Perovskite as a High-Energy radiation detector

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Abstract: This project is mainly focused on extracting interesting properties of the perovskite when working as a High-Energy radiation detector and afterwards, analysing them in order to understand better its behaviour. Furthermore, detecting single High-Energy photons with them has become a firm short-term objective.

I. INTRODUCTION

A perovskite is a semiconductor material with a band gap close to 1,5 eV and with an ionising energy of about 6 eV. In order to measure X and gamma rays we will work with two different kind of sensors: **thin perovskites** and **thick perovskites**. Thin sensors are composed by perovskite single crystals of 9 mm^2 with the layer configuration **FIG.1 (a)** shows. Thick perovskites are formed by single large crystals of perovskite, methylammonium bromide $MAPbBr_3$, of larger dimensions, with an External Quantum Efficiency (EQE) almost constant from 350 nm to 770 nm, as we can see from **FIG.1 (b)**. In order to decide which perovskite composition was more appropriate, some simulations which compared $MAPbI_3$ and $MAPbBr_3$ were done. **See TABLE I.**

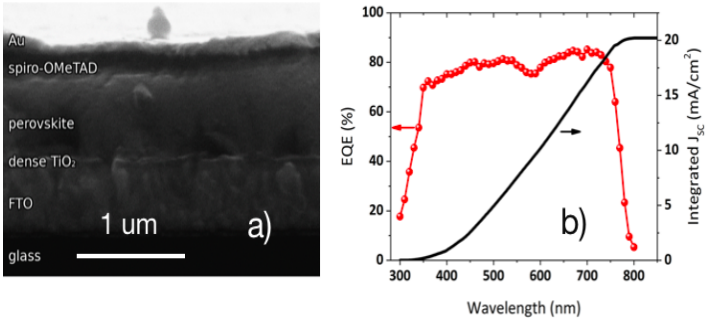

FIG. 1: (a) Cross-section images of a thin diode of perovskite (b) EQE spectrum (red and filled symbols) of a perovskite device and the integrated photocurrent of the solar spectrum (black line) to estimate the photocurrent expected from the diode.

Material	% Interact.	% Events	Energy Deposit
$MAPbI_3$	10,6	3,6	4,5 KeV
$MAPbBr_3$	6,0	3,1	4,8 KeV

TABLE I: GEANT4 simulations results for different crystal compositions using 6 keV incident photons.

The experiments done consist on a piece of perovskite with two metallic contacts connected to a circuit: when a X-ray source is applied through this detector some excited electrons are generated and forced to move around the circuit due to the intrinsic electric field our sensor has -because of the difference in the Fermi energy between the perovskite and the metallic contacts- giving place to an electric current J.

Considering the fact the sensor has an intrinsic potential difference, the external electric field applied is optional. Electrons are forced to move through the material by this intrinsic electric field anyway. But in the case of the thick perovskite (**See FIG.2 (b)**) the intrinsic potential won't be enough to collect these electrons before they recombine, so an external electric field would be useful in this case.

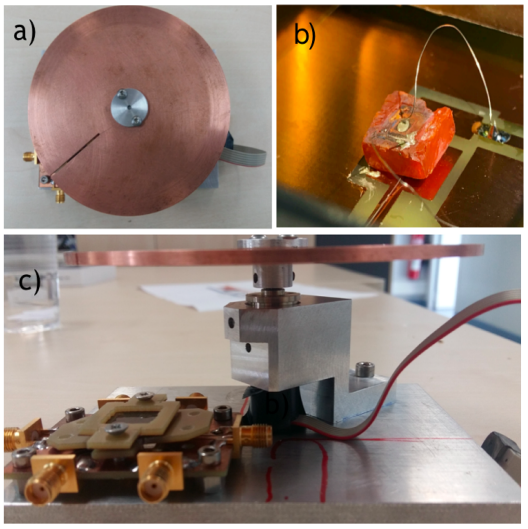

FIG. 2: (a) Rotor disk (b) Thick perovskite with guard-ring (c) Setup.

A. Physical processes involved

Photons of the visible spectrum (**See FIG.1(b)**)ionise electrons -primary electrons- initially bounded to their atoms, and the external electric field provide them with enough energy to ionise by scattering other bounded electrons, called secondary electrons. When the scattering process takes place some of the secondary electrons go from the valence band to the conduction band.

However, X-ray photons create primary electrons by accelerating them, with no ionisation.[1] This electrons ionise the perovskite producing secondary electrons.

When working at room temperature we should consider also thermal excitation as a common process of electron excitation, where lattice vibrations provide enough energy to transfer electrons to a higher energy band. This effect depends on the temperature, for a higher T of the system thermal excitation effects would be more relevant. Another process is related to the electromagnetic excitation: nuclei absorb energy through excitation releasing it as scintillation light.

B. Why do we use a semiconductor material?

Considering the fact that a conductor material has its conduction band closer to the valence band than a semiconductor material, an excitation of an electron in the valence band would be more probable in this case. That said, we will obtain a higher noise in our experimental results because we will be recollecting electrons in the conduction band that are not coming from an X-ray excitation but coming from a thermal excitation, so it will be more difficult to distinguish a peak of intensity of electrons in the circuit when working with a conductor material.

C. Why do we use perovskite?

A perovskite is a material with a large number of Z (protons) which means it also has a large number of electrons, in order to be an electrically neutral material. This is of an important interest due to four main reasons:

1. With respect to the photoelectric interaction there is a reduction on the Compton effect for the range of energies we are working with, which is α to Z. However the cross section is proportional to Z^4 and with more electrons filling the material, the process of scattering between them is more probable, so the signal would be increased. [2]

2. Perovskites form a crystal structure that in principle gives to it nice conducting properties that enhance the charge carriers mobility. This is convenient for extracting the signal minimising the trapping and the recombination.

3. Perovskites are made with very commonly available materials, and its production is rather simple in comparison to other materials as CdTe. This makes the perovskite a potentially very cheap material which is a very desired property in the industry. On top of that, perovskites can be grown at very low temperatures -close to 100°C- which also saves energy in the production.[3]

II. EXPERIMENTS

A. Constant X-ray radiation: comparison between thick and thin perovskite

To understand the transient behaviour of the sensors we illuminate them with a long X-Ray pulse and record the voltage across a 1MΩ resistor, for the thick perovskite and 1kΩ for the thin perovskite. We have seen that when illuminating the thick perovskite we obtained a constant voltage response, although if we illuminate the solar-cell like perovskite we observe an initial peak before obtaining a stable response: **See FIG.3**. This can be attributed to the fact we are observing at very different time scales and the difference in the resistance we used, but the important characteristic would be that the signal gets stable for both of them. More research is needed to understand the physical origin of this different behaviour, but there are many differences between the two sensors that might provide an explanation.

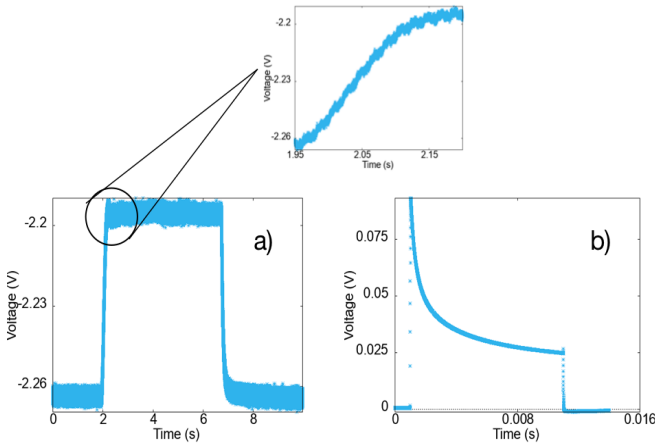

FIG. 3: Time evolution of a constant X-ray radiation response for the (a) Thick perovskite (b) Thin perovskite

B. Solar-cell-like Perovskite: Pulsed radiation

The second measurement was done with a periodical narrow signal and measuring the voltage drop across a resistor of 1MΩ in serial connection with the perovskite. This was achieved by introducing a rotor disk with an aperture of one degree approximately between the sensor and the X-ray source **See FIG.2 (a)**.By changing its rotation frequency, we could modify the radiation time exposition.

I will consider that a peak is symmetric if the *width right* is equal to the *width left*, both parameters are measured from the Full Width at Half Maximum (FWHM). The average width of the peaks is higher for lower than for higher frequencies, although for 5,8 Hz and 14 Hz

we observe that this parameter remains almost constant. **See FIG.4 (b)**. The explanation could be that for higher values of the frequency, as we can see from **FIG.3 (b)**, we are on the peak regime. However, for 0,58 Hz we are in the constant regime and the average width increases radically. Apart from that, it has been proved that for higher exposition times and higher intensities we obtain more signal. **See FIG.4 (a)**

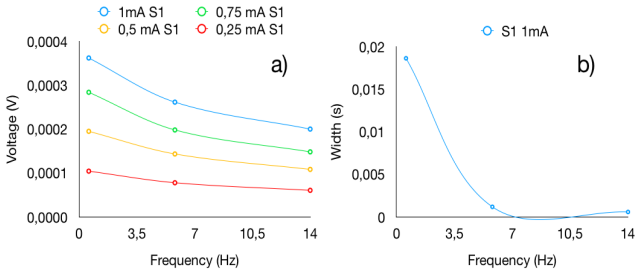

FIG. 4: (a) Representation of the signal measured in terms of the frequency of the rotor disk (b) Representation of the average width of the peak in terms of the frequency of the rotor disk.

Defining the asymmetry term as it follows, it could be obtained by analising the signal the average asymmetry for the peaks. **See TABLE II**

$$Asymmetry = \frac{\text{Average width left}}{\text{Average width}} \qquad (1)$$

Asymmetry	**0,58 Hz**	**5,8 Hz**	**14 Hz**
1 mA	0,5	0,56	0,63
0,75 mA	0,54	0,57	0,64
0,5 mA	0,53	0,57	0,65

TABLE II: This table recollects the asymmetry values for different frequencies of the rotor disk and for different X-ray intensities.

C. Thick Perovskite: Pulsed radiation

The experiment consisted on sending periodically X-rays to our sensor, with the same setup we used with the thin perovskite. We tried to see the dependence in the polarisation applied on the perovskite and the voltage response using a setup which consisted on a rotor disk with a constant frequency of 10,5 Hz and X-ray radiation intensity of 0,5 mA. **See FIG.5**. We observed that going from positive to negative voltages of polarisation the peaks increased constantly, but going from negative to positive voltages we get a maximum value of 3V and then it decreases: we will see the same dependence when studying the intensity-voltage curve.

If we analyse the peaks along the same lines in terms of the intensity of the incident radiation, we will see that

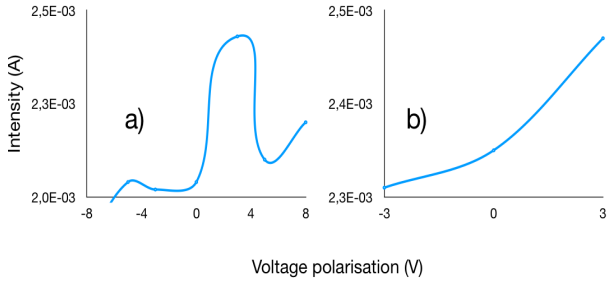

FIG. 5: Representation of the signal of the sensor, intensity, in terms of the voltage polarisation applied for the thick perovskite in a pulsed system (a) NegPos (b) PosNeg.

it has an almost linear response. For higher values of the intensity we obtain more signal. **See FIG.6**. It can be seen that using the same setup the thick perovskite gives us a signal 100 times higher than the thin perovskite, which was expected due to the larger interaction rate.

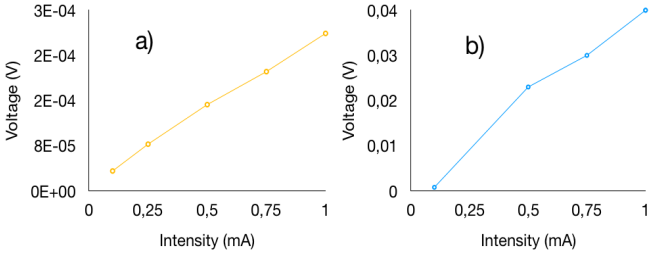

FIG. 6: Representation of the signal of the sensor, voltage, in terms of the X-ray source intensity for the (a) thin perovskite (b) thick perovskite.

D. Thick Perovskite: I-V curve characteristics

In order to study the Intensity-Voltage curve -from now on, I-V curve- we will apply a potential difference between this two surfaces, and that way, we will generate a current inside the sensor. The range of voltages we will be dealing with goes from 8V to -8V, and the measurements will be done in steps of 1V. In order to do that, we will use a program which controls the time for each measurement and records the value of the intensity for each polarisation.

After studying the I-V curves for the thick perovskites we can state that they do not have a linear response and its behaviour depends radically on the sense of the voltage scan, which can be interpreted as an hysteresis. **See FIG.7.** Fitting the I-V curves to the Schottky diode model provides insights into the operation of these photodetectors.

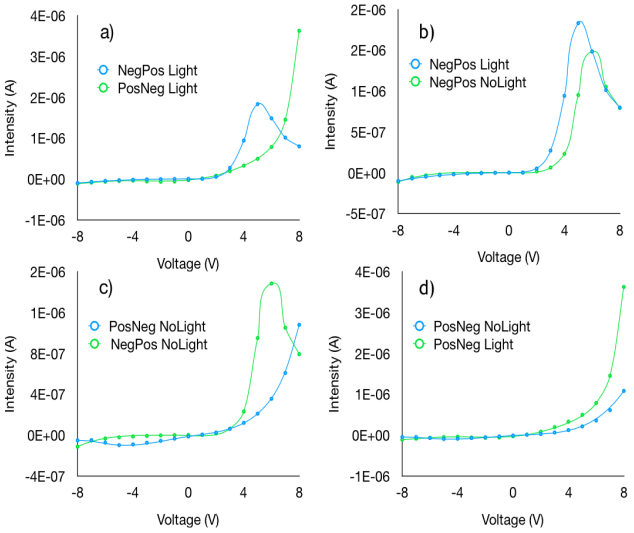

FIG. 7: I-V characteristics measured on the detector (a) under light conditions (c) in dark (b) comparing the response obtained when going from -8V to 8V under different light conditions (d) comparing the response obtained when going from 8V to -8V under different light conditions.

Cheung et al.[4] proposed the following equation to extract the diode parameters:

$$\boxed{\frac{dV}{d(lnI)} = IR_S + \frac{nkT}{q}} \tag{2}$$

where, R_S is the diode series resistance, n the ideality factor, T the temperature and k the Boltzmann constant. **FIG.8 (b)** shows the representation of $\frac{dV}{d(lnI)}$ in terms of the intensity, and from this plot we extracted Rs and n parameters.

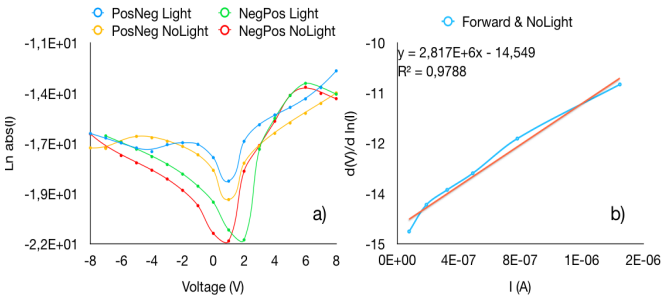

FIG. 8: Representation of the (a) Ln(I) in terms of the voltage applied under different light conditions (b) $\frac{dV}{d(lnI)}$ in terms of the intensity, R_S corresponds to the slope and n is easily defined with the independent term. **See Table III**.

From **FIG.8 (a)** we can state that going from negative voltages to positive voltages is a good way to reduce the noise of the system, because the minimum of Ln(I) is lower for this directionality.

In order to reduce the noise of our system as much as we can we changed our setup: we separated one contact into two metallic contacts, one surrounding the other forming a guard ring and a pixel (**See FIG. 2(b)**) -with no potential difference between them-, leaving the other intact. A voltage is applied between the two surfaces but now, considering that electrons move more easily along surfaces than in the bulk, by measuring the current in the pixel we obtain a more precise signal with less noise [5]. This way the pixel readout should follow closer the behaviour of the ideal Schottky diode.

In an attempt to extract the Schottky parameters for the I-V curve for this setup we found that the results approached more the expected model. **See TABLE III.**

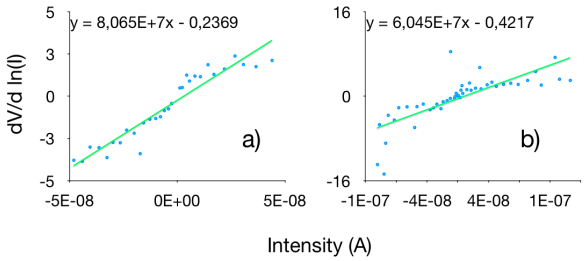

FIG. 9: Representation of the $\frac{dV}{d(lnI)}$ in terms of the intensity of the (a) pixel (b) guard ring.

Perovskite	n	R_s MΩ
Thick Perovskite	562	2,82
Thick Perovskite-Pixel	9,15	80,6
Thick Perovskite-Guard-Ring	16,24	60,4
Thick Perovskite-Pulsed setup	2,64	30,6

TABLE III: This table recollects the parameters extracted from the $\frac{dV}{d(lnI)}$ in terms of I curve for the pixel and the guard ring, for the thick perovskite and for a voltage pulsed setup, which will be commented hereafter. The ideality factor in this case approaches more to 1, which is the value of an ideal Schottky diode.

In order to reduce that hysteresis we have proved that it is effective to use a pulsed system in which the voltage is only applied a short time. In our setup we worked with a period of 0,2s, which is the pulse width in which the voltage is applied to the system. **See FIG.10**. The Schottky parameters for this setup match better to an ideal Schottky diode. **See TABLE III.**

We have also studied that if we go to 5V, polarisation in which the two I-V curves -NegPos and PosNeg- differed more, and we change the directionality, we return to the other curve, but not instantaneously. In **FIG.11** we went

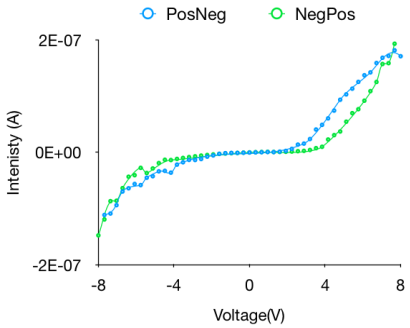

FIG. 10: Representation of the I-V curve for the thick perovskite with a pulsed voltage setup.
Period: 1s; Pulse width: 0,2s

from negative to positive voltages, from -8V to 5V, and then returned to -8V changing the directionality, all in the same measurement.

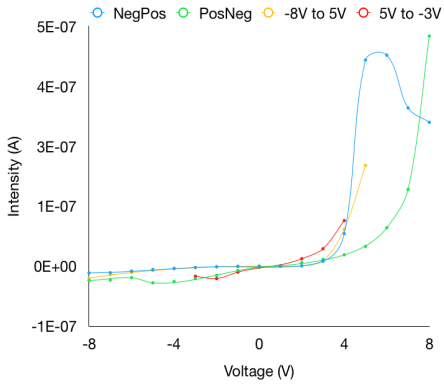

FIG. 11: I-V curve for the thick perovskite in a non-pulsed setup. This measurements are done under dark conditions. Blue and green curves go from -8V to 8V and from 8V to -8V respectively as a reference, and red and yellow form one single curve, but it has been plotted with different colours in order to distinguish between the two directionalities.

III. FUTURE WORK

1. Polish the perovskite surface before doing the metal deposition of the contacts in order to reduce the noise and be able to obtain a better signal.

2. Estimate the Fano factor associated to our experiments.

3. Repeat the same process with perovskites of different compositions.

4. Developing the electronics adapted to the perovskite properties, taking into consideration that the understanding of the I-V curves are critical to the design of the readout electronics.

5. Some reports show the existence of photoluminiscence. This might have applications in High Energy physics and requires its own set of studies.

IV. CONCLUSIONS

To conclude, we have shown that the perovskites are sensitive to X-Rays. We have developed new diodes, thicker than the usual solar cell perovskites, that are more suitable for this kind of applications. In the process of this research we have discovered a rich phenomenology and a wide field of research. Next steps go in the direction of trying to detect single X-Rays with high energy resolution. Once proven the spectrographic capabilities of the perovskites we can start thinking about possible applications. This will require more research, development and better understanding and quality control on the sensors. Working together with ICIQ has proven to be an important assist to develop radically new technologies.

Acknowledgments

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I would also want to thank Prof. Lluís Garrido for calling the results I obtained into question, that way I forced myself to go deeper in a concept and achieve a better understanding.

Finally, I would want to thank PhD Cesar Jesus, for all his help in the project: he provided me with new concepts and ideas.

[1] T.E.Schlesinger. Semiconductors for room temperature nuclear detector applications.
[2] Glen F. Knoll. Radiation detection and measure.
[3] Sergii Yakunin. Detection of gamma photons using solution-grown single crystals of hybrid lead halide perovskites.
[4] Parvez A. Shaikh. Schottky juntions on perovskite single crystals.
[5] Haotong Wei. Dopant compensation in alloyed perovskite single crystals for gamma-ray spectroscopy.