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Skolkovo Institute of Science and Technology

Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Olga Yamilova

PhD Program: Materials Science and Engineering

Title of Thesis: Revealing electrochemical degradation pathways in complex lead halides and design of stable perovskite solar cells

Supervisor: Professor Keith Stevenson

Name of the Reviewer: Annie Ng

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Date: 06-01-2023**

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

This thesis systematically designed the experiments to study the material stability and lifetime of solar cells. The presented results are interesting and useful for the PV community to understand the degradation mechanisms of perovskite solar cells. The thesis was well written with minor grammatical mistakes and wrong phases, which can be polished by the students before the oral defense. The student has good publications in the peer review journals and international conferences. The comments on this thesis are listed below:

- Page 18 : "The only remaining obstacle is a short lifetime of the devices under realistic operating conditions." Please note that short lifetime is not the only remaining obstacle. Please revise this statement.
- Chapter 1 Introduction: "*Unfortunately, among all aforementioned factors the bias-induced degradation processes remain the least elucidated.*" is the last sentence. However, no further information was introduced related to this work. It is better to elaborate further the motivation of this work and briefly introduce the designed experiments and related information.

- Page 23: ~~"On~~ Figure 4 you can see the extreme points" revise this sentence by deleting "on" and use passive voice.
- Page 25 "Typical EQE is presented on Figure 5." Replace "on" with "in". Check other parts of the thesis if there are similar issues.
- Page 26: *2.1.3 Requirements and problems* The focus should be placed on perovskite solar cells. Same as above, the requirements and problems are not the only issue. It is better to elaborate thoroughly.
- The permission should be granted by the journals for the figures which have been reported by the papers including other authors and own papers. This can be done in the journal websites. The statement should be also indicated in the figure caption. You can follow the style of review papers published in the journal.
- The 1-page Chapter 3 Research objectives is a separated chapter, which can be combined with Chapter 1 "Introduction".
- The title of Tables should be above the table.
- The figure caption of Figure 18 should be more clear. Please use a), b), c) etc to indicate each figure panel.
- Figure 19: Please further discuss the results of Figure 18 and Figure 19. Some description of the spectra and images are also needed and will be helpful.
- Page 64: "*N-i-p solar cells were fabricated using the configuration ITO|SnO_2|PCBA|perovskite|PTAA|V_2O_5|Al (Figure 20a) using various range of perovskite materials…..* " Please revise as below:

  ⇒ The n-i-p solar cells were fabricated in a configuration of ITO/SnO_2/PCBA/perovskite/PTAA/V_2O_5/Al as shown in Figure 20a. The perovskite with various compositions ($MAPbI_3$, $MA_{0.15}Cs_{0.1}FA_{0.75}PbI_3$, $Cs_{0.15}FA_{0.85}PbI_3$, $Cs_{0.12}FA_{0.8}PbI_{2.92}$, $Rb_{0.1}Cs_{0.15}FA_{0.75}PbI_3$, $Cs_{0.125}FA_{0.875}PbBr_{0.375}I_{2.625}$, $CsPbI_2Br$ and $MAPbI_xCl_{3-x}$) in the n-i-p structure were investigated for their lifetimes.

  ⇒ It is noted that the configuration of device is commonly represented by "/". Please revise for other parts of the thesis.

- Please explained clearly about the stability and device lifetime of $CsPbI_2Br$. The following statement cause confusion. Please revise properly. Meanwhile, if it is the factor of thickness, the experiment should exclude this uncertainty by preparing the same thickness for all kind of perovskites (e.g. all of them around 200 nm or 400 nm depending on the preparation technique.) The aim of this experiment is to compare the perovskite with different compositions. Therefore, thickness should be the same for fair comparison.

  ⇒ Page 62 "*Another candidate for stable devices is fully inorganic $CsPbI_2Br$ which does not contain any organic components prone to reduction process*."

  ⇒ Page 58-59 "*Unfortunately, we were not able to perform PL mapping for $CsPbI_2Br$ because this material could not sustain the transportation between the glovebox and measurement device*".

  ⇒ Page 64-65 "*And contrary to what was expected from AFM data, inorganic perovskite $CsPbI_2Br$ devices demonstrated the fastest*

degradation among all materials, despite their favorable chemical structure. The reason behind such behavior is the thickness of the photoactive film, which is around 200 nm for $CsPbI_2Br$ because of processing method, while for other materials thickness is around 400 nm. Thickness influences the voltage density per 1 nm in the biasing process, so it is obvious that thin film devices will surely degrade faster."

- Page 68: "*The existence of something like "threshold voltage" for PSCs was already observed previously in the publication of the Bae et al*." Please revise the this statement because *"something like"* is not an appropriate scientific phase in a thesis.
- Page 59: "*Behavior of the materials in the device channel after applying an electric field and also optical photographs are demonstrated in Figure 17" What is the meaning of device channel*? The optical photos of corresponding channel are also not very understandable. The section of "4.1.5 PL mapping" did not explain this concept also. Please elaborate the text and write comprehensive description in the figure captions. In fact, in this thesis, most of the figure captions even for the figures with a lot of panels are very general. The readers easily confuse with the plots and images. It would be great if the student check all figure captions again and revise accordingly.
- Page 74 "*Then go copper salts with direct perovskite contact, which could undergo partial flushing by perovskite solvents*." Revise this sentence. Also, what is the meaning of partial flushing? Please explain further in the text.
- In the chapter of conclusion, please suggest the potential methods and materials selection for achieving good stability and lifetimes of perovskite solar cells based on the findings in this thesis work.

Signature:

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*