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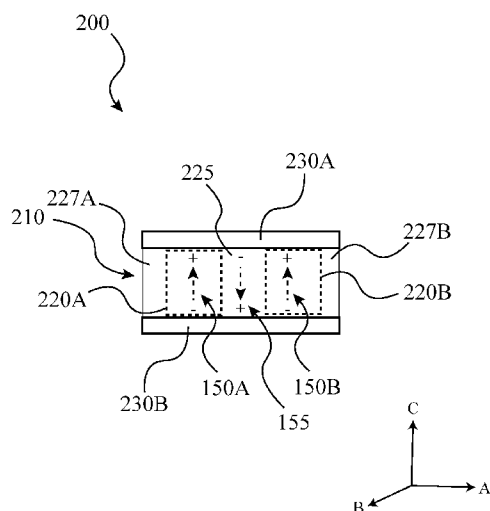


Figure 2

(57) Abstract: The present disclosure relates to a composition that includes a perovskite crystal having a ferroelectric domain aligned substantially parallel to a reference axis. In some embodiments of the present disclosure, the perovskite crystal may include ABX_3 , where A is a first cation, B is a second cation, and X is an anion. In some embodiments of the present disclosure, A may include an alkyl ammonium cation. In some embodiments of the present disclosure, B may include a metal element. In some embodiments of the present disclosure, the metal element may include lead. In some embodiments of the present disclosure, X may include a halogen. In some embodiments of the present disclosure, the perovskite crystal may include methylammonium lead iodide.



HYBRID PEROVSKITE BULK PHOTOVOLTAIC EFFECT DEVICES AND METHODS OF MAKING THE SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S Provisional Patent Application No. 62/476,492 filed
5 March 24, 2017, the contents of which are incorporated herein by reference in their entirety.

CONTRACTUAL ORIGIN

The United States Government has rights in this disclosure under Contract No. DE-AC36-08GO28308 between the United States Department of Energy and Alliance for Sustainable Energy, LLC, the Manager and Operator of the National Renewable Energy Laboratory.

BACKGROUND

10 Perovskite solar cells have shown remarkable progress in recent years with rapid increases in conversion efficiency, from initial reports of 2-3% in 2006 to 20% in 2015. Perovskite solar cells may offer the potential for an earth-abundant and low-energy-production solution to truly large-scale manufacturing of photovoltaic (PV) modules. While perovskite solar cells have
15 achieved very high efficiencies in a very short amount of time, a number of challenges remain before perovskite solar cells can become a competitive commercial technology.

Although organic-inorganic perovskite materials have been studied for more than a century, initial studies on methylammonium lead halides for semiconductor applications, including thin-film transistors and light-emitting diodes, started in the last two decades. The first
20 application of hybrid organic-inorganic perovskite absorbers in solar cells occurred in 2006. However, these early cells were of rather poor efficiency (<4%) due in part to the liquid electrolyte used, which limited both device stability and the open circuit voltage due to compromised interfacial chemistry and energetics. The application of a solid-state hole transport material (HTM), spiro-MeOTAD (2,2',7,7'-tetrakis(N,N-di-p-
25 methoxyphenylamine)-9,9'-spirobifluorene) improved the efficiency to 10% by 2012. Subsequent improvements in performance and stability have come through continued investigation of mixed halide perovskites, improved contact materials, new device architectures, and improved deposition processes, with 20% efficiency having been reported in late 2014. However, there remains a need for improved organic-inorganic perovskite
30 compositions and materials to further improve the performances of devices fabricated from these materials so that they can successfully compete with incumbent materials, both from technical and economical perspectives.

SUMMARY

An aspect of the present disclosure is a composition that includes a perovskite crystal having a ferroelectric domain aligned substantially parallel to a reference axis. In some embodiments of the present disclosure, the perovskite crystal may include ABX_3 , where A is a first cation, B is a second cation, and X is an anion. In some embodiments of the present disclosure, A may include an alkyl ammonium cation. In some embodiments of the present disclosure, B may include a metal element. In some embodiments of the present disclosure, the metal element may include lead. In some embodiments of the present disclosure, X may include a halogen. In some embodiments of the present disclosure, the perovskite crystal may include methylammonium lead iodide.

In some embodiments of the present disclosure, the ferroelectric domain may have a crystal structure that includes at least one of a tetragonal phase and/or an orthorhombic phase. In some embodiments of the present disclosure, the ferroelectric domain may be characterized by a Rayleigh response having a positive slope. In some embodiments of the present disclosure, the ferroelectric domain may be characterized by a d_{33} measurement having a value greater than zero pC/N. In some embodiments of the present disclosure, the d_{33} measurement may be between 0.1 pC/N and 10,000 pC/N.

An aspect of the present disclosure is device that includes a layer that includes a perovskite crystal that includes a ferroelectric domain aligned substantially parallel to a reference axis, where the perovskite crystal includes ABX_3 , where A is a first cation, B is a second cation, and X is an anion. In some embodiments of the present disclosure, the layer may further include a first surface and a second surface, the second surface may be substantially parallel to the first surface, the first surface and the second surface may define a thickness of the layer, and the reference axis may be substantially perpendicular to the first surface and the second surface. In some embodiments of the present disclosure, the thickness may be between 1 Å and 10 mm. In some embodiments of the present disclosure, the ferroelectric domain may have a length between 1 Å and 10 mm. In some embodiments of the present disclosure, the device may further include a first electrode that includes a first metal positioned against the first surface and a second electrode that includes a second metal positioned against the second surface, where the layer is positioned between the first electrode and the second electrode. In some embodiments of the present disclosure, the first metal and the second metal may be the same.

An aspect of the present disclosure is a method that includes applying a gradient to a perovskite crystal having a characteristic length, where the applying creates at least one ferroelectric domain within the perovskite crystal, the ferroelectric domain has a crystal structure that is not in a cubic phase, and the ferroelectric domain is aligned substantially parallel with the characteristic length. In some embodiments of the present disclosure, the applying may include at least one of applying an electric field gradient and/or a temperature gradient across the characteristic length. In some embodiments of the present disclosure, the applying the electric field gradient may include applying a voltage between 1 mV and 100 V across the characteristic length.

BRIEF DESCRIPTION OF THE DRAWINGS

Some embodiments are illustrated in referenced figures of the drawings. It is intended that the examples and figures disclosed herein are to be considered illustrative rather than limiting.

Figure 1 illustrates a perovskite crystal structure, according to some embodiments of the present disclosure.

Figure 2 illustrates a device that includes a perovskite having ferroelectric domains, according to some embodiments of the present disclosure.

Figure 3 illustrates a method for producing a perovskite having ferroelectric domains, according to some embodiments of the present disclosure.

Figures 4A-4E illustrate piezoresponse force microscopy (PFM) and temperature dependent ferroelectric response in large, high-quality MAPbI_3 single crystals, according to some embodiments of the present disclosure. Figure 4A illustrates the PFM small signal amplitude response trace (solid line) and retrace (dashed line). Figure 4B illustrates the PFM small signal phase response trace (solid line) and retrace (dashed line). Figure 4C illustrates an image of a single crystal of MAPbI_3 with natural faceting before metallization. Figure 4D illustrates the Rayleigh response, determined from the E_{AC} response of the permittivity measured at 1 MHz, from the lowest applied signal (9.2×10^{-4} kV/cm) increasing with applied voltage to the maximum (7.6×10^{-3} kV/cm); arrow indicates increasing applied E_{AC} . The Rayleigh response decreases with increasing temperature, collapsing near the global phase transition temperature for the cubic phase, which is an indication of the presence of ferroelectricity. Figure 4E illustrates a schematic of the material structure, the temperature dependence of the global phase transitions, possible mechanisms of structural modification, and Rayleigh response in MAPbI_3 .

Figures 5A and 5B illustrate Rayleigh coefficient and dielectric loss tangent for a single crystal

MAPbI₃ at 1MHz, according to some embodiments of the present disclosure. Figure 5A illustrates the Rayleigh coefficient, α calculated from the data in Figure 4D, as a function of temperature. Figure 5B illustrates dielectric loss measurements taken concurrently with the Rayleigh analysis indicating a decrease in V_{AC} dependence above the global phase transition temperature. The arrow indicates increasing Applied E_{AC} , from a low value of 9.2×10^{-4} kV/cm to a high value of 7.6×10^{-3} kV/cm

Figure 6A, 6B, and 6C illustrate poling induced macroscopic ferroelectric domains, according to some embodiments of the present disclosure. Figure 6A illustrates large voltage PFM amplitude and Figure 6B illustrates PFM phase. Figure 6C illustrates optical microscope image of crystal surface after poling showing stable periodic domain lines which extend across the face of the crystal.

Figures 7A and 7B illustrate various properties of perovskite-containing devices, according to some embodiments of the present disclosure. Figure 7A illustrates XPS measurements of the I 3d core level region. Figure 7B illustrates XPS measurement of the Pb 4f core level region. The top traces correspond to poled crystals and the bottom traces correspond to unpoled crystals.

Figures 8A-8E illustrate various properties of perovskite-containing devices, according to some embodiments of the present disclosure. Figure 8A illustrates AFM topography of domain lines, area delineated by dashed line corresponds to the electric force microscopy (EFM) amplitude scan area shown in Figure 8B in at 8V bias. Figure 8C illustrates line scans corresponding to the solid line in Figure 8A, showing the response for topography (dashed line, right axis), EFM amplitude signal at 0V bias (dotted line, left axis) and 8V (solid line, left axis). Figure 8D illustrates AFM topography image and line scan (Figure 8E) after aging a poled crystal for 3 weeks in ambient conditions.

Figures 9A and 9B illustrate the dielectric response of single crystal MAPbI₃ as a function of temperature and frequency, according to some embodiments of the present disclosure. Figure 9A illustrates the permittivity over a range of frequencies shows dispersion that decreases with increasing temperature above the global phase transition temperature. Figure 9B illustrates the concurrently measured dielectric loss as a function of temperature and frequency.

Figure 10 shows the piezoresponse (taken as the band excitation-PFM amplitude multiplied by the cosine of BE-PFM phase response) as a function of applied voltage, according to some embodiments of the present disclosure.

Figures 11 illustrates the read/write voltage steps used in the BE-PFM experiment, according to some embodiments of the present disclosure.

Figure 12 illustrates the dC/dV response of a BPE device, according to some embodiments of the present disclosure.

5	REFERENCE NUMBERS
	100..... perovskite
	110..... A-cation
	120..... B-cation
	130..... X-anion
10	140..... driving mechanism
	150..... first dipole
	155..... second dipole
	200..... device
	210..... perovskite layer
15	220..... first ferroelectric domain
	225..... second ferroelectric domain
	227..... non-ferroelectric domain
	230..... current collector
	300..... method
20	310..... depositing
	315..... perovskite film
	320..... treating
	325..... perovskite layer
	330..... applying
25	335..... final perovskite layer

DETAILED DESCRIPTION

The present disclosure may address one or more of the problems and deficiencies of the prior art discussed above. However, it is contemplated that some embodiments as disclosed herein may prove useful in addressing other problems and deficiencies in a number of technical areas.

Therefore, the embodiments described herein should not necessarily be construed as limited to addressing any of the particular problems or deficiencies discussed herein.

The present disclosure relates to ferroelectricity in organic-inorganic perovskite materials (e.g. single crystals of methyl ammonium lead iodide) and methods for making such materials, as well as the use of ferroelectric domain engineering to control the electronic response in these materials. A comprehensive set of methodologies including temperature dependent Rayleigh analysis, piezoresponse force microscopy, and d_{33} Berlincourt piezoelectric measurements have resulted in experimental results, described herein, that confirm relaxor ferroelectricity with nanoscale domain ordering. As will be described in more detail below, the ferroelectric response of the organic-inorganic perovskite materials studied exhibited sharp declines above 57 °C, which is consistent with the tetragonal-to-cubic phase transition temperature. Large signal poling greater than 16 V/cm induced permanent macroscopic ferroelectric domains (up to 40 μm wide, and between 0.01 mm and 1 mm in length), which demonstrated preferential stabilization over a period of weeks and a distinguishable domain specific electronic response. The impact of the ferroelectric domains on the opto-electronic response was characterized through X-ray photoemission spectroscopy (XPS), and electric force microscopy (EFM). The XPS results indicate a rigid shift of 400 meV in the binding energy of the iodine and lead core level peaks in the poled crystal with respect to the unpoled crystal. Additionally, there is a domain specific electrical response seen by EFM. The ability to control the ferroelectric response provides routes to increase both device stability and improve photovoltaic performance through domain engineering, and provides key insights for future designs of novel, high-efficiency photovoltaic materials. The ability to control the ferroelectric domain orientation allows for the development of bulk photovoltaic effect devices, which employ the ferroelectric polarization to separate photogenerated charge carriers.

Figure 1 illustrates that a perovskite 100, including an organic-inorganic perovskite, may organize into cubic crystalline structures and may be described by the general formula ABX_3 , where X (130) is an anion and A (110) and B (120) are cations, typically of different sizes with the A-cation 110 typically larger than the B-cation 120. In a cubic unit cell, the B-cation 120 resides at the eight corners of a cube, while the A-cation 110 is located at the center of the cube and is surrounded by six X-anions 130 (located at the face centers) in an octahedral $[\text{MX}_6]^{4-}$ cluster (unit structure). Typical inorganic perovskites include calcium titanium oxide (calcium titanate) minerals such as, for example, CaTiO_3 and SrTiO_3 . In some embodiments of the present invention, the A-cation 110 may include a nitrogen-containing organic compound such as an alkyl ammonium compound. The B-cation 120 may include a metal and the X-anion 130 may include a halogen. Although Figure 1 illustrates a perovskite having a cubic crystalline

structure, a perovskite may have other crystalline structures, including tetragonal or orthorhombic (e.g. I4cm). In some embodiments of the present disclosure, a perovskite 100 may include at least a first portion that is substantially in the cubic crystalline phase and a second portion that is substantially in a different crystalline phase, e.g. tetragonal, orthorhombic. In some embodiments of the present disclosure, a perovskite may have a combination of more than one crystal phase, for example a mixture of a cubic phase and a tetragonal phase and/or orthorhombic phase.

Additional examples for an A-cation 110 include organic cations and/or inorganic cations. A-cations 110 may be an alkyl ammonium cation, for example a C₁₋₂₀ alkyl ammonium cation, a C₁₋₆ alkyl ammonium cation, a C₂₋₆ alkyl ammonium cation, a C₁₋₅ alkyl ammonium cation, a C₁₋₄ alkyl ammonium cation, a C₁₋₃ alkyl ammonium cation, a C₁₋₂ alkyl ammonium cation, and/or a C₁ alkyl ammonium cation. Further examples of organic A-cations 110 include methylammonium (CH₃NH³⁺), ethylammonium (CH₃CH₂NH³⁺), propylammonium (CH₃CH₂CH₂NH³⁺), butylammonium (CH₃CH₂CH₂CH₂NH³⁺), formamidinium (NH₂CH=NH²⁺), and/or any other suitable organic compound. In other examples, an A-cation 110 may include an alkylamine. Thus, an A-cation 110 may include an organic component with one or more amine groups, or transition metal cations. For example, an A-cation 110 may be an alkyl diamine such as formamidinium (CH(NH₂)₂)⁺.

Examples of metal B-cations 120 include, for example, lead, tin, germanium, and or any other 2+ valence state metal that can charge-balance the perovskite 100. In some embodiments of the present disclosure, a metal B-cation 120 may have a 1+, 2+, 3+, or 5+ valence state, for example at least one of Na, K, Ba, Sr, Ca, Pb, Bi, Sn, and/or In. Examples for the X-anion 130 include halogens: e.g. fluorine, chlorine, bromine, iodine and/or astatine. In some cases, a perovskite 100 may include more than one X-anion 130, for example pairs of halogens; chlorine and iodine, bromine and iodine, and/or any other suitable pairing of halogens. In other cases, the perovskite 100 may include two or more halogens of fluorine, chlorine, bromine, iodine, and/or astatine. In some embodiments of the present disclosure, at least one X-anion 130 may be mixed with oxygen.

Thus, the A-cation 110, the B-cation 120, and the X-anion 130 may be selected within the general formula of ABX₃ to produce a wide variety of perovskites 100, including, for example, methylammonium lead triiodide (CH₃NH₃PbI₃), and mixed halide perovskites such as CH₃NH₃PbI_{3-x}Cl_x and CH₃NH₃PbI_{3-x}Br_x. Thus, a perovskite 100 may have more than one halogen element, where the various halogen elements are present in none integer quantities;

e.g. x is not equal to 1, 2, or 3. In addition, perovskite halides, like other organic-inorganic perovskites, can form three-dimensional (3-D), two-dimensional (2-D), one-dimensional (1-D) or zero-dimensional (0-D) networks, possessing the same unit structure.

As stated above, the A-cation 110 may include organic constituents in combination with each other. In some cases, the organic constituent may be an alkyl group such as straight-chain and/or branched saturated hydrocarbon group having from 1 to 20 carbon atoms. In some embodiments, an alkyl group may have from 1 to 6 carbon atoms. Examples of alkyl groups include methyl (C_1), ethyl (C_2), n-propyl (C_3), isopropyl (C_3), n-butyl (C_4), tert-butyl (C_4), sec-butyl (C_4), iso-butyl (C_4), n-pentyl (C_5), 3-pentanyl (C_5), amyl (C_5), neopentyl (C_5), 3-methyl-2-butanyl (C_5), tertiary amyl (C_5), and n-hexyl (C_6). Additional examples of alkyl groups include n-heptyl (C_7), n-octyl (C_8) and the like.

Referring again to Figure 1, and without wishing to be bound by theory, the application of a driving mechanism 140 in a particular orientation and/or direction, for example an electric field, appears to result in a structural reorientation (e.g. displacement of the center ion) within the perovskite 100 unit cell. In the example of Figure 1, the driving mechanism 140 is substantially parallel to the A-axis and results in at least a partial reorientation of the elements of the perovskite (cations and/or anions) along the A-axis, which further results in the alignment of charges within the perovskite. This alignment of charges creates a dipole 150 of at least some of the perovskite elements in three-dimensional (3D) space, as defined by the unit cell between the centers of the B-cation 120 octahedra, which is referred to herein as “polling”. Thus, depending on the driving mechanism 140 used, and the alignment of its forces in 3D space, a perovskite 100 may form a dipole 150 of its elements aligned along the A-axis, B-axis, and/or C-axis, and aligned substantially parallel with the driving mechanism 140. In Figure 1, the driving mechanism 140, e.g. an electric field, is shown to be substantially parallel to the C-axis, which results in the formation of a dipole 150 also substantially parallel with the C-axis. Polycrystalline materials, with crystal symmetries may accommodate the structural changes by re-orienting along the closest direction to the applied field. Regions where the structural distortions and the dipole 150 orient along the same axis and direction are referred to herein as “ferroelectric domains”, which may vary in size from two unit cells on the order of Angstroms, up to millimeters in length. Similar poling may be produced by driving mechanisms 140 such as at least one of strain, strain gradients, temperature gradients, and/or electric field gradients. The range of applied poling voltages may be between 1 mV and 100 V. A temperature gradient as a driving mechanism 140 may be between 50 °C/micrometer and 200° C/micrometer. In

some embodiments, the temperature gradient may be pulsed at regular time intervals. Thus, the application of an appropriate driving mechanism 140, e.g. electric field, may result in the alignment of at least one of an A-cation 110, a B-cation 120, and/or an X-anion 130 along an axis that is substantially parallel to at least one of the A-axis, the B-axis, and/or the C-axis, resulting in the creation of a dipole 150 and the creation of at least one ferroelectric domain positioned within the perovskite 100. These structural changes may also result in subsequent changes in at least one of an electrical, an optical, and/or a mechanical property. In some examples of the present disclosure, a perovskite material containing ferroelectric domains, treated according to at least some of the embodiments described herein, will exhibit the BPE response, a piezoelectric response, and birefringence, as demonstrated herein. The poling may remain oriented along the same direction after the driving mechanism is removed unless the material reaches some condition that provides enough energy (e.g. a temperature above the Curie temperature) that the material may rearrange and reassume a less-poled, less-ferroelectric state.

Figure 2 illustrates a device 200, for example a solar cell, that includes a perovskite layer 210 having a first dipole 150 (two shown; 150A and 150B) aligned along a dimension of the perovskite layer 210; e.g. aligned parallel to the perovskite layer 210 thickness dimension. In the example of Figure 2, the first dipole (150A and 150B) forms a first ferroelectric domain (two shown; 220A and 22B), represented by dashed rectangles spanning the entirety of the thickness of the perovskite layer 210. However, it should be understood that in some embodiments of the present disclosure, a perovskite layer 210 may have one or more ferroelectric domains. For example, at least one first ferroelectric first domain (220A and/or 220B) may be separated by non-ferroelectric domains (227A and 227B) and/or by at least one second ferroelectric domain 225 have a second dipole 155 oriented in a different and/or opposite direction relative to the first dipole (150A and 150B) of the first ferroelectric domain (220A and 220B). In some embodiments of the present disclosure, two or more ferroelectric domains (e.g. 220A, 220B, and/or 225) may have intersecting areas or volumes such that a single ferroelectric domain results; e.g. having no intervening, non-ferroelectric domains 227. Thus, a ferroelectric domain (220A, 220B, and/or 225) may be characterized by a thickness dimension that is substantially parallel its respective dipole (150A, 150B, and/or 155) (e.g. along the C-axis of Figure 2), where the thickness dimension may be between several Angstrom and several millimeters; e.g. the thickness dimension of a ferroelectric domain (220A, 220B, and/or 225) may be between 1 Å and 100 millimeters, or between 10 Å and 10 millimeters, or

between 100 Å and 1 millimeter. A ferroelectric domain (220A, 220B, and/or 225) may also have a characteristic width dimension (B-axis) and length dimension (A-axis), both of which may be at least orders of magnitude larger than the thickness dimension (C-axis) of the ferroelectric domains (220A, 220B, and/or 225). In addition, Figure 2 illustrates the ferroelectric domains (220A, 220B, and/or 225) as being rectangular in shape. However, this is for illustrative purposes only and a ferroelectric domain (220A, 220B, and/or 225) may have any geometric shape, which may be defined by the starting shape of the perovskite layer 210 and/or the conditions used during the formation of the ferroelectric domain (220A, 220B, and/or 225).

Thus, as shown herein, a device may include a perovskite (e.g. layer) having at least one ferroelectric domain. In addition, the perovskite (e.g. layer) may have a least one non-ferroelectric domain. The ferroelectric domain may be identified by the presence of a dipole, whereas the non-ferroelectric domain may lack a measurable dipole. The presence of the dipole of a ferroelectric domain, and conversely, the absence of a dipole in a non-ferroelectric domain, may be identified using the analytical methods described herein, which include Rayleigh analysis, polarization-electric field loops, d_{33} Berlincourt measurements, PFM, EFM, contact Kelvin probe force microscopy (cKPFM), scanning microwave impedance microscopy (sMIM), and/or visual inspection (e.g. optical microscopy). According to some of the embodiments described herein, the presence or absence of ferroelectric domains in a perovskite material (e.g. layer) may be indicated as summarize below in Table 1.

Table 1. Ferroelectric versus Non-Ferroelectric Indicators

Method	Measures	Ferroelectric	Non-Ferroelectric	See Figure
Rayleigh	C(Vac)	Positive slope.	Flat or negative slope.	4D, 5A, 5B
Polarization - Electric Field	$P(E) = I(V)$	Square in the second and fourth quadrant, hysteresis, pointy ends, discontinuous slope.	straight line, circle.	NA
d_{33}	strain induced charge	Between 0.1 pC/N and 10,000 pC/N ($d_{33} > 0$ pC/N).	No piezoelectric response, or no difference in response after poling in opposite direction.	NA
EFM	dC/dV, Voltage	Linearly segregated areas with distinct electrical response, change in surface charge buildup.	No difference, topographic induced differences.	8A, 8B, 8C
PFM	Displacement (Vdc)	Positive displacement, linear, hysteresis, crossing response at $x=0$.	No displacement, or quadratic displacement at high voltages.	4A, 4B, 6A, 6B
cKPFM	surface charge build-up	Two separate bands.	single band.	11
visual/SEM	-----	Observable surface domains.	No clear delineation.	6C
sMIM	dI/dV	At $V=0$, $I \neq 0$	At $V=0$, $I=0$	NA

The device 200 of Figure 2 also includes a first current collector 230A and a second current collector 230B, such that the device 200 may function as a bulk photo effect device. The bulk photovoltaic effect (BPE) is the separation of photogenerated charges due to the asymmetric wavefunction of the material, which in this case is provided by the coherent structural distortion within a ferroelectric domain, (and the difference in-built potential between and through ferroelectric domains). Open current voltages greater than the band gap may result from BPE. Any asymmetric material with a band gap may exhibit the BPE. Unlike a traditional solar cell, a BPE device does not require a junction, but instead, can utilize a single layer of active (ferroelectric) material. A BPE solar cell will be much different from a conventional p-n junction solar cell in a few key areas. For example, a BPE solar cell may utilize a band gap in the visible spectrum and it may generate a photo voltage and current much like a conventional solar cell. However, the photo voltage of BPE solar cell is not limited by the band gap such that open-circuit voltages on the kiloVolt magnitude are possible. In addition, the transport

mechanisms in a BPE device may be ballistic resulting in faster transport and higher efficiencies. Although Figure 2 illustrates a device 200 that may be a solar cell, other devices utilizing perovskite films having ferroelectric domains are contemplated and are considered within the scope of the present disclosure (e.g. transistors, sensors, energy harvesters, ferroelectric-random access memory, opto-electronics). In addition, the device 200 of Figure 2 may include other elements (e.g. layers) typically found within solar cells, for example, additional perovskite layers (e.g. designed to absorb light of different wavelengths).

Figure 3 illustrates a method 300 for making a final perovskite layer 335 having ferroelectric domains. The method 300 may begin with the depositing 310 of a perovskite film 315, for example the depositing of a perovskite film 315 by a solution method onto a substrate, according to methods known to one having skill in the art. The perovskite film 315 may be transformed into a solid perovskite layer 325 by treating 320 the perovskite film 315. For example, the treating 320 may include heating the perovskite film 315 to a temperature between 20 °C and about 200 °C. At this point, the perovskite film 315 may not contain a dipole or a ferroelectric domain. These may be formed by the subsequent applying 330 of a driving mechanism (e.g. poling), for example an electric field, resulting in the formation of a final perovskite film 315 having at least one ferroelectric domain. An electric field may be applied to a perovskite material by positioning the perovskite material between a first electrode and a second electrode and applying a voltage across the two electrodes. In some embodiments of the present disclosure, the applying 330 and the treating 320 may be performed substantially simultaneously. For the example of an electric field driving mechanism, the electric field may be applied during the heating of the perovskite film 315, such that the ferroelectric domains form as the perovskite transitions from a liquid solution to a solid. For the example of an electric field driving mechanisms, an electric field having a voltage between greater than 0 V and 100 V may be applied for a time period of between 1 second and 1000 seconds, or between 1 second and 100 seconds, or between 1 second and 10 seconds, while below, above or at room temperature, and along the [001] family of planes. As used herein, room temperature is defined to be between 15 °C and 25 °C.

The work present herein unequivocally confirms that MAPbI₃, with a near ideal band gap of 1.6 eV and verified solar cell efficiency over 19%, can be ferroelectric. These results run counter to the current prevailing view that ferroelectricity does not occur in MAPbI₃, which has come about in part due to the difficulties in making definitive measurements using conventional techniques, especially on thin film samples. These previous results highlight the

importance of developing appropriate methods in order to detect a ferroelectric response in semiconducting ferroelectrics. The ability to control the ferroelectric response is also demonstrated herein, which allows for the exploitation of benefits unique to ferroelectrics, such as increasing the material stability and controlling the opto-electronic properties through domain engineering and creating a BPE device.

As described herein, high quality single crystals and unique small signal electrical measurements were utilized to definitively confirm ferroelectricity in MAPbI₃. The characterization techniques employed to confirm the ferroelectric response included: temperature dependent Rayleigh analysis, dielectric measurements, piezoresponse force microscopy, electric force microscopy (EFM), and d₃₃ Berlincourt piezoelectric measurements. After identifying a ferroelectric response and determining the conditions for macroscopic domain control, the impact of poling on the material stability and electrical response were measured through EFM and X-ray photoemission spectroscopy (XPS),

Piezoelectricity is a prerequisite of ferroelectricity, making piezoresponse force microscopy (PFM) an effective initial screening method for ferroelectricity in MAPbI₃ single crystals. Figures 4A and 4B show representative PFM amplitude and phase as a function of applied V_{DC}. The offset minimum in the forward and reverse sweeps, the linear displacement with applied field, and the hysteresis in trace and retrace are indicative of a piezoelectric (rather than a pure electrostrictive) response associated with the reorientation of ferroelectric domains by an electric field. The concomitant phase shift of 180° is congruent with ferroelectric domain reversal. This fulfills the criteria of ferroelectricity, a spontaneous polarization that can be reoriented with the application of an electric field. Identifying a ferroelectric response and showing polarization reorientation under an electric field in polycrystalline thin films through large signal, small area PFM scans is problematic due to the convolution of electrostatic, electrostrictive, and topographic contributions to the signal. These issues were avoided herein by utilizing smaller signal (160 V/cm, <4V), large electrode area static PFM scans, making it unlikely that the response is field-induced. If the material was only piezoelectric, or electrostrictive, then no minimum offset, no significant hysteresis, and no phase shift would occur. Hence, the PFM data strongly supports ferroelectricity and the narrow hysteresis is indicative of ferroelectric ordering on the nanoscale, e.g. relaxor ferroelectricity.

Although PFM and PE loops are the most commonly reported ferroelectric measurements, these methods are sensitive to small changes in charge such that the movement of free charge can overwhelm the ability to see a ferroelectric response and are thus problematic in

semiconducting material Advanced alternative methodologies based on Rayleigh analysis were also employed in the work described herein. The Rayleigh response is the linear change in permittivity under an applied electric field, E_{AC} , due to the irreversible movement of domain walls, domain clusters, or phase boundaries. Rayleigh analysis can be used as an indicator for the presence of ferroelectric domain wall movement with a Gaussian distribution of restoring forces. Figure 4D shows the E_{AC} induced dielectric response measured under small signal conditions (<8.3 V/cm, <2 V) at 1 MHz with increasing temperature. The Rayleigh coefficient and concurrent loss are shown in Figures 5A and 5B. A clear Rayleigh response is apparent in MAPbI₃, indicating ferroelectric polar clusters, with mobile boundaries. This response decays with increasing temperature, sharply declining near 57 °C, and finally disappearing beyond 75 °C. The transition near 57 °C is consistent with previous reports of the temperature of transition between the tetragonal and cubic phase between 54 °C and 60 °C. The persistence of the Rayleigh response beyond the global phase transition temperature is a common characteristic of a relaxor ferroelectric, indicating that a few local polarized regions remain above the global phase transition temperature. The decrease in the loss tangent above the transition temperature indicates that the response is not dominated by ion movement and that there is a contribution from the ferroelectric response

The nano-polar regions in a relaxor ferroelectric can be transitioned into a macroscopic ferroelectric state with an applied electric field in a process called poling. Poling was confirmed through direct Berlincourt measurements of the d_{33} piezoelectric coefficient. Prior to the application of an electric field no piezoelectric response could be measured. After five minutes of poling at 21 V/cm, the d_{33} was found to be 54 pC/N. The measured d_{33} likely underestimates the actual piezoelectric response due to leakage currents, low applied poling voltages, and imperfect impedance. Interestingly, the DFT calculations of the piezoelectric tensor of MAPbI₃ are approximately an order of magnitude smaller than the experimental results. Note that the computational method has been compared to other piezoelectric materials in the literature and typically reproduces the measured response at an accuracy of $\pm 25\%$.

In addition to verifying the presence of ferroelectricity, the ability to pole the material into persistent macroscopic domains indicates that domain engineering can be used to select for a desired predominant polarization orientation and thus control the structure and electronic response. Figures 6A and 6B show the large signal PFM amplitude and phase. Simply stated, these data show the forward trace and backward trace for PFM amplitude and phase. The fact that the forward trace and backward trace do not fall directly on each other for the entire

duration indicate the presence ferroelectric domains in the perovskite. The development of hysteresis with increasing electric field above 12 V/cm is consistent with a transition from the slim relaxor ferroelectric response into an induced macroscopic ferroelectric structure. After removing the applied bias large visible domain structures remained. Periodic domain structures
 5 extended millimeters across the surface of the samples, with domain widths that varied with poling field and orientation, ranging from between 2 μm and 40 μm , shown in Figure 6C.

XPS was used to examine the impact of ferroelectricity on the electronic structure. The lead and iodine core level spectra of a poled and unpoled MAPbI_3 crystal are depicted in Figures 7A and 7B. Referring to Figure 7A, for the unpoled crystal (bottom trace), the main I $3d_{5/2}$ peak
 10 is centered at 619.3 eV which is consistent with an intrinsic response. Relative to the measurements taken on an unpoled crystal, the iodine core level peaks in the poled crystal exhibit a rigid shift in binding energy of 400 meV with a similar shift in the Pb 4f peaks (see Figure 7B and Table 2 below). This change in Fermi level, E_F , position could be associated
 15 with sampling over domains that are predominantly oriented in such a way that there is a net electric field resembling a positively charged surface. These shifts could be indicative of a change in Fermi level position that suggests dipole doping.

Table 2. Centroid positions of lead and iodine core level peaks before and after poling

	Unpoled	Poled
I $3d_{5/2}$	619.3 eV	619.7 eV
I $3d_{3/2}$	630.8 eV	631.2 eV
Pb $4f_{7/2}$	138.5 eV	138.9 eV
Pb $4f_{5/2}$	143.3eV	143.7 eV

While XPS provides specifics of the electronic structure, the macroscopic influence of ferroelectricity by performing EFM on poled crystals was also probed. These results strongly
 20 support the potential for a bulk photovoltaic response in this material and indicate the influence of ferroelectricity on the opto-electronic response.

The domain specific response was investigated through EFM. It is shown that domains of differing orientations exhibit a measurably different electrical response. Figures 8A and 8B
 25 show the results of both the topographical and EFM scans. The 0V, 8V and topographical line scans are shown in Figure 8C; the 0V scan shows no response verifying that the measured EFM signal is a function of a varied electrical response, and not due to topographical features or

surface chemical potential differences. In contrast, the 8V scan shows a specific electrical response that is coincident with the domain structures. Although a complete analysis and understanding of the EFM response is beyond the scope of this work, it clearly demonstrates domain-specific electrical response, which, in turn, implies that a built-in field can be engineered into working devices. The difference in chemical potential at the surface of different domains plays a large role in the stability of the material over time. The EFM/AFM images taken after a period of intentional etching in air for a month showed that domains in the dominant orientation remained relatively unchanged while preferential etching and degradation occurred in domains with the opposite orientation. This effect is shown in Figures 8D and 8E with the arrow indicating the domain boundary. By poling a crystal or film along this preferential direction the stability of the material could be increased. Observing these phenomena in MAPbI₃ highlights a route to increase the material and device stability and reliability of the material over time via targeted domain design.

Using a broad range of unique characterization techniques across multiple length scales the existence of ferroelectricity in single crystals of MAPbI₃ is confirmed by the work described herein. An important implication of this work is that any ferroelectric semiconductor, like MAPbI₃, may also exhibit the bulk photovoltaic effect. The bulk photovoltaic effect in ferroelectrics relies on the spontaneous polarization, which enables efficient separation of photo-excited charge carriers without a *p-n* junction. This work shows that MAPbI₃ is ferroelectric, that the polarization can be controlled through polling, and that the domain structure impacts the opto-electronic response, three critical criteria for the development of BPE devices. These results support the idea that the BPE effect in MAPbI₃ may contribute to the spectacular photovoltaic response observed in this material.

Figures 9A and 9B illustrate the dielectric response of single crystal MAPbI₃ as a function of temperature and frequency, according to some embodiments of the present disclosure. Figure 9A illustrates the permittivity over a range of frequencies shows dispersion that decreases with increasing temperature above the global phase transition temperature. Figure 9B illustrates the concurrently measured dielectric loss as a function of temperature and frequency.

Figure 10 shows the piezoresponse (taken as the band excitation-PFM amplitude multiplied by the cosine of BE-PFM phase response) as a function of applied voltage on a single crystal of methylammonium lead iodide. This measurement is the average response over ten areas on the sample. The sharp saturated response, with square corners and low injected charge are indicative of a ferroelectric response.

Figure 11 illustrates the read/write voltage steps used in the BE-PFM experiment (top two panels), the lower panel shows the measured, non-averaged response demonstrating the separation into two separate bands indicating a ferroelectric response.

Figures 12 illustrates the dC/dV response of a BPE device made from a single crystal of methylammonium lead iodide with symmetric gold contacts of 100nm thickness. The metal used can be any non-reactive metal of any thickness, the crystal can be any of those compositions included here and can range from 100nm to several millimeters in thickness. The initial scan shows the response of a typical resistor with the current equal to approximately zero (within the error of the instrument) when the voltage is 0. After poling the device, we get a non-zero current when $V=0$, both in the dark and under illumination. This demonstrates that poling has aligned the ferroelectric domains substantially and normal to the electrodes allowing for charge separation and collection.

Methods:

Crystal Growth, Characterization, and Preparation: Single crystals were prepared using an acid initiated solution growth method. Briefly, iodide salt solutions at 0.8 M in 4 ml fresh γ -butyrolactone were prepared by dissolving the salts at 55 °C with vigorous stirring for at least 30 minutes. The solution was filtered with a 0.45 μ m syringe filter and placed in an oil bath at 95 °C in a closed crystallization dish. After the initial seed growth, an appropriate seed crystal (~0.5mm) was placed in a similarly prepared solution and allowed to grow for 10-12 hours. The process was repeated multiple times until the crystal was of an appropriate size for the characterization technique. For the poling and EFM measurements double-sided, conductive copper tape was used to form electrical connection between the crystal and a conducting substrate. For the Rayleigh analysis and PFM 100 nm thick gold electrodes were thermally evaporated on opposite facets of the crystal; electrical connection was made by adhering the bottom facet to a metalized substrate using silver paste and using a micro-probe to contact the top electrode.

Table 3. Single Crystal X-Ray Diffraction Indexing Results

Compound	CH ₃ NH ₃ PbI ₃	
Growth temperature		
Measurement temperature	296 K	
Space group	<i>I4/m c m</i>	<i>I4cm</i>
Unit cell dimensions	$a = 8.9018 \pm 0.0003 \text{ \AA}$ $c = 12.6237 \pm 0.0005 \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$	$a = 8.9018 \pm 0.0003 \text{ \AA}$ $c = 12.6237 \pm 0.0005 \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$
Volume	1000.33 Å ³	1000.33 Å ³
Z	4	4
Reflections collected	19866	19866
Unique reflections	256	484
Inconsistent equivalents	18	32
R(int)	0.1083	0.1072
R (sigma)	0.0780	0.1320
Goodness-of-fit	1.110	1.203
Final R indices	0.0773	0.1316
Twin model	N/A	[1 0 0 0 1 0 0 0 -1]
Extinction coefficient	0.003594	0.007768
Wavelength	0.71073 Å	0.71073 Å
Weight scheme for the refinement	Weight = $1 / [\sigma^2(\text{Fo}^2) + (0.0681 * P)^2 + 82.13 * P]$ where $P = (\text{Max}(\text{Fo}^2, 0) + 2 * \text{Fc}^2) / 3$	Weight = $1 / [\sigma^2(\text{Fo}^2) + (0.0681 * P)^2 + 82.13 * P]$ where $P = (\text{Max}(\text{Fo}^2, 0) + 2 * \text{Fc}^2) / 3$

Piezoresponse Force Microscopy: A 2 N/m platinum-coated tip (SCM-PIT-V2 Bruker) was used on a Bruker atomic force microscope system (Billerica, MA). During PFM measurements, an ac signal ranging from 20 mV up to 10 V was applied at 750 kHz. This frequency was chosen to avoid resonance. The response was measured statically on a well-defined gold top electrode. The response did not change over multiple sweeps taken over multiple days. Further static measurements were taken on the bare surface of the material, which showed a similar

5

PFM response. All PFM and electrical measurements were taken with no illumination to reduce contributions from photo-generated carriers. For large signal measurements the domain reorientation by poling was duplicated in an external LCR measurement system.

Electrical Force Microscopy: The single crystals were mounted on an AFM sample holder via a conducting double-sided copper tape. The top surface of the crystal exposed to a high-voltage (i.e. poled) to facilitate ferroelectric domain formation (described in detail elsewhere). The EFM measurements were performed under ambient conditions using single pass mode on a Park AFM equipped with an XE-70 controller and an external lock-in amplifier (SR830, Stanford Research Systems). The external lock-in amplifier was used for electrical AC bias of the tip, lock-in detection and feedback at 18 kHz of the EFM signal. Conductive Pt/Ir-coated AFM tips (Multi-75EG, Budget Sensors) were used for the measurements. Topography was measured at the first resonance frequency (~75 kHz) and EFM was collected with a 1.00 V_{AC} bias at 18 kHz, well separated from the topography frequency. The scan rate was 0.1 Hz. Surface topography and EFM were mapped simultaneously, while varying the sample bias voltages (0 to +/- 10 V).

Electrical Measurements: The dielectric temperature and frequency dependence and Rayleigh behavior were measured using a precision LCR meter (Hewlett Packard 4284A, Palo Alto, CA). The heating and cooling rates were controlled by a Peltier heater, monitored by a type-K thermocouple, which was read via a digital multimeter (Hewlett Packard 3478). Samples were allowed to equilibrate for a two minutes prior to taking a measurement. Rayleigh behavior was characterized at 1 MHz. No changes were observed in the Rayleigh response upon multiple cycles of applied AC electric fields indicating that the response was not induced or affected by the application of this electric field. The temperature of the global phase transition temperature occurs at the same temperature for increasing and decreasing temperature sweeps within the limit of the experimental step size. Further information on the Rayleigh analysis methodology for indicating residual ferroelectricity can be found in Ref. ¹³. Polarization–electric field measurements were taken on a Precision Multiferroic materials analyzer (Radiant Technologies, Inc., Albuquerque, NM).

The Rayleigh coefficient (see Figures 5A and 5B) was calculated from the slope of the AC electric field dependence of the permittivity. The total dielectric response, including the dielectric loss, is a combination of semiconductor and ferroelectric contributions. If only space-charge mechanisms were present, the permittivity and loss tangent should increase with temperature. The fact that the permittivity decreases as the temperature increases is consistent

with relaxor ferroelectricity. This is also consistent with the loss of dispersion in the permittivity data above approximately 57 °C.

Relaxor ferroelectricity should also cause frequency dispersion in the permittivity below T_{\max} . Figures 9A and 9B show the dielectric response and loss for a MAPbI₃ single crystal as a function of temperature and frequency. Above 57 °C the frequency dispersion in the dielectric response does decrease but does not disappear, likely due to contributions from leakage current.

Density Functional Theory Calculations: First principles calculations were performed using the projector augmented wave (PAW) method as implemented in the Vienna Ab Initio Simulation Package (VASP). Structures were relaxed using the standard parameters of the Materials Project. Density functional perturbation (DFPT) calculations using the Perdew, Becke and Ernzerhof (PBE) Generalized Gradient Approximation (GGA) for the exchange-correlation functional, a plane wave cutoff of 1000 eV, and a k-point density of approximately 2,000 per reciprocal atom were employed to calculate the piezoelectric tensor. The elastic tensor was computed in DFT with a plane wave cutoff of 700 eV, and a k-point density of 7,000 per reciprocal atom using explicit perturbations of the lattice corresponding to the 6 principle deformations and fit assuming a linear relationship. The reported piezoelectric tensor was then computed by the dot product of the piezoelectric stress tensor computed via DFT and the computed compliance tensor.

XPS: Photoemission spectroscopy measurements were performed on a Kratos NOVA spectrometer calibrated to the Fermi edge and core level positions of sputter-cleaned metal (Au, Ag, Cu, Mo) surfaces. X-ray photoemission spectra were taken using mono-chromated Al K α radiation (1486.7 eV) at a resolution of 400 meV and fit using Pseudo-Voigt profiles. Spectral acquisition were performed without light bias and using low X-ray fluences at nominal 1.5 W anode power.

d_{33} Berlincourt Measurements and Analysis: The theoretical estimate calculated in this work for d_{33} of 2.9 pC/N significantly underestimates the piezoelectric response. Plane wave based DFT codes are effective at predicting properties of periodic coupled systems such as inorganic crystals, but poor at describing the localized waves of molecular systems. These calculations are likely under-representing the contribution of the methyl ammonium to the polarization, which should be significant at 2.3 Debye. The under-prediction of the piezoelectric response by DFT suggests that the methyl ammonium molecule is largely responsible for the measured piezoelectricity. But the presence of any piezoelectric response when no response could be

measured prior to poling further validates the presence of enduring reorientable dipoles within the material. Similar electrical measurements were taken on large, high quality single crystals of MAPbBr₃. MAPbBr₃ showed no Rayleigh response, or PFM response, which is consistent with the reported cubic crystal structure.

5 Examples:

Example 1. A composition comprising a perovskite crystal comprising a ferroelectric domain aligned substantially parallel to a reference axis.

Example 2. The composition of Example 1, wherein: the perovskite crystal comprises ABX₃, wherein: A is a first cation, B is a second cation, and X is an anion.

10 Example 3. The composition of either Examples 1 or 2, wherein A comprises an alkyl ammonium cation.

Example 4. The composition of any one of Examples 1-3, wherein B comprises a metal element.

15 Example 5. The composition of any one of Examples 1-4, wherein the metal element comprises lead.

Example 6. The composition of any one of Examples 1-5, wherein X comprises a halogen.

Example 7. The composition of any one of Examples 1-6, wherein the perovskite crystal comprises methylammonium lead iodide.

20 Example 8. The composition of any one of Examples 1-7, wherein the ferroelectric domain has a crystal structure comprising at least one of a tetragonal phase or an orthorhombic phase.

Example 9. The composition of any one of Examples 1-8, wherein the ferroelectric domain has a crystal structure that is not a cubic phase.

Example 10. The composition of any one of Examples 1-9, wherein the ferroelectric domain is characterized by a Rayleigh response having a positive slope.

25 Example 11: The composition of any one of Examples 1-10, wherein the perovskite crystal comprises MAPI.

Example 12. The composition of any one of Examples 1-11, wherein the ferroelectric domain is characterized by a d₃₃ measurement having a value greater than zero pC/N.

Example 13. The composition of any one of Examples 1-12, wherein the d_{33} measurement is between 0.1 pC/N and 10,000 pC/N.

Example 14. The composition of any one of Examples 1-13, wherein the ferroelectric domain is characterized by a characteristic value measured by at least one of piezoresponse force
5 microscopy, electric force microscopy, contact Kelvin probe force microscopy, scanning microwave impedance microscopy, or optical microscopy.

Example 15. A device comprising a layer comprising a perovskite crystal comprising a ferroelectric domain aligned substantially parallel to a reference axis, wherein: the perovskite crystal comprises ABX_3 , wherein: A is a first cation, B is a second cation, and X is an anion.

10 Example 16. The device of Example 15, wherein A comprises an alkyl ammonium cation.

Example 17. The device of either Examples 15 or 16, wherein B comprises a metal element.

Example 18. The device of any one of Examples 15-17, wherein the metal element comprises lead.

Example 19. The device of any one of Examples 15-18, wherein X comprises a halogen.

15 Example 20. The device of any one of Examples 15-19, wherein the perovskite crystal comprises methylammonium lead iodide.

Example 21. The device of any one of Examples 15-20, wherein the ferroelectric domain has a crystal structure comprising at least one of a tetragonal phase or an orthorhombic phase.

20 Example 22. The device of any one of Examples 15-21, wherein the ferroelectric domain has a crystal structure that is not a cubic phase.

Example 23. The device of any one of Examples 15-22, wherein the ferroelectric domain is characterized by a Rayleigh response having a positive slope.

Example 24. The device of any one of Examples 15-23, wherein the ferroelectric domain is characterized by a d_{33} measurement having a value greater than zero pC/N.

25 Example 25. The device of any one of Examples 15-24, wherein the d_{33} measurement is between 0.1 pC/N and 10,000 pC/N.

Example 26. The device of any one of Examples 15-25, wherein the ferroelectric domain is characterized by a characteristic value measured by at least one of piezoresponse force microscopy, electric force microscopy, contact Kelvin probe force microscopy, scanning
30 microwave impedance microscopy, or optical microscopy.

Example 27. The device of any one of Examples 15-26, wherein: the layer further comprises a first surface and a second surface, the second surface is substantially parallel to the first surface, the first surface and the second surface define a thickness of the layer, and the reference axis is substantially perpendicular to the first surface and the second surface.

- 5 Example 28. The device of any one of Examples 15-27, wherein the thickness is between 1 Å and 10 mm.

Example 29. The device of any one of Examples 15-28, wherein the ferroelectric domain has a length between 1 Å and 10 mm.

- 10 Example 30. The device of any one of Examples 15-29, further comprising: a first electrode comprising a first metal positioned against the first surface; and a second electrode comprising a second metal positioned against the second surface, wherein: the layer is positioned between the first electrode and the second electrode.

Example 31. The device of any one of Examples 15-30, wherein the first metal and the second metal are the same.

- 15 Example 32. The device of any one of Examples 15-31, wherein the first metal and the second metal comprise gold.

- 20 Example 33. A method comprising: applying a gradient to a perovskite crystal having a characteristic length, wherein: the applying creates at least one ferroelectric domain within the perovskite crystal, the ferroelectric domain has a crystal structure that is not in a cubic phase, and the ferroelectric domain is aligned substantially parallel with the characteristic length.

Example 34. The method of Example 33, wherein the applying comprises at least one of applying an electric field gradient or a temperature gradient across the characteristic length.

- 25 Example 35. The method of either Examples 33 or 34, wherein the applying the electric field gradient comprises applying a voltage between 1 mV and 100 V across the characteristic length.

Example 36. The method of any one of Examples 33-35, wherein the temperature gradient is between 50 °C/micrometer and 200° C/micrometer across the characteristic length.

Example 37. The method of any one of Examples 33-36, wherein the characteristic length is between 1 Å and 10 mm.

Example 38. The method of any one of Examples 33-37, wherein the applying is performed at a temperature between 15 °C and 25 °C.

Example 39. The method of any one of Examples 33-38, wherein the applying is performed for a period of time between 1 second and 100 seconds.

5 Example 40. The method of any one of Examples 33-39, wherein: the perovskite crystal comprises ABX_3 , wherein: A is a first cation, B is a second cation, and X is an anion.

Example 41. The method of any one of Examples 33-40, wherein A comprises an alkyl ammonium cation.

Example 42. The method of any one of Examples 33-41, wherein B comprises a metal element.

10 Example 43. The method of any one of Examples 33-42, wherein the metal element comprises lead.

Example 44. The method of any one of Examples 33-43, wherein X comprises a halogen.

Example 45. The method of any one of Examples 33-44, wherein the perovskite crystal comprises methylammonium lead iodide.

15 Example 46. The method of any one of Examples 33-45, wherein the ferroelectric domain has a crystal structure comprising at least one of a tetragonal phase or an orthorhombic phase.

Example 47. The method of any one of Examples 33-46, wherein the ferroelectric domain has a crystal structure that is not a cubic phase.

20 Example 48. The method of any one of Examples 33-47, wherein the ferroelectric domain is characterized by a Rayleigh response having a positive slope.

Example 49. The method of any one of Examples 33-48, wherein the ferroelectric domain is characterized by a d_{33} measurement having a value greater than zero pC/N.

Example 50. The method of any one of Examples 33-49, wherein the d_{33} measurement is between 0.1 pC/N and 10,000 pC/N.

25 Example 51. The method of any one of Examples 33-50, wherein the ferroelectric domain is characterized by a characteristic value measured by at least one of piezoresponse force microscopy, electric force microscopy, contact Kelvin probe force microscopy, scanning microwave impedance microscopy, or optical microscopy.

The foregoing discussion and examples have been presented for purposes of illustration and

description. The foregoing is not intended to limit the aspects, embodiments, or configurations to the form or forms disclosed herein. In the foregoing Detailed Description for example, various features of the aspects, embodiments, or configurations are grouped together in one or more embodiments, configurations, or aspects for the purpose of streamlining the disclosure.

- 5 The features of the aspects, embodiments, or configurations, may be combined in alternate aspects, embodiments, or configurations other than those discussed above. This method of disclosure is not to be interpreted as reflecting an intention that the aspects, embodiments, or configurations require more features than are expressly recited in each claim. Rather, as the following claims reflect, inventive aspects lie in less than all features of a single foregoing
- 10 disclosed embodiment, configuration, or aspect. While certain aspects of conventional technology have been discussed to facilitate disclosure of some embodiments of the present invention, the Applicants in no way disclaim these technical aspects, and it is contemplated that the claimed invention may encompass one or more of the conventional technical aspects discussed herein. Thus, the following claims are hereby incorporated into this Detailed
- 15 Description, with each claim standing on its own as a separate aspect, embodiment, or configuration.

CLAIMS

What is claimed is:

1. A composition comprising a perovskite crystal comprising a ferroelectric domain aligned substantially parallel to a reference axis.
2. The composition of claim 1, wherein:
the perovskite crystal comprises ABX_3 , wherein:
A is a first cation,
B is a second cation, and
X is an anion.
3. The composition of either claims 1 or 2, wherein A comprises an alkyl ammonium cation.
4. The composition of any one of claims 1-3, wherein B comprises a metal element.
5. The composition of any one of claims 1-4, wherein the metal element comprises lead.
6. The composition of any one of claims 1-5, wherein X comprises a halogen.
7. The composition of any one of claims 1-6, wherein the perovskite crystal comprises methylammonium lead iodide.
8. The composition of any one of claims 1-7, wherein the ferroelectric domain has a crystal structure comprising at least one of a tetragonal phase or an orthorhombic phase.
9. The composition of any one of claims 1-8, wherein the ferroelectric domain is characterized by a Rayleigh response having a positive slope.
10. The composition of any one of claims 1-9, wherein the ferroelectric domain is characterized by a d_{33} measurement having a value greater than zero pC/N.
11. The composition of any one of claims 1-10, wherein the d_{33} measurement is between 0.1 pC/N and 10,000 pC/N.

12. A device comprising
a layer comprising a perovskite crystal comprising a ferroelectric domain aligned substantially parallel to a reference axis, wherein:
the perovskite crystal comprises ABX_3 , wherein:
A is a first cation,
B is a second cation, and
X is an anion.
13. The device of claim 12, wherein:
the layer further comprises a first surface and a second surface,
the second surface is substantially parallel to the first surface,
the first surface and the second surface define a thickness of the layer, and
the reference axis is substantially perpendicular to the first surface and the second surface.
14. The device of either claims 12 or 13, wherein the thickness is between 1 Å and 10 mm.
15. The device of any one of claims 12-14, wherein the ferroelectric domain has a length between 1 Å and 10 mm.
16. The device of any one of claims 12-15, further comprising:
a first electrode comprising a first metal positioned against the first surface; and
a second electrode comprising a second metal positioned against the second surface,
wherein:
the layer is positioned between the first electrode and the second electrode.
17. The device of any one of claims 12-16, wherein the first metal and the second metal are the same.
18. A method comprising:
applying a gradient to a perovskite crystal having a characteristic length, wherein:
the applying creates at least one ferroelectric domain within the perovskite crystal,
the ferroelectric domain has a crystal structure that is not in a cubic phase, and
the ferroelectric domain is aligned substantially parallel with the characteristic length.

19. The method of claim 18, wherein the applying comprises at least one of applying an electric field gradient or a temperature gradient across the characteristic length.
20. The method of either claims 18 or 19, wherein the applying the electric field gradient comprises applying a voltage between 1 mV and 100 V across the characteristic length.

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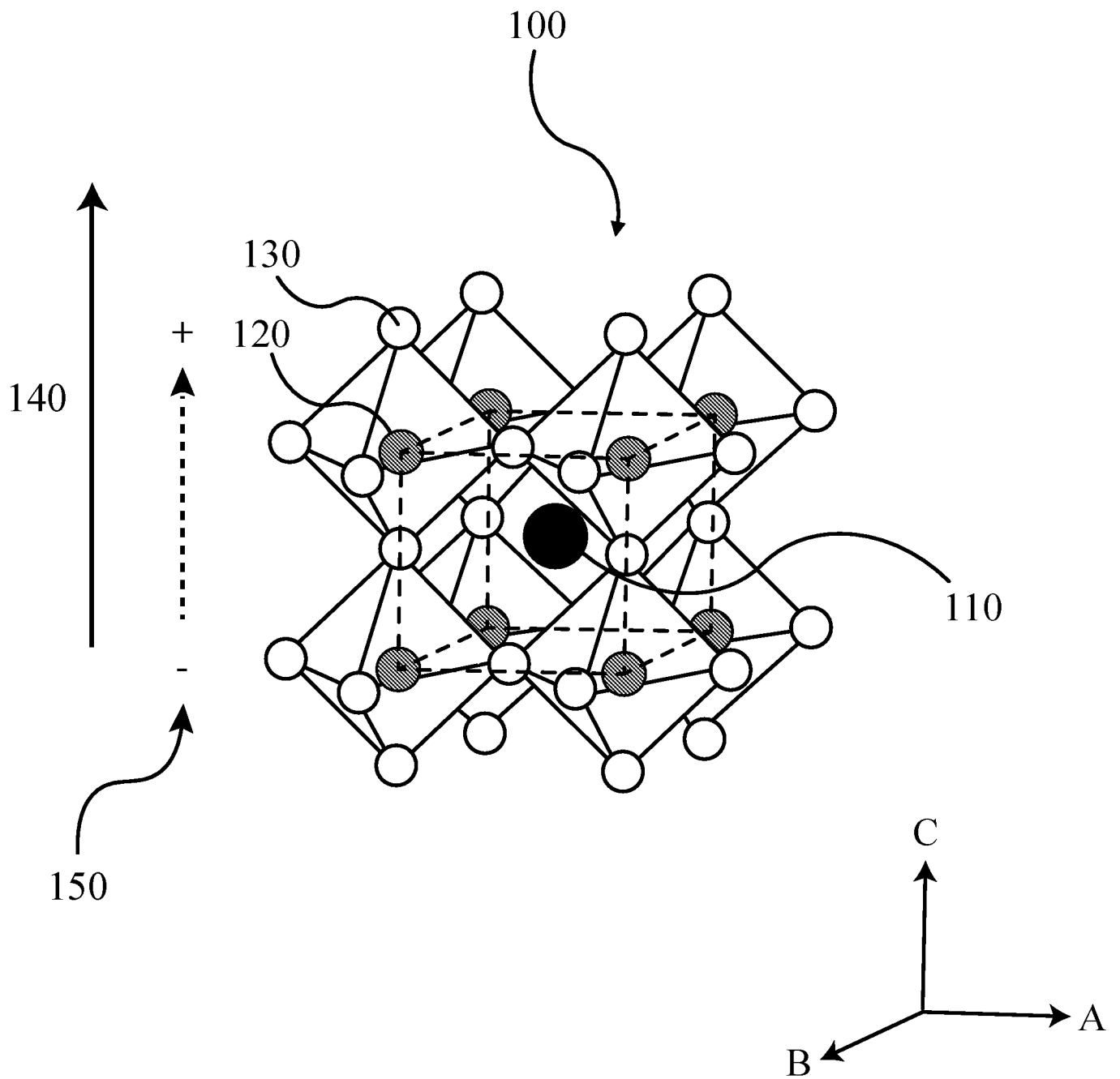


Figure 1

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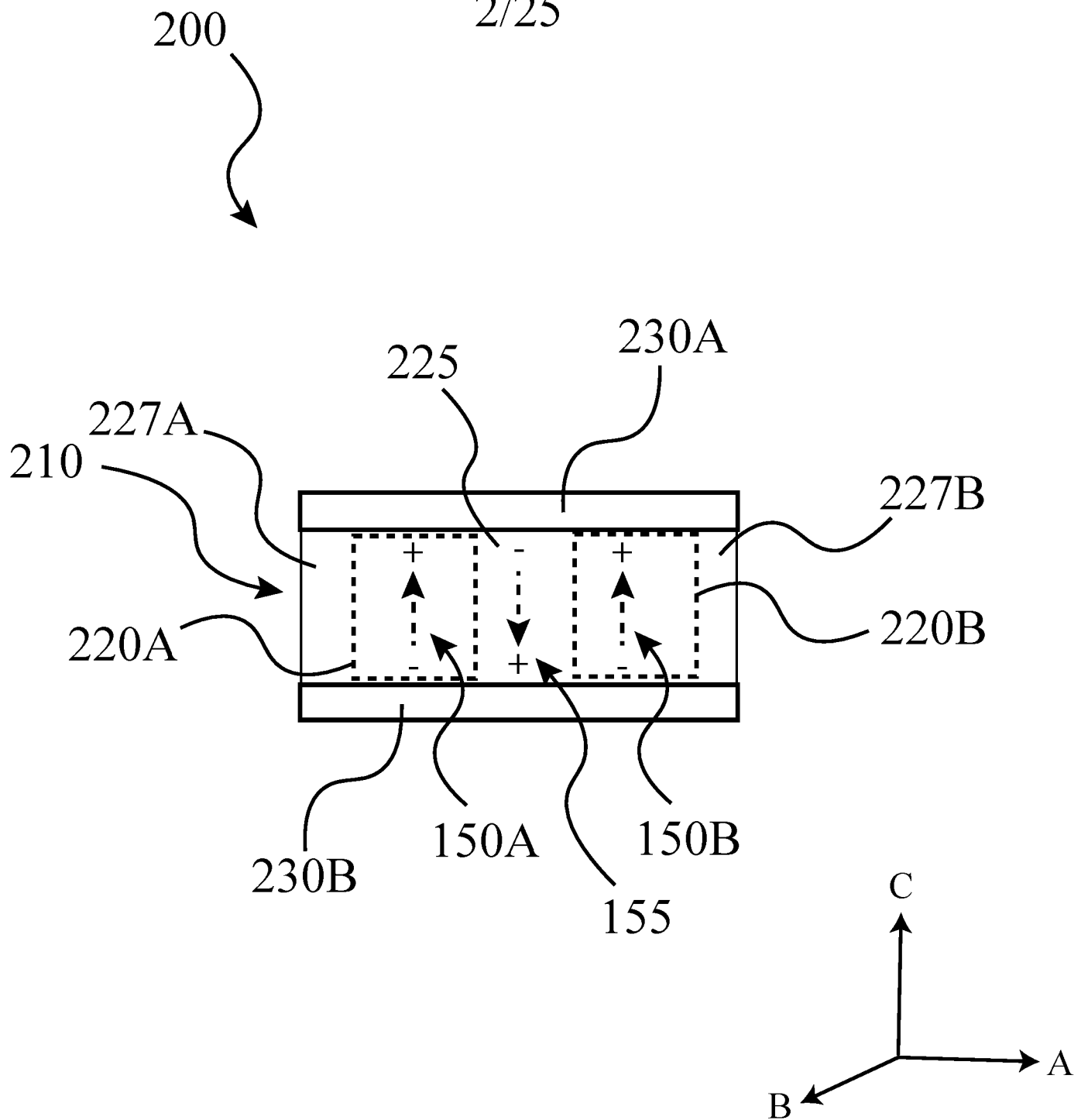


Figure 2

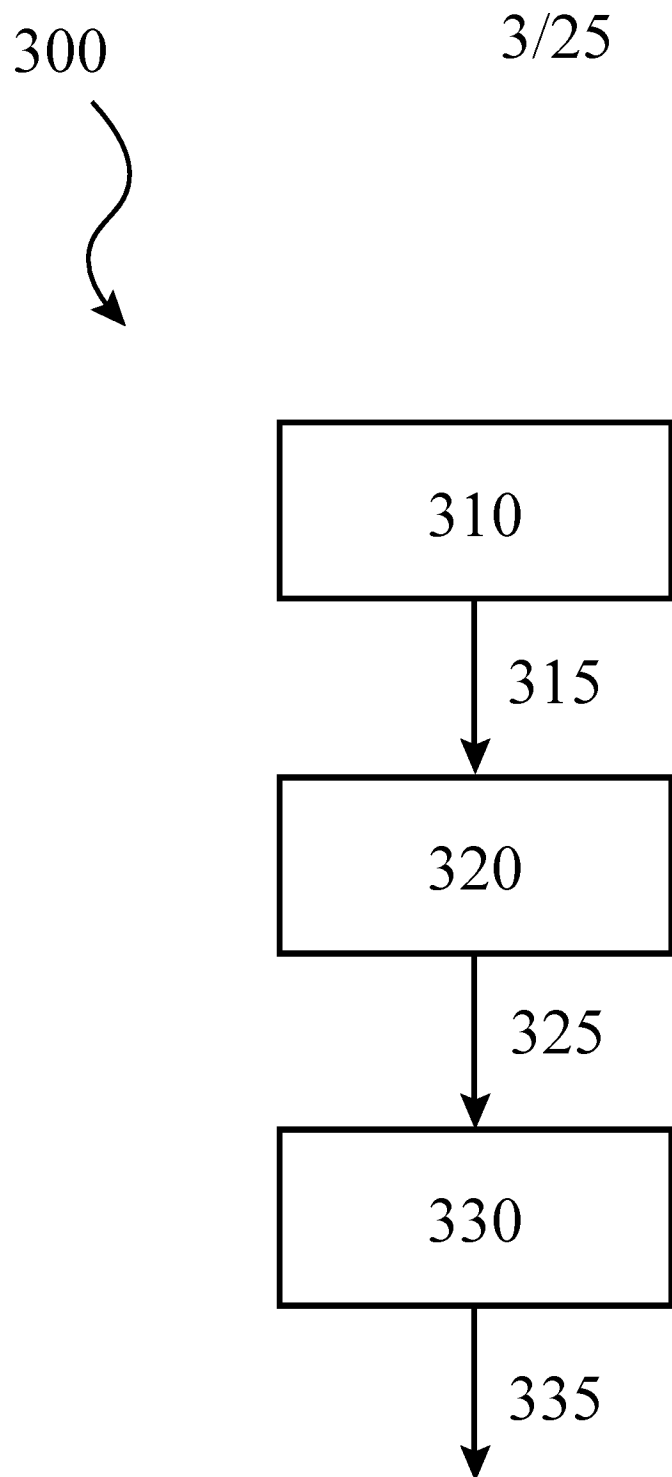


Figure 3

4/25

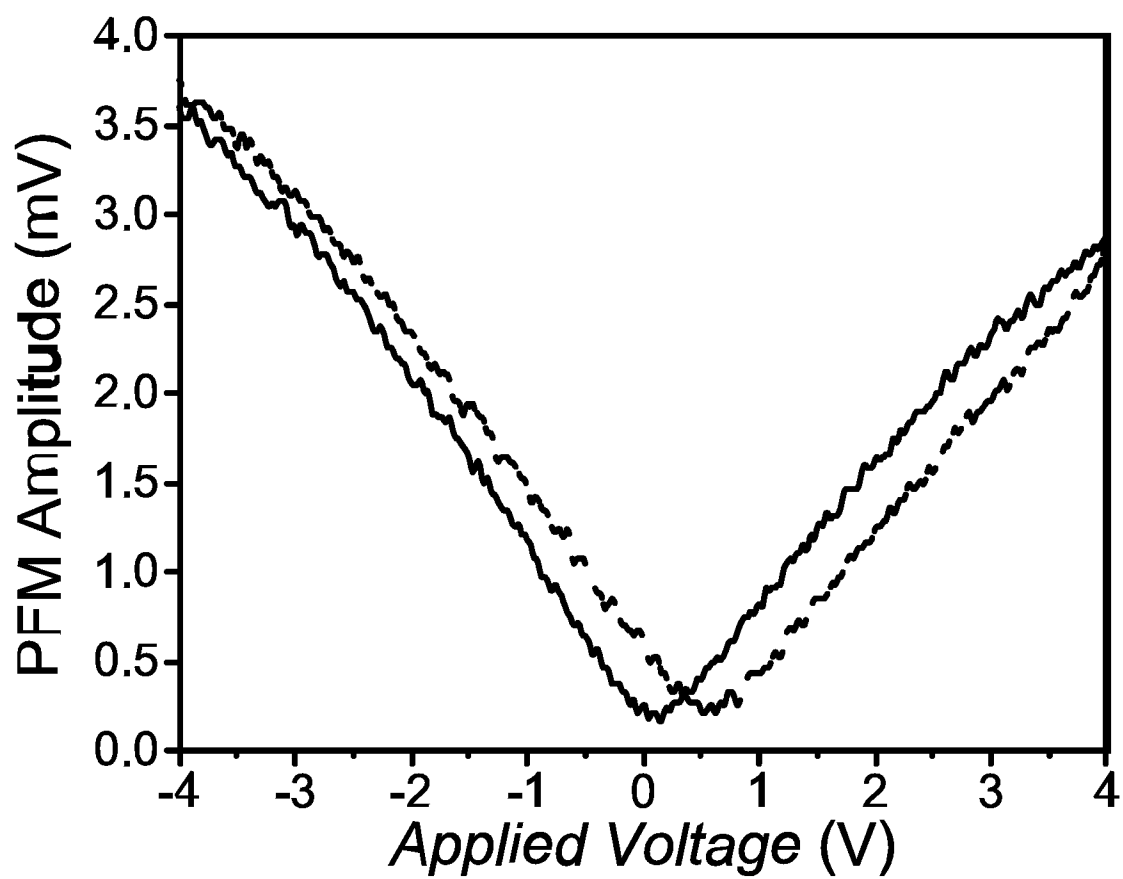


Figure 4A

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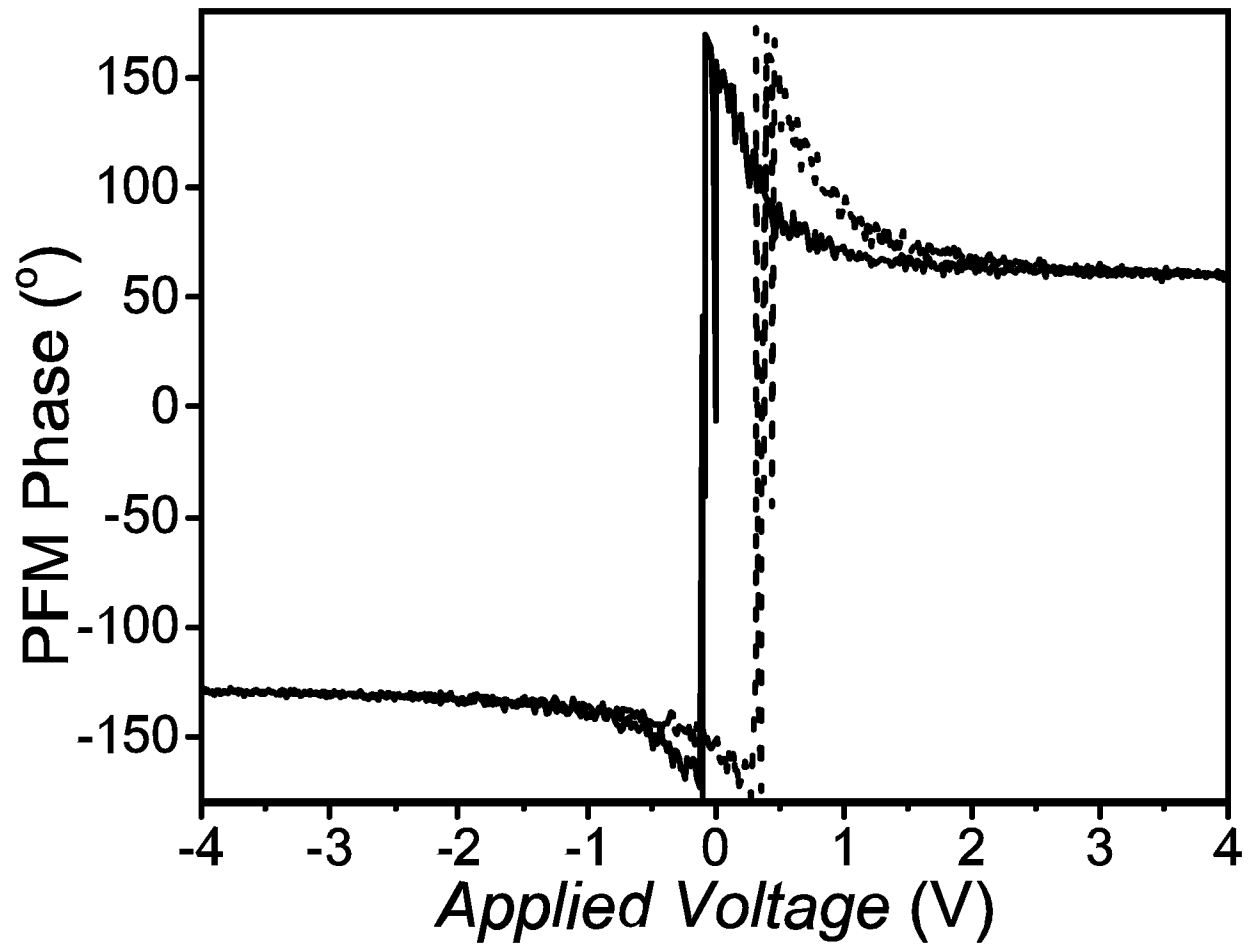


Figure 4B

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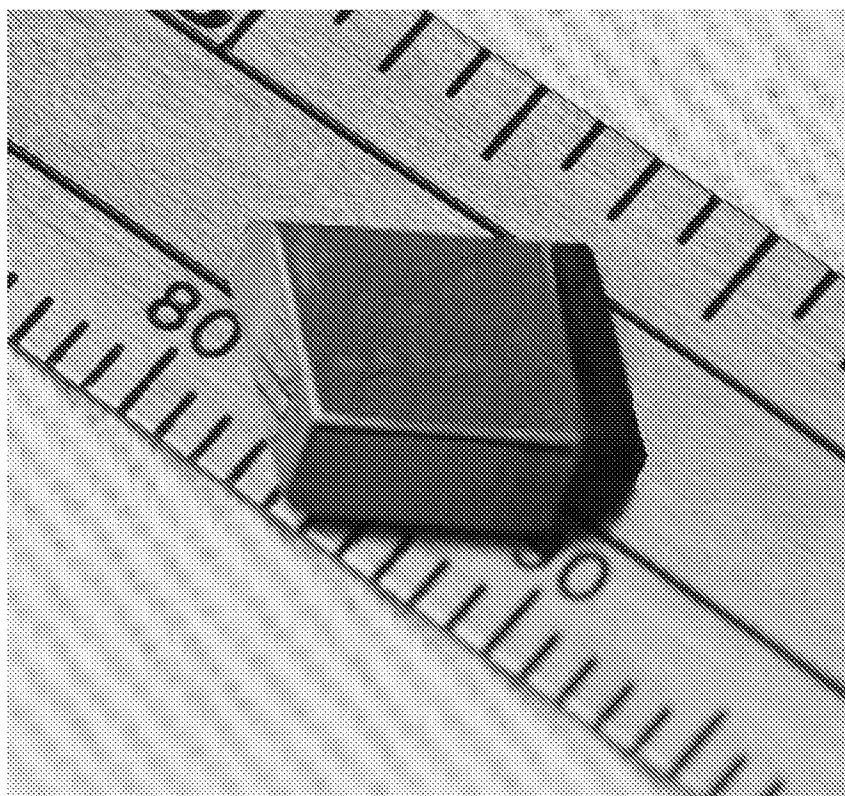


Figure 4C

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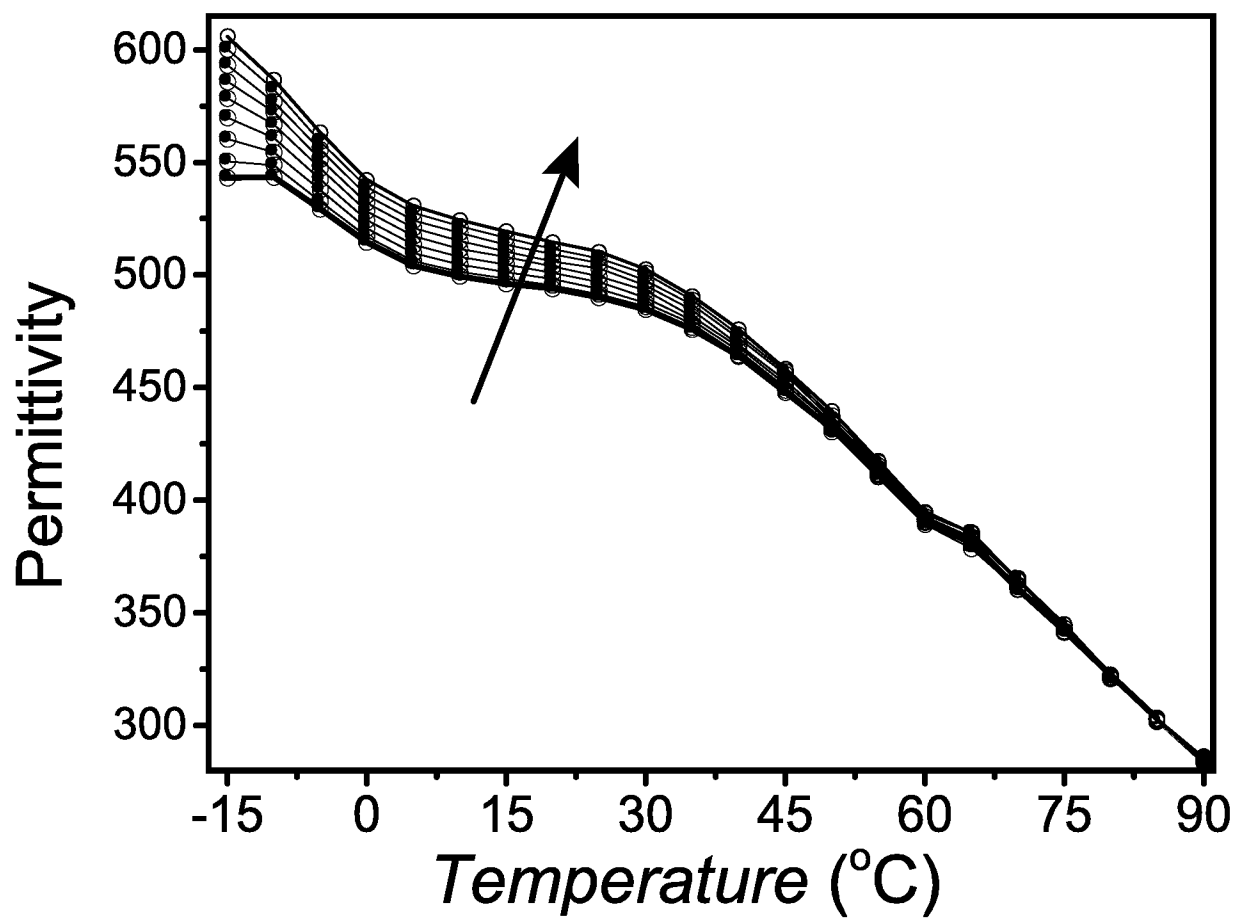


Figure 4D

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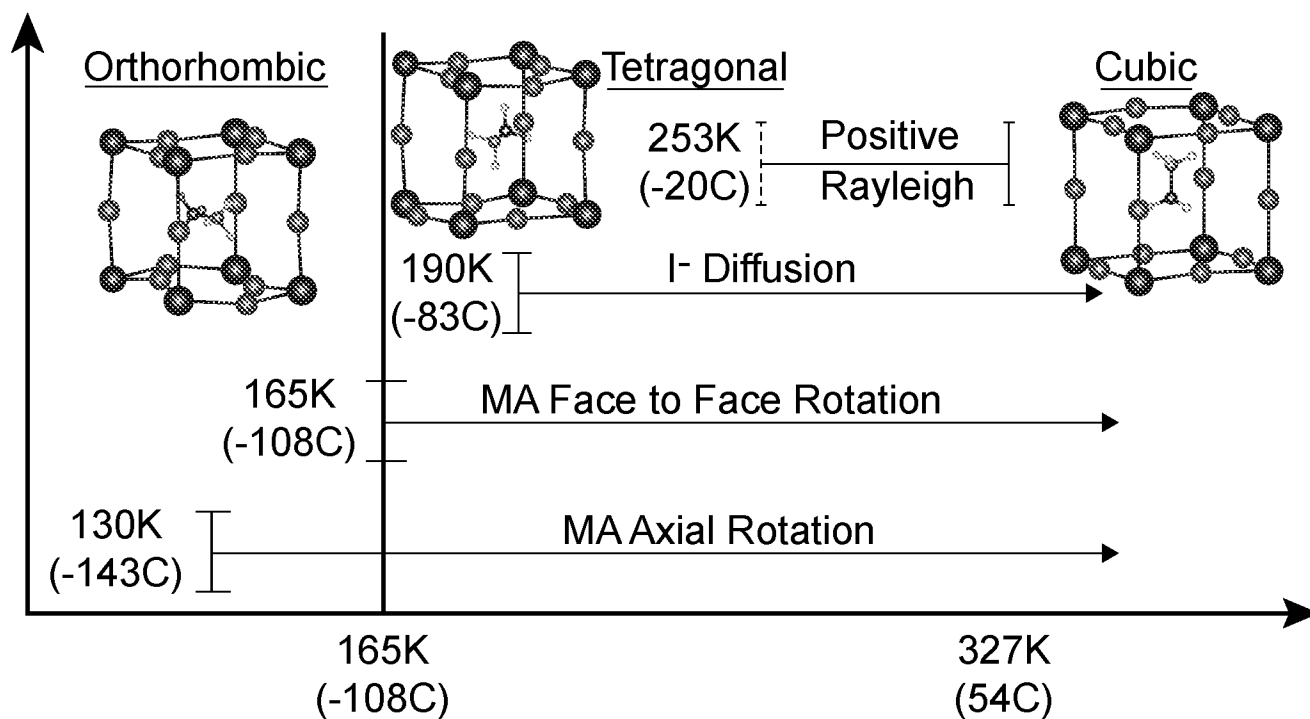


Figure 4E

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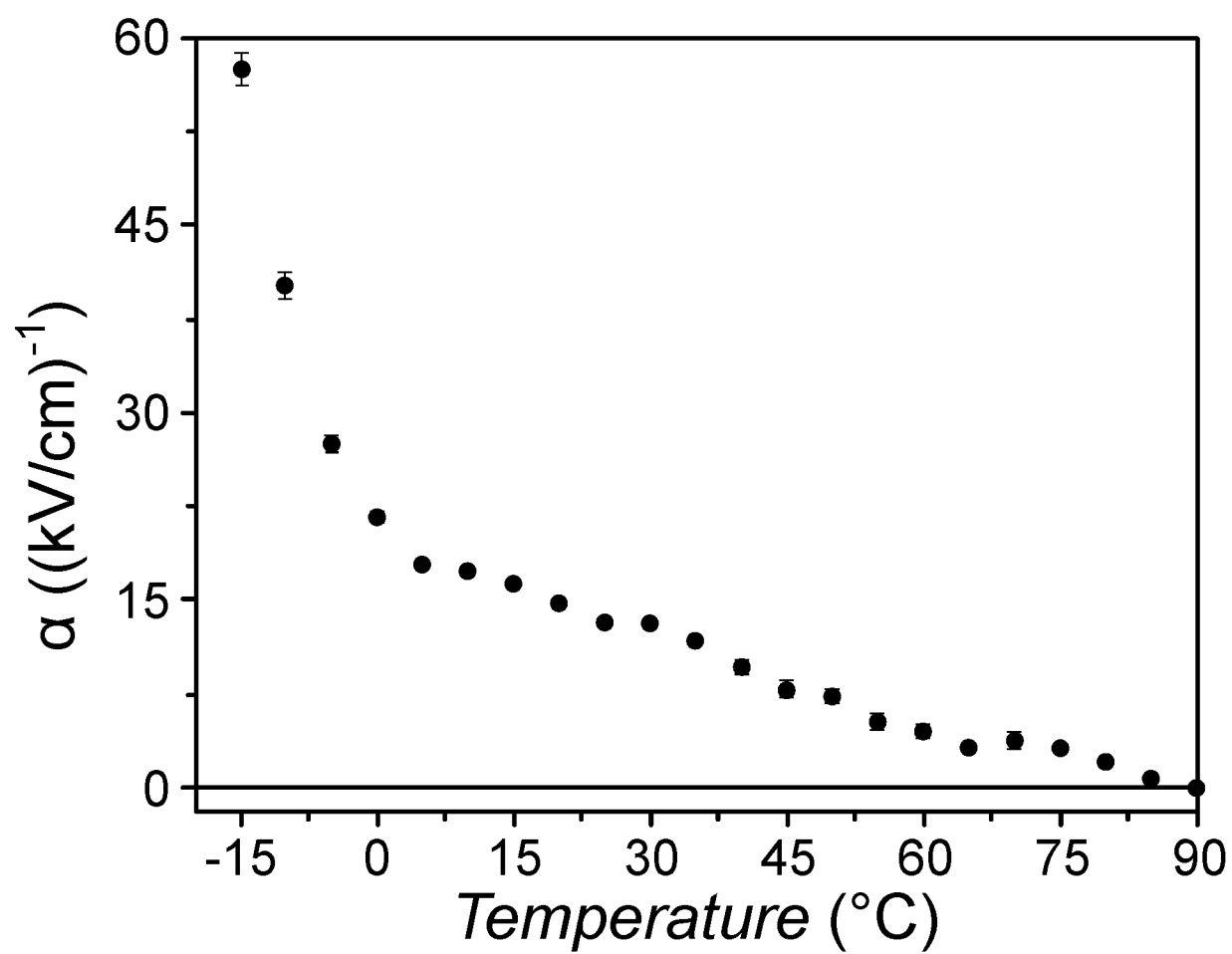


Figure 5A

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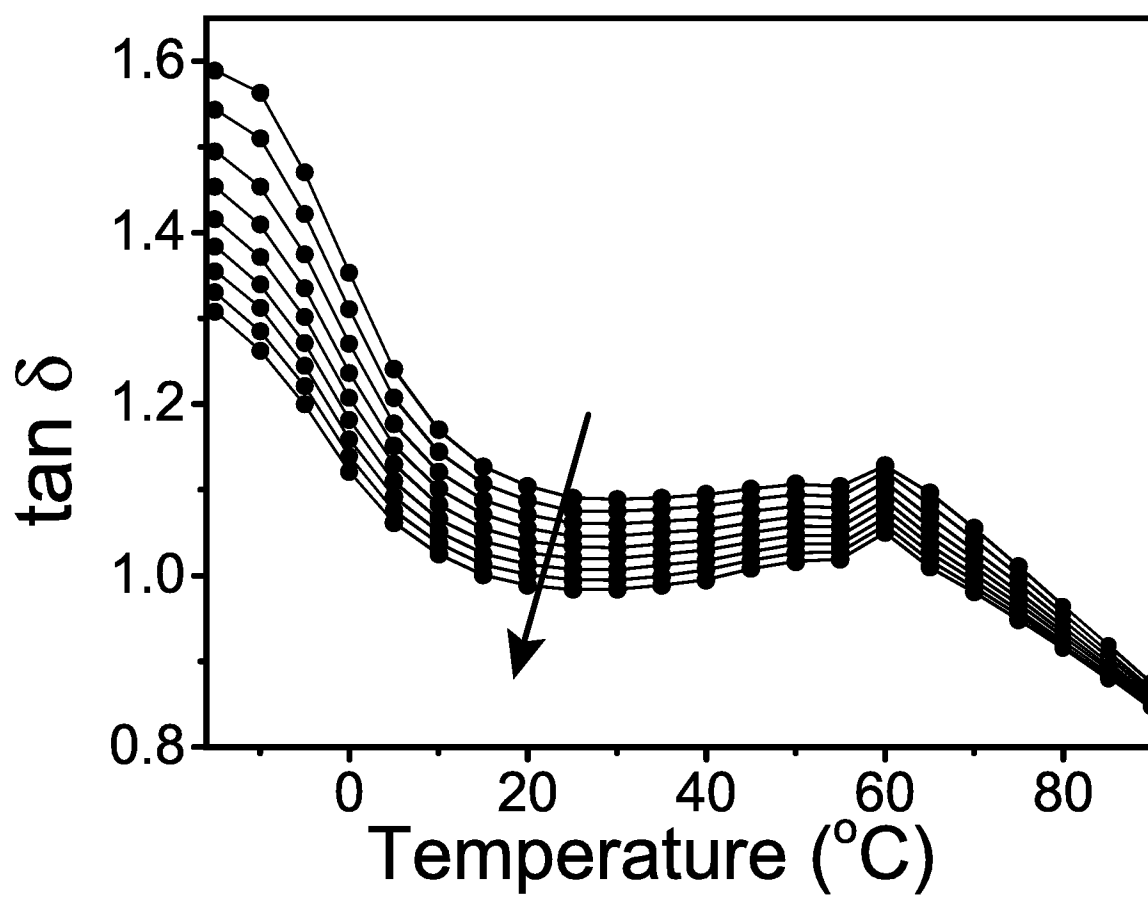


Figure 5B

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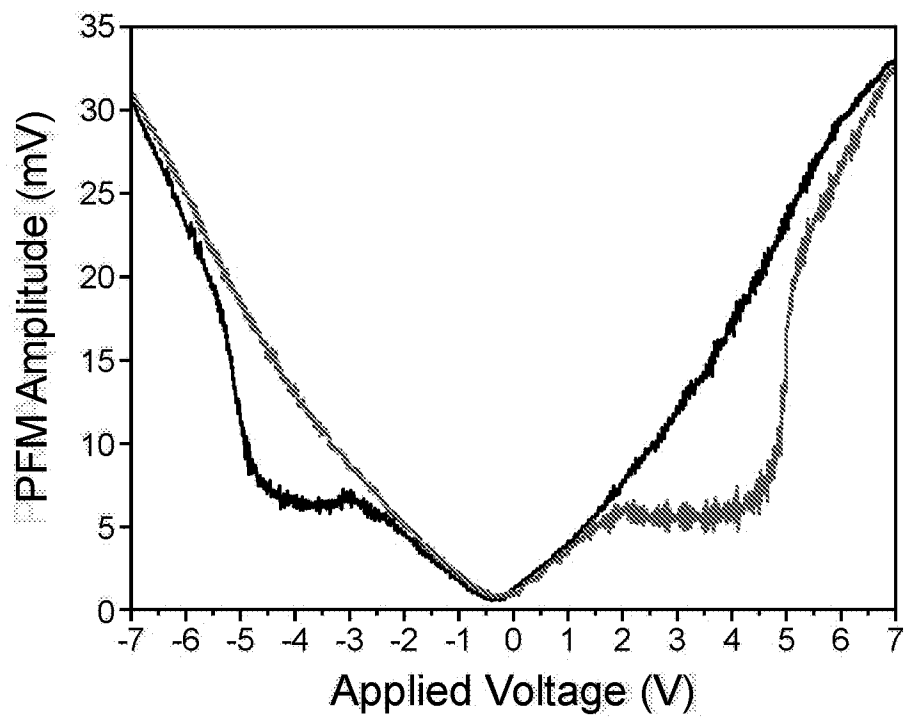


Figure 6A

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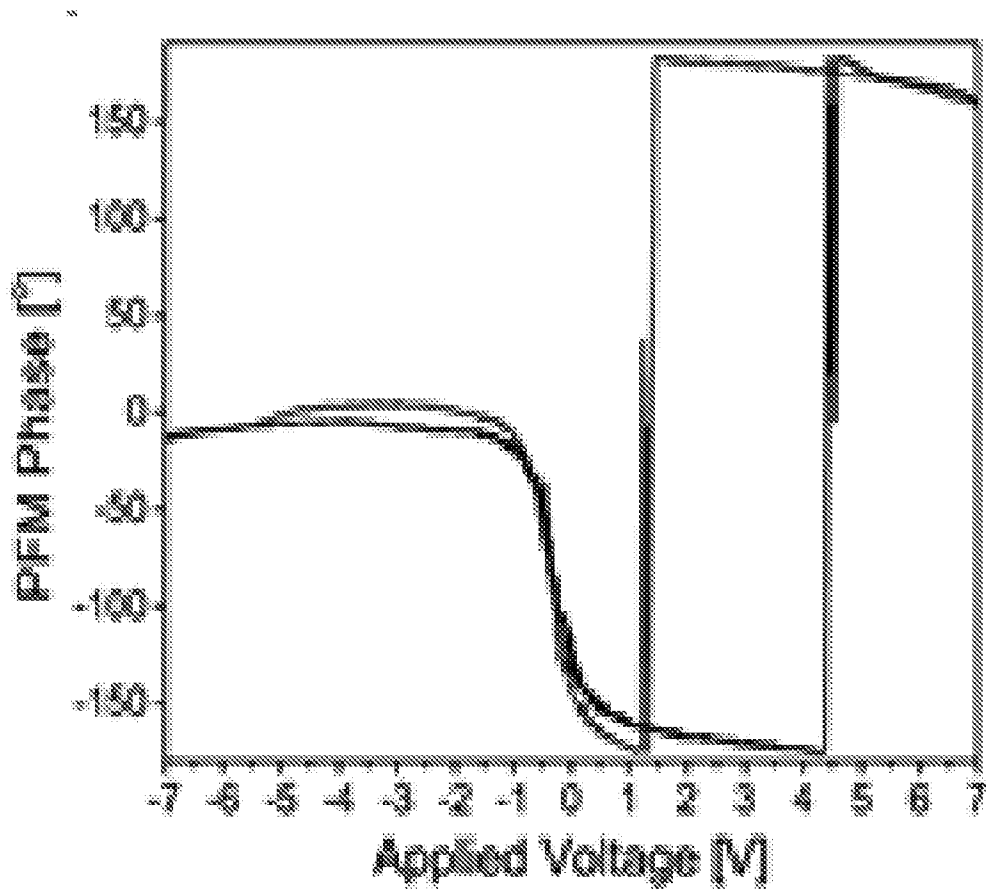


Figure 6B

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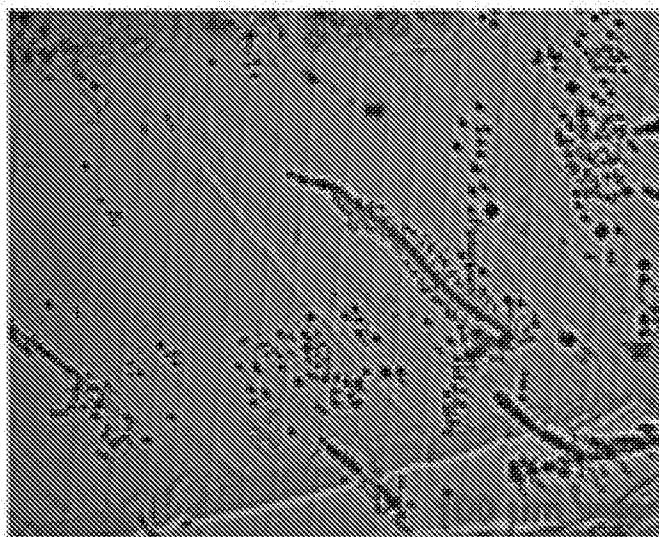


Figure 6C

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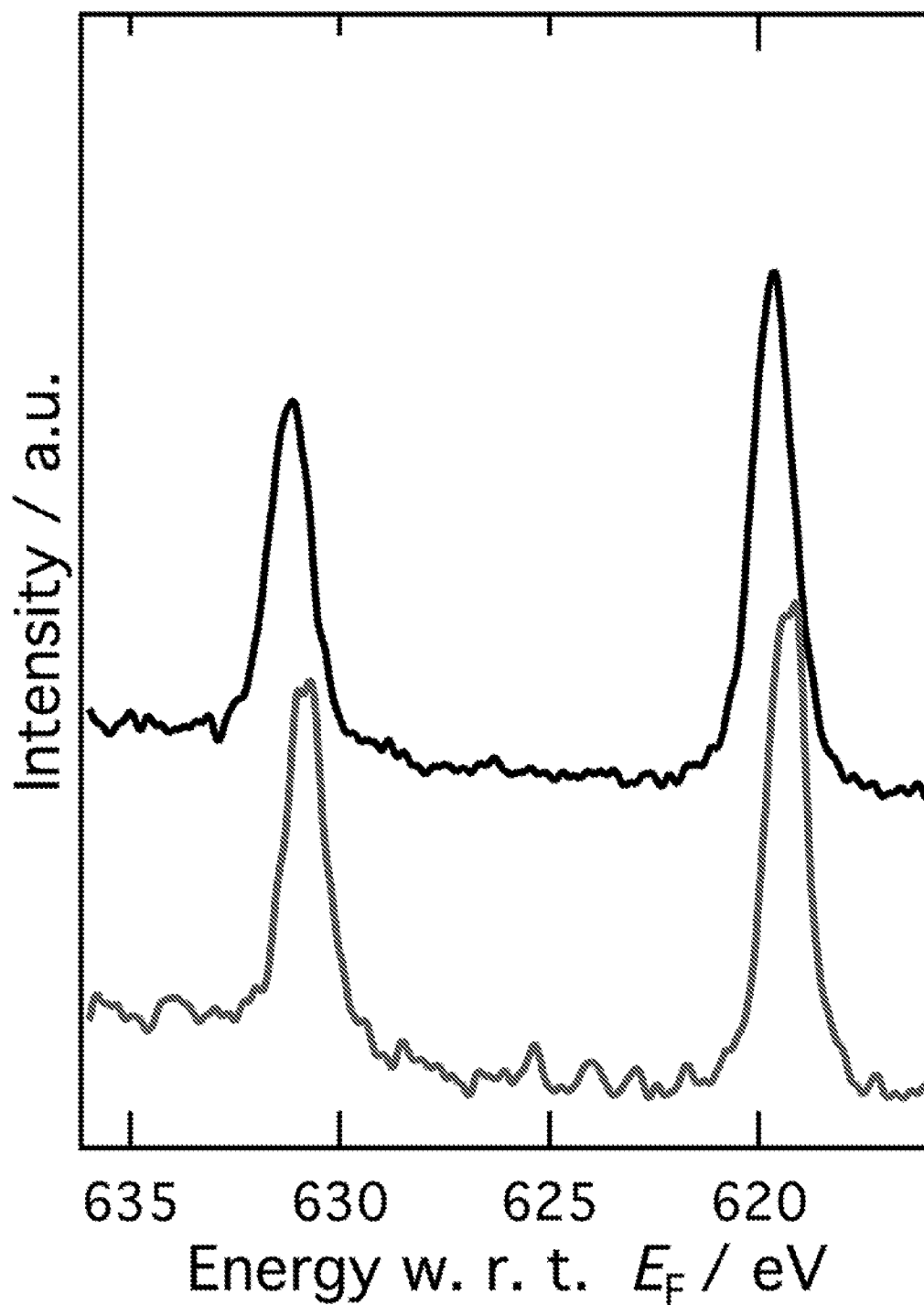


Figure 7A

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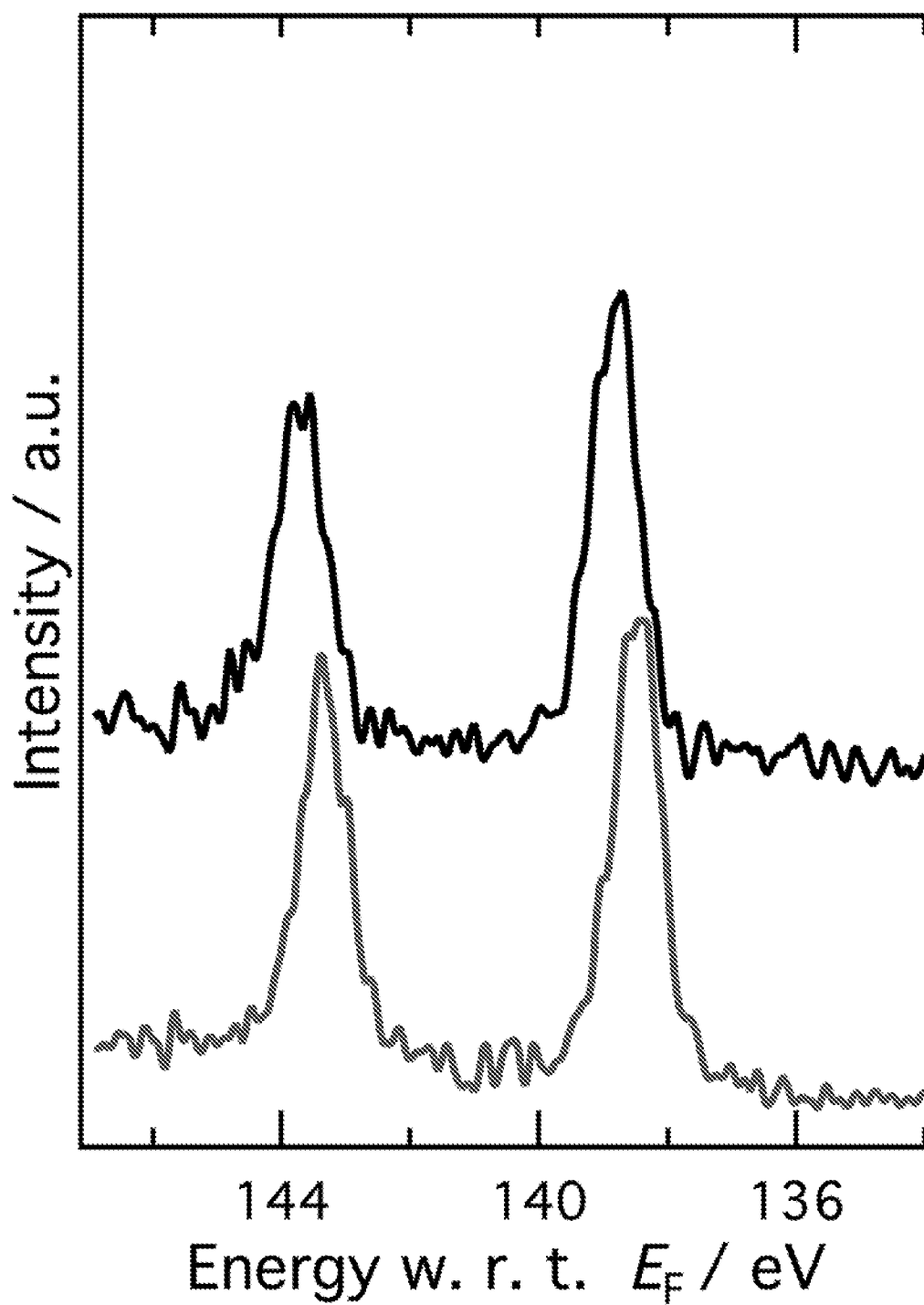


Figure 7B

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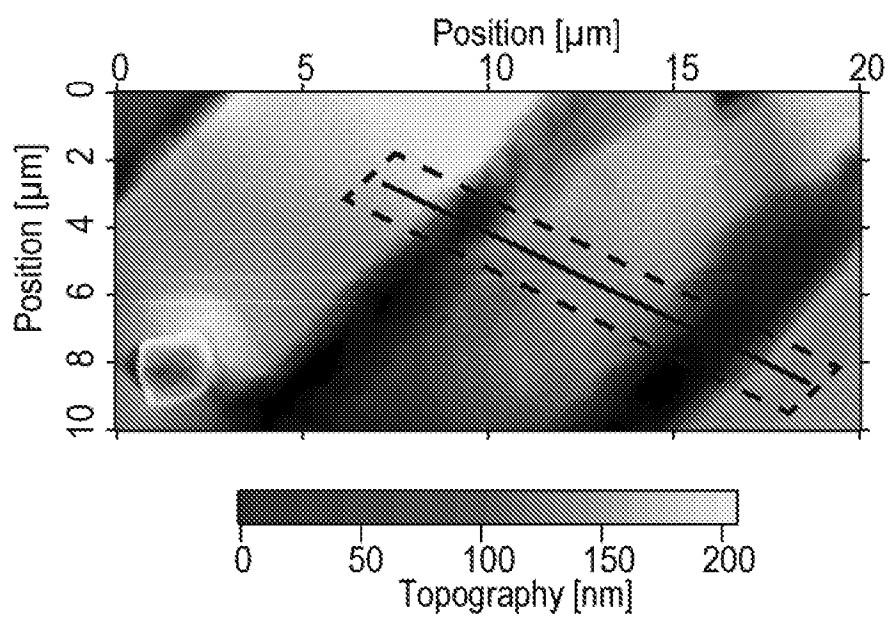


Figure 8A

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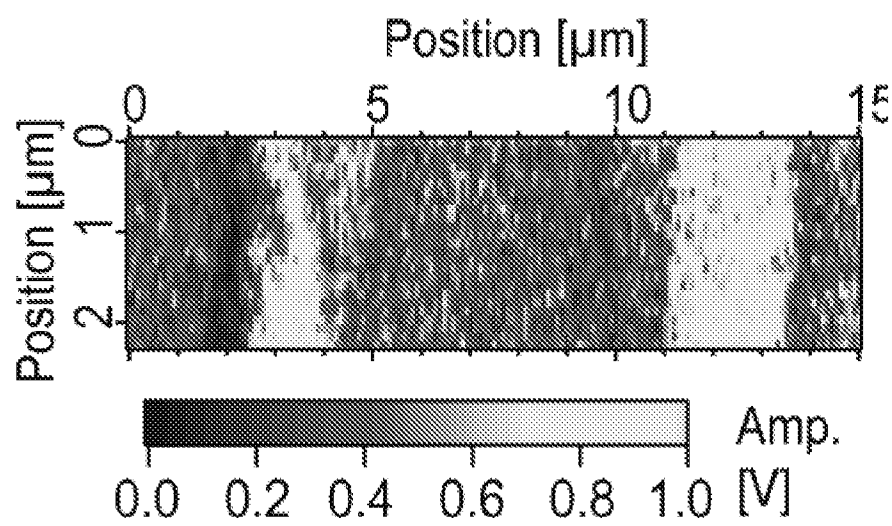


Figure 8B

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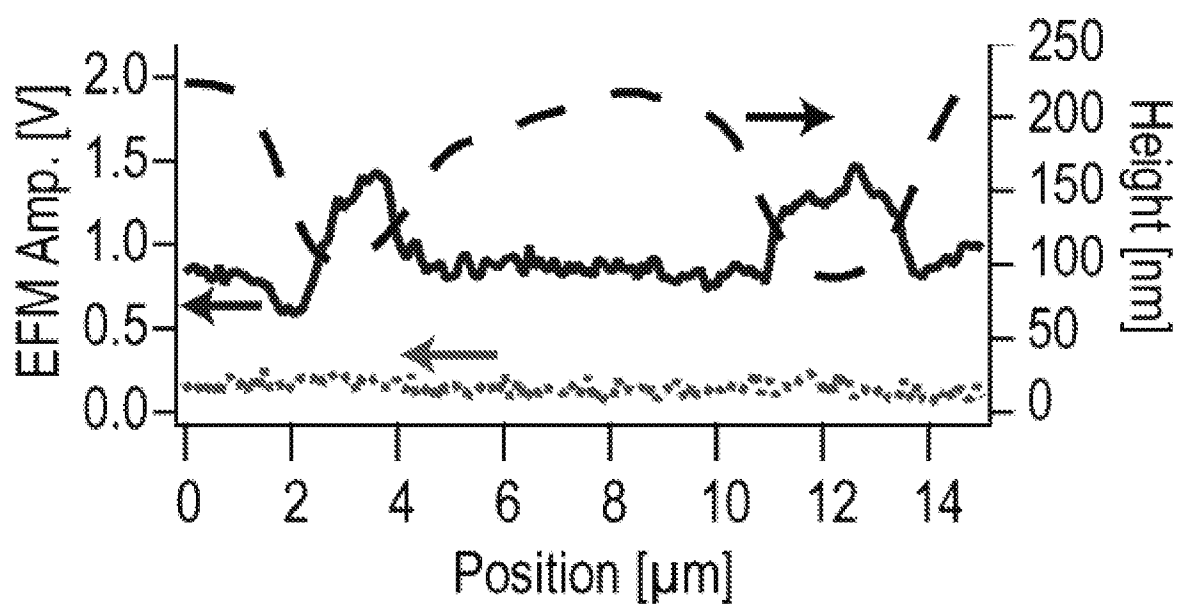


Figure 8C

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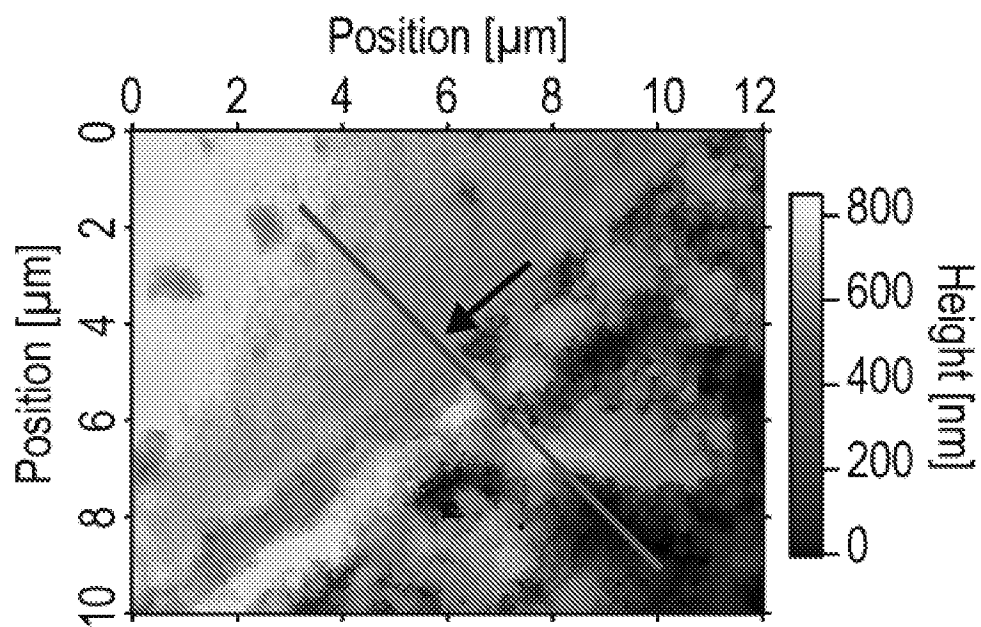


Figure 8D

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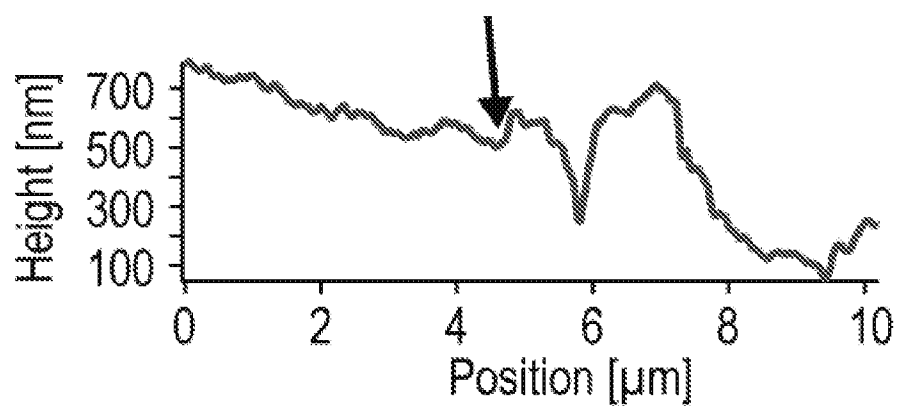


Figure 8E

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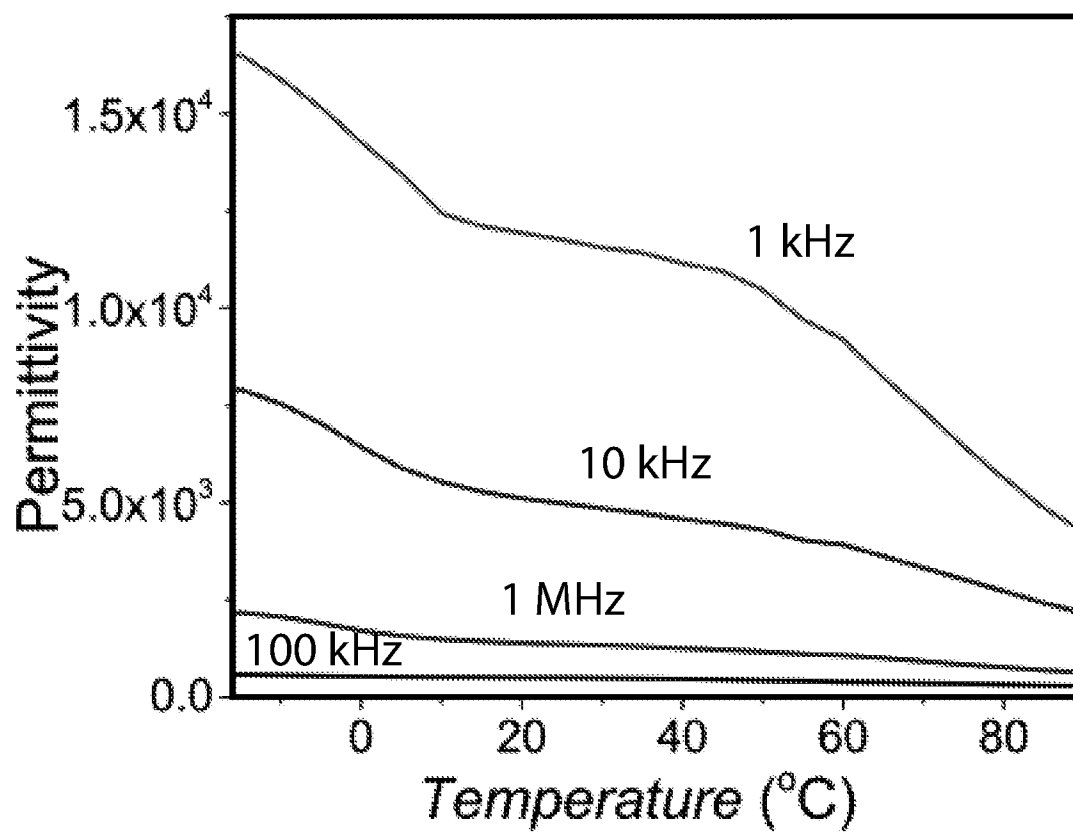


Figure 9A

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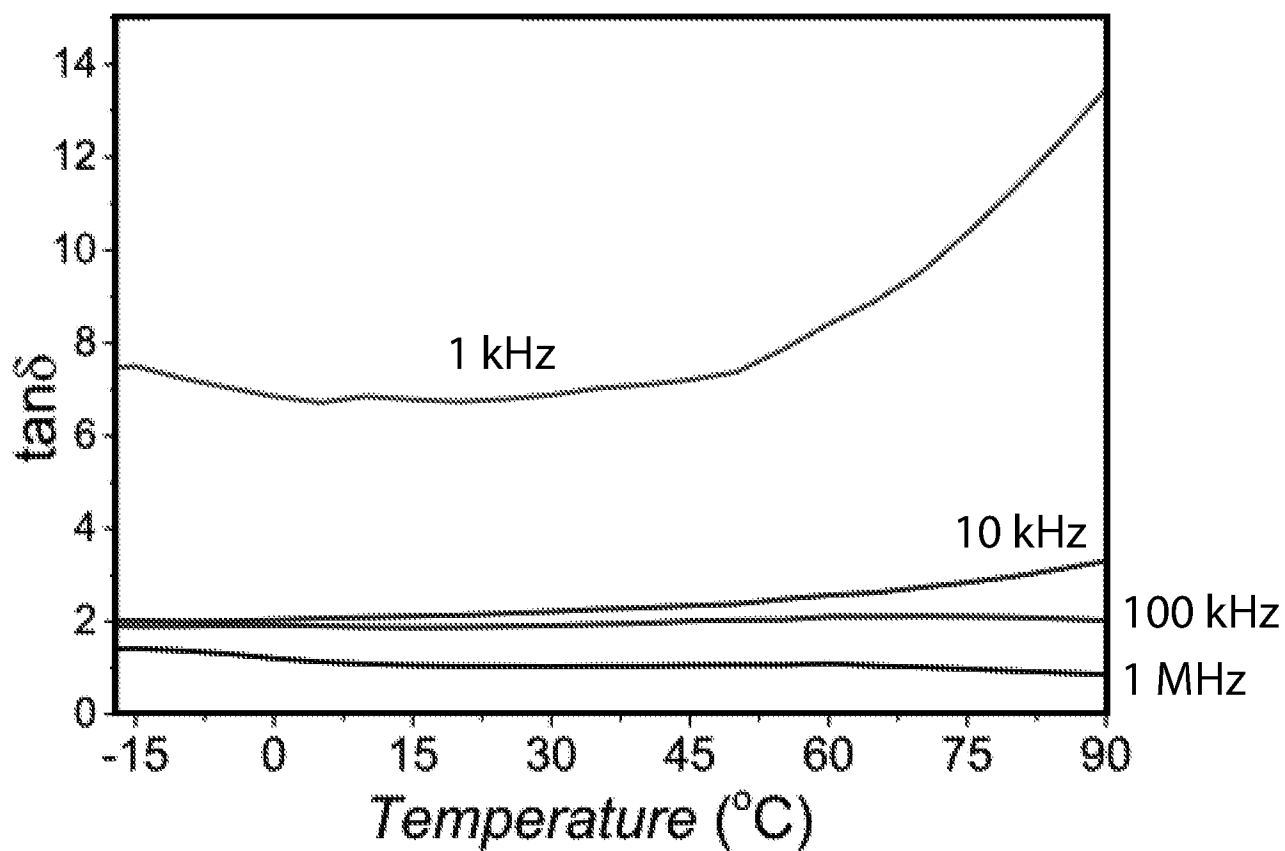


Figure 9B

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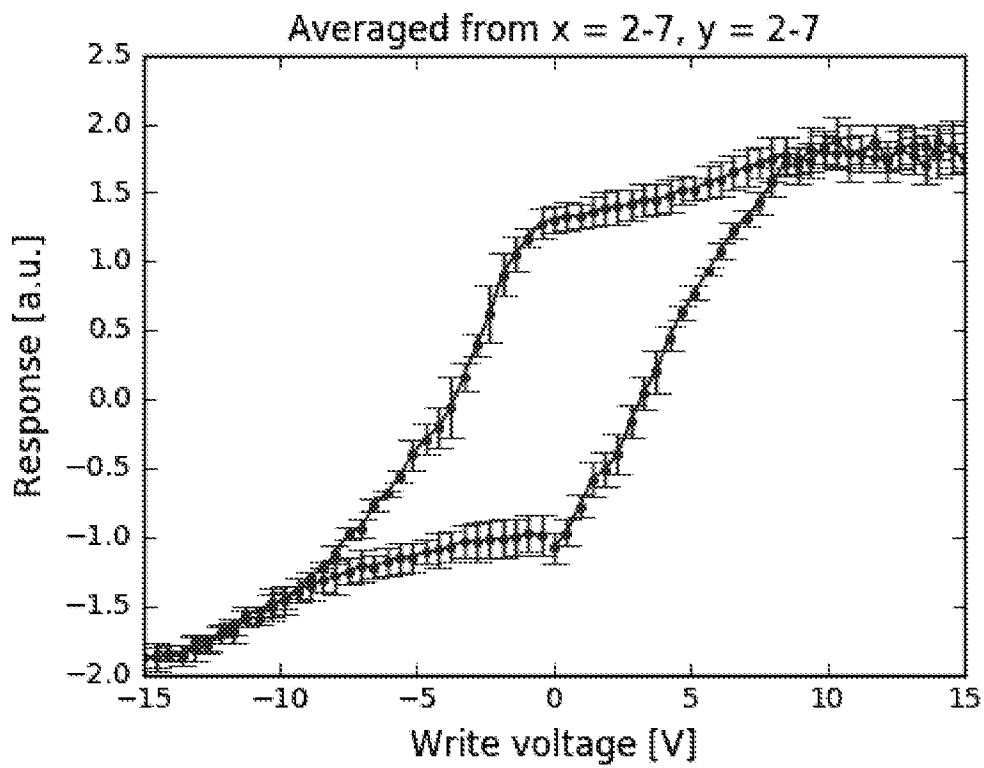


Figure 10

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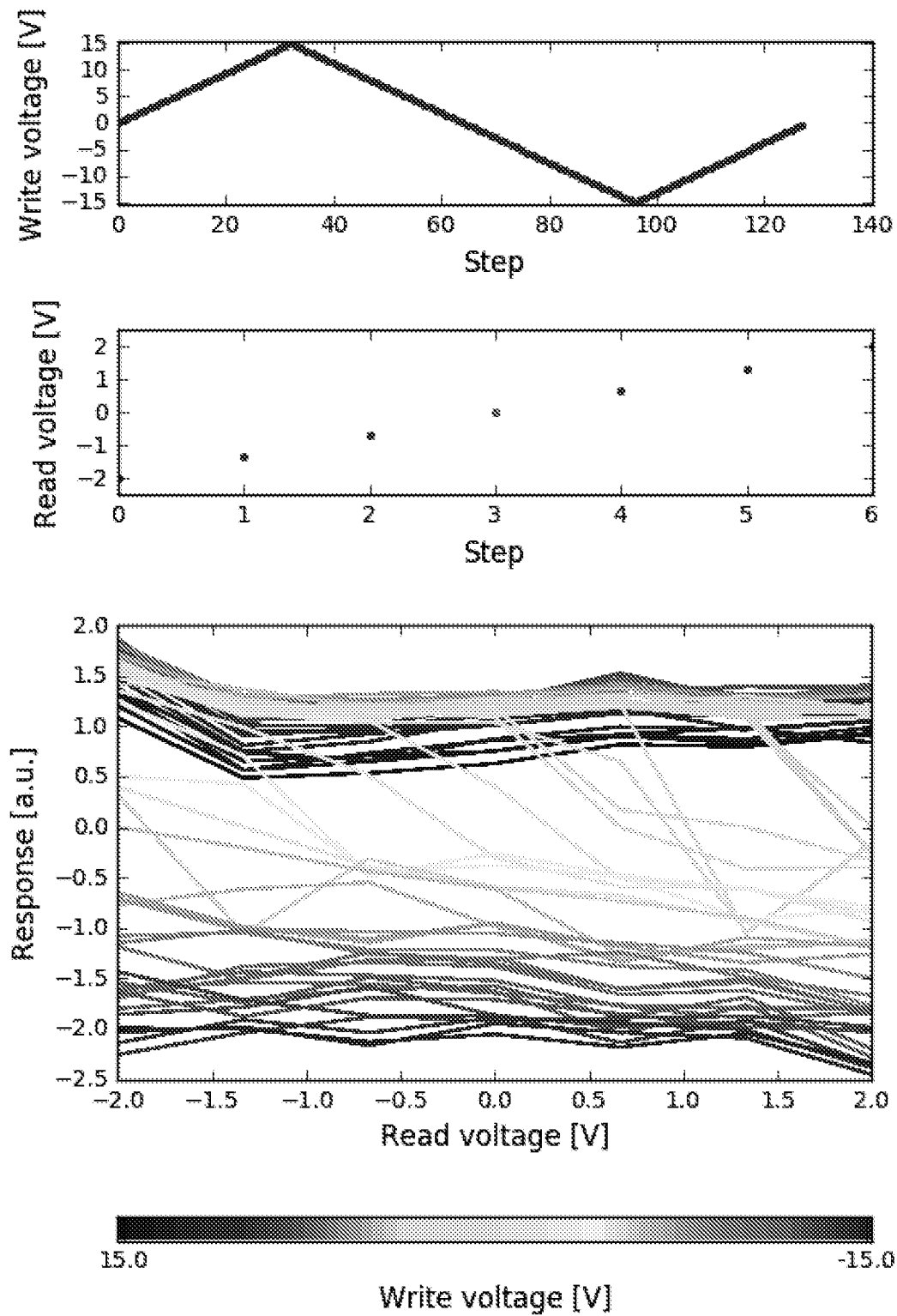


Figure 11

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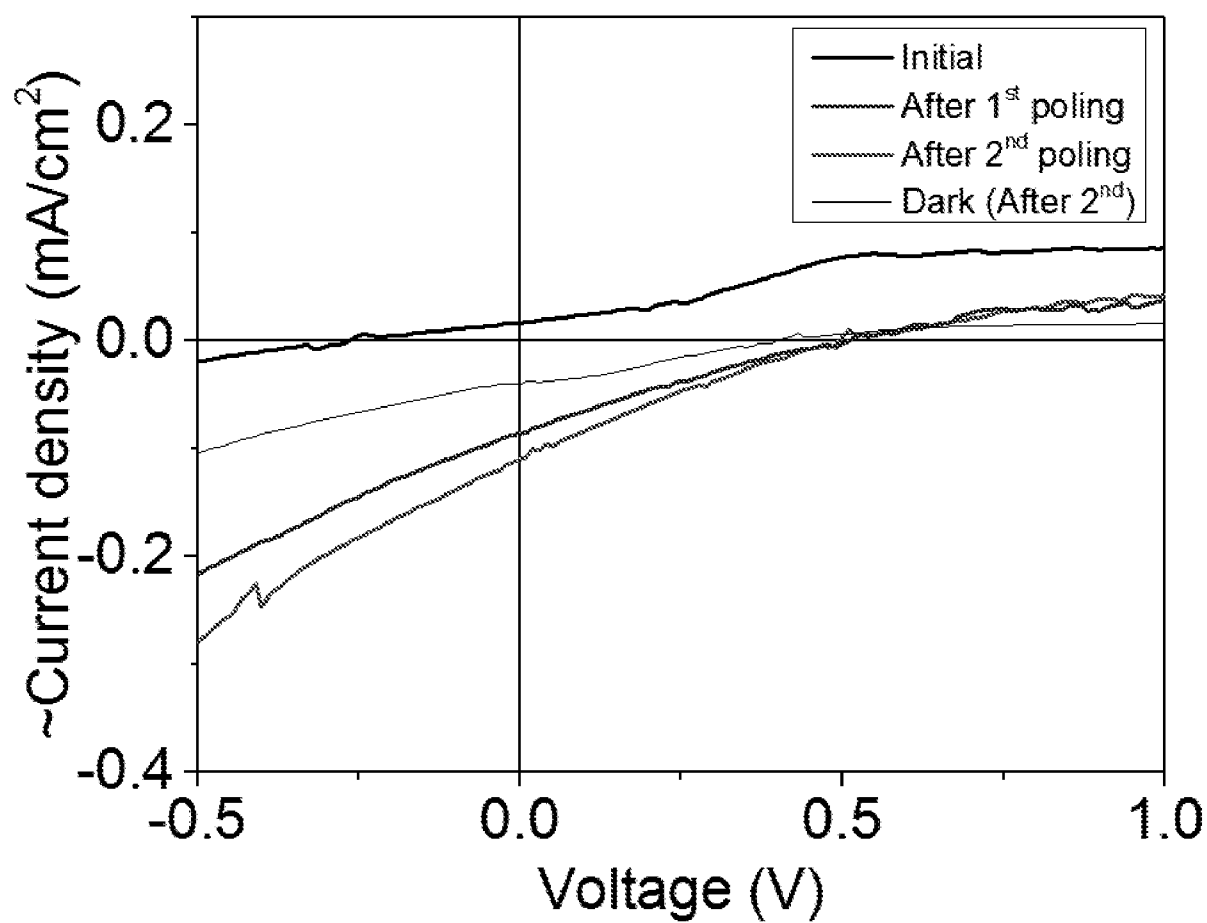


Figure 12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 18/24140

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 4-11, 15-17
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 18/24140

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - H01L 31/032 (2018.01)
CPC - C01G 33/00, C01G 53/66, C01P 2002/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History Document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History Document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KUTES et al, 'Direct Observation of Ferroelectric Domains in Solution-Processed CH ₃ NH ₃ PbI ₃ Perovskite Thin Films', The Journal of Physical Chemistry Letters, volume 5, 15 September 2014 (15.09.2014), pg 3335-3339 and associated Supporting Information.	1-3, 18-20
X	US 5,514,484 A (NASHIMOTO), 7 May 1996 (07.05.1996), figures 1-4; col 1 ln 11-12, col 3 ln 17-19, col 4 ln 39, col 6 ln 40-41, col 6 ln 61-66, col 7 ln 23-25.	12-14
X	US 2,852,400 A (REMEIKA), 16 September 1958 (16.09.1958), entire document.	1-2, 12-14, 18-20
X	US 5,248,564 A (RAMESH), 28 September 1993 (28.09.1993), entire document.	1-2, 12-14, 18-20
A	SCOTT et al, 'Ferroelectric Memories', Science, volume 246, 15 December 1989 (15.12.1989), pg 1400-1405.	1-3, 12-14, 18-20

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

22 May 2018

Date of mailing of the international search report

20 JUN 2018

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