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Peer Review File

Electrical De-poling and Re-poling of Relaxor-PbTiO3 Piezoelectric Single Crystals without Heat Treatment

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

In this study, the authors investigated the de-poling and re-poling of Relaxor-PbTiO_3 using alternative electric fields. Notably, their findings are compelling because no heat treatment is necessary to control the poling-repoling state. They demonstrate that low-frequency AC fields with amplitudes close to E_c could be employed to achieve this result. The experimental findings are supported by phase-field simulations. The work is interesting and compelling. Before recommending it for publication, I would like more details on the phase-field methodology and further phase-field analysis.

1/ Could the authors provide additional details on the phase-field methodology. What was the grid size employed? For solving the electrostatic and mechanical equilibriums, what methods were used for resolving the partial differential equations? Additionally, information on the boundary conditions utilized in both cases would be appreciated. Regarding the electrostatic equilibrium, how was the electric fields applied?

2/ Do you anticipate that employing different electrical boundary conditions, such as applying AC fields locally through an AFM tip, could yield varied results? Specifically, would it be feasible to control the poling/re-poling locally using this method, or do you think the influence of the surrounding domains would impede it?

3/ Do you anticipate that an elastic mismatch could influence the domain dynamics achieved through AC fields? If so, do you believe it could be advantageous in certain cases for achieving a more optimal time window of poling?

4/ In your opinion, could the demonstrated control of the domain structure be achieved without using voltage? Would tip-induced mechanical switching or other mechanical means be suitable for room temperature poling-repoling?

5/ The initial poled state was established using AC fields in the phase-field section. Could you please provide the values of both the electric field and its frequency during this process?

6/ In the phase-field simulations, could you specify the timestep used for the simulations? While acknowledging that phase-field simulations are often conducted in arbitrary units, as indicated in Fig 5, would it be feasible to estimate this timestep in real units? Could you discuss this value in relation to the experimental results, particularly in Fig 5.b?

7/ Observing Fig 5.c, I am curious to know whether modifying the frequency and/or field value would enable the maintenance of polarization within the ideal time window. Specifically, I am interested in understanding if adapting the frequency, once the polarization reaches the ideal window for the first time, could sustain the polarization in that region without reverting to its remanent value. Would it be beneficial ?

8/ In this study, the authors demonstrated a significant impact of AC field frequency on the experimental results. I believe the study could benefit from including an analysis of the frequency impact in the phase-field simulations as well. I would greatly appreciate the inclusion of some simulations in the phase-field section or SI, specifically highlighting the frequency trend observed in the experimental results.

Reviewer #2 (Remarks to the Author):

In this study, the authors introduced a novel method utilizing AC electric fields to depolarize ferroelectric single crystals, specifically Pb(In1/2Nb1/2)O3-Pb(Mg1/3Nb2/3)O3-PbTiO3 (PIN-PMN-PT), without the need for heat treatment. By applying AC electric fields with amplitudes near the coercive field at low frequencies, the authors successfully achieved depolarization of poled crystals at room temperature. Furthermore, this research investigated the reproducibility of depoling and repoling processes in single crystals of the piezoelectric device, supported by a phase field model. While the findings of this study are intriguing, significant revisions are necessary prior to publication.

1. Is this method could widely used for both single crystal and ceramic ferroelectrics, or is it primarily applicable to single crystals only? It would be beneficial to discuss the potential for general use in a broader context. While the method has been predominantly applied to single crystals in the current study, its adaptation and effectiveness in ceramic ferroelectrics merit consideration for broader applicability. Further research and experimentation could shed light on its viability across different material types.
2. While this method finds support in the phase field model, additional experimental verifications would enhance its credibility. The authors have conducted comparisons involving dielectric permittivity, piezoelectric coefficients, and impedance. However, incorporating information on phase transitions, possibly through techniques like X-ray diffraction (XRD), would provide a more comprehensive understanding.
3. Figure 5 illustrates the domain changes during the depoling and repoling process. It would be valuable to explore the feasibility of monitoring these domain changes using Piezoresponse Force Microscopy (PFM), particularly for comparing domain patterns post-DC depoling and AC depoling treatments.
4. An intriguing aspect to explore further is whether this method can depolarize the ferroelectric material to a specific polarization state. It would be insightful for the authors to provide commentary on this aspect, potentially elucidating the method's capabilities in achieving desired polarization states.
5. It would be beneficial for the authors to include figures depicting the experimental setup and the fabricated device, providing readers with a visual understanding of the methodologies employed and the resulting device architecture.
6. The authors should rectify certain errors within the main context. For instance, in Figure 2's caption, "impedance spectrum of initially DCP PIN-PMN-PT single crystals after being triggered by AC electric fields for depoling" should be corrected. Additionally, in the section discussing phase field simulation, the equation contains a discrepancy where "r" is mentioned but not included in the equation. The authors should ensure consistency and accuracy in all textual descriptions and equations throughout the manuscript.

Dear Editors and Reviewers,

We are pleased to resubmit our work, entitled “Electrical De-poling and Re-poling of Relaxor-$PbTiO_3$ Piezoelectric Single Crystals without Heat Treatment,” after taking the received comments into a serious consideration. We highly appreciate the editors and reviewers for all comments that are constructive and insightful to make the current manuscript improved. Specifically, we have conducted a series of experiments to properly address all the concerns and suggestions raised by the reviewers. We do hope that our revised manuscript meets the standards of *Nature Communications*. Here, we include our point-by-point responses to each comment, and corrections made to the previous manuscript are highlighted with yellow color.

Dear reviewers,

We really thank the reviewers for taking the time and efforts to review our recent manuscript and provide constructive comments. We are glad that our current work has been significantly improved with the corresponding revisions. Please find point-by-point responses to the remarks raised by the reviewers as attached below. We hope that this revision meets the standards of *Nature Communications*.

Reviewer #1 (Remarks to the Author):

In this study, the authors investigated the de-poling and re-poling of Relaxor-$PbTiO_3$ using alternative electric fields. Notably, their findings are compelling because no heat treatment is necessary to control the poling-repoling state. They demonstrate that low-frequency AC fields with amplitudes close to E_c could be employed to achieve this result. The experimental findings are supported by phase-field simulations. The work is interesting and compelling. Before recommending it for publication, I would like more details on the phase-field methodology and further phase-field analysis.

1. Could the authors provide additional details on the phase-field methodology. What was the grid size employed? For solving the electrostatic and mechanical equilibriums, what methods were used for resolving the partial differential equations? Additionally, information on the boundary conditions utilized in both cases would be appreciated. Regarding the electrostatic equilibrium, how was the electric fields applied?

Response: We really thank the reviewer for the acknowledgment that the work is interesting and compelling, and thank for their valuable questions. In our phase-field simulations, we used a quasi-two-dimensional (2D) system of 256 nm × 256 nm × 1 nm, which is discretized into 512 × 512 × 2 grids. Therefore, the grid sizes of *x*, *y*, *z* directions are equal to 0.5 nm. The electrostatic and elastostatic equilibrium equations were solved using the Fourier spectral method (**Ref**: Hu, H. L., & Chen, L. Q., *J. Am. Ceram. Soc* **81**(3) (1998) 492-500). When solving the equations, the three-dimensional periodic boundary condition is imposed. For the elastostatic equation, the average strain of the simulated system is fixed to be zero at all time steps, corresponding to a constrained mechanical boundary condition. For the electrostatic equation, the average electric field of the system is maintained to be equal to the applied electric fields for AC and DC poling and de-poling processes which vary as a function of time. The contribution from external electric field is included in the electrostatic energy,

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where $\mathbf{E}^{int}$ and $\mathbf{E}^{ext}$ denote the internal field and the external electric field, respectively. The external field $\mathbf{E}^{ext}$ is equal to the applied time-dependent AC or DC fields. The internal field $\mathbf{E}^{int}$ is then solved through the following electrostatic equation:

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where $\boldsymbol{\kappa_0}$ and $\boldsymbol{\kappa}^b$ are the vacuum permittivity and background dielectric constants, respectively. We added the detailed information of the phase-field simulation into the Method section **Phase-field simulations**.

2. Do you anticipate that employing different electrical boundary conditions, such as applying AC fields locally through an AFM tip, could yield varied results? Specifically, would it be feasible to control the poling/re-poling locally using this method, or do you think the influence of the surrounding domains would impede it?

Response: Thanks for the insightful questions. On the basis of our experimental results, the same phenomena should be observed regardless of methods to apply electric fields if depoling conditions are properly selected. However, this proper depoling conditions by AC electric fields may be highly dependent on given

ferroelectric materials. This is because depolarization fields inside ferroelectric materials should also be dependent on mechanical and electrical boundary conditions such as dimension, defects and surrounding domains. In this regard, as the reviewer mentioned, we argue that probe-based technologies may lead to varied results. For instance, when it comes to thin films, due to the existence of a non-ferroelectric layer, the distribution of depolarization fields near surface should be definitely dissimilar. It means that we need to find other suitable depoling/repoling conditions when we confirm the current depoling/repoling behaviors are really feasible througn AFM-based technologies. Therefore, our answer is “yes” but need to find suitable depoling/repoling conditions which are highly dependent on ferroelectric materials in use.

By the same token, the surrounding domains or structures likely impede the suggested depoling/repoling phenomena because they induce dissimilar boundary conditions. Hence, the distribution of depolarization field and domain dynamics may be disssimilar and thus impede or facilitate the depoling/repoling behaviors.

3. Do you anticipate that an elastic mismatch could influence the domain dynamics achieved through AC fields? If so, do you believe it could be advantageous in certain cases for achieving a more optimal time window of poling?

Response: Thanks for the questions. As we discussed above, mechanical boundary conditions influence not only domain dynamics but also the distribution of depolarization fields. So, it certainly impacts the suggested depoling/repoling results. Therefore, we carefully argue that the proposed stragtegy will be advantageous in achieving a more optimal time window for depoling/repoling. Our opinion can be supported by the fact that the ferroelectric properties of single crystals can be adjusted by mechanical stress [**Ref**: *Appl. Phys. Lett.* **102** (2013) 172902 & *J. Am. Ceram. Soc* **89** (2006) 775-785]. For example, if elastic mismatch induces mechanical constraint, domain dynamics may be more facilitated or impeded (it may depend on how mechanical constraint or elastic mismatch is applied on domains). Consequently, we will be able to achieve a more optimal time window (longer or shorter) for depoling/repoling by employing elastic mismatch.

4. In your opinion, could the demonstrated control of the domain structure be achieved without using voltage? Would tip-induced mechanical switching or other mechanical means be suitable for room temperature poling-repoling?

Response: We are so impressed by the reviewer's comment. Our answer is "yes" in that mechanical stress on a certain direction can bring about depolarization in ferroelectric materials [**Ref**: *Appl. Phys. Lett.* **112** (2018) 122903]. If a tip can be precisely controlled to apply mechancal constraint along a specfic direction, the suggeted depoling behaviors are also feasible without voltages. However, our concern is that a tip may damage the surface of ferroelectric materials, leading to other non-ferroelectric layers or phase transitions. Furthermore, its controllability is to some extent limited, that is, it is hard to apply mechanical confinement in a proper manner on the surface we want. Nevertheless, we need to actively investigate mechanical-stress dependent domain dynamics in nano-scaled ferroelectric materials for a state-of-the-art applications.

5. The initial poled state was established using AC fields in the phase-field section. Could you please provide the values of both the electric field and its frequency during this process?

Response: Thanks for the question. The amplitude of the applied AC electric field is 93 kV/cm and the frequency of the AC field is $1/(4\times10^5\ t_0)$ where t_0 is the real time of one simulation timestep. Please refer our answer to **Comment 6** below for the detailed discussion on the choice of t_0.

6. In the phase-field simulations, could you specify the timestep used for the simulations? While acknowledging that phase-field simulations are often conducted in arbitrary units, as indicated in Fig 5, would it be feasible to estimate this timestep in real units? Could you discuss this value in relation to the experimental results, particularly in Fig 5.b?

Response: Yes, we used normalized parameters in the phase-field simulations for the time-dependent equation for polarization evolution. Nevertheless, the real time per each timestep of the simulation can be determined by,

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where α_0 equals the Landau coefficient, α_1 at room temperature and L_0 equals to the kinetic coefficient of the time-dependent Ginzburg-Landau equation. For the Landau parameters used in this work, $\alpha_0 = 2.295 \times 10^5\ m^2N/C^2$, while L_0 for PMN-PT systems

has not been reported in the literature to our best knowledge. In fact, the estimated L_0 for $BaTiO_3$ in the literature can vary by 10 orders of magnitude. For example, it is calculated to be ~4×10^4 $C^2/(J\cdot m\cdot s)$ in the following reference (**Ref**: *Nanotechnology* **20** (2009) 105709) and ~4×10^{-6} $C^2/(J\cdot m\cdot s)$ in the reference (**Ref**: *J. Mech. Phys. Solids* **55** (2007) 280–305). To accurately quantify L_0, it is required to experimentally measure or theoretically calculate the mobility of domain walls subject to electrical fields, which depends on the domain wall types and the strength of the driving electric fields, and L_0 can also be an anisotropic tensorial quantity. Despite the importance of determining the absolute value of L_0 for a quantitative comparison with experiments, it is a non-trivial task and is beyond the scope of our current work. Therefore, we assume that the kinetic coefficient is a scalar constant with an arbitrary unit, and the simulation time step in this work can only be compared with experiments qualitatively.

7. Observing Fig 5.c, I am curious to know whether modifying the frequency and/or field value would enable the maintenance of polarization within the ideal time window. Specifically, I am interested in understanding if adapting the frequency, once the polarization reaches the ideal window for the first time, could sustain the polarization in that region without reverting to its remanent value. Would it be beneficial ?

Response: We are grateful for the reviewer's comment to complement our work. In our opinion, a polarization state which is close to the state where a polarization is close to 0 can be maintained within more extended time window if the frequency is lower, which is grapsed by the fact that low frequency driving fields usually lead to slower ferroelectric dynamics. However, we expect this is limited as a transient state should be unstable, implying that a maximum time window for depoling should be confined when we modifty the frequency of applied electric fields. For the field value (amplitude), it may "slightly" change the time window for a polarization state as the proper value exists and is considerably limited (in our simulation ~ 0.85 E_c) for depoling processes.

As the reviewer mentioned, if we readily control (sustain) polarizations, it means that we can achieve diversity in ferroelectric states. This is beneficial to ferroelectrics-based applications (for example, FeRam) where their functionality is, so far, usually originated from the direction of polarizations (up or down). If a variety of ferroelectric states is feasible in single materials, we will be able to achieve controbility in resistivity (conductivity) or polarization states (e.g. up, down, and zero: total 3 states) in ferroelectric appliations, which can result in new functionality. We hope that our strategy for single crystals will be extended to ferroelectric thin films for next generation ferroelectric devices.

8. In this study, the authors demonstrated a significant impact of AC field frequency on the experimental results. I believe the study could benefit from including an analysis of the frequency impact in the phase-field simulations as well. I would greatly

appreciate the inclusion of some simulations in the phase-field section or SI, specifically highlighting the frequency trend observed in the experimental results.

Response: Thanks for the great suggestion. Our results have shown that the depolarization of the single crystals can be realized near 0.85 E_C with one cycle of the applied field corresponding to an AC period of 400 k timesteps. To study the effect of AC frequencies on the depolarization behavior, we keep the applied electric field strength as 0.85 E_C. The polarization as a function of the number of cycles of the system exposed to AC electric fields at different frequencies is shown in **Figure R1** below. In these three cases, the period of the AC electric fields is 300 k, 400 k, and 500 k timesteps, corresponding to a high, medium, and low frequency, respectively. At the high frequency, the depoling is negligible. At the low frequency, despite that the depoling can occur at certain time windows, a well depoled state is unstable, and the sample tends to become repoled. At the medium frequency, a well depoled state can be achieved. The simulation agrees qualitatively well with the experimental observation. As can be seen in the blue line of **Figure 1c**, the sample remains poled when exposed to 4 kV/cm at a frequency higher than 10^3 Hz, while the sample is not well depoled when exposed to 4 kV/cm at a frequency of 10^{-2} Hz. We have included the new figure in the supplementary information and modified the manuscript to highlight the consistency of the simulation with the experimental results.

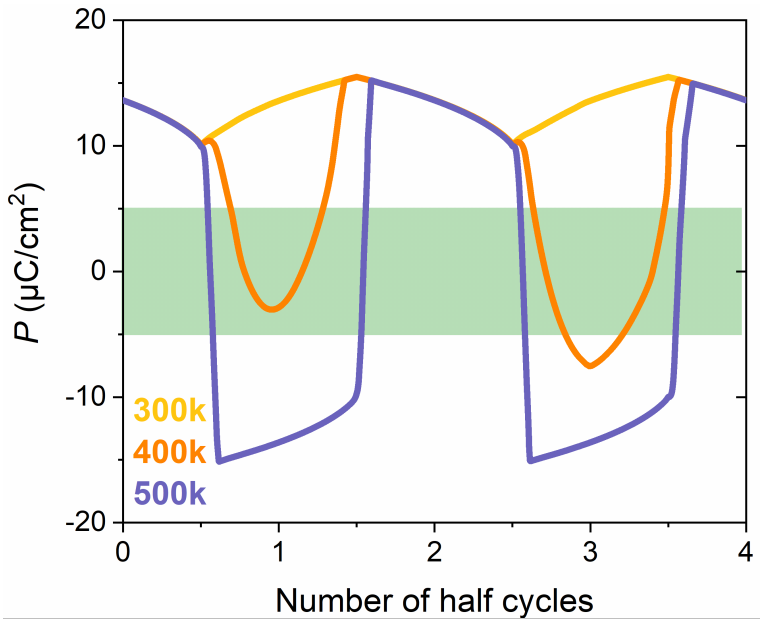

Figure R1 (Figure S7). Polarization as a function of the number of cycles of the investigated sample exposed to AC electric fields of 53.3 kV/cm (0.85E_C) at different AC periods, *i.e.*, 300 k timesteps, 400 k timesteps, and 500 k timesteps per cycle, corresponding to high, medium, and low frequencies, respectively. The simulation agrees qualitatively well with the experimental observation. As can be seen in the blue line of **Figure 1c**, the sample remains poled when exposed to 4 kV/cm at a frequency

higher than 10^3 Hz, while the sample is not well depoled when exposed to 4 kV/cm at a frequency of 10^{-2} Hz.

Reviewer #2 (Remarks to the Author):

In this study, the authors introduced a novel method utilizing AC electric fields to depolarize ferroelectric single crystals, specifically $Pb(In_{1/2}Nb_{1/2})O_3$-$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PIN-PMN-PT), without the need for heat treatment. By applying AC electric fields with amplitudes near the coercive field at low frequencies, the authors successfully achieved depolarization of poled crystals at room temperature. Furthermore, this research investigated the reproducibility of depoling and repoling processes in single crystals of the piezoelectric device, supported by a phase field model. While the findings of this study are intriguing, significant revisions are necessary prior to publication.

1. Is this method could widely used for both single crystal and ceramic ferroelectrics, or is it primarily applicable to single crystals only? It would be beneficial to discuss the potential for general use in a broader context. While the method has been predominantly applied to single crystals in the current study, its adaptation and effectiveness in ceramic ferroelectrics merit consideration for broader applicability. Further research and experimentation could shed light on its viability across different material types.

Response: We are grateful to the reviewer for the constructive comments. To confirm its further applicability, we have conducted the same experimental procedures on the representative polycrystalline piezoelectric ceramics, *i.e.*, $Pb(Zr,Ti)O_3$ (**Figure R2, Figure S12**). The dimension of the samples is 3 x 3 x 0.9*t* mm^3, which is similar to that of the crystals in this work. Given that its E_c is close to 8 kV/cm, an electric poling condition is 12.5 kV_{pp}/cm, 1Hz, 20 cycles while electric depoling was applied under different frequencies (0.1, 1, 10 and 100 Hz) and amplitudes (0.6, 0.8, 1.0 and 1.2 E_c) at a fixed cycle (10 cycles)

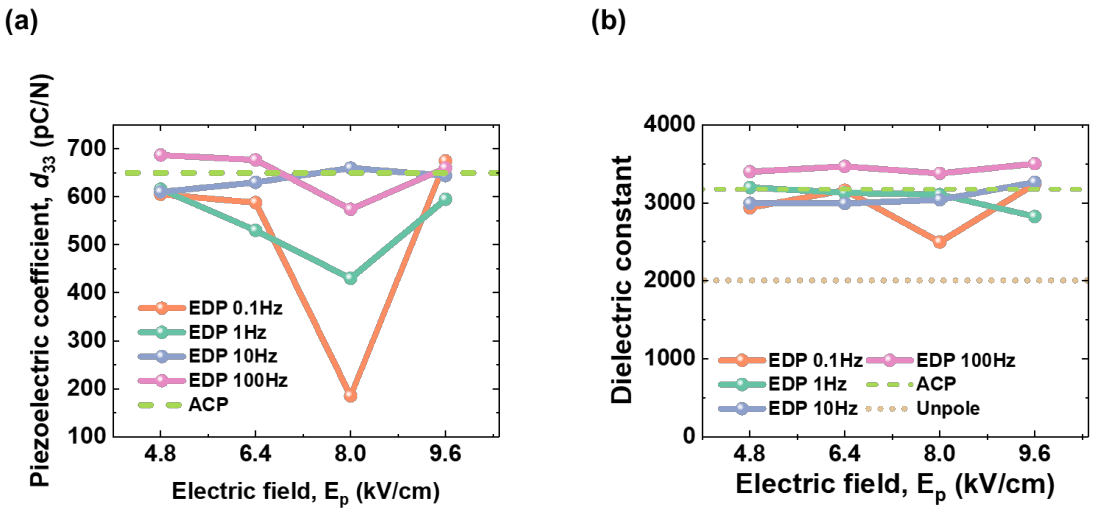

Figure R2 (Figure S12). (a) Piezoelectric coefficients and (b) dielectric constants of poled Pb(Zr,Ti)O_3 ceramics under AC electric fields for de-poling. The peak amplitudes and frequencies of the AC electric fields were varied to investigate how poled states change in response to external electric fields. The dimension of the samples is 3 x 3 x 0.9*t* mm^3, which is similar to that of the crystals in this work. Given that its E_c is close to 8 kV/cm, an electric poling condition is set as 12.5 kV_{pp}/cm, 1Hz and 20 cycles while electric fields for de-poling were applied under different frequencies (0.1, 1, 10 and 100 Hz) and amplitudes (0.6, 0.8, 1.0 and 1.2 E_c) at a fixed cycle (10 cycles).

In contrast to the single crystals, notable depoling behaviors were not observed over the experimental conditions except 1.0 E_c. However, their piezoelectric and dielectric properties at 1.0 E_c were not comparable to the unpoled counterpart. In this regard, we carefully argue that the strategy for depoling on ceramics should be different from single crystals. Given that constraint effects of polycrystalline ceramics, such as the grain boundaries, are likely larger than single crystals, harsh depoling conditions including mechanical confinements or higher energy electric fields may be required. Further investigations should be needed to broaden the feasiblity of the suggested idea for a different material type.

2. While this method finds support in the phase field model, additional experimental verifications would enhance its credibility. The authors have conducted comparisons involving dielectric permittivity, piezoelectric coefficients, and impedance. However, incorporating information on phase transitions, possibly through techniques like X-ray diffraction (XRD), would provide a more comprehensive understanding.

Response: Thanks for the good suggestion. As the reviewer pointed out, we have conducted *ex-situ* X-ray diffraction analyses at different poled states including ACP, ACP-EDP, DCP, DCP-EDP and thermal depoled state. The (400) reflection of the PIN-PMN-PT single crystals at the different poling conditions are shown in **Figure R3**

(Figure S13). On the basis of the XRD results, AC-poled crystals mainly consist of monoclinic phases as major one while DC-poled crystals have mixed phases (The highest peak of the AC-poled one is located at the higher angle than that of the DC-poled one). It is conistent with our previous work [**Ref**: W.-Y. Chang *et al. Mater. Res Lett.* **6** (2018) 537-544]. After applying AC electric fields for depoling on the AC-poled crystals (ACP-EDP), the highest peak is shifted to the lower angle, implying that other phases such as rhombohedral or tetragonal phases are induced or that their lattice parameters become larger (Reference XRD patterns are provided at the bottom). On the other hand, in the case of DCP-EDP, the highest peak is shifted to the higher angle when compared to DCP. This may be caused by AC electric fields for depoling because DC-poled one is transformed into an AC-poled state. It is supported by the fact that the higest peak of DCP-EDP is close to that of monoclinic phases (ACP). In constrast to thermal depoling where distinct phase identity cannot be discerned, electric depoling show specific phases. In this regard, the depoling process in this work may be associated with changes in domain distributions along with phase transformations and lattice parameter variations.

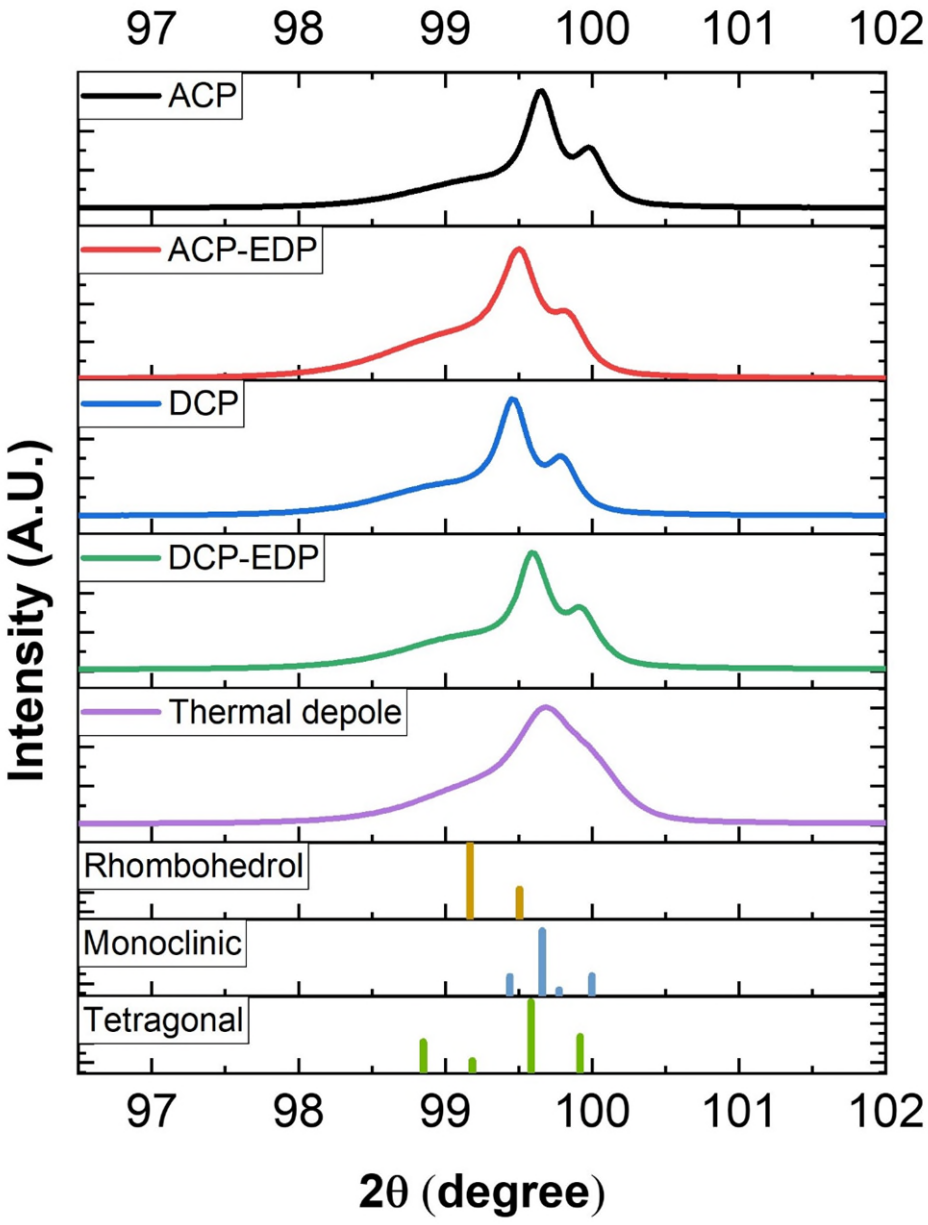

Figure R3 (Figure S13). X-ray diffraction (400) patterns of the PIN-PMN-PT single crystals at different poling conditions including ACP, ACP-EDP, DCP, DCP-EDP and thermal depoled state. The intensities have been normalized and reference patterns are shown in the bottom.

3. Figure 5 illustrates the domain changes during the depoling and repoling process. It would be valuable to explore the feasibility of monitoring these domain changes using Piezoresponse Force Microscopy (PFM), particularly for comparing domain patterns post-DC depoling and AC depoling treatments.

Response: Thanks for the good suggestions. We have conducted the visualization of ferroelectric domains regarding our current electric depoling experiments using a piezoresponse force microscopy (PFM). The phase and amplitude images of the PIN-PMN-PT single crystals at different poling conditions are shown in **Figure R4 (Figure S14).** We first scanned the domain structures of DCP and ACP crystals for better comparisons. As expected, dictinct ferroelectric domains are not observed in the unpoled one while DCP and ACP crystals consist of certain ferroelectric domains. It is widely known that ferroelectric domains of ACP crystals consist of stripe-like domains (109^o domains) parallel to their (001)- plane. On the contrary, irregular domains (109^o domains + 71^o domains) are captured in DCP crystals. To monitor domain changes during the depoling triggered by electric fields, we poled the single crystals (DCP: 10 kV/cm, 300s), followed by DC and AC electric field for depoling. Here, we tested only the samples which were well depoled (at least, d_{33} of the samples is less than 500 pC/N). For the DC-depoling case, their domain configurations are quite similar to the DCP crystals, indicating that both types of domains (109^o domains + 71^o domains) still remain. Furthermore, even the AC-depoling case also shows similar configurations. Given that our simulation results show that electrically-depoled crystals have irregular patterns similar to DC-poled crystals to some extent, our PFM results are well consistent with the computational calculations.

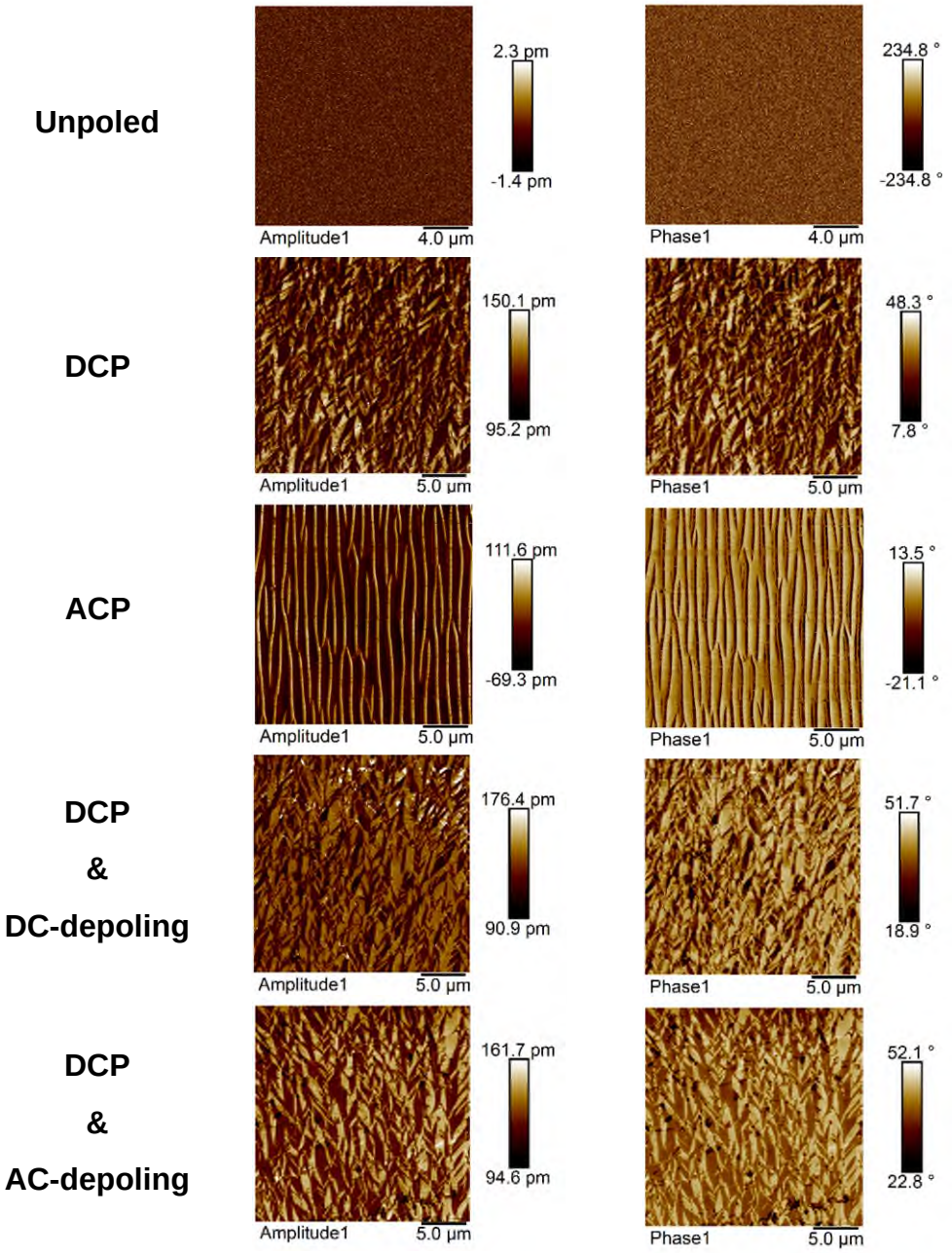

Figure R4 (Figure S14). Piezoresponse force microscopy (PFM) amplitude and phase images of unpoled, DCP, ACP, DC-depoled and AC-depoled PIN-PMN-PT crystals. Given that our simulation results show that electrically-depoled crystals have irregular patterns similar to DC-poled crystals to some extent, our PFM results are well consistent with the computational calculations.

4. An intriguing aspect to explore further is whether this method can depolarize the ferroelectric material to a specific polarization state. It would be insightful for the authors to provide commentary on this aspect, potentially elucidating the method's capabilities in achieving desired polarization states.

Response: We really appreciate the reviewer's comment to further complement our manuscript and works. In our opinion, it is not "perfectly" feasible for ferroelectric materials to be "directly" depolarized (switched) to a specific polarization state. However, as shown in **Figure 4**, once ferroelectric materials are depolarized through AC electric fields, we can freely control their final polarization states. By this way, the proposed method can depolarize ferroelectric materials and then achieve a specfic polarzation state. When it comes to the method's capabilities, we are considering the tunability of ferroelectric materials inside piezoelectric devices, which is usually impossible so far. For example, if we need higher transmitting sensitivity of a underwater transducer, we can depole ferroelectric materials and then repole it by AC-poling (higher piezoelectric properties). If we need higher voltage receiving sensitivity of an acoustic transducer, we can depole or partially ferroelectric materials. We argue that this is our selling point for the suggested method's capabilities in achieving desired polarization states. We have complemented our manuscript with our discussion added in the revised one as follows.

'We expect the suggested idea will be useful thanks to its capabilities in achieving desired ferroelectric states. In other words, the proposed method can depolarize ferroelectric materials and then achieve a desired polarization state without heat treatment and device disassembly. In this regard, the advantage of our idea is the tunability of ferroelectric materials inside piezoelectric devices, which is usually impossible so far. The idea can be also extended to ferroelectrics-based devices. More ferroelectric variants in ferroelectrics-based memory devices are definitely beneficial for next-generation applications to achieve new functionality. Therefore, investigating how to precisely control ferroelectric states is our principal goal for the future works."

5. It would be beneficial for the authors to include figures depicting the experimental setup and the fabricated device, providing readers with a visual understanding of the methodologies employed and the resulting device architecture.

Response: Thanks for the suggestion. We have complemented figures illustrating experimental setup and characterizations for better understanding.

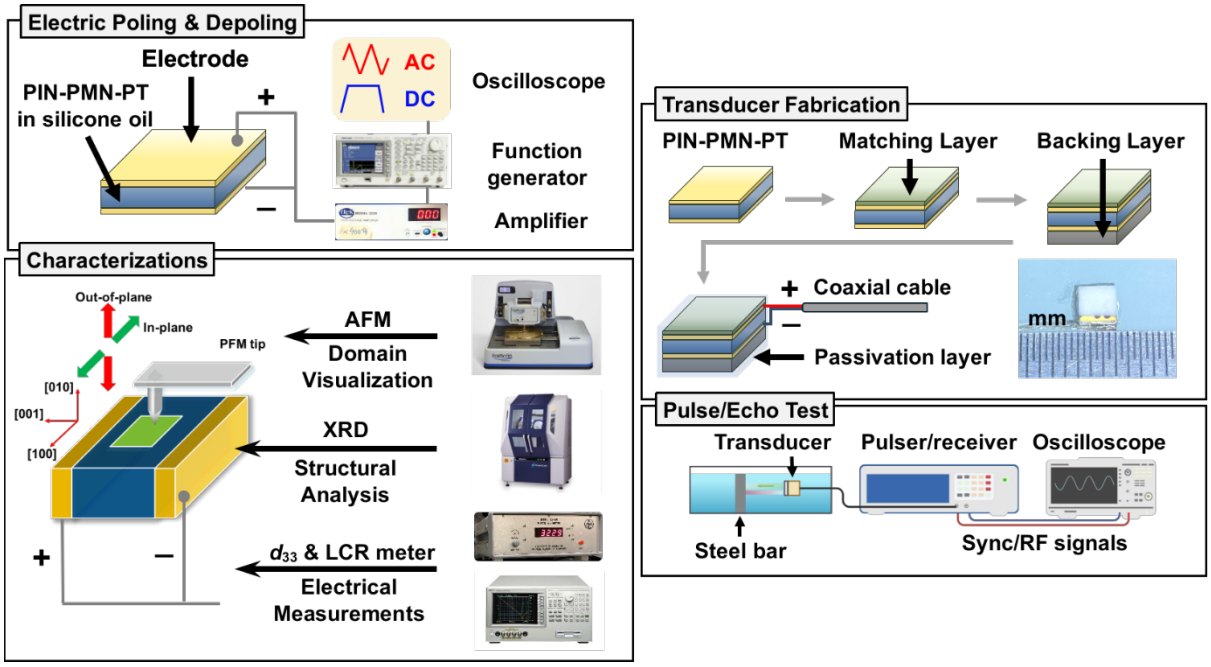

Figure R5 (Figure S15). Schematic illustrations dipicting the exeperimental procedures and characterizations in this work.

6. The authors should rectify certain errors within the main context. For instance, in Figure 2's caption, "impedance spectrum of initially DCP PIN-PMN-PT single crystals after being triggered by AC electric fields for depoling" should be corrected. Additionally, in the section discussing phase field simulation, the equation contains a discrepancy where "r" is mentioned but not included in the equation. The authors should ensure consistency and accuracy in all textual descriptions and equations throughout the manuscript.

Response: Thanks for the careful reading. To avoid any misunderstanding for potential readers, we have corrected the manuscript for better readability.

REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

The authors have addressed my comments and I think this manuscript is ready to be accepted for publication.

Reviewer #2 (Remarks to the Author):

The authors have provided additional experiments to improve the manuscript. The results are attractive and clear, so it meets the standards for a publication. However, before publication, a few things need to be addressed.

1. The authors provide some additional figures in the supplementary document, but it is better to give the main summary or brief discussion in the main context.

2. The authors should be careful about the figure captions to make them clearer.

Dear Editor and Reviewers,

We are grateful to the editor and reviewers for taking efforts to review our recent work, entitled “Electrical De-poling and Re-poling of Relaxor-$PbTiO_3$ Piezoelectric Single Crystals without Heat Treatment”. Thanks to all the constructive comments, our manuscript has been truly improved, and we are so delightful to receive the positive responses from the reviewers. Finally, according to the reviewer’s most recent comments, we have modified our recent submission for better clarity to potential readers. We do hope that our revised manuscript meets the standards of *Nature communications*. Any corrections made to the previous manuscript are highlighted with yellow color.

Reviewer #1 (Remarks to the Author):

The authors have addressed my comments and I think this manuscript is ready to be accepted for publication.

Reviewer #2 (Remarks to the Author):

The authors have provided additional experiments to improve the manuscript. The results are attractive and clear, so it meets the standards for a publication. However, before publication, a few things need to be addressed.

1. The authors provide some additional figures in the supplementary document, but it is better to give the main summary or brief discussion in the main context.

(**Response**) We are thankful for the reviewer to help us improve our manuscript. It will be surely helpful for better clarity to potential readers. Our manuscript has been complemented with additional information regarding the new figures in the supplementary document.

(**Before**) X

(**After**) To confirm our phase-field simulation results, we visualized ferroelectric domains of the single crystals using piezoresponse force microscopy (PFM) (**Figure S8**). The domain configurations were captured at different poling states for better comparisons. In contrast with ACP which generates periodic domain structures, de-poling by AC electric fields induces complex structures which are similar to DCP. Further, the simulation shows that de-poling by AC electric fields also leads to DCP-like irregular pattens. In this regard, our simulation results are consistent with the experimental results. In addition, we also measured X-ray diffraction patterns of the crystals to track crystallographic changes during de-poling by AC electric fields (**Figure S9**). When the initial poling state is ACP (ACP-EDP), the diffraction pattern after de-poling is shifted to a lower angle and consequently similar to DCP. This supports our argument from the simulation that de-poling by AC electric fields results in DCP-like domain configurations.

(**Before**) X

(**After**) To confirm its feasibility for other piezoelectric ceramics, we conducted the proposed de-poling experiments on $Pb(Zr,Ti)O_3$ (PZT) polycrystalline ceramics (**Figure S14**). The dimension of the ceramics is similar to that of the crystal in this work, and the amplitude of AC electric fields for de-poling is determined based on their E_c. Compared to PIN-PMN-PT single crystals, prominent de-poling behaviors were not observed in the PZT samples under the selected experimental conditions. Therefore, we can deduce that the optimized conditions for de-poling may be highly dependent on the types of materials. Further investigations are needed to study strategies to find optimum de-poling conditions for other types of piezoelectric ceramics.

2. The authors should be careful about the figure captions to make them clearer.

(**Response**) Thank you for the careful review on our manuscript. We have modified figure captions to avoid any misunderstanding.

Figure 1

(**Before**) **Figure 1**. (a) Schematic illustrations of poling and de-poling induced by AC electric fields. (b) Dielectric constants, (c) piezoelectric coefficients, and (d) impedance spectrum of ACP PIN-PMN-PT single crystals under AC electric fields for de-poling. The peak amplitudes, cycles, and frequencies of the AC electric fields were varied to investigate how poled states change in response to external electric fields. Compared to the de-poling by DC electric fields (**Figure S2**), AC electric fields can readily induce

an almost completely depoled state by simply adjusting the amplitude and frequency of AC electric fields.

(**After**) **Figure 1**. **AC electric field de-poling for AC poled PIN-PMN-PT single crystals.** (a) Schematic illustrations of experimental procedures for PIN-PMN-PT single crystals that were first poled by AC electric fields and then depoled by AC electric fields. (b) Dielectric constants, (c) piezoelectric coefficients, and (d) impedance spectrum of the PIN-PMN-PT single crystals after applying AC electric fields for de-poling. Error bars indicate the sample standard deviation of n = 3 measurements carried out on independent samples. The peak amplitudes, cycles, and frequencies of the AC electric fields were varied to investigate how poled states change in response to external electric fields. Compared to the de-poling by DC electric fields (Figure S2), AC electric fields can readily induce an almost completely depoled state by simply adjusting the amplitude and frequency of AC electric fields.

Figure 2

(**Before**) **Figure 2**. (a) Schematic illustrations of poling and de-poling induced by DC and AC electric fields, respectively. (b) Dielectric constants, (c) piezoelectric coefficients, and (d) impedance spectrum of DCP PIN-PMN-PT single under AC electric fields for de-poling. The peak amplitudes, cycles, and frequencies of the AC electric fields were controlled to investigate how poled states are destabilized in response to external electric fields. Similar to the DC electric field for de-poling (**Figure S3**), initial poled states are influential in conditions for de-poling.

(**After**) **Figure 2**. **AC electric field de-poling for DC poled PIN-PMN-PT single crystals.** (a) Schematic illustrations of experimental procedures for PIN-PMN-PT single crystals that were first poled by DC electric fields and then depoled by AC electric fields. (b) Dielectric constants, (c) piezoelectric coefficients, and (d) impedance spectrum of the PIN-PMN-PT single crystals after applying AC electric fields for de-poling. Error bars indicate the sample standard deviation of n = 3 measurements carried out on independent samples. The peak amplitudes, cycles, and frequencies of the AC electric fields were controlled to investigate how poled states are destabilized

in response to external electric fields. Similar to the DC electric field for de-poling (Figure S3), initial poled states are influential in conditions for de-poling.

Figure 3

(**Before**) **Figure 3**. *In-situ* electric field induced (a) dielectric constants and (b) piezoelectric coefficients of ACP PIN-PMN-PT single crystals during de-poling triggered by AC electric fields. The peak amplitude and frequency of the AC electric fields for de-poling were 4 kV/cm and 1 Hz, respectively. Variations in the properties were measured at each cycle. The results show that the poled crystals were clearly de-poled after AC electric fields were applied.

(**After**) **Figure 3**. *In-situ* electric field induced (a) dielectric constants and (b) piezoelectric coefficients of PIN-PMN-PT single crystals when AC electric fields are applied for de-poling. The peak amplitude and frequency of the AC electric fields for de-poling were 4 kV/cm and 1 Hz, respectively. Variations in the properties were measured at each cycle. The results show that the poled crystals were clearly depoled after AC electric fields were applied.

Figure 4

(**Before**) **Figure 4**. (a) Schematic illustrations of the repetitions for poling and de-poling of PIN-PMN-PT single crystals induced by AC electric fields. (b) Dielectric constants and (c) piezoelectric coefficients of PIN-PMN-PT single crystals with multiple poling and de-poling processes to confirm the reproducibility of the de-poling induced by AC electric fields. (d) Impedance spectrum of a crystal after multiple poling and de-poling processes to ensure its effectiveness. Here, the optimized ACP condition (a peak amplitude of 10 kV/cm, 20 cycles and 30 Hz) was used for the poling while a peak amplitude of 4 kV/cm, 10 cycles and 1 Hz were adopted for the de-poling.

(**After**) **Figure 4**. (a) Schematic illustrations of repetition tests with multiple poling and de-poling processes that were conducted with PIN-PMN-PT single crystals. Here, the optimized ACP condition (a peak amplitude of 10 kV/cm, 20 cycles and 30 Hz) was used for the poling while a peak amplitude of 4 kV/cm, 10 cycles and 1 Hz were adopted for the de-poling. (b) Dielectric constants and (c) piezoelectric coefficients of the PIN-PMN-PT single crystals during multiple poling and de-poling processes to confirm the reproducibility of the de-poling induced by AC electric fields. (d) Impedance spectrum of crystals after multiple poling and de-poling processes to ensure its effectiveness.

Figure S1

(**Before**) **Figure S1**. (a) Schematic illustrations of poling and de-poling induced by AC and DC electric fields, respectively. Here, the DC electric fields were applied along the same direction of the initial polarity of ACP crystals. (b) Dielectric constants, (c) piezoelectric coefficients, and (d) impedance spectra of the ACP PIN-PMN-PT single crystals under DC electric fields for de-poling. The amplitude and duration time of the DC electric fields were controlled to investigate their effects on the poled state in response to external electric fields.

(**After**) **Figure S1**. (a) Schematic illustrations of experimental procedures for PIN-PMN-PT single crystals that were first poled by AC electric fields and then depoled by DC electric fields. Here, the DC electric fields for de-poling were applied along the same direction of the initial polarity of ACP crystals. (b) Dielectric constants, (c) piezoelectric coefficients, and (d) impedance spectra of the PIN-PMN-PT single crystals after applying DC electric fields for de-poling. Error bars indicate the sample standard deviation of n = 3 measurements carried out on independent samples. The amplitude and duration time of the DC electric fields were controlled to investigate their effects on the poled state in response to external electric fields.

Figure S2

(**Before**) **Figure S2**. (a) Schematic illustrations of poling and de-poling induced by AC and DC electric fields, respectively. (b) Dielectric constants, (c) piezoelectric coefficients, and (d) impedance spectra of initially AC-poled (ACP) PIN-PMN-PT single crystals under DC electric fields for de-poling. The amplitude and duration time of the DC electric fields were controlled to investigate their effects on the poled state in response to external electric fields. Though a transient de-poled state can be achieved at certain amplitude and time of the electric field exposure, it is hard to find exact conditions for an almost completely de-poled state using DC electric fields because de-poling occurs over a very short period of time.

(**After**) **Figure S2**. (a) Schematic illustrations of experimental procedures for PIN-PMN-PT single crystals that were first poled by AC electric fields and then depoled by DC electric fields. Here, the DC electric fields for de-poling were applied along the opposite direction of the initial polarity of ACP crystals. (b) Dielectric constants, (c) piezoelectric coefficients, and (d) impedance spectra of the PIN-PMN-PT single crystals after applying DC electric fields for de-poling. Error bars indicate the sample standard deviation of n = 3 measurements carried out on independent samples. The amplitude and duration time of the DC electric fields were controlled to investigate their

effects on the poled state in response to external electric fields. Though a transient depoled state can be achieved at certain amplitude and time of the electric field exposure, it is hard to find exact conditions for an almost completely depoled state using DC electric fields because de-poling occurs over a very short period of time.

Figure S3

(**Before**) **Figure S3**. (a) Schematic illustrations of poling and de-poling induced both by DC electric fields. (b) Dielectric constants, (c) piezoelectric coefficients, and (d) impedance spectra of initially DC-poled (DCP) PIN-PMN-PT single crystals under DC electric fields for de-poling. The amplitude and duration time of the DC electric fields were controlled to investigate their effects on the poled state in response to external electric fields. Here, we found that conditions for a de-poled state are highly dependent on initial poled states; the amplitude and time for the DC (poling) – DC (de-poling) case are different from the AC (poling) – DC (de-poling) case shown in **Figure S2**.

(**After**) **Figure S3**. (a) Schematic illustrations of experimental procedures for PIN-PMN-PT single crystals that were first poled by DC electric fields and then depoled by DC electric fields. Here, the DC electric fields for de-poling were applied along the opposite direction of the initial polarity of DCP crystals. (b) Dielectric constants, (c) piezoelectric coefficients, and (d) impedance spectra of the PIN-PMN-PT single crystals after applying DC electric fields for de-poling. Error bars indicate the sample standard deviation of n = 3 measurements carried out on independent samples. The amplitude and duration time of the DC electric fields for de-poling were controlled to investigate their effects on the poled state in response to external electric fields. Here, we found that conditions for a depoled state are highly dependent on initial poled states; the amplitude and time for the DC (poling) – DC (de-poling) case are different from the AC (poling) – DC (de-poling) case shown in **Figure S2**.

Figure S14

(**Before**) **Figure S14**. (a) Piezoelectric coefficients and (b) dielectric constants of poled $Pb(Zr,Ti)O_3$ ceramics under AC electric fields for de-poling. The peak amplitudes and frequencies of the AC electric fields were varied to investigate how poled states change in response to external electric fields. The dimension of the samples is 3 × 3 × 0.9*t* mm^3, which is similar to that of the crystals in this work. Given that its E_c is close to 8 kV/cm, an electric poling condition is set as 12.5 kV_{pp}/cm, 1 Hz and 20 cycles while electric fields for de-poling were applied under different frequencies (0.1, 1, 10 and 100 Hz) and amplitutes (0.6, 0.8, 1.0 and 1.2 E_c) at a fixed cycle (10 cycles).

(**After**) **Figure S14**. (a) Piezoelectric coefficients and (b) dielectric constants of poled $Pb(Zr,Ti)O_3$ ceramics after applying AC electric fields for de-poling. The peak amplitudes and frequencies of the AC electric fields for de-poling were varied to investigate how poled states change in response to external electric fields. The dimension of the samples is $3 \times 3 \times 0.9t$ mm^3, which is similar to that of the crystals in this work. Given that its E_c is close to 8 kV/cm, an electric poling condition is set as 12.5 kV_{pp}/cm, 1 Hz and 20 cycles while electric fields for de-poling were applied under different frequencies (0.1, 1, 10 and 100 Hz) and amplitudes (0.6, 0.8, 1.0 and 1.2 E_c) at a fixed cycle (10 cycles).