Unveiling the ferrielectric nature of PbZrO₃-based antiferroelectric materials

Zhengqian Fu¹,6, Xuefeng Chen²,6, Zhenqin Li¹,3, Tengfei Hu¹,4, Linlin Zhang¹, Ping Lu¹, Shujun Zhang⁵, Genshui Wang¹,2, Xianlin Dong¹,2,4 & Fangfang Xu¹,4

Benefitting from the reversible phase transition between antiferroelectric and ferroelectric states, antiferroelectric materials have recently received widespread attentions for energy storage applications. Antiferroelectric configuration with specific antiparallel dipoles has been used to establish antiferroelectric theories and understand its characteristic behaviors. Here, we report that the so-called antiferroelectric (Pb,La)(Zr,Sn,Ti)O₃ system is actually ferrielectric in nature. We demonstrate different ferrielectric configurations, which consists of ferroelectric ordering segments with either magnitude or angle modulation of dipoles. The ferrielectric configurations are mainly contributed from the coupling between A-cations and O-anions, and their displacement behavior is dependent largely on the chemical doping. Of particular significance is that the width and net polarization of ferroelectric ordering segments can be tailored by composition, which is linearly related to the key electrical characteristics, including switching field, remanent polarization and dielectric constant. These findings provide opportunities for comprehending structure-property correlation, developing antiferroelectric/ferrielectric theories and designing novel ferroic materials.
Dielelectrics have been commercialized for a wide range of applications including pulsed power systems, electrical vehicles, and medical devices. Benefiting from the electrical field-induced reversible phase transition between antiferroelectric (AFE) and ferroelectric (FE) states, AFE perovskite oxides (ABO$_3$) become promising candidates for dielectric energy storage capacitors due to their high power density, good energy storage density, and long lifetime.

Early in 1951, Kittel theoretically defined AFE configuration in analogy with antiferromagnetism as neighboring lines of dipoles pointing in antiparallel directions, while Sawaguchi et al. experimentally observed AFE behavior in PbZrO$_3$ ceramic according to its characteristic dielectric response and hysteresis loops. Later on, the X-ray diffraction, neutron diffraction, convergent-beam electron diffraction, and high-resolution transmission electron microscopy have been applied to substantiate the AFE configuration in PbZrO$_3$. Based on these comprehensive structural investigations, the basic dipole ordering configuration of PbZrO$_3$ was established in which the two long right-handed dipole lines and two right-oriented dipole lines alternate. Therefore, the PbZrO$_3$ has become the prototypical AFE material for understanding the physics of AFE and exploring new AFE materials. For AFE physics, theoretical models always involve ferrielectric (FiE) phase when AFE order parameter is coupled with field-induced polarization, while the FiE configuration has never been experimentally established. For AFE materials, numerous chemical elements (A-sites: La$^{3+}$, Ba$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, etc.; B-sites: Sn$^{4+}$, Ti$^{4+}$, Nb$^{5+}$, etc.) have been attempted in PbZrO$_3$ for decreasing its extremities and optimizing energy storage characteristics. As a consequence, the large family PbZrO$_3$-based solid solutions were considered as AFE materials with specific antiparallel polarization configuration, which has been rarely challenged.

In PbZrO$_3$-based ceramics, the chemical doping generally drives the AFE phase from commensurate structure to incommensurately modulated structure (IMS). The complex IMS was firstly investigated by MacLaren et al. in (Pb$_{0.96}$La$_{0.04}$) (Zr$_{0.9}$Ti$_{0.1}$)$_{0.99}$O$_3$ ceramics on atomic-scale, where the modulation of A-site cations was found to exist in a sinusoidal fashion. Ma et al. further pointed out that the A-site cations were either antiparallel but imbalanced or in a nearly orthogonal arrangement in (Pb$_{0.9}$Nb$_{0.1}$$_{0.82}$) (Zr$_{0.8}$Sn$_{0.43}$)$_{1-y}$Ti$_{3y}$O$_{3}$ ceramics. These works have been regarded as an extraordinary step forward to the understanding of cation displacement in IMS. Nonetheless, early work has demonstrated that the prototypical PbZrO$_3$ showed multiple soft-mode vibrations, which mainly involved trilinear coupling between vibrations of Pb cations and librations of oxygen octahedra. Moreover, the recent work on the electron-beam illumination induced phase transition in PbZrO$_3$ single crystals clearly showed the hierarchical evolution of oxygen octahedra. Thus, as an important component in perovskite PbZrO$_3$-based materials, the information of oxygen density, good energy storage density, and long lifetime has been regarded as an extraordinary step forward to the understanding of cation displacement in IMS.

We demonstrate the so-called AFE PLZST system has actual arrangement of dipoles in FiE configuration. The coupling between A/B-cations and O-anions is explicitly elucidated. Based on the FiE configurations, the key electrical properties can be clearly understood upon varying the composition.

### Results

**Characterization of average structure.** Pb$_{0.97}$La$_{0.02}$Zr$_{0.50}$Sn$_{0.50}$Ti$_{0.50}$O$_3$ ceramics with $x = 0.50$, 0.45, 0.375 (hereafter denoted as PLZST 50/50/0, PLZST 50/45/5, and PLZST 50/37.5/12.5, respectively) were prepared by high temperature solid-state sintering method. X-ray diffraction studies reveal their crystal structures are periodically modulated because the characteristic superlattice reflections (marked by arrows) appear ahead of the [100] basic reflection (Fig. 1a, all crystallographic indices refer to the simple pseudocubic unit cell in this work). According to the crystal structure of PbZrO$_3$, these peaks are mainly associated with the displacement of cations. They gradually move upward to the [100] peaks indicating the modulation period ($N_{\text{IMS}}$) increases with decreasing Sn/Ti ratio. Compared with the selected area electron diffraction (SAED) patterns of [001], [100], and [112] zone axes (Fig. 1b and Supplementary Fig. 1), it is confirmed that the modulation wave is along [110] direction with average $N_{\text{IMS}}$ of 4.04, 6.15, and 9.37 for PLZST 50/50/0, PLZST 50/45/5, and PLZST 50/37.5/12.5, respectively (Fig. 1c). The fractional (irrational) values of $N_{\text{IMS}}$ indicate that all three PLZST compositions show IMS. Meanwhile, the appearance of characteristic superlattice reflections associated with oxygen octahedral tilts in XRD (Fig. 1a, marked by dash rectangle) and [1−12] SAED patterns (Supplementary Fig. 1a, marked by blue arrow) indicates that the octahedra of PLZST have the similar antiphase tilt with PbZrO$_3$. It
can be seen that the intensity of $1/2[11\bar{1}]$ reflections gradually decreases with decreasing Sn/Ti ratio. This implies the strong coupling of octahedra tilts with cations displacement, which is believed to stabilize the modulated structure$^{24,26,27}$ and will be further discussed in the following.

**Atomic-scale analysis of modulated structure.** Because spontaneous polarization ($P_s$) linearly relates with the atomic displacement, atomic-scale high-angle annular dark field (HAADF) imaging was performed to investigate the dipoles ordering configurations based on cations displacement in PLZST system. The picometer-precision fitting was applied to extract the cation column positions (see the details in Methods). Previous neutron diffraction studies on Zr-rich Pb(Zr,Ti)O$_3$ confirmed that Pb cations were responsible for the spontaneous polarization because the displacement magnitude of Pb cations was about three times that of Zr/Ti$^{20,29}$. Similarly, it can be immediately accessible by directly observing the experimental HAADF images (Supplementary Fig. 2) that the A-site cations have obviously larger displacement than B-site cations in our PLZST system. Thus, we define the atomic displacement vectors ($\mathbf{D}_{AB}$) as the relative offset of the A-site cations from the center of four adjacent B-site cations in the (001) plane. Displacement maps (Fig. 2) reveal that the dipoles are modulated periodically in all PLZST compositions, leading to the appearance of coherent fringes in medium-magnified TEM images (Supplementary Fig. 3). The modulation intervals are found to increase with decreasing Sn/Ti ratio, not necessarily only two dipole lines as modeled in the prototypical AFE ($\mathbf{D}_{AB}$) that the Pb cations have obviously larger displacement than B-site cations in our PLZST system. Thus, we define the atomic displacement vectors ($\mathbf{D}_{AB}$) as the relative offset of the A-site cations from the center of four adjacent B-site cations in the (001) plane. Displacement maps (Fig. 2) reveal that the dipoles are modulated periodically in all PLZST compositions, leading to the appearance of coherent fringes in medium-magnified TEM images (Supplementary Fig. 3). The modulation intervals are found to increase with decreasing Sn/Ti ratio, not necessarily only two dipole lines as modeled in the prototypical AFE structure in PbZrO$_3$. Actually, the distortion of oxygen octahedra should also have an important influence on the prototypical AFE structure, which can be clearly seen from the irregular shape of oxygen octahedra in Fig. 3a. The tilt and distortion of oxygen octahedra can be characterized by measuring the rippling of O-sublattice along x- and y-direction (Fig. 3i). Based on the experimental ABF images (Fig. 3b–d), we map the corner-shared BO$_6$ octahedra of PLZST system (Fig. 3i–l). The as-expected tilt and distortion of oxygen octahedra (see the irregular shape of oxygen octahedra and the rippling of O-row/column) was then found to occur simultaneously contributing to the observed FE configuration in PLZST system. Interestingly, the coupling along x-direction is manifested by the modulation of y-rippling for O-sublattice, i.e., the large/small magnitude of $\mathbf{D}_{AB}$ usually corresponds to the high/low degree of y-rippling of O-rows (Fig. 3f–h, n–p), which can be understood by the Coulomb interaction (Supplementary Fig. 6). Thus, it can be understood that the decrease of intensity of $1/2[11\bar{1}]$ reflections in XRD (Fig. 1a) and SAED (Supplementary Fig. 1a) is caused by the increase of volume fraction of the areas with small y-rippling amplitude. Compared with the one in PbZrO$_3$ (Fig. 3m), it can be clearly seen that the y-rippling of O-rows in PLZST system breaks the long-rang antiphase octahedral tilt of a–a–c$^0$ system and is periodically modulated with local disorder.

Similarly, the coupling along y-direction can be manifested by the modulation of horizontal component of atomic displacement (Fig. 4). In PbZrO$_3$, the coupling features the characteristic that Zr-cations move in the same direction as Pb-cations while O-anions move in the opposite direction (Fig. 4a). In contrast, the coupling behavior in PLZST is strongly dependent on composition although displacement of both A/B-cation and O-anion are

![Fig. 2 Polarization mapping based on cations displacement in PLZST system.](image)
modulated in corresponding period. Specifically, firstly, the PLZST 50/50/0 has a similar way to PbZrO₃, but there is a phase difference about one d₁₁₀ between A-cations and B-cations/O-anions (Fig. 4b). The horizontal displacement of O-anions in Fig. 4b refers to the data of odd column while its comparison to the displacement of even column and the sum of both columns are presented in Supplementary Fig. 7. Secondly, the PLZST 50/45/5 shows inverse behavior to PbZrO₃, i.e., B-cations move in the opposite direction to Pb-cations while O-anions move in accordance with A-site cations, synchronous alternation of large positive value and small negative value (Fig. 4c). Thirdly, the PLZST 50/37.5/12.5 presents nearly the same fashion as PbZrO₃, in which the displacement of O-anions has approximately equal positive and negative value (Fig. 4d). Apart from the difference in coupling behavior, the displacement amplitude of both A/B-cation and O-anion gradually decrease with decreasing of Sn/Ti ratio, consequently led to the decrease of intensity of 1/2{11\over 22} reflections in XRD (Fig. 1a) and SAED (Supplementary Fig. 1) as well. Of particular interest is that the displacement of O-anion gradually changes its position with the reference of zero-line while the A-cations maintain the unbalanced displacement in all three compositions. Thus, the displacement of O-anion is also strongly affected by the doping effect of B-site elements. For instance, the stronger hybridization between B-cation and...
The purple, green, orange, and red profiles represent the A-cations, B-cations, O-anions, and $P_s$, respectively. The value of these profiles are calculated from the Fig. 3a–d, where the displacement is defined as negative value when it aligns to the left. The corresponding profiles for vertical component are presented in Supplementary Fig. 8. The error bars represent the standard deviation measured from the experimental image.

O-anion occurs with higher Ti content in B-site (Zr/Sn/Ti) composition by taking account of difference in ionic radius and electronegativity.

Accompanied with the quantitative analysis of atomic displacement, the local polarization (Fig. 4 and Supplementary Fig. 8) is calculated in terms of standard definition $P_s = \frac{1}{V} \sum_i Z'_i$, where $V$, $\delta$, and $Z'_i$ are the volume of unit cell under consideration, atomic displacement with respect to the ideal position, and the Born effective charge, respectively. The $Z'_i$ values of cubic PbZrO$_3$ in ref. 30 are used for the PLZST system. Clearly, the horizontal $P_s$ is also periodically modulated because of the main contribution from the displacement of A-cations and O-anions. The $P_s$ of PLZST system have been substantially suppressed compared with PbZrO$_3$, especially in some local areas where structural disorder decreases the amplitude of the oxygen modulation. Thus, the O-anions should be taken into consideration for quantitative characterization of the polarization modulation. Nevertheless, the $P_s$ profiles also presents the FiE configuration in all three PLZST compositions, being consistent with the quantitative $D_{AB}$ mapping.

Structure–property correlation. According to the above structural characterizations, the interplay of FE, FiE, and AFE orderings and the structure–property relationship can be understood comprehensively. Figure 5 models the ideal FiE ordering configurations of PLZST system compared with the AFE ordering configuration of PbZrO$_3$. Here, only the dominant magnitude modulation mode is given for PLZST system. It should be noted that the dipoles ordering configurations in PLZST system actually have fluctuant periods and cyclic variation of magnitude, and in particular, the dipoles tend to be zero at the transitional area between dipole lines of different orientations (Figs. 2 and 4). Thus, the schematic illustrations with fixed modulated period and magnitude of dipoles in Fig. 5 are just the simplification of the experimental observations. Clearly, the AFE ordering originates from a couple of two-layer equivalent FE ordering segments with opposite directions (Fig. 5a) while the FiE ordering stems from two inversely polarized but nonequivalent FE ordering segments whose width is composition-dependent (Fig. 5b–d). The double/multiple hysteresis loops are so invertebrate for PbZrO$_3$-based materials that their AFE nature has been rarely challenged due to the similar polarization loops as observed in Fig. 5e. Nevertheless, some electric properties can hardly be understood based on prototypical AFE model. The FiE nature of PLZST system results in detectable remanent polarization ($P_r$), which increases linearly with the net polarization of FE segments ($\Delta P$). It should be noted that although the measured $\Delta P$ value in the FiE region of PLZST 50/50/0 is obviously larger than the one in PLZST 50/45/5, the existence of large areas with AFE ordering (see Supplementary Fig. 9 and circled region in Fig. 2a) eventually results in an overall smaller $P_r$ for PLZST 50/50/0. The modulation period ($N_{IMS}$) will increase by enlarging the FE ordering segments with decreasing the Sn/Ti ratio, i.e., 2 rows, 3 rows, and 5 rows for PLZST 50/50/0, PLZST 50/45/5, and PLZST 50/37.5/12.5, respectively, due to the fact that Ti favors the ferroelectricity while Sn favors the antiferroelectricity$^{19}$. In this case, the interactions between the nearest neighboring dipoles with opposite direction will decrease, which will lead to the increased dielectric constant ($\varepsilon_{RT}$) and decreased forward switching field ($E_{AF}$), as shown in Fig. 5f and Supplementary Table 1. We also correlated $N_{IMS}$ with $P_r$, $\varepsilon_{RT}$ and $E_{AF}$ in the Sr-doped PLZST system, where the similar trend was observed (Supplementary Fig. 10 and Supplementary Table 2), supporting the proposed correlation between modulation structure and macroscopic properties. Thus, the structure with antiparallel, equal and narrow FE segments is highly desired for high energy storage application because it has low $P_r$ and large forward switching field. This has been strongly evidenced in PLZST 50/50/0, which possesses the highest energy storage density of 9.82 J/cm$^2$ with satisfied energy efficiency of 84% (see the inset in Fig. 5e).

In summary, the current work determines the FiE nature of PLZST system, which has long been regarded as AFE materials. The FiE ordering originated from two unequal FE ordering segments with opposite directions (magnitude modulation) or two equal FE ordering segments with different orientations (angle modulation), which can be tailored by composition tuning, i.e., the Sn/Ti ratio in the studied PLZST system. The FiE ordering is mainly attributed to the coupling between A-cations and O-anions, which is strongly dependent on composition but has the

![Fig. 4 Quantitative analysis of coupling between O-anions displacement and A/B-cations displacement.](image-url)
common characteristics including, (a) both A-cations and O-anions are periodically modulated, breaking the long-range order of equally antiparallel cation displacement and antiphase octahedral tilt of the a–a–c0 system in PbZrO3; (b) the FE segments with large/small A-cations displacement correspond to the O-subbattice with high/low degree of γ-rippling; (c) the tilt and distortion of oxygen octahedra simultaneously occur to stabilize the IMS. The relationship of composition, structure, and property has been established, providing a solid ground for materials design of Pb during sintering. Raw materials were ball-milled for 6 h and dried at 120 °C. Then they were calcined at 900 °C for 2 h. The PLZST powders were ball-milled for 24 h, dried, mixed with 6 wt% PVA as binding agent and then pressed into pellets of 13 mm in diameter at 150 MPa. Finally, the binder was burnt out at 800 °C for 2 h and the pellets were sintered at 1300 °C for 2 h.

Methods

Materials synthesis. Pb0.97La0.02(Zr0.50Sn0.50)O3 ceramics with x = 0.50, 0.45, 0.375 (hereafter denoted as PLZST 50/50/0, PLZST 50/45/5, and PLZST 50/37.5/12.5, respectively) were prepared by high temperature solid-state sintering method. PbO, ZrO2, TiO2, La2O3, and SnO2 powders with the purity of at least 99.0% were weighted and 0.5 wt% excess PbO were added to compensate for the volatilization of Pb during sintering. Raw materials were ball-milled for 6 h and dried at 120 °C. Then they were calcined at 900 °C for 2 h. The PLZST powders were ball-milled again for 24 h, dried, mixed with 6 wt% PVA as binding agent and then pressed into pellets of 13 mm in diameter at 150 MPa. Finally, the binder was burnt out at 800 °C for 2 h and the pellets were sintered at 1300 °C for 2 h.

Electric properties characterization. All samples were polished to the thickness of 0.10–0.15 mm and the silver thin film was sputtered with the diameter of 0.75 mm as electrode. The room temperature polarization-electric field (P–E) hysteresis loops were characterized by aix ACCT TF 2000 analyzer FE measurement system (aix ACCT Co., Aachen, Germany) at 10 Hz and different electric fields.

Transmission electron microscopy (TEM). TEM specimens were prepared by a conventional approach combining mechanical thinning and finally Ar + ion-milling in a Gatan PIPS II. The ion-milling voltage was gradually decrease from 3 keV to 0.5 keV to reduce ion-beam damage. Specimens were then coated with a thin-layer of carbon to minimize charging under the electron beams. The dark-field (DF) images and select-area electron diffraction (SAED) patterns were carried out on JEOL JEM-2100F microscope. The atomic-scale high-angle annular dark-field (HAADF) and annular bright-field (ABF) images were carried out on Cs-corrected JEOL JEM- ARM300F and Hitachi HF5000 microscopes. The experiment conditions were: probe size in 7C mode and convergence semi-angle of 20 mrad and collection semi-angle of 40–80 mrad (HAADF) and 10–20 mrad (ABF) for JEOL microscope; probe size in UHR mode and convergence semi-angle of 20 mrad and collection semi-angle of 60–320 mrad (HAADF) and 11–22 mrad (ABF) for Hitachi microscope.
The accurate and precise extraction of atomic column positions from HRSTEM images permits to quantify crystal structure parameters along the selected direction. In this case, the dipole ordering configuration can be immediately accessible by direct imaging of the crystal structure. In this work, the picometer-precision fitting of atomic columns was done by MATLAB code, a least squares estimation algorithm for accurate and precise quantification of the atomic column positions and intensities with considering overlap between neighboring atomic columns which has been used in previous literatures. Considering the fact that the B-cations have very small displacement, the B-cations positions are averaged as reference points to calculate the displacement of A-cations, B-cations, and O- anions. The fitting of the atomic columns for A-cations, B-cations, and O-anions in this work has a 95% confidence interval of 4 pm, 3 pm, and 7 pm, respectively. The larger deviation of A-site columns than the one of B-site columns represents an overestimation of the precision of the fitting algorithm due to the modulated structure, which leads to a large fluctuation in distance between adjacent columns. Nevertheless, the polarization maps and profiles reveal the same evolution of modulation period with XRD (Fig. 1a), SAED (Fig. 1b and Supplementary Fig. 1) and modulation fringes (Supplementary Fig. 3), implying that the calculation results in this study are reliable and secure.

Data availability
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Received: 21 June 2019; Accepted: 12 July 2020;
Published online: 30 July 2020

References
1. Yao, Z. et al. Homogeneous/Inhomogeneous-structured dielectrics and their energy-storage performances. Adv. Mater. 29, 1601727 (2017).
2. Pan, H. et al. Ultrahigh-energy density lead-free dielectric films via polymorphic nanodomain design. Science 365, 578–582 (2019).
3. Wang, G. et al. Ultrahigh energy density lead-free multilayers by controlled electrical homogeneity. Energy Environ. Sci. 12, 582–588 (2019).
4. Yang, L. et al. Perovskite lead-free dielectrics for energy storage applications. Prog. Mater. Sci. 102, 72–108 (2019).
5. Hao, X., Zhai, J., Kong, L. B. & Xu, Z. A comprehensive review on the progress of lead zirconate-based antiferroelectric materials. Prog. Mater. Sci. 63, 1–57 (2014).
6. Zhao, L., Liu, Q., Gao, J., Zhang, S. & Li, J. F. Lead-free antiferroelectric silver niobate talcaltate with high energy storage performance. Adv. Mater. 29, 1701824 (2017).
7. Wang, H., Liu, Y., Yang, T. & Zhang, S. Ultrahigh energy-storage density in antiferroelectric ceramics with field-induced multphase transitions. Adv. Funct. Mater. 29, 1807321 (2019).
8. Chen, M. J., Ning, X. K., Wang, S. F. & Fu, G. S. Significant enhancement of energy storage density and polarization in self-assembled PbZr2O5: NiO nano-columnar composite films. Nanoscale 11, 1914–1920 (2019).
9. Kittel, C. Theory of antiferroelectric crystals. Phys. Rev. 82, 729–732 (1951).
10. Shirane, G., Sawaguchi, E. & Takagi, Y. Dielectric properties of lead zirconate. Phys. Rev. 84, 476–481 (1951).
11. Corker, D. L. et al. A Re-investigation of the crystal structure of the364 Perovskite PbZrO3 by X-ray and Neutron Diffraction.Acta Crystallogr B 53, 135–142 (1997).
12. Teslic, S. & Egami, T. Atomic structure of PbZrO3, determined by pulsed neutron diffraction. Acta Crystallogr B 54, 750–765 (1998).
13. Zhang, N. et al. A neutron diffuse scattering study of PbZrO3 and Zr-rich PbZr1−xTixO3. J. Appl. Crystallogr. 48, 1637–1644 (2015).
14. Tanaka, M., Saito, R. & Tsuzuki, K. Determinations of space group and oxygen coordinates in the antiferroelectric phase of lead zirconate by neutron diffraction. J. Phys. Soc. Jpn. 51, 2635–2640 (1982).
15. Wei, X. K. et al. Ferroelectric translational antiphase boundaries in nonpolar materials. Nat. Commun. 5, 3031 (2014).
16. Tomé, P. & Guennou, M. Theory of antiferroelectric phase transitions. Phys. Rev. B 94, 014107 (2016).
17. Tolédano, P. & Khlayvin, D. D. Symmetry-determined antiferroelectricity in PbZrO3, NaNbO3, and PbHfO3. Phys. Rev. B 99, 024105 (2019).
18. Shirane, G. Ferroelectricity and Antiferroelectricity in Ceramic PbZrO3. Containing Ba or Sr. Phys. Rev. 86, 219–227 (1952).
19. Berlincourt, D. Transducers using forced transitions between ferroelectric and antiferroelectric states. IEEE Trans. Sonics Ultrason. 13, 116–130 (1966).
20. Lu, B. et al. Large electrocaloric effect in relaxor ferroelectric and antiferroelectric lanthanum doped lead zirconate titanate ceramics. Sci. Rep. 7, 15335 (2017).
21. Zhuo, F. et al. Large field-induced strain, giant strain memory effect, and high thermal stability energy storage in (PbLa)(ZrSn,Ti)O3 antiferroelectric single crystal. Acta Mater. 148, 38–37 (2018).
22. MacLaren, I., Villaurrutia, R., Schaffer, B., Houben, L. & Peláiz-Barranco, A. Atomic scale imaging and quantification of electrical polarisation in incommensurate antiferroelectric lanthanum-doped lead zirconate titanate. Adv. Funct. Mater. 22, 261–266 (2012).
23. Ma, T. et al. Uncompensated polarization in incommensurate modulations of perovskite antiferroelectrics. Phys. Rev. Lett. 123, 217602 (2019).
24. Hlinka, J. et al. Multiple soft-mode vibrations of lead zirconate. Phys. Rev. Lett. 112, 197601 (2014).
25. Wei, X. K. et al. An unconventional transient phase with cycloidal order of polarization in energy-storage antiferroelectric PbZrO3. Adv. Mater. 32, 1907208 (2020).
26. Tagantsev, A. K. et al. The origin of antiferroelectricity in PbZrO3. Nat. Commun. 4, 2229 (2013).
27. Lu, T. et al. Critical role of the coupling between the octahedral rotation and A-site ionic displacements in PbZrO3-based antiferroelectric materials investigated by intris neutron diffraction. Phys. Rev. B 96, 214108 (2017).
28. Zhang, N., Yokota, H., Glazer, A. M. & Thomas, P. A. Neutron powder diffraction refinement of PbZr1−xTixO3. Acta Crystallogr B 67, 386–398 (2011).
29. Zhang, N. et al. The missing boundary in the phase diagram of PbZr1−xTixO3. Nat. Commun. 5, 5231 (2014).
30. Ghosez, P., Cockayne, E., Waghmare, U. V. & Rabe, K. M. Lattice dynamics of BaTiO3, PbTiO3, and PbZrO3: a comparative first-principles study. Phys. Rev. B 60, 836–843 (1999).
31. Yang, L. et al. Observation of a periodic array of flux-closure quadrants in strained ferroelectric PbTiO3 films. Science 348, 547–551 (2015).
32. Yadav, A. K. et al. Observation of polar vortices in oxide superlattices. Nature 530, 198–201 (2016).
33. Das, S. et al. Observation of room-temperature polar skyrmions. Nature 568, 368–372 (2019).
34. De Bakker, A. et al. StatEM: an efficient approach for accurate and precise model-based quantification of atomic resolution electron microscopy images. Ultramicroscopy 171, 104–116 (2016).
35. Van Aert, S. et al. Advanced electron crystallography through model-based imaging. IUCrJ 3, 71–83 (2016).

Acknowledgements
We thank Prof. Junming Liu, Prof. Rong Huang, and Prof. Yun Liu for stimulating discussions. This work is supported by National Key R&D Program of China (2016YFA0201103), the National Natural Science Foundation of China (51672296, 1177436), the Equipment Advanced Research Fund (Grand No. 61409220107) and Shanghai Technical Platform for Testing and Characterization on Inorganic Materials (19D22290700).

Author contributions
Z.F., F.X. and X.D. conceived the experiments. X.C. carried out the synthesis and electrical characterization. Z.F. and X.D. performed SAED and XRD characterizations. F.X., S.Z., G.W., T.H., P.L. and L.Z. conceived the experiments. X.C. carried out the synthesis and electrical characterization. Z.F. and Z.L. did the atomic-scale HAADF and ABF experiments. T.H., P.L. and L.Z. performed SAED and XRD characterizations. F.X., Z.F., Z.E. and X.C. analyzed the data and co-wrote the paper. F.X., G.W. and X.D. supervised the research. All authors contributed to the discussions and paper preparation.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary information is available for this paper at https://doi.org/10.1038/s41467-020-17664-w.

Correspondence and requests for materials should be addressed to G.W., X.D. or F.X.

Peer review information Nature Communications thanks Yui Noguchi and Xiankui Wei for their contribution to the peer review of this work.

Reprints and permission information is available at http://www.nature.com/reprints

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.
