Skoltech
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:

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Date: 10-12-2022**

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

Dear Members of the Examination Committee,

I hereby provide the evaluation of the **PhD Thesis of Olga Yamilova** on ***"Revealing electrochemical degradation pathways in complex lead halides and design of stable perovskite solar cells"*** for which I serve as thesis examination jury member.

The thesis focuses on the investigation of field-induced degradation pathways of hybrid organic-inorganic metal halide perovskites and the corresponding solar cells. This has involved three distinct investigation stages. Specifically, a model perovskite material based on methyl ammonium iodide was investigated, which was followed by the analysis of electrochemical stability of other perovskite compositions. Finally, the role of external bias was investigated on complete solar cells to assess their operational stability from the perspective of the role of other elements, including charge-extraction layers and metal contacts. The study reveals that redox processes of organic components are involved in the degradation through a combination of complementary techniques. Moreover, the effect of external factors, such as oxygen and water, was considered, as well as the overall device structure, proposing a strategy to enhance stability.

The thesis is structured in six chapters which are accompanied by an Appendix section with supplementary materials and the Bibliography. Chapter 1 provides a general introduction to the topic, which is complemented by a detailed literature review in Chapter 2 and research objectives defined in Chapter 3. The experimental details are outlined in Chapter 4, whereas Chapter 5 details the main results of the thesis. In particular, the redox processes involving organic components of perovskite materials are revealed and it is shown that replacing highly volatile methylammonium cation with less volatile formamidinium or inorganic cations (e.g., Cs) can improve material stability under operating conditions. Moreover, a more general electrochemical degradation pathway for perovskite solar cells is identified that involves the analysis of a range of charge-extraction layers under voltage bias that contributes to losses in performances due to increase in charge-carrier accumulation and ion migration. This process was also found to be affected by oxygen and water. Apart from these electrochemical factors affecting perovskite solar cell stability, the work points at the role of the metal electrode in the stability. Finally, Chapter 7 provides a conclusion based on the key findings across chapters with a perspective. ***The topic and methods are highly relevant to the stability of perovskite photovoltaics, and the results are of high quality and scientific significance with respect to state-of-the-art. Moreover, they are relevant to photovoltaic applications. This is further reflected in the high-quality publication output.***

I recommend to consider the following **minor remarks** that can be addressed before/after thesis defense.

- *In general, the thesis* is very well structured and clearly presented. I wonder whether "literature review" chapter could be part of the introduction, unless this is based on the internal policies.
- *In the introduction*, it is pointed out that "the only remaining obstacles is a short lifetime of devices under realistic operating conditions". This claim is made once more in the next chapter, providing more information from the literature reports. While instability is indeed one of the most pressing challenges, there are others that remain towards practical applications of these materials and devices. In particular, this refers to the toxicity of lead-based components, which is not relevant to this particular thesis. The candidate should however revise the statement to point at the instabilities as "*one of the most important obstacles" rather than "the only ones"*.

- *In the experimental section*, the preparation procedures are outlined for different perovskite compositions. This involves different (anti)solvents and annealing temperature conditions without information about the basis for these experimental details. Even though some of these aspects are further discussed in the other sections, the candidate should briefly comment on whether these are optimized conditions or those based on literature reports and provide the corresponding literature (e.g., in Table 2). Similarly, the candidate should briefly comment on the reasons behind the selection of specific solar cell architectures in the first two studies.
- *In the discussion of results,* the candidate points at the reaction of iodine with "virtually all iodides to form polyiodides" under experimental conditions, which can be misleading as it is not specifically put into context with respect to experimental evidence. It is important to note that iodine could engage in other reactions at the contacts and its volatility could also contribute to degradation. Similarly, the reduction of ammonium cations is implied and it is important to put these conclusions into context with respect to experimental evidence and discuss briefly whether there are other reactivities that could be considered. Finally, in the third part of the study, the normalized PCEs should include a comment on the range of values of initial PCEs in the caption or the Appendix for clarity and comparison with other devices.
- *In terms of language,* the thesis is very well written, clear and coherent. On a minor note, the candidate refers to "iodine ions" where iodide might be more appropriate. Also, there is a reference to perovskite materials "recommending themselves" (page 35) and their sustainability (page 65) which could be revised as it might not reflect the intended meaning. Moreover, in terms of the thesis format, the candidate should ensure the appropriate use of formulae and units (i.e., applying subscripts or superscripts, such as on page 37/41, where some of them are not formatted), the use of space between the unit and the value (e.g., page 38), and a consistent use of units of time (s/min/h). Finally, even though the candidate introduces abbreviations at the beginning, it might be helpful to also introduce them upon first use as well.
- *The literature* discussed in the thesis is comprehensive and involves relevant work on the topic.

All in all, the thesis presents a comprehensive analysis of operational instabilities of hybrid metal halide perovskite materials and the corresponding solar cells. It substantially contributes to the research developments on hybrid perovskite materials and solar cells, opening a path for advancing the material/device design by increasing the stability under operating conditions. The work resulted in 3 publications and a submitted article, as well as 6 conference presentations. Considering the quality of the research and presentation, I strongly **recommend the thesis for acceptance without reservation**.

I appreciate your consideration and look forward to the thesis defense.

Sincerely,

Dr. Jovana V. Milić

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*