Skoltech
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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: Sergey Levchenko

I confirm the absence of any conflict of interest 	**Date:** 07.09.2021

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

All comments are meant to be addressed by changing directly the text of the thesis, except where an answer is specifically requested.

- Brief evaluation of the thesis quality and overall structure of the dissertation.

The research presented in the thesis is of very high scientific quality. In addition to the immense amount of experimental results, the work contains global analysis of the data based on simple physico-chemical arguments, which helps to systematize all the data in the field reported to date. This makes the presented work very valuable for further data analysis and ultimately development of best additives for inorganic-organic perovskite solar cells.
The structure of the thesis is overall clear, although the introduction seems too detailed and therefore very long. Also, the English writing should be improved, but it is clear enough for understanding all the statements. My detailed comments and particular concerns with writing and clarity are summarized below.

- The relevance of the topic of dissertation work to its actual content

The actual content of the thesis is directly related to the topic.

- The relevance of the methods used in the dissertation

The methods used are directly relevant for the research tasks formulated in the thesis.

- The scientific significance of the results obtained and their compliance with the international level and current state of the art

The scientific significance of the results obtained is very high. The obtained experimental data give important insights into the connection between features of additives and their effect on solar cell performance. In particular, it is found that the effect of over-stoichiometric PbI2 crucially depends on the choice of solvent. New additives have been tested, and an important general conclusion is made that amine groups have crucial role in stabilizing the perovskite layer. The high level of synthesis control and thorough materials' characterization are beyond current state-of-the-art. It has allowed to get the above insights which were not reported before. These advances are documented in four peer-reviewed first-author publications.

- The relevance of the obtained results to applications (if applicable)

The obtained results are directly tied to a particular application – solar cells. The research addresses an important challenging problem with inorganic-organic hybrid perovskite solar cell materials – their low stability under operational conditions.

- The quality of publications

These advances are documented in four peer-reviewed first-author publications. All publications do not only report experimental results, but also provide rational analysis of the obtained data and clearly put it in the broader context of the immense knowledge accumulated in the literature on this topic.

The summary of issues to be addressed before/during the thesis defense

It is often unclear why reported results or conclusions from experiments are relevant for the topic of the thesis (see detailed comments below).

Please explain from very beginning what is meant by additives. At which stage of synthesis are they added?

"The poor stability of the perovskite layer often disintegrates perovskite into either PbI2, metallic lead or some volatile species, creating defects at the surface, grain boundaries." – clarify why this is bad

"due to HAI incorporation" – explain abbreviation HAI

"The author prepared sampled" - ... samples

"Besides, their application became limited to powering satellites and some other space applications." – why "besides"? in this context, "Therefore, ..." would be better

"These choices are of the cation and anion relies on Goldschmidt tolerance factor (t), which predicts a stable crystal structure of perovskite." -> "The choices of the cation and anion rely on Goldschmidt tolerance factor (t), which predicts a stable crystal structure of perovskite."

"long diffusion lengths of charge carriers >1 um" – um?

"Further, low trap states" – do you mean "low density of trap states"?

"Since perovskite solar cells showed rapid progress of improvement in the efficiencies within a decade, it has emerged as future generation PV technology" – "...they have emerged ..."

"On the contrary, perovskite solar cells are reported to be stable only for a few hundred hours to a maximum of one year 5. Thus faces serious stability issues..." -> "On the contrary, perovskite solar cells are reported to be stable only for a few hundred hours to a maximum of one year 5, thus facing serious stability issues..."

"Reports have shown that upon exposure to these external factors, PSCs degrades and loses their operational stability." -> "Reports have shown that upon exposure to these external factors, PSCs degrade and lose their operational stability."

"In the presence of light and heat, PbI2 is further decomposed and results in the formation of metallic lead and ionic iodine" – what do you mean by "ionic iodine"? how is this possible when lead is metallic?

"Majorly the additives have opted" – "Majority of the additives"

"Majorly the additives have opted from already available literature or experimental data related to dye-sensitized solar cells (DSSC)" – DSSC abbreviation was used before but not explained; explain it above

"Majorly the additives have opted from already available literature or experimental data related to dye-sensitized solar cells (DSSC). For which additives are often categorized..." -> "Majorly the additives have opted from already available literature or experimental data related to dye-sensitized solar cells (DSSC), for which additives are often categorized..."

"Unfortunately, the addition of MACl was reported to form mixed halide perovskite CH3NH3PbI3-xClx" – explain why this is bad

"For instance, the introduction of 4, 4'-bipyridine in MAPbI3 demonstrated complex formation with PbI" – explain what it means "demonstrated complex formation with PbI" and why this is good

"Additionally, it has been shown that the presence of N atoms prevents the loss of volatile species..." – I guess you do not really mean free N atoms, but it sounds like this; please re-write to clarify this

"eliminated ion migration. While the hydrophobic C60 unit does not let moisture directly affect the film" – "eliminated ion migration, while the hydrophobic"; as you can see from previous similar comments, this is a common mistake in the text: you use part of a sentence as a separate sentence, which is strange to read; please revise your writing

"In an investigation, Zhang and co-workers demonstrated that NMP as a solvent additive (when added in DMF) – explain abbreviation NMP, DMF; also further on, please introduce abbreviations first time they appear in the text

"when the intermediate phase was found to be vanished with CHP solvent additive" – "to vanish"

“and ambient stability due to hydrophobicity of N atoms with ring like structure” – “N atoms within ring-like structure”?

“The oxygen atoms act as Lewis base. Whereas Pb2+ acts as Lewis acid” – this is ONE sentence: “The oxygen atoms act as Lewis base, whereas Pb2+ acts as Lewis acid”

“This adduct formation further results in large, flat grains” – explain why this is important

“Moreover, it was shown that incorporating amides in MAPbI3 reduces the Fermi level by interacting I- defect vacancy, reducing the trap sites and increasing the work function of MAPbI3 perovskite.” – very unclear sentence; what does it mean “reduces the Fermi level”, “I- defect vacancy”, “reducing the trap sites”? Also, why is it good to increase the work function of MAPbI3 perovskite?

“Recently, a variant of urea, biuret incorporation in MAPbI3 precursor attributed the intermediate formation with PbI2 to the electron delocalization in the N-C=O-N system in the presence of carbonyl group and explained this is why the peak shift for C=O vibration is noticed in FTIR spectra. (in the case of biuret-modified MAPbI3 film from 1722 to 1713 cm-1) 68” -> revise this sentence, it is impossible to understand

“This further reflected improvements in the contact angles of the film (so that the hydrophobicity of the films)” – the phrase in parentheses looks unfinished

“could inhibit the raid of moisture to MAPbI3 films” – what is “raid of moisture”?

“However, both IDIC-Th and IDIS-Th are known for their hydrophobic nature.” – Why “however”? In the previous sentence you wrote that hydrophobic is good

“Although the purpose of using the azo group was to reduce the stiffness of the perovskite film 91.” – this is not a properly finished sentence

“Although the purpose of using the azo group was to reduce the stiffness of the perovskite film 91. However, due to the hydrophobic nature of attached cation in the acid-containing additive, most of them increase ambient stability.” -> “Although the purpose of using the azo group was to reduce the stiffness of the perovskite film 91, due to the hydrophobic nature of attached cation in the acid-containing additives, most of them also increase ambient stability.”

“Further, cyclic ether compound THF (Tetrahydrofuran) also reported improving stability in ambient air” -> “Further, cyclic ether compound THF (Tetrahydrofuran) was also reported to improve stability in ambient air”

“which was used to achieve fast electron transport rates toward the anode, including the growth of large, uniform, smooth and crystalline perovskite film” -> “which was used to achieve fast electron transport rates toward the anode and growth of large, uniform, smooth and crystalline perovskite film”

“At the same time, quantum dot improves the crystallinity of film due to the quantum confinement effect” – are you sure? how can quantum confinement effect improve crystallinity? please explain the mechanism of this effect

“However, as the size of nuclei increases, the perovskite shows partial replacement” – do you mean weight of nuclei?

“Further, the transitional metal halides,” – “transition metal halides”

"over stoichiometric PbI2" – explain what this means

"Whereas Pb2+ defects sites that act as Lewis acid." – this is not a complete sentence

"In the scope of this thesis, selection criteria for choosing additives for the MAPbI3 active layer have been presented, which was absent otherwise." – The state-of-the-art overview pointed out several selection criteria for choosing one or another additive. In what sense was this absent? Or was the literature reviewed in the light of the knowledge obtained in this thesis? It is very important to make this very clear.

"The organic additives were later subcategorised based on N donor atom, O donor atom and S donor atom mainly with the associated functional group. Inorganic additives were subcategorised based on the group in the periodic table." – related to the previous question; is this kind of classification your idea, based on your research, or not?

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*