

# Ideal antiferroelectricity with large digital electrostrain in PbZrO<sub>3</sub> epitaxial Thin Films

Corresponding Author: Professor Zuhuang Chen

**This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.**

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The author presents an effective methodology for designing ideal antiferroelectric thin film materials, which holds significant guiding implications for both lead-free and lead-containing antiferroelectric thin film materials. Furthermore, this approach provides crucial guidance for the application of antiferroelectric materials in various fields. However, several issues must be addressed by the author before the manuscript can be accepted.

1. It would be beneficial to provide the electrode area diagram used for measuring the P-E hysteresis loop to verify the accuracy and authenticity of the polarization intensity measurements.
2. How can the accuracy of the test results for 60  $\mu\text{C}/\text{cm}^2$  be validated? For ferroelectric materials, the Pund test is commonly employed to assess their properties. What method can be used to validate antiferroelectric materials?
3. The authors should present antiferroelectric hysteresis loops obtained after various fatigue to demonstrate the superior anti-fatigue properties of the PZO films. Does  $P_r$  increase after fatigue?
4. Regarding the comparison of  $P_{\text{max}}$  and  $P_r$  for AgNbO<sub>3</sub>, PbZrO<sub>3</sub>, PbHfO<sub>3</sub>, PbSnO<sub>3</sub>, and NaNbO<sub>3</sub> films as shown in Fig. 3(d), the author should consult the most recent research findings. For instance, the latest sol-gel combined with plasma technology has achieved a  $P_{\text{max}}$  of 58.6  $\mu\text{C}/\text{cm}^2$  and a  $P_r$  of 7.44  $\mu\text{C}/\text{cm}^2$  for AgNbO<sub>3</sub>. Additionally, it would be beneficial to design a comprehensive parameter that reflects the advantages and disadvantages of antiferroelectric properties, such as  $(P_{\text{max}} - P_r) / P_r$ . Alternatively, the author could propose a superior factor for evaluating antiferroelectricity.
5. Why do the results in Fig. 4 (b) and Fig. 4 (d) differ? In Fig. 4 (b), an evident displacement jump occurs at approximately 7V when the electric field is applied, whereas in Fig. 4 (d), the corresponding jump is observed at around 8V. What could be the underlying reasons for this discrepancy? Please provide an explanation.
6. The author should provide a detailed explanation of the underlying mechanisms that lead to frequency independence in digital electromechanical behavior.
7. Fig. 4 (b)-(e) should include the data of PZO(100) film for comparison and explanation to validate the accuracy of the conclusions. Additionally, it would be investigated whether frequency independence also holds for this sample. If it exists, for what reason? Or if it doesn't exist, for what reason?
8. The author duplicated Supplementary Table 1 twice in the supplementary material. The author should carefully review and revise the manuscript to ensure accuracy and consistency.
9. There are multiple grammatical and structural errors in the article that require correction. For example, consider the following sentence: Moreover, a new ferrielectric structure has been observed recently in (100)-oriented PZO films. indicating that there could be a transient state between the AFE and FE structures under an electric field<sup>19, 20</sup>.
10. The reference format in the paper lacks consistency, which is an issue that should not be present in a scholarly manuscript.

Reviewer #2

(Remarks to the Author)

This study, reported by Zuhuang Chen et al., presents atomistic models for controlled antiferroelectric-ferroelectric phase transitions along specific crystallographic directions. (111)-oriented PbZrO<sub>3</sub> thin films achieved nearly ideal antiferroelectricity with square double hysteresis loops, high polarization, negligible remnant polarization, fast response, and fatigue-free performance, which solve the typical problem of Distorted Switching Behavior in the present related AFE studies. In addition, a significant bipolar, frequency-independent digital electrostrain (~0.83%) was observed, driven by field-

induced structural transitions. This interesting manuscript presents high-quality and convincing data that deserves publication. However, some minor questions still need to be addressed before publishing.

1. According to the authors, the triple-splitting observed in the out-of-plane RSM of the PZO (111) diffraction, as shown in the inset of Fig. 2(a), is not easily understood. Based on my knowledge, these three spots result from the alignment of the PZO c-axis along each of the three cubic STO axes. However, the correlation with 60°/120° domains remains unclear and requires a clearer explanation. For example, how do two domains contribute to three spots? What is the rotation symmetry for each domain? There should be a clearer definition for these domains. Additionally, the designation of 60°/120° domains may not be precise, as PZO lacks 3-fold or 6-fold symmetry. If possible, please identify the actual angles of these domains to enhance accuracy.

Additionally, please address why the  $\theta/2\theta$  line scan shows only a single diffraction peak while the RSM reveals a triple-splitting for the same diffraction Miller index. Clarifying this difference is crucial for understanding the underlying structural characteristics.

2. In Fig. 4c, using “strain” to describe the lattice change during the phase transition may lead to confusion, as the film could already experience biaxial strain from the substrate. Therefore, it would not be zero even without applying the bias if using a broad definition of “strain”. I recommend the authors redefine the longitudinal axis title as “electrostrain” in the figure caption for greater clarity. In addition, please also provide the strain information of the PZO film caused by the STO substrate.

3. In some figures, the data lacks clear and sufficient labeling.

For example, in Fig. 2c-e, the STEM images should include axis or orientation information to provide proper context.

In Fig. 3a, the hysteresis and switching current loops are not clearly identified in the figure or its caption. Please ensure these are explicitly labeled for clarity.

### Reviewer #3

(Remarks to the Author)

Journal: Nature Communication

Paper: NCOMMS-24-82107

Authors: Zuhuang Chen, Yangyang Si, Ningbo Fan, Yongqi Dong, Zhen Ye, Shiqing Deng, Yijie Li, Chao Zhou, Qibin Zeng, Lu You, Yimei Zhu, Zhenlin Luo, SUJIT DAS, L. Bellaiche, Bin Xu, and Huajun Liu

Title: Ideal antiferroelectricity with large digital electrostrain in PbZrO<sub>3</sub> epitaxial Thin Films

I have reviewed the manuscript "Ideal antiferroelectricity with large digital electro strain in PbZrO<sub>3</sub> epitaxial Thin Films" by Zuhuang Chen et al.

This paper reports the production of the PbZrO<sub>3</sub> epitaxial thin film in (111)P with preservation of the antiferroelectric order. Such a preservation is a challenge and it is fundamental to the potential application of digital strain and the mechanism of swing motion devices. Moreover, they apply atomistic models to propose the mechanism of the antiferroelectric to ferroelectric phase transition as a function of the electric field in PbZrO<sub>3</sub> thin films. After the electromechanical characterization, in-situ XRD was an important tool to evaluate their hypothesis.

The methodology and the way they show the problem are excellent. I hope to see the application of this pathway to evaluate the crystallographic phase transition of all the other AFE materials. Therefore, their methodology will be widely cited. The combination of this methodology and different AFE thin films exploring different AFE-FE phase transition mechanisms would be a complete publication of nature (not communication) complete publication.

The manuscript provides important findings about antiferroelectricity, and phase transition mechanisms and I think it is worth publishing in Nature Communication with minor revisions.

A few comments and questions on the text follow:

#### Abstract:

1 - by definition, displacive polar and antipolar materials are anisotropic. What do you mean by orientation design? Is the polarization rotation possible into monoclinic intermediate phase? Terms such as polarization rotation and extension should be explored all over the discussion.

2 – Every time you use crystallographic direction there it is hard to understand what direction you are talking about. For example: thin film grows in (111) sound that the octahedron is oriented in (111) (Glazer reference as the prototype). However, the direction you use at the TEM results sound to be related to the Pbam reference. I strongly recommend you use the subscript “P” when you are using the octahedra reference. This is worse when you are using the semi-inter superlattice peak, as the semi-inter are always referent to the prototype structure. (Obs: I checked the indexation of the semi-inter and it is correct).

Therefore, it sounds like the [11-2] you mention in HAADF is the [110]P. The support information with the projection is in reference of Pbam and is correct.

#### Introduction:

3 - General question: what is the digital, analogue and their relation to displacive and order-disorder phenomena?

4 - In the Pbam space group there is 8 oxygen octahedrons. The notation of the antipolar perovskite structure in orthorhombic symmetry Pbam is not taking into account the pseudocubic (prototype) direction of a perovskite structure. Taking into account the prototype structure, what would be the direction of the antiphase dipoles?

#### Atomistic modeling of AFE-FE phase transition.

5 - There is confusion when one says pseudo-tetragonal symmetry and cites the space group Pbam (orthorhombic group).

You should justify or at least use the subscript indices P (from prototype) at the lattice parameters ( $a_P$  and  $b_P$ ) with the equation to convert them from the orthorhombic space group (Pbam) to the pseudo tetragonal.

In-situ structural analysis of antiferroelectric and field-induced ferroelectric phase

6 - You mention that the “structural phase transition is the major contribution to the observed large digital strain”. What would be the other hypothesis for the strain? Is it possible to be from another thing that is not the lattice?

7 - You affirm that the “splitting of main spots is clearly from the as-grown film, implying the existence of multidomain structure”. The disappearance of the main spots splitting indicated the formation of a single domain. How was it when the electric field was removed?

8 - How could you be sure about the phase transition to rhombohedral if you looked at only one direction of the thin film? Did you compare with lattice parameters of monoclinic phase (DFT) as well?

9 - What was the applied electric field in the in-situ measurement? The procedure of electric field application is not clear.

Typing errors:

Page3. There is a dot followed by a non-capital latter. I think this dot is a comma.

Page6 – change HADDF by HAADF.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The author achieved ideal antiferroelectricity with square double hysteresis loop, large saturated polarization ( $\sim 60 \mu\text{C}/\text{cm}^2$ ), near-zero remnant polarization, fast response time ( $\sim 75 \text{ ns}$ ), and near-fatigue-free performance ( $\sim 10^{10}$  cycles) in (111)P-oriented PbZrO<sub>3</sub> epitaxial thin films. Moreover, a bipolar and frequency-independent digital electrostrain ( $\sim 0.83\%$ ) were demonstrated in this archetype antiferroelectric system. This work holds significant importance for this field and related areas. It demonstrates advancement compared with existing literature. This work can support the conclusion and claim without the need for additional evidence. The data analysis, interpretation and conclusion are feasible and do not require further modification. The methodology is reasonable and the work meets the expected standards in my field. The method provides sufficient details to reproduce the work.

Reviewer #2

(Remarks to the Author)

The authors have provided clear responses to the questions, and the manuscript has been well reorganized. I have no further concerns regarding its acceptance.

Reviewer #3

(Remarks to the Author)

Dear Dr. Jiajun Zhu,

I am writing to inform you that I have reviewed the revised manuscript titled “Ideal antiferroelectricity with large digital electrostrain in PbZrO<sub>3</sub> epitaxial Thin Films” from Zuhuang Chen, Yangyang Si, Ningbo Fan, Yongqi Dong, Zhen Ye, Shiqing Deng, Yijie Li, Chao Zhou, Qibin Zeng, Lu You, Yimei Zhu, Zhenlin Luo, SUJIT DAS, L. Bellaiche, Bin Xu, and Huajun Liu. I am pleased to report that the authors have satisfactorily addressed all my comments and suggestions. The revisions have improved the quality and clarity of the manuscript.

Additionally, all discussions related to my comments have been incorporated into the text or included in the supplementary material. Some of my comments regarding crystallographic notations were challenging to verify, and the authors have carefully ensured the correct notation was added. They are to be commended for their thorough and meticulous work.

Therefore, I am happy to recommend accepting this manuscript for publication in Nature Communications.

Thank you for the opportunity to review this work. Please let me know if you need any further information.

Best regards,

Flávia Regina Estrada

Full Researcher

Brazilian Synchrotron Light Laboratory

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## Overall Response to Editor and Reviewers

We sincerely thank the editor and reviewers for their precious time and valuable comments on our manuscript. We have carefully considered all comments and made revisions accordingly, as reflected in the point-by-point response below. We believe that the revisions have significantly improved the quality of the manuscript and hope the reviewers find the updated version suitable for publication.

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### Reviewer #1

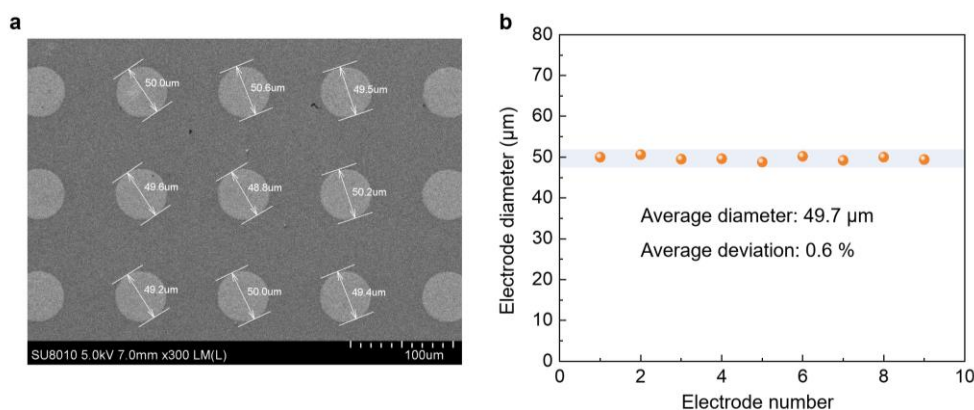
**General Comment:** The author presents an effective methodology for designing ideal antiferroelectric thin film materials, which holds significant guiding implications for both lead-free and lead-containing antiferroelectric thin film materials. Furthermore, this approach provides crucial guidance for the application of antiferroelectric materials in various fields. However, several issues must be addressed by the author before the manuscript can be accepted.

**Response:** We sincerely thank the reviewer for his/her positive evaluation and constructive comments, which have greatly helped improve the quality of the manuscript. Please find our detailed point-by-point response below.

**Comment 1.** It would be beneficial to provide the electrode area diagram used for measuring the P-E hysteresis loop to verify the accuracy and authenticity of the polarization intensity measurements.

**Response:** We thank the reviewer for this comment. Indeed, the accurate top-electrode area is essential for the measurement of *real* polarization. In this manuscript, we used ultraviolet lithography (NXQ4006. Ultraviolet wavelength  $\lambda = 385$  nm) and contact exposure method to transfer the electrode pattern, which provide the equipment accuracy less than 1  $\mu\text{m}$ . We then used magnetron sputtering (Arrayed Materials RS-M) to fabricate the top-electrode Pt layer, and remove the photoresist with acetone.

For the hysteresis-loop measurement, we used circular electrodes with a diameter of 50  $\mu\text{m}$  from the mask (Fig. R1). To calibrate the electrode area, we measured the electrode diameter under scanning electron microscopy (SEM). As shown in Fig. R1, the electrode diameters from 9 individual electrodes are all around 50  $\mu\text{m}$ , 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



**Fig. R1 Characterization of Pt electrode diameter under SEM. a,** SEM image of Pt electrode pattern; **b,** Plot of diameters of 9 individual Pt electrodes from **a**.

and corresponding polarization intensity is around 1.2%, which have negligible influence on the polarization calculation. We thank the reviewer again for this constructive suggestion, and we are pleased to add these to the Supplementary Fig. 12 and Supplementary Note 4 to illustrate and strengthen the reliability of the data.

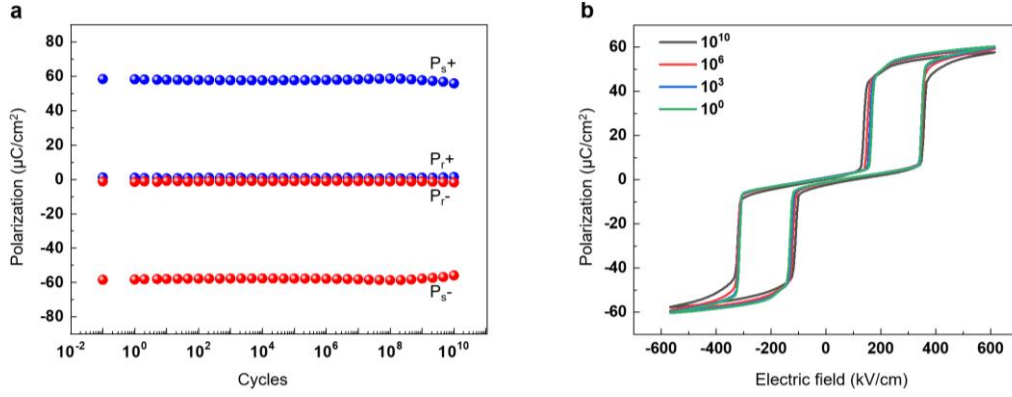
**Comment 2.** How can the accuracy of the test results for  $60 \mu\text{C}/\text{cm}^2$  be validated? For ferroelectric materials, the Pund test is commonly employed to assess their properties. What method can be used to validate antiferroelectric materials?

**Response:** Again, we thank the reviewer for this comment. For ferroelectric materials, PUND test is an effective method (using a series of voltage pulses and measuring the current transients) to obtain the switchable polarization while excluding the leakage and capacitive contributions<sup>1</sup>. However, for ideal antiferroelectric materials, the field-induced ferroelectric state is not stable, and the reversible AFE-FE phase transition inherently results in zero remanent polarization. Therefore, due to this intrinsic nature of antiferroelectric materials, the PUND test is not suitable for evaluating the effective polarization.

To validate the accuracy of test results, let us take the leakage contribution into account first. It has been widely noted that the existence of leakage current may result in the overestimated remanent polarization and distortion of hysteresis in leaky ferroelectrics and other nonlinear dielectrics<sup>1, 2</sup>. In this work, the hysteresis loop of the (111)<sub>P</sub>-oriented PZO film is square with near-zero remanent polarization, indicating a minimal leakage contribution on the polarization calculation. Instead, the hysteresis loops of leaky dielectrics are typically rounded at the top and/or the bottom of the loop. This is further supported by the leakage current measurements (Supplementary Fig. 10). At an electric field of  $40 \text{ kV}\cdot\text{cm}^{-1}$ , the leakage current density of our film is only  $\sim 10^{-7} \text{ A}\cdot\text{cm}^{-2}$ . Meanwhile, we also corrected the electrode area carefully to validate the accuracy of polarization measurement, which has been discussed in the response of Comment 1. Finally, the result of polarization is also highly reproducible across different samples during the experimental measurement, which would further validate the accuracy of the test. Additionally, the measured polarization values of  $\sim 40 \mu\text{C}/\text{cm}^2$  in our (100)<sub>P</sub>-oriented  $\text{PbZrO}_3$  films is consistent with previous experimental reports<sup>3-5</sup>, and  $\sim 60 \mu\text{C}/\text{cm}^2$  in our (111)<sub>P</sub>-oriented  $\text{PbZrO}_3$  films are very consistent with not only our own first-principles results, but also many other previous theoretical reports<sup>6-8</sup>. In summary, the three points discussed above, including the minimized leakage contribution, the corrected electrode area, and the reproducible measurement, would validate the results for  $60 \mu\text{C}/\text{cm}^2$  in this manuscript. Again, we totally agree with the Reviewer that careful consideration is necessary to obtain reliable polarization measurements in antiferroelectric samples with poor quality, where the leakage contribution is severe and cannot be eliminated.

**Comment 3.** The authors should present antiferroelectric hysteresis loops obtained after various fatigue to demonstrate the superior anti-fatigue properties of the PZO films. Does Pr increase after fatigue?

**Response:** We thank the reviewer for this constructive suggestion. Here we provided the hysteresis loops after  $10^0$ ,  $10^3$ ,  $10^6$ ,  $10^{10}$  switching cycles for comparison in Fig. R2. It's noted that the maximum polarization and remanent polarization remains stable before  $10^{10}$ -cycle fatigue measurement. After  $10^{10}$  cycles, the maximum polarization shows slight degradation, while the remanent polarization slightly increases simultaneously, indicating the beginning of material fatigue.

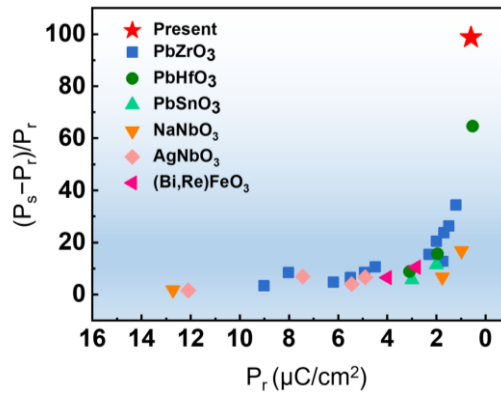


**Fig. R2 Fatigue performance of (111)-oriented PZO.** **a**, The maximum polarization and remanent polarization under electric field cycles. **b**, Double hysteresis loop of (111)-oriented PZO thin film after  $10^0$ ,  $10^3$ ,  $10^6$ ,  $10^{10}$  electric field cycles.

We thank the reviewer again for pointing this out and we are glad to add the hysteresis loops in Supplementary Fig. 13 to make the paper more solid.

**Comment 4.** Regarding the comparison of  $P_{\text{max}}$  and  $P_r$  for  $\text{AgNbO}_3$ ,  $\text{PbZrO}_3$ ,  $\text{PbHfO}_3$ ,  $\text{PbSnO}_3$ , and  $\text{NaNbO}_3$  films as shown in Fig. 3(d), the author should consult the most recent research findings. For instance, the latest sol-gel combined with plasma technology has achieved a  $P_{\text{max}}$  of  $58.6 \mu\text{C}/\text{cm}^2$  and a  $P_r$  of  $7.44 \mu\text{C}/\text{cm}^2$  for  $\text{AgNbO}_3$ . Additionally, it would be beneficial to design a comprehensive parameter that reflects the advantages and disadvantages of antiferroelectric properties, such as  $(P_{\text{max}} - P_r) / P_r$ . Alternatively, the author could propose a superior factor for evaluating antiferroelectricity.

**Response:** We thank the reviewer for this insightful suggestion. We completely agree with the reviewer's approach to define the antiferroelectric superior factor as  $(P_{\text{max}} - P_r) / P_r$ . This factor effectively incorporates both the maximum polarization and remanent polarization, providing a meaningful parameter to evaluate antiferroelectricity. We have updated Fig. 3(d) to include the antiferroelectric superior factor, and have also cited the most recent research findings for  $\text{AgNbO}_3$  (*J. Eur. Ceram. Soc.* 2024, 44, 2923-2933),  $\text{NaNbO}_3$  (*Nature* 2024, 633, 798-803), and  $\text{PbZrO}_3$  films (*Nature* 2025, 637, 1104-1110, *Nat. Mater.* 2024, 23, 944-950).



**Fig. R3 Comparison of superior factors and remanent polarization of our films with representative reported perovskite AFE thin films, including  $\text{PbZrO}_3$  thin films,  $\text{PbHfO}_3$  thin films,  $\text{PbSnO}_3$  thin films,  $(\text{Bi,Re})\text{FeO}_3$  thin films,  $\text{AgNbO}_3$  thin films, and  $\text{NaNbO}_3$  thin films.**

**Comment 5.** Why do the results in Fig. 4 (b) and Fig. 4 (d) differ? In Fig. 4 (b), an evident displacement jump occurs at approximately 7V when the electric field is applied, whereas in Fig. 4 (d), the corresponding jump is observed at around 8V. What could be the underlying reasons for this discrepancy? Please provide an explanation.

**Response:** We thank the reviewer for the careful reading. In this work, we performed the electromechanical measurement with many capacitors on different 5mm×5mm samples. While the AFE-FE transition is sharp for (111)<sub>P</sub>-oriented PZO films, any fluctuation would cause the deviation of critical transition point among different electrode. From Fig. 4(b), we can see the displacement jump to an unsaturated point at 7 V and saturate quickly at 8 V. Therefore, 7 V is close to and slightly higher than the critical point for the sharp AFE-FE transition. In Fig. 4(d), the displacement at 7 V show no jumps but a slight increase, then saturated at 8 V. This indicate 7 V is close to but slightly lower than the critical point. This variation can be attributed to the fluctuation of sample conditions. For example, the thin-film thickness can slightly vary among different samples, where multiple factors can introduce thickness variations, such as laser energy fluctuation, and relative position of sample and laser plume<sup>9</sup>.

**Comment 6.** The author should provide a detailed explanation of the underlying mechanisms that lead to frequency independence in digital electromechanical behavior.

**Response:** We thank the reviewer for this comment. Considering intrinsic property of antiferroelectricity, where the antipolar and polar phase are energetically close to each other, a first-order field-driven structural phase transition, characterized by a dramatic change in lattice structure at a critical electric field, would lead to a digital strain response. The corresponding driving force for the phase transition can be attributed to the electric-field induced increasement of electrostatic energy and entropy of AFE ground state, leading to an energetically favorable FE state under high field. Therefore, the most important factor that determine the phase transition is the external electric field. While the external electric field reach up to the critical transition point, the phase transition happens dramatically at nanosecond level (that is, within MHz-GHz frequency range) as revealed by pulse measurement in Fig. 3c in our manuscript. Therefore, the digital electromechanical behavior shows wide-range frequency independence as long as the frequency not exceed the switching dynamic limit.

We thank the reviewer again for this valuable suggestion and are pleased to incorporate the discussion into the manuscript as follows: “This frequency-independence behavior arises from the first-order, field-driven structural phase transition. When the external electric field reaches the critical transition point, the phase transition occurs on a nanosecond timescale (Fig. 3c). Therefore, the digital electromechanical behavior exhibits broad frequency independence, provided that the measurement frequency does not exceed the switching dynamics limit.”

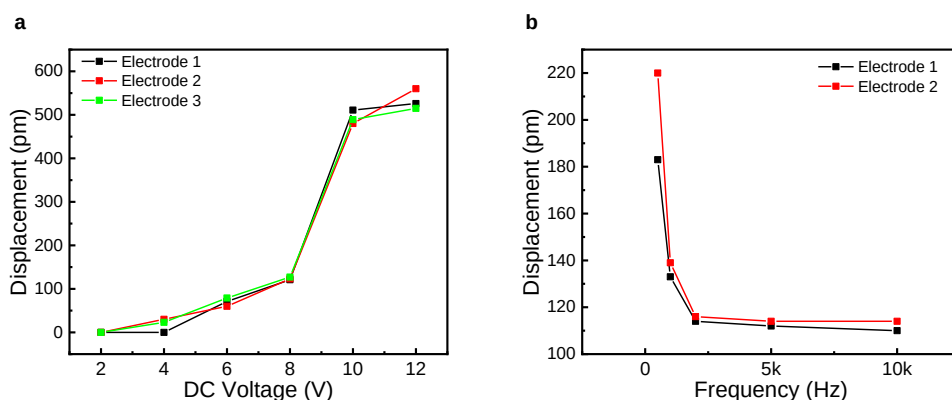
**Comment 7.** Fig. 4 (b)-(e) should include the data of PZO(100) film for comparison and explanation to validate the accuracy of the conclusions. Additionally, it would be investigated whether frequency independence also holds for this sample. If it exists, for what reason? Or if it doesn't exist, for what reason?

**Response:** We thank the reviewer for this comment. As shown in Fig. R4a, the displacement of (100)<sub>P</sub>-oriented PZO film is plotted for comparison. It can be clearly seen that the (100)<sub>P</sub> PZO film exhibits an analog response, where the displacement increases continuously at a wide voltage range.

In contrast, the displacement of (111)<sub>P</sub>-oriented PZO film shows a sharp switching at a critical point, representing a typical digital response. For PZO (100)<sub>P</sub>, the electric field-induced AFE-FE transition exhibits multistep phase transition and experiences several intermediated ferrielectric phases. These metastable ferrielectric phases are competitively distributed on the phase transition pathway between AFE and FE phases. Considering the polar structure of the metastable ferrielectric phases, the displacement would be sensitive to external electric field, leading to the continuous analog response.<sup>10</sup> In comparison, the phase transition of PZO (111)<sub>P</sub> 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)<sub>P</sub> exhibit digital responses.

We also measured the displacement of (100)<sub>P</sub>-oriented PZO film under different frequency. As shown in Fig. R4b, the displacement of (100)<sub>P</sub>-oriented PZO film shows obvious frequency dependence. The lower frequency would lead to higher displacement. This phenomenon is usually observed in systems with competing ferroic order<sup>10</sup>, where the domain wall and interphase boundary motion under electric field may account for the frequency dependent behavior. Here, the (100)<sub>P</sub>-oriented PZO film would experience multiple ferrielectric phases 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<sup>11, 12</sup> or Schottky barrier<sup>13</sup> may also contribute to the analog-like, frequency-dependent electromechanical response.

We thank the reviewer again for the constructive comment, and are glad to add the discussion into Supplementary Fig. 14 and Supplementary Note 5 to make the manuscript more solid.



**Fig. R4 Electromechanical measurement of (100)<sub>P</sub>-oriented PZO thin films. a,** Electric field induced displacement of (100)<sub>P</sub>-oriented PZO thin films. **b,** Frequency dependence of the displacement in (100)<sub>P</sub>-oriented PZO thin films.

**Comment 8.** The author duplicated Supplementary Table 1 twice in the supplementary material. The author should carefully review and revise the manuscript to ensure accuracy and consistency.

**Response:** We thank the reviewer for this comment. We have removed the duplicated Table 1 from the Supplementary Information and carefully reviewed the manuscript to ensure its clarity and accuracy.

**Comment 9.** There are multiple grammatical and structural errors in the article that require

correction. For example, consider the following sentence: Moreover, a new ferrielectric structure has been observed recently in (100)-oriented PZO films. indicating that there could be a transient state between the AFE and FE structures under an electric field<sup>19, 20</sup>.

**Response:** We thank the reviewer for this comment. We have carefully reviewed the manuscript sentence by sentence and revised any grammatical and structural errors.

**Comment 10.** The reference format in the paper lacks consistency, which is an issue that should not be present in a scholarly manuscript.

**Response:** We thank the reviewer for this comment. We have unified the reference format in accordance with the requirements of Nature Communications.

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## Reviewer #2

**General Comment:** This study, reported by Zuhuang Chen et al., presents atomistic models for controlled antiferroelectric-ferroelectric phase transitions along specific crystallographic directions. (111)-oriented PbZrO<sub>3</sub> thin films achieved nearly ideal antiferroelectricity with square double hysteresis loops, high polarization, negligible remnant polarization, fast response, and fatigue-free performance, which solve the typical problem of Distorted Switching Behavior in the present related AFE studies. In addition, a significant bipolar, frequency-independent digital electrostrain (~0.83%) was observed, driven by field-induced structural transitions. This interesting manuscript presents high-quality and convincing data that deserves publication. However, some minor questions still need to be addressed before publishing.

**Response:** We are grateful to the reviewer for his/her encouraging and constructive feedbacks, which has significantly helped to improve the quality of the manuscript. Please find our detailed point-by-point response below.

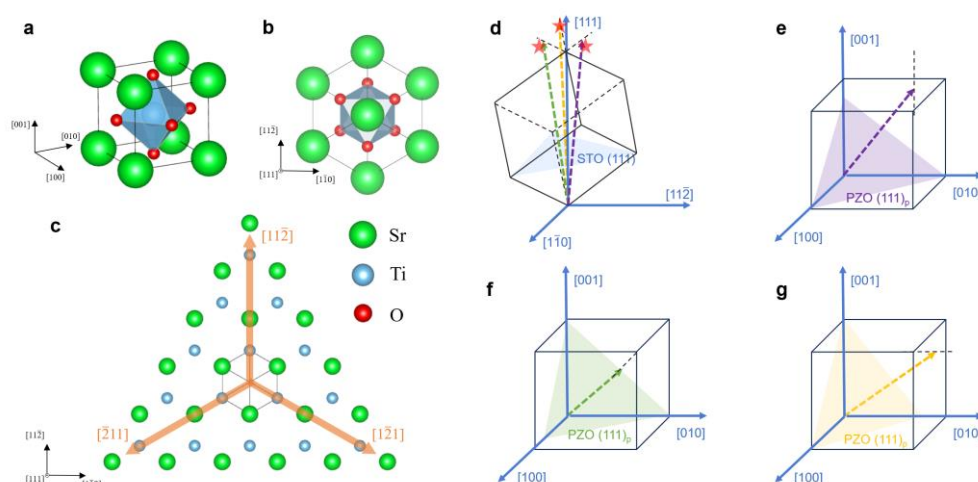
**Comment 1.** According to the authors, the triple-splitting observed in the out-of-plane RSM of the PZO (111) diffraction, as shown in the inset of Fig. 2(a), is not easily understood. Based on my knowledge, these three spots result from the alignment of the PZO c-axis along each of the three cubic STO axes. However, the correlation with 60°/120° domains remains unclear and requires a clearer explanation. For example, how do two domains contribute to three spots? What is the rotation symmetry for each domain? There should be a clearer definition for these domains. Additionally, the designation of 60°/120° domains may not be precise, as PZO lacks 3-fold or 6-fold symmetry. If possible, please identify the actual angles of these domains to enhance accuracy. Additionally, please address why the  $\theta/2\theta$  line scan shows only a single diffraction peak while the RSM reveals a triple-splitting for the same diffraction Miller index. Clarifying this difference is crucial for understanding the underlying structural characteristics.

**Response:** We thank the reviewer for this constructive comment and sincerely apologize for the confusion. Firstly, the Reviewer is right that the observation of three spots is related to the triple rotation symmetry of (111)-oriented cubic SrTiO<sub>3</sub> substrate. When we used the cubic (111)-oriented SrTiO<sub>3</sub> substrate to epitaxially grow the PZO film, the (111) plane of SrTiO<sub>3</sub> is in-plane. The (111) surface has a hexagonal symmetry, as shown in Fig. R5a-c. Thanks to the cubic feature of SrTiO<sub>3</sub>, where  $a = b = c$ , this arrangement would give birth to the triple rotation symmetry around the out-of-plane [111] axis (Fig. R5c). However, considering the pseudo tetragonal nature of PZO lattice, where  $a_p = b_p = 4.16 \text{ \AA}$  and  $c_p = 4.11 \text{ \AA}$ , the shorter  $c_p$  disrupts the triple rotation symmetry. The (111)<sub>p</sub> plane exhibits three distinct tilts, as the  $c_p$  of PZO can align either with  $a$ , or  $b$ , or  $c$  of SrTiO<sub>3</sub> substrate, resulting in the triple splitting of PZO(111)<sub>p</sub> diffraction (Fig. R5d-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 (please note that the 60°/120° domains mentioned in our original manuscript did 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). To avoid the confusion, we have replaced the word “60°/120°” with “60°” to avoid any confusion.

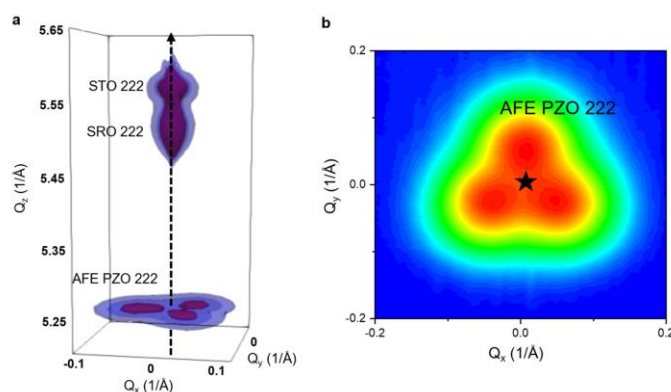
Finally, we need to distinguish the difference between  $\theta/2\theta$  line scan and RSM. As previously discussed, the (111)<sub>p</sub> plane of PZO would slightly tilt away from the out-of-plane direction due to the shorter  $c_p$  axes, causing the three PZO(111)<sub>p</sub> diffraction spots all deviate from the out-of-plane

direction, forming the triple splitting spots as our RSM revealed in Fig. R6a. However, the symmetric  $\theta/2\theta$  line scan are strictly along out-of-plane direction, therefore, the line scan could not cross any of the three PZO (111)<sub>P</sub> diffraction spots, but the center of the triangle (black pentagram in Fig. R6b) the three spots forms, therefore resulting in a single diffraction peak.

We thank the reviewer for this comment again and are glad to add the discussions above into the Supplementary Fig. 7, Supplementary Fig. 15, and Supplementary Note 6.



**Fig. R5 Structure geometry of SrTiO<sub>3</sub> and PbZrO<sub>3</sub>.** **a**, 3-dimensional atomic model of cubic perovskite SrTiO<sub>3</sub>. **b**, 2-dimension atomic model of cubic SrTiO<sub>3</sub> projected along [111]. **c**, plane-view of two adjacent atom layer of Sr and Ti projected along SrTiO<sub>3</sub> [111]. **d**, Schematic view of *c<sub>P</sub>*-axes tilting induced three PZO [111]<sub>P</sub> direction. **e-g**, Three kinds of PZO (111)<sub>P</sub> plane tilts with respect to cubic SrTiO<sub>3</sub>.



**Fig. R6 Reciprocal space mapping of PZO thin films.** **a**, 3-dimensional reciprocal space mapping around STO 222 spot, the dotted line represents the direction of out-of-plane  $\theta/2\theta$  scan crossing STO 222 spot. **b**, In-plane HK- reciprocal space mapping crossing the triple splitting PZO 222<sub>P</sub> spots, the black pentagram indicates the position where out-of-plane  $\theta/2\theta$  scan passes by.

**Comment 2.** In Fig. 4c, using “strain” to describe the lattice change during the phase transition may lead to confusion, as the film could already experience biaxial strain from the substrate. Therefore, it would not be zero even without applying the bias if using a broad definition of “strain”. I recommend the authors redefine the longitudinal axis title as “electrostrain” in the figure caption for greater clarity. In addition, please also provide the strain information of the PZO film caused by the STO substrate.

**Response:** We thank the reviewer for pointing this out. We have redefined the longitudinal axis title in Fig. 4c as “electrostrain” to avoid potential confusion between substrate misfit strain and electrostrain. Meanwhile, we also resolved the lattice parameter of PZO from the 3-dimensional reciprocal space mapping at zero field, where  $a_p = 4.113 \text{ \AA}$ ,  $b_p = 4.152 \text{ \AA}$  and  $c_p = 4.100 \text{ \AA}$ . In its bulk form, the pseudotetragonal lattice parameters of PZO are previously reported as  $a_p = b_p = 4.16 \text{ \AA}$  and  $c_p = 4.11 \text{ \AA}$ <sup>14</sup>. Therefore, we could calculate the misfit strain from the substrate along three axes, that is  $\varepsilon_a = -1.13\%$ ,  $\varepsilon_b = -0.19\%$ , and  $\varepsilon_c = -0.24\%$ . The results indicate the crystal lattice withstand compressive strain along all three pseudo cubic axes, which is similar with previous report on  $\text{PbTiO}_3$  on (111)-oriented  $\text{SrTiO}_3$  substrate<sup>15</sup>.

We thank the reviewer again for this suggestion and are glad to add this information in Supplementary Table 3.

**Table R1** Lattice parameter comparison and corresponding strain

| Lattice             | Thin film | Bulk | Strain |
|---------------------|-----------|------|--------|
| $a_p \text{ (\AA)}$ | 4.113     | 4.16 | -1.13% |
| $b_p \text{ (\AA)}$ | 4.152     | 4.16 | -0.19% |
| $c_p \text{ (\AA)}$ | 4.100     | 4.11 | -0.24% |

**Comment 3.** In some figures, the data lacks clear and sufficient labeling.

For example, in Fig. 2c-e, the STEM images should include axis or orientation information to provide proper context.

In Fig. 3a, the hysteresis and switching current loops are not clearly identified in the figure or its caption. Please ensure these are explicitly labeled for clarity.

**Response:** We thank the reviewer for the careful reading and also for the constructive comment. We have checked the figures thoroughly and revised the corresponding labels.

### Reviewer #3

**General Comment:** This paper reports the production of the PbZrO<sub>3</sub> epitaxial thin film in (111)<sub>P</sub> with preservation of the antiferroelectric order. Such a preservation is a challenge and it is fundamental to the potential application of digital strain and the mechanism of swing motion devices. Moreover, they apply atomistic models to propose the mechanism of the antiferroelectric to ferroelectric phase transition as a function of the electric field in PbZrO<sub>3</sub> thin films. After the electromechanical characterization, in-situ XRD was an important tool to evaluate their hypothesis. The methodology and the way they show the problem are excellent. I hope to see the application of this pathway to evaluate the crystallographic phase transition of all the other AFE materials. Therefore, their methodology will be widely cited. The combination of this methodology and different AFE thin films exploring different AFE-FE phase transition mechanisms would be a complete publication of nature (not communication) complete publication.

The manuscript provides important findings about antiferroelectricity, and phase transition mechanisms and I think it is worth publishing in Nature Communication with minor revisions.

A few comments and questions on the text follow:

**Response:** [We sincerely thank the reviewer for their thoughtful evaluation and insightful comments, which have been invaluable in enhancing the quality of our manuscript. Please find our detailed point-by-point response below.](#)

Abstract:

**Comment 1.** - by definition, displacive polar and antipolar materials are anisotropic. What do you mean by orientation design? Is the polarization rotation possible into monoclinic intermediate phase? Terms such as polarization rotation and extension should be explored all over the discussion.

**Response:** [We thank the reviewer for pointing this out. As discussed in the manuscript, the electric field-induced AFE-FE transition in PZO is anisotropic. When the external electric field is applied along the \[111\]<sub>P</sub> direction of the PZO crystal, the AFE-FE transition would exhibit the largest polarization change and volume expansion, the lowest transition field, as well as the ideal one-step AFE-FE transition without the presence of intermediate metastable phases. By contrast, when the applied field is along the \[100\]<sub>P</sub> direction of the PZO crystal, we observed small polarization change and volume expansion, large transition field, as well as multistep AFE-FE transition. In our experiment, we selectively epitaxially grow PZO single crystal films on commercial \(111\)-oriented SrTiO<sub>3</sub> single crystal substrates. By applying an out-of-plane electric field \(\*i.e.\*, \[111\]<sub>P</sub> direction\), we can obtain the desired one-step AFE-FE transition with exceptional properties. Therefore, orientation design here means the selective choice of the anisotropic AFE-FE transition pathway and consequently desired electro- and mechanical- properties via epitaxially growing the PZO films on the designed oriented single-crystal substrates<sup>16</sup>.](#)

[From the NEB calculations, we discovered that when the electric field was applied along \(111\)<sub>P</sub>, it would result in the rhombohedral FE phase while electric fields along other directions would distort the FE phase as monoclinic phase. Considering the transition from orthorhombic AFE to rhombohedral FE, the initial antipolar dipole point along \[110\]<sub>P</sub> and the final polar dipole point along \[111\]<sub>P</sub>. The polarization would rotate in the \(110\)<sub>P</sub> plane during the transition. Therefore, dipole rotation is possible in the monoclinic intermediate phase during orthorhombic AFE to rhombohedral FE transition.](#)

We also apologize for using the term “polarization rotation” in our original Supplementary Information. As reported in Dragan Damjanovic, Appl. Phys. Lett. **97**, 062906 2010,<sup>17, 18</sup> the polarization extension usually refers to the colinear polarization change between nonpolar (probably not be antiferroelectric) and polar structure, whereas polarization rotation refers to the polarization change between two polar structures with different polarization orientation<sup>17</sup>. Therefore, we agree with the reviewer that “polarization rotation between IM\*, IM\*\* and FE structure” might not be the right term, as both two metastable transient states IM\* and IM\*\* are ferroelectric phase. In our original manuscript, we just intended to use polarization rotation to literally explain the dipole reorientation. We thank the reviewer again for this comment and would replace the term “polarization rotation” with “dipole reorientation”.

**Comment 2.** – Every time you use crystallographic direction there it is hard to understand what direction you are talking about. For example: thin film grows in (111) sound that the octahedron is oriented in (111) (Glazer reference as the prototype). However, the direction you use at the TEM results sound to be related to the Pbam reference. I strongly recommend you use the subscript “P” when you are using the octahedra reference. This is worse when you are using the semi-inter superlattice peak, as the semi-inter are always referent to the prototype structure. (Obs: I checked the indexation of the semi-inter and it is correct).

Therefore, it sounds like the [11-2] you mention in HAADF is the [110]P. The support information with the projection is in reference of Pbam and is correct.

**Response:** We thank the reviewer for pointing this out and apologize for the confusion. We have reconsidered the crystallographic notation in this manuscript, and have used the subscript “*P*” to denote the octahedra reference. Meanwhile, the zone axis  $[11\bar{2}]_P$  mentioned in HAADF analysis corresponds to the prototype structure, which is usually used to analysis cross-section information of (111)<sub>P</sub>-oriented perovskite thin films<sup>15</sup>. (See also Supplementary Fig. 9). For clarity, we have added the subscript “*P*” in the figures as well.

Introduction:

**Comment 3.** - General question: what is the digital, analogue and their relation to displacive and order-disorder phenomena?

**Response:** We thank the reviewer for this insightful comment. First, we would attribute the digital response in this manuscript 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.

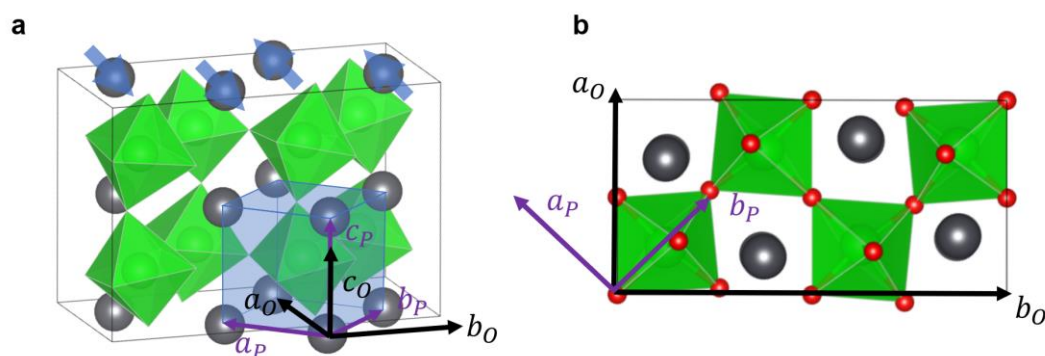
Then we consider the displacive and order-disorder phenomena. The displacive and order-disorder phenomena are usually considered as the dynamics of temperature-driven ferroelectric or antiferroelectric phase transition<sup>19</sup>. When a long wavelength optic mode frequency slow down with decreasing 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<sup>19</sup>. 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<sup>20, 21</sup>. 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.

We thank the reviewer again for this constructive suggestion on discussing the phase transition mechanisms, and are glad to add this discussion into Supplementary Note 7.

**Comment 4.** - In the  $Pbam$  space group there is 8 oxygen octahedrons. The notation of the antipolar perovskite structure in orthorhombic symmetry  $Pbam$  is not taking into account the pseudocubic (prototype) direction of a perovskite structure. Taking into account the prototype structure, what would be the direction of the antiphase dipoles?

**Response:** We thank the reviewer for this comment. In the orthorhombic axes, the antipolar dipole is oriented along  $[100]_o$  ( $a_o$ ) and arranged antiparallel along  $[010]_o$  ( $b_o$ ) direction, while in the pseudocubic axes, the antipolar dipole aligns along the  $[110]_p$  direction. We apologize for any confusion regarding the coordinate transformation and have included a diagram in Supplementary Fig. 1 (shown in Fig. R7) to illustrate the geometric relationship between the orthorhombic and pseudocubic axes.



**Fig. R7 Transformation between the orthorhombic and pseudocubic geometry. a,** Atomic model of the orthorhombic PZO and corresponding pseudocubic axes. **b,** atomic model of orthorhombic  $a$ - $b$  plane and corresponding pseudocubic axes.

Atomistic modeling of AFE-FE phase transition.

**Comment 5.** - There is confusion when one says pseudo-tetragonal symmetry and cites the space group  $Pbam$  (orthorhombic group). You should justify or at least use the subscript indices P (from prototype) at the lattice parameters ( $a_P$  and  $b_P$ ) with the equation to convert the from the orthorhombic space group ( $Pbam$ ) to the pseudo tetragonal.

**Response:** We thank the reviewer for pointing this out. We have checked the manuscript thoroughly, providing the conversion equation and using the subscript “P” to indicate the pseudo tetragonal lattice. In the manuscript now it read as “In its bulk form, PZO possesses an orthorhombically distorted perovskite structure with space group  $Pbam$  and lattice constant of  $a_o = 5.884 \text{ \AA}$ ,  $b_o = 11.768 \text{ \AA}$ , and  $c_o = 8.220 \text{ \AA}$  at room temperature<sup>22</sup>. The orthorhombic unit cell of PZO can

alternatively be described as a simplified pseudotetragonal perovskite unit cell with constants  $a_p = a_o/\sqrt{2} = 4.16 \text{ \AA}$ ,  $b_p = b_o/2\sqrt{2} = 4.16 \text{ \AA}$  and  $c_p = c_o/2 = 4.11 \text{ \AA}^2$  (The subscript “O” denotes orthorhombic indices while the subscript “P” denotes pseudo-tetragonal indices, Supplementary Fig. 1).”

In-situ structural analysis of antiferroelectric and field-induced ferroelectric phase

**Comment 6.** - You mention that the “structural phase transition is the major contribution to the observed large digital strain”. What would be the other hypothesis for the strain? Is it possible to be from another thing that is not the lattice?

**Response:** We thank the reviewer for this comment and feel sorry for the confusion. In fact, the structural phase transition here means the field-induced AFE-to-FE phase transition, which provide sharp lattice expansion at critical point. Indeed, the strain of materials should all come from the lattice, and we are glad to potentially list some of the origin of the electrostrains, including the piezoelectricity, electrostriction, chemopiezoelectric effect and AFE-FE structural phase transition for discussion.

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)<sub>P</sub>-oriented PZO, before the jump of digital strain (i.e., the applied field is below the critical transition point), 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<sup>11, 12</sup>. This is clear not the case in our manuscript, where the digital strain shows broad 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)<sub>P</sub>-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 large volume expansion during the structural phase transition, giving birth to the sharp contrast of digital electromechanical responses.

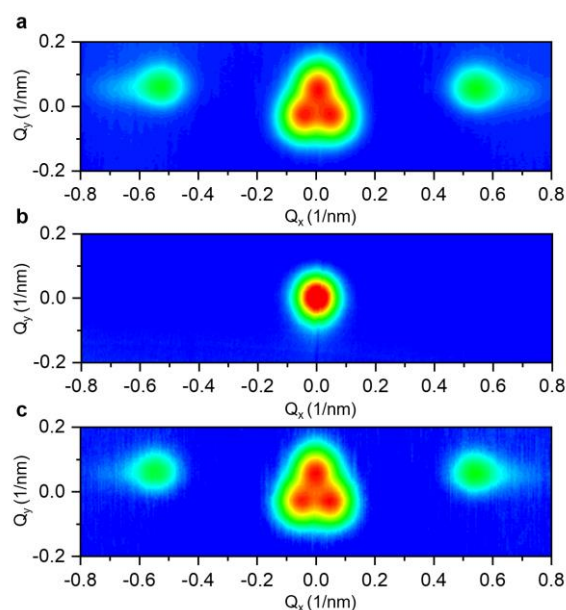
To avoid possible confusion, we would like to replace the sentence by “the **field-driven AFE-to-FE** structural phase transition is the major contributor to the observed large digital displacement” and add above discussion into Supplementary Note 8 to make the conclusion solid.

**Comment 7.** - You affirm that the “splitting of main spots is clearly from the as-grown film, implying the existence of multidomain structure”. The disappearance of the main spots splitting indicated the formation of a single domain. How was it when the electric field was removed?

**Response:** We thank the reviewer for this comment. We performed the reciprocal space mapping focusing on the region around main reflections of 222<sub>P</sub>-spot and nearby superstructure spots before (Fig. R8a), during (Fig. R8b), and after (Fig. R8c) applying the electric field over the critical

transition field.

In Fig. R8a, we can see the main-Bragg-spot splitting of  $(222)_P$  reflections before applying the electric field, indicating the pseudo tetragonal structural feature of AFE PZO. Meanwhile we can see the  $1/4$  superstructure spots in line with one of the triple-splitting main spots, which denote the corresponding AFE-order induced four-fold lattice period increasement. As increasing the electric field, the AFE-to-FE transition happens and triple splitting main spots merge into one spot in Fig. R8b, denoting the crystal symmetry changes. Moreover, the  $1/4$  satellite peaks disappear, confirming the annihilation of AFE order and completion of AFE-to-FE transition. When the electric field is removed, as shown in Fig. R8c, we can see the reappearance of  $1/4$  superstructure spots and triple splitting of main reflections. These features indicate the recovery of AFE structure at zero field, which is consistent with the proposed reversible AFE-FE phase transition.



**Fig. R8 In-situ characterization of in-plane reciprocal space mapping around  $222_P$ -spot.** a, Before, b, during and c, after applying electric field over the critical switching point.

We thank the reviewer for this comment and are glad to include this discussion into Supplementary Fig. 16 and Supplementary Note 9.

**Comment 8.** - How could you be sure about the phase transition to rhombohedral if you looked at only one direction of the thin film? Did you compare with lattice parameters of monoclinic phase (DFT) as well?

**Response:** We thank the reviewer for this comment. Firstly, we need to explain how we determine the rhombohedral symmetry. In this manuscript, we used synchrotron-based 3-dimensional reciprocal space mapping to in-situ monitor the AFE-to-FE phase transition. This method could collect the wide-range diffraction information of the films, providing 3-dimensional reciprocal space coordinate of main Bragg spots<sup>22</sup>. If we could find out three linear-independent Bragg spots, the reciprocal space lattice can be calculated and further converted to lattice parameter at real space. As shown in Fig. 5c and Fig. 5e, we collected the coordinates of asymmetric  $(123)_P$ ,  $(132)_P$ ,  $(213)_P$ ,  $(231)_P$ ,  $(312)_P$ , and  $(321)_P$  main Bragg spots as well as the symmetric  $(222)_P$  main Bragg spot, resolving the lattice parameter for FE PZO in Supplementary Table 1, where  $a_p \approx b_p \approx c_p = 4.147 \text{ \AA}$

and  $\alpha \approx \beta \approx \gamma = 89.52^\circ$  within experimental errors. Here, we also provide the lattice parameter of monoclinic phase in PZO(100)<sub>p</sub> from DFT calculations, where  $a_p = 4.141 \text{ \AA}$ ,  $b_p = 4.142 \text{ \AA}$  and  $c_p = 4.174 \text{ \AA}$ . The angles between two lattice axes are  $\alpha = \gamma = 90^\circ$  while  $\beta = 91.32^\circ$ . Both the lattice parameters and angles differ a lot between in-situ results and DFT monoclinic phase.

**Comment 9.** - What was the applied electric field in the in-situ measurement? The procedure of electric field application is not clear.

**Response:** We thank the reviewer for this comment. During our in-situ measurement, we first collected wide-range main Bragg spots at zero field, observing the triple splitting of main spots, as shown in Fig. 5c. Since a wide-range scan takes approximately 15 minutes, we applied the voltage incrementally at 1 V per step and monitored the evolution of the (222)<sub>p</sub> main spot by keeping the diffraction geometry and detector fixed at the corresponding position. When the applied voltage reaches 8 V, the splitting of main spots fully merge into a single peak, indicating the completion of the AFE-to-FE transition. We then performed three-dimensional reciprocal space mapping (RSM) with holding on the applied electric field and using the same scan parameters, which yielded the main Bragg spots of the FE PZO phase, as shown in Fig. 5e. Finally, we rapidly removed the electric field and repeated the same zero-field measurement to confirm the reversible AFE-FE structural phase transition. We have added this clarification into Supplementary Note 10 to prevent any confusion from the reviewer and readers.

**Comment 10.** Typing errors:

Page3. There is a dot followed by a non-capital latter. I think this dot is a comma.

Page6 – change HADDF by HAADF.

**Response:** We thank the reviewer for pointing these errors out. We have checked the manuscript carefully and revised the typing errors accordingly.

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## Overall Response to Editor and Reviewers

We sincerely express our gratitude to the editor and reviewers for their precious time and valuable comments on our manuscript. We also thank the reviewers for their highly praise on the revised version of this manuscript, and the editor for the acceptance of our manuscript in Nature communications. Finally, we hope this manuscript would contribute to the communities.

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### Reviewer #1 (Remarks to the Author):

**General Comment:** The author achieved ideal antiferroelectricity with square double hysteresis loop, large saturated polarization ( $\sim 60 \mu\text{C}/\text{cm}^2$ ), near-zero remnant polarization, fast response time ( $\sim 75 \text{ ns}$ ), and near-fatigue-free performance ( $\sim 10^{10}$  cycles) in (111)P-oriented PbZrO<sub>3</sub> epitaxial thin films. Moreover, a bipolar and frequency-independent digital electrostrain ( $\sim 0.83\%$ ) were demonstrated in this archetype antiferroelectric system. This work holds significant importance for this field and related areas. It demonstrates advancement compared with existing literature. This work can support the conclusion and claim without the need for additional evidence. The data analysis, interpretation and conclusion are feasible and do not require further modification. The methodology is reasonable and the work meets the expected standards in my field. The method provides sufficient details to reproduce the work.

**Response:** We would like to extend our appreciation to the Reviewer once again for providing us with valuable comments to enhance the manuscript and for recommending it for publication.

### Reviewer #2 (Remarks to the Author):

**General Comment:** The authors have provided clear responses to the questions, and the manuscript has been well reorganized. I have no further concerns regarding its acceptance.

**Response:** We would like to thank the Reviewer once again for all the valuable comments and recognition of our manuscript.

### Reviewer #3 (Remarks to the Author):

**General Comment:** I am writing to inform you that I have reviewed the revised manuscript titled "Ideal antiferroelectricity with large digital electrostrain in PbZrO<sub>3</sub> epitaxial Thin Films" from Zuhuang Chen, Yangyang Si, Ningbo Fan, Yongqi Dong, Zhen Ye, Shiqing Deng, Yijie Li, Chao Zhou, Qibin Zeng, Lu You, Yimei Zhu, Zhenlin Luo, SUJIT DAS, L. Bellaiche, Bin Xu, and Huajun Liu. I am pleased to report that the authors have satisfactorily addressed all my comments and suggestions. The revisions have improved the quality and clarity of the manuscript.

Additionally, all discussions related to my comments have been incorporated into the text or included in the supplementary material. Some of my comments regarding crystallographic notations were challenging to verify, and the authors have carefully ensured the correct notation was added. They are to be commended for their thorough and meticulous work.

Therefore, I am happy to recommend accepting this manuscript for publication in Nature Communications.

Thank you for the opportunity to review this work. Please let me know if you need any further information.

**Response:** We gratefully acknowledge once again the Reviewer for the detailed review and the support in the publication of our manuscript.