

An opinion concerning the thesis “Magneto-optical and microscopic properties of organo-lead halide perovskites” by Krzysztof Gałkowski submitted as a partial fulfilment of the requirements to obtain a degree of doctor of physics

First, a formal remark: my information is that the doctoral procedure of Mr. Krzysztof Gałkowski is carried out within the agreement between Université de Toulouse and the Department of Physics of the University of Warsaw. The thesis does not state this fact anywhere. Also, my information is that the defense is to be held in Warsaw at the Department of Physics while the thesis mentions Toulouse as the place planned for this event. Please, check and correct if necessary these two pieces of information.

The thesis is written in English which is obviously a foreign language to Mr. Gałkowski (as it is to this reviewer). In particular usage of definite/indefinite articles and prepositions is often wrong and sometimes makes it hard to comprehend the text (e.g., “...for the further controlled development...”, see page 15, “...in more a cubic-like character...”, see page 23, “In order to avoid the formation of eddy currents...”, see page 29 and/or “composed from”, see abstract, etc.). Another example of bad language may be found in the last paragraph of Section 1.3.2 where the sentence beginning with “Theoretical calculations,...” does not contain any verb in its first part. This is particularly true in the case of the introductory parts of the thesis. As the reading progresses the language of the text becomes better and better. But still what is “spin-coated nature”, see page 67? I think that the entire text should undergo a thorough linguistic smoothing before it goes to the printers.

The thesis consists of 7 Chapters including an Introduction, short conclusions, descriptions of the experimental equipment and set-ups used by Mr. Gałkowski (by the way, did Mr. Gałkowski contributed to the construction of some the equipment or, possibly, software? I do not find such information in his thesis) and four main Chapters containing results obtained by him during his studies. The thesis contains also a list of publications in various journals co-authored by Mr. Gałkowski and an extensive bibliography of papers quoted in the main text. Such composition of the thesis is quite standard and complies with the usual layout expected of a doctoral thesis.

The introduction shows that Mr. Gałkowski is familiar with a broad spectrum of problems that one faces when attempting to fabricate efficient solar cells made of perovskite materials. On the other hand, his main goal was not directly connected to this effort. He was, for instance, not involved in measurements of photon conversion efficiency of the perovskites. (Parenthetically, I do not see any activity of his that would provide a useful feedback the material growers in the UK, where the samples studied by Mr. Gałkowski were

obtained from. This is rather a weakness of the whole project. I only hope that such feedback loop does exist in reality.) With this fact in mind the Introduction contains a lot of information that is not directly connected to the thesis itself and, thus, the text could be made shorter (pages 20-24). The same is true for the part describing the equipment, in particular that generates intense magnetic fields, and even more precisely, the information on pages 27-28. The same is true for the part describing fabrication of the samples which were prepared by others (pages 36 – 37) .

The following Chapters 4, 5 and 6 contain the main body of new results obtained by Mr. Gałkowski, namely the magneto-transmission study and spatially resolved microluminescence of hybrid perovskites APbX_3 , where X is either Br or I, and A is either methylammonium or formamidinium ions or their mixture. (The case of X=Chlorine mentioned in the abstract is actually only fragmentarily studied by the author in Chapter 4 and 5 where crystals with mixtures of I-Cl were experimented upon). In Chapter 6 the organic ions are replaced by inorganic Cs ions. I have an impression that the study of the crystals with Cs as described in the thesis is only at a very initial stage. In this latter case only the transmission and magneto-transmission experiment were performed. The materials, as the author emphasizes in several places, are promising materials for making cheap and efficient solar cells. Therefore, the contribution made by Mr. Gałkowski represents a part of an important line of studies performed presently worldwide aimed at optimization of the materials from that point of view. Since these materials undergo structural phase transitions as the temperature is varied (which changes their usefulness for solar cells) the author had to study their properties as a function of the temperature. Also, as he shows, different crystalline phases may coexist in some temperature ranges. Thus, the part of work related to microluminescence described in Chapter 5 is an important fragment of the program.

Samples were examined very carefully before making optical experiments and a careful procedure was developed in order to avoid degradation of the perovskite structure that may result when exposition to moisture takes place.

The center of gravity lies, however, in the part related to optical transmission and magneto-transmission. From those measurements Mr. Gałkowski is able to extract such important parameters of the studied crystals as exciton binding energy and the effective mass of the charge carriers with an unprecedented accuracy. He also makes some general remarks concerning trends in the values of these parameters in the entire family of organic lead halide perovskites connecting them to the energy gap value. This is a useful and important result. Equally important is determination of the effective dielectric constant for the studied compounds. The data are nicely presented in tables and in figures (e.g., figure 4.12) that summarize the discussion in a convincing way.

The method of microluminescence is not as quantitative neither it is very predictive. It may be, however, equally useful to people assessing the quality of the materials, as the results of

the magneto-transmission. Definitely, it should be made more directly accessible to them and become an important link in the feedback loop mentioned above.

I have several remarks of minor importance: (i) the author should decode an acronym LUMNP on page 32; (ii) Figures 3.5 a and 3.5 b use completely different vertical axis scales and show different parts of the spectrum. So they cannot be called a comparison of the data for pristine and degraded samples; (iii) Equation 4.7 cannot be true since the units of particular terms are different; (iv) Figure 4.6b repeats the data already presented in Fig. 4.6a; In Fig. 4.8 the effective Rydberg constant is denoted by a and the reduced exciton mass by m while in the text the author uses, respectively, R^* and μ to denote these two quantities; (v) on page 40 and ff Mr. Gałkowski several times writes about "absorption minima" while it is the transmission curves are shown in this Chapter that display the minima. Thus the absorption shows local maxima, in fact; (vi) why Fig. 5.1a and 5.1b are repeated on page 69 (they appear for the first time on page 41).

Some of the results that the thesis contains were already published in a regular refereed journal. In fact, this is the most frequently cited paper co-authored by Mr. Gałkowski (19 times according to Web of Science database). There is another paper on the microluminescence studies that has been submitted to prestigious *Nanoletters*, however I do not see it listed in this database. In both these papers Mr. Krzysztof Gałkowski is the first author which indicates his leading role in their preparation.

To sum up, this is an interesting thesis where important questions are asked and answered. The logic of the discussion of the experimental data obtained in the course of the work is clear and convincing. In my opinion the thesis presented by Mr. Krzysztof Gałkowski is very good and solid and certainly sufficient to be a basis for application for a degree of doctor of physics. I am formally requesting that he is permitted to publicly defend it.

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