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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: Andriy Zhugayevych

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	 **Date: 08-09-2021**

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 thesis research is targeted on improvement of the stability of hybrid perovskite solar cells (PSCs). The operational instability is a major problem of this class of photovoltaic materials, therefore the thesis work is very important for practical applications, as well as for fundamental understanding of degradation processes in PSCs. More specifically, the thesis is focused on experimental study of influence of additives to MAPbI3 precursor solution on the stability of the resulting thin film and the solar cell constructed of this thin film as the active layer. Several classes of organic and inorganic additives are considered. Among them, three best performing additives are studied in details (UV-Vis & PL, XRD, FTIR, AFM & SEM, XPS, device performance): excess of PbI2, hydrazinium iodide and 4,4'-bipyridine. The maximum stability is achieved for the second additive: 4400 hours of continuous illumination in an inert environment.

Results of the thesis work have been published in 4 articles, most of them in topical impactful journals. In all four articles, the candidate is the writing author and the main contributor. All this proves that the quality and amount of thesis work fully meet PhD requirements.

However, there are some comments to the thesis itself. I will start with quality of scholarly presentation. Results and Discussion session is only 28 pages long and has no explicit connection to thesis publications. Also, there are some important figures discussed in that session (e.g. XPS results) but moved to Supporting Information which is inconvenient for reading. Formula 1 (Goldschmidt tolerance factor) is mistyped. There are multiple minor grammatical errors/mistypes or text requiring clarity improvement, already at the beginning of the thesis, for example:

1) Improper punctuation in Figure 2 caption.

2) In sentence "Thus, destabilize the solar cells" (p.31) it is unclear what does destabilize the cells.

3) The same page, grammar/mistype in "This reactive O_2^- species".

4) Unclear meaning of the phrase "to improve the intrinsic stability challenge of MAPbI" in p.33.

At the end of the thesis, the writing style of "Results and Discussion" session requires improvement to meet common requirements of scientific publications, e.g. in p.101 what is "absorbance characteristic", what is meant by "perovskite production had occurred". Also, in Fig.12 the caption is split across pages.

Considering scientific aspects of the thesis, I have the following questions and comments to be discussed before or on the Defense:

1) The selection of additives for the investigation is not explained. Is there some rationale behind Table 15? This is also related to the literature review – it ends with too short summary, not providing useful keys for rationalization of additives.

2) The strategy of the thesis work is unclear: from the presentation it looks like the candidate studied additives sequentially for the entire duration of the thesis work. Given a huge number of possible additives, such "enumeration" approach seems to be inefficient. Is it possible to make a more rational design of additives?

3) Why does hydrazinium iodide additive produce the most stable device among studied additives?

4) How the achieved stability of 4400 hours compares to current state of the art for the studied materials and overall for PSCs?

Provisional Recommendation

I recommend that the candidate should defend the thesis by means of a formal thesis defense