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Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Mayuribala Mangrulkar

PhD Program: Materials Science and Engineering

Title of Thesis: Design and engineering of additives for improving the stability of hybrid perovskite solar cells

Supervisor: Professor Keith Stevenson

Name of the Reviewer: Prof. Alexei Buchachenko

I confirm the absence of any conflict of interest	**Date:** Sep 7, 2021

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 PhD research work by Mayuribala Mangrulkar lies in extremely hot, challenging and practically-driven direction of improving stability of the perovskite materials for solar cell applications. Since 1999, more than 100 records featuring the «perovskite .AND. stability» query in WoS® had been publishing annually, heating the bar of 1000 records per year in 2016 and 4000 records per year already in 2020. The reason for so intent interest is obvious, as the stable perovskite photovoltaics (PV) is expected to revolutionize the solar energy generation. The reason why so huge efforts invested still not solved the problem well enough for commercial applications, is the overwhelming complexity. The problem has dozens of dimensions. Variety of the degradation paths broadly classified as extrinsic and intrinsic, the choice and the synthesis of the generating perovskite layer, its combination with charge-transfer layers (ETL and HTL), a plethora of approaches to cell assembly and different means to suppress the degradation form an infinite variety of the approaches to be tried dwarfing some 200 hundred papers already published on the topic.

The research presented in the thesis comprises four publications in respectful professional journals with an average impact factor 2.7 (still falling in Q2-Q3 of the overheated Materials Science category) and one more Q1 paper less related to the focus of the thesis. Such a productivity is above an average for Skoltech Materials Science & Engineering Doctoral Program and is not negligible comparing to the 200 most relevant papers in a narrow thesis field. All papers, published in 2020 and 2021, were cited 13 times (WoS®), which is quite an impact. Less impressive is the conference record – all 5 contributions were made to local (though relevant) events. As most of the publishable results came out in 2020 or later, one can see here the pandemic effect.

Now, from the formal assessment to essentials. Below the critical comments and questions, which I consider worthy of discussion, are highlighted in *italics*.

First, I would like to acknowledge the composition and logic of the thesis. It starts with the well-written introductory Sec. 1, which channels a broad perovskite PV landscape into the extrinsic and intrinsic stability issues and use of additives as a particular remedy (I do not like the term «additive engineering» in this context as it sounds misleading for additive manufacturing and additive technology). The aim of the thesis formulated in Sec. 1.6 looks a bit vague, but clear enough to justify the literature review that follows.

Literature review presents a kind of masterpiece. Search of suitable additives has no less dimensions than the whole perovskite PV stability problem and the current status resembles a patchwork. It required a lot of knowledge, scrutiny and intelligence to classify existing information by the chemical nature of additives, evaluate their impacts and compile these into the very telling comparative tables 1-14 and summary graphs presented in Appendix. No wonder that the material of this section has been published as the self-contained review. Well, it still does not point out the route towards the stability problem solution, but give a map for searching the directions. Certainly, the literature review is not the only and main achievement of the author, but in a sense it certifies her qualification and maturity as a scientist in the most spectacular way.

Sec. 3 describes experimental approaches, methodology, materials and characterization techniques. Everything is on the up-to-date level and suits the aims of the thesis. *However, I found it strange that the protocols for stability testing of the films and cells are not explicitly given in this section. Moreover, I did not see a reference on the recently published 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)].* Such statements help to reduce the dimensionality of the problem*, so I think that the relation of the conducted stability test to the consensus protocol should at least be commented.* Less important comment is that the preselection of additives for in-depth study, well justified and illustrated by Table 15, could be better placed in the very beginning of Sec. 3 for clear connection with the lessons of literature review and reiteration of the thesis aim at an elevated level.

The research workflow is logically organized and presented is Sec. 4. Describing briefly the results of screening the preselected set of additives for the film stabilization, the author turns to three most promising candidates identified, N-Methyl-2-pyrrolidone, hydrazinium iodide and \Gamma-bipyridyl. Special section is devoted to the performance of each of this agent in a cell, comprehensive characterization and attempt to establish the stabilization mechanism in each case in terms of morphology improvement and adduct formation. Quite impressive results for intrinsic stability at very reasonable power conversion efficiencies were achieved with the additives studied. Concluding chapter provides clear and concise summary of the thesis. All results and conclusions are firmly justified by the high level of experimental techniques, studies of concentration and ageing dependences, robust systematics in the measurements and careful analysis.

My questions actually address the lessons that one can take away of this work rather than to the work itself.

How general the conclusions are? For instance, a unified typical cell architecture is used for stability tests - n-i-p Glass/TCO/ETL/Passivation layer/$MAPbI_3$+additive/HTL/electrode with ETL = SnO_2, Passivation layer = PCBM /PCBA, HTL = PTA or PTAA. *To what extent the present results can be used to predict the effect of the additive in a cell with different configuration and CT layer compositions? Would the mechanisms proposed be helpful for such predictions?*

The author sees this main future prospect for using additives for perovskite stability improvement in the *«developing an artificial intelligence-based system/ machine learning/ depository» because «there was no proper rule to select the correct/suitable material to achieve stabilization effect until now».* On the one hand, artificial intelligence is indeed a proper means for solving multidimensional problem. *On the other, does this statement mean that efforts based on the human chemical knowledge and intuition are hopeless?* The question is not solely philosophical, as the answer determines experimental strategy: artificial intelligence would prefer wide screening for a few target parameters, human one – deep comprehensive exploration of the physical and chemical phenomena in a limited number of examples. As the thesis under review certainly belongs to a latter case, it is interesting to learn why this experience turned to be so disappointing for the author.

To conclude, the thesis presented by Mayuribala Mangrulkar 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 complies with all the requirements to the PhD Thesis set at Skoltech. PhD qualification of the author is out of question.

Unfortunately, the thesis text suffers from many misprints, stylistic problems (broken sentences, missing or excessive punctuation marks) and formatting inaccuracies.

The need for careful proofreading is the only reason why I claim the revision of the thesis before the defense. Other comments and questions may well be addressed during the defense – it is up to the author how to handle them.

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*