Photoinduced Giant Dielectric Constant in Lead Halide Perovskite Solar Cells

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ABSTRACT: Organic—inorganic lead trihalide perovskites have emerged as an outstanding photovoltaic material that demonstrated a high 17.9% conversion efficiency of sunlight to electricity in a short time. We have found a giant dielectric constant (GDC) phenomenon in these materials consisting on a low frequency dielectric constant in the dark of the order of $\varepsilon_0 = 1000$. We also found an unprecedented behavior in which $\varepsilon_0$ further increases under illumination or by charge injection at applied bias. We observe that $\varepsilon_0$ increases nearly linearly with the illumination intensity up to an additional factor 1000 under 1 sun. Measurement of a variety of samples of different morphologies, compositions, and different types of contacts shows that the GDC is an intrinsic property of MAPbX$_3$ ($\text{MA} = \text{CH}_3\text{NH}_3$). We hypothesize that the large dielectric response is induced by structural fluctuations. Photoinduced carriers modify the local unit cell equilibrium and change the polarizability, assisted by the freedom of rotation of MA. The study opens a way for the understanding of a key aspect of the photovoltaic operation of high efficiency perovskite solar cells.

SECTION: Energy Conversion and Storage; Energy and Charge Transport

Perovskite solar cells have emerged as a major topic of research in photovoltaics because of the promising properties of the solution processed, low cost, and high efficiency solar cells for large-scale solar energy production.1,2 Perovskite is the denomination for any material with the general chemical formula ABX$_3$ that adopts the crystalline structure of calcium titanate, CaTiO$_3$. Compositional combinations provide hundreds of materials with perovskite structure, and many display a fascinating variety of electric, piezoelectric, and electro-optical properties, such as high polar behavior and structural and ferroelectric phase transitions.3,4 These last properties rely on a complex interplay between the substitutional chemistry and the lattice displacements.5,6

Since the 1990s, organic—inorganic hybrid halide perovskites have been investigated for their promising semiconductor properties.7 Recently, photovoltaic behavior was discovered using the methylammonium lead trihalide perovskite (MAPbX$_3$, MA = CH$_3$NH$_3$; X$_i$ = Br, I$_1$, I$_3$,Cl$_3$) as light absorber5,9 and further developments in the last two years reached nearly 18% conversion efficiency of sunlight to electricity that already overcomes the performance of some established thin film photovoltaic technologies.10–12 These results have boosted the research on these materials to further improve their photovoltaic efficiencies. Consequently, there is a growing interest to understand the detailed physical properties of MAPbX$_3$ perovskites in order to develop better photovoltaic structures as well as new applications of these semiconductors. We have conducted a number of studies of their electrical and electro-optical properties that have provided basic insights to the photovoltaic mechanisms.13,14 Here, we report an outstanding and unique physical behavior in the photovoltaic classes of materials, a carrier-induced giant dielectric constant (GDC). The large dielectric relaxation is a central element to understand the physical processes in the perovskite photovoltaic devices13 and opens up these materials for unexpected new applications.

The structure of the perovskite plays a significant role in the observed phenomena.6–18 In the high temperature cubic phase, it has a B cation in 6-fold coordination with an octahedron of X anions (a corner sharing [BX$_6$] octahedra) and the A cation occupying the 12-fold cuboctahedral coordination site. Under application of stress or electrical field, two main distortions can be distinguished: a polar displacement of both A and X atoms (off-centering), or a nonpolar rotation of [BX$_n$] octahedra. In many cubic materials, off-centering leads to a ferroelectric phase transition, but in a majority of perovskites,

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the [BX₃] octahedra are tilted and they are not ferroelectric. In contrast with oxide based perovskites, the halide perovskites as MAPbI₃ show the cubic symmetry phase transition at relatively low temperature, 56 °C, and the tetragonal lattice, Figure 1b, is maintained until −112 °C when it undergoes phase transition to orthorrombic phase, Supporting Information Figure S11. Very recently, Frost et al. have discussed theoretically the presence of ferroelectric domains in MAPbI₃.¹⁹

GDC is observed in materials in which the low frequency limit of the real part of the dielectric constant becomes large, ε₀ > 1000. Provided that ε₀ shows small temperature dependence, these materials are applied to high dielectric constant capacitors for energy or memory storage devices. GDC was suggested in polaronic conductors as a possible cause for high Tₜ superconductivity,²⁰ and it has also been reported for inorganic and hybrid metal oxide perovskites²¹,²² and in molecular crystals.²³ The origin of GDC in several classes of materials is a subject of debate, as it can be ascribed to different causes, namely, an intrinsically high polarizability due to either ionic displacements or to dipolar or hopping contributions of polarons,²⁰,²⁴ or alternatively, morphology features as interfacial polarization at the insulating boundaries between semiconducting grain or polarization at the metal/dielectric interface.²⁵,²⁶ In either case, in the previous literature reports the GDC is caused by inherent electronic carriers in the material, whereas a photoinduced effect has been only rarely observed.²⁷ Below, we report the observation of GDC in MAPbX₃ perovskites that can be achieved by injection of carriers induced either by photogeneration or applied voltage, in a diode structure.

At present, there are two main kinds of perovskite photovoltaic films where MAPbX₃ is deposited inside of a metal oxide nanostructured scaffold that may be semiconducting (TiO₂)³⁰,³¹ or an insulator (Al₂O₃)³² and alternatively as planar film without scaffold.¹¹,³³ We prepared a variety of films on these configurations, see Figure 1a, using different contacts combinations: (i) diode (solar cell) structure, with asymmetric electron and hole selective contacts, (ii) symmetric contacts that allow injection of only one kind of carrier, either electrons or holes, and (iii) films with blocking insulator layers that prevent carrier injection. The dielectric constant ε'(ω) = ε′ − iε″ was measured as a function of frequency under different conditions of bias voltage, illumination, and temperature. The experimental details of materials, device preparation and their characterization measurements are described in Supporting Information.

The characteristic behavior of the frequency dependent real part of the dielectric constant is shown in Figure 1c. In the dark, the permittivity of the perovskite film decreases from a low frequency value of about ε₀ ≈ 1000, showing already GDC, to the high frequency value ε∞ in the order of tens. The decrease of ε′ shows a number of features. A relaxation peak is observed in the dielectric loss ε″ at the frequency f₀ = 0.5 Hz, and it can be ideally described by the generic Debye expression

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\frac{\omega}{\tau_\omega}}$$

where τ₀ = (2πf₀)⁻¹ is a temperature-dependent constant, the relaxation time. At the high frequency side of the ε″ peak, the real part of the permittivity (associated with the system’s capacitance) does not abruptly decay as would be expected from eq 1. This feature is related, on one hand, to the presence of a capacitance not related to dielectric polarization, to the chemical capacitance thirty¹ that has been emphasized in a previous report,¹³ and in addition, to a distribution of relaxation times which gives rise to well-known dielectric functions can also contribute to the smoothness in the ε″ step. Due to the effect of the dc conductance, the dielectric loss ε″ increases at the low frequency side of the relaxation peak at τ₀. Identical features have been observed either with TiO₂ scaffold or with no scaffold, Supporting Information Figure S12. Also, with different contacts, symmetric, asymmetric or blocking, see Supporting Information Figure S13. Furthermore, GDC is not exclusive of the MAPbI₃ perovskite and it has been also observed for CH₃NH₂PbI₃, see Supporting Information Figure S14.

Illumination of the perovskite samples produces a significant increase of charge carrier density in the perovskite layer due to the high extinction coefficient of organic—inorganic lead halide perovskite.²⁷ Figure 1c shows that upon application of 1 sun illumination intensity to the sample, ε∞ is not modified but there is a prodigious shift of the permittivity from intermediate to low frequencies that produces a change of the dielectric constant until a plateau is attained at values as high as ε₀ ≈ 10⁸–10¹⁰ implying a photoinduced variation of factor ≈1000. Dependence of the permittivity vs incident light intensity, Φ₀ is further analyzed in Figure 2, that shows a relationship ε₀ = k(Φ₀)γ with γ = 1.1.

In order to discriminate between bulk and interfacial effect, different contact configurations have been explored, including the diode structure, the blocking of one of the contacts, and
symmetric contacts, see Figure 3a and Supporting Information Figure SI3. The effect of front contact (illumination side) can be appreciated only at high and intermediate frequencies. However, at low frequency when GDC is observed, $\varepsilon'$ values are independent of front contact. A similar trend is observed for $\varepsilon'$ when the back contact is modified, see Supporting Information Figure SI3. The increase of GDC observed cannot be attributed to an effect related with the photocurrent as it is also obtained when blocking contacts (20 nm of CaO) are inserted in the front or in the back contact. In this sense, the independence of the phenomena with the kind of contact suggests an intrinsic effect related with bulk perovskite. The application of bias voltage at room temperature, from 0 to 1 V, with this last value being similar to the photovoltage in the solar cell at 1 sun, increases markedly, the $\varepsilon'$ and finally provokes a similar GDC effect to that of photogeneration, see Supporting Information Figure SI5. These results point to a direct relation between the charge carrier density and the increase of the giant permittivity, which indistinctly occurs due either to photogeneration or to carrier injection by applied bias.

Voltage and temperature dependence of the GDC effect are analyzed in Figure 3b and Supporting Information Figures SI5 and SI6. At 0 V and low temperature, a relative permittivity of $\varepsilon_\infty \approx 7$ is observed at high and intermediate frequencies. This is a realistic value for the geometric dielectric permittivity of the sample, considering that a value of 7.1 has been recently calculated for the CH$_3$NH$_3$PbI$_3$ perovskite. At high $T$, a richer permittivity pattern is obtained, Figure 3b. There is a first step at high frequency bringing $\varepsilon'$ to values $\sim 100$ in a thermally activated process. This increase of $\varepsilon'$ should be related with a capacitance at the contacts. At temperature of 273 K and higher, see Supporting Information Figure SI6, a second step appears that increases real permittivity to $10^2$–$10^3$. Finally, a third step appears at low frequency promoting real permittivity to high GDC of $10^3$–$10^5$. Results in Figure 3 confirm that the giant dielectric permittivity is related with the increase in carrier density due to illumination, charge injection, or temperature. Although the dielectric permittivity has been previously studied for these perovskite materials, there are no reports of studies under illumination or at frequencies as low as the analyzed in this paper, and consequently GDC has not been previously reported. Nevertheless, previous results of $\varepsilon'$ as high as 200 have been reported for X = (Cl, Br) perovskite single crystals at 50 Hz. These values are in the range of the results shown here.

In summary, the large number of samples investigated, with a wide variation of internal morphologies, compositions, and contacts, including samples with insulating contacts, show the GDC effect in all cases. Therefore, it is reasonable to assume that the large dielectric constant is an intrinsic effect related to increased population of electronic carriers and not an interfacial one.

Already in the dark (without added carriers), the perovskite shows a very large static dielectric constant. This feature reflects the response of small dipolar domains to the external electrical field. The large native dielectric constant could be induced by structural fluctuations of the perovskite cell, aided by the large freedom of rotation of the polar CH$_3$NH$_3^+$ cation. The dipole–dipole interaction is weak so that the correlation length $\xi_\infty$ of the dipolar domains may comprise only a few unit cells. These domains tend to align to the external field. According to our observations, when carriers are injected, an enhanced polarizability is induced by electronic carriers located in the conduction band and holes in the valence band, corresponding
in the first case to the hybridizations of the 6p orbitals of B (lead) and to hybridizations of the 6s orbitals of B and 5p orbitals of X (halide) for the valence band. However, in a highly polar crystal, the electronic carriers become strongly localized by electron–phonon coupling. The self-stabilized electronic charge in a deformable polar medium is termed a polaron, and its slow motion, which drags the lattice distortion, is denoted polaron hopping. The presence of excess localized charge, with a relative positional freedom to move under external or thermal force, modifies the ionic bonding balance of the unit cell and causes local distortion. Previous experimental results reveal a high mobility of carriers but those measurements are obtained at 10^9 Hz which is 9 orders of magnitude faster than the dynamic polarization observed here. Terahertz conductivity only probes the electronic carrier dynamics in a very short scale vibrational motion. The carrier-induced enhanced polarization is on a very slow scale vibrational motion. The low frequency conductivity decreases by 2 orders of magnitude due to long-range carrier transport. As the experimental results reveal a high mobility of carriers but those are only observed at 10^9 Hz which is 9 orders of magnitude faster than the dynamic polarization observed here. Terahertz conductivity only probes the electronic carrier dynamics in a very short scale vibrational motion. The large dielectric constant removes Coulomb attraction between carriers and facilitates ambipolar transport by electronic charge screening. These facts could have profound implications for the development of new optoelectronic devices as photonic control of memory devices or capacitance based photodetectors. The authors declare no competing financial interest.

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Supporting Information

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Fig. S11. Methylammonium (MA) lead triiodide perovskite, MAPbI$_3$, building blocks and unit cells of (a) the orthorhombic phase ($T < 170$ K) $^1$, (b) the tetragonal phase ($170 – 329$ K) and (c) the cubic phase ($T > 329$ K) $^2$. Blue point is Pb cation and red point is I anion, white and cyan spheres represent C and N atoms from MA. Note that MA ions are fully disordered in the cubic phase (respect to the orientation of the C-N axis itself and around the C-N), the order increases in tetragonal and orthorhombic phases $^3$.

**Experimental methods:**

*Cleaning and pre-treatment of the FTO substrates*

The pre-patterned FTO substrates (2.5 x 2.5 mm, TEC15) were thoroughly cleaned with aqueous soap and rinsed with MiliQ water. Then, the substrates were immersed in a mixture of acetone:isopropanol (1:1 v/v) and sonicated for 15 minutes. The sonicated substrates were rinsed with ethanol and dried with compressed air. Next,
a UV/ozone treatment was performed for 20 minutes. Finally, the layers of the materials employed for the device preparation were deposited by following the methodologies mentioned below.

**Deposition of the materials**

**TiO$_2$ Compact Layer**

TiO$_2$ blocking layer was deposited by spraying a solution of titanium diisopropoxide bis(acetylacetonate) (75% in 2-propanol, Sigma-Aldrich) diluted in ethanol (1:39, v/v), using nitrogen as carrier gas, onto the hot substrates (450 °C). The FTO-TiO$_2$ electrodes were kept at this temperature for 30 minutes and then cooled down to room temperature.

**Mesoporous TiO$_2$ layer**

The mesoporous TiO$_2$ layer (~200 nm) was deposited by spin coating at 5000 rpm during 30 s using a TiO$_2$ paste (Dyesol 18NRT, 20 nm average particle size) diluted in terpineol (1:3, w/w). After drying at 80 °C during 15 min, the TiO$_2$ layers were heated up to 470 °C for 15 min and cooled to room temperature.

**Mesoporous Al$_2$O$_3$ layer**

The mesoporous Al$_2$O$_3$ layer (~400 nm) was deposited by spin coating a colloidal dispersion of Al$_2$O$_3$ (Sigma-Aldrich, product number 702129, < 50 nm particle size) diluted (1:2 v/v) in isopropanol at 1500 rpm during 60 s followed by a drying process at 135 °C during 30 minutes.

**Thin-film layer of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$**

The perovskite precursor solution (100 µl), which consists of 5.32 mmol of methylammonium iodide (845.6 mg), 1.77 mmol of PbCl$_2$ (492.6 mg) and 2 ml of anhydrous DMF, was spin-coated onto the substrates inside the glove-box at 2000 rpm during 60 s. After the deposition, the substrate was kept at room temperature for 15 min and then heated up to 100°C during 2 hours in an oven under air atmosphere.

**Embedding process of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ in a mesoporous scaffold**

The perovskite precursor solution (CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$) was spin-coated onto a substrate with a mesoporous layer following the above mentioned thin-film layer deposition procedure. In this case, the substrate was kept at 80 °C for 10 min inside the glove-box and then heated up to 100°C during 2 hours in an oven under air atmosphere.

**Embedding process of CH$_3$NH$_3$PbI$_3$ in a mesoporous TiO$_2$ scaffold**

The CH$_3$NH$_3$PbI$_3$ perovskite film was deposited using a two-step sequential deposition method. The PbI$_2$ was dissolved in N,N-dimethylformamide at a concentration of 33 % (w/w) under stirring at 80 °C. The PbI$_2$ solution was spin-coated
onto the substrate with the corresponding mesoporous layer at 6500 rpm during 90 s and dried at 80 °C for 30 min. After cooling down to room temperature, the films were dipped in a solution of CH$_3$NH$_3$I in 2-propanol (10 mg/ml) for 30 s, rinsed with 2-propanol and dried at 80 °C during 30 min.

**Spiro-OMeTAD HTM layer**

The Spiro-OMeTAD solution was prepared by dissolving 72.3 mg (2,2′,7,7′-tetrakis(N, N-di-p-methoxyphenylamine)-9,9-spirobifluorene) (spiro-OMeTAD), 28.8 µl of 4-tert-butylpyridine and 17.5 µl of a stock solution of 520 mg/ml lithium bis(trifluoromethylsulphonyl)imide in acetonitrile in 1 mL of chlorobenzene. The spin-cast film deposition was carried out by spreading 100 µl of the Spiro-OMeTAD solution on the substrate and rotating the sample at 4000 rpm during 30 s under air conditions.

**P3HT HTM layer**

The P3HT solution was prepared by dissolving 15 mg of P3HT in 1 ml of anhydrous chlorobenzene and it was deposited by a two step spin-cast recipe (500 rpm, 30 s and 1500 rpm, 30 s).

**CaO blocking layer**

For the devices with charge blocking contacts, a 20 nm thick layer of Ca was deposited by thermal evaporation of calcium under ultrahigh vacuum conditions and subsequent oxidation under room conditions for 24 hours to afford the desired CaO layer.

**Au electrodes deposition**

The deposition of the metal contacts was performed by thermal evaporation of a 60 nm layer of gold under ultrahigh vacuum conditions using a commercial MBraun vacuum chamber. (0.2 Å/s during the first 10 nm, then the rate was gradually increased up to 1.5-2 Å/s).

**Characterization of the devices**

The electrochemical impedance spectroscopy (EIS) measurements were carried out by means of a FRA equipped PGSTAT-30 from Autolab under 1 sun illumination (100 mW·cm$^{-2}$) conditions at different forward voltages and applying a 20mV A/C voltage perturbation over the DC bias with a frequency ranging, in most of the cases, between 1 MHz and 0.05 Hz (5 points/decade). White LEDs were used for illumination, controlling light intensity with neutral filters.

The temperature controlled EIS measurements were carried out by using a potentiostat coupled with a temperature controlled sample holder, ranging from -100 °C to +100 °C with 25°C steps, in dark conditions. A series of DC voltage were applied (from -1 V to +1 V in 0.5 V steps), the frequency range was comprised between 1 MHz and 0.05 Hz (5 points/decade) and the A/C voltage perturbation was 20 mV. The
microstructural features and cross sectional thickness of the active layers of the prepared devices were analyzed using a JEOL-JSM-7001F field emission scanning electron microscope (FE-SEM).

**Dielectric relaxation data**

![Dielectric Relaxation Data](image)

Figure SI2: Effect of film structure on dielectric constant and conductivity. Bode plot of the real and Imaginary part of dielectric permittivity under dark and 1 sun illumination conditions for thin film of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ perovskite using (a) and (b) Al$_2$O$_3$ scaffold; (d) and (e) TiO$_2$ scaffold; and (g) and (h) no scaffold. Bode plot of the real part of conductivity under dark and 1 sun illumination conditions for thin film of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ perovskite using (c) Al$_2$O$_3$ scaffold; (f) TiO$_2$ scaffold; and (i) no scaffold. Samples present asymmetric (diode) configuration with compact TiO$_2$ front contact and spiro-OMeTAD/Au as back contact. Measurements were carried out at room temperature and 0 V applied bias.
Figure SI3: Effect of different contact. (a) Different front contact (contact through which the sample is illuminated, see Fig. 1a). Three different front contacts are checked FTO/TiO$_2$, FTO/spiro-OMeTAD and bare FTO, with the same back contact spiro-OMeTAD. Real part of dielectric permittivity under dark and 1 sun illumination conditions for thin film of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ perovskite without scaffold using different front contact, with spiro-OMeTAD as back contact; (b) different back contact with FTO as front contact except for sample with Au in which compact TiO$_2$ has been used as front contact in order to avoid short-circuits; and (c) blocking contacts with a thin CaO (~20 nm) isolating layer at the front or at the back contact. Measurements were carried out at room temperature and 0 V applied dc bias in all the cases.

The effect of front contact can be appreciated only at high and intermediate frequencies, as we have recently point out $^4$. But at low frequency when GDC is observed, $\varepsilon'$ values are independent of front contact. Similar trend is observed for $\varepsilon'$ when it is the back contact the modified one, see Figure SI3b. In this case just FTO is used as front contact, except for sample with Au back contact for which TiO$_2$ compact is deposited on top of FTO in order to avoid shortcuts. In addition the giant $\varepsilon'$ observed
cannot be attributed to an effect related with the photocurrent as it is also observed when blocking contacts (20 nm of CaO) are inserted in the front or in the back contact, see Fig. SI3c. The independence of the phenomena with kind of contact points to an effect related with bulk perovskite.

**Figure SI4:** Permittivity for CH$_3$NH$_3$PbI$_3$ perovskite. Bode plot of the real part of dielectric permittivity under dark and 1 sun illumination conditions for thin film of CH$_3$NH$_3$PbI$_3$ perovskite. Samples present asymmetric (diode) configuration with compact TiO$_2$ front contact and spiro-OMeTAD/Au as back contact. Measured at room temperature with 0.1 V of applied DC bias.
Figure SI5: Effect of applied bias voltage. Bode plot of the real part of dielectric permittivity at different applied bias conditions for thin film of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite without scaffold using asymmetric contacts, TiO$_2$ and spiro-OMeTAD, (a) under dark and (b) 1 sun illumination. Real part of dielectric permittivity at different applied bias conditions for thin film of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite without scaffold using symmetric contacts, spiro-OMeTAD, (c) under dark and (d) 1 sun illumination. All measurements have been carried out between 75 kHz and 50 mHz. For some samples the results at low frequency are not represented as negative capacitance has been found in this range.

Fig. SI5 shows the effect on $\varepsilon'$ of applied bias for samples with symmetric and asymmetric contacts, under dark and 1 sun illumination conditions. Taking as reference the sample with asymmetric contacts positive voltage in Fig. SI5 is forward bias and negative potential is reverse bias. Note that for asymmetric device the photoinduced effect on permittivity is clear. Under dark no giant dielectric constant (GDC) is observed at low frequencies due to the apparition of negative capacitance at high forward bias, see Fig. SI5a.

Asymmetric cell under illumination exhibits giant dielectric permittivity independently of the applied voltage, see Fig. SI5b, even reversely biased. Just at high forward bias, again negative capacitance appears. It is interesting to compare these results with the results from a sample with symmetric contacts of spiro-OMeTAD in both sides of perovskite layer. Similar behavior than for asymmetric samples is observed under illumination, Fig. SI5d, but now the negative capacitance is observed at high reverse bias, this fact is probably due to an incomplete symmetry of both contacts.
Symmetric sample under dark, shows negative capacitance at reverse applied bias. At 0 V there is no negative capacitance and $\varepsilon_0 \approx 1000$ at low frequencies. Interestingly just an applied forward bias of 0.1 V is enough to trigger the GDC two orders of magnitude to $\varepsilon' \approx 10^5$, see Fig. SI5c. Further increase in $\varepsilon'$ is observed as the forward bias increases. The apparition of negative capacitance prevent the observation of the GDC at high forward bias in the cases of asymmetric contacts, see Fig. SI5a. The origin of this negative capacitance and its dependence is currently under study. We have observe experimentally that the observation of the negative capacitance is reduced as the performance of the solar cell increases.

Results depicted in Fig. SI5 points to a direct relation between charge carrier density and GDC due to illumination and carrier generation or to carrier injection by applied bias. In the last case, another effect, the negative capacitance, is also acting, especially when high voltages are applied.

![Figure SI6: Effect of temperature. The effect of temperature on dielectric permittivity has been studied under dark for an asymmetric sample under different applied bias. Bode plot of the real part of dielectric permittivity at different temperatures at three different applied bias conditions for thin film of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ perovskite without scaffold using asymmetric contacts, TiO$_2$ and spiro-OMeTAD. Arrow indicates the temperature increase. The lowest temperature was -100ºC and the highest 100ºC, dielectric permittivity was measured each 25ºC.](image)

At 0 V and low temperature a $\varepsilon_x \approx 7$ is observed at high and intermediate frequencies. This is a realistic value for the geometric dielectric permittivity of the sample. This value is of the same order than the $\varepsilon_x \approx 23.3$ obtained from powdered CH$_3$NH$_3$PbI$_3$ crystals pressed to form disks $^3$. Note that significantly different configurations are used for both samples justifying the different obtained value.

As T increases a first step in bringing it to values $\sim$100 is thermally activated. This increase of $\varepsilon'$ should be related with a capacitance at the contacts $^4$. This step is also clearly appreciated at higher applied forward bias. For 0 and positive T in the Celsius scale a second step appears increases the low frequency $\varepsilon'$ to $10^3$-$10^4$. At higher applied forward bias this second step is difficult to appreciate due to the apparition of third step which leads the permittivity to reach extremely values. Note that T also affects negative capacitance apparition and it is not observed at high T. Results in Fig. SI6 confirm that
the giant dielectric permittivity is related with the increase in carrier density due to illumination, charge injection or temperature.

References


