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An Explanation of the Photoinduced Giant Dielectric Constant of Lead Halide Perovskite Solar Cells.

Darryl P Almond and Chris R Bowen.

Material Research Centre, Department of Mechanical Engineering, University of Bath, Bath, BA2 7AY, UK.

ABSTRACT

A photoinduced giant dielectric constant of ~10^6 has been found in impedance spectroscopy measurements of lead halide perovskite solar cells. We report similar effects in measurements of a porous lead zirconate titanate (PZT) sample saturated with water. The principle effect of the illumination of the solar cell and of the introduction of water into the pore volume of the PZT sample is a significant increase in conductivity and dielectric loss. This is shown to exhibit low frequency power law dispersion. Application of the Kramers-Kronig relationships show the large measured values of permittivity to be related the power law changes in conductivity and dielectric loss. The power law dispersions in the electrical responses are consistent with an electrical network model of microstructure. It is concluded that the high apparent values of permittivity are features of the microstructural networks and not fundamental effects in the two perovskite materials.

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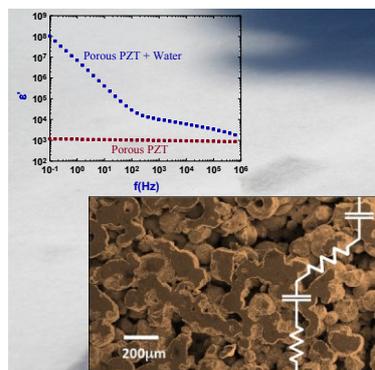
KEYWORDS: perovskite; giant dielectric constant; impedance spectroscopy; permittivity; conductivity; dielectric; porosity

Recently, a giant dielectric constant has been reported in lead halide perovskite solar cells [1]. The relative permittivity in the dark was found to be ~10^3 when measured at very low frequencies (<1 Hz) and to rise under the illumination of 1 sun to ~10^6. The authors suggest the large relative permittivity is induced by structural fluctuations.

Photoinduced carriers modify the local unit cell equilibrium and change the polarisability which is assisted by the freedom of rotation of CH_3NH^{3+}.

The purpose of this work is to point out that somewhat similar dielectric phenomena are observed in many other materials and that these can be explained as being characteristics of materials that have microstructures containing conducting and dielectric phases. The increase in relative permittivity, ε', with the reduction in measurement frequency, over many decades of frequency in a power law fashion, is a part of the "Universal Dielectric Response" identified by Jonscher [2, 3]. The phenomenon is said to be universal because it has been reported in measurements of a very wide range of materials and material types. A key feature of this "Response" is an accompanying increase in the imaginary part, ε'', of the permittivity (the dielectric loss) with reduction in measurement frequency; as also reported for the lead halide perovskite solar cells [1]. This was shown by Jonscher [4] to be a consequence of the Kramers-Kronig relationships for materials exhibiting a fractional power law frequency dependence of permittivity. The relationship may be summarised as: if $\varepsilon' \propto \omega^{n-1}$ then $\varepsilon'' \propto \omega^{n-1}$ and $\varepsilon''/\varepsilon'=\cot(n\pi/2)$ where ω is angular frequency and $0<n<1$. Or, alternatively, if $\varepsilon'' \propto \omega^{n-1}$ then $\varepsilon' \propto \omega^{n-1}$ and $\varepsilon''/\varepsilon'=\cot(n\pi/2)$. Dielectric loss is related directly to the conductivity, σ, of a material ($\varepsilon''=\sigma/\varepsilon_0\omega$, where ε_0 is the permittivity of free space) which in the case of the lead halide perovskite solar cells is greatly enhanced by illumination. "Pure" conductivity is, by definition, frequency independent and the resulting dielectric loss $\varepsilon'' \propto \omega^{-1}$. For such "pure" conductivity the above exponent n=0 and the Kramers-Kronig relationships predict no accompanying permittivity, ε'. However, there is evidence that the low frequency photoinduced conductivity of the lead halide perovskite solar cells shows a weak frequency dependence, n>0, and we will show that this is sufficient to explain the high measured values of ε' at low frequencies.

The authors of this work have shown [5, 6] that the above defined fractional power law behaviour of ε' and ε'' is also a characteristic of large networks of randomly positioned resistors and capacitors. These networks were suggested to be equivalent circuits for materials having complex microstructures containing conductive and insulating/dielectric phases. In many materials conductive phases form microscopic resistors imbedded in an insulating/dielectric matrix. These microscopic resistors are separated from each other by microscopic regions of matrix that act as microscopic capacitors which also contribute to AC conductivity. The frequency dependences of the AC conductivities of the large networks were traced to those of the admittances, $Y_c=i\omega C$, of the capacitors that contribute to the random conduction paths in these networks. The authors went on to show [7] that the electrical responses of these networks were exactly reproduced by measurements of a porous sample of the perovskite lead zirconate titanate (PZT) with

the pore volume filled with water. The water became a conductive phase within the insulating/dielectric PZT host. This acted as a model of a material in which an electrically conductive microstructural phase is present within an insulating/dielectric host material. An example of such a material would be a polymer into which graphite flakes or nanoparticles had been mixed.

In the solar cells the perovskite is a polycrystalline thin film. The perovskite crystallites are separated from one another by grain boundaries or voids. Grain boundaries are rich in defects that cause the trapping of carriers, band bending and depletion layers. These effects lead to grain boundary capacitance. Consequently, whilst regions within the bulk of the crystallites become electrically conductive on illumination, they are surrounded by capacitive material, or indeed voids between poorly connected grains. We suggest the effect of illumination on the lead halide perovskite solar cell is to produce an electrical microstructure that is essentially a conductive microstructural phase present within an insulating/dielectric host. This suggestion is supported by the similarity of the AC electrical characteristics of the porous PZT water filled samples with those of the lead halide perovskite solar cells that will be shown below.

The experimental measurements of the effects of filling the pore volume of porous PZT with water [7] are reproduced here in figure 1 because we believe it is instructive to compare them with the measurements of the lead halide perovskite solar cells. The AC conductivity and relative permittivity of the water filled porous PZT sample are shown in figures 1c and 1d.
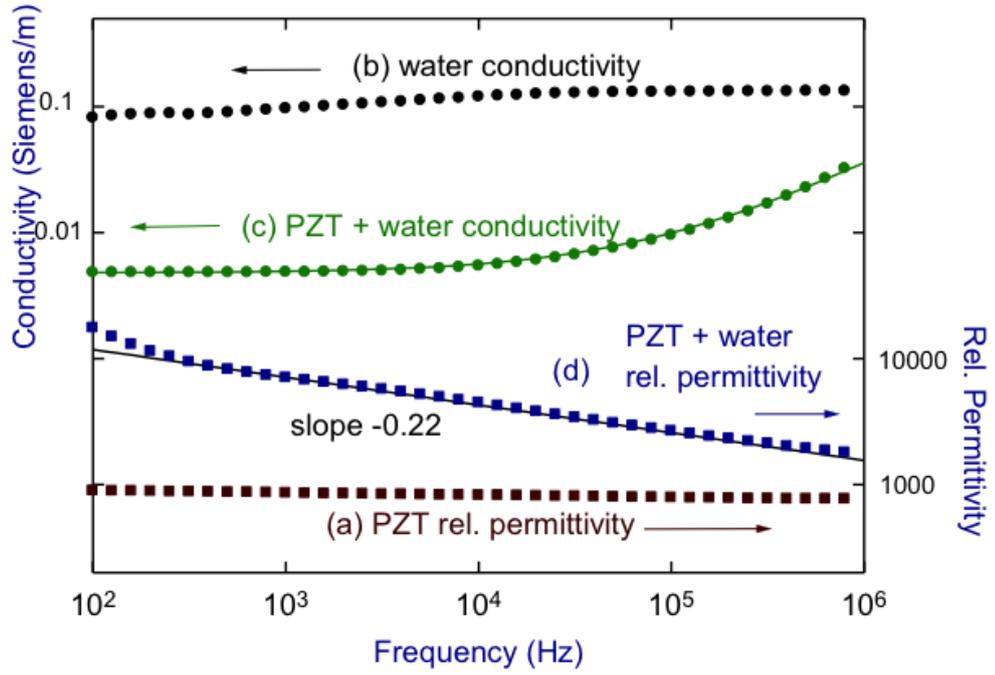
Figure 1. Measurements of (a) relative permittivity of a porous PZT sample, (b) conductivity of water at equilibrium immersed PZT fragments [7], (c) the conductivity and (d) the relative permittivity of the sample saturated with water.

Also shown in the figure are measurements of the AC conductivity of the water and the relative permittivity of the porous PZT sample. PZT is a ferroelectric material with a relative permittivity of 1500. The PZT sample used was 22% porous and found to have a reduced relative permittivity of ~900 that was fairly frequency independent across the frequency range shown in the figure, fig 1a. When the pores were filled with water this rose to 1.75×10^4 at a measurement frequency of 100 Hz and fell in a power law fashion across the frequency range 200 Hz to 1 MHz. The power law exponent, -0.22, matched the proportion of the sample filled with the conductive water, ie the 22% porosity. The solid line shown with the experimental measurements of relative permittivity, fig 1d, was obtained from the expression:

$$\varepsilon_{meas} = (\varepsilon_0 \omega)^{n-1} \varepsilon^n \sigma^{1-n} \sin(n\pi/2) \tag{1}$$

This expression was obtained from the logarithmic mixing rule [8] and found [5,6] to account for the responses of the large networks of randomly positioned resistors and capacitors. To obtain the solid line in fig. 1d, ε was set to equal the relative permittivity of bulk PZT (1500), σ was matched with the measured conductivity of the water (0.1 S/m), fig 1b, and n with the proportion of the sample filled with capacitive material ie the relative density of the PZT

sample = 0.78.   The solid line shown with the AC conductivity data, fig 1c, was obtained by adding the low frequency plateau value of conductivity to the expression for network conductivity:

$$\sigma_{meas}=(\omega\varepsilon\varepsilon_0)^n(\sigma)^{1-n}\cos(n\pi/2) \tag{2}$$

The low frequency plateau value of conductivity (0.0048 S/m) was attributed to the percolation paths of the water through the sample. The match between the experimental data and the prediction based on the network results is excellent.

The high value of relative permittivity (1.75×10^4) measured in the sample at low frequencies is that of the very complex network of microscopic conductors and capacitors formed naturally within the porous sample when pore volume is filled with conductive water.   It does not indicate that the fundamental relative permittivity of PZT has been changed by filling the pores of the sample with water or that any new physics has to be found to explain the enhanced permittivity.   The results, fig 1d, are similar in character to the enhancement of relative permittivity reported [1] for the lead halide perovskite solar cells. Differences are that: the magnitude of the relative permittivity in the solar cells rises to ~10^6 and that measurements extend to the far lower frequency of 0.04 Hz.
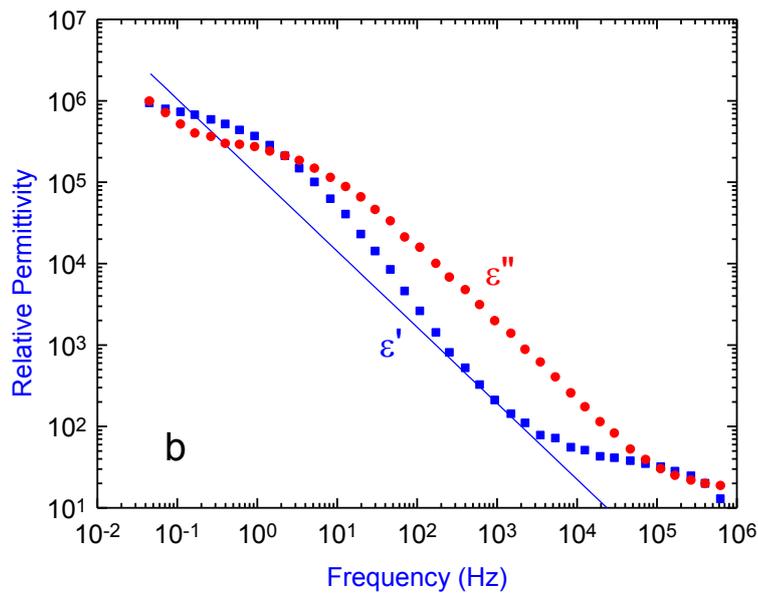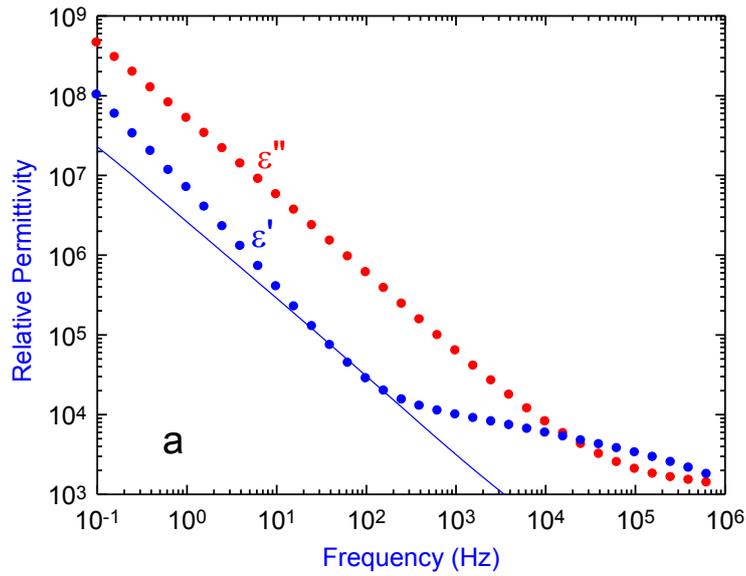
Figure 2. Measurements of the real and imaginary parts of the relative permittivities of (a) a 26% porous PZT sample saturated with water and (b) a lead halide perovskite solar cell, ref.1. The solid lines are the Kramers-Kronig predictions of relative permittivity, $\varepsilon'= \varepsilon''/\cot(n\pi/2)$, where n is obtained from the ω^n frequency dependence of the conductivity plateau, see text and Fig. 3.

For this work, the relative permittivities of a further five water filled porous PZT samples were measured across the wider frequency range of 0.1 Hz to 1 MHz. These five samples had porosities in the range 26 to 32%. All exhibited characteristics that are very similar to those of the 26% porous sample shown in figure 2a. These measurements

show real part of relative permittivity, ε', rising to values exceeding 10^8 at the lowest frequencies. The overall form of this relative permittivity vs. frequency characteristic is very similar to that reported for the lead halide perovskite solar cell under a 1 Sun illumination [1], shown here for comparison in figure 2b. In both the solar cells and the water filled PZT samples the introduction of a significant internal conductivity leads to a massive enhancement of measured relative permittivity and dielectric loss, ε'', at low frequencies. The frequency dependences of the AC conductivities, obtained from the measurements of the dielectric loss, are shown in figure 3.
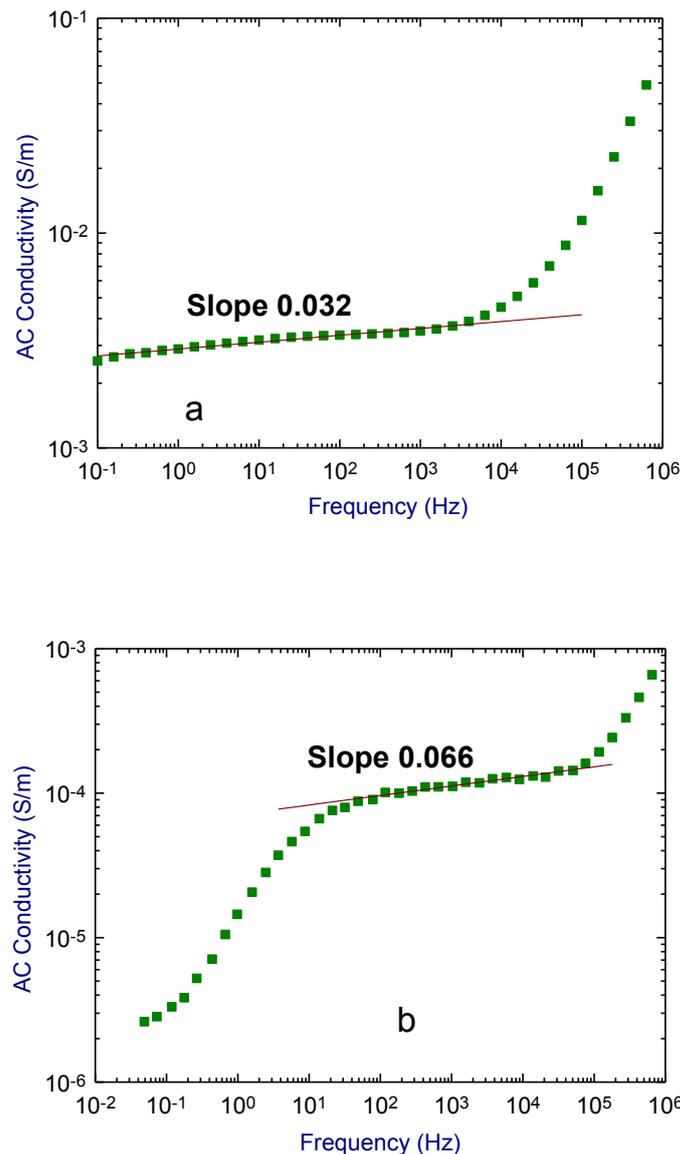

Figure 3. Measurements of the AC conductivities of (a) a 26% porous PZT sample saturated with water and (b) a lead halide perovskite solar cell, ref.1. The solid lines are power law fits, $\sigma \propto \omega^n$, to the low frequency dispersion in conductivity where n=0.032 for water filled porous PZT and n=0.066 for the lead halide perovskite, see text.

The solar cell measurements, fig 3b, are typical the AC conductivities of real complex materials. Across the central range of frequencies there is a "plateau" in conductivity that is usually identified with the potential bulk DC conductivity. At low frequencies, conductivity falls due to electrode polarisation effects at electrodes that block the carriers producing the conductivity. At high frequencies ($>10^5$Hz) there is a power law increase in conductivity, high frequency dispersion, that is fully explained by the results, fig 1, and eqns. 1 and 2 above. The measurements of the water filled porous PZT sample, fig. 3a, differ in that there is far less evidence of electrode polarisation at low frequencies, indicating more effective electrodes. However, the DC conductivity of this sample was found to be 1.4 x 10^{-3} S/m which is significantly lower than the lowest frequency AC conductivity measurement, 2.5 x 10^{-3} S/m, showing some electrode blocking to be present.

A close examination of the "plateaus" in the conductivities of both samples reveals that they exhibit power law increases with frequency. The measurements of the conductivity of solar cell, fig 3b, across the frequency range 10^2 to 10^5 Hz were found to have an ω^n frequency dependence with the power law exponent n=0.066 and for those of the water filled porous PZT sample, fig 3a, across the frequency range 10^{-1} to 10^3 Hz n=0.032. These shallow power law increases in AC conductivity are known as low frequency dispersions [4]. Associated with them, by the Kramers-Kronig relationships above, or explicitly by eqns. 1 and 2, are power law decreases in permittivity across the frequency ranges over which the power law dependence of conductivity is found. These contributions to relative permittivity are shown as solid lines figures 2a and 2b.

At low frequencies, the real part of the measured relative permittivity of the water filled porous PZT sample, fig.2a, is close to the component (the solid line) obtained by the Kramers-Kronig relationships. The additional permittivity found at lowest frequencies is attributed to a weak electrode polarisation effect. This effect produces a more substantial addition to the permittivity of the solar cell, fig.2b; in agreement with the strength of this effect evident in the frequency dependence of AC conductivity shown in fig. 3b. In both cases, the large measured values of relative permittivity at low frequencies and their rapid decrease with frequency can be understood as being a consequence of the observed low frequency dispersion in AC conductivity and its related effect on dielectric loss.

Low frequency dispersion is found to be a feature of the plateau in AC conductivity that is generally interpreted as the potential bulk DC conductivity of a sample, given perfectly conducting electrodes. In real solid samples, this bulk DC conductivity is formed by numerous filamentary percolation paths of a conductive phase that link the electrodes.

It has been seen that for the two cases under discussion here that the power law exponents are small (0.066 and 0.032). The power law exponents for high frequency dispersion were shown to match the proportion of the material occupied by a dielectric/insulating phase. If low frequency dispersion is caused by a similar phenomenon, the small power law exponents indicate effects caused by small quantities of dielectric/insulating material.

The model that we propose to explain low frequency dispersion is a simple refinement of the accepted percolation model for DC conductivity. We suggest that in addition to the continuous percolation paths of conducting phase there are likely to be numerous incomplete percolation paths in which only small quantities of a dielectric/insulating phase are present. These small quantities of the dielectric/insulating phase block the use of these paths for DC conduction but they act as microscopic capacitors that enable these paths to contribute to AC conduction. As frequency is raised the admittances, $i\omega C$, of the small capacitive regions increase, enabling additional percolation paths to contribute to electrical conduction, resulting in the shallow increase in conductivity with frequency known as low frequency dispersion.

Further evidence of the physical phenomena occurring in the two cases is provided by the frequency dependences of the phases of the electrical responses shown in figure 4. The phase, or phase shift, of an electrical response is the difference in phase between AC current and voltage. In a purely conductive material, current and voltage are in phase and this phase is 0°. By contrast, in a purely capacitive material AC current lags AC voltage by 90° producing a phase, or phase shift, of -90°. The phase, θ, is related to the real and imaginary parts of dielectric response by:

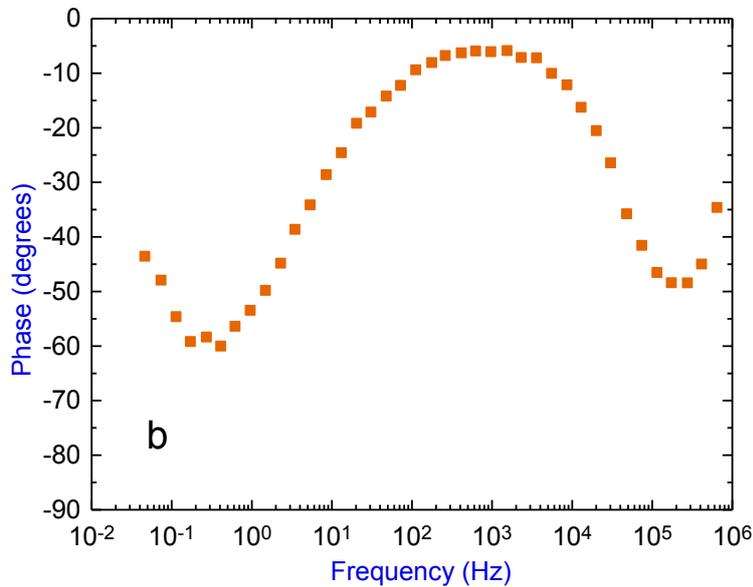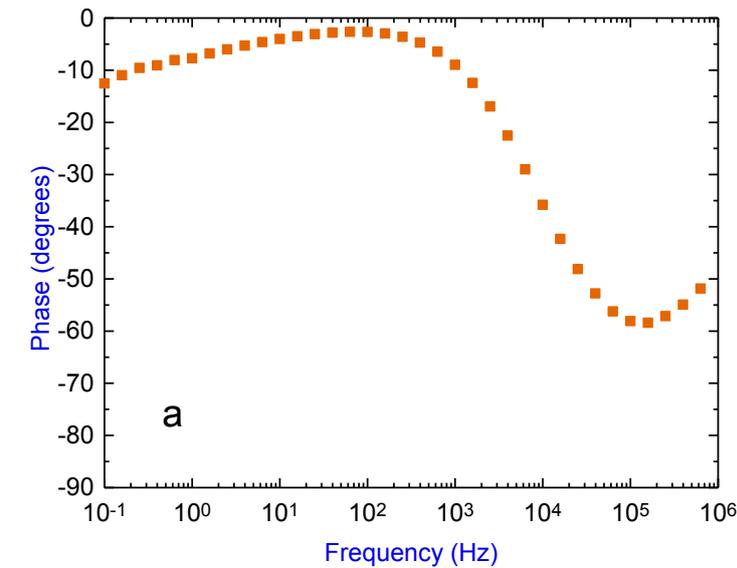$$\Theta = -\tan^{-1}(\varepsilon'/\varepsilon'') \qquad\qquad (3)$$

Figure 4. Measurements of the phases of the electrical responses of (a) a 26% porous PZT sample saturated with water and (b) a lead halide perovskite solar cell, ref.1.

The frequency dependence of the phase of the water filled porous PZT sample, fig 4a, indicates the sample to be neither purely conductive nor purely capacitive across the whole frequency range. At low frequencies (< 100 Hz) phase has small negative values indicating an AC response that is predominantly conductive (carrier based) but having a small capacitive displacement current contribution. This is consistent with the suggested interpretation of the low frequency dispersion in AC conductivity. At higher frequencies (>10^4 Hz) phase drops to <-60° where high frequency dispersion occurs. This is again consistent with the explanation for high frequency dispersion above that

involves AC conduction throughout the bulk of the sample by utilising both carrier conduction through the water and displacement currents through the PZT. The simulations of the electrical responses of large networks of randomly positioned resistors and capacitors [5] show phase to be simply related to the proportion of the network, n, occupied by capacitors: $\theta=-n\pi/2$.

The frequency dependence of the phase of the solar cell, fig. 4b, has small negative values across the intermediate frequency range where the plateau in conductivity, fig. 3b, is found, again indicating this to be predominantly conductive (carrier based) but having a small capacitive displacement current contribution. At higher frequencies the phase drops to ~-50° where the onset of high frequency dispersion occurs. At low frequencies there is also a fall corresponding to the decrease in conductivity, fig 3b, resulting from electrode polarisation effects caused by blocking electrodes.

The principle effect of illumination on the lead halide perovskite solar cell and of the addition of water to porous PZT is to significantly raise electrical conductivity. However, neither material/system becomes perfectly conductive and the consequence of this is the high relative permittivity obtained by impedance spectroscopy measurements. These relative permittivity measurements do not indicate that a super high permittivity material has been formed or that there is unexplained new physics occurring in the materials. The principle characteristic of both is that they are conductive, and measurements of this conductivity or of the imaginary part of relative permittivity dominate the electrical response. However, because there is a very small capacitive contribution to the AC conduction processes impedance spectroscopy indicates a related real part of relative permittivity, required by the Kramers-Kronig relationships as explained above.

It is concluded that the impedance spectroscopy measurements of the lead halide perovskite solar cells do not indicate the fundamental relative permittivity of the perovskite to have been massively enhanced by illumination and that there is no need to find new physical models to explain such an effect. The very significant electrode blocking effect evident in the conductivity data, fig 3b, is a concern as it indicates that the electrodes are very inefficient.

In general, reports of exceptionally high measurements of dielectric permittivity are for materials that also have a high electrical conductivity. This may be provided by the inclusion of a second conductive phase or internally by free carrier creation. Such materials are of no practical value for capacitive devices because their conductivities provide

leakage currents that prevent the storage of charge and because their high dielectric losses make them worthless for resonator or filter applications.

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