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# PHOTOCURRENT SPECTRA AND TRANSPORT CHARACTERIZATIONS ON HALIDE PEROVSKITES THIN FILMS

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**ABSTRACT:** In this study we present a study of the transport parameters of multi-cation halide perovskite thin films under different states: as-deposited, light-soaked and after several days of recovery. These transport parameters were investigated by steady state dark and photo-current measurements as well as with advanced characterization techniques such as Fourier transform photocurrent spectroscopy (FTPS) and steady state photocurrent grating (SSPG) experiment. FTPS is a powerful technique that allows to analyze the weak absorption due to states present in the gap of semiconductor materials down to photon energy of 1 eV or even smaller. With the SSPG technique one has access to the ambipolar diffusion length of the same type of materials. Deduced from these three experiments, the evolution of the transport parameters (dark and photo- conductivity, density of states, diffusion length) of triple cation perovskite with light-soaking and recovery will be underlined in this communication.

**Keywords:** Multi-cations perovskite thin films, FTPS, SSPG, aging influences

## 1 INTRODUCTION

In the field of semiconductor material characterizations, spectroscopic methods have been widely applied. It is especially important for optoelectronic devices such as solar cells and light emitting diodes. Since the photo-effect phenomenon is highly sensitive to scanning wavelengths, the material spectral photoresponse bridges illumination light and its photoconductivity. Besides, the semiconductor density of states can be also associated closely with light absorption and photocurrent. Obtaining the absorption spectrum is therefore an easy way to derive information on the band gap structures such as energy bandgap and deep states. The determination of the material absorption spectrum can be done directly by optical spectroscopy from the measured reflection and transmission spectra. However, when considering a very weak light absorbance, as in the case of below gap photon energy, it becomes very hard to measure this spectrum reliably. To overcome this issue in the weak absorption region, several techniques have been proposed, combining photocurrent spectrum measurement upon light illumination instead of only the optical way via a UV-Visible spectrometer.

Among the photoconductivity-based methods developed to investigate on the absorption spectrum of a material, we can quote the Constant Photocurrent Method (CPM) [1] and Dual Beam Photoconductivity (DBP) (See for instance Ref. [2]). However, Fourier Transform Photocurrent Spectroscopy (FTPS) [3, 4] presents at least two advantages over the aforementioned approaches. First, the Fourier transform method can provide a fast measurement within only few minutes. Indeed, in the CPM method, each wavelength is selected from the light source with a monochromator and the photocurrent is adjusted to a constant value which requires hours of measurement. Secondly, to perform absorption measurements, the resolution of FTPS is nanometric, far better than the CPM resolution.

In this paper we have also investigated on some of the transport properties of perovskite thin films by measuring the carrier diffusion length. For this purpose

we have used the steady state photocurrent grating (SSPG) technique, originally proposed by Ritter and coworkers [5], since this technique allows to directly measure the ambipolar diffusion length ( $L_{amb}$ ). For extended details on this experiment see for instance the review proposed by R. Brüggemann [6].

In addition, to these sophisticated techniques the very simple and well-known dark conductivity measurements as well as the steady state photocurrent (SSPC) experiment can bring valuable information of the properties of the material under investigation.

These characterization techniques (SSPC, SSPG, FTPS) have been applied to the study of opto-electronic properties of perovskite (PVK) thin films, the experiments being performed either under air or under vacuum ( $\sim 10^{-6}$  mBar) on samples either in their as-deposited states or after light-soaking.

## 2 EXPERIMENTAL CONFIGURATIONS

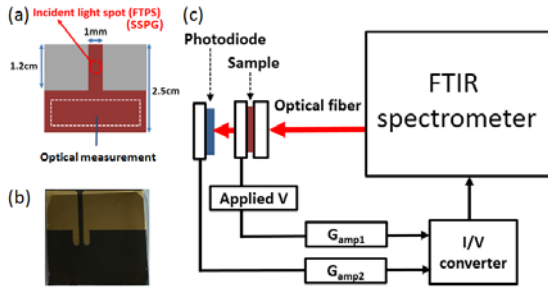
We fabricated triple-cation perovskite thin films (MaFaCs) from a mixture of methylammonium (Ma), formamidinium (Fa) and cesium which was spin-coated on glass with 5% Cs and 10% excess  $\text{PbI}_2$ . For details concerning the preparation of the PVK thin films please refer to [7]. After that, parallel planar gold electrodes were deposited via thermal evaporation, to end with a coplanar geometry as shown in Figure 1(a), in order to perform the electrical measurements such as FTPS, conductivity and SSPG. A typical sample with the PVK film deposited on glass and fitted with gold electrodes is shown in Figure 1(b).

In Figure 1(c), a schematic diagram of the home-made FTPS set-up designed to investigate on the variation of the absorption spectrum above and below semiconductors bandgap is shown. The light coming out of a Fourier transform infrared (FTIR) spectrometer is sent toward the sample via an optical fiber bundle. The current generated by this illumination is amplified and converted into a voltage signal via a current/voltage amplifier and this signal is sent back to the FTIR for

Fourier transform treatment. To derive the FTPS spectra the fluxes, either impinging the film or transmitted through it, are measured via calibrated photodiodes placed immediately behind the sample and the responses of these photodiodes are also treated by the FTIR spectrometer. Details on this bench can be found in [8].

The relative variations of the absorption coefficient  $\alpha$  are proportional to the FTPS spectra calculated from the ratio of the photocurrent to the flux of light used to generate it via the equation [3, 4]

$$\alpha \propto \frac{I_{ph}(A)}{F(A)} \quad (1)$$



**Figure 1:** (a) Sample configuration (Au/ PVK/ glass) for the measurements of FTPS, SSPG and SSP, (b) picture of an as-deposited sample, and (c) FTPS system set-up

A classical configuration of the SSPG set-up is shown in Figure 2(a). A HeNe laser (633 nm) beam, the light of which is polarized perpendicularly to the plane of the figure, is split in two by a beam splitter. One beam, the probe beam is attenuated by a factor between 10 to 30 and chopped before being sent back in between the electrodes of the sample. On the path of the other beam, the main beam, is placed a  $\lambda/2$  plate to rotate the light polarization and this beam is subsequently sent onto the sample to superimpose with the probe beam. A bias is applied in between the electrodes and this main beam fixes the steady state of the sample generating a current  $I_{ss}$  while the probe beam creates a small perturbation of this situation.

When the two beams have the same light polarization, parallel to the electrodes, they create interferences on and in the sample, the grating period  $\Lambda$  of which depends on the angle  $\theta$  between the two beams via the equation

$$\Lambda = \frac{\lambda}{2 \sin(\theta/2)} \quad (1)$$

and one measures the current  $I_{wi}$  generated by these interferences in excess of  $I_{ss}$ .

When the two beams have crossed polarizations the interferences disappear and one measures the current  $I_{woi}$  generated in excess of  $I_{ss}$  by the superimposition of the two beams. A sketch of the light illuminating the sample with and without interferences is displayed in Fig. 2(b).

To measure these two excesses of current the probe beam is chopped at a low frequency (say 10 Hz) and the currents are measured via a lock-in amplifier, a method that improves the signal to noise ratio.

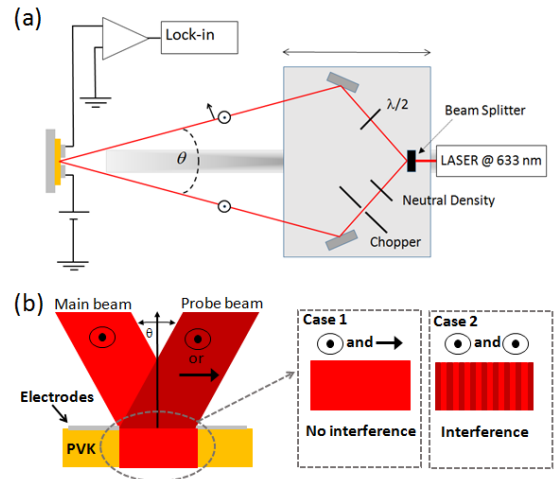
The grating period  $\Lambda$  is modified by changing the angle  $\theta$  between the beams and one finally plots the variations of the ratio  $\beta = I_{wi} / I_{woi}$  as function of  $\Lambda$ . Ritter *et al.* have shown that an expression of  $\beta(\Lambda)$  is

$$\beta(\Lambda) = 1 - \frac{2\phi}{\left[1 + \left(\frac{2\pi\Lambda}{\lambda}\right)^2\right]} \quad (2)$$

where  $\phi$  is a parameter that depends on the conductivity of the material and the quality of the interferences, and  $L_{amb}$  is the ambipolar diffusion length. Consequently, a fit of the  $\beta(\Lambda)$  curve with Eq. (2) brings information on the diffusion length of the carriers.

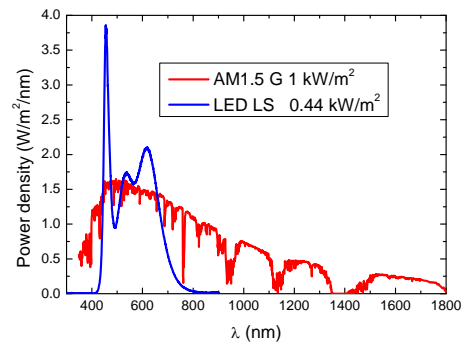
The major problem of the ‘classical’ SSPG experiment is that the modification of  $\theta$  is done manually. In the case of the bench displayed in Fig. 2(a), the optical components are fixed on a plateau that can be moved on a rail perpendicularly to the sample. For each  $\theta$  the plateau is displaced and the superimposition of the beams on the sample is adjusted by rotating both mirrors manually which is time consuming, prohibiting systematic characterizations.

To save time an automatic SSPG set-up was designed with which  $\beta(\Lambda)$  curves can be recorded with almost no adjustments and within 5 mins [9]. It is this bench that was used to perform the PVK characterizations.



**Figure 2:** (a) Standard SSPG set-up, (b) is an illustration of two incident laser beams collected on the PVK sample with two different polarizations of the beams.

Light-soaking of the films was achieved under air with a high power LED the spectrum of which is presented in Fig. 3 and compared to the AM1.5G solar spectrum.



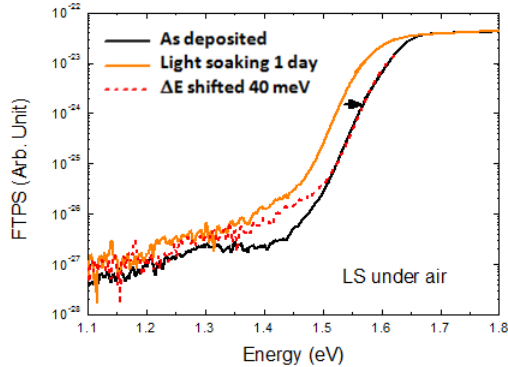
**Figure 3:** Spectrum of the high power LED used to light-soaked the PVK films (Blue line) compared to the AM1.5G solar spectrum (Red line).

It can be seen that the LED light is concentrated in the visible range of the solar spectrum and reaches a total power density of  $0.44 \text{ kW/m}^2$ , to be compared to the  $1 \text{ kW/m}^2$  of the AM1.5 G spectrum. The fact that the LED light has no infrared component is not critical for the light-soaking process since according to the FTPS spectra the light is not, or very weakly, absorbed by the perovskite film for wavelengths larger than  $800 \text{ nm}$  (energy lower than  $1.55 \text{ eV}$ ).

### 3 RESULTS

#### 3.1 Fourier Transform Photocurrent Spectroscopy

The FTPS spectrum of a triple cation PVK thin film (MaFaCs) in its as-deposited (AD) state at room temperature is displayed in Fig. 4 (Black line). This spectrum presents a sharp drop between  $1.45$  and  $1.65 \text{ eV}$  corresponding to the onset of the band edge. This decrease is characterized by an Urbach energy of the order of  $E_U = 17 \text{ meV}$ . For energies lower than  $1.4 \text{ eV}$  the FTPS spectrum presents a bump that could be linked to a distribution of deep gap states. This film was subsequently light-soaked (LS) under air during 24 hours under the light provided by a high power LED, the spectrum of which is shown in Fig. 4. After light-soaking, and normalization of the LS FTPS spectrum to the AD FTPS spectrum in the high energy region ( $\sim 1.8 \text{ eV}$ ), we observe that the band edge is shifted to lower energies (Orange line in Fig. 4), corresponding to a shrinking of the band gap without modification of  $E_U$ . In addition, at low energies, the distribution of deep states increases. All these behaviors (Same  $E_U$ , increase of deep states) are clearly seen by shifting upward by  $40 \text{ meV}$  the LS FTPS spectrum (Dashed red line in Fig. 4).



**Figure 4:** Comparison of FTPS spectra of a triple cation PVK thin film in its AD (Black line) and LS (Orange line) states. The dashed red curve is the translation of the LS spectrum by  $40 \text{ meV}$  along the energy axis.

The interesting point is that, as observed on many samples, after a few days of recovery in the dark and under vacuum, the band edge comes back to its original AD position while the deep defect distribution stays unchanged. Thus, after light-soaking we have a partial recovery of the transport properties of the PVK thin film if maintained in the dark and under vacuum.

#### 3.2 Dark and photo- conductivity

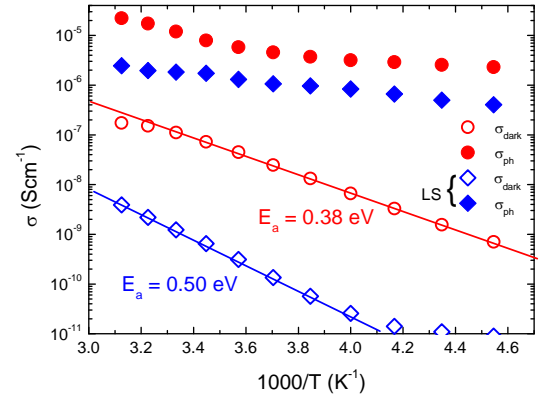
On the same type of material as studied with FTPS, MaFaCs with  $5\% \text{ Cs}$  and an excess of  $10\% \text{ PbI}_2$ , we have performed dark conductivity and photoconductivity

experiments as function of temperature on a PVK thin film in its AD and LS states. As for the previous sample LS was done under air but the dark and photoconductivity experiments were done under vacuum ( $\sim 10^{-6} \text{ mBar}$ ) in a range of temperature  $220 \text{ K} - 320 \text{ K}$  in  $10\text{-K}$  steps. For the photoconductivity measurements we used the light coming out of a He-Ne laser with a flux of  $4 \times 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$ . The results are presented in an Arrhenius plot displayed in Fig. 5.

From these plots we can see that the activation energy in the AD state is  $E_a = 0.38 \text{ eV}$ . Light-soaking results in a decrease of the dark conductivity  $\sigma_{\text{dark}}$  by a factor of the order of 20 and an increase of the activation energy to  $E_a = 0.50 \text{ eV}$ . Note that the increase of the activation energy is not systematic since, for some films we have not observed an increase of  $E_a$  though we do observed a decrease of the dark conductivity.

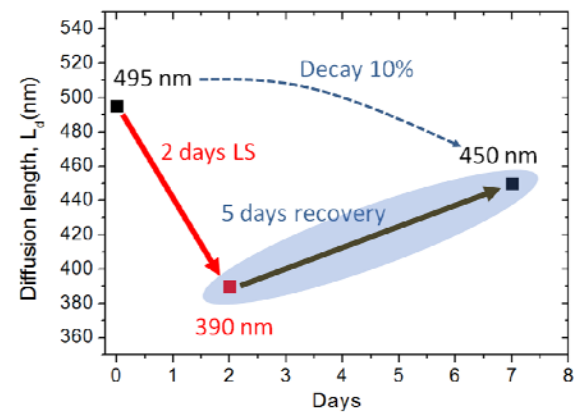
Concerning the photoconductivity  $\sigma_{\text{ph}}$ , we also observe that it decreases with light-soaking though with a smaller ratio than for  $\sigma_{\text{dark}}$  (of the order of 10).

We want to stress that even after leaving the film to recover in the dark and under vacuum for several days we observed a very slight increase of  $\sigma_{\text{dark}}$  and  $\sigma_{\text{ph}}$ , but these quantities remained close to their LS values.



**Figure 5:** Arrhenius plots of dark (Open symbols) and photoconductivity (Full symbols) obtained on a triple cation PVK thin film in its AD (Circles) and LS (Diamonds) states. The straight lines are guides for the eyes.

#### 3.3 Steady state photocarrier grating



**Figure 6:** Diffusion length of a PVK sample measured at room temperature by the SSPG technique in the AD ( $495 \text{ nm}$ ) and LS ( $390 \text{ nm}$ ) states as well as after 5 days of recovery in the dark and under vacuum ( $450 \text{ nm}$ ).

In the last set of measurements we have applied the SSPG technique to the study of PVK thin films. The flux of the main beam was the same as for the SSPC experiments:  $F = 4 \times 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$ . We have investigated on the evolution of the ambipolar diffusion length  $L_{amb}$  with light-soaking. This evolution is displayed in Fig. 6. It can be seen that, after 45 hours of light-soaking under air,  $L_{amb}$  decreases from 495 nm down to 390 nm.

However, after 5 days of recovery in the dark and under vacuum, the ambipolar diffusion length almost comes back to its AD value, eventually reaching 450 nm.

### 3.4 Discussion

According to the above measurements we can draw the following conclusions concerning the aging and recovery of triple-cation PVK thin films. Under light soaking we observe:

i/ A shrinking of the band gap and an increase of the deep gap states,

ii/ A decrease of the dark and photo-conductivity along with an increase of the activation energy,

iii/ A decrease of the ambipolar diffusion length.

After several days of recovery ( $\sim 1$  week) of the film in the dark and under vacuum we have seen:

i/ The band gap returning to its AD position whereas the deep states remain at the same value as in the LS state,

ii/ A very small increase of the dark and photo-conductivity that stay close to their values obtained after light-soaking,

iii/ A rise of the diffusion length that increases from its LS value to a value only 10 % lower than the AD value.

These results show that light-soaking and recovery, in the dark and under vacuum, have definitely an influence on the transport parameters of triple cation PVK as expected. However, upon recovery at room temperature, some of these parameters present some self-healing properties since they come back to, or return to values close to, those of the AD state, whereas the degradation of some other parameters seems to be irreversible.

Clearly, these various evolutions of the transport parameters have different origins and more work is needed to fully understand all the processes behind the observed behaviors. For instance, we may try to anneal the film under vacuum at different temperatures to check if some of the evolution irreversible at room temperature can be triggered at higher temperature. However, we shall have to be very cautious not introducing irreversible changes by heating at a too high temperature.

## 4 CONCLUSION AND OUTLOOKS

In this work, we have investigated the phenomena of light-induced degradation and self-recovery on triple cation (MaFaCs) PVK thin films. These investigations were performed via a powerful photocurrent spectrum technique (FTPS), steady state conductivity and photoconductivity and steady state photocarrier grating experiments. We have observed that, as expected, most of the parameters measured with the above techniques changed with light-soaking indicating a degradation of the transport properties of the material (Decrease of the photoconductivity, decrease of the diffusion length, increase of deep gap states).

However, after a recovery of a few days in the dark and under vacuum, some of the studied parameters returned back to their as-deposited values or very close to them, whereas some others remained in their degraded state.

This indicates that light-soaking has not a simple influence on the material properties such as, for instance, an increase of the deep defect density that would result in a decrease of the photoconductivity because of an increase of recombination. The fact that the diffusion length recovers almost completely its AD value indicates that other mechanisms are involved in the degradation process and more work has to be done for these mechanisms to be revealed.

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