“Forbidden” Polarisation and Extraordinary Piezoelectric Effect in Organometallic Lead Halide Perovskites

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Organometallic lead halide perovskites are highly efficient materials for solar cells and other optoelectronic applications due to their high quantum efficiency and exceptional semiconducting properties. A peculiarity of these perovskites is the substantial ionic motion under external forces. Here, it is revealed that electric field-and light-induced ionic motion in MAPbX₃ crystals (X = Cl, Br, I and MA = CH₃NH₃) leads to an unexpectedly high piezoelectric-like response that is at low frequencies an order of magnitude larger than in ferroelectric perovskite oxides. The nominal macroscopic symmetry of the crystals is broken by redistribution of ionic species, which can be controlled deterministically by light and electric field. The revealed piezoelectric response is possibly present in other materials with significant ionic activity, but the unique feature of organometallic perovskites is the strong effect on the piezoelectric-like response of interplay of ionic motion (MA⁺ and X⁻) and photoelectrons generated with illumination.

1. Introduction

Organometallic lead halide perovskites, represented by methylammonium (MA) lead halides MAPbX₃ (X = Cl, Br, I), exhibit unusually broad spectrum of properties attractive for optoelectronic applications such as solar cells, radiation detectors, light-emitting diodes, and photodetectors.[1] Despite extensive studies, some key aspects of MAPbX₃ behavior are still poorly understood. Among the most intriguing are the nature of ionic defects, their interaction with external fields, and the role of their transport on properties.[2] MA⁺, Pb²⁺, X⁻ and H⁺ are directly or indirectly known to form vacancies and possibly interstitials.[3,4] Substitutional defects Xₚb, Xₘₐ, and Pbₓ have also been reported.[5,6] The charge-compensating species (electrons, holes or other ionic defects) for each defect are most often not identified. There is substantial evidence that ionic defects in MAPbX₃ are more much mobile at ambient temperature than their counterparts in oxide perovskites.[4] Additionally, the MA⁺ molecule (with an equivalent radius of 2.17 Å[12] it is comparable in size with X⁻ and Pb²⁺ ions[13]), and defect associates (clusters that ionic defects form with their charge-compensating species) may reorient in external electric field. Since charged point defects have a different size than the host site, they exert strain on their lattice surrounding deforming the unit cell and distorting halide octahedra, X₆. Various orientations of MA⁺ and defect clusters also deform the lattice. The charged ionic defects, orientable molecules, and defect clusters therefore interact with both electric field and stress, i.e., they are electro-mechanically active.[14] Potential for a strong electro-mechanical effect in these materials is significant: for example, a high concentration of charged iodine vacancies in apical position of I₆ octahedra can contract the unit cell by 11%.[10] Three electro-mechanical effects are usually considered in deformable, polarizable materials. Electrostriction, which is present in all materials regardless of their symmetry, has been reported to be large in MAPbI₃, when compared to oxide perovskites. Flexoelectric effect may also appear in all materials, but requires stress (strain) or polarization (electric field) gradients and is thus usually negligible in bulk samples. Strong light-assisted flexoelectric effect has been measured in thin sheets of MAPbX₃ for X = Cl, and Br.[16] Piezoelectricity is the most interesting electro-mechanical effect for applications and is the largest of the three in a given bulk material.

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Importantly, piezoelectricity is forbidden in centrosymmetric crystals.\cite{17} The nominal average crystal structure of the bromide and chloride is considered cubic centrosymmetric, space group type $Pm-3m$, at room temperature\cite{18} and thus does not support piezoelectricity. The symmetry of the iodide at room temperature is usually given as centrosymmetric tetragonal $I4/mcm$. Therefore, even if individual defects and charged molecules in an MAPbX$_3$ crystal are electro-mechanically active, the sample will not be piezoelectric if the arrangement of defects and orientation of molecules is random. Ferroelectric-like polar behavior has been reported for MAPbI$_3$\cite{19,20} in which case the proposed symmetry is $I4cm$ and the material is potentially piezoelectric.\cite{19,21,22} Macroscopic polarity in MAPbI$_3$ has been associated with the ordering of MA$^+$ molecules.\cite{23} It has been inconclusively speculated that polarization may enhance optoelectronic properties.\cite{24} In materials with substantial concentration of mobile ionic defects electro-chemo-mechanical coupling arises in addition to purely electro-mechanical coupling.\cite{25–27} The thermodynamic model of electro-chemo-mechanical response of nanoscale systems with mixed ionic and electronic conductivity has been proposed and discussed by Morozovska et al.\cite{28,29}

In this paper, we report experimental results of substantial electro-chemo-opto-mechanical effects in millimeter-size bulk crystals. We show that bulk samples of MAPbX$_3$ single crystals exhibit macroscopic polarity and an enormous apparent converse piezoelectric-like response at low frequencies. The presented evidence points toward ionic rearrangement as the main cause of the symmetry breaking and ensuing polarity and piezoelectricity. It is shown that the “forbidden” polarization and piezoelectricity can arise spontaneously, during the crystal growth, and may be triggered and controlled by electric field and UV light. The results imply that the electrically and optically generated piezoelectric strain may affect operation of optoelectronic devices.\cite{30,31,32}

2. Results and Discussion

Crystals were prepared by the inverse crystallization method (see Methods).\cite{33} Electrodes were deposited on two opposite faces of as-received crystals shaped as cuboids ($X = \text{Cl, Br}$) or irregular polyhedra ($X = \text{I}$), Figure 1a. Electric field of variable frequency and strength was applied on the electrodes and mechanical displacement was measured in longitudinal mode with a linear variable differential transformer (LVDT). The current through the samples is measured by connecting a resistor in series with the sample and measuring the voltage drop across the resistor. Experimental details are given in Experimental Section and Figures S1 and S2 (Supporting Information).

2.1. Induced Piezoelectricity

Figure 1b–d illustrates mechanical displacement generated in the examined crystals upon application of an electric field. In all sufficiently insulating materials an alternating electric field $E_{ac} = E_0 \sin (\omega t)$ induces electrostrictive strain $x = ME_{ac}$, where $M$ is the electrostrictive coefficient.\cite{34} The piezoelectric

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Three aspects of induced piezoelectricity. a) Examples of MAPbX$_3$ crystals. The sides of the crystals in the plane of the image are perpendicular to the growth direction. The field was applied along the growth direction for $X = \text{Cl, Br}$ and perpendicular to it for $X = \text{I}$. b) Coexistence of electrostriction and piezoelectricity in an MAPbCl$_3$ crystal at small $E_{dc}$ ($\sim 34 \text{ V cm}^{-1}$) and large $E_{ac}$ ($\sim 250 \text{ V cm}^{-1}$). The field was applied along the thickness $t = 2.15 \text{ mm}$. c) Change in the sign of the bias field $E_{dc}$ flips the phase of the displacement in an MAPbBr$_3$ sample indicating that the piezoelectric coefficient $d$ is controlled by $E_{dc}$. $t = 1.32 \text{ mm}$. d) Asymmetric and hysteretic displacement-voltage relationship in an MAPbI$_3$ crystal. $t = 5.68 \text{ mm}$. All samples had sprayed graphite electrodes.
effect may be induced in centrosymmetric materials if a direct electric-field bias $E_{dc}$ is applied together with the $E_{ac}$. The role of the $E_{dc}$ is to break the crystal’s centric symmetry and bias electrostriction, similar to what polarization does in ferroelectrics. The total strain $x$ is then given by $x = M(E_{ac} + E_{dc})^2$. The piezoelectric (linear) component of the strain is $x = (2ME_{dc})E_{ac}$, where $d = 2ME_{dc}$ is the apparent piezoelectric coefficient (Figure S3, Supporting Information). This simultaneous appearance of the electrostrictive and piezoelectric strains is illustrated in Figure 1b, which shows the displacement of an MAPbCl$_3$ crystal on which an alternating field with a frequency of 10 mHz, amplitude $\approx 230$ V cm$^{-1}$, and an offset of $\approx -34$ V cm$^{-1}$ was applied. The electrostrictive strain is identified in the graph as the second harmonic response (twice the frequency of the applied field) whereas the piezoelectric strain appears as the first harmonic response. In a general case, electric field induced alternating strain in a material that exhibits both piezoelectric and electrostrictive effects are given by equation $x = ME_{ac}^2 + dE_{ac}$ (see Figure S3, Supporting Information). The fit (purple dots) of the data (blue line) in Figure 1b with this equation leads to $M = 1.45 \times 10^{-12}$ m$^2$ V$^{-2}$ and $d = 16$ 900 pm V$^{-1}$. For comparison, the latter value is 30–80 times larger than in Pb(Zr,Ti)O$_3$ ceramics ($d = 200$–500 pm V$^{-1}$) and up to ten times larger than in relaxor ferroelectric Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_5$-PbTiO$_3$ single crystals ($d = 1500$–2000 pm V$^{-1}$). In those ferroelectric oxide perovskites, which are presently the most widely used piezoelectric materials, the origin of the piezoelectric effect is in small distortions of chemical bonds, small displacements of ions around equilibrium positions, and displacement of domain walls, maintaining a high value of the piezoelectric coefficient over a broad frequency range. In organometallic halide perovskites, the origin of the large displacement is obviously different and limited to low frequencies, as will be discussed later. This difference can be understood by looking at the polarization-related electrostrictive coefficient, $Q$, which is defined by relationship $x = QP_{tot}$. $P_{tot}$ is the polarization induced by the electric field $E_{dc}$ and is related to it by relationship $P_{tot} = \chi E_{ac}$ where $\chi$ is the dielectric susceptibility. It follows that $d = 2ME_{dc} = 2\chi QP_{tot} = 2\chi E_{dc}$, where $\varepsilon = \varepsilon_0 + \chi$ is the dielectric permittivity and $\varepsilon_0$ permittivity of the free space. The origin of the large induced piezoelectric coefficient in organometallic perovskites can now be interpreted qualitatively as follows: in materials with a substantial ionic mobility, it is reasonable to expect that both $\varepsilon$ and $P_{tot}$ become very large at low frequencies as indeed seen experimentally (Figures S6 and S4, Supporting Information). This situation is analogous to that in oxides with fluorite structure where large induced piezoelectric response is also related to a high mobility of oxygen ions via oxygen vacancy migration. In contrast, in ferroelectric oxide perovskites the origin of the intrinsic piezoelectric effect is in electrostriction biased by the spontaneous polarization, $P_s$, and intrinsic permittivity, where long range motion of ionic defects does not contribute substantially to the polarization and permittivity. Note that we compare MAPbX$_3$ with perovskite oxides only to demonstrate how various contributions to the polarization may have vastly different effect on the electro-mechanical coupling in materials with the same crystal structure. No implication is made on the suitability of MAPbX$_3$ for piezoelectric applications.

The extracted electrostrictive coefficient $M$ for the examined MAPbCl$_3$ and MAPbBr$_3$ samples is several orders of magnitude larger than in a broad class of materials, including MAPbI$_3$, as shown in Figure S5 (Supporting Information). This result is again consistent with the large apparent permittivity of the crystals ($M = \varepsilon_0^2 Q$).

To further confirm the piezoelectric-like nature of the strain signal, we illustrate in Figure 1c inversion of the strain phase angle in MAPbBr$_3$ when the sign of $E_{dc}$ is switched, as expected from relation $x = (2ME_{dc})E_{ac}$. In contrast to the data for the chloride in Figure 1b, only the first harmonic is observed in this bromide sample. Because of the large $E_{dc}$ (in this experiment, $V_{dc} = \pm 50$ V, $V_{ac} = 50$ V) the piezoelectric term dominates the total strain and the electrostrictive component of the strain is not readily apparent. The value of $d$ in bromide crystals is also exceptionally large, around 3000 pm V$^{-1}$, and values over 9000 pm V$^{-1}$ have been observed in some samples (Figure S6, Supporting Information). Figure 1d shows displacement-voltage relationship for an MAPbI$_3$ sample. The observed electro-mechanical hysteresis is similar to the current-voltage hysteresis, which has been in hybrid perovskites commonly attributed to ionic migration. The asymmetry of the displacement-voltage graph for the positive and the negative $V_{dc}$, indicates asymmetry of the sample. The equivalent piezoelectric coefficient in this sample is about 350 pm V$^{-1}$, much larger than previously reported using local techniques ($\approx 5$ to 25 pm V$^{-1}$) and direct piezoelectric measurements ($\approx 50$ pm V$^{-1}$).

We presume that one of the reasons why the large values of piezoelectric coefficients reported here were not detected by AFM-based local techniques is because in those experiments the driving frequency is usually in kHz range (50 kHz in Ref. [44]), compared to 10 mHz to 4 Hz in our work. As discussed below, the electro-mechanical response of investigated bulk crystals decreases rapidly with an increasing frequency of the driving field. This rapid decrease of signal with increasing frequency is consistent with dominant slow ionic contribution to the electro-mechanical signal at low frequencies.

### 2.2. Evidence of Internal Asymmetry

The apparent piezoelectric coefficient obtained from $x = ME_{ac}^2 + dE_{ac}$ was compared with the piezoelectric coefficient expected from $d = 2ME_{dc}$ using the value of $M$ extracted from the former equation. We get discrepancy that, generally, depends irregularly on $E_{dc}$ (Figure S7, Supporting Information). In the case of MAPbCl$_3$ in Figure 1b, the estimated $d = -10$ 000 pm V$^{-1}$, which is just over half of the value calculated from the experimental data. This discrepancy suggests that the sample has an internal bias field in addition to experiencing the external $E_{dc}$. Another evidence of built-in asymmetry is the piezoelectric displacement generated by an $E_{dc}$ signal (no $E_{dc}$ offset) applied on an as-grown MAPbBr$_3$ crystal, Figure 2a. Combination of the electrostrictive and piezoelectric response is clearly seen, which is inconsistent with the nominal $Pm-3m$ structure, where only an electrostrictive response is expected. The displacement shown in Figure 2a was measured along the growth direction of the sample, where growth facets could be clearly observed on one side of the crystal.
is expected in samples with different electrodes, as commonly supported by Supporting Information. It should be noted that asymmetry of MAPbX$_3$ samples, we utilized the putative high 

2.3. Poling of Crystals

To confirm the likely role of defect distribution in the asymmetry of MAPbX$_3$ samples, we utilized the putative high mobility of ions to manipulate defect distribution by applying $E_{dc}$ for 10 min and removing it before applying only $E_{ac}$. By this “poling” procedure$^{[48]}$, we are able to rearrange defects and deterministically induce strong piezoelectric effect and invert its sign, as shown in Figure 2d–e. The evolution in the amplitude of the piezoelectric response immediately after $E_{dc}$ removal indicates that a fraction of defects population displaced by $E_{dc}$ tends to redistribute to a new equilibrium position without external $E_{dc}$ (Figure S9, Supporting Information). Interestingly, a negative poling field $E_{dc}$ (Figure 2e) leads to an increase in the piezoelectric response with time after removal of $E_{dc}$. This could be related to the injection of electrons, which interferes with the mobility and distribution of ionic defects.

2.4. Frequency Dependence of Properties

Analysis of the temporal characteristics of the electro-mechanical response gives further insight into processes involved in the symmetry breaking and the large electro-mechanical response. Data in Figure 1 show time delay between the driving field and strain on the order of several seconds. Hysteresis in electric current–voltage relationship has been reported by many authors for MAPbX$_3$ samples$^{[49]}$ and has been attributed to the motion of ionic defects and reorientation of groups of ions. We report a similar hysteresis in the electrically triggered mechanical displacement, Figure 1d. Evolution of the displacement hysteresis with the field amplitude is illustrated in Figure 10 (Supporting Information). The time lag translates into a large frequency dependence of the piezoelectric, Figure 3a, and electrostrictive responses (Figures S11 and S14a, Supporting Information). The broad, non-Debye-like relaxation seen in the permittivity (Figures S11 and S14b, Supporting Information) is typical for disordered systems$^{[40]}$. The broad relaxation suggests different strain and polarization environments for ionic defects.

Figure 2. Asymmetry and poling. Electromechanical displacement of: a) an as received MAPbBr$_3$ sample with only $E_{ac}$ applied along the growth direction. The piezoelectric signal is dominant. b) another as received MAPbBr$_3$ sample, measured applying only $E_{dc}$ along a direction orthogonal to the growth direction. The response is dominantly electrostrictive but with a non-negligible piezoelectric contribution. c) the same sample and direction as in (b) after driving the sample for additional 108 min with $E_{ac}$. The asymmetry and piezoelectric response are nearly eliminated by homogenizing the defect distribution resulting in only electrostrictive response. d) the sample as in (a), after being poled by $+E_{dc}$ for 10 min. The measurements were performed by applying only $E_{ac}$, e) the same sample as in (a,d), after being poled by $-E_{dc}$ for 10 min and then driven by applying only $E_{ac}$. Note the expected change in the phase of displacement between (d) and (e). Both MAPbBr$_3$ samples had graphite sprayed electrodes. Thickness $t = 1.54$ mm along the growth direction in (a), (d), (e), and $V_{dc} = 150$ V. Thickness $t = 6.40$ mm along the direction orthogonal to the growth direction in (b–c) and $V_{dc} = 150$ V. Insets in Figure 2d,c show crystals with electrodes deposited on faces perpendicular and parallel, respectively, to the growth direction. (Figure S1, Supporting Information). While it is reasonable to interpret the symmetry breaking by inhomogeneous distribution of charged ionic defects or preferential orientation of MA$^{+}$ along the growth direction, the inspection of crystals along a direction orthogonal to the growth direction, Figure 2b, also reveals piezoelectric effect, indicating a complex distribution of defects along different crystal axes. When alternating field is applied for a prolonged time, nearly pure electrostrictive effect can be observed, Figure 2c. This suggests that the alternating field homogenizes defects' distribution throughout the crystal, removing the internal field.

Another evidence of macroscopic asymmetry of the samples is seen in the voltage signal generated by UV radiation (Figures S8 and S10, Supporting Information), and asymmetrical current measured under $E_{dc}$ (Figures S8 and S11, Supporting Information). It should be noted that asymmetry is expected in samples with different electrodes, as commonly used in optoelectronic applications such as solar cells$^{[45,46,47]}$. However, in our case, the two electrodes are the same (both either Pt or C) and the electrode-crystal interface effects$^{[47]}$ can be excluded as a significant contributor to the asymmetry.
throughout the crystal and trapping-detrapping events with different activation energies indicating multiple interactions among defects.\(^{[9]}\) The decrease of the mechanical displacement with increasing frequency shows that the electric-field induced strain is dominated by slow defects; the electrical signature of this activity is the current which roughly follows the same trend as the piezoelectric coefficients, Figure 3b. Because of the slowness of the process and long settling times each experiment captures just a snapshot of the sample behavior. If measurements are continued for sufficiently long time, properties evolve, sometimes radically changing behavior and even switching internal polarization (Figure S12, Supporting Information). This may explain why many studies of organometallic halides report mutually inconsistent behaviors.\(^{[3]}\) In our experience, this is caused by the strong sensitivity of samples on time and mechanical, electrical, and optical boundary conditions.

2.5. Origin of Asymmetry

We next comment on the nature of species responsible for the strong and slow piezoelectric response. We consider two main candidates: i) field-driven ionic diffusion via ionic and molecular vacancies and ii) reorientation of organic molecules and defect clusters. There is a considerable controversy about mobility of various defects in MAPbX\(_3\).\(^{[9]}\) Evidence has been presented about substantial migration of MA\(^{+}\)\(^{[46,52]}\) whereas activation energy for Pb\(^{2+}\) motion via its vacancies is much higher and motion probably insignificant.\(^{[53,58]}\) Reorientation of MA\(^{+}\) is considered (much) faster than the time scales in our experiments.\(^{[55]}\) However, because of a presumed high concentration of defects their interaction cannot be neglected and will likely modify characteristic times of individual defects.

It is tempting to correlate the general trend of the piezoelectric coefficients \(d\), Figure 3a, where \(d(\text{MAPbCl}_3) > d(\text{MAPbBr}_3) > d(\text{MAPbI}_3)\), with the ionic radius \(r\) of the halides \((r(\text{Cl}) = 1.81 \text{ Å} < r(\text{Br}) = 1.96 \text{ Å} < r(\text{I}) = 2.20 \text{ Å})\).\(^{[13,53]}\) However, this empirical inverse correlation of \(d\) with ionic radius should be taken with caution: it may imply that motion or reorientation of MA\(^{+}\) may be easier if the halide ions (or their vacancies) sitting on vertices of the X\(_6\) octahedra are smaller. Furthermore, an origin of the spontaneous poling effect in as-grown crystals could be related to orientation of MA\(^{+}\) or defect clusters (e.g., halide vacancy-lead vacancy pair\(^{[8]}\)). Despite being fast, reorientation of MA\(^{+}\) molecules under \(E_{dc}\) and \(E_{ac}\) field probably depends on each molecule’s immediate surrounding consisting of slow ionic defects so that the whole charge migration and strain propagation process – diffusion of ions, electronic conductivity which may screen ionic charges and reorientation of organic molecules and defect clusters – are intermingled. How these processes control ion migration is still open to debate.\(^{[53]}\)

Note that the long times observed in our experiments may suggest migration of ions over longer distances, not only vibration, orientation or jumps within a unit cell.

2.6. Effect of UV Light on Strain

The UV light is applied (see Figure S2, Supporting Information) while the sample was driven by electric field, as shown in Figure 4a for MAPbBr\(_3\). The data demonstrate that the UV light plays multiple roles in the photo-electro-mechanical coupling. The jump in the displacement signal when the UV light is turned on and off, Figure 4b–d is caused by the photostrictive effect, already reported for MAPbX\(_3\).\(^{[56,57]}\) Notably, the data reveal that the UV light polarizes samples. In the sample with graphite electrodes, Figure 4b, the pure electrostrictive response observed without UV light becomes partly piezoelectric under the light. Since the electric field is applied without a dc bias, this is possible only if the sample became polarized by the light (compare with Figures S8 and S10, Supporting Information). An indication of the possible mechanism which governs the piezoelectric effect is seen in the sample with Pt electrodes, Figure 4c. The apparent absence of the displacement
for this sample under $E_{dc}$ field means that the signal is either absent or too small to be detected by the instrument. However, turning on the light reveals both electrostriction and piezoelectricity. The same sample under $E_{ac} + E_{dc}$, Figure 4d, shows that the light increases the piezoelectric signal by factor of four. It has been demonstrated that UV light promotes the migration of MA$^{+}$ ions, but does not affect significantly the motion of X$^{-1}$ ions\[46,52\]. This selective action of light on ions could suggest an important role of MA$^{+}$ ions in the generation of strain. As the UV light also creates electron-hole pairs the whole charge balance in the crystal will be affected under the light, a new charge environment will develop over time, making deconvolution of different contributions to strain difficult.

2.7. Thermal Expansion

MAPbX$_3$ is known to exhibit a large thermal expansion and a low thermal conductivity.$^{[58]}$ The concern is that the electric-field-generated current could raise the temperature of the sample through Joule heating, with resulting thermal strain interfering with electro-mechanical strain$^{[59]}$ (see Figure S13, Supporting Information). To gain further insights into the structural mechanisms of the electric-field-induced strain, we investigated MAPbBr$_3$ using single crystal x-ray diffraction$^{[60]}$ (see Experimental Section and Figure S14, Supporting Information).

All the measured Bragg peaks are sharp and single (FWHM = 0.1°), indicating a mono-domain nature of MAPbBr$_3$ crystals. Figure 5a shows the time-dependent rocking curve of 004 reflection in the negatively biased sample and the strain calculated from the shift of the reciprocal space position of 004 peak, Figure 5b. The electric field shifts the position of the rocking curve while preserving its sharp profile, indicating that the electric-field induced strain is associated with the change of the corresponding lattice parameters. The process responsible for the strain produces therefore an uniform long-range strain field extending over entire crystal, as would be expected for chemical expansion effects$^{[61]}$ and other processes such as local, reversible decomposition-recomposition events under electric field.$^{[62,63]}$ Figure 5c shows the strain-voltage “butterfly loops”, calculated from the reciprocal space position of 004 peak. The agreement with the macroscopic strain measured by LVDT is remarkable.

We investigated next if a significant contribution to the strain originates from the thermal expansion of the sample generated by electric-field-induced Joule heating. The pure thermal behavior of the crystal was probed by measuring the 004 Bragg peak between 20 and 80 °C (Figures S19a and S14, Supporting Information). The corresponding thermal expansion coefficient $\alpha = 0.36 \times 10^{-4}$ K matches well the literature value.$^{[58]}$ Additionally, we calculated the evolution of integrated intensity of the Bragg peaks from which we can determine the dependence of the integrated intensity on thermal strain. We use the decay of intensity with strain as a “fingerprint” of the thermal origin of the strain (Figures S19b and S14, Supporting Information).

Figure 5c, shows the dependence of relative Bragg peak’s intensity on the electric-field induced strain. Notably, the electric-field induced strain is accompanied by the increase of the integrated peak intensity. This behavior is opposite to

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**Figure 4.** Effect of UV light on strain in MAPbBr$_3$. a) a crystal in the LVDT setup with the fiber optic UV light guide in the back. The light beam is perpendicular to the plane of the picture. b) electro-mechanical displacement measured in a sample with sprayed graphite electrodes, thickness $t = 5.23$ mm, and $V_{ac} = 150$ V applied perpendicular to the growth direction. c) displacement in a sample with sputtered Pt electrodes, $t = 3.59$ mm and $V_{pp} = 125$ V applied along the growth direction. d, the same as in (c) with additional $V_{dc} = -100$ V.
the one for thermally induced strain (Figures S19c and S14, Supporting Information) which is also shown by the dashed lines in Figure 5d). This indicates that the electric-field-induced strain is different from the strain of purely thermal origin.

We have finally measured sample temperature while applying electric field and compared strains from thermal expansion and electric-field, Figure 5e. The electric-field induced strain is nearly four times larger than the thermal strain.

3. Conclusion

Experimental and theoretical investigations of organometallic lead halides mostly focus on electrical properties and electric interactions of ionic defects whereas the strain is usually considered only as an external parameter.\cite{30,31,64} We show that the strain associated with charged ionic defects (effect known as “chemical expansion or contraction”\cite{61}) leads to remarkable electro-mechanical activity resulting in huge macroscopic piezoelectric and electrostrictive responses, much higher than those in oxide perovskites. Local strain resulting from rearrangement of ionic defects under external and internal electric field is expected to interact with and affect the recombination of electrons and holes, thus directly influencing the performance of optoelectronic devices. A better theoretical understanding of electro-mechanical interactions among defects may help shed light on the importance of each defect in the overall performance of these materials. The effects of long-range ionic displacement on electro-mechanical properties revealed in our work should not be limited to organometallic perovskites but are expected to be present in other materials with substantial ionic migration, such as family of fluorites.\cite{41} These effects can be classified under the general category of ferroionic-like\cite{65} phenomena, even if ferroelectricity is absent.

4. Experimental Section

Preparation of Crystals: MAPbBr\textsubscript{3} single crystals were grown using the inverse temperature crystallization method\cite{33} from its saturated solution in dimethylformamide (DMF). MAPbI\textsubscript{3} and MAPbCl\textsubscript{3} were grown using the identical method, with \(\gamma\)-butyrolactone (GBL) and 50 v/v\% DMF/50 v/v\% dimethyl sulfoxide (DMSO). Crystals (Figure 1a; Figure S1, Supporting Information), typically a few millimeters in size, were used as-grown. Electrodes are either sprayed graphite or sputtered platinum, as specified in the text. The electrodes were applied on a parallel pair of \{100\} faces for X = Br, and Cl and parallel to \{100\} direction for the iodide. Electroded faces for X = Cl, and Br were thus either perpendicular or parallel to the crystal growth direction, as shown in Figure S1 (Supporting Information).

Mechanical Displacement Measurements: Mechanical displacement of the samples was measured using a LVDT. The LVDT consists of one...
central primary and two outer secondary coils placed in a tube, forming a transformer. Application of ac voltage on the primary coil induces magnetic field in the transformer. A ferromagnetic core, connected to the sample, moves along the tube axis as the sample size changes under electric field. The magnetic flux changes as the core moves and the voltage difference of the two secondary coils was proportional to the core (sample) displacement. The small voltage difference was read with a lock-in amplifier. The sample was held in contact with the core via a nonmagnetic rod which was supported by two leaf springs that provide restoring force and keep the sample in contact with the core. The displacement on the order of 1 nm can be really measured, in the frequency range from a few mHz to ~10 Hz. The device was calibrated and the linear range determined with a micrometer. The calibration was verified by measuring displacement of piezoelectric ceramics and crystals with known piezoelectric coefficient. (Figure S2, Supporting Information) Further experimental details could be found in the Ph.D. thesis by Matthew Davis, EPFL[66].

**Conflict of Interest**

The authors declare no conflict of interest.

**Author Contributions**

M.V. performed all electrical, mechanical displacement, and optical experiments analyzed and interpreted the data. M.K. and E.H. grew crystals. L.F. coordinated the crystal growth work. D.S. and S.G. performed X-ray diffraction measurements, analysed and interpreted the data. L.R. constructed the setup for UV measurements. All coauthors discussed the results. D.D. conceived the idea, supervised the work, and participated in the experimental work, data analysis, and interpretation. M.V., S.G., and D.D. wrote the paper with input from all coauthors.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords**

electrostriction, halide perovskites, ionic defects, piezoelectricity

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**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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