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Name and surname: Wiktor Żuraw

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Abstract of the doctoral dissertation „Development of lead-reduced perovskite photovoltaics"

Perovskite solar cells (PSCs) are the most promising technology among third-generation solar cells and by far the most efficient solution-processable solar cells. Their greatest advantage is low-energy production and their fabrication ability on lightweight and flexible substrates. Currently, research is primarily focused on lead-based PSCs, which are the most efficient and stable of those being explored. Although they offer the potential for efficient technologies, lead toxicity is one of the factors hindering the commercialization of these solutions and poses problems related to subsequent management and disposal. Minimizing lead content in fabricated devices is the preferred approach to reducing potential lead exposure. In this dissertation, two main strategies were explored for minimizing lead content: (i) decreasing perovskite thickness and (ii) replacing lead with non-toxic tin in the perovskite composition. The next challenge in real commercialization is that most research efforts have focused on enhancing power conversion efficiency on small-area (~0.1 cm^2) cells made on rigid substrates, which are far from being commercialized. Therefore, this thesis also considers advancing the development of large-area (≥1 cm^2) flexible perovskite solar cells and modules using various perovskite compositions.

The first chapter provides a brief introduction to PSC technology, outlining its theoretical aspects, working principle, and key features. The second chapter discusses concerns about lead toxicity, including environmental and health impacts associated with lead-based perovskites. It also analyses the main challenges associated with tin-based perovskites, proposed as the main alternative to lead-based ones. The third and fourth chapters provide a detailed overview of deposition and characterization techniques employed in the experimental section. The experimental section consists of a series of three publications and one patent application, all of which focus on the development and fabrication of PSCs with reduced lead content.

The first experimental chapter (Chapter 5) describes the reduction of the lead content by reducing the perovskite thickness. However, the formation of very thin, homogeneous perovskite layers becomes a challenge due to the strains present in the fabricated layers, and thus the generation of discontinuities that reduce photovoltaic performance. The study presents a working PSC with the thinnest perovskite layer reported so far, obtained using the spin-coating technique. The produced PSCs contain up to 50 times less lead than standard ones. By reducing the thickness of the remaining layers, semi-transparent PSCs have been obtained, with an application area far beyond the currently available opaque heavy silicon cells.

The second work (Chapter 6) focuses on the fundamental problem with the easy oxidation of Sn^{2+} into Sn^{4+}, resulting in poor stability of tin-based perovskites. It presents the development of a novel method for the synthesis of tin(II) iodide, a key precursor for the production of tin-based perovskites. The resulting perovskite ink and perovskite layers were characterized by

significantly higher purity and stability compared to commercial precursors. This was achieved by eliminating Sn^{4+} impurities, which have an impact on material degradation and consequently reduce PSC performance. The work also demonstrates a flexible tin-based PSC with an active area of 1 cm^2. The designed method has improved the performance and stability of the fabricated cells, which represents a further step towards the development of lead-free tin perovskite technology.

The third publication (Chapter 7) presents the first-ever report on a tin-based perovskite solar module fabricated by a scalable blade-coating technique. This result was achieved through a comprehensive approach that involved optimizing the perovskite composition, improving its deposition process, and enhancing crystallization by replacing the commonly used hole transport layer with its non-aqueous equivalent. An important part of the work was also optimizing the laser ablation process, which enabled an electrical connection between adjacent cells in the module. The champion device achieved 5.7% power conversion efficiency on a 25 cm^2 total module area.

The last part of the experimental section (Chapter 8) is about the patent application extending the method presented in Chapter 6. The described method allows to obtain a variety of metal halide salts, as well as perovskite precursor inks and powders. Perovskite layers prepared from the perovskite precursor ink, using metal halides synthesized according to the described method, are characterized by a lack or reduced amount of impurities compared to conventional synthesis or commercially available precursors.

This work aims to push further the development of sustainable photovoltaics and demonstrate that lead-reduced and lead-free PSCs can be produced on a large scale, giving them real potential for commercialization. The hypothesis that large-area perovskite solar cells and modules with a significant lead reduction can be successfully fabricated using perovskite ink engineering will be proven.