce novel functional structures. Here, we show that nanoscale defects, such as nonstoichiometric nanoregions (NSNRs), can act as nano-building blocks for creating complex electrical polarization structures in the prototypical multiferroic BiFeO₃. An array of charged NSNRs are produced in BiFeO₃ thin films by tuning the substrate temperature during film growth. Atomic-scale scanning transmission electron microscopy imaging reveals exotic polarization rotation patterns around these NSNRs. These polarization patterns resemble hedgehog or vortex topologies and can cause local changes in lattice symmetries leading to mixed-phase structures resembling the morphotropic phase boundary with high piezoelectricity. Phase-field simulations indicate that the observed polarization configurations are mainly induced by charged states at the NSNRs. Engineering defects thus may provide a new route for developing ferroelectric- or multiferroic-based nanodevices.

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Quasi-1D ferroic states arising from the interplay of spin, charge, orbital, and/or lattice degrees of freedom in strongly correlated oxides usually exhibit complex polarization or spin textures and unique properties that hold great promise for the development of new device paradigms [1]. Examples include vortices, hedgehogs, and Skyrmions that have been discovered and extensively studied in magnetic materials [2–4]. These magnetic states can be efficiently manipulated by magnetic fields [5,6] or driven by a spin-transfer torque at ultralow current densities [7] and thus can be potentially applied for high-density magnetic memories or current-driven devices. At the same time, considerable interest has also been given to exploring new polarization states in ferroelectrics, because the use of ferroelectric states that are much smaller than their counterparts in magnets as functional elements in nanodevices is particularly attractive. For example, advances in the synthesis of ferroelectric thin-film heterostructures have enabled the creation of periodic patterns of polarization vortices through tuning the boundary conditions at film interfaces [8–10]. It is also theoretically predicted that Skyrmion-like polarization patterns can be stabilized in ferroelectric nanocomposites through the application of external electric fields [11]. Yet, another type of quasi-1D ferroelectric state known as the polarization hedgehog, in which all the polarization vectors diverge from the center of the structure, remains relatively unexplored. This is partially because such a hedgehog state is generally

considered unstable, unless the inevitable accumulation of a large amount of polarization bound charge at the center of the structure can be compensated by some strong driving force. An intriguing theoretical work has predicted that the hedgehog states can be stabilized in BaTiO₃ nanowires under specific boundary conditions, where surface effects play a critical role [12]. But these hedgehog states have not yet been experimentally confirmed.

On the other hand, the recent observation of a strong interaction between ferroelectric polarization and built-in fields induced by charged impurity defects embedded in the ferroelectric matrix suggests that these defects may be used as nano-building blocks that can provide a strong electrostatic-driven force for stabilization of complex domain structures [13,14]. For example, it has been shown that nanoscale planar charged defects in BiFeO₃ thin films can induce novel head-to-head mixed-phase polarization structures [13]. Nevertheless, these observed impurity defects were accidentally introduced in those films, and the possibility to precisely control the formation of the defects and thus to generate the desired domain structures has not been studied. Here, we show that, by controlling the substrate temperature during the growth of a BiFeO₃ thin film, an array of nonstoichiometric nanoregions (NSNRs) can be deliberately introduced as charged defects into the host material matrix, which leads to the stabilization of novel hedgehog or antihedgehog nanodomains. These

nanodomains present exotic patterns of polarization rotation that form mixed-phase structures and can be coupled with polarization vortices. Their novel properties could be useful for nanoelectronic and electromechanical applications.

BiFeO_3 is a room-temperature multiferroic with a rhombohedral lattice structure, exhibiting coupled ferroelectric ($T_C \sim 1103$ K) and antiferromagnetic ($T_N \sim 650$ K) order [15]. In pseudocubic unit cells [Fig. 1(a)], the oxygen octahedra and the central Fe cation are displaced from their respective positions at the face and body centers, giving rise to a large spontaneous polarization ($\sim 100 \mu\text{C cm}^{-2}$) along the $\langle 111 \rangle_{\text{PC}}$ directions [15–19], where the PC subscript represents pseudocubic indices. Using aberration-corrected high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) imaging, the atomic-scale structure within a BiFeO_3 thin film can be directly visualized, and the polarization vector within each pseudocubic unit cell can be measured. For example, in the HAADF image shown in Fig. 1(b), where the Bi columns appear as the brighter dots, the Fe columns show weaker contrast, and the oxygen atoms are not visible, a vector, \mathbf{D}_{FB} , can be defined as the atomic displacement in the image plane of the Fe cation from the center of the unit cell formed by its four Bi neighbors. This \mathbf{D}_{FB} vector is exactly opposite to the projection of the polarization vector in the image plane and can be directly measured by fitting the atomic columns as two-dimensional (2D) Gaussian peaks to locate their centers and recording the offset [8,20].

The growth of BiFeO_3 films is very sensitive to deposition parameters, and by most deposition techniques phase-pure BiFeO_3 can be obtained only within a narrow combination of growth parameters [21]. An alternate

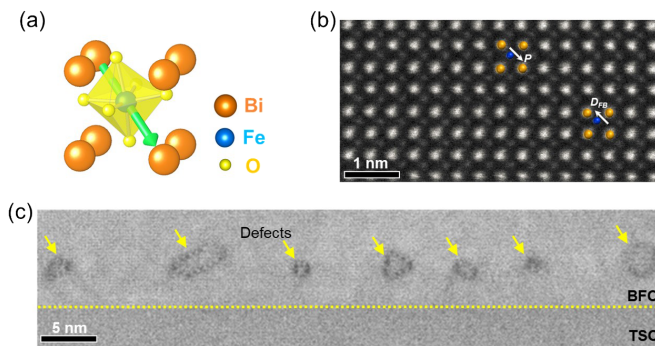


FIG. 1. Atomic structure and defects in a BiFeO_3 thin film. (a) Atomic model of the pseudocubic structure of BiFeO_3 . Polarization is shown by a green arrow. (b) HAADF STEM image of a BiFeO_3 thin film viewed in cross section along the $[100]_{\text{PC}}$ zone axis. The \mathbf{D}_{FB} vector, defined as the atomic displacement in the image plane of the Fe cation from the center of the unit cell formed by its four Bi neighbors, is opposite to the polarization vector (\mathbf{P}). (c) HAADF STEM image of the BiFeO_3 (BFO)/ TbScO_3 (TSO) interfacial region, where the interface is indicated by the yellow dashed line and an array of defects are observed at a uniform height of 3 nm above the interface.

method enabling the growth of phase-pure BiFeO_3 for a broader range of growth parameters, referred to as the “growth window,” is what we use when synthesizing BiFeO_3 by molecular-beam epitaxy (MBE). In this process, BiFeO_3 is formed by flooding the growing film with excess bismuth and oxidant and relying on thermodynamics to desorb the excess of both of these constituents, resulting in a phase-pure BiFeO_3 film for conditions within the growth window. Our prior MBE work mapping out the adsorption-controlled growth conditions for BiFeO_3 indicates that a change of the substrate temperature during film growth, given a constant bismuth and oxygen overpressure at a fixed Bi:Fe flux ratio, can result in three different products: (I) $\text{BiFeO}_3 + \gamma\text{-Fe}_2\text{O}_3$ (at a higher than optimal temperature), (II) BiFeO_3 (within the growth window, i.e., at an optimal temperature), and (III) $\text{BiFeO}_3 + \text{Bi}_2\text{O}_{2.5}$ (at a lower than optimal temperature) [22]. The formation of the Fe-rich or Bi-rich defects can be directly monitored during film growth by *in situ* RHEED, since these defects can generate additional spots in the RHEED pattern [22].

In this work, we grew epitaxial $(001)_{\text{PC}}$ -oriented BiFeO_3 thin films on $(110)_O$ TbScO_3 single crystal substrates (where the O subscript represents orthorhombic indices) by MBE, monitoring the growth by RHEED. The films were grown at constant bismuth (Bi flux = 1.4×10^{14} Bi/cm² s) and oxygen ($\text{O}_2 + \sim 10\% \text{ O}_3$ background pressure = 1×10^{-6} Torr) with pressure over a fixed Bi:Fe flux ratio of 8:1. Film growth was initiated at a substrate temperature of $\sim 680^\circ\text{C}$ (higher than the optimal temperature) until additional spots in the RHEED pattern, indexed to diffraction from (111) -oriented $\gamma\text{-Fe}_2\text{O}_3$, were observed (Supplemental Fig. S1 [23]) [22]. Upon seeing these spots, the substrate temperature was decreased to 610°C and the RHEED pattern, which is very surface sensitive, went back to that of phase-pure BiFeO_3 . As a result, an array of Fe-rich defects were inserted into the BiFeO_3 matrix at a uniform height along the film thickness, several unit cells above the bottom interface of the film, evident in the HAADF STEM image shown in Fig. 1(c). In this way, control of the temperature lends control of the placement of defects in the film.

The atomic-scale structure of the defects is examined in Fig. 2(a), where a magnified HAADF image of an interfacial region containing one typical semicircular loop defect in the BiFeO_3 matrix is shown. As there are no other elements introduced during film growth, the defect should also be composed of Bi, Fe, and O atoms, with the brighter dots in the HAADF image corresponding to the heavier Bi columns and the weaker dots corresponding to the lighter Fe columns. This defect is generally composed of two parts. The first part is a short vertical segment on the right (highlighted in brown) with a distorted pseudocubic perovskite lattice, where an apparent lattice expansion is observed along the horizontal direction. The second part is a long curved or inclined segment on the left (highlighted

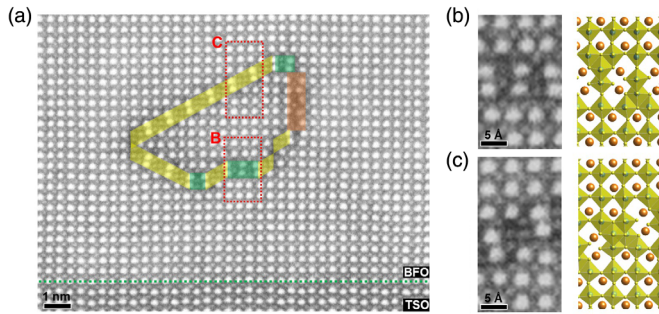


FIG. 2. Atomic structure associated with a semicircular loop defect in the BiFeO_3 thin film. (a) HAADF STEM image of the BiFeO_3 (BFO)/ TbScO_3 (TSO) interfacial region containing one typical semicircular loop defect. The defect is composed of a vertical segment (highlighted in brown) with distorted pseudocubic perovskite lattices and nonstoichiometric planar (highlighted in green) and stepped (highlighted in yellow) structural units. (b) Magnified image of the nonstoichiometric planar unit in the defect [red rectangular highlighted region “B” in (a)] and a model of its corresponding atomic structure on the right. (c) Magnified image of the nonstoichiometric stepped unit in the defect [red rectangular highlighted region “C” in (a)] and a model of its corresponding atomic structure on the right.

in yellow and green) with a structure and stoichiometry different from the BiFeO_3 matrix, forming NSNRs. Furthermore, these NSNRs in the defect are composed from two structural units—planar units (highlighted in green) and stepped units (highlighted in yellow). While the planar unit is oriented on the horizontal $(001)_{\text{PC}}$ plane of BiFeO_3 and adopts the structure of one pair of Bi atoms alternating with one pair of Fe atoms, the stepped unit has an inclined orientation and is formed from one pair of Bi atoms alternating with two pairs of Fe atoms.

The same types of planar and stepped NSNRs have also been observed in previous studies of Nd- and Ti-doped antiferroelectric BiFeO_3 by MacLaren *et al.* [24,25]. Their

detailed structural study suggests that the Fe atoms within the NSNRs are coordinated by six oxygens in the form of edge-sharing oxygen octahedra, resembling the structure of $\gamma\text{-Fe}_2\text{O}_3$ and forming the planar and stepped structural units shown schematically in Figs. 2(b) and 2(c), respectively. As a result, there is an excess of anions (more oxygen) at the NSNRs, which produces a net local negative charge density. Assuming Bi^{3+} , Fe^{3+} , and O^{2-} at the defects, the charge density is calculated to be -1.4 C/m^2 at the planar unit and -1.1 C/m^2 at the stepped unit. Another feature associated with the NSNRs is an atomic shift of one-half of a pseudocubic unit cell of the BiFeO_3 lattice across the planar units in the $[001]_{\text{PC}}$ direction and a shift of one-half of a pseudocubic unit cell of the BiFeO_3 lattice across the stepped units in both the $[010]_{\text{PC}}$ and $[001]_{\text{PC}}$ directions, as evident in the Fourier-filtered images shown in Supplemental Fig. S3 [23]. These shifts, however, do not induce obvious strain in the BiFeO_3 matrix, as shown by the quantitative analysis of the high-resolution HAADF images using geometric phase analysis (GPA) in Supplemental Fig. S4 [23]. The shift in the lattice occurs mainly through atomic rearrangement at the boundary of the NSNRs and the shifted BiFeO_3 lattices are separated, accommodating the strain and forming an isolated region enclosed by the loop defect.

The polarization distribution in the BiFeO_3 lattice adjacent to the defect was determined by mapping the $-\mathbf{D}_{\text{FB}}$ vectors [Fig. 3(a)]. Within the region enclosed by the semicircular defect (marked as region “1”), a hedgehog polarization state can be identified. While the polarization vectors of each unit cell in the middle of this region are attenuated and oriented along multiple directions, the unit cells that are in contact with the defect forming the periphery of the NSNRs (the unit cells highlighted by red rectangles) show significant lattice distortions with enhanced polarization pointing outward, towards the

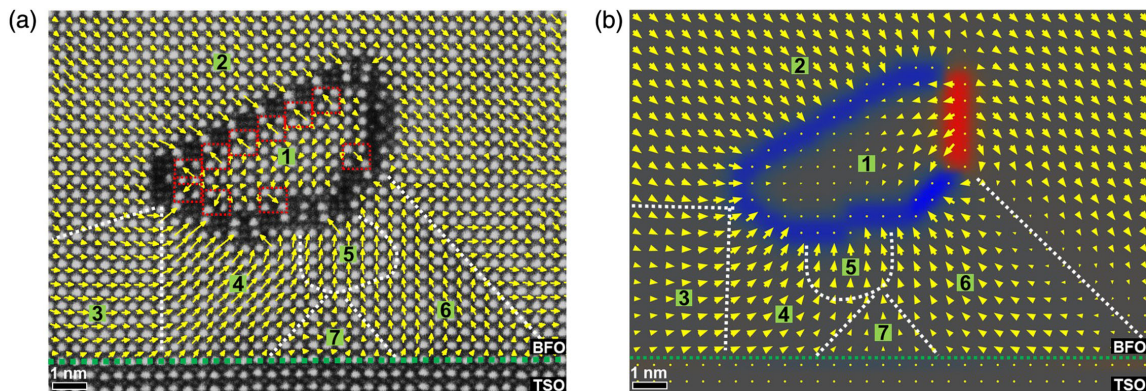


FIG. 3. Polarization map of the nanodomains surrounding the semicircular loop defect in the BiFeO_3 thin film. (a) The same HAADF STEM image as Fig. 2(a) overlaid with the polarization vectors ($-\mathbf{D}_{\text{FB}}$, shown by yellow arrows). The white dashed lines represent the positions of domain walls. (b) Phase field simulation of the polarization distribution in the image plane of the domain structure stabilized by a charged defect with a configuration similar to the experimental observation. The polarization vectors are overlaid on a color map of the charge distribution, where the red, blue, and gray colors represent positive ($+1.1 \text{ C/m}^2$), negative (-1.1 C/m^2), and zero charge densities, respectively.

NSNRs. In contrast, the BiFeO₃ lattice outside of the defect presents a continuous rotation of polarization, with polarization vectors generally pointing inward towards the defect, except for the right-side region where the polarization vectors are pointing outward. This arrangement leads to the formation of six different nanodomains [marked “2”–“7” in Fig. 3(a)] surrounding the defect. Some of these domains also experience a change in lattice symmetry, forming mixed-phase structures. Particularly, the “2,” “4,” and “6” domains possess normal *rhomboidal-like* (*R-like*) structures with polarizations oriented along the diagonal directions. In contrast, the “3” and “5” domains adopt polarizations along [010]_{PC} and [001]_{PC} directions, respectively, resembling horizontal or vertical *tetragonal-like* (*T-like*) structures [26]. Within region 7, significantly attenuated polarizations were observed.

Since the polarization directions are generally pointing toward the NSNRs in the defect and these NSNRs are negatively charged, a plausible mechanism is that the polarization distortions of the BiFeO₃ lattices are modified by the built-in fields induced by the charge on the NSNRs. To gain further insight of the driving force for the formation of the nanodomains, we employ phase field simulations to calculate the stable polarization configuration in the presence of a charged defect. In the simulated BiFeO₃ thin film, we created a defect with a similar shape to what we observed in the experiment in Fig. 2 and then applied an additional charge at the defect, with no additional eigenstrain introduced by the defect from the lattice mismatch between the defect and the matrix, as the defect-induced strain has a minimal effect on the polarization (see Supplemental Material [23] for a discussion). Since the left curved or inclined part of the defect is mostly composed of the stepped units, for simplicity a uniform charge density of -1.1 C/m^2 was applied there. Although the defect chemistry of the vertical segment on the right side of the defect cannot be directly determined by STEM imaging, its lattice expansion along the horizontal direction could indicate a local accumulation of oxygen vacancies and thus a positive charge density [27,28]. Simulations allow the effect of charge density to be studied, and a comparison of simulated results with different values of charge densities ranging from -1.1 to $+5.5 \text{ C/m}^2$ at the right-side segment of the defect is shown in Supplemental Fig. S5 [23]. The result with a charge density of $+1.1 \text{ C/m}^2$ [Fig. 3(b)] is most consistent with the experimental observation, indicating that the existence of a moderate positive charge is the most probable situation. Note that in each case a random polarization distribution was set as the initial structure, and simulations repeated with different initial random polarization distributions were found to yield consistent final configurations.

In the simulated polarization configuration around the defect [Fig. 3(b)], attenuated polarization is observed within the semicircular region enclosed by the defect

(region 1), with the exception of the very large polarization of a few unit cells at the region boundary. This could be a result of the exclusion of the experimentally observed distorted unit cells at the region boundary [red rectangular highlighted unit cells in Fig. 3(a)] from the simulation. Nevertheless, the simulated results reproduced almost all of the features in the polarization configuration outside of the defect captured in the experiment, including the polarization reorientation around the defect with the formation of six different polarized regions (regions 2–7), the change of lattice symmetries into *T-like* structures in region 3 and 5, and the attenuated polarization in region 7. These results indicate that the charge on the NSNRs should be the major driving force inducing the observed nanodomain structures, in which the gradient energy from the polarization rotation is counterbalanced by the corresponding reduction in overall electrostatic energy.

The hedgehog and antihedgehog domains are ubiquitous around the defects composed of NSNRs in the BiFeO₃ thin films, and they can also induce polarization vortices, as shown by three examples in Figs. 4(a)–4(c). Similar to the previous case shown in Fig. 2, these defects are mainly comprised of the same types of nonstoichiometric planar units and stepped units, with the same excess of oxygen and thus local net negative charge. Some additional variations were noted. For example, within the circular defect in Fig. 4(a), an inclined segment is observed on the right side. It is composed of five consecutive pairs of Fe atoms with no Bi atoms in between them. Examination of the polarization shows that the hedgehog and antihedgehog domains around the defects are also accompanied by the formation of multiple different polarized regions and mixed-phase structures. In Fig. 4(a), a tiny hedgehog polarization state with a diameter of 4 unit cells was observed within the nanoregion encircled by the defect. In both Figs. 4(a) and 4(b), antihedgehog polarization states are stabilized at the shell regions surrounding the defects. On larger length scales outside of these defects, the overall continuous polarization rotation patterns lead to flux-closure vortex structures. In Fig. 4(c), a pair of polarization semivortex and semiantivortex structures form at the left and right sides of this nearly linear defect as a result of the formation of a “head-to-head” polarization configuration above and below the defect.

In conclusion, we have demonstrated the stabilization of novel hedgehog and antihedgehog nanodomains in multiferroic BiFeO₃ thin films by making use of nanoscale charged defects. These nanodomains offer new opportunities to explore the complex interplay of spin, charge, orbital, and lattice degrees of freedom in systems with strong electron correlations. As the hedgehog states are confined within the nanosized structure defects, they can approach sizes down to several unit cells and have a much higher density than the bulk domains in the film. Our finding therefore opens the door for creating high-density

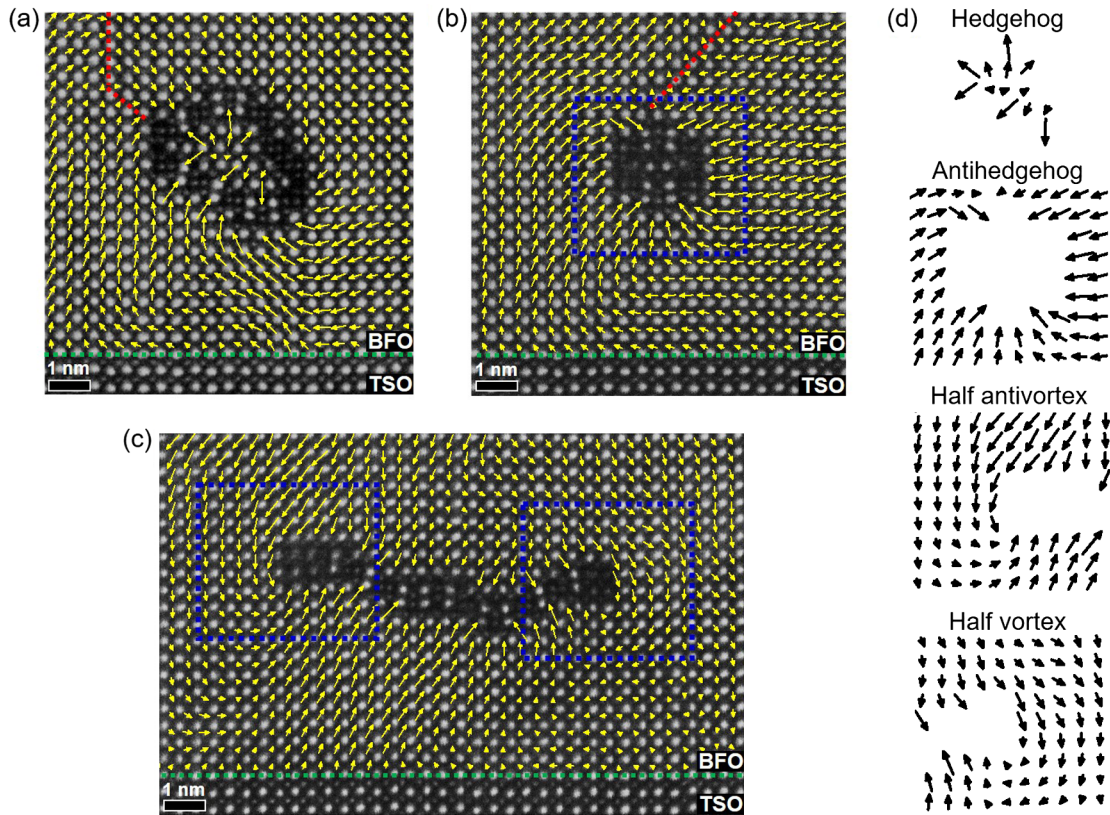


FIG. 4. Polarization maps of nanodomains induced by three different defects in the BiFeO_3 thin film. (a)–(c) HAADF STEM images of three different defects above the BiFeO_3 (BFO)/ TbScO_3 (TSO) interface, where the polarization vectors ($-\mathbf{D}_{\text{FB}}$, shown by yellow arrows) are overlaid on the BiFeO_3 lattice. The dashed red line marks the domain walls that penetrate to the top surface of the thin film. (d) Magnified map of the polarization vectors in the nanoregion enclosed by the loop defect in (a) and in the three different nanoregions highlighted by the blue rectangles in (b) and (c).

nanodomains in relatively thick ferroelectric films, which can overcome the limit on domain size or density imposed by the scaling law that states the domain width is proportional to the square root of the sample's thickness [29,30]. The polarization component perpendicular to the hedgehog plane (the image plane in our study) may be switchable. Therefore, further study of the electrical and magnetoelectric properties and dynamics under applied fields may assist future development of nanoelectronic devices such as high-density memories. On the other hand, it is well known that defect engineering through adding small amounts of donor dopant to a ceramic can create randomly oriented defect dipoles between donors and cation vacancies in the crystal structure, which promotes domain wall motion leading to enhanced piezoelectric properties [31]. Here, the antihedgehog polarization states stabilized by the nanoscale impurity defects possess mixed-phase structures that are reminiscent of the ferroelectric domains near a morphotropic phase boundary. These states may also exhibit enhanced properties such as giant piezoelectricity and thus are potentially attractive for electromechanical applications.

As it is known that nonstoichiometric phases can commonly occur in functional oxides due to different

mechanisms, such as cation doping [24,25], stoichiometric fluctuation [21], and temperature variation during film growth [22], our observation of topological states induced by NSNRs in BiFeO_3 should stimulate efforts to design functional patterns of ferroelectric or multiferroic nanodomains or nanopolymorphs with a focus on controlling the intrinsic defect structures and motivate a search for a similar mechanism in other functional oxide systems. While conventional chemical engineering methods (composition tuning) and interface engineering methods (boundary condition tuning) produce only structure changes uniformly distributed within the whole material, defect engineering can generate functional structures at local nanoregions without the disruption of the bulk structural patterns, which is desirable as the dimensions of individual elements in nanodevices continue to shrink. Further developments may allow the NSNRs to be introduced in a fine controlled fashion, enabling their configurations to be adjusted during material synthesis, or allow the charge states of the NSNRs to be modified by external charge injection methods, opening the door to the control of nanodomain structures and the customized creation of topological states in complex materials through defect engineering.

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