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Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Aleksandra Boldyreva

PhD Program: Materials Science and Engineering

Title of Thesis: Unraveling bulk and interfacial degradation mechanisms in perovskite solar cells

Supervisor: Prof. Pavel Troshin

Name of the Reviewer:

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Signature:** Aldo Di Carlo **Date: 07-06-2020**

The purpose of this report is to obtain an independent review from the members of PhD defense Jury before the thesis defense. The members of PhD defense Jury are asked to submit signed copy of the report at least 30 days prior the thesis defense. The Reviewers are asked to bring a copy of the completed report to the thesis defense and to discuss the contents of each report with each other before the thesis defense. *If the reviewers have any queries about the thesis which they wish to raise in advance, please contact the Chair of the Jury.*
Reviewer's Report

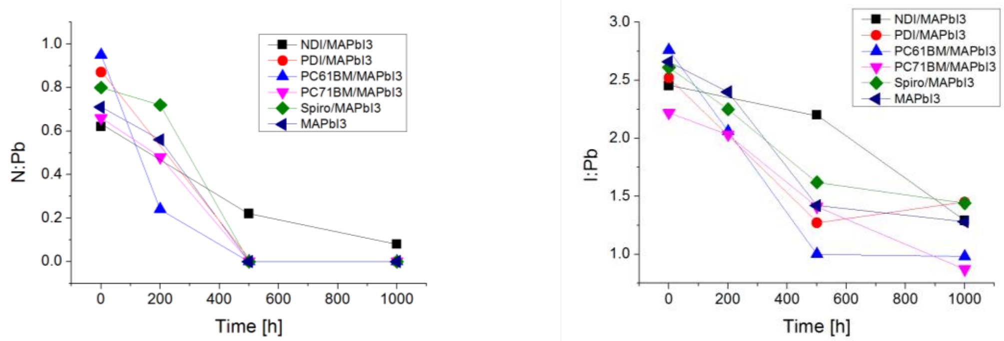
The PhD Thesis Aleksandra Boldyreva focusses on a fundamental and timely issue in the halide perovskite solar cell context, namely the stability of the materials forming the cell and the stability of the cell itself. A plethora of effects can rule the stability of cells and materials and only a very methodological approach to the problem with a clear plan of experiments and characterization techniques can be used to extract the relevant information. In fact, differently to other issues in solar cell development, such as efficiency, stability studies require time consuming experiments needed to stress the cell in specific conditions. A miss planning of experiments and characterization would results in a loss of time that could not be compatible with a PhD thesis. Aleksandra Boldyreva successfully addressed the study of stability with rigor, precise planning of the experiment and conclusion supported by clear experimental evidences. It is rare, nowadays, to read a PhD thesis with a precise strategy with a clear statement of the thesis, the identification of the hypothesis and the proofs supported by clear experimental evidences.

In the introductory part of the thesis, the candidate presents the field of halide perovskite solar cells (PSCs) and a literature review related to the main issues concerning the stability of cells, namely extrinsic stability, intrinsic stability and interface stability. Moreover, an additional section was devoted to radiation stability with the main intent to discuss space application of PSC. The introductory chapter is well written, few minor points should be considered and are reported as comments in the thesis. On point deserve an additional discussion:

- pag. 28. It is written "The main advantages of PTA over PTAA is deeper-lying HOMO and Fermi energy levels resulting in higher VOC…" The relation between HTL Fermi level and Voc is not direct. It depends on the dominant recombination mechanism. For a good solar cell, it is only related to the absorption layer, while in other cells could also be related to the CTL. See for example Matthias Auf der Maur and Aldo Di Carlo Solar Energy 187 (2019) 358–367. I suggest to put this observation in the right framework

Chapter 2 is devoted to a study of the impact of charge transport layers (CTLs) on the light-soaking stability of $MAPbI_3$ and PSCs. Here the candidate performs a detailed experimental/characterization analysis to investigate the stability of $MAPbI_3$, $MAPbI_3$ on CTL and CTL on MAPbI3 by using XRD, XPS, AFM and SEM. Degradation reaction were proposed and related to experimental data. The stability analysis has been extended also to devices where the possible degradation induced by the contact were avoided by adding contacts after aging. It is show that, even for the very stable structural configuration (PCBM on perovskite) electrical properties could degrade due to interface instability. A good compromise for stability has been obtained with Spiro-OMeTAD even though, as revealed by ToF-SIMS characterizations, MAPbI3 degradation products can be absorbed into this CTL. Based on these experiments, the candidate propose a new strategy to improve PCBM CTL by filling with inert material the space between C61/C71 spheres. The chapter is well written, has a very logical sequence of investigation, a detailed characterization and results as of absolute importance ad international level for the development of the field. Few minor points have been commented directly in the thesis, while the following deserve some additional discussion:

- The discussion on the impact of the CTL in the stack glass/CTL/Perovskite is performed also considering XPS data. The ratios I:Pb, N:Pb have been calculated and reported in the tables 1-3. The graphical representation of these ratios is shown in the following figures:



As we can see, the general degradation trend is observed already in the pristine sample with only MAPbI3. Some differences among the structures enter in the sample-to-sample variation (as for example the t=0 difference). I think the only remarkable difference can be found for NDI (less degradation) and PC61BM (higher degree of degradation). I suggest to rephrase this part of the thesis starting from the very beginning with pristine MAPbI3 XPS data (now it is at the end) and then showing the evolution of the others, and considering the sample to sample variation.

- On pag. 51, when discussing about PCBM effect on MAPbI3, the candidate focusses on the encapsulation property of PCBM without considering that PCBM could passivate grain boundaries avoiding the decomposition of MAPbI3 as it has been shown in several publications. The candidate should extend the discussion here also to consider literature data on grain passivation induced by PCBM.
- On Scheme 2 at pag 48, both light stress heat stress are reported, however all the results presented were related to light stress. Is there any evidence about heat stress?

Chapter 3 extends the stability study of the previous chapter to better investigate the stability of PCBM in inverted PSC configuration considering also mixed perovskites. The first section is dedicated the light stability of HTL. The candidate founds, by using XRD, XPS, SEM and ToF-SIMS that PTAA/$MAPbI_3$ presents the most stable interface without intermixing and with a low perovskite decomposition. Other interface, including the one with inorganic oxides (NiOx/MAPbI3) are not stable and present strong intermixing. In particular for NiO_x it is found that NiI_2 forms. This investigation is also extended to mixed perovskite and a similar conclusion is made on the superior stability of PTAA/Perovskite (as well as PTA/Perovskite). A light-induced perovskite crystallization phenomena has been found and related to the HTL/Perovskite interface. An interesting and novel discussion/evidence on the amorphization of $CsMAFAPbI_3$ is presented. Mixed halide perovskite (with I and Br) are less stable and a clear Hoke effect is found and related to segregation of the halides. Such halide segregation is shown to be suppressed by PCBM ETL. In fact, the ITO/HTL/Perovskite/PCBM is much more stable than the one without PCBM. So PCBM has a strong impact on the light soaking stability of the stack. In particular the most stable configurations are ITO/PTAA/$MAPbI_3$/PCBM; ITO/PTAA/ $CsMAFAPbI_3$/PCBM; ITO/PTA/ $CsMAFAPbI_3$/PCBM. The last section of the chapter is related to light soaking stability of electrical parameters of the cell. Here to avoid the degradation already demonstrated in chapter 2, the candidate perform a refresh of the PCBM after light soaking. The simple $MAPbI_3$ perovskite results more stable than the others do. The chapter is well organized and important conclusions are obtained with a complete characterization. Few minor points are outlined directly in the Thesis. A point deserve some additional discussion:

- I suggest, if available, to report the results of light soaking stability of electrical parameters even without PCBM refresh as done for MAPbI3 in chapter 2.

Chapter 4 studies the degradation under gamma ray. A very systematic study is performed on the different layers forming the solar cell. Structural stability under gamma radiation is shown for glass/ITO/PEDOT:PSS/perovskite stack (ad single layers). A new phenomena of gamma-ray induced halide segregation has been found and related to the Hoke effect induced by the light. Fabricated solar cells shown a gamma-ray induced degradation of the overall efficiency mainly related to J_{SC}. This is more evident in the PSCs where also PCBM were irradiated. The impact of the gamma-ray on PCBM has been studied and correlated to the further reduction of the PSC efficiency. The research presented in the chapter is well performed and permits to understand clearly the impact of gamma-ray on the materials and PSC performances. The only point which deserve further discussions is the following:

- Pag. 108 it is written " The main contribution to solar cell degradation comes from the severe photocurrent losses (25-35% of the initial value) suggesting the accumulation of the radiation-induced defects facilitating the recombination of charge carriers." As the candidate shows, the main contribution comes from J_{SC} and not from V_{OC}. Recombination physics mainly rules the value of V_{OC} (this is also briefly discussed in the chapter). I ask the candidate to elaborate better this conclusion and how recombination could impact J_{SC} instead of V_{OC}.

The final Chapter of the thesis extends the investigation performed in Chapter 4, considering several perovskite compositions to assess the stability under gamma-ray stress. Very surprisingly, even if mixed cation perovskite and Br-based perovskite are showing a higher material stability than MAPbI3, the opposite is true for the complete cell. The reason for this behavior is well explained and related to self-healing property of $MAPbI_3$ and, on the opposite, to the gamma-ray induced segregation in mixed halide.

In conclusion, I deeply appreciate the work present in this PhD thesis. It is complete and push the knowledge of the radiation (light and gamma-ray) stability of perovskite cell and materials well beyond the state of art. This is also shown by the number of high-level scientific publications of the candidate related to the PhD thesis.

Provisional Recommendation

☐ *I recommend that the candidate should defend the thesis by means of a formal thesis defense*

X *I recommend that the candidate should defend the thesis by means of a formal thesis defense only after appropriate changes would be introduced in candidate's thesis according to the recommendations of the present report*

☐ *The thesis is not acceptable and I recommend that the candidate be exempt from the formal thesis defense*