

Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Olga R. 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: Professor Evgeny Antipov

I confirm the absence of any conflict of interest

(Alternatively, Reviewer can formulate a possible conflict)

Date: 19-12-2022

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

Olga Yamilova's dissertation is well structured and organized, it includes six chapters: Introduction, Review of the Literature, 3 main chapters: Research objectives, Experimental section, Results and discussion, and a Conclusions summarizing and discussing main important outcomes of the research.

Chapter 2 contains the overall literature review and provides important general information on key parameters of perovskite solar cells, possible pathways of the device degradation, an overview of electrochemical degradation of bulk perovskite materials and solar cells. The experimental part describes the preparation of materials and devices, methods of analysis. The results and discussion chapter provides an in-depth investigation of electrochemical degradation processes in perovskite materials and solar cells. The conclusions chapter combines key achievements and outcomes of the work. The thesis contains 28 figures, 3 tables and supporting materials that include additional 4 figures representing supplementary experimental data; the bibliography list consists of 130 references.

Olga Yamilova's thesis contains original work on revelation of the field-induced degradation mechanism of complex organo-inorganic lead halides with perovskite structure used as photoactive materials in solar cells and also the influence of the complete solar cell structure on the stability of the device. This work offers a contribution in the field of perovskite photovoltaics since it paves the way towards direct design of photoactive and charge transport materials for electrochemically stable perovskite solar cells. Thesis proves that the nature of the material adjacent to the perovskite in solar cell structure is the most important for the device stability.

The conclusions of this work are validated with experimental data. Among used physicochemical methods there are chronoamperometry, spectroscopy PL mapping technique, atomic force microscopy, highly informative and sensitive ToF-SIMS technique.

The scientific outcomes are reflected in 3 publications and 1 submitted manuscript. They are published in the journals of high impact and reputation.

The most important achievement of this work is the proposing of the mechanism of electrochemical decomposition of perovskite materials and of a general pathway for electrochemical degradation of solar cells. Overall, the obtained results are definitely of high reliability and cannot be questioned.

The dissertation of Olga Yamilova is the complete research which meets the requirements for awarding a PhD degree according to the criteria of relevance, scientific novelty, validity and reliability of the conclusions.

The following remarks can be made on the content of the thesis:

- 1) P. 20. The statement "Perovskite is a type of crystal with a cubic structure and orthorhombic, tetragonal or trigonal symmetry" is not correct and should be corrected.
- 2) P.26 kW/h – should be corrected
- 3) P.35 . What does it mean "Nevertheless, according to the XDR measurements of the films, they fully correspond to the required materials"? If XDR means X-ray powder diffraction, the experimental data should be presented in the thesis to prove this statement.

- 4) P.35. How the compositions of the anion-deficient perovskites ($\text{Cs}_{0.125}\text{FA}_{0.875}\text{PbBr}_{0.375}\text{I}_{2.625}$ and $\text{Cs}_{0.12}\text{FA}_{0.8}\text{PbI}_{2.92}$) were determined? Please, provide the reliable own or literature data confirming the anion deficiency in these perovskites.
- 5) P.38. What does it mean “NiO_x and CuO_x”?
- 6) P.51. Fig.13. ToF-SIMS chemical maps show the distribution of different ions in the cells. The most remarkable changes were revealed at the maps of CH₃NH₃⁺ cations while the changes for the other ions are much less. Please, provide an explanation what are the probable products of the perovskite degradation when positively charged ions are deintercalated from the perovskite structure to the PEDOT:PSS hole selective layer with the formation of methylammonium salt of polystyrene sulfonic acid.
- 7) P. 54. Why “The oxidation of I⁻ with formation of I₂ seems to be reversible”? The probable formation of polyiodides does not prove the reversibility of the redox process.
- 8) P. 60. What does it mean “Nevertheless Cs⁺ cations partially migrate from anode to the cathode, leading to **the chemical shift in the structure**”?
- 9) P. 65 What does it mean “Also, excess of PbI₂ in the chemical structure”?
- 10) P.65. What does it mean “...chemical structure of perovskite material influences the stability of bulk material” ?
- 11) P. 68. What does it mean “NiO_x system ”?

These remarks do not reduce the significance of the obtained results and do not affect the overall very positive evaluation of Olga Yamilova’s dissertation. Overall, this thesis work represents a significant step in understanding of degradation behavior of this family of perovskite materials. Olga Yamilova has done original work and addresses many challenges of this field. She deserves to be awarded a PhD degree.

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