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Transparent Ferroelectric Crystals with Ultrahigh Piezoelectricity

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Transparent piezoelectrics are highly desired for numerous hybrid ultrasound-optical devices ranging from photoacoustic imaging transducers to transparent actuators for haptic applications[1,2,3,4,5,6,7]. However, it has long been challenging to simultaneously achieve high piezoelectricity and perfect transparency, since most high-performance piezoelectrics are ferroelectrics that contain high-density light-scattering domain walls. Here, through a combination of phase-field simulations and experiments, we demonstrate a relatively simple method of using an *AC* electric-field to engineer the domain structures of originally opaque rhombohedral $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) crystals to simultaneously generate near-perfect transparency, ultrahigh piezoelectric coefficient d_{33} (>2100 pC N^{-1}), outstanding electromechanical coupling factor k_{33} (~94%), and large electro-optical coefficient γ_{33} (~220 pm V^{-1}), far beyond the performance of the commonly used transparent ferroelectric crystal $LiNbO_3$ (d_{33} ~ 40 pC N^{-1}, k_{33} ~ 47%, and γ_{33} ~ 30 pm V^{-1}). We find that increasing the domain sizes leads to a higher value of d_{33} for the [001]-oriented rhombohedral PMN-PT crystals, challenging the conventional wisdom that decreasing the domain sizes always results in higher piezoelectricit[8,9,10]. This work presents a paradigm to achieve an unprecedented combination of properties and functionalities through ferroelectric domain engineering, and the new transparent ferroelectric crystals reported here are expected to open up a wide range of hybrid device applications, such as medical imaging, self-energy-harvesting touch screens and invisible robotic devices.

37 Achieving simultaneous high piezoelectricity and perfect transparency in a piezoelectric material has

38 long been a great challenge. For example, traditional high-performance piezoelectric transducers are

39 typically made from perovskite ferroelectric ceramics and crystals with chemical compositions around

40 their morphotropic phase boundaries (MPBs), e.g., $Pb(Zr,Ti)O_3$ (PZT) ceramics and domain-

41 engineered $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) crystals. These materials possess very high d_{33} and k_{33}

42 [11,12,13,14], but they are usually opaque in the visible light spectrum. On the other hand, the commonly

43 used transparent piezoelectrics, $LiNbO_3$ crystals and polyvinylidine fluoride (PVDF) polymers[6,7], have

44 good transparency but much lower values of d_{33} and k_{33} ($LiNbO_3$: $d_{33}<40$ pC N^{-1}, $k_{33} \sim 47\%$; PVDF: d_{33}

45 ~ 20 pC N^{-1}, $k_{33} \sim 16\%$), which severely limit the acoustic source level, bandwidth, and sensitivity of

46 the transparent transducers.

47 In addition to the extrinsic effects, such as porosity and grain boundaries which exist ubiquitously in

48 ceramics, the poor transparency in PZT ceramics and domain-engineered PMN-PT crystals is closely

49 associated with the light scattering and reflection by their ferroelectric domain walls. One can think of

50 two possible approaches to reduce the light-scattering domain walls. The first is to pole a ferroelectric

51 crystal along the polar direction to achieve a single-domain state. However, the value of d_{33} for such

52 single-domain PMN-PT crystals is generally very low,[13,14] much below that of [001] poled multi-

53 domain rhombohedral PMN-PT crystals (>1500 pC N^{-1}). In principle, one can first pole a

54 rhombohedral PMN-PT crystal along the [111] direction to achieve a single domain state with good

55 transparency, then rotate the crystal to [001] direction to guarantee the high longitudinal

56 piezoelectricity. However, this approach is not feasible in practice as detailed in the Methods section.

57 The second approach is to dramatically reduce the domain sizes by breaking the domains into polar

58 nanoregions whose spatial sizes (a few to tens of nanometres) are much smaller than the wavelength of

59 visible light, thus greatly improving the light transparency as observed in La-doped PZT[15,16]. However,

60 improving the transparency using polar nanoregions was achieved at the expense of a drastically

61 reduced remanent polarization and thus very low values of d_{33}. Therefore, optical functionalities in

62 high-performance piezoelectrics have not been realized despite more than 50 years of efforts.

63 In this work, we show that one can use AC electric-fields to effectively eliminate light-scattering 71°

64 domain walls for [001]-oriented rhombohedral PMN-PT crystals to achieve both near-perfect

65 transparency and ultrahigh piezoelectricity. We first perform phase-field simulations to study the

66 domain evolution of a [001]-oriented $0.72Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.28PbTiO_3$ (PMN-28PT) rhombohedral

67 crystal using both conventional DC and AC electric-fields. We generate the initial pristine unpoled state

68 starting from a random distribution of small polarizations representing a high-temperature paraelectric

69 state. The obtained multi-domain state contains all eight possible <111> rhombohedral domain variants

70 with an average size of ~ 20 nm. Three types of domain walls are present in the unpoled rhombohedral

71 crystal, i.e., 71°, 109° and 180° domain walls.

72 Under a DC electric-field along the [001] direction, the four domain variants with polarizations along

73 $[11\bar{1}]$, $[\bar{1}1\bar{1}]$, $[\bar{1}\bar{1}\bar{1}]$ or $[1\bar{1}\bar{1}]$ are switched to the [111], $[1\bar{1}1]$, $[\bar{1}\bar{1}1]$ or $[\bar{1}11]$ directions. Thus,

74 only 71° and 109° domain walls survived while the 180° domain walls were eliminated by poling, as

75   shown **Fig. 1a**. The horizontal layers are separated by a set of 109° domain walls parallel to the (001)

76   plane, while within each lamina, there are 71° domain walls approximately parallel to {011} planes. It

77   should be noted that 71° domain walls can scatter light since the refractive indices n_o and n_e (the

78   subscript letters 'o' and 'e' represent ordinary and extraordinary light, respectively) change as light

79   travels across a 71° domain wall, as shown in Extended Data Fig. 1. In contrast, 109° domain walls do

80   not induce light scattering since the refractive indices are the same for the domains on both sides of a

81   109° domain wall.

82   Our phase-field simulations demonstrate that the application of an *AC* electric-field effectively reduces

83   the number of 71° domain walls with only two 71° domain walls left in each lamina after *AC*-poling,

84   leading to the much larger domain size within each lamina. To understand the reason for the

85   elimination of 71° domain walls by *AC*-poling, we analyse the domain evolution during the

86   polarization reversal process, as shown in Fig. 1b and SI Videos 1&2. One can see that the reversal of

87   electric field causes the "swinging" of 71° domain walls, i.e., 71° domain walls alternating between

88   (011) and (01$\bar{1}$) planes. During this process, the contiguous 71° domains tend to merge with each other,

89   and thus a significant increase in 71° domain size after *AC*-poling. In addition, as presented in Extended

90   Data Fig. 2, the total free energy of the system is reduced during *AC*-poling since the energies arising

91   from the discontinuities of polarization/strain associated with domain walls decrease as the domain

92   wall density decreases. In other words, alternating the polarity of the electric-field back and forth

93   lowers the free energy of a ferroelectric crystal, leading to a domain structure with reduced domain

94   wall density. As discussed above, due to the significantly decreased 71° domain wall density, the light

95   transmission of the *AC*-poled sample is expected to be superior to a corresponding *DC*-poled sample.

96   Following the phase-field simulations, we characterized the domain structures of *AC*-poled and *DC*-

97   poled PMN-28PT crystals. Using birefringence imaging microscopy (BIM)[17], we characterized the

98   orientation (φ) of the principal axis of the optical indicatrix projected on the (001) planes, as shown in

99   **Fig. 2a**. For a rhombohedral single domain, the projection of the optical axis is along the face diagonal.

100   Therefore, the orientation φ of a rhombohedral domain would be 45° or 135°, which are represented by

101   blue and red colours respectively, as shown by the colour bar in Fig. 2a. A multi-domain crystal may

102   show two or more colours simultaneously in the projection map due to the overlap of ferroelectric

103   domains and domain walls along the light propagation path.

104   For the unpoled sample, the orientation map shows an irregular colour distribution on a very fine scale.

105   This is because the domain size of the as-grown PMN-PT is much smaller than the experimental

106   resolution (i.e., the wavelength of the light: 590 nm); therefore, the exact domain pattern may not be

107   clearly revealed. Compared to classical ferroelectrics (e.g., $BaTiO_3$), the relatively small domain size in

108   relaxor ferroelectrics (on the order of several tens of nanometres before poling [18,19,20]) is attributed to

109   the presence of random fields/bonds that inhibits the growth of ferroelectric domains [21,22,23,24].

110   After *DC*-poling, the regions with the same colour increase in size, and cross-like boundaries are

111   approximately along the [100] and [010] directions, which are associated with the projections of 71°

112 domain walls [(101), (10$\bar{1}$), (011) or (01$\bar{1}$) planes] on the (001) plane. In this image, the colours of
113 most regions are neither red nor blue. Of particular importance is the significantly enlarged domain size
114 in the *AC*-poled sample where the in-plane size of the rhombohedral domain is on the millimetre scale.
115 It should be noted that the domain size obtained from phase-field simulation is much smaller than that
116 from experiments. This is due to the fact that the spatial scale in the phase-field simulation (512 nm) is
117 much smaller than that of the materials in experiments (millimeter scale). By increasing the scale in
118 phase-field simulation, the domain size of *AC*-poled crystal is found to increase (Extended Data Fig. 3).
119 It is difficult to perform a phase-field simulation on millimeter scale and at the same time to revolve the
120 polarization profiles across domain walls of the thickness of ~1 nm. In this work, we used phase-field
121 simulations to qualitatively analyse the domain evolution of PMN-28PT crystals during *AC*-poling. We
122 also characterized the cross-section domain structure of *AC*-poled and *DC*-poled samples to investigate
123 the domain size for the out-of-plane direction. As shown in Extended Data Fig. 4, we found that the
124 width between two neighbouring 109° domain walls is similar for both samples (~ 1 micron), indicating
125 that most 109° domain walls survived after *AC*-poling, which is consistent with phase-field simulations.

126 X-ray diffraction patterns confirm the main observations from the BIM images. Fig. 2b shows the {222}
127 reflections for the [001]-oriented PMN-28PT crystals. In this measurement, if the rhombohedral
128 domain variants are evenly distributed in the sample, there should be two diffraction peaks in the 2θ-ω
129 map: one peak is associated with the (222) plane at a lower 2θ, and the other peak is associated with the
130 remaining three {222} planes at a higher 2θ. Thus, the integrated intensity of the high-2θ reflection is
131 supposed to be three times that of the low-2θ reflection. This is approximately what has been observed
132 in the unpoled sample. The diffuse distribution of the diffraction along the ω axis is associated with the
133 lattice distortions due to the existence of domain walls. After *DC*-poling, the diffraction peaks converge
134 into distinctive sharper reflections, indicating that the domains become larger and the volume fraction
135 of domain walls is decreased. Eventually, in the *AC*-poled sample, only the high-2θ diffraction peak is
136 observed, and the diffusiveness of the diffraction peak along the ω axis is much smaller than that of the
137 *DC*-poled and unpoled samples (Extended Data Fig. 5). These features reveal that the X-ray beam is
138 almost incident on a single domain of *AC*-poled sample. The size of the beam here is approximately 1
139 mm^2, which leads us to believe that the in-plane domain size of the *AC*-poled sample is equal to or
140 greater than this value.

141 Due to the unique domain structure, *AC*-poled PMN-28PT crystals exhibit numerous attractive
142 properties in addition to their ultrahigh piezoelectricity, including a high electro-optical coefficient γ_{33}
143 of 220 pm V^{-1}, near-perfect light transmittance, and an enhanced birefringence (Extended Data Table 1).
144 **Fig. 3a** shows photos of the *AC*-poled and *DC*-poled samples, where *AC*-poled samples are clearly
145 transparent. The light transmittance of *AC*-poled sample is found to be very close to its theoretical limit
146 and is much higher than that of the *DC*-poled sample, especially for the visible light spectrum, as
147 shown in Fig. 3b. The light with a wavelength below 400 nm is completely absorbed due to the optical
148 absorption edge (~3.10 eV), which is similar to most oxygen-octahedral perovskites[25,26]. At a
149 wavelength above 400 nm, the light absorption coefficient of the *AC*-poled sample is found to be

150 almost zero, while the absorption coefficient of the *DC*-poled sample remains large and monotonically
151 decreases with increasing wavelength (Extended Data Fig. 6).

152 The birefringence of the *AC*-poled crystals is approximately one order of magnitude higher than that of
153 their *DC*-poled counterparts, as shown in Fig. 3c. This difference is associated with the different
154 domain structures. The principle axis of the optical indicatrices of the domains on both sides of a 71°
155 domain wall are perpendicular to each other on the (001) plane, resulting in cancellation of the
156 birefringence as light travels through a 71° domain wall (see Methods section for *Polarized Light*
157 *Microscope*). For *AC*-poled crystals, however, the birefringence is approximately equal to that of the
158 intrinsic value of a single-domain rhombohedral PMN-28PT crystal due to the substantially decreased
159 number of 71° domain walls.

160 In addition, the *AC*-poled crystals exhibit a 30% enhancement in d_{33} over the *DC*-poled crystals. This
161 phenomenon was observed in many *AC*-poled relaxor-PT crystals[27,28,29,30]. To understand the
162 mechanism for the enhanced piezoelectricity, we conducted phase-field simulations to calculate the
163 piezoelectricity of PMN-28PT with different 71° domain sizes, as shown in **Fig. 4a**. The variation of
164 polar vectors around a 71° domain wall is depicted in Fig. 4b. For an ideal rhombohedral domain, the
165 polar vectors are along <111> directions, and the angle between the polar vector and [011] direction is
166 35.3°. However, the presence of 71° domain walls causes the polar vectors to rotate towards the [011]
167 direction to minimize the polarization gradient and elastic energies associated with the
168 polarization/strain discontinuities around the domain walls. With decreasing domain size, the impact of
169 the domain walls on the polarization becomes more prominent, resulting in a larger deviation of
170 polarization from the <111> directions, as shown in Fig. 4c. Because of variations in polarization, the
171 free energy profile of the system is also affected. As shown in Fig. 4d, the averaged free energy profile
172 of the system as a function of ΔP_z is flattened with the increase in the 71° domain width, i.e., the

173 curvature of free energy profile $\left(\frac{\partial^2 G}{\partial P_z^2}\Big|_{\Delta P_z=0}\right)$ decreases with increasing 71° domain width. Thus, the

174 calculated dielectric permittivity ε_{33} and d_{33} increase with enlarging 71° domain width, as shown in
175 Figs. 4e&f.

176 It should be noted that the observed enhancement in piezoelectricity with increasing domain size is not
177 universal to all ferroelectric crystals. It is expected that the piezoelectricity of ferroelectrics is also
178 related to the symmetry of ferroelectric phase and domain configurations[31,32]. For example, in
179 tetragonal BaTiO_3 [8,9,10] and high-temperature-poled PZN-PT crystals[33], where domain configurations
180 are very different from PMN-28PT, the domain-size-dependence of piezoelectricity shows an opposite
181 trend to that we observed here.

182 For the purpose of practical applications, we also studied the temperature stability of properties of *AC*-
183 poled PMN-28PT crystals (Extended Data Fig. 7), which indicates that the temperature dependent
184 electromechanical behaviors of *AC*- and *DC*-poled samples are very similar. Of particular interest is
185 fact that at temperatures below rhombohedral-tetragonal phase transition temperature (~95 °C), the

186 domain structure remains essentially the same, and no depolarization behaviour is observed, indicating
187 *AC*-poled crystals can be used up to their respective phase transition temperatures.

188 In summary, we report a simple approach of using AC electric-fields to simultaneously achieve near-
189 perfect transparency, enhanced piezoelectricity and birefringence for rhombohedral PMN-PT crystals.
190 Such transparent crystals are expected to find a wide range of applications in electro-optical-
191 mechanically coupled devices. Both experimental and simulated results demonstrate that the enhanced
192 piezoelectricity of [001]-poled rhombohedral PMN-PT crystals through AC-poling is due to the
193 increased domain size, in contrast to the long-standing belief that decreasing domain size always leads
194 to higher piezoelectricity.

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268

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Author Contributions

The work was conceived and designed by S.Z., L.Q.C., and F.L.; C.Q. performed the piezoelectric and optical experiments; F.L. and Z.X. supervised the piezoelectric and dielectric measurements; N.Z. and F.L. supervised the optical experiments; B.W. performed the phase-field simulations and discussed with F.L.; L.Q.C. supervised the simulation work; J.L. assisted piezoelectric measurements; N.Z. and D.W. performed XRD experiments; Y.W. and H.T. assisted the optical measurements; F.L. drafted the manuscript; S.Z., N.Z., L.Q.C. and T.R.S. revised the manuscript; and all authors discussed the results. The authors declare no competing financial interests.

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Figure 1 Phase-field simulations of the domain structures and evolution of [001]-oriented rhombohedral PMN-28PT single crystals via *DC* and *AC* poling. a, Domain structures for unpoled, *DC*-poled and *AC*-poled samples. The black and white vectors on the right show the polarization directions, where the colour denotes the positive (white) and negative (black) polarization components along the [100] direction, respectively. The colours represent different ferroelectric domains, where the corresponding polar directions are illustrated on the right of the figure. Examples of 71° and 109° domain walls are indicated by the red arrows. A beam of light is schematically illustrated in the *DC*- and *AC*-poled cases, indicating that the light may not be scattered as it travels through the *AC*-poled sample. **b**, Snapshots of the domain pattern evolution during the reversal of polarization under *AC* poling. The initial state (i.e., $E = 0.0$ kV cm^{-1}) is the DC-poled sample. The dimensions of all the domain structure plots are 512 nm × 512 nm. The videos illustrating the domain evolution under an *AC* electric field are shown in SI Videos 1&2. For comparison, a video illustrating the domain evolution under a *DC* electric field is shown in SI Video 3.

Figure 2 Analysis of the domain structures for the [001]-oriented PMN-28PT crystals. a, Birefringence imaging microscopy (BIM), where the colours indicate the orientations (φ) of the projection of the principal optical axis on the (001) plane. The red and blue colours represent the projection of the principal axis of the optical indicatrix along the face diagonals on the (001) plane, i.e., orientation angles φ of 45° and 135°, respectively. For example, the projections of the principal axis of the optical indicatrix of the $[\bar{1}\bar{1}1]$ and $[1\bar{1}1]$ domains are illustrated in the schematics on the right of the figure. **b**, Reciprocal space maps of the {222} reflections from differently treated samples measured with high-resolution single-crystal XRD. The colour bars on the right of the figure indicate the intensity of the diffractions. The thickness of the samples is 175 μm.

Figure 3 Comparison of the properties for *AC*-poled and conventional *DC*-poled [001]-oriented PMN-28PT crystals. a, Photo of *AC*-poled and *DC*-poled PMN-28PT crystals. The thicknesses of the crystals are 0.5 mm and 1.8 mm, respectively. **b**, Light transmittance of the *AC*-poled and *DC*-poled PMN-28PT crystals. **c**, Piezoelectric coefficient d_{33} and birefringence of the *AC*-poled and *DC*-poled PMN-28PT crystals. Ten AC-poled and ten DC-poled samples are used for the characterization of piezoelectric coefficient d_{33}, while birefringence is determined from seven points of the AC-poled and DC-poled samples. The error bars in Fig. 3c present the standard deviations (SD) of the corresponding data.

Figure 4 Phase-field simulations of the domain size effect on the polarization, free energy density and properties of the PMN-28PT crystal. a, a 2D schematic of an [001]-poled PMN-28PT with different 71° domain width (D_{71}). D_{71}=inf. means there are no 71° domain walls in the system. The polar directions for different colors are depicted on the right of the figure. **b**, Schematic of polar vectors around a 71° domain wall as marked by the green line in Fig. a. The colours represent the angles (deg.=degree) between each polar vector and the [011] direction. The 71° domain width in this schematic is 64 nm. **c**, The averaged magnitude of the spontaneous polarization components P_x ([100]), P_v ([010]) and P_z ([001]) of a ferroelectric domain as a function of the 71° domain width. **d**, The averaged free energy density of the system with respect to the variation of polarization P_z. The free energy density at the stable state (i.e., ΔP=0) is selected as the reference in this figure. **e**, Dielectric permittivity as a function of 71° domain width. **f**, Piezoelectric coefficient as a function of 71° domain width.

Methods

Sample preparation

To achieve high transparency of rhombohedral PMN-PT crystals, we choose crystal compositions to avoid the presence of multiple phases, e.g., a mixture of rhombohedral, monoclinic, and orthorhombic phases within a MPB region. In particular, we selected the 28%PT composition to stay away from the MPB region (around 33%PT). The PMN-28PT single crystals were grown by a modified Bridgman method at Xi'an Jiaotong University. The crystals were oriented by an X-ray diffraction method with the x, y and z axes along the [100], [010] and [001] directions, respectively, and then cut into the required dimensions for different experiments. The thickness of the samples for the domain observation and birefringence measurement was 0.175 mm. For the other experiments, the thickness of the samples was in the range of 0.5 mm to 4 mm. Vacuum-sputtered gold was applied to both (001) faces of the samples as electrodes.

The *AC* and *DC* poling experiments were performed by using a ferroelectric test system (TF Analyzer 2000E, aixACCT) with a high-voltage amplifier (TREK 610E). The samples were immersed in silicone oil during the poling process. For *AC* poling, a bipolar triangle wave was applied to the samples with a frequency of $0.1 \sim 10^2$ Hz, a cycle number of 5~20, an amplitude of 5 kV cm^{-1} and a poling temperature of 20~60°C [34]. We discovered that essentially all the 71° domain walls could be effectively eliminated by using *AC* electric fields with a broad range of frequencies from 0.1 to 100 Hz (see Extended Data Fig. 8). The cycle number was selected to be larger than 10, since the enhancement of dielectric permittivity was found to saturate after 10 cycles, as shown in Extended Data Fig. 9. To minimize the fluctuation of dielectric and piezoelectric properties among different samples, the frequency of AC electric field was selected to be below 10 Hz in this work, as shown Extended Data Fig. 9. To avoid the influence of internal stresses generated during polishing and sputtering of PMN-28PT crystals, a thermal annealing process was applied to the PMN-28PT crystals before AC-poling[34]. Specifically, the samples were first annealed at 300°C for 5 h and then slowly cooled down to room temperature. The samples then dwelled at room temperature for 5-7 days until the dielectric loss was reduced from 4~5% right after the annealing to around 2%. For *DC*-poling, a conventional poling process of PMN-PT crystals was adopted with a DC electric field amplitude of 5 kV cm^{-1} and a dwelling time of 5 min.

For the optical and XRD experiments, the gold electrodes were removed by a solution of potassium iodide and iodine (the mass ratio of KI, I$_2$ and H$_2$O was 4:1:40) without affecting the polarization. The (001) surfaces were then carefully polished to optical quality using diamond polishing paste decreasing the average grit size down to 0.05 μm. In the electro-optic measurements, a thin layer of gold film (~15 nm) was deposited on the polished surfaces as electrodes. Silver leads were attached by conductive epoxy to apply a voltage.

Here, we would like to note that there are two technical issues associated with the idea using crystals poled along the [111] direction and then cut along the [001] direction to achieve both high piezoelectric coefficient d$_{33}$ and light transparency rather than AC-poling employed in this work.

(1) The limitation of crystal size and difficulty to achieve a single domain state by poling [111] oriented rhombohedral crystals: For example, if one needs a [001]-oriented crystal plate with the size of 20mm×20mm×1mm (for medical transducers, practical size of piezoelectric materials is in the range of 20 – 60 mm), one first needs a [111]-oriented crystal with the size of ~30×30×30 mm. To pole a crystal with the thickness of 30 mm along its spontaneous polarization direction is almost an impossible task due to the severe cracking as a result of the internal stress development during poling[35]. In addition, one cannot guarantee the composition homogeneity for the [001]-oriented crystal plates made by this process because of the composition segregation along the crystal growth direction of Bridgman grown PMN-PT crystal boules.

384 (2) The instability of a single domain state and the issue of depolarization: Preparing the [111]-poled
385 samples with rotated d_{33} involves high-temperature processes, such as attaching a crystal onto a sample
386 holder for cutting, heat generation during cutting, and sputtering transparent electrodes (the temperature
387 for sputtering of ITO electrodes is 300$^\mathrm{o}$C~600$^\mathrm{o}$C). One may argue that we can adopt careful low
388 temperature processes and utilize low temperature transparent electrodes (e.g., silver nanowires) to
389 prepare the samples. However, based on our experiences, this is really a difficult task, as we need to
390 use special binders and sample holders and drastically slow down the cutting speed of the cutting
391 machine; meanwhile, the adhesion of electrodes will be greatly affected by using silver nanowires to
392 replace ITO. Even by using all these precautions and approaches, the samples are still likely to be
393 depolarized to some extent because of the instability of a single domain state. In addition, the [001]-
394 oriented samples made by this process cannot be re-poled if they are de-poled accidentally. This is due
395 to the fact that we cannot recover the original [111]-oriented samples.

396

397 **Dielectric and piezoelectric measurements**

398 The piezoelectric coefficients were determined by a combination of a quasi-static d_{33} metre (ZJ-6A)
399 and an electric-field-induced strain measurement. The electric-field-induced strain was measured by a
400 ferroelectric test system (TF Analyzer 2000E, aixACCT, Germany) with a laser interferometer (SIOS
401 SP-S 120E, Germany). The dielectric permittivity was measured using an LCR metre (E4980A,
402 KEYSIGHT technologies, CA, USA). In the measurements of temperature-dependent properties, the
403 piezoelectric coefficient d_{33} and electromechanical coupling factor k_{33} of PMN-PT crystals are
404 determined by the resonance method according to IEEE Standard.

405 **Optical transmittance measurement**

406 Transmission spectra were measured by a UV–VIS–IR spectrophotometer (JASCO V–570, Japan) at
407 wavelengths ranging from 300 to 2500 nm. The incident light was set to transmit through the crystal
408 along the poling direction, which was perpendicular to the (001) surface.

409 According to the Fresnel equations, the reflection loss at two faces of the crystal plate was calculated
410 from 450 to 850 nm through,

411 $$R = \frac{(n-1)^2}{n^2+1} \qquad (1)$$

412 where n is the wavelength-dependent index of refraction, calculated from the Sellmeier equation for a
413 PMN-28PT single crystal given in Refs. 36&37.

414 The effective loss coefficient α_{eff}, a combination of the scattering coefficient κ and the absorption
415 coefficient, α ($\alpha_{eff} = \kappa + \alpha$), was calculated using the transmission data from samples of different
416 thicknesses,

417 $$\alpha_{eff} = -\frac{\ln(T_2/T_1)}{t_2 - t_1} \qquad (2)$$

418 where T_1 and T_2 are the transmittances of the two samples with thicknesses t_1 and t_2, respectively.

419 **Domain characterizations by optical methods**

420 *Polarized light microscope (PLM).* The domain patterns and their extinction behaviours were observed
421 using a PLM with a 0°/90° crossed polarizer/analyser (P/A) pair (OLYMPUS BX51, Japan). The
422 optical retardation was measured using a thick Berek compensator (OLYMPUS U-CTB ranging from
423 0~10λ) and an interference filter (IF546, λ=546.1 nm). The birefringence was calculated as the ratio of
424 the retardation to the sample thickness. In the following, we would like to explain the cancellation

11

425 effect of birefringence as light travels across a 71° domain wall. For a single domain rhombohedral
426 ferroelectric, the parameters n_o and n_e are the refractive indices for the ordinary light and extraordinary
427 light propagating along z-axis, respectively. The parameters Δn_1 and Δn_2 are the birefractive indices of
428 two different domains on both sides of a 71° domain wall. Since the principal axes of the optical
429 indicatrices of the domains on both sides of a 71° domain wall (e.g., the domains with polar vectors
430 along [111] and [1$\bar{1}$1] directions) are perpendicular to each other on the (001) plane, the relation
431 between Δn_1 and Δn_2 is: $\Delta n_1 = -\Delta n_2$. Thus as the light travels across a 71° domain wall, the measured
432 birefringence can be expressed by the following equation:

433 $$\Delta n^* = \frac{\Delta L}{d} = \frac{\Delta n_1 \cdot d_1 + \Delta n_2 \cdot d_2}{d_1 + d_2} = \Delta n_1 \cdot \frac{d_1 - d_2}{d} \quad (3)$$

434 where d_1 and d_2 are the lengths of optical path within the [111] and [1$\bar{1}$1] domains, respectively, ΔL is
435 the optical retardation caused by birefringence, and d is a sum of d_1 and d_2. It is obvious that the
436 measured birefringence will be quite small if the values of d_1 and d_2 are similar.

437

438 *Birefringence imaging microscopy (BIM)*. The domain orientation measurements were performed using
439 BIM equipment (Metripol, Oxford Cryosystems, UK). Monochromatic light with a wavelength of 590
440 nm was used as the light source. A quarter-wave plate and a polaroid (P$_2$) were placed at a 45° position
441 to produce circularly polarized light. The circularly polarized light was converted to elliptical
442 polarization after passing through an optically anisotropic specimen. The light then transmits through a
443 linear analyser (P$_2$) rotating about the microscope axis at a frequency of ω. Finally, the intensity
444 measured by the charge-coupled device (CCD) camera as a function of ω is given by

445 $$I = \frac{1}{2}I_0[1 + \sin 2(\omega t - \varphi)\sin \delta] \quad (4)$$

446 where t is time, φ is the angle between the horizontal direction and the principal axis of the optical
447 indicatrix, δ is the phase shift introduced to the light rays passing through the anisotropic sample with a
448 certain thickness, and I_0 is the intensity of the unpolarized light. After rotating the analyser 10 times, it
449 is possible to obtain the intensity of each pixel on the recorded image, refine the I_0, $|\sin \delta|$, and φ values,
450 and construct the false-colour images.

451 **High-resolution X-ray diffraction experiments**

452 High-resolution single-crystal XRD experiments were carried out to analyse the {222} Bragg
453 reflections for (001)-oriented PMN-PT crystals. A high-resolution diffractometer (PANalytical X'Pert
454 Pro MRD), equipped with Cu$K\alpha_1$ radiation, a hybrid mirror monochromator, an open Eulerian cradle
455 and a solid-state PIXcel detector, was used for a precise two-dimensional 2θ-ω scan of the {222} Bragg
456 peaks. The reciprocal space maps were collected with step sizes of 0.004° in ω and 0.004° in 2θ. The
457 intensity of the patterns was accumulated along the ω or 2θ direction and then fitted to the pseudo-
458 Voigt function:

459 $$f(x) = a_1 \left\{ a_4 \cdot \frac{1}{1 + \left(\frac{x - a_2}{a_3}\right)^2} + (1 - a_4)\exp\left[-\left(\frac{x - a_2}{a_3}\right)^2\right] \right\} \quad (5)$$

460 where a_1 is the intensity of the peak, a_2 is the position of the peak, a_4 is the mixing parameter of the
461 Gaussian and Lorentzian profiles, and a_3 is proportional to the FWHM, which can be calculated using
462 the equation,

463 $$\text{FWHM} = 2\sqrt{\ln 2} \cdot a_3 \quad (6)$$

464 **Electro-optic measurements**

465 The electro-optic (E-O) coefficients of the samples were measured using a modified Mach-Zehnder
466 interferometer. The light source was a 632.8 nm He–Ne laser. For the longitudinal mode, the light
467 beam and the applied electric field were both parallel to the poling direction. In this mode, the
468 longitudinal effective linear E-O coefficient ($\gamma^{L}_{c}{}^{*}$) was measured.

469 For the transverse mode, the light beam travels along the [110] direction, and the electric field was
470 applied along the [001] poling direction of the sample. The linear E-O coefficients $\gamma_{13}{}^{*}$ and $\gamma_{33}{}^{*}$ were
471 measured when the polarization directions of the laser beam were perpendicular and parallel to the
472 poling direction, respectively. The transverse effective linear E-O coefficient ($\gamma^{T}_{c}{}^{*}$) was calculated by
473 the equation:

474 $$\gamma^{T^*}_{c} = \gamma^{*}_{33} - n^{3}_{o}\gamma^{*}_{13}/n^{3}_{e} \quad (7)$$

475 where n_o and n_e are the refractive indices of the ordinary and extraordinary light, respectively. The
476 refractive indices were calculated from the data of mono-domain crystals[36,37]. The marker (*) indicates
477 that the measured E-O coefficient is a combination of the inverse piezoelectric effect and the intrinsic
478 E-O effect.

479 **Phase-field simulations**

480 The domain evolution and piezoelectric responses were obtained by performing phase-field simulations.
481 A domain structure is described by the spatial distribution of the ferroelectric polarization **P**. The
482 temporal evolution of the polarization and thus the domain structure is described by the time-dependent
483 Ginzburgh-Landau (TDGL) equation:

484 $$\frac{\partial \boldsymbol{P}}{\partial t} = -L\frac{F(\boldsymbol{P})}{\delta \boldsymbol{P}} \qquad (8)$$

485 where t is time, F is the total free energy, and L is the kinetic coefficient. The total free energy contains
486 contributions from the bulk, elastic, electric, and gradient energies. Details of using the phase-field
487 method to simulate the switching behaviours of ferroelectric single crystals can be found in Ref. 38&39.
488 The Landau coefficients were adapted from Ref. 40 using the experimental ferroelectric, piezoelectric,
489 and dielectric properties of PMN-28PT crystals at room temperature[40]. Based on this thermodynamic
490 potential, the calculated equilibrium phase is rhombohedral at room temperature with a spontaneous
491 polarization of ~ 0.38 C m^{-2}, a relative dielectric constant of ~ 5500 along [001], and a longitudinal
492 piezoelectric coefficient ~ 1850 pC N^{-1} along [001], which are in reasonable agreement with our
493 experiments. The electrostrictive coefficients measured by Li et al.[41] for PMN-28PT were adopted.
494 The gradient energy coefficients were assumed to be isotropic, and the domain wall width was assumed
495 to be approximately ~ 2 nm. It should be noted here that the Landau potential used in this work
496 represents the averaged free energy of a single-domain PMN-28PT crystal, which incorporates the
497 impacts of the nanoscale heterogeneous polar regions (several nanometres) in the free energy and
498 electromechanical properties[42].

499 To simulate the *AC* and *DC* poling processes, we first obtained an unpoled domain structure from a
500 random noise distribution of the polarization within a quasi-2D grid with 512 Δx ×512 Δx ×1 Δx grid
501 points (Δx = 1 nm). Then, a low-frequency triangle wave was applied to mimic the *AC* poling, whereas
502 a single-step square wave was used to represent the *DC* poling. The magnitude of the poling electric
503 field was 10 kV cm^{-1}. We performed phase field simulations at different mechanical boundary
504 conditions, i.e., the stress-free condition which assumes the averaged stress of the simulated system
505 equal to zero, and the clamped condition which assumes the averaged strain equal to zero. Fig. 1 shows
506 the simulated results for the clamped condition, and the simulation results at stress-free condition are
507 presented in Extended Data Fig. 3b. The practical condition in experiments is likely between these two
508 extreme mechanical conditions. The conclusion that the sizes of 71° domains in AC-poled samples are

509 always much larger than the DC-poled ones holds for both mechanical boundary conditions while the
510 109° domain layer thickness is similar in AC- and DC-poled samples. It is interesting to note that the
511 AC-poling can lead to completely layered 109° domain structure without $71°$ domain walls under the
512 stress-free condition.

513 The dielectric permittivity ε_{33} and piezoelectric coefficient d_{33} were obtained by evaluating the
514 variations of polarization and longitudinal strain under a small electric field of 0.5 kV cm^{-1} along the
515 [001] direction. We also calculate the free energy by applying small test electric fields (E_z is from 0 to
516 1 kV cm^{-1}, which is sufficient small without causing domain wall motion or phase transition) and plot
517 the averaged free energy density as a function of the change of overall the polarization P_z along the
518 poling direction.

519 The computer simulations were performed on the ICS-ACI Computing Systems at Pennsylvania State
520 University and at the Extreme Science and Engineering Discovery Environment (XSEDE) cluster,
521 which is used the Bridges system at the Pittsburgh Supercomputing Center (PSC)[43,44].

522

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Extended Data Figure Legends

Extended Data Figure 1│Schematic diagrams of the projections of optical indicatrices on both sides of a domain wall. a, 109°-domain wall; **b**, 71°-domain wall. The prerequisite of the light scattering and reflection at an interface is the difference of refractive indices between the optical media on each side of the interface. As shown here, the principal axes of the optical indicatrix projected on the (001) planes are the same for domains on each side of a 109° domain wall. Thus, the refractive indices n_o and n_e do not change as the light goes across a 109° domain wall, resulting in the absence of light scattering and/or reflection. In contrast, the principal axis of the optical indicatrix projected on the (001) plane rotates by 90° as the light travels across a 71° domain wall, resulting in the alternating of refractive indices n_o and n_e. This is the reason that 71° domain walls scatter and/or reflect the light.

Extended Data Figure 2│The variation of various energies of PMN-28PT during the first four cycles of *AC*-poling. The data are obtained by phase-field simulations. Here we plot the normalized energies that are dimensionless.

Extended Data Figure 3│Effects of system size and mechanical boundary conditions on the AC- and DC-poled domain structures from phase-field simulations. a, Effects of system size (at the clamped boundary condition). **b**, Effects of mechanical boundary condition (the scale of the simulation is 512×512 nm).

Extended Data Figure 4│Characterization of the domain size along the poling direction for [001]-oriented rhombohedral relaxor-PT crystals. a, PLM images on the (100) face for [001]-poled PMN-28PT crystals by AC poling. **b**, PLM images on the (100) face for [001]-poled PMN-28PT crystals by DC poling. **c**, Distribution of the thickness of laminar domains for AC-poled sample measured from Fig. **a**. **d**, Distribution of the thickness of laminar domains for DC-poled sample measured from Fig. **b**. The thickness of the samples is around 100 μm. As shown in these figures, no clear difference is observed for the thickness of laminar domains between AC- and DC-poled samples.

Extended Data Figure 5│Pseudo-Voight fittings of the {222} diffraction peaks at high-2θ. a and **b** are for the unpoled sample; **c** and **d** are for the *DC*-poled sample; **e** and **f** are for the *AC*-poled sample; **a, c,** and **e,** the intensity of the patterns, accumulated along Ω direction. **b, d** and **f,** the intensity of the patterns, accumulated along 2θ direction.

Extended Data Figure 6│ Effective light absorption coefficients of *AC*- and *DC*-poled PMN-28PT crystals.

Extended Data Figure 7│The temperature stability of AC-poled and DC-poled PMN-28PT crystals. a, Piezoelectric coefficient d_{33}, dielectric permittivity $\varepsilon_{33}^T/\varepsilon_0$ and electromechanical coupling factor k_{33} as a function of temperature. For each testing temperature, the dwelling time is 10 mins. **b**,

591   Domain structure of AC-poled PMN-28PT crystals as a function of temperature. For this experiment,
592   the temperature is increased from 25 to 100°C. The increase rate is 1°C/min. For each testing
593   temperature, the dwelling time is 30 mins. At temperatures below rhombohedral-tetragonal phase
594   transition temperature (~95 $^{\circ}$C), the domain structure remains essentially the same and no
595   depolarization behaviour is observed, indicating AC-poled crystals can be used up to their respective
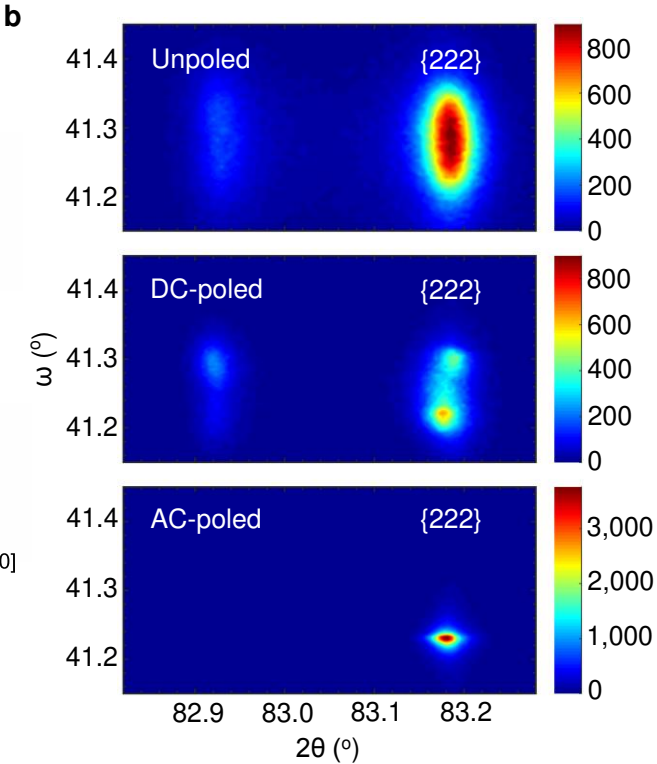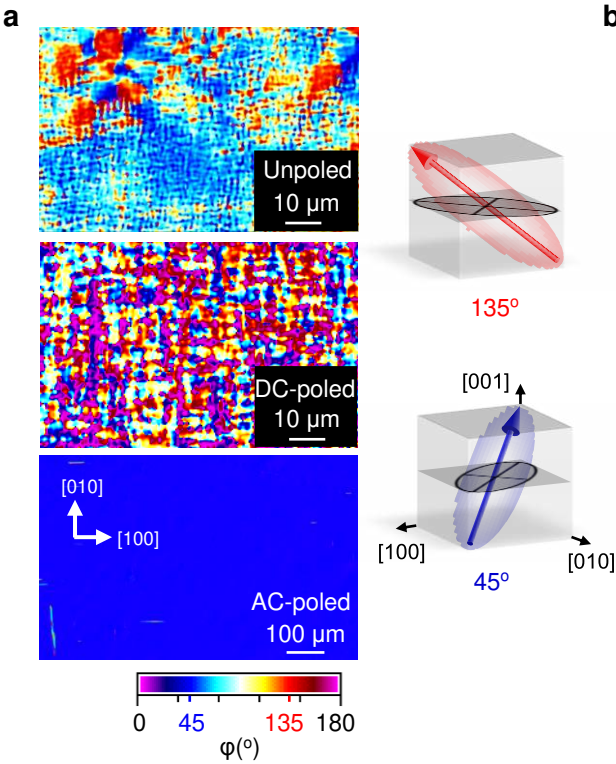596   phase transition temperatures.

597   **Extended Data Figure 8│Polarized light microscopic (PLM) images of [001]-oriented PMN-28PT**
598   **crystals with different poling conditions.** Images **a**, **b**, **c**, and **d** are obtained from the crystals poled at
599   frequencies of 0.1 Hz, 1 Hz, 10 Hz and 100 Hz, respectively. Images **e** and **f** are the enlarged ones of
600   the regions of **b** and **c**, respectively. Images **g**, **h** and **i** are obtained from the crystals poled by a DC
601   electric field. The thickness of the samples is 0.5 mm. For DC-poled samples, there are numerous
602   cross-like domain walls while these types of domain walls are removed by an AC electric field. For this
603   experiment, the thickness of the samples is 0.5 mm.

604   **Extended Data Figure 9│Dielectric permittivity and piezoelectric coefficient of the AC-poled**
605   **PMN-28PT crystal as a function of the cycle number and frequency. a**, Dielectric permittivity as a
606   function of the cycle number. **b**, Dielectric permittivity as a function of the frequency. **c**, Piezoelectric
607   coefficient as a function of the frequency. Five samples are used for each frequency. The error bars
608   indicate the standard deviations (SD) of the corresponding data.

609

610   **Extended Data Table 1│ Electromechanical and electro-optical properties of [001]-oriented**
611   **PMN-28PT crystals via *AC*- and *DC*-poling.** To measure coefficient $\gamma_{\mathrm{c}}^{\mathrm{L}*}$, both the applied electric
612   field and the light beam are along the [001] direction. To measure coefficients γ_{33}^{*} and γ_{13}^{*}, the applied
613   electric field is along the [001] direction, and the light beam is along the [110] direction. Note: it is
614   difficult to obtain accurate electro-optical coefficients for *DC*-poled samples, owing to the strong light
615   scattering by the high density of ferroelectric domain walls. The errors indicate the standard deviations
616   (SD) of the corresponding data (more than five samples/data-points are used for each measurement).

617

a

Unpoled
10 μm

DC-poled
10 μm

AC-poled
100 μm

[010]
[100]

135°

[001]
[100]
[010]
45°

0   45   135   180
φ(°)

b

Unpoled   {222}

DC-poled   {222}

ω (°)

AC-poled   {222}

82.9   83.0   83.1   83.2
2θ (°)

a

Unpoled
10 μm

DC-poled
10 μm

[010]
[100]

AC-poled
100 μm

135°

[001]

[100]

[010]

45°

0   45   135   180
φ(°)

b

Unpoled   {222}   800
                                               600
                                               400
                                               200
                                               0

DC-poled   {222}   800
                                               600
                                               400
                                               200
                                               0

AC-poled   {222}   3,000
                                               2,000
                                               1,000
                                               0

ω (°)

41.4
41.3
41.2

82.9   83.0   83.1   83.2
2θ (°)

a AC-poled DC-poled

b

Surface reflection loss

Visiable light

AC-poled (0.5 mm)
AC-poled (1.8 mm)
DC-poled (0.5 mm)
DC-poled (1.8 mm)

c

Birefringence
Piezoelectric coefficient

a

D_71 = Inf.   D_71 = 256 nm   D_71 = 128 nm   D_71 = 64 nm

Polar directions for different colors

$[\bar{1}\bar{1}1]$ $[\bar{1}11]$ $[1\bar{1}1]$ $[111]$

b

Angle (deg.)

c

P_z P_y P_x

Average polarization (C m^{-1})

Rotation angle from $[111]_{pc}$ (°)

D_{71} (nm)

d

Change of free energy density (a.u.)

D_71=64nm
D_71=128nm
D_71=256nm
D_71=Inf.

Change of polarization ΔP_z (μC cm^{-2})

e

4,480   4,700   4,890   5,500

$\varepsilon_{33}/\varepsilon_0$

64   128   256   Inf.

D_{71} (nm)

f

1,560   1,610   1,650   1,850

d_{33} (pC N^{-1})

64   128   256   Inf.

D_{71} (nm)