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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: Danila S. Saranin (Ph.D. in technical sciences)

I confirm the absence of any conflict of interest	**Date: 17-11-2022**

Reviewer's Report

The dissertation work of O.L. Yamilova is a completed research work performed by the author at a high scientific and technical level. The results and conclusions of the thesis are reliable and scientifically grounded. The abstract and publications fully and correctly reflect the content of the thesis and its main provisions and conclusions. The thesis consists of an introduction, 5 chapters, a conclusion, and a list of references. On the topic of the dissertation, 3 scientific papers were published in the editions indexed by Web of Science & Scopus.

The thesis topic fully corresponds to the direction from the Strategy of the Russian Federation's Scientific and Technological Advancement: Transition to environmentally friendly and resource-saving energy, increasing the efficiency of hydrocarbon production and deep processing, formation of new sources, methods of transportation and storage of energy.

The relevance of the key tasks and general topic:

- determination of the perovskite material electrochemical degradation pathway,
- defining the chemical structure of the most electrochemically stable perovskite material,
- comparative analysis of different adjacent charge-transport materials and metal electrodes,

are completely supported with the content of the dissertation work.

O.L. Yamilova performed a complex study of the thin-films and various device structures based on halide perovskites. For the device fabrication, O.L. Yamilova used conventional solution processing, typical for the lab-research approach in the field of perovskite photovoltaics. The morphology, surface, optical and structural properties of the thin-films of perovskite absorbers and charge transporting layers were studied with:
AFM measurements,
Chronoamperometry measurements,
PL mapping,
ToF-SIMS analysis.
The device performance was studied with IV scans, EQE spectral measurements, Maximum power point tracking and light soaking stress tests.
All used methods in the dissertation are relevant for the multidisciplinary approach of the investigation on revealing electrochemical degradation pathways in PSCs.

The investigation of O.M. Yamilova contains several parts with significant achievements. It should be noted that research work was done in straight consequent way with step-by-step Complication Of the experiment. For the simplest device structure (photoconductive resistor) Yamilova found, that applying electric bias (340 h) results in severe depletion of organic cations near the cathode thus implying that they undergo electrochemically induced degradation via reduction of $CH_3NH_3^+$ to form methylamine CH_3NH_2 and molecular hydrogen H_2 at the interface between metal contact and perovskite absorber.

For the multilayer p-i-n device architecture, Yamilova revealed that the $CH_3NH_3^+$ in the device structure induced by the electric field. At the end of the first chapter, Yamilova formulated the conclusion for the major mechanisms of the electrochemical corrosion in PSCs.

For the conclusions at the third stage, Yamilova explained the benefits of the use of double CTLs consisting of an organic layer in direct contact with perovskite and supporting metal oxide due to the encapsulation properties of the multilayer stacks.

The main achievements of the work have a full set of the analysis: thin-films properties, proposed chemical mechanism of the electrochemical degradation, high level of the device performance (PCE >18%) and device stability over 1000H before T80 conditions (time to reach 80% of the initial PCE value). Accord to the presented thesis of O.M. Yamilova, it's possible to conclude that the scientific significance of the results completely fits to the current state-of-the-art in the field of HP PV.

The results of this dissertation work can be recommended for review and use by thin-film optoelectronics specialists at leading research organizations and industrial enterprises: Russian Center for Flexible Electronics, Ledingrad LLC, Central Research Institute (TsNII) Cyclone, Roselectronics Holding, A.F. Ioffe Physico-Technical Institute of RAS, A.N. Frumkin Institute of Physical Chemistry and Electrochemistry of RAS, NUST MISIS, National Research

University ITMO, N.S. Enikolopov Institute of Synthetic Polymeric Materials RAS and V.I. Ulyanov Saint Petersburg State Electrical Engineering University "LETI".

The quality of the papers published on the topic of the present thesis shows the high – international level. All three papers are published in first quartile journals recognized in the Web of Science and Scopus.

However, several parts of the thesis require additional comments from the applicant:

The author should provide the additional comments on the motivation of using different device architectures (p-i-n and n-i-p) in different chapters. This makes the interpretation of the obtained results a bit more complex.

The applicant describes the data for the process of electrochemical doping with simple charge – current dependence. The specific conductivity and/or the difference in dielectric constants values could give an impact on the process of the current flow. It's necessary to consider the differences between the set of the transport properties to make the logical conclusion.

TOF -SIMS evaluation data presented on the fig.18 is very complex for analysis, the upscale of the figures is preferable.

The evolution of normalized PCE during the "stepwise" biasing presented on the fig.22 have a sharp difference between the configuration of the devices based on organic/inorganic HTLs. The reasons of the different light-soaking behavior at the starting periods of testing require additional comments and interpretation.

In the second part of the thesis, O. Yamilova formulated the conclusion: "The major factor here is the sustainability of the material to the accumulated charge carriers of defects. Of course, replacement of highly volatile MA_+ to the bigger cation FA_+ or inorganic Cs_+ and Rb_+". The integration of the large Rb ions to crystal lattice of hybrid halide perovskites creates some doubts. Probably author could give some comment on this point.

In the last chapter the applicant demonstrates the investigation focused on the impact of different electrodes versus PCSs stability under exploitation stress effects. The choice of proper chemically stable electrodes is well established topic in wafer and thin-film solar cells. The interpretation of results requires the comments for the choice of metal contacts used in the research work.

The comments made are of a private nature and do not call into question the major results and conclusions of the thesis, nor do they reduce the scientific and practical significance of the thesis. I recommend approving this thesis in conditions "as is."

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*