UNIWERSYTET KAZIMIERZA WIELKIEGO W BYDGOSZCZY

KAZIMIERZ WIELKI UNIVERSITY
Faculty of Physics
Powstańców Wielkopolskich 2, 85-090 Bydgoszcz

Dr. hab. Paweł Szroeder, University professor

Bydgoszcz, July 18th, 2025

Review of PhD Thesis "Nanostructures and thin films of metal-organic complexes and hybrid perovskites for applications in optoelectronics and photovoltaics" by Amina Laouid

Supervisor: dr hab. Anna Zawadzka, University professor, Nicolaus Copernicus University
Co-supervisor: dr hab. Amine Alaoui Belghiti, University professor, Chouaib Doukkali University

Scope and significance of the thesis

Demand for new environmentally compatible optoelectronic materials with improved performance and stability stimulates basic research into systems in which electron and optical properties can be tailored for specific applications. In particular, this area of research considers such phenomena as quantum confinement, as well as intra- and inter-molecular interactions in multicomponent systems. Quantum confinement effect makes it possible to control the electron and optical properties of materials by reducing their size, while intermolecular interactions in multicomponent systems enable to take advantage of such phenomena as energy transfer between molecules.

In the last two decades, special attention of researchers has been paid to organometallic complexes and perovskites, which show particular flexibility in matching their electronic and optical properties. Organometallic complexes are being studied extensively for applications in LED and nonlinear optics, while perovskites are attracting attention because of their high light absorption, efficient charge transport, and ease of fabrication. The application potential of these materials in photovoltaics and optoelectronics is fully manifested as long as they are in the form of thin films with reduced dimensionality.

Faculty of Physics, Kazimierz Wielki University, Powstańców Wielkopolskich 2, 85-090 Bydgoszcz, Poland
E-mail: psz@ukw.edu.pl https://www.ukw.edu.pl/pracownicy/strona/pawel_sz/ Phone: +48 52 321 61 91

Mrs. Amine Lauoid's doctoral dissertation fits perfectly into this stream of research. She chose thin films of two-component materials with limited dimensionality obtained by PVD and thin-film perovskites as the subject of her research. The PVD technique chosen by the doctoral candidate allowed to obtain high quality films with thicknesses on the order of 100 nm, which is crucial from the point of view of fundamental research.

In selecting the luminescent materials to be studied, the PhD candidate was guided by criteria such as high luminescence efficiency, stability, cost-effectiveness, environmental friendliness and the suitability to form thin films. These criteria are met by bis(8-hydroxyquinoline) zinc (Znq_2), which can act as an electron donor or acceptor, depending on its molecular environment. The original idea is co-doping of Znq_2 with the red merocyanine dye, 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl) -4H-pyran (DCM), which is known as a push-pull system having an electron donor-acceptor architecture. Another luminescent material under consideration was zinc sulfide, a direct bandgap semiconductor. Luminescence characteristics of ZnS thin films were tailored by doping with Ca and Mn. Additionally, Mrs. Amina Laouid conducted research of the thin film solar cells based on lead-free perovskite $RbSn_{0.5}Ge_{0.5}I_3$ and hybrid organic-inorganic perovskite $CH_3NH_3PbI_3$ (methylammonium lead iodide) to optimize the geometry and parameters of the cells for the greatest efficiency.

In summary, the scope of the thesis and proposed approaches are relevant to current trends and challenges in photovoltaics and optoelectronics.

Form and content

The basis of the submitted doctoral dissertation is a thematically coherent collection of 6 scientific papers published in the highly ranked journals. The collection of articles is preceded by a general introduction, in which the most important achievements and challenges related to the properties of thin films and nanostructures composed of metal-organic complexes and perovskites in the context of their optoelectronic and photovoltaic applications are outlined. In the introduction, which serves as a guide to the collection of publications, the doctoral candidate defined the research objectives and briefly described and justified the experimental and numerical methods used to achieve them. In this section, Mrs. Amina Laouid summarizes the most important results reported in each article and provides perspectives for further research.

All articles included in the dissertation were published in JCR-indexed journals, whose impact factor ranged between 3.8 and 6.3. The total IF of the collection of articles is 28,6. In the creation of five of the six scientific articles, the Mrs. Laouid's contribution is leading. According to the co-authorship statement, contribution of the doctoral student to article I is 64%, to article II – 50%, to article III – 57%, to article IV – 62%, to article V – 60. Only in the last paper, Mrs. Laouid is not the first author and her declared contribution is 6%.

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E-mail: psz@ukw.edu.pl https://www.ukw.edu.pl/pracownicy/strona/pawel_sz/ **Phone:** +48 52 321 61 91

Ca and Mn. Similarly to the two-component CMG-Znq_2 layers, they were fabricated using the PVD method. In this work, the influence the concentration of Ca and Mn on surface morphology was investigated by AFM and optical microscopy. In general, Ca dopant influences the surface roughness more than Mn, which is explained by the larger size of Ca ions. The optical transmittance data of Ca-ZnS and Mn-ZnS were used for studying the influence of dopants on energy gap, E_g. The increase in Ca concentration leads to a reduction of the energy gap from 3.05 eV (0%) to 2.7 eV (50%). This behavior of Ca-ZnS films is attributed to the decrease of the number of grain boundaries with increasing Ca concentration. On the other hand the addition of Mn has almost no effect on energy gap. PL data were used for investigation of transitions that occur in doped ZnS thin films. The Mn doping results in appearing of another peak in the yellow-orange region of luminescence spectrum attributed to the $^4T_1 \rightarrow {}^6A_1$ transition of Mn_2^+ ions. Moreover, this peak has tendency to red-shift with increasing concentration of Mn. Of particular note in this work is the demonstration that by changing the Ca or Mn concentration it is possible to control the chromaticity of LEDs based on thin ZnS layers deposited by the PVD method.

Article **IV**, *Enhancing the efficiency and stability of non-toxic $RbSn_{0.5}Ge_{0.5}I_3$ based perovskite solar cells through optimization*, is a comprehensive study of the efficiency of solar cell with perovskite active layer. Using SCAPS software, Mrs. Laouid consider such issues as absorber layer thickness, electron and hole transport layer doping density, absorber defect density, back contacts, series and shunt resistance and temperature effect. Using $RbSn_{0.5}Ge_{0.5}I_3$ as a lead-free perovskite solar cell active layer, it has been shown that in optimization of the solar cell performance the hole and electron transport layer properties play crucial role. Appropriate selection of these materials and geometric parameters can result in an efficiency of 24.3%.

The contribution of the doctoral student to the creation of **article VI**, *Low-temperature influence on the properties and efficiency of thin-film perovskite solar cells fabricated by the PVco-D technique*, is not leading (6%), but some of the research results that were carried out by Mrs. Laouid complete the previous ones and at the same time open new research topics. The main author of this work is Prof. Anna Zawadzka, who is the supervisor of the doctoral student. This work concerns perovskite solar cells that can operate in space, i.e. in conditions of low temperature and pressure. For the purpose of this work, Ms. Amina Laouid performed simulations of the perovskite cell operation in order to optimize the cell geometry. Simulations performed by Mrs. Laouid show that the thickness of electron and hole transport layers does not affect the efficiency of the solar cell and the optimal thickness of the methylammonium lead iodide perovskite photoactive film is in the range between 500 and 600 nm. This allows to achieve the efficiency of 18.5% in the wide range of temperatures from 10K to 320K.

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in which the phenomenon of quantum confinement could be observed? What effects would be expected?

In summary, the reviewed dissertation is cognitively interesting and is an original contribution to the study of thin-film optoelectronic materials based on organometallic compounds and perovskites.

Conclusion

Considering the important results obtained by Mrs. Amina Laouid, good mastery of the research technique which combines experimental and theoretical approaches, herein it can be concluded that her doctoral dissertation meets all conditions specified in Article 187 of Act of July 20, 2018, Law on Higher Education and Science (Journal of Laws of 2018, item 1668, as amended). **I apply for Mrs. Amina Laouid admission to further stages of the procedure leading to obtaining a doctoral degree.**

Since the results presented in the dissertation are distinguished by the originality of the methods and research tools used (see section: Scientific content and substantive aspects) and include scientific achievements published in reputably international journals (*Environ. Sci. Pollut. Res.* IF 5.8; *Vacuum* IF 3.8; *Mater. Chem. Phys.* IF 4.3; *Mater. Sci. Eng. B* IF 4.6; Opt. Mater. IF 3.8; *Sol. Energ. Mat. Sol. Cells* IF 6.3), I request the Council of the Discipline of Physical Sciences of Nicolaus Copernicus University **to award this doctorate with distinction**.

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Paweł Szroeder

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