

PEROVSKITE STRUCTURE, PROCESS FOR PRODUCTION AND USE THEREOF

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority of Singapore Patent Application No. 10201902526R, filed March 21, 2019, the contents of it being hereby incorporated by reference in its entirety for all purposes.

TECHNICAL FIELD

[0002] Various aspects of this disclosure relate to a perovskite structure with switched polarization and a systematic approach for tuning the ferroelectric properties of a perovskite for optoelectronic device applications. Aspects also relate to a process for the production of the perovskite structure as well as a use thereof as a memory device. In some embodiments, this disclosure provides a method for tuning ferroelectric properties in the perovskite structure through engineering its composition and crystal plane orientations.

BACKGROUND

[0003] Perovskites have attracted tremendous attention due to their potential for facile high efficiency low-cost photovoltaic technology. Their outstanding properties such as large absorption coefficient, tunable band gap, long charge carrier diffusion length, high charge carrier mobility, low exciton binding energy also makes them suitable for a broad range of optoelectronic applications other than solar cells. These include light emitting devices, transistors, memory devices, lasers and photodetectors. Amidst the intense debate over the origin(s) of the hysteresis effects (i.e., over the contributions from defects, ion migration, and ferroelectricity) in perovskite solar cells, the ferroelectric nature of perovskite materials was thrown into the limelight. This sparked yet another controversy as various groups had encountered grave difficulties in establishing the ferroelectric behavior in the 3-dimensional (3D) halide perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$). While the 3D halide perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) is reported to be ferroelectric, no ferroelectric behavior has been reported for layered perovskite structures such as the Ruddlesden–Popper (RP) phase perovskite structures.

[0004] In view of the before mentioned, there is a need for a layered perovskite structure with enhanced ferroelectric properties.

SUMMARY

[0005] In a first aspect, there is provided a perovskite structure. The perovskite structure may comprise a composition comprising a first organic cation, a second cation, a metal cation and a counter anion. The perovskite structure may comprise layers stacked in a stacking direction. The perovskite structure may further comprise polarized charge domains arranged along a horizontal direction which is perpendicular to the layers stacking direction.

[0006] In a second aspect, there is provided a process for the production of a perovskite structure comprising polarizable charge domains. The process may comprise: a) forming a perovskite structure from a first organic cation, a second cation, a metal cation and a counter anion on a substrate. The process may further comprise: b) applying an external electric field through at least one polarizable charge domain of the polarizable charge domains to modify a polarization of the at least one polarizable charge domain.

[0007] In a third aspect, there is provided use of a perovskite structure comprising a composition comprising a first organic cation, a second cation, a metal cation and a counter anion, wherein the perovskite structure may comprise layers stacked in a stacking direction and wherein the perovskite structure may have polarizable charge domains arranged in a horizontal direction which is perpendicular to the layers stacking direction, as a memory device structure, wherein a polarization of a domain of the polarizable charge domains represents a unit of information.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] The invention will be better understood with reference to the detailed description when considered in conjunction with the non-limiting examples and the accompanying drawings, in which:

- **FIG. 1A** shows a schematic view of the structural orientation in Ruddlesden-Popper (RP) perovskites $((\text{PEA})_2(\text{MA})_{\bar{n}-1}\text{Pb}_{\bar{n}}\text{I}_{3\bar{n}+1})$ for $\bar{n} = 2, 3, 4, 5$ and 3D sample ($\bar{n} = \infty$) on conducting substrate, wherein PEA stands for phenylethylammonium and MA stands for methylammonium;
- **FIG. 1B** shows RP perovskites $((\text{PEA})_2(\text{MA})_{\bar{n}-1}\text{Pb}_{\bar{n}}\text{I}_{3\bar{n}+1})$ for $\bar{n} = 2, 3, 4, 5$ and 3D sample ($\bar{n} = \infty$) excited by a p-polarized laser beam at an incident angle $\theta = 60$ degrees to the normal of the sample surface;

- **FIG. 1C** shows the second harmonic generation intensity and out-of-plane component of $\chi^{(2)}$ as a function of $\bar{n}$. The error bars represent the uncertainties in the determination of SHG intensities;
- **FIG. 2** shows the X-ray diffraction patterns of RP perovskites $((\text{PEA})_2(\text{MA})_{\bar{n}-1}\text{Pb}_{\bar{n}}\text{I}_{3\bar{n}+1})$ $\bar{n} = 1$, to 7 and 3D sample (MAPbI_3);
- **FIG. 3** shows the local piezo phase remnant hysteresis loops switching by piezo force microscopy (PFM) spectroscopy on RP perovskite $(\text{PEA})_2(\text{MA})_{\bar{n}-1}\text{Pb}_{\bar{n}}\text{I}_{3\bar{n}+1}$ (where $\bar{n} = 2$ to 5) and MAPbI_3 thin films respectively;
- **FIG. 4** shows PFM images of RP perovskites. The sample is $(\text{PEA})_2(\text{MA})_4\text{Pb}_5\text{I}_{16}$ ($\bar{n} = 5$). **FIG. 4A** and **FIG. 4C** show the PFM image after -4V DC poling and +4V DC poling, respectively. **FIG. 4B** and **FIG. 4D** indicate 180 degree difference of reference AC external electric field applied on tip. The arrow directions represent the dipole directions on the sample. Thus it was found that the dipole flipped after poling from -4V to +4V by comparing the arrow directions in **FIG. 4B** and **FIG. 4D**;
- **FIG. 5A** shows the second harmonic generation (SHG) anisotropy pattern of RP perovskites under p polarized laser beam. The sample is $(\text{PEA})_2(\text{MA})_4\text{Pb}_5\text{I}_{16}$ ($\bar{n} = 5$);
- **FIG. 5B** shows the SHG intensity as a function of $\bar{n}$;
- **FIG. 6A** shows the current hysteresis in $\bar{n} = 5$ $((\text{PEA})_2(\text{MA})_4\text{Pb}_5\text{I}_{16})$ sample measured under dark condition. A thin layer of phenyl-C61-butyric acid methyl ester (PCBM) (<10 nm) was inserted to prevent silver migration into perovskite as shown in inset schematic;
- **FIG. 6B** shows the macroscopic polarization- electric field hysteresis loops of $\bar{n} = 2, 3, 4, 5$ and MAPbI_3 devices;
- **FIG. 6C** shows the variation in coercive electric field (E_c);
- **FIG. 6D** shows remnant polarization (P_r), in RP perovskite $(\text{PEA})_2(\text{MA})_{\bar{n}-1}\text{Pb}_{\bar{n}}\text{I}_{3\bar{n}+1}$ for $\bar{n} = 2, 3, 4, 5$ and MAPbI_3 devices;
- **FIG. 7A** shows the surface morphology of RP perovskites $((\text{PEA})_2(\text{MA})_{\bar{n}-1}\text{Pb}_{\bar{n}}\text{I}_{3\bar{n}+1})$ for a sample with $\bar{n} = 3$;
- **FIG. 7B** shows the surface morphology of RP perovskites $((\text{PEA})_2(\text{MA})_{\bar{n}-1}\text{Pb}_{\bar{n}}\text{I}_{3\bar{n}+1})$ for a sample with $\bar{n} = 5$;

- **FIG. 7C** shows the surface morphology of RP perovskites $((\text{PEA})_2(\text{MA})_{\bar{n}-1}\text{Pb}_{\bar{n}}\text{I}_{3\bar{n}+1})$ for a sample with $\bar{n} = 7$;
- **FIG. 7D** shows the surface morphology of RP perovskites $((\text{PEA})_2(\text{MA})_{\bar{n}-1}\text{Pb}_{\bar{n}}\text{I}_{3\bar{n}+1})$ wherein the sample is MAPbI_3 ;
- **FIG. 8A** shows the differential scanning calorimetry of RP perovskites, in particular the thermal stability for a sample with $\bar{n} = 2$;
- **FIG. 8B** shows the differential scanning calorimetry of RP perovskites, in particular the thermal stability for a sample with $\bar{n} = 3$;
- **FIG. 8C** shows the differential scanning calorimetry of RP perovskites, in particular the thermal stability for a sample with $\bar{n} = 4$;
- **FIG. 8D** shows the differential scanning calorimetry of RP perovskites, in particular the thermal stability for a sample with $\bar{n} = 5$ sample;
- **FIG. 9A** shows the plot for SHG intensity versus detection wavelength for RP perovskites for a sample with $\bar{n} = 2$;
- **FIG. 9B** shows the plot for SHG intensity versus temperature for RP perovskites for a sample with $\bar{n} = 2$;
- **FIG. 9C** shows the plot for SHG intensity versus detection wavelength for RP perovskites for a sample with $\bar{n} = 3$;
- **FIG. 9D** the plot for SHG intensity versus temperature for RP perovskites for a sample with $\bar{n} = 3$;
- **FIG. 9E** shows the plot for SHG intensity versus detection wavelength for RP perovskites for a sample with $\bar{n} = 4$;
- **FIG. 9F** shows the plot for SHG intensity versus temperature for RP perovskites for a sample with $\bar{n} = 4$;
- **FIG. 9G** shows the plot for SHG intensity versus detection wavelength for RP perovskites for a sample with $\bar{n} = 5$;
- **FIG. 9H** shows the plot for SHG intensity versus temperature for RP perovskites for a sample with $\bar{n} = 5$;
- **FIG. 10** shows the variation of dielectric constant as a function of temperature for showing the ferroelectric phase (FEP) to paraelectric phase (PEP) transition for different RP perovskite films;

- **FIG. 11** shows the local piezo phase remnant hysteresis loops switching by PFM spectroscopy on n-BA based RP perovskite $(n\text{-BA})_2(\text{MA})_4\text{Pb}_5\text{I}_{16}$;
- **FIG. 12** shows the change of the absorption edges, which indicates lower bandgap with larger $\bar{n}$ values. The Absorption spectra is in excellent agreement with published reports. Linear absorption spectra of RP perovskites for $\bar{n} = 1, 2, 3, 4, 5$, (i.e., RP1, RP2 ..., RP5) and MAPbI_3 samples (3D).
- **FIG. 13A** shows the square power dependence of SHG signals on RP perovskites for a sample with $\bar{n} = 3$;
- **FIG. 13B** shows the square power dependence of SHG signals on RP perovskites for a sample with $\bar{n} = 4$;
- **FIG. 13C** shows the square power dependence of SHG signals on RP perovskites for a sample with $\bar{n} = 5$;
- **FIG. 13D** shows the square power dependence of SHG signals on RP perovskites, wherein the sample is MAPbI_3 ;
- **Figure 14A** shows the SHG spectra and schematic crystalline structure of RP perovskites. SHG signals were obtained for RP1 photoexcited by 800 nm p polarized pulsed laser at $\theta = 0^\circ$ and $\theta = 60^\circ$ incidence indicating larger value of in plane second order susceptibility than out plane;
- **Figure 14B** shows the SHG spectra and schematic crystalline structure of RP perovskites. SHG signals were obtained from samples photoexcited by 800 nm p polarized pulsed laser at normal incidence ($\theta = 0^\circ$) - indicating a small value for in plane second order susceptibility;
- **FIG. 14C** is a schematic diagram to illustrate the in-plane and the out-of-plane second order susceptibility with respect to the substrate for $\bar{n} = 1$ and $\bar{n} \neq 1$;
- **FIG. 14D** shows the SHG anisotropy pattern of RP5 perovskites under p -polarized laser beam;
- **FIGS. 15A – 15D** show the local switching behavior of RP perovskites. The graphs are the remnant PFM phase and amplitude hysteresis loops from samples of different batches by switching spectroscopy piezo force microscope under a scan speed of 0.112 V/s/nm. The results are consistent and reproducible; and

- **FIG. 16** shows the current hysteresis in $\bar{n} = 5$ RP perovskite based device (glass/indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS)/perovskite (~300 nm)/PCBM/silver (Ag)) measured under dark condition.

DETAILED DESCRIPTION

[0009] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the disclosure may be practiced. These embodiments are described in sufficient detail to enable those skilled in the art to practice the disclosure. Other embodiments may be utilized and structural, and logical changes may be made without departing from the scope of the disclosure. The various embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

[0010] In a first aspect, the present disclosure refers to a perovskite structure comprising a composition comprising a first organic cation, a second cation, a metal cation and a counter anion, wherein the perovskite structure comprises layers stacked in a stacking direction and polarized charge domains arranged along a horizontal direction which is perpendicular to the layers stacking direction.

[0011] In general, the typical perovskite structure is extended in three dimensions where a first organic cation is attached to an octahedral structure (**FIG. 1A**) with the formulation AMX_3 ; wherein A may represent the second cation, M may represent the metal cation and X may represent the counter anion. The perovskite structure may comprise octahedral layers of $[MX_6]^{4-}$ octahedral sheets formed from M^{2+} and X^- . Insertion of the first organic cation between two consecutive octahedral layers of $[MX_6]^{4-}$ may yield the two dimensional (2D) perovskite structure. Such structures are very useful for devices where higher in-plane charge carrier mobility is important. The approach of mixing the pure 2D and 3D perovskite precursors results in a category of layered perovskites known as the Ruddlesden–Popper (RP) phase perovskite. These perovskites are a type of perovskite structure that consists of 2D perovskite-like sheets interleaved with the first organic cation.

[0012] Accordingly, in various embodiments of this disclosure, the perovskite structure disclosed herein is a “Ruddlesden-Popper perovskite”. In this disclosure, the perovskite structure comprises three different cations, and a counter anion. The three different cations are

termed herein as “first organic cation”, “second cation” and “metal cation”. Each has its own characteristics and function which will be discussed further below.

[0013] The perovskite structure may comprise octahedral sheets of $[\text{MX}_6]^{4-}$ formed from M^{2+} and X^- , wherein the octahedral sheets are perpendicular to the layers of the perovskite structure. The octahedral layers $[\text{MX}_6]^{4-}$ may be made from inorganic matter, *i.e.*, in some embodiments, they may contain no organic matter. In those embodiments, the octahedral layers are inorganic octahedral layers.

[0014] The plurality of $\bar{n}$ octahedral layers may form the octahedral sheet. One of the octahedral sheets, or a majority of the octahedral sheets, may have a smallest width of at least about 5 Å, or of at least about 10 Å, or of at least about 15 Å. The width of the octahedral sheets may be dependent on the number $\bar{n}$ of octahedral layers, and may increase with the number $\bar{n}$ of octahedral layers. Advantageously, a small width of the above values may be sufficient to lift the inversion symmetry. This may be due to the interplay between the $\bar{n}$ octahedral layers and the first organic cation, giving rise to nonpolar structural distortions (from rotation or tilt) of the octahedral cage, thus maximizing the second harmonic generation of the perovskite structure.

[0015] Accordingly, due to the lift of the inversion symmetry, the perovskite structure may be non-centrosymmetric. By being non-centrosymmetric, ferroelectricity, and thereby directed net polarization of the perovskite structure, may be enhanced.

[0016] Ferroelectricity is the ability of a dielectric material to spontaneously switch the polarizations under external electric field that persist even when the electric field is removed. Ferroelectricity has a strong influence on spatial charge separation and carrier transfer. The induced spontaneous polarizations within the optoelectrical material can play an important role to enhance the performance of perovskite devices. To further improve the performance and stability of electronic devices, it is important to enhance or suppress the ferroelectricity in perovskites for specific applications. For instance, spontaneous spatial charge separation is beneficial for photovoltaic operation, while this is undesirable for light emitting diodes as it could lead to reduced emission efficiency as well as decreased emission color purity under sustained operations.

[0017] The perovskite structure may comprise several layers. Firstly, there are layers stacked in a stacking direction. The composition of the layers stacked in the stacking direction generally follows the sum formula AMX_3 , and further includes the first organic cation. In some

embodiments, wherein the perovskite structure may further comprise a substrate, the layers stacked in the stacking direction may be parallel to the substrate. The layers stacked in the stacking direction are different from the octahedral layers discussed above, and may be perpendicular to the octahedral layers.

[0018] Each octahedral layer may have a number of $[\text{MX}_6]^{4-}$ octahedral units interrupted by the first organic cation. The polarized charge domains are arranged along a horizontal direction which is perpendicular to the layers stacking direction.

[0019] The term “polarized charge domains” as used herein refers to domains within the perovskite structure wherein a net charge is present in a predetermined direction. In this instance, the predetermined direction is perpendicular to the layers stacking direction. “Net charge”, as used herein, indicates that at least 60%, or at least 70%, or at least 80%, or at least 90% of the perovskite structure has a dipole that is present in the predetermined direction. The term “polarized charge domains” as used herein is also used in contrast to “random charge domains”. Random charge domains may be present by natural dipoles within the perovskite structure, occurring due to differing electronegativities between different elements. However, “random charge domains” would not have a net charge being present in a predetermined direction.

[0020] The perovskite structure comprises a “first organic cation”. The first organic cation may be a cation that comprises, or essentially consists of, an organic moiety. Advantageously, by comprising an organic moiety, the first organic cation may be an insulating organic cation layer between two consecutive octahedral layers. The first organic cation may have a stacking direction that may be aligned in a direction out of plane (or normal) to the substrate surface. The first organic cation therefore has the function as an organic spacer cation, wherein different organic species can be accommodated in the intervening organic layers to induce distortions of the $[\text{MX}_6]^{4-}$ octahedral units and the interplay of dipole-dipole interactions between the second cation to influence the ferroelectric properties. Accordingly, the first organic cation may be an insulating material. Hence, it may have the function of a barrier. The width of the organic cation may be a spacer within the perovskite structure to produce a well.

[0021] In some embodiments, the first organic cation may comprise an ammonium functional group. The ammonium functional group may be a primary, a secondary, a tertiary or a quaternary ammonium ion. The ammonium functional group may be substituted with an organic moiety. Depending on whether the ammonium functional group is a primary, a

secondary, a tertiary or a quaternary ammonium ion, the first organic cation may comprise one, two, three or four organic moieties.

[0022] The term “organic moiety” as used herein refers to carbon-containing moieties. These moieties can be linear or branched, substituted or unsubstituted, and are derived from hydrocarbons, typically by substitution of one or more carbon atoms by other atoms, such as oxygen, nitrogen, sulfur, phosphorous, or functional groups that contain oxygen, nitrogen, sulfur, phosphorous. The organic moiety can comprise any number of carbon atoms, but has preferably a molecular weight of above 80 g/mol, or above 100 g/mol.

[0023] In a preferred embodiment, the organic moiety can be a linear or branched, substituted or unsubstituted alkyl with 1 to 10 carbon atoms; linear or branched, substituted or unsubstituted alkenyl with 2 to 10 carbon atoms; linear or branched, substituted or unsubstituted alkynyl with 2 to 10 carbon atoms; linear or branched, substituted or unsubstituted alkoxy with 1 to 10 carbon atoms; substituted or unsubstituted cycloalkyl with 3 to 10 carbon atoms; substituted or unsubstituted cycloalkenyl with 3 to 10 carbon atoms; substituted or unsubstituted aryl with 6 to 10 carbon atoms; and substituted or unsubstituted heteroaryl with 3 to 9 carbon atoms.

[0024] The organic moiety can also be a combination of any of the above-defined groups, including but not limited to alkylaryl, arylalkyl, alkyl heteroaryl and the like, to name only a few, all of which may be substituted or unsubstituted.

[0025] The term “substituted” as used herein in relation to the above moieties refers to a substituent other than hydrogen. Such a substituent is preferably selected from the group consisting of halogen, -OH, -OOH, -NH₂, -NO₂, -ONO₂, -CHO, -CN, -CNOH, -COOH, -SH, -OSH, -CSSH, -SCN, -SO₂OH, -CONH₂, -NH-NH₂, -NC, -CSH -OR, -NRR', -NR, -C(O)R, -C(O)OR, -(CO)NRR', -NR'C(O)R, -OC(O)R, aryl with 5 to 10 carbon atoms, cycloalk(en)yl with 3 to 10 carbon atoms, 3- to 8-membered heterocycloalk(en)yl, and 5- to 10-membered heteroaryl, wherein R and R' are independently selected from hydrogen, alkyl with 1 to 10 carbon atoms, alkenyl with 2 to 10 carbon atoms, alkynyl with 2 to 10 carbon atoms, aryl with 5 to 10 carbon atoms, cycloalk(en)yl with 3 to 10 carbon atoms, 5- to 10-membered heteroaryl, comprising 1 to 4 heteroatoms selected from nitrogen, oxygen, and sulfur, and 5- to 10-membered heterocycloalk(en)yl, comprising 1 to 4 heteroatoms selected from nitrogen, oxygen, and sulfur. Any of these substituents may again be substituted, it is however preferred that these substituents are unsubstituted.

[0026] In some embodiments, the organic moiety may be at least one alkyl moiety. The alkyl moiety may be branched or linear. In some embodiments, the at least one alkyl moiety may be at least one linear alkyl moiety. In some embodiments of the first organic cation, the organic moiety may be a substituted alkyl moiety.

[0027] The first organic cation may comprise a linear or branched C₂-C₁₀ alkyl substituted with a phenyl moiety. Advantageously, one phenyl moiety extending from one of the octahedral sheets may engage into van der Waals interactions with another phenyl moiety extending from one of one of the adjacent octahedral sheets. Particularly, the first organic cation may comprise a phenylethyl moiety. By comprising a phenylethyl moiety, advantageously, an optimal insulating space is provided by the ethyl moiety for the phenyl moieties to engage into van der Waals interactions.

[0028] The perovskite structure comprises a “second cation”. The second cation may comprise or consist of any functional group which possesses a net positive charge and is stable under the reaction conditions which result in the perovskite structure. In some embodiments, the second cation may comprise an ammonium ion. In some embodiments, the second cation may be a monovalent cation. “Monovalent” refers to the second cation being present in the oxidation state +I. According to some embodiments, the second cation may comprise an ammonium ion. Additionally or alternatively, the second cation may be any one selected from a group consisting of a methylammonium ion, a formamidinium ion, a hydroxylammonium ion, a hydrazinium ion, an azetidinium ion, an imidazolium ion, a dimethylammonium ion, an ethylammonium ion, a phenethylammonium ion, a guanidinium ion, a tetramethylammonium ion, a thiazolium ion, a 3-pyrrolinium ion, a tropylium ion, a piperazinium ion, and a dabconium ion. In one example, the second cation is a methylammonium ion. In another example, the second cation may be a formamidinium cation.

[0029] In some embodiments, both the first organic cation and the second cation may comprise an ammonium functional group. In particular embodiments, the ammonium functional group may be a primary ammonium ion. Advantageously, when both the first organic cation and the second cation comprise a primary ammonium ion, the interaction with the octahedral units may be enhanced. Between the first organic cation and the second cation, the first organic cation may be larger than the second cation. For example, the first organic cation may have a higher molecular weight and/or a higher ionic radius. Thus, the first organic cation may function as an organic spacer cation.

[0030] The perovskite structure further comprises a “metal cation”. The metal cation may occupy the M-site of the formula AMX_3 described above. In some embodiments, the metal cation may be a divalent metal cation. “Divalent metal” in this context refers to any metal which may form the perovskite structure as described above and is present in the oxidation state +II. Notably, the divalent metal may be selected from the group consisting of transition metals, lanthanoids, post-transition metals and heavy metals. In some embodiments, the metal cation is any metal of group 11, group 14 or group 15 of the periodic system or a mixture of these. Consequently, the metal cation may be selected from the group consisting of copper, silver, gold, germanium, tin, lead, arsenic, antimony, bismuth, and a combination thereof. In some embodiments, the metal cation may be a heavy metal cation. In some embodiments, the metal cation may be a mixture of several heavy metal cations. Heavy metals may be associated with a higher density and a lower reactivity than other (light) metals. As such, the divalent heavy metal may be selected from zinc, mercury, lead, iron, copper, tin, silver, gold, platinum, gallium, thallium, hafnium, cobalt, ruthenium and indium. In one example, the heavy metal cation is lead.

[0031] Additionally or alternatively, the metal cation may be a post-transition metal. Post-transition metals may refer to the metallic elements in the periodic table located between the transition metals (to their left) and the metalloids (to their right). These elements may include gallium, indium, thallium, tin, lead, bismuth, cadmium, mercury and aluminum. In one example, the post-transition metal cation is lead.

[0032] The perovskite structure further comprises a “counter anion”. The counter anion may be selected from any anion which may form the perovskite structure as described above. Preferably, the weight of one counter anion may not exceed about 100 g/mol. More preferably, the counter anion is selected from the group of the non-metals. More preferably, the counter anion is selected from the group of the halogens. The disclosure may refer to a counter anion at several sections and for several functions, wherein each may be the same or they may be different from each other. The counter anion may be a monovalent anion. In some embodiments, the counter anion may be a halide. The halide may be an iodide, a bromide, a chloride or a mixture thereof. In one example, the halide is an iodide.

[0033] The composition may be of the general formula $((RNH_4)^+)_2(A^+)_{\bar{n}-1}M^{2+}_{\bar{n}}X_{3\bar{n}+1}^-$.

[0034] In this formula, R may be a linear or branched, substituted or unsubstituted C_2 - C_{10} alkyl; linear or branched, substituted or unsubstituted C_2 - C_{10} alkenyl; linear or branched,

substituted or unsubstituted C₂-C₁₀ alkynyl; linear or branched, substituted or unsubstituted C₁-C₁₀ alkoxy; substituted or unsubstituted C₃-C₁₀ cycloalkyl; substituted or unsubstituted C₃-C₁₀ cycloalkenyl; substituted or unsubstituted C₆-C₁₀ aryl; substituted or unsubstituted C₃-C₁₀ heteroaryl. Alkyl refers to a saturated hydrocarbon moiety, such as methyl, ethyl, and the like. Alkenyl and Alkynyl comprise at least one carbon-carbon double bond or triple bond, respectively, and are otherwise defined as alkyl above.

[0035] Cycloalkyl refers to a non-aromatic carbocyclic moiety, such as cyclopentanyl, cyclohexanyl, and the like.

[0036] Cycloalkenyl refers to non-aromatic carbocyclic compounds that comprise at least one C-C double bond.

[0037] Similarly, heterocycloalk(en)yl relates to cycloalk(en)yl groups wherein 1 or more ring carbon atoms are replaced by heteroatoms, preferably selected from nitrogen, oxygen, and sulfur.

[0038] Aryl relates to an aromatic ring that is preferably monocyclic. Preferred aryl substituents are moieties with 6 carbon atoms, such as phenyl.

[0039] Heteroaryl refers to aromatic moieties that correspond to the respective aryl moiety wherein one or more ring carbon atoms have been replaced by heteroatoms, such as nitrogen, oxygen, and sulfur.

[0040] All of the afore-mentioned groups can be substituted or unsubstituted. When substituted, the substituent can be selected from the above list of substituents.

[0041] The term ‘at least one’ as used herein relates to one or more, for example 1, 2, 3, 4, 5, 6, 7, 8, 9 or more of the referenced species.

[0042] Halogen as used herein refers to F, Cl, Br, and I.

[0043] $\bar{n}$ may be an integer selected from 2 to ∞ . $\bar{n}$ may signify a number of consecutive layers in the octahedral sheets and may be selected from 2 to ∞ , or from 2 to 1000, or from 2 to 100, or from 2 to 20, or from 3 to 10, or preferably from 4 to 7. In one example, $\bar{n}$ is 5 and/or 6. The term “ $\bar{n}$ ”, as used herein, may refer to an average value n of the actual composition, because the multiphases nature in the perovskite structure cannot be ruled out. In general, it is estimated that more than 50%, or more than 70%, or more than 90% of the perovskite structure is present in the stated n value.

[0044] A⁺ may be the monovalent cation as discussed above, M²⁺ may be the divalent metal cation as discussed above and X⁻ may be the monovalent anion as discussed above.

[0045] The perovskite structure may be present in a grain size having an average diameter of about 50 nm to 200 nm. Interestingly, the grain size may increase with increasing $\bar{n}$ value. At an $\bar{n}$ value of about 4 to 7, defects in the structure may be minimized.

[0046] The perovskite structure may have a phase transition temperature, indicating the temperature at which the ferroelectric phase transforms into the paraelectric phase, whereby the paraelectric phase does not bear spontaneous polarization. In some embodiments, this phase transition temperature may be above 100 °C, or above 130 °C, or above 160 °C.

[0047] The perovskite structure may be deposited on a substrate. The substrate may be a hydrophilic substrate. The substrate may be selected from the group consisting of glass, quartz, polyethylene terephthalate (PET), polyethylene naphthalate (PEN), silicon dioxide etc. The substrate may be coated with indium tin oxide (ITO), fluorine-doped tin oxide (FTO) or any other conducting layer. The substrate may further comprise an electrode. In some embodiments, ITO may be the electrode.

[0048] The perovskite structure may be present as a film on the substrate. Hence, there is provided a perovskite film a substrate. The perovskite film may be polycrystalline. Additionally or alternatively, the perovskite film may have a film thickness of about 10 nm to about 1000 nm, or about 100 nm to about 500 nm, or about 200 nm to about 400 nm. The above-mentioned range may be suitable for the applications of the perovskite structure in solar cells, light emitting diodes etc. A film thickness of about or less than 1000 nm, and particularly of about or less than 400 nm may advantageously allow for higher charge carrier mobilities due to lower series resistance, and thus be particularly useful for the applications.

[0049] In another aspect, there is provided a process for the production of a perovskite structure comprising polarizable charge domains. The process comprises: a) forming a perovskite structure from a first organic cation, a second cation, a metal cation and a counter anion on a substrate. The process further comprises: b) applying an external electric field through at least one polarizable charge domain of the polarizable charge domains to modify a polarization of the at least one polarizable charge domain.

[0050] Step a) of the process may further comprise preparing a precursor solution from the first organic cation, the second cation, the metal cation and the counter anion. The precursor solution may further comprise a solvent. The solvent may be chosen from a polar aprotic solvent. The polar aprotic solvent may be selected from the group consisting of tetrahydrofuran, ethyl acetate, acetone, N,N-dimethylformamide, acetonitrile, dimethyl sulfoxide, nitromethane

and propylene carbonate, and mixtures thereof. In one example, the polar aprotic solvent is N,N-dimethylformamide (DMF).

[0051] Step a) of the process may further comprise heating the precursor solution to a temperature above room temperature. "Room temperature", as used herein, refers to a temperature greater than 4° C, preferably from 15 °C to 40 °C, 15 °C to 30 °C, and 15 °C to 24 °C, and 16 °C to 21 ° C. Such temperatures may include, 14 °C, 15 °C, 16 °C, 17 °C, 18 °C, 19 °C, 20 °C, and 21 °C. Step a) of the process may further comprise depositing the precursor solution on the substrate. Heating the precursor solution may comprise to proceed at elevated temperature, such as between 40 °C to 200 °C, preferably at between 40 °C to 100 °C, more preferably at about 50 °C. The precursor solution may be heated for more than one hour, or for more than two hours, or for about 2 hours to 5 hours, or for about 2 hours to 10 hours.

[0052] Depositing the precursor solution on the substrate may proceed by any methodology. For example, the deposition may be carried out by spin coating, doctor blading or inkjet printing. The deposition may be carried out at room temperature or at the elevated temperature. The deposition may further comprise the production of the perovskite film as discussed above.

[0053] The external electric field which is applied through the at least one polarizable charge domain of the polarizable charge domains of the perovskite structure may be chosen from about 0.1 kV/cm to about 100 kV/cm, or from about 0.5 kV/cm to about 80 kV/cm, or from about 1.0 kV/cm to about 60 kV/cm, or from about 2.0 kV/cm to about 40 kV/cm, or from about 5.0 kV/cm to about 10 kV/cm. During the application of the external electric field, the dipoles induced by the spacing between two consecutive first organic cation layers may align and oscillate with the external electric field direction.

[0054] In another aspect, there is provided use of a perovskite structure comprising a composition comprising a first organic cation, a second cation, a metal cation and a counter anion, wherein the perovskite structure comprises layers stacked in a stacking direction and wherein the perovskite structure has polarizable charge domains arranged in a horizontal direction which is perpendicular to the layers stacking direction, as a memory device structure, wherein a polarization of a domain of the polarizable charge domains represents a unit of information. Since the perovskite structure as disclosed herein exhibits hysteresis, it may be applied as a memory device structure.

[0055] Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments. Features that are described

in the context of an embodiment may correspondingly be applicable to the other embodiments, even if not explicitly described in these other embodiments. Furthermore, additions and/or combinations and/or alternatives as described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments.

[0056] In the context of various embodiments, the articles “a”, “an” and “the” as used with regard to a feature or element include a reference to one or more of the features or elements.

[0057] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

EXAMPLES

[0058] Ruddlesden–Popper (RP) halide perovskites may be used for high-performance perovskite photovoltaics with excellent ambient stability. The layered nature of these perovskites offers an exciting possibility of harnessing their ferroelectric property for photovoltaics. Adjacent polar domains in a ferroelectric material allow the spatial separation of electrons and holes. In this disclosure, tunable ferroelectricity in 2-phenylethylammonium (PEA) and methylammonium (MA) RP perovskite $(\text{PEA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ is realized. Second harmonic generation (SHG) confirms the non-centrosymmetric nature of these polycrystalline thin films, whereas piezoresponse force microscopy and polarization–electric field measurements validate the microscopic and macroscopic ferroelectric properties. Temperature-dependent SHG and dielectric constant measurements uncover a phase transition temperature at around 170 °C in these films. Extensive molecular dynamics simulations support the experimental results and identified the correlated reorientation of MA molecules and ion translations as the source of ferroelectricity. Current–voltage characteristics in the dark reveal the persistence of hysteresis in these devices, which has profound implications for light-harvesting and light-emitting applications. Importantly, the findings herein disclose a viable approach for engineering the ferroelectric properties of RP perovskites that may unlock new functionalities for perovskite optoelectronics. For instance, ferroelectricity in RP perovskites can lead to the formation of distinct electron and hole diffusion pathways toward the respective electrodes, thereby avoiding the chance encounters of opposite charges and suppressing recombination losses in solar cell devices. These diffusion pathways are mainly located at the boundaries of the ferroelectric domains inside the bulk film. The spontaneous spatial charge separation and suppression of the recombination losses yield a higher open-circuit voltage and

thus better efficiency in photovoltaics. On the other hand, such avoidance is undesirable for light-emitting diodes (LEDs) as it could lead to reduced emission efficiency as well as decreased emission color purity under sustained operations.

[0059] RP halide perovskites exhibit favorable photovoltaic efficiency (power conversion efficiency (PCE) = 20.6%) and LED performance (EQE = 14.4%) with excellent moisture stability. RP perovskites have a general formula $(\text{RNH}_3)_2\text{A}_{\bar{n}-1}\text{M}_{\bar{n}}\text{X}_{3\bar{n}+1}$ ($\bar{n}= 1, 2, 3, 4, \dots$), where RNH_3 is a large organic ammonium-insulating spacer cation [e.g., 2-phenylethylammonium (PEA), n-butylammonium (n-BA), etc.], and A represents a monovalent organic cation [e.g., $\text{CH}_3\text{NH}_3 + (\text{MA}^+)$, $\text{HC}(\text{NH}_2)_2 + (\text{FA}^+)$, etc.]. M is a divalent metal cation such as Pb and Sn, whereas X represents a halide anion and $\bar{n}$ is the number of $[\text{MX}_6]^{4-}$ octahedral layers within each organic spacer. Essentially, RP halide perovskites can be considered as $\bar{n}$ layers of $[\text{MX}_6]^{4-}$ octahedral sheets sandwiched by two layers of large organic spacer cations that are held together by weak van der Waals forces (FIG. 1A).

[0060] In this disclosure, it is posited that the “soft nature” of layered RP halide perovskites and its rich chemistry could be leveraged to engineer the ferroelectric properties. Different organic species can be accommodated in the intervening organic layers to induce distortions of, e.g. the $[\text{PbI}_6]^{4-}$ octahedral and the interplay of dipole–dipole interactions between methylammonium (MA) molecules to influence the ferroelectric properties.

[0061] The generation of the second harmonic signal evidences the presence of non-centrosymmetry in the structures where dipole–dipole interactions offer an unprecedented degree of freedom to maximize ferroelectric polarization of these structures.

[0062] Furthermore, the coercive electric field and remnant polarization are well-captured by molecular dynamics (MD) simulations proving the orchestrated origin of the ferroelectricity.

[0063] Temperature-dependent SHG and dielectric constant measurements of the phase transition temperature around 170 °C in these films provide unequivocal proof of the existence of ferroelectricity.

[0064] In general, the typical perovskite structure is extended in three dimensions where the organic cation is attached to lead halide octahedral structure (**FIG. 1A**) with the formulation AMX_3 ; A represents the large organic/inorganic cations ($\text{MA}^+/\text{FA}^+/\text{Cs}^+/\text{Ru}^+$), M is the heavy metal cations ($\text{Pb}^{2+}/\text{Sn}^{2+}$) and X represents the halide anions X ($\text{I}^-/\text{Br}^-/\text{Cl}^-$). In contrast thereto, insertion of an insulating organic cation layer between two consecutive inorganic octahedral

layers yields the two dimensional (2D) perovskite structure. These perovskites are represented by the formula $(\text{RNH}_3)_2\text{A}_{\bar{n}-1}\text{M}_{\bar{n}}\text{X}_{3\bar{n}+1}$ ($\bar{n} = 1, 2, 3, 4, \dots$), where RNH_3 represents a large aliphatic or aromatic alkylammonium spacer cation. For example, 2 phenylethylammonium (PEA) and n-butylammonium (n-BA), while A, M and X are monovalent organic cation, divalent metal cation and halide anion respectively. Here, $\bar{n}$ represents the number of $[\text{MX}_6]^{4-}$ octahedral layers within two consecutive organic spacer layers and represents a potential well. Since these organic spacers are non-conducting in nature, they are therefore representative of potential barriers in the structure. **FIG. 1A** shows the crystal structures of the representative RP family ($\bar{n} = 2, 3$ and 5) in this disclosure as compared to conventional MAPbI_3 ($\bar{n} = \infty$ (3D)). RP perovskites can be considered as $\bar{n}$ layers of $[\text{MX}_6]^{4-}$ octahedral sheets sandwiched by two layers of large organic spacer cations. In this disclosure, the ferroelectricity of the RP perovskites may be controlled by tuning the width of 3D potential wells with a constant width of an organic spacer as the barrier. In addition, the orientation of the organic spacer's plane normal to the substrate is another primary requisite. In combination, the disclosure presents an in-depth investigation on the ferroelectric tuning by (i) microscopically switchable polarization ferroelectric domains and remnant ferroelectric hysteresis loops using PFM, (ii) validating their non-centrosymmetry, which is one of the fundamental properties of the conventional ferroelectric materials and finally (iii) correlation of polarization electric field ($P \sim E$) hysteresis with number of $\bar{n}$ layers in RP perovskite.

[0065] In the present disclosure, an easier and well-controlled single-step spin coating method is developed to make high quality layered RP perovskite $(\text{PEA})_2(\text{MA})_{\bar{n}-1}\text{Pb}_{\bar{n}}\text{I}_{3\bar{n}+1}$ (for $\bar{n} = 1$ to 7 and 3D). These films are polycrystalline and exhibit multiple phases as observed by X-ray diffraction pattern shown in **FIG. 2**. In $(\text{PEA})_2\text{PbI}_4$, the observed peak at $2\theta = 10.8^\circ$ (004) shows that the PEA planes are aligned parallel to the substrate for $\bar{n} = 1$. On the other hand, for $\bar{n} \geq 2$, the peak at $2\theta = 14.8^\circ$ (101) shows that the PEA planes are aligned in a direction out of plane (or normal) to the substrate surface.

[0066] **FIG. 3** shows the local polarization switching at nano-scale measured by PFM. PFM visualizes the existence of ferroelectric domains and local polarization switching at the nano-scale. In order to test the polarization switching in thin films, the phase variation was first measured by applying pulsed tip bias across the $\bar{n} = 2$ to 5 and MAPbI_3 films (**FIG. 3**). The emergence of rectangular shape in phase hysteresis loop provides the first evidence of the ferroelectric polarization reversal in all RP films. Moreover, the ferroelectric coercivity and

area under the phase loops increase from $\bar{n} = 2$ to 5, and subsequently drop for larger $\bar{n}$ values. This variation indicates that ferroelectricity in RP perovskites can be controlled by tuning the width of the potential barrier through varying the composition. The optimal is the $\bar{n} = 5$ composition which shows the strongest ferroelectricity among these samples (**FIG. 3**).

[0067] Generally, ferroelectric domains have the switching ability under the influence of an external electric field larger than the coercive magnitude. Based on the hysteresis loop evolution, the best composition as $\bar{n} = 5$ (that yielded the largest ferroelectric response) was used to investigate the polarization switching at microscopic scale. **FIGS. 4 A-D** show the ferroelectric domain microscopically in $1 \times 1 \mu\text{m}^2$ scanned area of $\bar{n} = 5$ thin film. A DC bias of $V = -4 \text{ V}$ on the conductive tip with substrate as ground was applied to polarize the sample. The PFM images were subsequently obtained with AC signals near resonance cantilever under Dual AC Resonance Tracking (DART) PFM mode. Based on the DC voltage polarity, the equally grey regions in the phase image represent the ferroelectric domains oriented out of the plane along the applied field direction while black regions represent the domain oriented opposite to the field direction (representation in **FIG. 4B**). The phase image shows that majority of the domains in $\bar{n} = 5$ film is readily polarized by negative 4 V biasing. To prove the switching ability of these polarized domains, an opposite voltage DC bias ($V = \text{positive } 4 \text{ V}$) was further applied on the cantilever tip. In order to avoid the phase wrapping effect (which means the PFM phase is either lower than -180° or higher than $+180^\circ$), the phase offset was manually tuned to be -90° before the acquisition of PFM images just after positive poling (see **FIG. 4C and FIG. 4D**). Since the reference phase was manually tuned 180° , the polarization of areas that remained the same phase (or same color) under both positive and negative poling conditions were switched 180° . Based on the areal phase changes, the majority of the polarized domains are switched (**FIG. 4C**) *i.e.* undergo the phase change on switching the external field direction and thus qualify the test of switchable spontaneous polarization, one of the fundamental properties of ferroelectric materials.

[0068] In hybrid perovskite optoelectronic devices, defects, ion migration, and ferroelectricity are considered as the probable origin(s) of the current hysteresis in the 3D MAPbI_3 perovskites. Most reports attributed ion migration as the origin for the current hysteresis, even though the ferroelectric nature of the material cannot be discarded. Meanwhile, the 3D MAPbI_3 perovskite is reported to be ferroelectric.

[0069] Generally, the absence of the inversion symmetry or being non-centrosymmetric is another fundamental condition of conventional ferroelectric materials. Since second harmonic generation (SHG) is strongly associated with the symmetry of the object, therefore SHG is generated only from those materials which crystalize in non-centrosymmetric space group and are ferroelectric in nature. Therefore, an optical technique was utilized (to discount any possibility of ion migration arising from current injection) to validate the ferroelectric nature of these RP phase hybrid perovskites. **FIG. 1B** shows a schematic of the experimental setup to excite the samples and collect the SHG signal in optical microscopy. A plane polarized laser at an incident angle of 60° to the normal of sample surface was used to excite the film. In this configuration both out-plane as well as in-plane non-centrosymmetry of the perovskite contribute to the SHG signal. **FIG. 5A** exhibits the anisotropy patterns for sample $\bar{n} = 5$ which evolve by changing the angle between input and output polarizer. In order to detect the SHG signal, films coated on quartz substrates are excited with laser at 800 nm wavelength and the SHG signal is detected at 400 nm wavelength. The investigation was further extended to the other samples and the variation in SHG signal intensity from $\bar{n} = 2$ to $\bar{n} = 7$ and 3D samples as shown in **FIG. 5B** confirms that RP perovskites break their centrosymmetry at various extent. It shows that the degree of the non-centrosymmetry is dependent on the width of the 3D octahedral structure or the spacing between two consecutive organic spacer layers (*i.e.*, PEA in this disclosure), which induces dipoles to align and oscillate with the incident electric field direction. The presence of SHG signal in $\bar{n} = 2$ confirms that a smaller spacing between two consecutive PEA layers ($\sim 10 \text{ \AA}$) is enough to demonstrate the non-centrosymmetry in these perovskite samples. Moreover, the SHG intensity increases with the number of layers and peaked at $\bar{n} = 6$ with drastic drop in signal intensity on further increase of the layers (**FIG. 5B**). The rise of the SHG intensity shows the increase in the breaking of the strong centrosymmetry of the structure *i.e.*, the ratio of PEA, MA and PbI_2 is optimum to show the strongest non-centrosymmetry and hence strongest ferroelectricity in $\bar{n} = 6$. The observation of the optimal composition for the strongest ferroelectricity between $\bar{n} = 5$ and $\bar{n} = 6$ could be due to two different techniques used for the investigation, though these compositions are very similar, as shown in **Table 2**.

[0070] In 3D perovskite-based solar cells as well as light emitting devices, current-voltage hysteresis is commonly found. This leads to problems of accurately measuring the power conversion efficiency in solar cells and severe color change in light emitting devices,

respectively. In order to reveal the current hysteresis exists in RP samples, a device configuration glass/ITO/PEDOT:PSS(~ 30 nm)/Perovskite(~ 300 nm)/PCBM(< 10 nm)/Ag(~ 100 nm) was prepared as shown in the inset of **FIG. 6A** with optimum composition $\bar{n} = 5$ for strongest ferroelectricity. A thin layer of PCBM was inserted to prevent the migration of silver (Ag) into the perovskite. The current-voltage characteristics were measured under dark conditions and presented in **FIG. 6A**. The variation in measured current depending on the voltage sweep direction confirms the existence of hysteresis in RP based hybrid perovskite thin film. This is the first time that current hysteresis in a hybrid RP perovskite system is presented. To further validate ferroelectricity as the origin of current hysteresis, P - E (polarization-electric field) loops were measured on these macroscopic devices using a virtual ground assembly method at room temperature with varying electric field. The P - E loop for $\bar{n} = 5$ was further compared and correlated with other devices prepared with $\bar{n} = 2, 3, 4$ and MAPbI₃ perovskites as shown in **FIG. 6B**. The thickness that was used for all of these perovskite films was ~ 300 nm, which was enough to prevent the leakage current as shown in the measured dark current which is lower (at 1 V) than the set compliance value (1 mA) in **FIG. 6A**. The measured P - E hysteresis loop of different RP films (**FIG. 6B**) confirms the nonlinear dependence of polarization on an external electric field, which is evidence to reveal the ferroelectric nature of the RP system.

[0071] Based on the further in-depth evaluation, the remnant polarization, as well as the coercive electric field, rises with the number of layers peaking at $\bar{n} = 5$ with subsequent drop, which is consistent with microscopic measurements (**FIGS. 6C and 6D**). Correlating with the film morphology, the perovskite grain size also increases with a drop in the voids from $\bar{n} = 3$ to $\bar{n} = 5$ thin films and shows a very non-uniform morphology with larger voids for $\bar{n} = 7$ films (**FIGS. 7A to 7D**). Moreover, smaller perovskite grains with plenty of grain boundaries in MAPbI₃ are observed. Thus, PEA molecules tune the morphology and act as the defects passivating agent with optimum fraction in $\bar{n} = 5$ samples to provide the minimum defects (in terms of grain boundaries, voids etc.); while defects are higher in MAPbI₃ film (**FIGS. 7A to 7D**).

[0072] On the other hand, the presence of the defects is also beneficial since the polarization switching of the area around the defects is easier compared to switching in a crystallized domain. Therefore on correlating with defects, the decreasing trend of coercivity in these films is well-matched with the trend of the defects in these films with the increase of $\bar{n}$.

[0073] **Example 1: Temperature dependent measurements**

[0074] Differential scanning calorimetry is used to detect the phase transition Curie temperature by measuring the variation of heat flow due to the specific heat change during structural phase transition of samples. In **FIGS. 8A to 8D**, the main peak between 170° - 176° for $\bar{n} = 2, 3, 4$ and 5 RP perovskites represents the first-order reversible phase transition with latent heat hysteresis during heating and cooling processes. These dominant peaks represent the ferroelectric to paraelectric (*i.e.* the phase to which the ferroelectric phase transforms above T_c and does not bear spontaneous polarization) phase transition temperature. RP perovskite films shows the higher T_c than recently reported organic based ferroelectric materials. On the other hand, no phase transition is observed in RP perovskites at room temperature accordingly.

[0075] For a ferroelectric material, a significant change of the SHG signal around the ferroelectric-paraelectric phase transition temperature is another key signature. **FIGS. 9A to 9H** show the SHG as a function of temperature for RP films where SHG signal increases close to the phase transition temperature above 140 °C and drops immediately above the temperature 170 °C. It shows that non-centrosymmetry is present in RP films below phase transition temperature and it maximizes around phase transition temperature while it breaks down immediately after RP system turns into the paraelectric phase.

[0076] Furthermore, the variation of dielectric constants for different RP perovskite films was also measured by measuring the device capacitance at as a function of temperature. These devices were prepared by depositing 300 ± 20 nm perovskite films on cleaned ITO glass substrates and deposited gold on top as the second electrode (see the experimental details). Capacitance of these devices at 0.5V/54 kHz were measured from room temperature to 180 °C. **FIG. 10** shows the dielectric constant ε_0 ($\varepsilon = \varepsilon_0 + i\varepsilon_i$, where ε_0 is the real part and ε_i is the imaginary part) as the function of temperature. At room temperature, the $\bar{n} = 5$ perovskite thin film shows the relatively highest dielectric constant among these RP perovskite films, consistent with SHG and PFM measurements indicating the strongest ferroelectric properties among these RP perovskite films. The value of the dielectric constant remains almost invariant up to 100 °C and increases drastically afterwards peaking between 170-180 °C for all these perovskite films. Higher peak values of dielectric constant *i.e.* > 300 are much larger than the value at the room temperature stable state, which is the fundamental property of the ferroelectric phase transition. This trend is similar to the traditional ferroelectric material such

as PZT where it follows Curie-Weiss law and thus verifies the existence and tunability of ferroelectricity from $\bar{n} = 2$ to $\bar{n} = 5$ RP perovskite films.

[0077] The disclosure is further extended to the other organic spacer with different molecular structure. N-butylammonium iodide based $\bar{n} = 5$ RP perovskite ((n-BA)₂(MA)₄Pb₅I₁₆) films also demonstrate the local piezo phase remnant hysteresis measured using PFM spectroscopy as shown in **FIG. 11**.

[0078] **Table 1:** Details of the composition of different RP and 3D perovskite films to achieve ~50 nm thickness to conduct the PFM measurements.

RP Perovskites ($\bar{n}$)	Molarity	PEA (mg)	MAI (mg)	PbI ₂ (mg)	DMF
1	0.125 M	31.1	0	28.8	0.5 ml
2	0.1 M	24.9	7.9	46.1	0.5 ml
3	0.08 M	19.9	12.7	55.3	0.5 ml
4	0.05 M	12.4	11.9	46.1	0.5 ml
5	0.04M	10.0	12.7	46.1	0.5 ml
3D	0.17 M	0	13.5	39.0	0.5 ml

[0079] **Table 2:** Details of the composition of different RP and 3D perovskite films to achieve ~300 nm thickness to conduct optical characterization and device fabrication.

RP Perovskites ($\bar{n}$)	Molarity	PEA (mg)	MAI (mg)	PbI ₂ (mg)	DMF
1	0.5 M	124.5	0	115.3	0.5 ml
2	0.31 M	77.2	24.6	142.9	0.5 ml
3	0.25 M	62.3	39.7	172.9	0.5 ml
4	0.22 M	54.8	52.5	202.8	0.5 ml
5	0.15 M	37.4	47.7	172.9	0.5 ml
6	0.13 M	32.4	51.7	179.8	0.5 ml
7	0.11 M	27.4	52.5	177.5	0.5 ml
3D	1.2 M	0	95.4	276.6	0.5 ml

[0080] **Example 2: Thin film fabrication for microscopic and optical measurements**

[0081] The formula for RP perovskite used in this disclosure is $(\text{PEA})_2(\text{MA})_{\bar{n}-1}\text{Pb}_{\bar{n}}\text{I}_{3\bar{n}+1}$ with $\bar{n}$ equals to 1, 2...7. Note that here, an average value of n is used, because the multiphases nature in the samples cannot be ruled out except for the pure 2D sample. $\bar{n}$ represents the dominating n component for each sample. Different precursor solutions were prepared by dissolving different concentrations of PEA₂I, MAI and PbI₂ in 0.5 ml DMF as shown in Table 1 (for PFM characterizations) and Table 2 (for other optical, electrical and structural characterization) and heated on a hot plate at 50 °C for 2 hours. All these steps were performed in a nitrogen filled glove box with <0.1 ppm H₂O and <2.0 ppm oxygen level. The cleaned ITO (indium tin-oxide) coated glass substrates and quartz substrates were used to prepare the thin films for microscopic and optical measurements, respectively. Substrates were cleaned by soap solution followed by ultrasonication in deionized water, acetone, and isopropanol. To make the surface hydrophilic, substrates were also treated with air plasma just before spin coating the solution. All RP precursor solutions were filtered through 0.45 µm PTFE filter and spin coated on these cleaned substrates at 4000 rpm for 30s at room temperature in a nitrogen-filled glovebox. On the other hand, filtered 3D perovskite solution was spin coated at 5000 rpm for 12s for thicker film and 4000 rpm for 30s for thinner film with toluene anti-solvent treatment. All RP films were subsequently annealed at 70 °C for 15 min while 3D films were annealed at 100 °C for 30 min to remove the solvent residue. The thickness of these films which was measured to be 50 ± 10 nm by surface profilometer was used for PFM studies, while solution concentration was increased to a film thickness of $300 \text{ nm} \pm 20 \text{ nm}$ for optical characterization and device fabrication. X-ray diffraction patterns were collected using a Bruker-AXS (D8 Advance) X-ray diffractometer equipped with Cu K α ($\lambda = 1.5418 \text{ \AA}$) X-ray source.

[0082] **Example 3: SHG signal measurements:**

[0083] SHG anisotropy patterns were obtained by transmission mode with excitation at 800 nm wavelength pulsed laser and SHG signal detection at 400 nm by a monochromator with proper filters. As the depth of focus for the lens that was used is larger than the thin film thickness, it was confirmed that the signals are generated from the bulk thin film instead of the surface. In this disclosure, SHG transmission mode was used to collect the signal with a fixed 60 degree angle between the incident p -polarized laser beam and the thin film surface. It is important to exclude false signals in the measurement generated by the filter. The power of incident laser source was carefully controlled to avoid damaging the thin film samples. A linear polarizer was placed before the samples to generate p -polarized beam only. Then a lens was

used to focus the beam in the samples. Another polarizer was placed after the samples, which was used to collect signals at *p*-polarization. For out plane nonlinear susceptibility measurements, the incident beam was at 60 degrees to the sample's normal, while for in plane nonlinear susceptibility measurements, the laser beam was at normal incidence on the samples. For temperature dependent SHG signal measurements, the rotational sample stage was replaced by a hotplate. The sample temperature was monitored by a non-contact infrared thermometer at a 1 cm distance away from the sample surface. At the same time, the incident beam was carefully aligned at 60 degrees to the sample's normal.

[0084] **Example 4: Device fabrication**

[0085] The capacitor structured devices as shown in the inset of **FIG. 6A** were fabricated on 1.0 cm x 1.0 cm pre-cleaned and dried ITO glass substrates. These cleaned substrates were treated with plasma for 7 min to make the ITO surface hydrophilic. A thin film of PEDOT:PSS layer of approximately 30 nm was deposited by spin-coating on these substrates (at 3000 rpm for 60 s), followed by annealing at 130 °C for 15 min. Later, these substrates were transferred to a nitrogen-filled glove box and different 300 ± 20 nm perovskite thin films were prepared as stated above.

[0086] A thin layer (< 10 nm) PCBM (5 mg/ml in chlorobenzene) was subsequently deposited on different perovskite layers by spin-coating at a speed of 4000 rpm for 30 seconds. The presence of a very thin layer of PCBM (< 10 nm) was used to prevent Ag migration into the perovskite. A metal shadow mask was attached to electron acceptor layer coated substrates and transferred to the thermal evaporation chamber. Finally, first 20 nm silver was deposited by 0.1-0.2 Å/s deposition rate and 80 nm by the deposition rate of 1.0 Å/s was used to complete the 100 nm silver thickness. The effective device area was 0.78 mm². The current-voltage characteristics of these devices were measured using Keithley and ferroelectric measurements (polarization hysteresis loops (P-E loops)) were carried out using a TF Analyzer 2000 ferroelectric test system applying triangular pulses from 0 kV/cm to 10 kV/cm across the samples.

[0087] **Example 5: Dielectric constant measurements**

[0088] A simple device configuration glass/ITO/Perovskite/Au was prepared to measure the capacitance of these materials under electric field of 1.67V/μm. Different perovskite films were prepared using the same conditions as described above on clean ITO substrates. A thin layer ~80 nm of gold was thermally deposited on these films under high vacuum through a

metal mask with the device area of approximately $7 \times 10^{-3} \text{ cm}^2$. The capacitance of these devices was measured using Agilent 4294A, precision impedance analyzer.

[0089] While the disclosure has been particularly shown and described with reference to specific embodiments, it should be understood by those skilled in the art that various changes in form and detail may be made therein without departing from the spirit and scope of the invention as defined by the appended claims. The scope of the invention is thus indicated by the appended claims and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced.

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CLAIMS

1. A perovskite structure comprising a composition comprising a first organic cation, a second cation, a metal cation and a counter anion, wherein the perovskite structure comprises layers stacked in a stacking direction and polarized charge domains arranged along a horizontal direction which is perpendicular to the layers stacking direction.
2. The perovskite structure of claim 1, wherein the first organic cation comprises an ammonium functional group, wherein the second cation is a monovalent cation, wherein the metal cation is a divalent metal cation and wherein the counter anion is a monovalent anion.
3. The perovskite structure of claim 2, wherein the composition is of the general formula $((\text{RNH}_4)^+)_2(\text{A}^+)_{\bar{n}-1}\text{M}^{2+}_{\bar{n}}\text{X}^{-}_{3\bar{n}+1}$, wherein:
R is a linear or branched, substituted or unsubstituted C₂-C₁₀ alkyl; linear or branched, substituted or unsubstituted C₂-C₁₀ alkenyl; linear or branched, substituted or unsubstituted C₂-C₁₀ alkynyl; linear or branched, substituted or unsubstituted C₁-C₁₀ alkoxy; substituted or unsubstituted C₃-C₁₀ cycloalkyl; substituted or unsubstituted C₃-C₁₀ cycloalkenyl; substituted or unsubstituted C₆-C₁₀ aryl; substituted or unsubstituted C₃-C₁₀ heteroaryl;
A⁺ is the monovalent cation;
 $\bar{n}$ is an integer selected from 2 to ∞ ;
M²⁺ is the divalent metal cation; and
X⁻ is the monovalent anion.
4. The perovskite structure of claim 3, comprising octahedral sheets of [MX₆]⁴⁻ formed from M²⁺ and X⁻, wherein the octahedral sheets are perpendicular to the layers of the perovskite structure.
5. The perovskite structure of claim 4, wherein $\bar{n}$ signifies a number of consecutive layers in the octahedral sheets.

6. The perovskite structure of claim 4 or 5, wherein one of the octahedral sheets has a smallest width of at least about 5 Å.
7. The perovskite structure of any of claims 1 to 6, being non-centrosymmetric.
8. The perovskite structure of any of claims 1 to 7, wherein the second cation comprises an ammonium ion.
9. The perovskite structure of any of claims 1 to 7, wherein the second cation is any one selected from a group consisting of a methylammonium ion, a formamidinium ion, a hydroxylammonium ion, a hydrazinium ion, an azetidinium ion, an imidazolium ion, a dimethylammonium ion, an ethylammonium ion, a phenethylammonium ion, a guanidinium ion, a tetramethylammonium ion, a thiazolium ion, a 3-pyrrolinium ion, a tropylium ion, a piperazinium ion, and a dabconium ion.
10. The perovskite structure of any of claims 1 to 9, wherein the second cation is a methylammonium ion.
11. The perovskite structure of any of claims 1 to 10, wherein the first organic cation comprises a linear or branched C₂-C₁₀ alkyl substituted with an aryl moiety.
12. The perovskite structure of any of claims 1 to 11, wherein the first organic cation comprises a phenylethyl moiety.
13. The perovskite structure of any of claims 1 to 12, wherein the counter anion is a halide.
14. The perovskite structure of claim 13, wherein the halide is an iodide, a bromide, a chloride or a mixture thereof.
15. The perovskite structure of claim 13, wherein the halide is an iodide.

16. The perovskite structure of any of claims 1 to 15, wherein the metal cation is any metal of group 11, group 14 or group 15 or a mixture of these.
17. The perovskite structure of any of claims 1 to 15, wherein the metal cation is a heavy metal cation or a mixture of several heavy metal cations.
18. The perovskite structure of claim 17, wherein the heavy metal cation is lead.
19. A process for the production of a perovskite structure comprising polarizable charge domains, the process comprising:
 - a) forming a perovskite structure from a first organic cation, a second cation, a metal cation and a counter anion on a substrate; and
 - b) applying an external electric field through at least one polarizable charge domain of the polarizable charge domains to modify a polarization of the at least one polarizable charge domain.
20. The process of claim 19, wherein step a) further comprises preparing a precursor solution from the first organic cation, the second cation, the metal cation and the counter anion.
21. The process of claim 20, wherein step a) further comprises heating the precursor solution to a temperature above room temperature, and depositing the precursor solution on the substrate.
22. The process of any of claims 19 to 21, wherein the external electric field through the at least one polarizable charge domain of the polarizable charge domains is chosen from about 0.1 kV/cm to about 100 kV/cm.
23. Use of a perovskite structure comprising a composition comprising a first organic cation, a second cation, a metal cation and a counter anion, wherein the perovskite structure comprises layers stacked in a stacking direction and wherein the perovskite

structure has polarizable charge domains arranged in a horizontal direction which is perpendicular to the layers stacking direction, as a memory device structure, wherein a polarization of a domain of the polarizable charge domains represents a unit of information.