

# Inverse Melting of Polar Order in Chemically Substituted BaTiO<sub>3</sub>

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In many condensed matter systems, long-range order emerges at low temperatures as thermal fluctuations subside. In the presence of competing interactions or quenched disorder, however, some systems can show unusual configurations that become more disordered at low temperature, a rare phenomenon known as “inverse melting.” Here, we discover an inverse melting of the polar order in a ferroelectric oxide with quenched chemical disorder (BaTi<sub>1-x</sub>Zr<sub>x</sub>O<sub>3</sub>) through direct atomic-scale visualization using *in situ* scanning transmission electron microscopy. In contrast to the clean BaTiO<sub>3</sub> parent system in which long-range order tracks lower temperatures, we observe in the doped system BaTi<sub>1-x</sub>Zr<sub>x</sub>O<sub>3</sub> that thermally driven fluctuations at high temperature give way to a more ordered state and then to a reentrant disordered configuration at even lower temperature. Such an inverse melting of the polar order is likely linked to the random field generated by Zr dopants, which modulates the energy landscape arising from the competition between thermal fluctuations and random field pinning potential. These visualizations highlight a rich landscape of order and disorder in materials with quenched disorder, which may be key to understanding their advanced functionalities.

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The concepts of order and disorder permeate a broad spectrum of physical phenomena, spanning condensed matter [1], liquids [2], and living cells [3]. Transitions from disorder to order can be described by an “order parameter” whose value changes from zero conventionally in the disordered phase to finite in the ordered phase [4]. Temperature plays a key role in this process: disorder is generally associated with high temperatures because thermal fluctuations encourage the exploration of microstates, disrupting perfect arrangements and decreasing the order parameter. Because thermodynamic systems minimize their free energy, the energy cost of misalignment can be overcome as the system gains entropy. As temperature decreases, disordered configurations yield to increasingly aligned and low energy arrangements. A classic example is the transition from paramagnetism to ferromagnetism, where the magnetization, representing the sum of spins, serves as the order parameter [5]. In the paramagnetic phase, spins are disordered and uncorrelated, resulting in an average magnetization of zero. Upon cooling, spins

increasingly align with one another and lead to long-range correlations and finite magnetization.

The picture of thermodynamic order and disorder, however, becomes blurry when real materials incorporate quenched or frozen disorder in their structure [6,7]. These imperfections introduce random fields into the system that can pin local configurations and give rise to near degeneracies or frustration, leading to rich phenomena like memory, hysteresis, and temperature chaos [8–10]. One such disorder-induced phenomenon is inverse melting, in which order gives way to a more disordered state at low temperature [11]. Proposed a century ago [12], this unusual melting has been observed sparingly in systems such as polymers [13], metal alloys [14], magnetic thin films [15], vortex lattices in superconductors [16], and more recently in ferroelectric domains [17]. Various spin models realizing inverse melting show that the transition can be either first-order or continuous, depending on the parameters and nature of disorder [18–20]. In all these cases, the inverse melting can be divided into two categories: changes in states of matter, like crystalline to amorphous transitions, or variations of large mesoscale structures on the order of 0.1–10 μm, such as magnetic and ferroelectric domains.

An intuitive question arises: can inverse melting emerge from atomic-scale and nanoscale fluctuations of the local order instead of changes to mesoscale domains or states of matter? Spin glasses provide a realization of this scenario in magnetic systems, where the reentrant spin glass transition can be achieved at lower temperature by balancing the spin

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interaction and internal frustration [21,22]. But in their ferroelectric counterparts, this phenomenon remains unexplored. The order parameter in a ferroelectric is polarization, arising from the off-centering of ions and the breaking of inversion symmetry [23]. Typically, ferroelectricity requires the long-range alignment of polarization. However, random fields created by quenched disorder may suppress the long-range order of polarization and broaden or blur phase transitions, leading to new ferroelectric phases with polar order fluctuating at nano or atomic scale, such as relaxor and superparaelectric states [24,25]. Despite their broad appeal across fields [26,27], how random fields regulate the local structure, spatial correlations, and detailed structure of disorder in ferroelectrics remains mostly inaccessible [28–31], particularly how they evolve with temperature [32]. In this work, we studied a chemically doped ferroelectric oxide  $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  (BZTO) which exhibits a rich phase diagram with different ferroelectric states. The random field in this system arises from chemical dopants that modify the local environment. With 20% Zr doping, the BZTO exhibits novel ferroelectric states with so-called “diffuse phase transition,” where the well-known ferroelectric state of  $\text{BaTiO}_3$  (BTO) no longer appears. This state is distinct from relaxors, as it does not show frequency dependent behavior [25]. To reveal the fluctuations of microscopic order parameters, we employed aberration-corrected scanning transmission electron microscopy (STEM), which is powerful for capturing polar order at atomic scale in ferroelectric oxides [33–35]. Through direct, atomic-scale mapping of the polar order and its nanoscale fluctuations across various temperatures, we discover that polar order in this doped oxide exhibits inverse melting at low temperature.

We first illustrate how a random field promotes degenerate energy landscapes and reentrant disordered states at low temperature, using a simple two-dimensional spin-1 random field Ising model (see SM). We define the order parameter, or polarization, at site  $i$  as  $P_i \in \{0, \pm 1\}$ , where  $P_i = 0$  represents the nonpolar phase and  $P_i = \pm 1$  two distinct polar states. The Hamiltonian,  $H$ , is given by

$$\mathcal{H} = -J \sum_{\langle ij \rangle} P_i P_j - \sum_i h_i P_i,$$

where  $J > 0$  is the exchange energy,  $h_i$  is a local random field normally distributed around zero, and  $\langle .. \rangle$  is the sum over nearest neighbors. The system can lower its energy through the first term by aligning to a finite polarization. but the random field locally favors or disfavors a specific polarization state. Figure 1(a) shows the temperature evolution of the order parameter and energy in the absence of a random field; as expected, the disordered state at high temperature gives way to a uniform long-range ordered state at low temperature. Upon adding a random field, the thermodynamics of the order parameter are

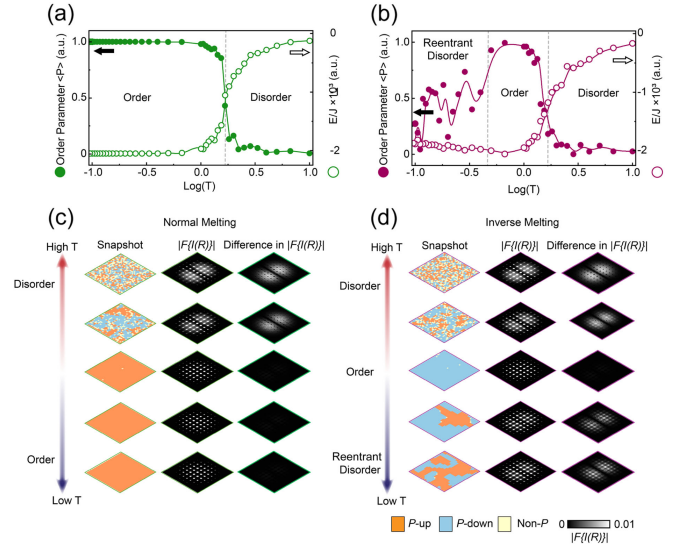


FIG. 1. Inverse melting in the presence of a random field. (a), (b) Evolution of the order parameter (solid circle) and energy (hollow circle) as a function of temperature in a two-dimensional spin-1 random field Ising model. The (a) and (b) represent the evolution in the absence and presence of random field, respectively. (c), (d) Left panels: snapshots of real-space configurations extracted at different temperatures in the absence (c) and presence (d) of a random field. The orange, blue, and yellow represents that order parameter equal to 1 (polar up),  $-1$  (polar down), and 0 (nonpolar), respectively. Middle panels: Fourier transformation of two-dimensional pattern constructed from real-space configurations [see Supplemental Material (SM) [36]]. Right panels: 2D difference plot after subtraction with Fourier transformation of ordered 2D pattern, which is used to highlight the diffuse intensity. The presence of diffuse intensity reflects the degree of disorder.

altered (Fig. S1). Within a specific range, the system first enters a more ordered state at intermediate temperatures and then, a reentrant disordered phase emerges as pinned regions and near degeneracies break and reform at different temperatures. Figure 1(b) shows this increase in the energy and a drop in the average polarization with decreasing temperature. The left panels of Figs. 1(c) and 1(d) show representative real-space snapshots of the order parameter at different temperatures without and with the random field, highlighting the emergence of inverse melting in the latter case. These two different melting behaviors can also be recognized by the change of diffuse intensity in reciprocal space. Disorder contributes diffusion around the sharp peak, as shown in the middle and right panels of Figs. 1(c) and 1(d). Such an evolution is consistent with the presence of a rough energy landscape and frustrated, highly degenerate, metastable configurations induced by the random fields.

Using atomic-resolution imaging of polar order, we explore the evolution of the local ordering across temperature without and with a random field. We first exemplify such capability through atomic-scale visualizations of pure

BTO. Pure BTO is an archetypal ferroelectric oxide, whose order parameter relates to the off-center displacement of Ti atoms relative to the neighboring O atoms [37]. Such displacements can be mapped quantitatively for each unit cell by fitting atomic positions of Ba and Ti in annular dark-field (ADF-STEM) data, a capability extended to both cryogenic and high temperature. The upper panel of Fig. 2(a) shows an ADF-STEM image of BTO at 104 K, with the Ba atoms appearing brighter than Ti atoms due to their larger atomic number. The lower panel shows a ADF-STEM image overlaid with the arrows representing Ti displacements and the color representing the direction of the displacements. The displacements are oriented toward the projection of the  $\langle 111 \rangle$  direction, consistent with the rhombohedral phase of BTO at this temperature [38].

Figure 2(b) shows the evolution of the real-space maps of polar displacements at 104, 300, and 473 K. In contrast to the uniform ordered state at low temperature, domains with spatially fluctuating polar angles appear at room temperature (see SM notes for more details). The polar histograms shown in the insets reveal that the average amplitude of polar displacements increases from 10 to 14 pm, and further

to 19 pm as the temperature decreases. Spatial fluctuations of polar order increase significantly at higher temperature, with a transition to local polar domains (see SM notes for more details). We note that the size of these polar domains is usually underestimated due to the projection nature of STEM imaging. This melting from an ordered to disordered state upon heating is further confirmed through the diffuse intensity in the Fourier transforms. While the sharp Bragg peaks encode the primary crystalline periodicity of the lattice, diffuse intensity encodes disorder and fluctuations in the positions of the atomic positions (Fig. S3). Figure 2(c) shows a Fourier transform of the real-space Ti positions [inset of Figs. 2(c) and S4(a)]. With higher temperature, this diffuse intensity between Bragg peaks becomes more prominent, consistent with evolution shown in Fig. 1(c). At high temperature, the effect of oxygen vacancies is ruled out (Fig. S8).

To quantify the degree of order ferroelectric displacements, we extract polar displacement angles,  $\phi(\mathbf{r})$ , their standard deviation,  $\sigma_\phi$ , and the correlation function,  $A[\phi(\mathbf{r})]$ . Figure 2(d) depicts  $\sigma_\phi^{-1}$  measured from the statistical distribution of the polar order at three

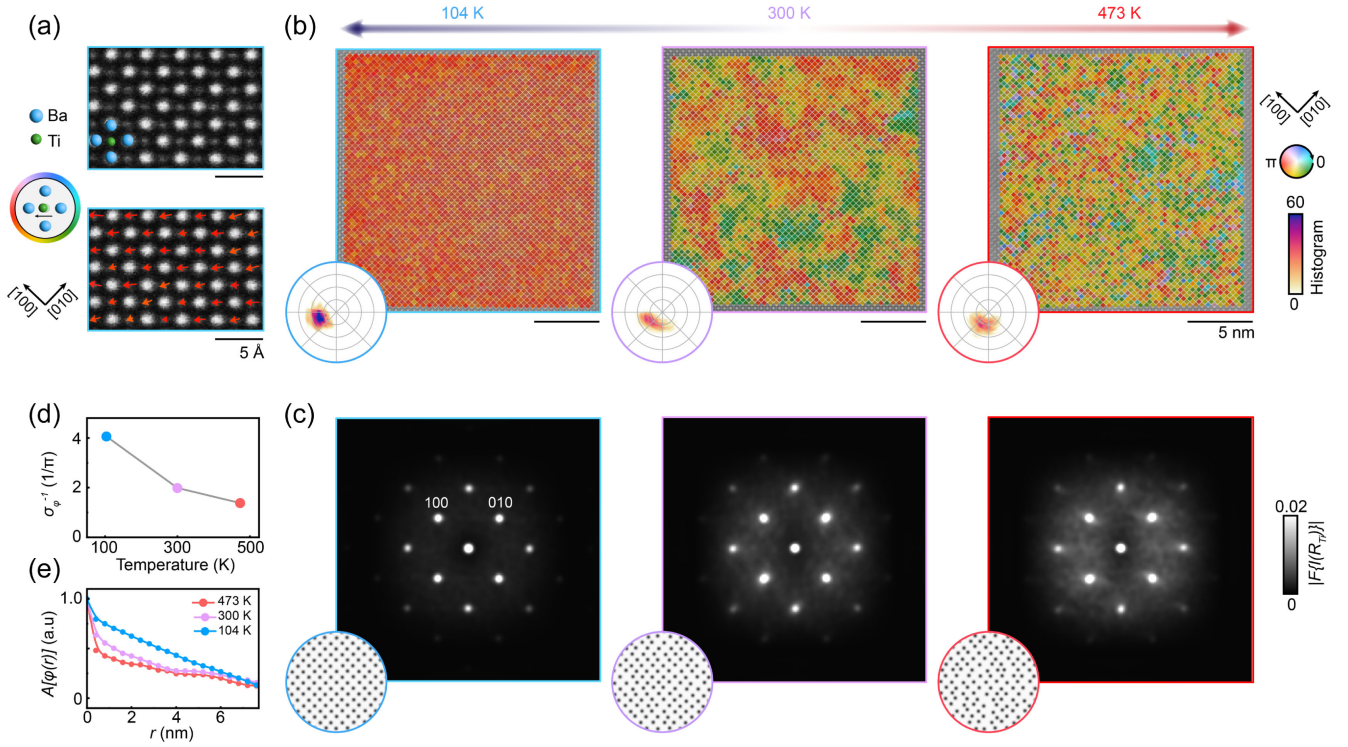


FIG. 2. Atomic-scale visualizations of polar order across normal melting in BaTiO<sub>3</sub>. (a) Upper panel: the ADF-STEM image of [001]-projected BaTiO<sub>3</sub> collected at 104 K. The atomic model of Ba and Ti is overlaid on the image. Lower panel: the measured polar displacement of Ti deviating from the central position determined by four neighboring Ba atoms. The color represents the angle of polar displacement. (b) Real-space maps of polar displacement angles at three temperatures: 473, 300, and 104 K. The color and transparency represents the direction and amplitude of polar displacement. The left corner is the polar histogram plot of polar displacements at the three temperatures. The radius is from 0 to 40 pm. (c) Fourier transform of the real-space Ti positions at three temperatures. The left corner shows the cropped real-space Ti positions [raw data is shown in Fig. S4(a)]. The amplitude of polar displacements is magnified 10 times to highlight the difference in positional disorder across the three temperatures. (d) The polar displacement angle deviations ( $\sigma_\phi^{-1}$ ). (e) Autocorrelation function of polar displacement angle  $A[\phi(r)]$  at three temperatures.

temperatures [inset of Fig. 2(b)]. The increase in  $\sigma_\phi^{-1}$  at 104 K is consistent with the ordered state that we visualize in the real space. Figure 2(e) shows the profiles of the autocorrelation function extracted from [110] direction,  $A[\phi(\mathbf{r})]$ , whose decay encodes the correlation length of the polar order. From 104 to 473 K, the decay behavior of  $A[\phi(\mathbf{r})]$  shows slower drop at lower temperature, as expected from thermally driven fluctuations. The evolution of the degree of polar order can therefore be directly visualized in ADF-STEM images and quantified by changes in  $\sigma_\phi^{-1}$  and decay in  $\phi(\mathbf{r})$  correlations.

The random field in real materials can have multiple characters such as electrostatic (due to charge disorder), magnetic (due to magnetic impurities), or elastic (due to local strain). In BTO, isovalent dopants, such as  $\text{Sn}^{4+}$ ,  $\text{Zr}^{4+}$ , do not introduce significant charge disorder and have been found to be an effective means to tune polar order without the complications of charge inhomogeneity [39]. The Zr dopants will alter polar order of BZTO in two ways [Fig. 3(a)]: (i) the mismatch between the Zr dopants and the pristine Ti will create an internal strain field around the doping sites. (ii) The Zr dopants are polar inactive [40], which breaks the local alignment of ferroelectric correlation between polar active Ti ions. In this way, if there exists the

atomic-scale fluctuations of the Zr dopants, it will generate a random field in the material. Using atomic-resolution energy-dispersive dispersion spectroscopy, we visualize the distribution of Zr dopants in BZTO. Figure 3(b) reveals fluctuations in Zr and Ti signals, and a homogeneous Ba signal, ruling out chemical segregation of Zr dopants. The effect of Ga injection during sample preparation is excluded (Fig. S9). Moreover, there exists a negative correlation between Zr and Ti, with some representative sites highlighted by white circles.

To confirm the random field into the system, we then compare the internal strain field and polar order in the presence and absence of Zr dopants. Measurements of the relation between lattice constant and Zr occupation show that BZTO exhibits an evidently positive correlation (Figs. S10, S11), confirming the role of Zr dopants on creating an internal strain field. The pair distribution  $g(r)$  can be employed to compare the inhomogeneity of strain field. By taking the atomic position fits in the ADF-STEM data, we calculated  $g(r)$  of BTO and BZTO at 104 K, respectively (see SM for more details). As shown in Fig. 3(c), the  $g(r)$  peaks of BZTO appear broader than those of BTO at 104 K, indicating the existence of an inhomogeneous strain fields and positional disorder in BZTO. Furthermore, the polar order in BZTO at 104 K [Fig. 3(d)] shows considerably more spatial fluctuations at the nanoscale when compared to the undoped system. This highlights that fluctuation of Zr dopants does indeed create a random field to induce inhomogeneous internal strain and disturb the alignment of ferroelectric polarization.

Remarkably, the random field generated by Zr dopants creates an inverse melting, whereby the low-temperature state is more disordered than the room-temperature phase. Figure 4(a) displays the real-space distribution of polar displacement at the three representative temperatures. At 473 K, polar displacements are highly disordered but still measurable, with an average amplitude of 7 pm (see SM notes for additional details). As the system cools to room temperature, the displacements begin to show increasing order, and the average amplitude rises to 11 pm. Upon further cooling to 100 K, the average amplitude continues to increase, reaching 17 pm; however, the system remains disordered rather than forming a uniform state—markedly contrasting the behavior of undoped BTO. These observations are further supported by the diffuse intensity in the Fourier transforms of atomic positions [Fig. 4(b)], which strongly resembles the behavior shown in Fig. 1(d). This diffuse intensity in the Fourier transform represents disorder in the polar displacement instead of size effects (see SM notes for more details). Additionally, by extracting  $\sigma_\phi^{-1}$  and  $A[\phi(\mathbf{r})]$ , we observe that the 100 K phase is, in fact, more disordered than the 300 K phase [Figs. 4(c) and 4(d)]. The variation of  $\sigma_\phi^{-1}$  is larger than the measured precision estimated by  $\text{BaTiO}_3$  (Fig. S15). The  $A[\phi(\mathbf{r})]$  shows nonmonotonic change, first increasing from 473 to

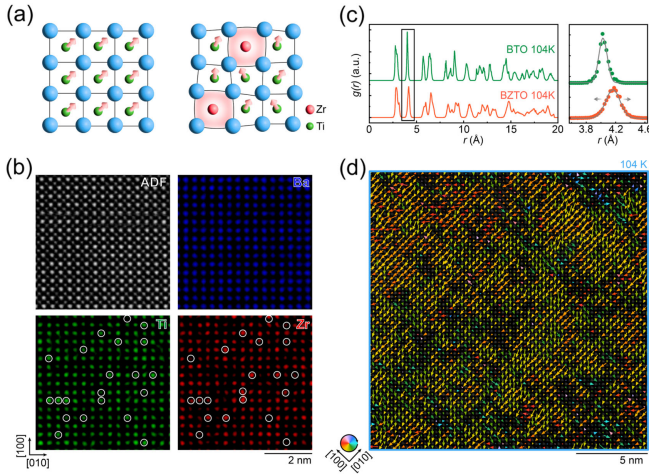


FIG. 3. Atomic-scale mapping of chemically quenched disorder and accompanied random field in  $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ . (a) The schematic shows the generation of random field by Zr-doping. The Zr dopant locally expands the lattice and disturbs ferroelectric order. (b) Atomic-resolution energy-dispersive dispersion spectroscopy chemical mapping of Ba, Zr, and Ti signals collected at 300 K. The white circles highlight representative positions with negative correlation between Zr and Ti. (c) Radial pair distribution function  $g(r)$  of  $\text{BaTiO}_3$  and  $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  at 104 K. The right panel shows an enlarged view of the next-nearest atomic spacing. The gray line shows a Gaussian fit to the peaks. The arrow helps distinguish the broadening of the peak in  $\text{Ba}(\text{Ti}, \text{Zr})\text{O}_3$ . (d) ADF-STEM image overlaid with polar displacements in  $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  at 104 K. The projection is along the [001] zone axis. The scale bar is 5 nm.

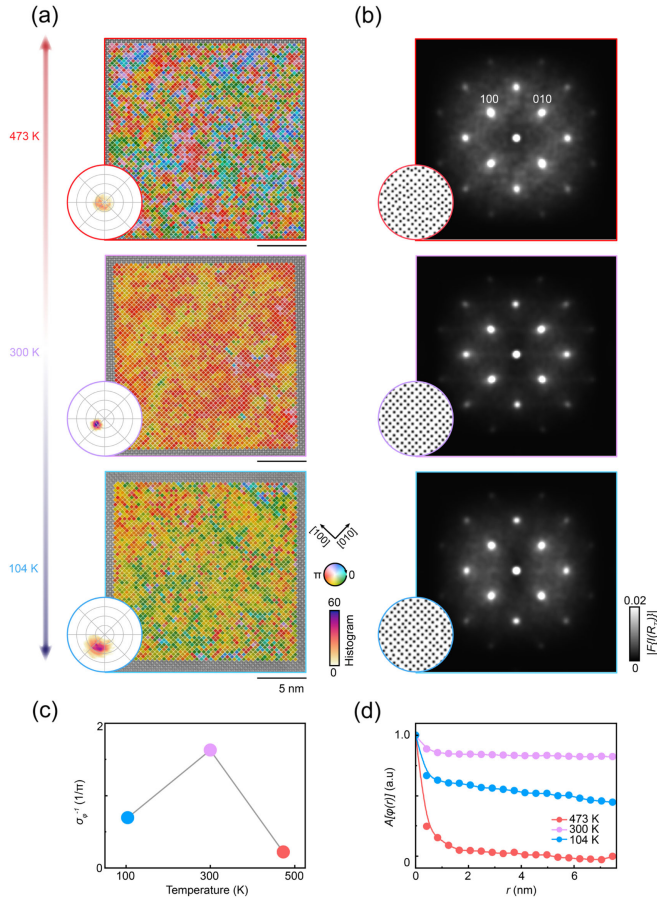


FIG. 4. Inverse melting of polar order in  $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ . (a) Real-space maps of polar displacement angles at three temperatures: 473, 300, and 104 K. The color and transparency represents the direction and amplitude of polar displacement. The left corner is polar histogram plot of polar displacement at three temperatures. The radius is from 0 to 40 pm. (b) Fourier transform of the real-space Ti positions with normalized displacement at three temperatures. The left corner shows the cropped real-space Ti positions [raw data in Fig. S4(b)]. The amplitude of polar displacement is magnified 10 times to highlight the difference among three temperatures. (c) The polar displacement angle deviation ( $\sigma_\phi^{-1}$ ) measured at three temperatures. (d) Autocorrelation function of polar displacement angle  $A[\phi(r)]$  at three temperatures.

300 K and then dropping at 104 K. Data collected across different regions and domains shows the same evolution (Fig. S16). This indicates an inverse melting involving reentrant disordering of polar order upon cooling. This abnormal dynamic behavior is different from the evolution of competing order in relaxors [32] (Fig. S17).

Our ability to map and analyze the correlations of polar order across temperature proved instrumental in unraveling the inverse melting phenomenon in a ferroelectric at the atomic scale. Inspired by the visualizations, we presented a simple mapping between BZTO and a spin-1 random field Ising model. Despite its simplicity, this model shows that a

random field, which can be generated by the presence of Zr dopants, mediates the following sequence of transitions: (i) at high temperature, large thermal fluctuations dominate the disordering process regardless of the strength of the random field; (ii) at intermediate temperature, thermal fluctuations are reduced but still significant enough to overcome and smear the random field potential, and so the system takes advantage of the exchange energy by aligning polarization; (iii) finally, at much lower temperature, the system is strongly pinned to the local random field, and so the local correlations are dominated by the coupling to the quenched disorder, leading to more disordered configurations than at higher temperature. The role of Zr dopants suggests that this phenomenon might prove more general and applicable to other chemically doped ferroelectric systems, when the random field is strong enough to pin the polar order at low temperature. In addition to these isovalent dopants, heterovalent dopants will further induce an electrostatic random field, potentially driving more complex melting behavior of polar order in ferroelectric systems. A compelling next step is to systematically investigate the relationship between doping levels and inverse melting by probing low-temperature polar correlations in ferroelectrics at the atomic scale across a range of chemical elements and dopant concentrations.

Beyond the intriguing fundamental aspects, inverse melting holds appeal for its potential for practical applications. Thermodynamic properties, such as thermal expansion and electrocaloric effects, are intimately linked to changes in entropy within a system [41–43]. A state of increased disorder at low temperature could theoretically exhibit negative thermal expansion [44–46], which plays a key role in tailoring the overall thermal expansion coefficient of materials [47,48].  $g(r)$  extracted from atomic-resolution data show that while the BTO lattice contracts as polar order from 300 to 104 K, the BZTO lattice expands in the low temperature disorder phase (Fig. S18). This behavior suggests that inverse melting and random fields may be unexplored, generic mechanisms for generating negative thermal expansion. These atomic-scale visualizations open new avenues for probing and designing material properties by means of controlled disorder and correlations.

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Y.Z. and I.E. conceived the study. S.-W.C provided bulk samples. Y.Z. prepared the *in situ* TEM samples, performed *in situ* electron microscopy experiments, and analyzed data with help from S.H.S. and I.E.I.E. and C.B.C. carried out theoretical calculations. Y.Z. and I.E. wrote the paper. All authors discussed the results and commented on the manuscript.

The authors declare no conflict of interest.

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