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2015 J. Phys.: Conf. Ser. 609 012001

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# Light induced structural changes in $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite Solar Cells

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**Abstract.** Perovskite solar cells have recently become one of the most promising alternative to the current solar cell technologies by achieving efficiencies superior to 20%. Owing to their distortable structure these devices have proven to show unusually slow relaxation processes upon illumination. We have identified this phenomenon in the frequency domain by impedance spectroscopy (IS) and in the time domain by transient photovoltage decay (TPD) and open circuit voltage decay (OCVD). However the origin of this process is still unclear although three main hypotheses have been proposed in the literature: i) high internal electric field, ii) ferroelectric domains and iii) ion/defect diffusion. In this conference paper we first present our works on light induced structural changes in perovskite and then discuss the main hypotheses previously mentioned with the insight of first principle calculations.

## 1. Introduction

$\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite has proven to be very successful as a light absorber, leading to solar cells with efficiencies as high as 20.1% [1]. This material is composed of an organic methyl ammonium cation,  $\text{CH}_3\text{NH}_3^+$ , which is located in an inorganic framework composed of four  $\text{PbI}_6$  octahedra.  $\text{CH}_3\text{NH}_3^+$  has been shown to be bound to the inorganic  $\text{PbI}_6$  octahedra through Van der Waals interactions. In such material the lowest conduction band is formed of the  $\text{Pb}^{2+}$   $6p$  orbitals, while the highest valence band is constituted by the  $\text{I}$   $5p$  orbitals [2]. Moreover, this perovskite structure displays a gap of 1.5 eV. Note that the gap of lead halide perovskite is strongly influenced by the nature of the halide anion [3, 4].

Structurally speaking this type of perovskite undergoes three phase transitions with temperature.  $\text{CH}_3\text{NH}_3\text{PbI}_3$  is in the orthorhombic phase at low temperature ( $T < 161.4$  K), in the tetragonal phase at higher temperatures below 330.4 K and in the cubic phase above 330.4 K [2]. At room temperature  $\text{CH}_3\text{NH}_3^+$  is therefore in the tetragonal phase and its crystallographic structure is distortable. This latter point is of considerable interest for photovoltaic applications since various studies have shown that perovskite undergoes structural changes under illumination.

In the following we first summarize the works published in our group, showing through electrochemical techniques the light induced structural changes in the perovskite absorber. Then we discuss, with the insight of first principle calculations, the main possible causes that can be found in the literature for such peculiar behaviour. Finally we give our conclusions on the topic.

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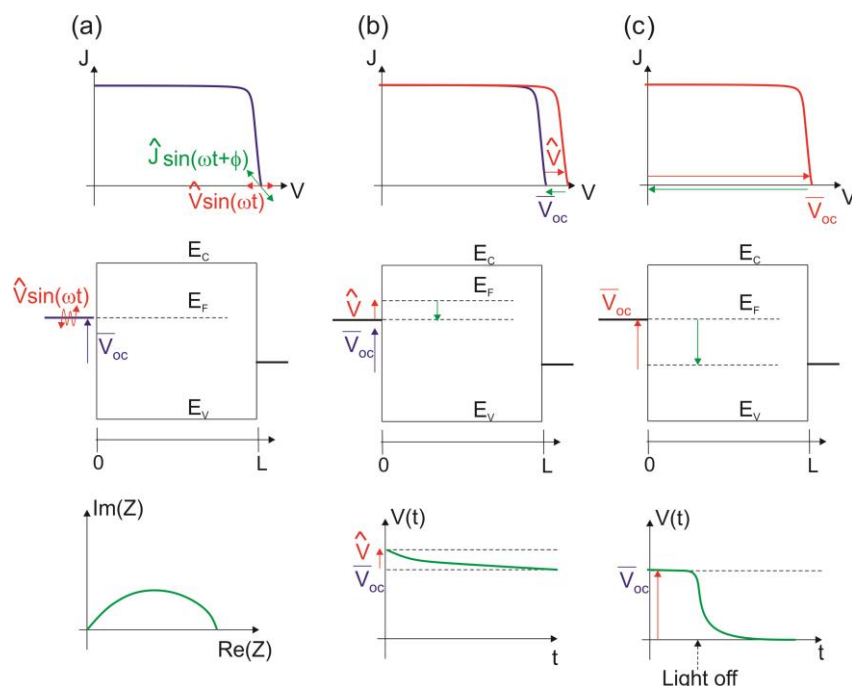
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## 2. Light induced structural changes in $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite.

Recently we have probed the relaxation processes in  $\text{CH}_3\text{NH}_3\text{PbI}_3$  solar cells by means of electrochemical techniques. Mainly we have used impedance spectroscopy (IS), transient photovoltage decay (TPD) and open circuit voltage decay (OCVD). Before entering into the details of our results, let us briefly explain the basic principles underlying these techniques.

### 2.1. Probing $\text{CH}_3\text{NH}_3\text{PbI}_3$ structural changes by electrochemical techniques



**Figure 1.** Underlying principles of (a) impedance spectroscopy, (b) transient photovoltage decay and (c) open circuit voltage decay. For each method, we show how the J-V curve (first row) and the energy diagram (second row) are modified when applying these techniques and we show how the response signal is typically represented (third row). Note that for simplification of the energy diagram, only the Fermi level of the minority carrier is represented. In this scheme blue lines and arrows refer to the steady state, red ones to the state resulting from the excitation (by light or voltage) and green ones to the response of the system after excitation.

In figure 1, we present a scheme that summarizes the techniques mentioned above. The strength of these techniques relies in their ability to decouple the different faradic (i.e. resistive) and capacitive processes that occur in a solar cell, which is impossible to achieve through steady state measurements. IS and TPD are small perturbation methods unlike OCVD. The main difference between IS and TPD relies in the nature of the small perturbation. In IS the perturbation is a sinusoidal, frequency dependent voltage,  $\hat{V}$  that is added to a steady state voltage,  $\bar{V}$ , and the resulting perturbation of the current,  $\hat{J}$ , is measured. IS measurements are usually represented in terms of impedance ( $Z = \hat{V}/\hat{J}$ ) in the complex plane and are interpreted with equivalent electrical circuits. In TPD a small pulse or step of voltage is applied at open circuit and one monitors the open circuit voltage decay to the steady state voltage. These measurements are interpreted in terms of decay times, which can be related to the electrical elements used for the interpretation of IS. Finally, the OCVD technique differs from the TPD in that the large perturbation of voltage decays to the ground state and not to a given steady state. The advantage of this technique over the TPD is that the measured signal is less noisy. It should be noted however that the OCVD is not necessarily reconstituted from the superposition of TPDs and both techniques may give different information.

### *2.2. Detection of anomalous relaxation processes in $\text{CH}_3\text{NH}_3\text{PbI}_3$ upon illumination.*

Our impedance measurements revealed the presence of a very high capacitive effect at low frequency upon illumination of the perovskite solar cell. From this measurements we could evaluate the static dielectric constant to take values as high as  $10^6 - 10^7$  whereas in dark conditions it was assessed to be around  $10^2 - 10^3$  [5]. These measurements suggest that light activates a new polarization process, which is coupled to the classical electronic drift diffusion recombination [6]. These measurements were confirmed by TPD where slow decay times (around 1.5 seconds) have been measured [7]. More evidence has been suggested by our recent work on the OCVD technique applied to perovskite solar cells where decay times of the order of 10 – 100 seconds have been measured [8]. Moreover we have analyzed the shape of these decays and found out that they follow a power law time dependence, which suggests cooperative polarization/depolarization processes. Our results do shine light on a new polarization process in  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite solar cells but the nature of this process is still unknown. For this latter purpose, first principle calculations are needed.

### **3. Insight from first principle calculations.**

Three main hypotheses have been suggested in order to explain the high polarization of the perovskite at low frequency: the existence of a strong internal electric field, ferroelectric domains and ion/defect diffusion in the perovskite absorber. Let us quickly review and discuss these hypotheses with the insight of first principle calculations, which have been performed by other groups.

#### *3.1. High internal electric fields.*

DFT calculations have shown that effective masses for both  $n$  and  $p$  type  $\text{CH}_3\text{NH}_3\text{PbX}_3$  perovskites are unusually low (0.12 – 0.14) [9, 10]. These results suggest a low density of states for electrons and holes. In fact, Manser et al. [11] have measured a density of states for the lower edge of the conduction band of the order of  $10^{17} \text{ cm}^{-3}$ , which is two orders of magnitude less than the one of silicon. It is therefore likely that strong electric fields are present in lead halide perovskite cells. Note however that these fields are strongly dependent on the contacting materials and fabrication method of the perovskite absorber. It should also be remarked that neither the theoretical nor the experimental studies explain how the generation of free carriers by illumination of the lead iodide perovskite influences this electric field.

#### *3.2. Ferroelectric domains.*

Several groups have studied the possible existence of ferroelectric domains in  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite based solar cells. Three causes have been identified: distortion of the inorganic octahedra, off centering of the  $\text{Pb}^{2+}$  cation and rotation of the  $\text{CH}_3\text{NH}_3^+$  ion in its inorganic “cage” [12–14]. However this last process is unlikely to cause the low frequency polarization observed experimentally since at room temperature the rotation time of the organic cation is of the order of picoseconds. It is worthwhile noticing that the effect of light on ferroelectric domain formation has not been considered in these studies.

#### *3.3. Ion/defect diffusion*

The possibility and conditions for a possible ion/defect diffusion in perovskite solar cells have still not been proven theoretically. However the existence of low formation energy defects has been demonstrated through DFT calculations. Wan-Jian Yin and co-workers have shown that deep defects resulting from the covalent bonds formed by Pb (dimers) and I (trimers) have a high formation energy and are consequently unlikely to be formed [15]. On the contrary, shallow defects arising from ionic interaction between  $\text{CH}_3\text{NH}_3^+$  and the inorganic  $\text{PbI}_6$  cage have a low formation energy. In particular lead vacancies and methyl ammonium interstitials are more likely to be formed. In addition shallow defects of the Frenkel type (interstitials) could act as dopants. However the one of the Schottky type (vacancies) are more likely to dominate the defect

population with a formation energy of 0.14 eV and could reach concentrations higher than 0.4 % [16].

#### 4. Conclusions.

Through three electrochemical techniques (IS, TPD and OCVD), we have shown that perovskite based solar cells display unusually slow relaxation processes, which are associated to the polarization of the perovskite absorber at low frequency. These findings have considerable importance for the field of photovoltaics since solar cells work in steady state condition (zero frequency). However the origin of such process is still under discussion. In the literature, three main possible reasons have been suggested: high internal electric field, ferroelectric domains and ion diffusion. The first one could be justified by the low density of states measured experimentally and calculated with DFT. The second hypothesis has been analysed by DFT and the distortion of the  $\text{PbI}_6$  cage, the off-centering of the  $\text{Pb}^{2+}$  cation and the rotation of the  $\text{CH}_3\text{NH}_3^+$  cation have been regarded as possible reasons for the creation of ferroelectric domains. Finally, ion/defect diffusion has not been demonstrated theoretically but the likely existence of shallow defects has been shown due to their low energy formation. Nevertheless none of these studies has been performed under illumination conditions, i.e. only the ground state perovskite absorber has been studied. The important problem of the structural changes induced by light therefore remains. In other words, one fundamental question is: how does light induce ferroelectric domains, ion diffusion or any other process that could cause the low frequency polarization?

#### Acknowledgments

The author wishes to thank Dr. Rafael S. Sanchez and Prof. Juan Bisquert for reading the manuscript and acknowledge funding from the European Union Seventh Framework Program [FP7/2007–2013] under grant agreement 316494.

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