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Poznań, 12nd March 2026

Review of the doctoral thesis of Ms Agnieszka Marjanowska, *M.Sc. in Technical Physics*
entitled: *Photovoltaic and nonlinear optical effects of thin films based on perovskites*

This research work was accomplished at the

NICOLAUS COPERNICUS UNIVERSITY IN TORUN, Institute of Physics
Faculty of Physics, Astronomy and Informatics
Doctoral School of Exact and Natural Sciences Scientific
under supervision of **dr hab. Anna Zawadzka,** Professor, Nicolaus Copernicus University
and
UNIVERSITY OF ANGERS, Institute of Sciences and Molecular Technologies of Angers,
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under supervision of **Prof. Bouchta Sahraoui**, Professor of University of Angers

The doctoral dissertation Ms Agnieszka Marjanowska is written on **170** pages and consists of: introduction, 4 numbered chapters, summary and lists of figures and tables. Each chapter contains its separate literature (chapter 1 – 33 references, chapter 2 – 41 references, chapter 3 – 33 references, chapter 4 – 27 references), which in total gives a very extensive bibliography (**134** literature items). There are also abstracts in English, Polish and French. Moreover, the authoress included the list of her publications (**19**) including **7** publications from the *JCR* list and **11** publications in conference materials and the list of conference presentations: oral presentations (**8**) and poster presentations (**3**). Ms Agnieszka Marjanowska was the first&corresponding author of **2** papers from the *JCR* list.

Nowadays, one of the most crucial ecological challenges is development of new technologies for production environmentally safe energy. The Sun, which is one of the natural sources of energy, provides the cleanest and relatively easily harvested energy. In recent years high dynamics in modification of conventional solar cells technology to improve efficiency in conversion of the natural solar energy into electric energy by the photovoltaic effect was observed. Among the materials that are being consider to use in new generation solar cells are hybrid perovskites. The materials investigated in the dissertation are hybrid perovskite thin films consisted of an organic part - the methylammonium part $CH_3\,NH_3^+$ and an inorganic part in the form of iodide (PbI_2), chloride ($PbCl_2$) or bromide ($PbBr_2$). The systematic study of the series of mentioned above materials were presented in the doctoral dissertation. The main part of the dissertation was preceded by the Introduction, in which the authoress presents some general information about the properties of hybrid perovskites and their potential application in photovoltaics, optoelectronics and nonlinear optics. The description of the theoretical issues considered in the doctoral dissertation and obtained experimental results were included in the 4 chapters. The dissertation ends with a summary including an analysis of the obtained experimental data, final conclusions, and perspectives for future research directions on perovskite materials in the context of photovoltaics and nonlinear optics applications.

Chapter 1 entitled *Photovoltaics* contains description of the energy band model of inorganic semiconductors (the energy levels structure of intrinsic, *p-type*, *n-type* doped semiconductors and semiconductor *p-n* junction). Moreover, the energy levels structure and conductivity of organic materials were described. The energy levels below the HOMO (the Highest Occupied Molecular Orbital) and the LUMO (the Lowest Unoccupied Molecular Orbital) considered equivalent to the valence and conduction bands is comparable to the energy gap E_g. In this chapter the structure and electrical model of solar cells was also described. In the subsection 1.4. *Classification of solar cells* the classification of photovoltaic materials: inorganic, organic and hybrid types (combination of inorganic and organic materials) were presented. The perovskite materials used in solar cells were described in the subsection 1.5. *Perovskite solar cells*. In the subsection 1.7. *Solar cell parameters* the parameters characterizing the photovoltaic cell determined from the *I-V* characteristics were defined.

Chapter 2 entitled *Nonlinear Optics* is focused on description of the theory of NLO phenomena including the Second Harmonic Generation (SHG), Third Harmonic Generation (THG), nonlinear absorption, and nonlinear refractive index. Moreover, the electromagnetic waves propagation in a medium was described on the basis of Maxwell's equations and the dependence of the electrical polarization P on the electric field E (linear and nonlinear electrical susceptibilities) was discussed. The second-order nonlinear susceptibility $\chi^{(2)}$ and third-order nonlinear susceptibility $\chi^{(3)}$ tensors were precisely described. Additionally, the second-order and third-order optical phenomena produced due to the interaction of an electromagnetic waves with the strong external electromagnetic field with a medium such as: SHG, THG, Sum-Frequency Generation (SFG), Difference-Frequency Generation (DFG), and Pockel's Effect were described. This chapter is very well written and illustrated based on the classical literature for NLO phenomena (41 references) and in my opinion may be very useful for the students, who are active in the field of NLO.

Chapter 3 contains description of the experimental techniques used to prepare and characterize the thin film perovskite samples. The low-dimensional structures were produced using the Physical Vapor Deposition (PVD) technique (the system - NANO 36™ /Kurt J. Lesker Company) supported by the material co-deposition process, called Physical Vapor co-Deposition (PVco-D). The obtained materials were characterized using the following experimental methods/technics: Atomic Force Microscopy (AFM) (the NanoSurf EasyScan 2 instrument), the optical spectroscopy in UV-VIS-NIR spectral range 250 – 1100 nm (the Analytik Jena UV-VIS-NIR spectrometer), PL spectra measurements (the Horiba FluoroMax®-4 spectrometer). The mentioned above experimental methods/technics and setups were described. In particular, the AFM technique provides information on topography, structure, roughness, crystallite size or type of the examined surface. A more detailed analysis was performed using the Minkowski Functionals Method (MFM) (Minkowski Volume $V(h)$, Minkowski Boundary $S(h)$, Minkowski Connectivity $\chi(h)$).

Moreover, the following experimental setups for determination of NLO properties of the thin film perovskite samples were described: experimental setup for SHG and THG measurements using Maker fringe technique, Corona Poling setup (for SHG study of centrosymmetric materials by creating macroscopic noncentrosymmetry), Z-scan technique (for measuring the third-order nonlinear optical properties of materials, such as the nonlinear refractive index n_2, nonlinear absorption coefficient β, and real and imaginary parts of $\chi^{(3)}$). In this chapter the following theoretical models used for analysis of experimental results were described: the Lee model used to determine the second-order nonlinear susceptibility $\chi^{(2)}$, the Kurtz-Perry model developed for microcrystalline powders based on comparison of the macroscopic second-order NLO of the samples with reference material, the Herman-Hayden model used for characterization of thin films and solid materials, the Kubodera-Kobayashi model used for calculation $\chi^{(3)}$, the Reintjes model, in which attempts were made to explain the phenomena responsible for the formation of the so-called Maker's fringes.

Additionally, the setups for testing the electrical properties of thin films and thin film solar cells under illuminated and dark conditions were presented.

Chapter 4 entitled *Characterization of perovskite thin films* presents the experimental results for the studied perovskite materials. In particular, description of perovskites (crystal structure) and their application in the photovoltaics and nonlinear optics were described. Moreover, the results of the investigation of the following organic-inorganic halide perovskites: $MAPbI_3$ (3 samples), $MACdI_3$ (1 sample), $MAGeI_3$ (1 sample), $MASnI_3$ (1 sample), $MAZnI_3$ (1 sample), $MAPbCl_3$ (3 samples), $MAPbBr_3$ (3 samples) and $MASnBr_3$ (1 sample) were presented and analysed. Mentioned above samples consisted of an organic part - the methylammonium part $CH_3\ NH_3^+$ (otherwise MA) and an inorganic part - in the form of iodide (PbI_2), chloride ($PbCl_2$) or bromide ($PbBr_2$). The samples made with various compositions of organic and inorganic part were assigned as follows: I.1, I.2, I.3, I.4, I.5, I.6, I.7, Cl.1, Cl.2, Cl.3, Br.1, Br.2, Br.3 and Br.4.

In particular, in this chapter the preparation of the hybrid perovskite thin film samples were described. All thin film samples investigated in this study were prepared by the PVD technique or its modification, PVco-D, using the Thin Film Deposition System - NANO 36™ apparatus (Kurt J. Lesker Company). Thin films were deposited onto transparent BK7 borosilicate glass substrates. The surface topography of the investigated hybrid perovskite thin films were characterized using the contact-mode AFM (2D and 3D AFM images); on the basis of AFM measurements the following parameters of hybrid perovskite thin films were determined and discussed: profiles, Minkowski Functionals (V, S, c), mean crystallite height (h_{ave}) and Mean Square Roughness (MSR). The described data set allows comparison of the surface topography of perovskites differing in B cation and X anion (based on the general formula of perovskites ABX3) and provides information on the influence of perovskite composition on its structure. Based on the above data, it was concluded that the perovskites forming the most homogeneous structures are the perovskites containing iodine and bromine. The compositions 50% MAX : 50% PbX_2 (X = I, Cl, Br) and the composition 70% MAI : 30% PbI_2 stand out in terms of layer quality compared to the others, and these could be the best candidates for further applications in optoelectronics.

Spectroscopic studies in the UV-VIS-NIR wavelength range were conducted for the following hybrid perovskite thin films: with iodide (I.1-I.7), chloride (Cl.1-Cl.3), and bromide (Br.1-Br.4). On the basis of transmission spectra of the mentioned above samples the absorption coefficients α for the 355 and 532 nm wavelengths were determined and the wavelengths for maximum transmittance λ_{trans} were given. The strongest absorption properties and the widest absorption range are exhibited by the samples with iodine I.1-I.3 and I.6. The absorption range for these samples was in the wavelength range 300 - 800 nm. The weakest absorption is shown by perovskites with chlorine, for which the absorption range is between 300 and 410 nm. Perovskites with bromine have an intermediate absorption bandwidth (300 - 590 nm) compared to the other materials tested.

The aging tests were carried out on the following hybrid perovskite thin films: I.1-I.3, Cl.1-Cl.3, and Br.1-Br.3. For the iodine perovskites 2D AFM images were presented for samples as fabricated, after 1 week, 1 month; mean crystallite height (h_{ave}) and Mean Square Roughness (MSR) and transmission spectra of samples with subsequent measurements were carried out after 1 week, 1 month, 2 months, and 6 months. For the chloride perovskites (highly degradable) 2D AFM images were presented for samples as fabricated, after 1 week, 2 months, mean crystallite height (h_{ave}) and Mean Square Roughness (MSR) and transmission spectra of samples with subsequent measurements were carried out after 1 week, 2 months. For the bromide perovskites (degrade over time more slowly) 2D AFM images were presented for samples as fabricated, after 1 week, 2 months, mean crystallite height (h_{ave}) and Mean Square Roughness (MSR) and transmission spectra of samples with subsequent measurements were carried out after 1 week, 1 month, 2 months, and 6 months. The investigated degradation processes in surface topography and transmission spectra indicate that, among the investigated perovskites, I.1 as well as Br.1 and Br.3 are the most stable due to surface structure for up to 6 months. On the other hand, due to optical transmission properties, I.1, I.3 and Br.1 are stable for up to 6 months. Perovskite containing chloride anions shows the greatest instability.

The phase transitions of the following hybrid perovskite thin films: I.1-I.3, Cl.1-Cl.3, and Br.1-Br.3 were studied by measuring UV-VIS-NIR transmission spectra and photoluminescence spectra as a function of temperature in the range from 80 to 310 K. The dependences of the maximum intensity and wavelengths of the selected peaks detected in PL spectra as a function of temperature were analysed. The following phase transitions were determined and analysed: from orthorhombic to tetragonal (I.1 and I.2) or cubic (I.3) and from orthorhombic to tetragonal and from tetragonal to cubic phases (Cl.1-Cl.3). Only one bromide perovskite (Br.3) showed changes in the transmission spectra, from which the phase transitions from orthorhombic to tetragonal phase at 110 K and from tetragonal to cubic phase at 240 K were determined.

Nonlinear optical effects were studied for the selected perovskite thin films with iodine, chlorine, and bromine. SHG and THG were analysed using the Lee (SHG) and Kubodera-Kobayashi (THG) theoretical Models, used in thin film analysis, and consider linear absorption coefficients. In particular, SHG measurements were carried out with two laser light polarization configurations (S-P and P-P). Most of the materials tested did not exhibit second-order nonlinear optical effects, so the Corona Poling (CP) technique was used to obtain the uniaxial orientation of the molecules. The SHG signals as a function of rotation angle for the selected perovskite materials: I.1-I.3, Cl.1-Cl.3 and Br.1-Br.3 were measured and analysed. The second-order nonlinear susceptibility $\chi^{(2)}$ values of perovskites I.1-I.7, Cl.1-Cl.3 and Br.1-Br.4 before and after application of the Corona Poling (CP) technique were calculated with the help of the theoretical Lee Model. The THG signals as a function of incidence angle of an S-P polarized laser beam were measured for the following materials: I.1-I.3, Cl.1-Cl.3 and Br.1-Br.3. The third-order nonlinear susceptibility $\chi^{(3)}$ values of the following perovskites: I.1-I.7, Cl.1-Cl.3 and Br.1-Br.4 were calculated with the help of the Kubodera-Kobayashi Model. The signals obtained by the Z-scan technique of I.4 and Cl.1 samples were measured and analysed and the values of the nonlinear absorption coefficient β of I.1, I.4-I.7 and Cl.1 materials were calculated.

In the subsection 4.8. *Application in photovoltaic cell* the authoress present the parameters determined for the selected hybrid perovskite thin films $MAPbI_3$, $MAPbCl_3$, and $MAPbBr_3$ used in a photovoltaic cells. The structure of the proposed cell consists of four thin layers: an ITO thin layer, acting as a transparent conductive electrode, a SnO_2 layer, an electron transport layer, a perovskite thin layer, which is the active layer that absorbs light, and a Spiro-MeOTAD layer responsible for hole transport. All thin layers were fabricated using the PVD technique and deposited on a transparent BK7 glass substrate. Characterization tests of the photovoltaic cells on the basis of I-V characteristics and power curves were carried out and the following parameters were determined: V_{OC} – open circuit voltage, J_{sc} – short circuit current density, P_{max} – maximum power point, FF – fill factor describing the quality of the cell, and energy efficiency coefficient η. The results obtained in this section confirm that thin films of hybrid perovskites $MAPbI_3$, $MAPbCl_3$, and $MAPbBr_3$ respond well to light and that solar cells containing these perovskite active thin films can generate current. Moreover, the efficiencies of the devices with $MAPbBr_3$ and $MAPbI_3$ are comparable. Measurements of electrical properties (dark and light I-V characteristics) showed that the cell with the $MAPbI_3$ perovskite active layer had the strongest light sensitivity. Cells with $MAPbCl_3$ and $MAPbBr_3$ light sensitivity was lower than that of the $MAPbI_3$ cell.

In addition, the following points should be clarified:

- Chapter 4 of the doctoral dissertation presents results, which were already published in the following articles:

  1. Marjanowska, A.; Wiśniewski, K.; Płóciennik, P.; Sahraoui, B.; Zawadzka, A. Role of Composition and Temperature in Shaping the Structural and Optical Properties of Iodide-Based Hybrid Perovskite Thin Films Produced by PVco-D Technique. Materials (2025) 18, 1336.

  2. Marjanowska, A.; El Karout, H.; Guichaoua, D.; Sahraoui, B.; Płóciennik, P.; Zawadzka, A. Topography and Nonlinear Optical Properties of Thin Films Containing Iodide-Based Hybrid Perovskites. Nanomaterials (2024) 14, 1, 50.

In my opinion these articles should be used as references in Chapter 4. Additionally, the same figures were used in the doctoral dissertation (Fig.3.8, Fig.4.22, Fig.4.23, Fig.4.24 and Fig.4.2.) and mentioned above articles without citations.

- Among the 14 samples investigated of the hybrid perovskite thin films 9 samples contains Pb and 1 sample contains Cd. Moreover, according to the obtained results the best structure parameters were obtained for the samples with the compositions 50% MAX : 50% PbX_2 (X = I, Cl, Br) and the composition 70% MAI: 30% PbI_2; from the UV-VIS-NIR spectroscopy $MAPbI_3$ and $MASnI_3$ are the most promising materials; from the analysis of the degradation processes $MAPbI_3$ as well as $MAPbBr_3$ are the most stable due to surface structure for up to 6 months. Finally, 3 samples $MAPbI_3$, $MAPbCl_3$ and $MAPbBr_3$ were selected for construction and characterization of photovoltaic cells. Could the authoress comment on the fact that the best materials with great optoelectronic potential for production the next-generation photovoltaic cells contain the toxic elements (Pb). Is there any chance to replace the components of the hybrid perovskite thin films with more environmentally friendly elements.

The most important achievements of the doctoral dissertation include:

- Develop a technique for fabricating of a series of new organic-inorganic hybrid perovskite thin films consisted of an organic part - the methylammonium part $CH_3\ NH_3^+$ and an inorganic part - in the form of iodide (PbI_2), chloride ($PbCl_2$), or bromide ($PbBr_2$) using the PVco-D method. Preparing the following samples with various percentages of organic and inorganic components: $MAPbI_3$ (3 samples), $MACdI_3$ (1 sample), $MAGeI_3$ (1 sample), $MASnI_3$ (1 sample), $MAZnI_3$ (1 sample), $MAPbCl_3$ (3 samples), $MAPbBr_3$ (3 samples) and $MASnBr_3$ (1 sample).
- The systematic study of the mentioned above materials using AFM, UV-VIS-NIR spectroscopy, photoluminescence spectroscopy techniques and electrical properties measurements important from the point of view their potential applications in photovoltaics or NLO optoelectronics.
- Construction and characterisation of the three prototypes of the perovskite photovoltaic cells on the basis of the selected hybrid perovskite thin films with the optimal parameters: $MAPbI_3$, $MAPbCl_3$ and $MAPbBr_3$.

Summary

Analyzing the above-described content of the doctoral dissertation Ms Agnieszka Marjanowska, it should be noted that in terms of technology as well as characterization of the selected physical properties of a group of new organic-inorganic hybrid perovskite thin films, the dissertation covers a very extensive research material. Moreover, an important aspect of the research was a comprehensive approach to the subject of the study with the use of many advanced experimental techniques in order to obtain new materials with the excellent photovoltaic and NLO properties. The application of the above-mentioned advanced experimental methods, requires knowledge of selected issues from the theory of the linear and nonlinear optics, solid state physics, chemistry of materials, technology for production thin films as well as the ability to analysis the experimental data using appropriate methods of numerical analysis, and finally to interpret the results of complex issues. It was a considerable challenge met excellently by Ms Agnieszka Marjanowska. Results of investigations of the mentioned above new organic-inorganic hybrid perovskite thin films contribute to the search for new advanced materials for photovoltaics and NLO based optoelectronics and in my opinion also bring a significant contribution to the materials science.

In summary, this work fully deserves the title of Doctor of physics of the Nicolaus Copernicus University in Torun, given the high quality of the scientific work presented and the doctoral student's success in achieving the requested objectives. I consider that the whole research activity of the candidate Ms Agnieszka Marjanowska and the scientific work presented for this thesis fulfil all the requirements and fully qualify Ms Agnieszka Marjanowska to obtain the degree of "Doctor in Physics". Moreover, I highly evaluate the doctoral dissertation of Ms Agnieszka Marjanowska and I think that the dissertation deserve to be distinguished for its originality, innovation and performing comprehensive research on new materials for photovoltaics. Consequently without any hesitation that I strongly recommend that Ms Agnieszka Marjanowska to be authorized to defend her doctoral thesis in physics at the Nicolaus Copernicus University in Torun.

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Poznań, 27th March 2026

Justification for awarding distinction to the doctoral dissertation
of Ms Agnieszka Marjanowska, *M.Sc. in Technical Physics*
entitled: *Photovoltaic and nonlinear optical effects of thin films based on perovskites*

The doctoral dissertation of Ms Agnieszka Marjanowska covers a very extensive research material in terms of technology as well as characterization of the selected physical properties of new organic-inorganic hybrid perovskite thin films – the group of materials considered as one of the most promising materials for photovoltaics. Nowadays the perovskites based solar cells are not yet widely used in commercial photovoltaics but they are widely researched in laboratories. In this sense, the doctoral dissertation of Ms Agnieszka Marjanowska fits perfectly into the topic of searching for new materials for photovoltaics. In particular, the materials investigated in the dissertation are hybrid perovskite thin films consisted of an organic part - the methylammonium part $CH_3\ NH_3^+$ and an inorganic part in the form of iodide (PbI_2), chloride ($PbCl_2$) or bromide ($PbBr_2$) produced using the Physical Vapor Deposition (PVD) technique supported by the material co-deposition process/Physical Vapor co-Deposition (PVco-D).

The most important achievements of the doctoral dissertation include:

- Develop a technique for fabricating of a series of new organic-inorganic hybrid perovskite thin films consisted of an organic part - the methylammonium part $CH_3\ NH_3^+$ and an inorganic part - in the form of iodide (PbI_2), chloride ($PbCl_2$), or bromide ($PbBr_2$) using the PVco-D method. Preparing the following samples with various percentages of organic and inorganic components: $MAPbI_3$ (3 samples), $MACdI_3$ (1 sample), $MAGeI_3$ (1 sample), $MASnI_3$ (1 sample), $MAZnI_3$ (1 sample), $MAPbCl_3$ (3 samples), $MAPbBr_3$ (3 samples) and $MASnBr_3$ (1 sample).
- The systematic study of the mentioned above materials using AFM, UV-VIS-NIR spectroscopy, photoluminescence spectroscopy techniques and electrical properties measurements important from the point of view their potential applications in photovoltaics or NLO optoelectronics.
- Construction and characterisation of the three prototypes of the perovskite photovoltaic cells on the basis of the selected hybrid perovskite thin films with the optimal parameters: $MAPbI_3$, $MAPbCl_3$ and $MAPbBr_3$.

Results of investigations of the mentioned above series of organic-inorganic hybrid perovskite thin films contribute to the search for new advanced materials for photovoltaics and NLO based optoelectronics. Moreover, in my opinion the doctoral dissertation of Ms Agnieszka Marjanowska deserve to be distinguished for its originality (proposed technique for fabricating of a series of organic-inorganic hybrid perovskite thin films, innovation (proposed technique for production), performing comprehensive research (AFM, UV-VIS-NIR spectroscopy, photoluminescence spectroscopy techniques and electrical properties measurements) and finally construction and characterisation of three prototypes of the perovskite photovoltaic cells on the basis of the selected hybrid perovskite thin films.