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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

Co-advisor:

Chair of PhD defense Jury: Prof. Alexei Buchachenko **Email**: *a.buchachenko@skoltech.ru*

Date of Thesis Defense: June 30, 2020

Name of the Reviewer: Prof. Alexei Buchachenko

X I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Signature:** **Date: June 3, 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 Thesis submitted by Aleksandra Boldyreva addresses the problem of degradation mechanisms controlling the stability of the perovskite-base solar cells (PSC). As the poor stability is deemed to be the main obstacle to commercialization of otherwise prospective perovskite photovoltaics, the topic is of high practical interest. As such, it attracts huge attention of academic and industrial research groups and the number of works devoted to PSC stability grows up enormously. To be competitive on this overheated ground, one should follow specific research strategies driven not only by knowledge, but also by intuition, picking up and testing different materials and architectures. To produce coherent, logical and self-consistent treatise, like PhD Thesis, one should be systematic and attentive to details. To my opinion, the Thesis by Aleksandra Boldyreva provides good example how these partially conflicting strategies can be compromised.

The main concepts behind the research presented in the Thesis are

- PSC is a complex device, whose function integrates the functions of individual bulk materials;
- The dependence is not additive, as the interfaces typical to layered PSC architectures create interference;
- Interface chemistry, physics and morphology effects are much richer than bulk chemistry and phase composition;
- Understanding of both interface and bulk degradation phenomena is in need for improving the stability of PSCs as an integrated device.

Though the introductory chapter of the Thesis may not be literally qualified as the comprehensive literature review (hardly possible in the field of study), it is fully in line with the underlying concepts providing the concise overview of the stability factors and summarizing the main pathways of intrinsic degradation of the bulk perovskite layer and main conclusions of the previous studies on interfacial stability and radiation damage. The introduction clearly identifies the major white spots in the current knowledge and approaches to fill them out are immediately converted to the research goals and concepts of the Thesis.

For intrinsic PSC stability, Chapters 2 and 3 constitute the core of the Thesis. The former provides the systematic comparative analysis of five organic charge transport layers (CTL) in two different architecture and MAPbI3 as absorber. It identifies the fullerene derivative PC61BM as prospective the CTL due to its good encapsulating properties that suppress reversible photoinduced bulk perovskite degradation. Chapter 3 capitalizes on this finding addressing the choice of the hole-transport materials (HTL), among which the polyarylamines are shown to be promising. It also extends the range of perovskite formulations, but no one studied behaves better than MAPbI3. This part nicely illustrates the benefits of the chosen research strategy. If I do not miscount, the full screening would require trials on 200 samples/devices. The Thesis shows that only 30 are enough to reach solid conclusions. It is the understanding that comes from in-depth study of a few subject that brings the benefit over sequential standard testing of a large array, which probably requires more time and efforts.

Similar strategy is followed in Chapters 4 and 5, which address another topic, namely, the stability of the PCS with respect to gamma-radiation. Studies of the radiation resistance of the particular PSC based on complex triple-cation perovskite are presented in Chapter 4. Like in the previous chapters, effects of radiation damage are considered for each layered component and for assembled device. Novel process of the radiation-induced phase segregation is documented. Chapter 5 provides the analysis of radiation stability of six different perovskite formulations and emphasizes the superior behavior of MAPbI3.

All chapters are well structured and logically expose the results for the target layers, layer combinations and assembled devices. Materials, methods and protocols are presented clearly and completely. Not being an experimentalist, I still can suggest that the descriptions given make the work and results reproducible. Chemical and phase compositions of the samples are characterized by a variety of modern methods. The results of different methods are related to each other and carefully interpreted. Comparisons of different samples or different protocols are made in a uniform style and very pictorial way. Nice and comprehensive illustrations are very useful helping the reader quickly spot confirmation of the findings described in the text.

The nice feature of the Thesis – an inherent part of its concept - is the discussion of the nature of distinct degradation pathways. In all cases the efforts are made to extract relevant information from the measured data (sometimes taken specifically on the purpose) and put forward plausible explanations. Well, I would not call them mechanisms (only the model for MAPbI3 radiation stability in Chapter 5 is close to what I consider as mechanism), but physical and chemical nature of the degradation pathways is formulated clearly enough to allow both more detailed exploration and qualitative predictions.

The Thesis is well written (a handful of inaccuracies I found is summarized at the end) and reflects enormous experimental work in clear and relatively concise manner. The size is well justified by the fact that the Thesis can serve as a good reference for future research. Author's contribution is highlighted. The quality and novelty of the results are confirmed by impressive list of publications in the most influential professional journals in the field, where Aleksandra Boldyreva is the first co-author.

My first comment is related to space applications pointed out as a motivation to the radiation stability study. To me, the problem is interesting per se, while prospects for space require more caution. First, early NASA report [T. W. Kerslake and E. D. Gustafson, On-Orbit Performance Degradation of the International Space Station P6 Photovoltaic Arrays, NASA/TM—2003-212513] mentions contamination, ultraviolet light, proton/electron bombardment, ion sputtering and elevated temperature due to intense solar radiation among the main factors causing the degradation of solar panels installed on International Space Station. So gamma-radiation is not the only issue. Second, in space all these factors, including solar and gamma-radiation, act simultaneously, which implies a complex interplay of various mechanisms. I would not say that the results presented in the Thesis are directly relevant to space applications, though certainly give a message to. On the other hand, the testing of PCS at ISS launched recently [https://news.gatech.edu/2019/11/06/novel-solar-cells-arrive-international-space-station-testing] may indicate that I am simply lacking an optimism.

The second comment is related to a long-waited [C. C. Boyd, Understanding Degradation Mechanisms and Improving Stability of Perovskite Photovoltaics, Chem. Rev. 119, 3418 (2019)] consensus statement on the perovskite stability assessment [M. V. Khenkin et al. Consensus statement for stability assessment and reporting for perovskite photovoltaics based on ISOS procedures, Nature Energy, 5, 35 (2020)]. With all understanding that most of the Thesis work had been accomplished before it came to the light of the day in Jan 2020, I would be pleased to see a reference and few words on compliance.

To conclude, the Thesis presented by Aleksandra Boldyreva is a comprehensive and self-contained work that clearly states the problem, identifies solid concepts for seeking the solutions, provides well-justified and reproducible novel results of practical importance and develops valuable knowledge to drive future research. It certainly complies with all requirements to the PhD Thesis set at Skoltech. PhD qualification of the author is out of question.

Saying that, I would like to list misprints and inaccuracies deserving attention.

p.5: Update references to papers 1, 2 and 6.

p.33: ***C****lass/CTL/MAPbI3*

p.65: *XRD patterns presented in Fig.****2b*** check reference to figure

p.83: *particular*ly *exciting*

Figure 45. Architecture and ***protocol*** Protocol is something formal; I would call it sketch or workflow

p.105, 106: Wrong formatting, no figure caption

p.130: The vacancies are displayed as yellow balls… Refer to Fig.70

Eq.(2): Better to emphasize that both T_x and T_0 depend on the wavelength

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*