Experimental report

17/02/2020

Proposal: **1-04-170** **Council:** 4/2019

Title: Organic cation segregation and degradation in perovskite solar cells:a neutron scattering study

Research area: Materials

This proposal is a new proposal

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Samples: Si/[(MA)x(FA)1-x]PbI3
Si/[(MA)x(Cs)1-x]PbI3
Si/MAPbI3
Si/FAPbI3

Instrument	Requested days	Allocated days	From	To
D17	6	4	27/09/2019	01/10/2019
D33	6	0		

Abstract:

In recent years, perovskite solar cells (PSC), have stunned the photovoltaic field owing to their unique combination of high performance and low-cost fabrication process. Compared with the existing technology, PSCs have demonstrated their potential by establishing an unprecedented increment in the power conversion efficiency (PCE) from 3.8% to >23.2% in less than a decade. Typically, hybrid perovskites are used, where the organic cations inside the perovskite satisfy the Goldschmidt tolerance factor, but present an oriental disorder in the crystal which increases with the temperature. In this context, in the present proposal we aim to perform a combination of neutron reflectometry and SANS experiments to study the structural part of the perovskite layer of the solar cells, paying special attention to the degradation of the perovsike and the organic cation segregation inside the perovskite structure. We will add up the results of these experiments with measurements of the PCE of each sample fresh and degraded. This will provide us with a scenario where we will be able to correlate the efficiency of the PSC with the degradation and organic cation distribution in the perovskite layer.

EXPERIMENT N°: 1-04-170 **INSTRUMENTS:** D17

DATES OF EXPERIMENT 27/09/2019-01/10/2019

TITLE: Organic cation segregation and degradation in perovskite solar cells: a neutron scattering study

REPORT 17/02/2020

In recent years, perovskite solar cells (PSCs), have stunned the photovoltaic field owing to their unique combination of high performance and low-cost fabrication process, achieving efficiency higher as the conventional ones.

Hybrid organic-inorganic perovskites like CH3NH3PbI3 are mostly used in the photovoltaic field. However, it presents several stability issues when external factors (e.g. temperature, humidity, oxygen) are present. In order to avoid that, more complex perovskites (triple cation) as well as protection methods (passivation, fluorinated compounds) have been developed to increase efficiency as well as long-term stability. Despite, with the addition of a mixture of different cations and halides devices a higher crystalline and stable perovskite is obtained, some reports suggest the existence of a non-perfectly homogeneous crystalline structure, but by a nanoscale segregation of multiple perovskite compositions.

In this context, our aim was to perform structural study of the perovskite layer of the solar cells, paying special attention to the organic cation segregation and possible nanolayer formation at interface. Thin film layer of perovskites of different compositions was spun-coated on top of a silicon substrate and measured at D17 reflectometer when humidity and temperature degradation processes took place.

The present reflectometry measurements provided information about the depth profile of the PSCs once the degradation process is initiated. The experiments performed in D17 clearly demonstrate that there is no any nanoscale layer formation at interface. In addition, they also indicate that the humidity and temperature degradation processes take place via different dissociation routes of the initial perovskite compounds, as is evidenced from the data presented in Fig.1 (NR data for only one kind of PSC sample were presented as an example).

The initial fittings performed in the temperature degraded PSCs indicate that no layer is formed in the interface between the PSCs and the Si substrate, while a change in the SLD of the degraded PSC layer occurs. Nonetheless, the fittings performed in the humidity degraded PSCs evidence the formation of dense (SLD~$6 \cdot 10^{10}$ cm^{-2}) ultrathin layers between 5 and 15 Å at the interface. Further to this, in the highest humidity measurement the critical edge is clearly observed in the reflectivity curve, meaning that in that case the average SLD of the degraded PSC products sample/layer become higher than the SLD of the Si substrate. According to the proposed scheme of degradation, four different main compounds could be formed in the sample. We have estimated the SLD values for all of them and divided them into "low SLD components" (SLD~$0.1\text{-}0.4 \cdot 10^{10}$ cm^{-2} – MAPbI$_2$, d-MAPbI$_2$, PbI$_2$), "intermediate SLD components" (SLD~$5 \cdot 10^{10}$ cm^{-2} – I2 ions) and "dense SLD component" (SLD~$6.7 \cdot 10^{10}$ cm^{-2} – d-MA). It should be mentioned that the SLD for MA is negative and ~ $-0.8 \cdot 10^{10}$ cm^{-2}.

The temperature degradation processes show no clear changes to the NR curves measured in the samples studied, as can be observed in Fig. 1a. This is attributed to the fact that the only non-gaseous resulting product from the temperature degradation in our PSCs is PbI2, whose SLD and that of the initial perovskite measured are low close to each other and, therefore, it is difficult to follow the PbI$_2$ formation during degradation. Nonetheless, the humidity degradation processes show evident changes to the NR curves, as it is observed in Fig.1b. The resulting products from the humidity degradation process include solid PbI$_2$, I$_2$ and MA, the latter two having higher SLDs than the former and the initial PSC. Thus, although the absence of fringes in the NR curves indicate that no continuous layer of any degradation product is formed in the interface between the substrate and the PSCs, the vertical shift of the NR curves indicates that the average SLDs from the degradation products change with respect to the initial PSC one.

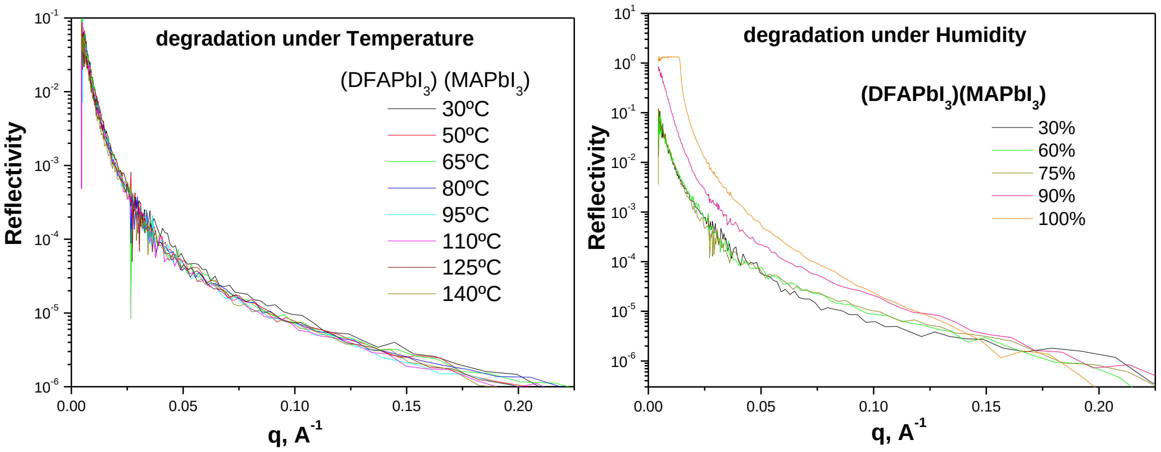

Fig.1. *(a) NR curves for the temperature degradation process of a mixed cation PSC. (b) NR curves for the humidity degradation process of the same mixed cation PSC.*

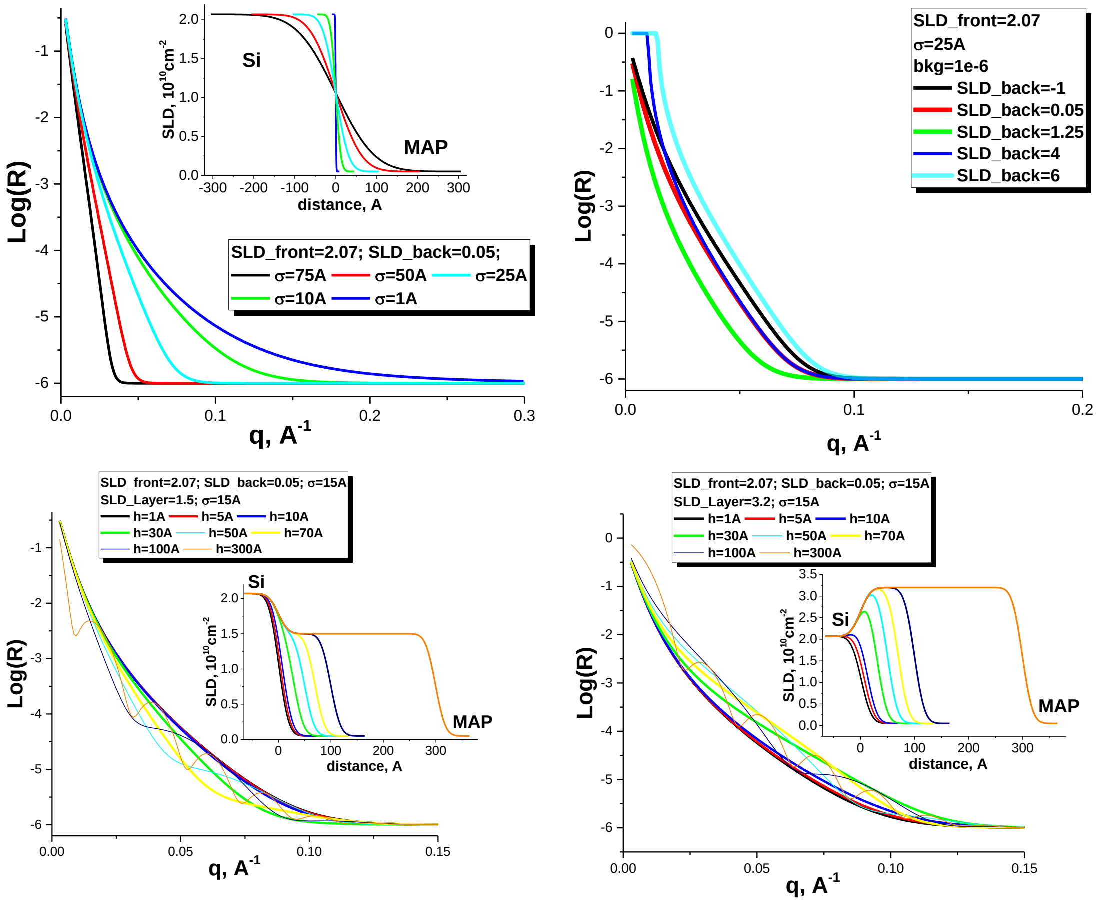

Fig.2. Modeling of various scenario for PSC degradation by neutron reflectometry (increasing of roughness at interface PSI/Si; change of the sample`s SLD; formation of nanoscale layer with SLD below and higher SLD of Si substrate).

Our further step is to perform detail fitting procedure for the whole NR curves and follow changes of PSC`s SLD&roughness and also additional layer (if any) vs temperature or humidity for the studied perovskite layers.