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Conc.: Referee report for Agnieszka Marjanowska's doctoral dissertation entitled: *Photovoltaic and nonlinear optical effects of thin films based on perovskites*.

Dear Colleagues,

With great pleasure I read the doctoral dissertation of Agnieszka Marjanowska, which contains a considerable amount of interesting and very valuable research that was done on a very timely subject. I sincerely hope that my report will be in the right form, and that it will be detailed enough to swiftly and successfully complete the ongoing graduation process.

Background:

Perovskite solar cells are still one of the hottest topics in state-of-the-art photovoltaics. Efficiencies of the order of 26% have repeatedly been reported for perovskite solar cells under laboratory conditions. This result seriously challenges Si-based solar cell technologies. But perovskite solar cells can also be fabricated with the help of thin-film technologies, which is yet another distinct advantage over the relatively complex and costly fabrication of conventional solar cells based on Si.

On the other hand, many of the highly efficient perovskite solar cells, like the ones containing $MAPbI_3$ (methyl-ammonium lead iodine) as an absorber layer, involve environmentally problematic elements. They are also subject to rapid degradation, compared to a 20-30 years lifespan of a typical commercial Si-based solar panel.

To make some serious progress towards commercialization of perovskite solar cells, and to challenge other commercially available solar cell technologies, one must probably try to understand the physical processes behind the unusually high efficiency of the perovskite solar cells on an atomistic level, and then try to eliminate all physical processes, which lead to the rapid decay of the most promising candidate perovskite absorber materials. And finally, one must also be able to identify more eco-friendly materials.

With perovskites dominating so much of the current literature about photovoltaics, one might be tempted to assume that these problems have all been solved, due to the sheer bulk of the already existing literature. But this is not the case, and it is quite typical for many (over-)hyped scientific topics these days, where a lot of work quickly becomes rather shallow, repetitive and only reports incremental progress, at best.

What the field would really need in such a situation are very systematic studies on carefully selected types of materials using established analysis methods and device technologies, as exemplified by the present dissertation. And there is always a need for fresh new ideas, which tackle aspects that have been neglected or explored rather poorly up to now. Like nonlinear optical properties in the case of perovskite materials, which is the other main topic of this dissertation.

Summary and appraisal of dissertation:

The dissertation describes research on perovskite materials and perovskite solar cells, which was completed under a joint supervision by Prof. Anna Zawadzka from the Nicolaus Copernicus University in Torun (Poland) and Prof. Bouchta Sahraoui from the University of Angers (France). The title of the thesis is: *Photovoltaic and nonlinear optical effects of thin films based on perovskites*, and the whole dissertation is structured accordingly.

Brief overview:

The dissertation starts with a two-page Introduction, where the candidate gives a clear and convincing motivation for the work completed in this thesis, and where she also guides the reader through the rest of the dissertation. Chapters 1-3 cover the necessary scientific background and make up for approximately half of the thesis, and a longer Chapter 4 describes detailed experimental studies of perovskite materials and perovskite solar cells. All Chapters have their own list of references, which makes each Chapter very self-contained, and the whole dissertation is a lot easier to read.

The scientific parts of the dissertation close with four pages of a general Summary. It should however be pointed out that in Chapter 4, which describes most of the scientific results of this dissertation, the candidate had already summarized and critically assessed many of her experimental results using separate conclusion Sections. This was very helpful, due to the bulk of the reported experimental results.

The remaining parts of the thesis contain the usual lists of figures and tables, and a list of published papers, oral presentations and poster contributions. Published worked comprises about 9 papers that appeared in decent international journals, and about 10 conference contributions. This output is very respectable and must be highly commended. The candidate also lists a total of 8 oral contributions and 3 poster contributions at leading international conferences (or as invited seminars), which shows that the candidate has regularly and very successfully presented her ongoing work to a larger audience of international peers.

Detailed summary and assessment:

Chapter 1 provides some technical background information about solar cells in general, and perovskite solar cells in particular. It states all the important facts, which are necessary to understand the fabrication and characterization of solar cell, and which are described in later Chapters of the dissertation. I also appreciated the short Section 1.8 very much, which summarizes the current state-of-the-art in photovoltaics, and which is indeed a strong motivation for the kind of research presented in this dissertation.

Chapter 2 tackles the second major topic of this thesis, which is the nonlinear optical properties of thin film perovskite materials. It contains a description of all the essential theoretical background to understand the nonlinear optical properties of bulk materials. Starting from the corresponding nonlinear wave equation, we get some insight into second and third harmonics, and the underlying light-matter interactions described by higher-order susceptibilities. The Chapter also discusses derived optical properties like nonlinear absorption and nonlinear contributions to the refractive index of a given material. And it closes with 3 pages that describe potential applications as another strong motivation for the research carried by the candidate.

Chapter 3 describes the experimental background of this dissertation, which starts with an outline of physical vapour co-depositions, being the method of choice to prepare the samples for this thesis. This Section is followed by a description of various standard analysis methods like atomic force microscopy and spectroscopic methods, both of which were particularly useful to study the ageing of the fabricated films, which is the topic of Section 3.4. A larger part of Chapter 3 is then devoted to the determination of nonlinear optical properties based on Maker fringes and Z-scan type of techniques. As the systematic measurements of nonlinear optical materials for a series of perovskite materials is one of the novel aspects of this thesis, a more detailed description of the corresponding experimental techniques is perfectly justified and very welcome. Chapter 3 closes with a short one-page description of photovoltaic measurements, which is all very easy to grasp, because the background material to understand these measurements had already been provided in Chapter 1.

Before I finally come to the main results of this dissertation, which are described in Chapter 4, I would like to point out that all the technical Chapters 1-3 were nicely written and nicely illustrated. The material was restricted to the bare essentials and nothing more, which for me is always a good sign, that a candidate has really understood the focus and the scope of his/her scientific work.

Let us now come to Chapter 4, which contains the main scientific results of this thesis. Here, the reader is greeted with a sound motivation for the reported research, and a brief overview of the perovskite materials that are supposed to be studied, and another brief overview of the various experimental techniques that were used to study each of them.

Section 4.1 reminds the reader of the structural properties of perovskites, which is very important information to understand the chemical and physical properties of these materials. It also lists a series of 8 closely related perovskite materials, which were fabricated in different compositions as basic materials for the reported research.

The fabrication of thin film samples is described in Section 4.2 using physical vapour co-deposition. All materials are related to methylammonium lead iodine, where iodine has been substituted by bromine and chlorine, and the lead atom has been substituted by germanium, cadmium, tin and zinc, some of which are eco-friendly choices, and some are not. A very useful nomenclature is introduced to distinguish between the different materials.

Section 4.3 describes the surface structural properties that were determined for each of the perovskite materials. We see very detailed 3D AFM scans, and we also see derived properties referring to the connectivity and the roughness of the fabricated thin films. This information is quite dense, but the candidate has added Section 4.3.4, where she critically assesses the quality of the fabricated thin films based on the reported surface properties, and where she also suggests potential applications.

Section 4.4 describes the measured linear optical properties of the perovskite thin films. For potential applications as absorber materials in perovskite solar cells, the key linear optical property will be strong absorption over a wide range of frequencies, and particularly in the visible range. To measure nonlinear optical properties, one would require high transmission at the wavelength of the incoming laser beam, and the assessment of linear absorption at the frequencies of the generated second and third harmonics, in order to choose the right model for the analysis of the experimental data. All the essential data has been provided by the candidate in quite some detail, and a summary and a critical assessment of the reported results is given in Section 4.4.4.

Another systematic study of materials properties, which are key to the development of largely improved perovskite solar cells, is the aspect of ageing and degeneration of thin films, which is described in Section 4.5. These tests were carried out over weeks and months, and they were monitored by performing AFM scans and by carrying out optical transmission measurements. Again, all results are summarized and critically assessed in a concluding Section 4.5.4, which shows that each sample was subject to degradation over time, but with chlorine-based samples showing the fastest ageing, and bromine-based samples being somewhat more stable.

A related problem are phase transitions within the perovskite samples, which might occur as a function of sample temperature. These phase transitions involve stable orthorhombic, tetragonal and cubic structures at different temperatures. The candidate examined that important aspect of perovskite thin films in Section 4.6 by measuring the related optical transmission and photoluminescence spectra as a function of temperature. The reported results look very consistent, and they are also consistent with the existing literature.

Section 4.7 contains a very detailed and very systematic study of the nonlinear optical properties of the fabricated perovskite thin films. This data is extremely valuable, also because the candidate has studied changes in the second order and third order nonlinear susceptibilities over time. Second order susceptibilities were taken under different polarizations and with and without employing corona poling. The candidate also determined third-order susceptibilities for a large series of samples, and she measured the nonlinear absorption of selected iodine-based and chlorine-based samples using Z-scans. The results are summarized and critically assessed in Section 4.7.4. Many samples showed weak second-order nonlinear effects, which often improved after corona poling. Concerning third order nonlinear susceptibilities, the candidate has measured strong nonlinear effects for all samples, also compared to the reference material. This is very interesting. As for nonlinear absorption, both iodine-based samples show negative nonlinear absorption coefficients, which corresponds to saturable absorption, whereas the nonlinear absorption coefficient for the chlorine-based sample was positive, which corresponds to reverse saturable absorption.

Section 4.8 finally describes measurements on three different types of lead-based perovskite solar cells, where the halogen components of the perovskite absorber layers changes from sample to sample. The candidate has followed a standard layout for this type of solar cells, which involves a perovskite absorber layer, tin oxide as electron transport layer and Spiro-MeOTAD as hole transport layer. Other standard layers were ITO and gold as upper and lower contact materials. The whole assembly was deposited on a glass substrate using physical vapour deposition. The basic photovoltaic properties of the three solar cells are shown in Fig. 4.43 and Table 4.22. All specimen act as solar cells and show the expected general behaviour of such devices. Efficiencies however are somewhat low in all three cases, which is a pattern that we also observe quite often, and which strongly depends on the laboratory conditions. Nevertheless, interesting information can always be extracted from the measured data on such samples. The candidate has convincingly carried out such an analysis to identify effects that clearly depend on the varying chemical composition of the absorber layers, and effects that influence the series and shunt resistances of the solar cells. The low efficiencies of the specimen were also contrasted to much larger efficiencies predicted by numerical device simulations for the same type of devices. This is a known problem and, in my eyes, says very little about the quality of the specimen, but instead raises some serious questions about the practical value of these device simulations. Because experimental studies always tend to report much lower efficiencies for the same types of perovskite solar cells.

Finally, the Summary gives a nice overview of the reported findings. The candidate rightfully points out that all the milestones of the PhD project had been reached, and that the reported results might be very useful to develop more stable and more efficient types of perovskite solar cells, which are also eco-friendly. The candidate also emphasizes the value of the reported results when it comes to potential applications of perovskite thin films in nonlinear optics. Here I also agree with her. The reported results are indeed very encouraging, and they strongly suggest interesting follow-up work.

Minor issues (which could be addressed during the defense):

- P. 3: "The energy gap has no energy levels, so electrons cannot reside there." I understand what the candidate wants to say, but this is only correct for Bloch states. Surface states, localized states, impurity-related states etc. can all exist in the band gap.
- P. 17 bottom: " … photovoltaic cell composed of a single semiconductor layer …" is formally correct but a bit misleading. Real solar cells always involve several functional

layers, including differently doped semiconductor layers. The Shockley-Queisser limit refers to a highly idealized model of a single-junction solar cell, where functional layers other than the absorber layer are all substituted by highly idealized processes to describe charge carrier transport and charge carrier extraction.

- P. 30 Eqs. (2.20): I cannot entirely follow the logic of the proof. Which statement about polarization would follow from inversion symmetry, and which statement follows from formally inserting an inverted electric field? I think this is where the contradiction originates.
- P. 31, top: " … the first term describes the static field …". Statement is correct, but in nonlinear optics this term is usually referred to as optical rectification.
- P. 43: "The most popular nonlinear crystals used for frequency conversion are BBO, KTP, LBO crystals, and perovskites". What do these abbreviations mean?
- P. 159: "The potential applications in nonlinear optics are enormous, and subsequent research should include a thorough analysis of NLO using quantum chemical simulations." I agree, but I would have appreciated that the candidate had given some examples of possible applications of perovskite thin films in nonlinear optics. And I also would like to point out that standard quantum chemical simulations of nonlinear optical properties are only possible for molecular systems. For bulk perovskites, one would need solid state simulations of nonlinear optical properties, which are not very well-developed up to now.

All formal criteria are met by this dissertation:

1. The candidate demonstrates profound theoretical and practical knowledge when it comes to the synthesis, analysis and characterization of perovskite thin films, and the fabrication and analysis of solar cell devices. What I see is a complete mastery of all these aspects to perform detailed and independent work in the field of perovskite solar cells, and at the very forefront of the field.
2. The thesis is original concerning the systematic choice and the synthesis of a family of 8 perovskite materials, and a very detailed analysis of these materials across an impressive suite of methods. The focus on nonlinear optical properties positively stands out, because the corresponding analysis methods are not among the typical standard methods used to characterize perovskite materials. Equally impressive are microscopic and optical studies of phase transitions, the aspect of ageing among the different perovskite materials, and the fabrication and the detailed analysis of the perovskite solar cells.
3. The thesis has been submitted as a complete and very well-edited written dissertation, together with a list of references to other published work by the candidate, including conference contributions and oral presentations.
4. Abstracts have been provided in English, French and Polish. Unfortunately, I cannot assess the Polish abstract. But the abstracts written in English and French are surely consistent.

Overall assessment:

My general impression of this dissertation is a very positive one. The thesis is very systematic and well-structured from a theoretical and experimental point of view. And it is also marked by a sound interpretation of the scientific results, which demonstrates a profound knowledge of the methods used in this work and of their potential limitations.

The danger with research being done in a very popular field like perovskite solar cells is that results are often obtained in a rush. Thus, the underlying research is often not very systematic, because people tend to mass produce and divide results into the smallest publishable units. The present work clearly goes against such a trend, which must be very highly commended.

So even if, as usual, some results might have been difficult to obtain, and/or some experiments did not give the expected "killer" results, I would like to emphasize again that it is the very systematic work on some well-selected perovskite materials across a whole suite of analysis methods and device applications, which makes this thesis so valuable and novel. This kind of work not only helps to further develop standard perovskite devices, but it is also essential to achieve more realistic solar cell device simulations, to suggest new device applications using nonlinear optical effects, and to guide the field towards new eco-friendly and stable bulk perovskite materials.

Distinction:

I would like to suggest a distinction for this thesis, not only because it is well-structured and well-written. But because it also contains many sound and novel results, which are likely to lead to some progress and to some new ideas in the field of nonlinear optics and perovskite solar cells.

Final remark:

Should you still have some open questions, please feel free to contact me again.

Sincerely,

Prof. Alexander Quandt
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