CARL VON OSSIETZKY universität OLDENBURG
FAKULTÄT V
MATHEMATIK- UND NATURWISSENSCHAFTEN

Institute of Chemistry Chemical Technology 1
Photocatalysis & sustainable feedstock utilization

Prof. Dr. Michael Wark

TELEPHONE
+49- 441-798 – 3675

E-MAIL
michael.wark@uni-oldenburg.de

INTERNET
www.uni-oldenburg.de/tc-wark/

OLDENBURG

Date
January 28th, 2022

POSTAL ADDRESS
D-26111 Oldenburg
FOR PARCEL SERVICE
Carl-von-Ossietzky –Str. 9 - 11
D-26129 Oldenburg

Natalya Karpova

St. Petersburg State University

Russia

Report on the PhD work of Ali Ibrahim Mohammed Sharafeldin

Title of the PhD thesis: Effect of heterovalent doping on structure and photostimulated processes in $CsPbBr_3$ halide perovskite

Mr. Sharafeldin worked on perovskite-based photoactive materials which became in the last year very attractive because with the class of inorganic-organic perovskite solar cells with very high efficiencies could be developed. Although being completely inorganic also the $CsPbBr_3$ is included in that development for photovoltaics since it turned out that the use of Cs^+ ions instead of ammonium-based cations strongly improved the stability of such cells.

Since in photovoltaics as well as in photocatalysis the absorbance of light in the layers plays a crucial role, it is obvious that the research on these kind of compounds with respect to photocatalysis is prospective as well.

To optimize the materials in both directions of application a good understanding of the photophysical processes of the perovskite materials is of high important. Since doping with more metal ions is a common technique to alter the photophysical properties, it is obvious that also Mr. Sharafeldin used this approach.

In chapter 1 of his thesis Mr. Sharafeldin describes very clearly the basics of perovskites, why dopants are attractive and how they act in the structure of perovskites, i.e., which kind of defects can be formed. Very illustrative is, for example, Figure 1.8. in chapter 1.2.4 Mr. Sharafeldin explains why he chose Bi^{3+} and Ag^+ as doping ions for his experiments. For this also DFT calculations were taken as arguments. Although the necessary citations are always given in the text, what I miss is a direct citation of the figures used from literature in the captions of the Figures in this chapter.
Very instructive is chapter 1.2.5 about photoinduced defects. All the discussions and equations listed there are very convincing, however I ask myself what the reason in the inconsistence of the style of the equations might be; some are given in *Times*, some in *Arial*.

In total the literature review in Chapter 1 is very extensive (about 160 citations), informative and conclusive. It provides a very good overview and motivation for the own study.

Chapter 2 describes the used methods – as far as I see the descriptions are complete and should allow a reproduction of the material syntheses. what I wonder about is the use of "gr" as the unit for the weights – usual is "g". Also, the use of "M" for **m**illigram and deci**m**eter in Table 2.1 is not common – and again in this Table two text styles are mixed as well as the use of "." and "," in numbers is not consistent.

Chapter 3 demonstrates that the doping with Ag^{+} or Bi^{3+} ions does not influence the stability of the perovskite structure much. But the lattice cell increase with the content of e.g. Bi^{3+} ions (Table 3.2) clearly shows that the doping was successful. A bit questionable is whether the direct linking of the measured points in Fig. 3.9 is favorable, I think considering some measurement errors would be better. in Fig. 3.10 the connection of the obtained data points is even more doubtful; I see no reason/evidence for the shown curvatures.

Chapter 4 discusses the formation of defects due to the doping. The doping with both ions results in redistributions of the intrinsic defects and formation of the dominating types of the defect states depending on the type of the dopant to compensate the charge excess of the corresponding dopant cations. However, the photostimulation of defect formation is much higher for doped silver ions. To my opinion the argumentation in the chapter is very clear – and the findings are very fruitful for further doping optimizations.

Chapter 5 finally concentrates on the effect of doping on the luminescence behavior of the doped perovskites. A convincing correlation to the defect formation is given. It is obvious that especially doping with Bi^{3+} ions strongly influences the luminescence band. In chapter 5 the style of the Figures is not always consistent; for example, Figs. 5.20 and 5.21 look different in style to the others; furthermore, again the use of decimal point and comma are not consistent again in some Figures (throughout the chapters 3 to 5).

Finally, in the Conclusion chapter Mr. Sharafeldin summarizes the most important results in a numbered list and draws 10 conclusions from those (again in a numbered list). To my opinion a discussion in a running text, giving the chance to better correlate results and conclusions to each other would have been better, but this might be a personal view. What I really miss is the reflect the obtained results in a broader approach, giving more general statements about the effects of doping on defects and optical (luminescence) properties, because as it was said in the Introduction chapter much more other doping ions can be used as well.

Based on the information given on pages 9 and 10 of his thesis Mr. Sharafeldin published 4 papers up to now. In Web of Science only two of them are listed; the one in ACS Appl. Mater. Interfaces from 2021, where Mr. Sharafeldin is the 4^{th} author and what deals with another perovskite material, and the one in Mendeleev Communications as well from 2021 with Mr. Sharafeldin as first author and the doping in $CsPbBr_3$ as topic. Both papers have not been cited yet, which, however, is understandable, since they were only published middle of 2021. Unfortunately, I had no access to the paper in Mendeleev Communications, so that I could not read the paper by my own. Although the impact factor of the journal is with 1.786 not high, the acceptance of the paper documents that the results discussed in it passed a critical review process.

Furthermore Mr. Sharafeldin discussed his scientific results on 6 scientific conferences, mainly in Russia.

In summary, with full conviction I recommend the acceptance of the PhD work and I propose that Mr. Sharafeldin is awarded with the doctoral degree.

Although there are some shortcomings in the style of the presentation of the results in the thesis, the high quality of the obtained results is convincing. Thus, in Germany, I would award the grade **"very good" ("magna cum laude")** – and I hope this recommendation is also helpful for you in St. Petersburg.

Yours sincerely

Prof. Dr. Michael Wark