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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:** **Date:** 05-06-2020

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

Reviewers report should contain the following items:

- Brief evaluation of the thesis quality and overall structure of the dissertation.
- The relevance of the topic of dissertation work to its actual content
- The relevance of the methods used in the dissertation
- The scientific significance of the results obtained and their compliance with the international level and current state of the art
- The relevance of the obtained results to applications (if applicable)
- The quality of publications

The summary of issues to be addressed before/during the thesis defense

The PhD thesis “Unraveling bulk and interfacial degradation mechanisms in Perovskite Solar Cells (PSCs)” presented by Aleksandra Boldyreva is focused on the study of the degradation pathways taking place in PSCs. The understanding and correction of these issues will permit the enhancement of the PSC lifetime and the prompt commercialization of the technology.

The thesis is divided in 5 chapters: 1) Introduction, 2) Impact of CTLs, 3) Impact of HTL, 4) the effect of Gamma rays on the halide perovskite absorber for space applications and 5) the effect of the composition of the absorber under Gamma Rays irradiation. The manuscript ends with conclusions and bibliography. **The topic of the PhD thesis is state of the ar**t and the results obtained from it will be a reference for the PV community in PSCs in the future. In general, the manuscript is of **high quality, very well written and well organized, it describes clearly the work developed step by step, from introduction, aims, experimental, discussion and conclusions**. This makes the writing very easy and straight forward. The fact that the application of this work is related to space applications (effect of Gamma Rays) makes it very attractive and clearly demonstrates research beyond current trends.

The PhD thesis covers the different degradation mechanisms taking place in the most fragile places of a PSC: at the absorber and at the interfaces. The work analyses the degradation taking place at the charge transport layer (CTL) (Chapter 2), the hole transport layer (HTL) (Chapter 3) and the absorber (Chapter 4 and 5). It is highly appreciated the schematics used to describe the methodology and procedures for aging experiments. It permits a clear understanding of the experiments and results. Moreover, the experimental results not only provided with the isolated results that prove degradation of materials, **the author used the synergy of different analytical techniques to understand the degradation from a more complete and open perspective**. As important as the latter, the aging experiments takes place for periods of time up to 1000 h which makes the work of great importance and can be used as a reference by the PSC community. Some of the conclusions involve CTL materials highly applied in the PSC community due to their stability. This PhD work demonstrates how those materials (e.g. PCBM family) bring stability. With respect to the HTL materials (Chapter 3), the work describes stability studies for the four most applied HT materials like the oxide NiO, the organic molecule Spiro-OMeTAD or the polymers PTTA and PTA. The application of oxides like NiO is well known for their stability. However, **this work proves the degradation of the oxide into NiI_2**, while the use of polymers like PTTA were reported to be highly stable. This is highly important since many are the studies and reviews from the PV community describing the stability of NiO. Another interesting finding is the enhanced stability observed for simple halide perovskites in comparison to mixed cation halides perovskites. The work also describes **methods to avoid this degradation**, for example, by the application of the top ETL, PCBM. However, the degradation mechanisms occurring in

PSCs are not simple but the **effect of multiple parameters taking place at the same time**, as corroborated by this PhD thesis work. Finally, the effect of gamma rays was also investigated in this work with the aim of study the possible use of PSCs for space applications. Especially interesting is the effect of gamma rays on the halide perovskite material. It was found, **for the first time**, that the segregation of the mixed halide perovskite is induced by high radiation doses. To overcome the issue, in the final experimental chapter (5), different halide perovskites under different radiation dose were analysed. The results revealed that is especially the surface of the thin film, and not the bulk, the most damaged part. In a complete device, the multication absorber devices showed the worse stability of all the materials, while the simple MAPI demonstrated the highest stability.

All these results were only possible thanks to a **careful selection and combination of the appropriate characterization tools**. From materials properties to thin films and complete devices, the single and combined use of analytical techniques is one of the main accomplishments of this work which permitted to understand the **multiparameter complexity** of the degradation of PSC.

In my point of view, the work developed under this **PhD thesis is one of a kind**: only a few research laboratories in the world are able to combine such amount of materials, device architectures and analytical methods to study the degradation of PSCs in a deep level, which makes this work of high relevance and unique. The work will certainly impact the PSC technology and will provide new perspectives to improve PSC stability. Moreover, the results are also highly applicable, not only to simple PSCs technology but also to PSCs to be used for space applications, which require a complete new perspective on testing conditions. The **excellence of this PhD work** is clearly demonstrated by the multiple (at least 6) **publications in international scientific journals of high impact factor**. Among them are J. Mater. Chem. A (Impact factor 10.73), J. Phys. Chem. Letters (IF=7.32), ACS Appl Mater Interf (IF=8.45) or Sust. Energ. Fuels (IF=4.9).

For all the above, I certify the high quality of the PhD these work and highly support it for public defence.

Provisional Recommendation

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

☐ *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*