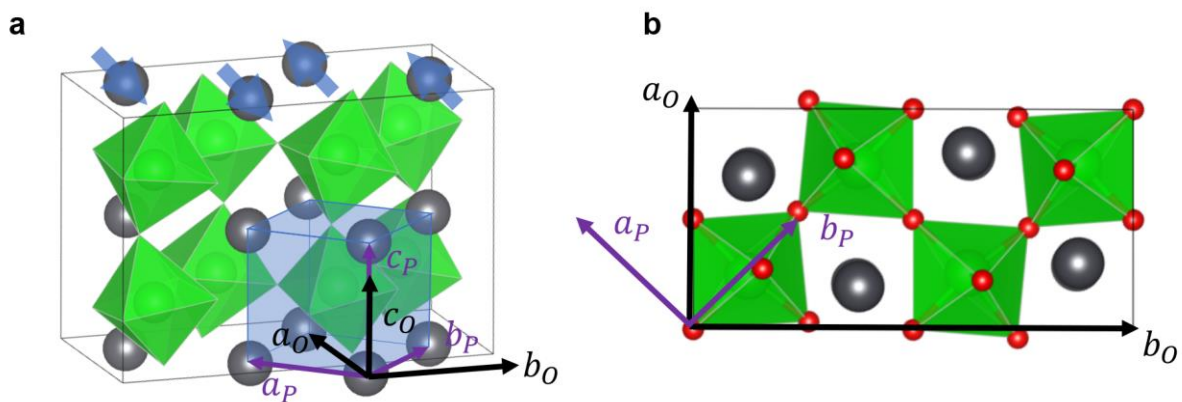
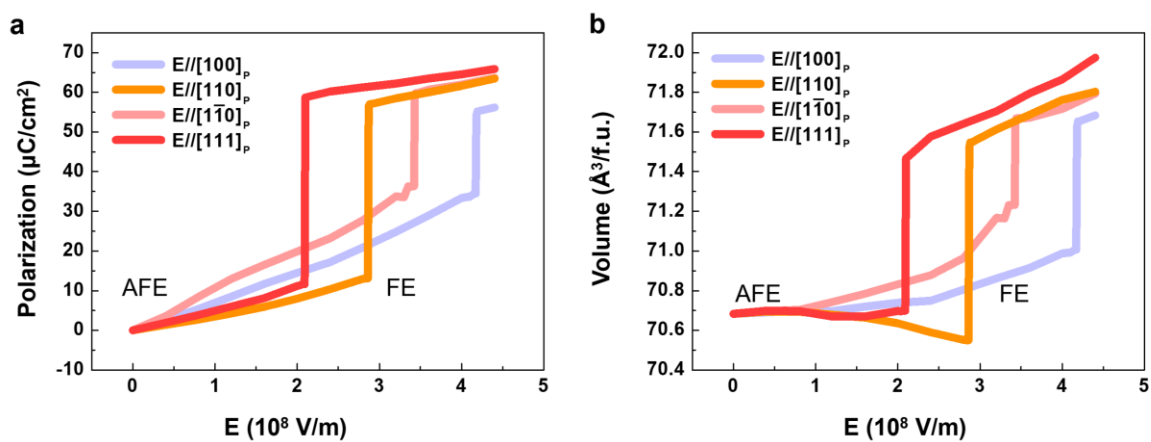


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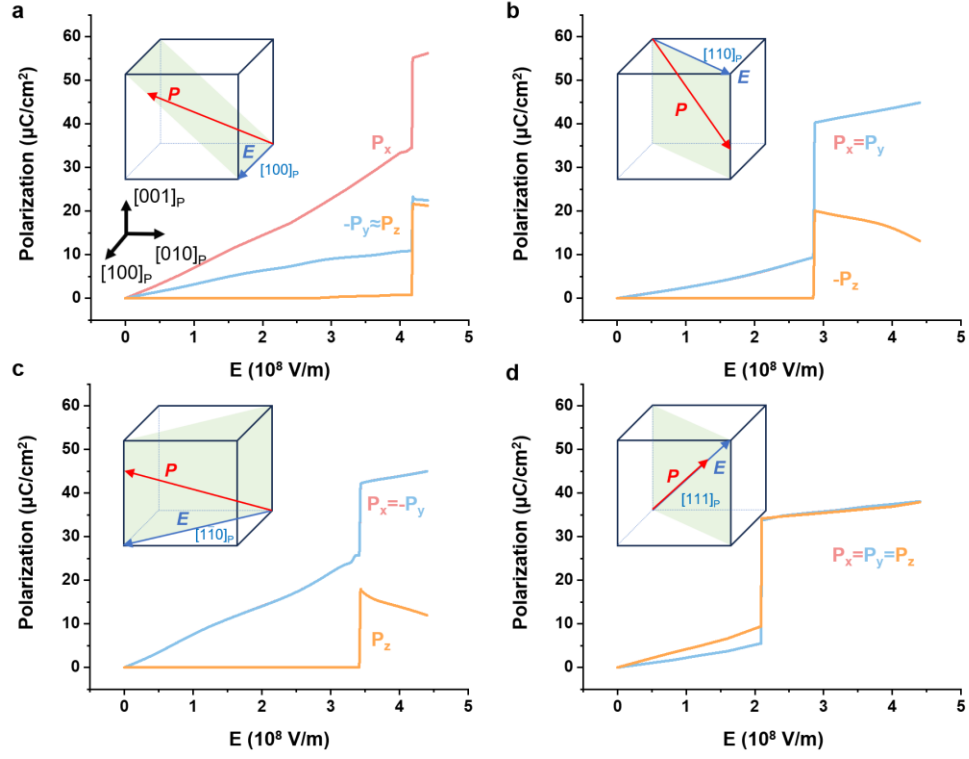
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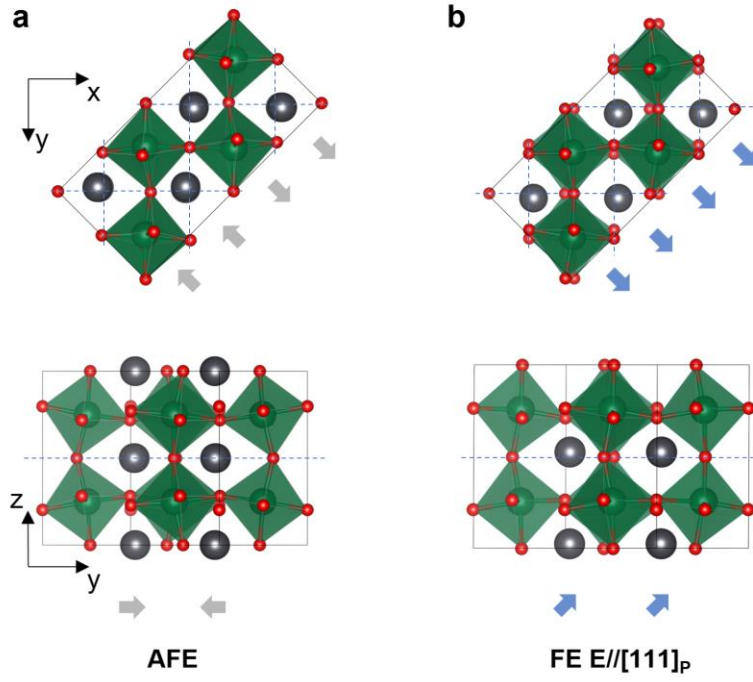
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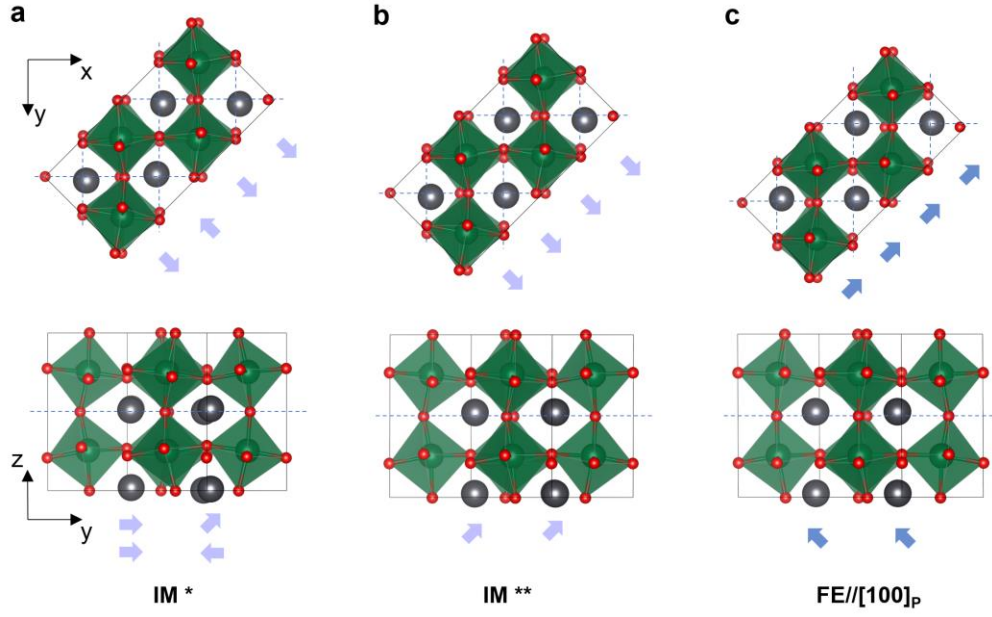
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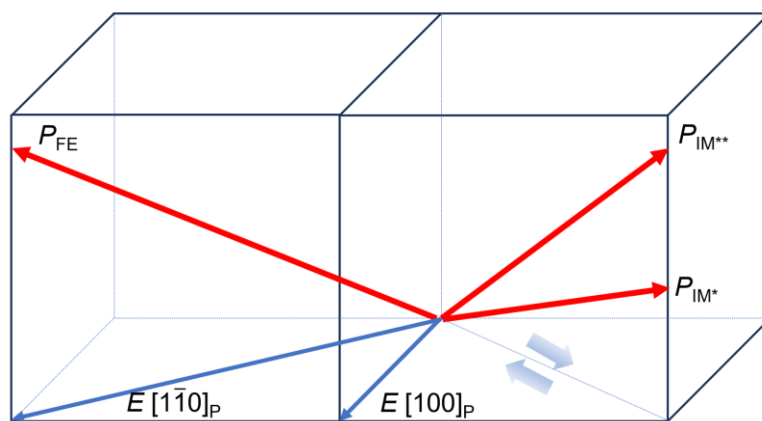
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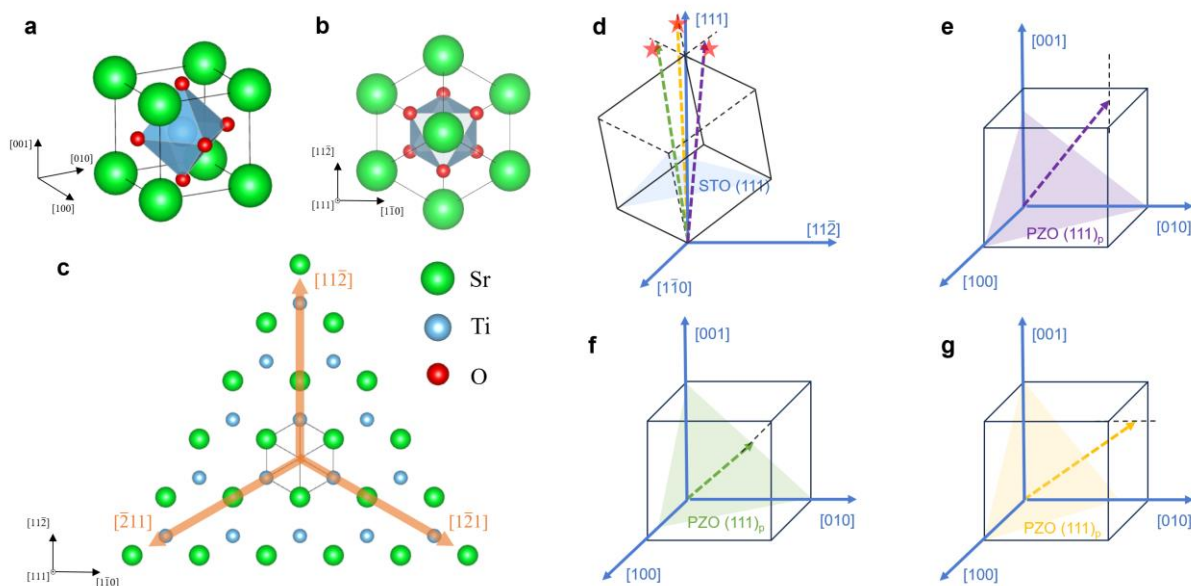
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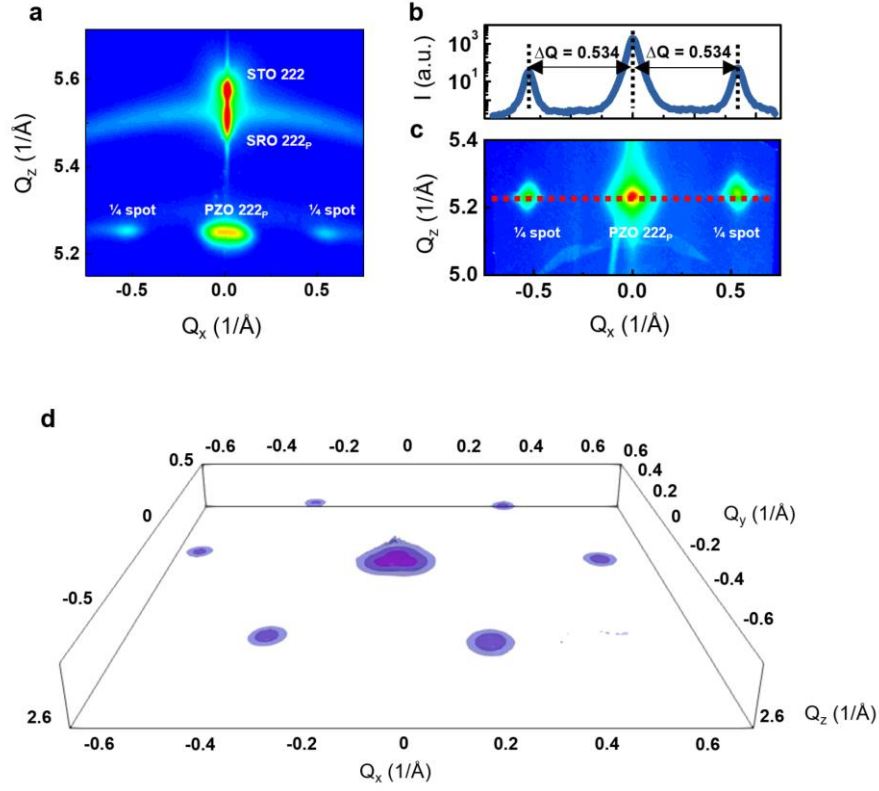
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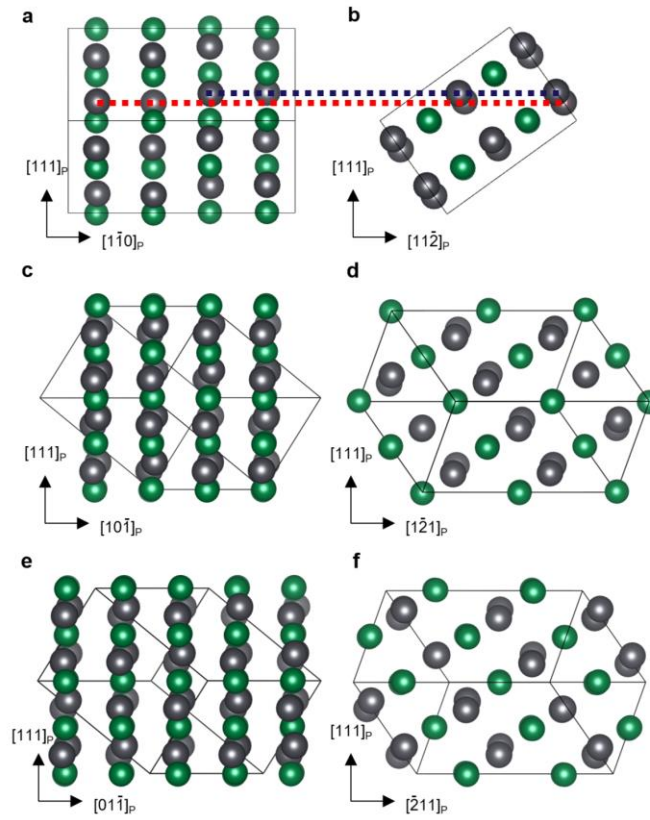
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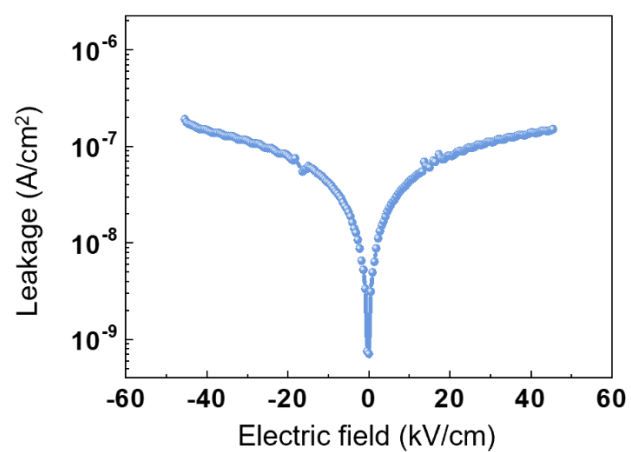
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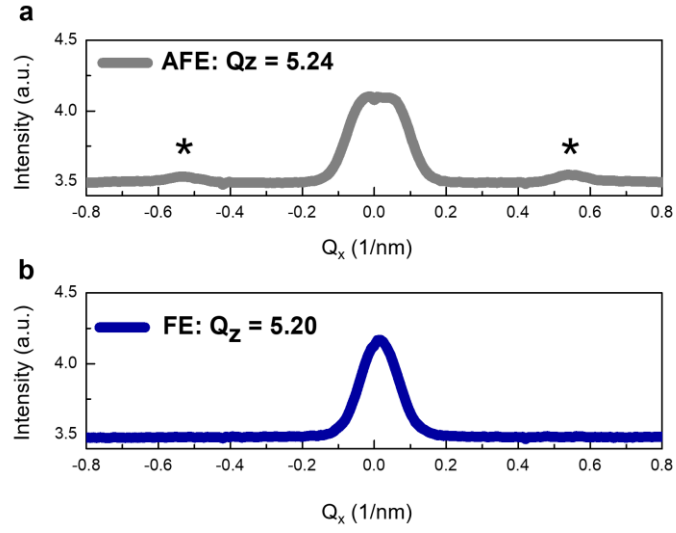
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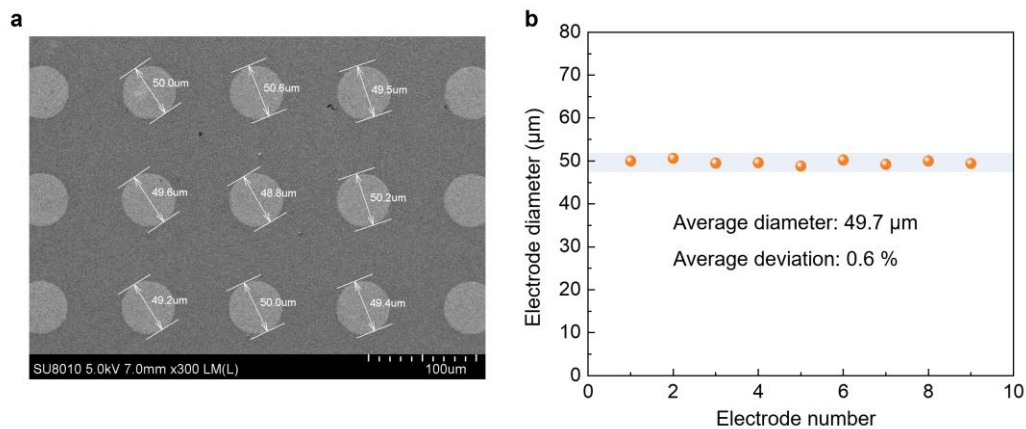
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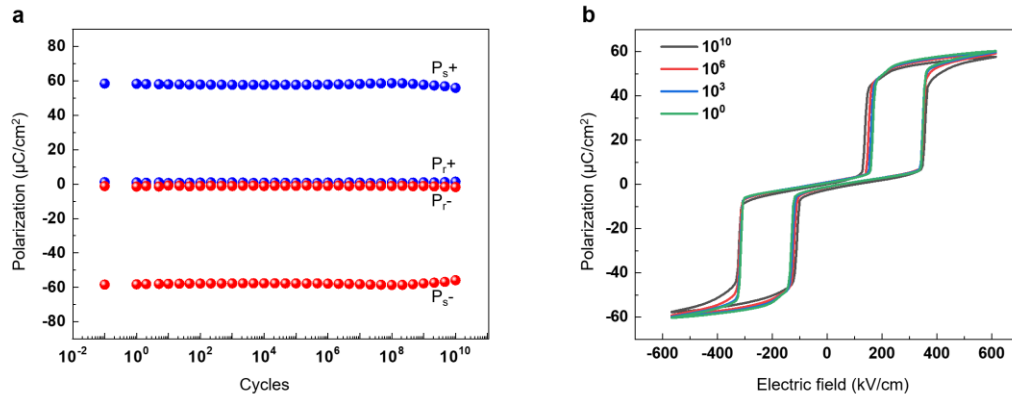
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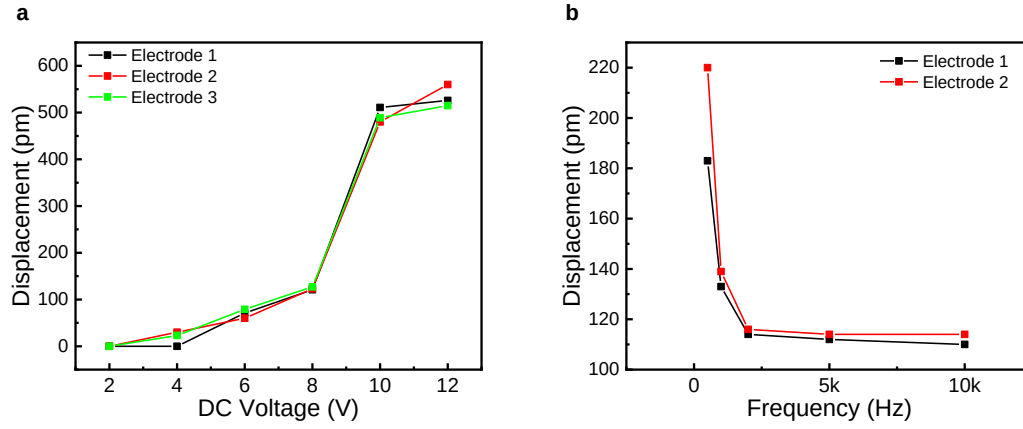
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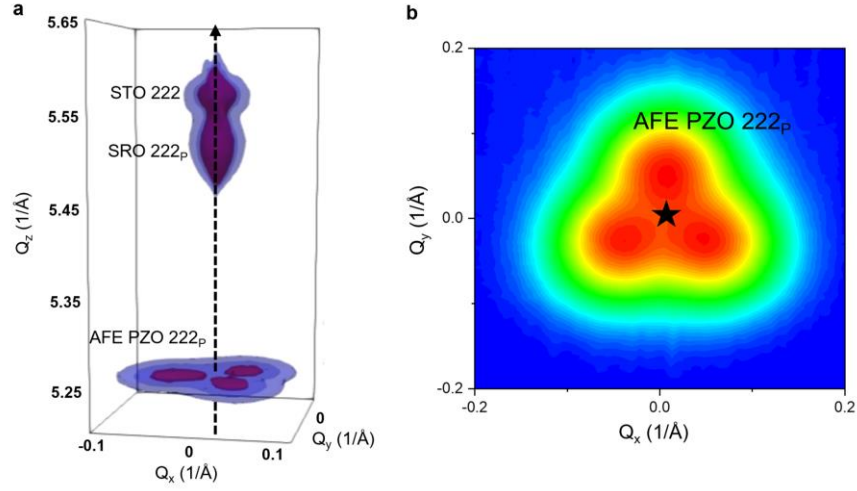
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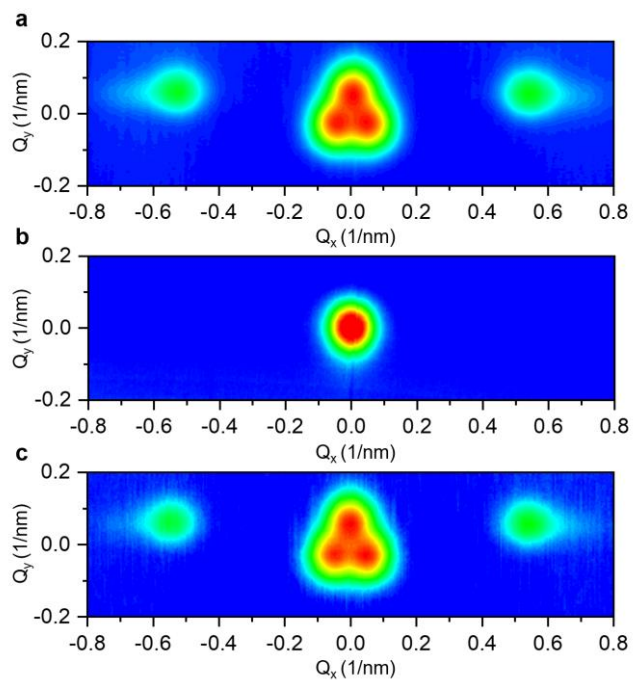
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Supplementary Fig. 16 In-situ characterization of in-plane reciprocal space mapping around PZO 222_p-spot. **a**, before, **b**, during and **c**, after applying electric field over the critical switching point.

Supplementary Table 1. Structure parameters of AFE *Pbam* and FE *R3c* phases of PbZrO_3 from DFT results.

DFT results	AFE	FE (Hexagonal axis)	FE (Rhombohedral axis)
a (Å)	5.87	5.84	5.87
b (Å)	11.77	5.84	5.87
c (Å)	8.18	14.41	5.87
α (°)	90	90	59.70
β (°)	90	90	59.70
γ (°)	90	120	59.70
Space group	<i>Pbam</i>	<i>R3c</i>	<i>R3c</i>

Supplementary Table 2 Comparison of structure parameters derived from In-situ experiment and DFT results.

	In-situ Results	DFT Results
a (Å)	4.147 ± 0.004	4.14
b (Å)	4.144 ± 0.003	4.14
c (Å)	4.147 ± 0.006	4.14
α (°)	89.61 ± 0.12	89.73
β (°)	89.53 ± 0.14	89.73
γ (°)	89.52 ± 0.07	89.73

Supplementary Table 3 Comparison of structure parameters of (111)_P-oriented PZO thin film and PZO bulk in pseudocubic axes.

Lattice	Thin film	Bulk	Strain
a_p (Å)	4.113	4.16	-1.13%
b_p (Å)	4.152	4.16	-0.19%
c_p (Å)	4.100	4.11	-0.24%

Supplementary Note 1. Atomistic simulations of AFE-to-FE phase transition

The polarization and volume expansion evolution of PbZrO_3 under electric fields are presented in Supplementary Fig. 2. With increasing electric field, the obvious jump of polarization and volume expansion indicate the occurrence of AFE-FE phase transition. It can be concluded that PbZrO_3 under $[111]_p$ field exhibit the largest polarization and volume expansion as well as the smallest critical electric field. The merits of $[111]_p$ field on PbZrO_3 can be attribute to the $[111]_p$ -preferred polarization in the field-induced ferroelectric structure. When the polarization switches to the $[111]_p$ direction, the electric field is collinear with the polarization and a maximum of effective electric field can be applied to the electric dipoles. As a result, the electrostatic energy can be fully minimized by polar dipole elongation and volume expansion.

Meanwhile, it is interesting to note that the results under electric field with $[110]_p$ and $[1\bar{1}0]_p$ direction exhibit nearly the same trend after AFE to FE phase transition, indicating that the field-induced structure and electric field geometry are symmetric in both conditions. This can be originated from the coupling between orientation symmetry of electric field along $[110]_p$ and $[1\bar{1}0]_p$ and structure symmetry of polarization along $[111]_p$ and $[1\bar{1}1]_p$. The diverse in their transition points can be attributed to the angle between initial antipolar dipole orientation and electric field direction, providing different driving force for AFE-to-FE phase transition with $[110]_p$ - and $[1\bar{1}0]_p$ - fields.

In FE materials, the direction of polarization is usually used to reflect the structure symmetry. To analysis the structure symmetry of field-induced FE structure, the polarizations during electric field increase are projected to $[100]_p$, $[010]_p$, and $[001]_p$ direction as P_x , P_y , and P_z , respectively. From Supplementary Fig. 3a, the absolute value of P_y and P_z are nearly the same while P_x shows larger value, result in the deviation from rhombohedral to monoclinic structure. The difference between P_x and other two polarization parameters can be attribute to the $[100]$ field, which can drag polarization close to $[100]_p$ direction and increase P_x to reduce the electrostatic energy. Similarly, electric field along $[110]_p$ and $[1\bar{1}0]_p$ would simultaneously enhance P_x , and P_y and result in monoclinic structure with $P_x = P_y > P_z$ as shown in Supplementary Fig. 3b and 3c. In contrast, when electric field point along $[111]_p$ direction, the polarization of rhombohedral structure are elongated equally along three directions as $P_x = P_y = P_z$ as shown in Supplementary Fig. 3d. Taking the antiphase rotation along $[100]_p$, $[010]_p$, and $[001]_p$ into consideration, the structure symmetry can be deduced as Cc for FE $[100]_p$, FE $[110]_p$, FE $[1\bar{1}0]_p$, *versus* $R3c$ for FE $[111]_p$, respectively.

Supplementary Note 2. Selective AFE-to-FE phase transition pathway

NEB calculation reveal that structure evolution from AFE to FE phase experience no transient state under electric field along $[111]_P$ and $[110]_P$. Taking the condition under $[111]_P$ -electric field for example, the AFE structure are presented in Supplementary Fig. 4a. The upper panel clearly shows the in-plane antipolar dipoles pointing along the $[110]_P$ direction with $\uparrow\uparrow\downarrow\downarrow$ modulation and antiphase octahedral rotation along $[100]_P$ and $[010]_P$ direction. The lower panel shows the absence out-of-plane polarization and antiphase octahedral rotation. During the structure evolution from AFE to FE, the field-induced FE structure under $[111]_P$ field can be directly obtained in Supplementary Fig. 4b, which can be seen as one-step structure phase transition as expected in conventional AFE materials. As compared with the original AFE structure, the antipolar dipole modulation disappear and all dipole switch to the same direction. The polar dipoles exhibit an out-of-plane polarization projection, giving rise to the $[111]_P$ -oriented polarization. Meanwhile, antiphase octahedral rotation appears along $[001]$ direction. As a results, one-step AFE-to-FE phase transition can be achieved under $[111]_P$ field by polarization switching to $[111]_P$ direction and antiphase octahedral rotation along $[001]_P$ direction simultaneously. The situation under $[110]_P$ -electric field is similar to that under $[111]_P$ field, and complete transition process can be seen in Supplemental Video S1 and S2.

Multistep phase transition can be observed under $[100]_P$ -electric field. Two transient states appear during AFE to FE phase transition. The IM* state as shown in Supplementary Fig. 5a exhibit ferrielectric structure with partially antipolar dipole switching from AFE structure. Simultaneously, out-of-plane polarization and antiphase rotation appear. Furthermore, IM** structure shows fully polarized dipoles along $[111]_P$ direction and antiphase rotation along $[001]_P$. This transient state is the same/similar with the final FE $[111]_P$ and FE $[110]_P$ structure. However, the polarization can be further switched to $[1\bar{1}0]_P$ direction to reach FE $[100]_P$ structure due to the considerable angle between external electric field and $[111]_P$ -oriented polarization, causing extra electrostatic energy gain for dipole switching. It is also interesting to note that during the transition from IM** to FE $[100]_P$, the octahedral rotation along $[100]_P$ direction inversely rotate so as to assist the **dipole reorientation**. The situation under $[1\bar{1}0]_P$ -electric field is similar to that under $[100]_P$ -electric field, and complete transition process can be seen in Supplemental Video S3 and S4.

Supplementary Note 3. Examination of AFE thin-film structure

As shown in Supplementary Fig. 8a, three-fold PZO 222_P main spots and satellite 1/4 superstructure diffraction spots can be observed along the $[1\bar{1}0]_P$ direction. The modulation period can be calculated by the distance between main spot and superstructure diffraction spot. To obtain the highest in-plane intensity distribution crossing the main spot and 1/4 superstructure diffraction spot, reciprocal space mapping and line scans are conducted crossing one of the three splitting main spots as presented in Supplementary Figs. 8b and 8c. The real space modulation period can be calculated to be $1/2\pi\Delta Q = 11.76 \text{ \AA}$, which is equal to the results in bulk PbZrO₃ thin films. 3D view of hexagonal satellite superstructure diffraction spot together with three-fold main spot are provided in Supplementary Fig. 8d, with this hexagonal feature also provides the evidence of 60°/120° domains. It is also interesting to note that although this kind of orientational domains present in $[111]_P$ -oriented PbZrO₃ thin films, the antipolar dipoles in different orientation domains exhibit triple rotation symmetry and the same tilt angle from out-of-plane direction, which can be estimated by angle between two vectors as:

$$\delta = \arccos \frac{[111] \cdot [110]}{|[111]| |[110]|} = 35.26^\circ.$$

A thorough comparison of various zone axes typically used in cross-section imaging of $[111]_P$ -oriented thin films (Supplementary Fig. 9), it can be seen that projecting along the $[11\bar{2}]_P$ zone axis is a viable approach to effectively capture the antiferroelectric modulation. It is noted that in AFE PbZrO₃ structure, the pseudo tetragonal structure with AFE modulation along $[1\bar{1}0]_P$ results in the degeneration of $[11\bar{2}]_P$, $[1\bar{2}1]_P$ and $[\bar{2}11]_P$ axis, which are usually overlooked in FE structure analysis. However, the TEM sample are prepared within the SrTiO₃ geometry, where the cubic structure exhibit highly symmetric features with exactly equivalent $[11\bar{2}]$, $[1\bar{2}1]$ and $[\bar{2}11]$ axis. Therefore, if one overlooks the degeneration and accidentally selects TEM image areas with $[1\bar{2}1]_P$ and $[\bar{2}11]_P$ zone axis of AFE crystal, the antipolar modulation may not be observed, potentially causing incorrect conclusions. It should be noted that Pb²⁺ and Zr⁴⁺ columns still exhibit slight overlap along this zone axis, which would bring in potential inaccuracies in determining precise atomic positions, and consequently may lead to the deviation in dipole orientation in the mapping.

Supplementary Note 4. Electrode area and polarization correction

The ultraviolet lithography (NXQ4006. Ultraviolet wavelength $\lambda = 385$ nm) and contact exposure method were used to transfer the electrode pattern, which provide the equipment accuracy less than 1 μm . Then magnetron sputtering (Arrayed Materials RS-M) was used to fabricate the top-electrode Pt, and remove the photoresist with acetone. For the hysteresis-loop measurement, the circular electrodes were used with a diameter of 50 μm from the mask. To calibrate the electrode area, the electrode diameter was measured under scanning electron microscopy (SEM). As shown in Supplementary Fig. 12, the electrode diameters from 9 individual electrodes are all around 50 μm , with average error less than $\sim 0.6\%$. Considering the electrode area is proportional to the square of the diameter, the average error of the electrode area and corresponding polarization intensity is around 1.2%, which have negligible influence on the polarization calculation.

Supplementary Note 5. Electromechanical response of PZO (100)_p

While PZO (111)_p exhibit digital electromechanical response, PZO (100)_p behaves much different. As shown Supplementary Fig. 14a, it can be clear seen that PZO (100)_p exhibit an analog response, where the displacement increases continuously at a wide voltage range. In contrast, the displacement of PZO (111)_p show a sharp switching at a critical point, representing a typical digital response. For PZO (100)_p, the electric field-induced AFE-FE transition exhibit multistep phase transition and experience intermediated ferrielectric phases. These metastable ferrielectric phase is competitively distributed on the phase transition path way between AFE and FE phase. Considering the polar structure of the metastable ferrielectric phase, the displacement would be sensitive to external electric field, leading to the continuous analog response. In comparison, the phase transition of PZO (111)_p shows one-step sharp transition, and the nonpolar AFE structure is not sensitive to external electric field when the field is below the critical transition point. Therefore, the displacement of PZO (111)_p exhibit digital responses.

The displacement of PZO (100)_p under different frequency are characterized as well. As shown in Supplementary Fig. 14b, the displacement of PZO (100)_p show obvious frequency dependence. The lower frequency would lead to higher displacement. This phenomenon is usually observed in systems with competing ferroic order¹, where the domain wall and interphase boundary motion under electric field may account for the frequency dependent behavior. While PZO (100)_p would experience competitive ferrielectric phase during phase transition, the competing ferroic orders can therefore possibly attributed to the frequency dependent behavior. Meanwhile, possible electrochemical effects such as the electric-field-induced rearrangement of defects^{2, 3} or Schottky barrier⁴ may also contribute to the electromechanical response.

Supplementary Note 6. The origin of triple splitting PZO (111)_P spot and scanning geometry

The triple rotation symmetry of (111)-oriented cubic SrTiO₃ substrate can be represent in Supplementary Fig. 7. While the cubic SrTiO₃ substrate is used to epitaxial grow the PZO single crystal film, the (111) plane of SrTiO₃ is in-plane and act as the interface between SrTiO₃ and PZO. As shown in Supplementary Fig. 7a, by looking at the interface in the out-of-plane [111] direction, the atoms are arranged in a hexagonal in Supplementary Fig. 7b. Thanks to the cubic feature of SrTiO₃, where $a = b = c$, this arrangement would give birth to the triple rotation symmetry around the out-of-plane [111] axis (Supplementary Fig. 7c). However, considering the pseudo tetragonal feature of PZO, where $a_p = b_p = 4.16 \text{ \AA}$ and $c_p = 4.11 \text{ \AA}$, the short c_p would broken the triple rotation symmetry. The (111)_P plane have three kinds of tilts as c_p of PZO can pair either with a , or b , or c of SrTiO₃ substrate, resulting in the triple splitting of PZO(111)_P diffraction (Supplementary Fig. 7d-g). Considering the connection of these three kinds of tilting PZO domains, they can rotate 60° or 120° to coincide with each other, therefore constituting the proposed 60° or 120° domains. It should be also noted that the 60°/120° domains do not mean they are only two structural domains, instead, it means that the neighboring domains are rotated by 60° or 120° with respect to each other.

The difference between $\theta/2\theta$ line scan and RSM can be understood in Supplementary Fig. 15. As previously discussed, the (111)_P plane of PZO would tilt from the out-of-plane direction due to the shorter c_p axes, causing the three PZO(111)_P diffraction spots all deviate from the out-of-plane direction, forming the triple splitting spots as the RSM revealed in Supplementary Fig. 15a. However, the $\theta/2\theta$ line scan are strictly along out-of-plane direction, therefore, the line scan could not cross any of the three PZO(111)_P diffraction spots, but the center of the triangle (black pentagram in Supplementary Fig. 15b) the three spots forms, therefore resulting in a single diffraction peak.

Supplementary Note 7. Discussion on the type of AFE-FE phase transition relating to the digital responses

The digital response can be attributed to the sharp first-order AFE-FE phase transition, where the volume changes dramatically at the critical transition point. In contrast, a second-order phase transition, characterized by a continuous change in structure with respect to the increasing or decreasing external electric field, would result in an analog electromechanical response.

The displacive and order-disorder phenomena are usually considered as the dynamics of temperature-driven ferroelectric or antiferroelectric phase transition⁵. When a long wavelength optic mode frequency slow down with decreasing temperature and freezes out at transition temperature, the corresponding ionic displacement would result in the polar or antipolar structure, which can be seen as the displacive transition. In contrast, ions already occupy various equivalent lattice sites, hopping between those dynamically above transition temperature, and into either of these sites at transition temperature, giving birth to the order-disorder transition. In this manuscript, the situation can be neither displacive nor order-disorder. In contrast, the AFE-to-FE phase transition can be reconstructive phase transition, where the lack of group-subgroup relation between the AFE and FE phases causes significant strains from the initial to the final phase^{6, 7}. At zero field, AFE PZO possesses orthorhombic *Pbam* space group and the Pb ions in PZO are strictly arranged according to the antiparallel displacement. With increasing the electric field to the transition point, the antipolar dipoles switch to the same direction uniformly, resulting in the reconstructive phase transition to FE PZO with rhombohedral *R3c* space group for (111)-oriented PZO and digital electromechanical responses.

Supplementary Note 8. Discussion on other factors potentially contributing to digital electromechanical responses

Some factors that would result in electromechanical response include piezoelectricity, electrostriction, chemopiezoelectric effect and AFE-FE structural phase transition. Piezoelectricity widely exists in centrosymmetric-broken materials while electrostriction can exist among all dielectrics. Both piezoelectricity and electrostriction can provide electric-field induced strains. However, piezoelectricity usually show linearly dependence on the external field, and electrostriction is proportional to the square of the external field. For (111)_p-oriented PZO, before the jump of digital strain, there is negligible electromechanical responses, indicating that the piezoelectricity and electrostriction could not contribute to the observed large digital electrostrain. Considering the recent defect migration-driven strain (*i.e.*, chemopiezoelectric effect), where large strain could be induced by external electric field, it is highly frequency dependent and change continuously under electric field^{2,3}. This is clear not the case in this manuscript, where the digital strain shows frequency independence. Finally, considering the first-order field-driven AFE-FE structural phase transition reported here, both the DFT calculation and in-situ structural measurement confirmed the sharp lattice expansion during the AFE-FE transition under external field, which is fully consistent with the digital strain. Moreover, in the (111)_p-oriented PZO, the remanent polarization is extremely small, indicating that there is little ferroelectric phase concentration before AFE-FE phase transition, which would greatly eliminate the piezoelectric responses before the phase transition. After the AFE-FE phase transition, the piezoelectric response from the field-induced FE structure is also small as compared with the volume expansion during the structural phase transition, giving birth to the sharp contrast of digital electromechanical responses.

Supplementary Note 9. Reversible AFE structure under electric field cycling

The reciprocal space mappings are performed by focusing on the region around main reflections of 222_P -spot and nearby superstructure spots before, during, and after applying the electric field over the critical switching point.

In Supplementary Fig. 16a, the main-Bragg-spot splitting of $(222)_P$ reflections can be seen before applying the electric field, indicating the pseudo tetragonal structural feature of AFE PZO. Meanwhile the superstructure spots are in line with one of the triple-splitting main spots, which denote the corresponding AFE-order induced four-fold lattice increase. As increasing the electric field, the AFE-to-FE transition happens and triple splitting main spots merge into one spot in Supplementary Fig. 16b, denoting the crystal symmetry changes. Moreover, the satellite superstructure spot disappears, confirming the annihilation of AFE order and completion of AFE-to-FE transition. When the electric field is removed, as shown in Supplementary Fig. 16c, the superstructure spots and triple splitting of main reflections reappear. These features indicate the recovery of AFE structure at zero field, which is consistent with the proposed reversible AFE-FE phase transition.

Supplementary Note 10. The procedure of in-situ reciprocal space mapping

During the in-situ measurement, the wide-range main Bragg spots at zero field are collected first, including the triple splitting of main spots as provided in Fig. 5c. While it takes time about 15 minutes to finish one wide-range scan, the voltage is applied slowly in 1 V per step. During increasing the voltage, the evolution of the main 222_P spot can be noticed by fixing the diffraction geometry and detector at corresponding position. When the applied voltage reaches at 8 V, the splitting of main spots totally merge into one, indicating the finish of AFE-to-FE transition. Then 3-dimensional reciprocal space mapping with the same scan condition is performed with holding on the applied voltage, giving the main Bragg spots of FE PZO as shown in Fig. 5e. Finally, we quickly removed the electric field and reconducted the same zero-field measurement to confirm the reversible AFE-FE structural phase transition.

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