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Title of the doctoral dissertation: **“Synthesis, characterization, and evaluation of the properties of new halide materials with perovskite structure”.**

Abstract

Organic-inorganic hybrid perovskite materials have recently become dominant in the field of photovoltaic. The efficiency of perovskite solar cells (PSCs) has increased from 3,8% in 2009 to 27%, making them the fastest-growing technologies in photovoltaics. After reaching an efficiency level of 25%, research on perovskite photovoltaics cells shifted from the race for efficiency to focusing on their stability and scalability of production.

This, the main challenges on the road to commercialization remain their limited phase stability and susceptibility to degradation under environmental conditions. One strategy improving the stability and functionality of ABX_3 perovskite materials is the search for new compounds and compositional engineering involving the introduction of oversized cations at the A site, which strengthens the crystal structure and increase the material's resistance to external factor.

The subject of the presented doctoral dissertation is the development of perovskite chemistry through synthesis and detailed physicochemical chatacterization of new compositions of perovskite materials, including three-dimensional (3D) structures, two-dimensional (2D) structures, and the increasingly studied one-dimensional (1D) materials. Particular attention was paid to the innovative mechanochemical synthesis method developed in the parent research group, which was recognized by the International Union of Pure and Applied Chemistry (IUPAC) as one of the world-changing technologies in the near future. Mechanochemistry has a numer of advantages, including eliminating the need for high temperatures or environmentally harmful

solvents. Above all, it allows one to bypass difficulties arising from the insolubility of substrates, making it an excellent alternative to solvothermal reactions.

The first part of dissertation involves compositional engineering and stabilization of the prototypical FAPbI₃ material (FA = formamidinium cation) by gradually introducing oversized dimethylammonium (DMA) cations into its crystal lattice. An integral part of the study was determining the structure of the resulting compositions, their physicochemical properties and phase transitions induced by external factors such as high temperature and pressure. Using in-situ Variable-Temperature Powder X-Ray Diffraction (VT-PXRD), it was shown that the perovskitoid δ -DMA_xFA_{1-x}PbI₃ undergoes a series of transformations into different polytypic forms. In the case of DMAPbI₃ single crystals, however, only a single pressure-induced structural transformation was observed.

The next part of the dissertation focuses on compositional engineering using the mechanochemical method, with particular emphasis on the incorporation of DMA into FAPbBr₃ and FASnI₃ matrices. The studies aimed to determine the cation mixing limit in double-cation perovskites, as well as the effect of ion incorporation on the optoelectronic properties of the resulting materials. The results obtained provided significant insights into the possibilities for structural stabilization of the studied materials and the modification of their properties through the application of compositional engineering. This constitutes a key step toward the rational design of new compositions with controlled properties.

Another partial task of the presented dissertation was the use of solvent-free mechanochemical method to obtain phase-pure layered 2D Ruddlesden-Popper perovskites of the formula A₂MA_{n-1}Pb_nI_{3n+1}. The research focused on synthesis involving three spacer cations of varied chain length: n-butylammonium (BA), hexylammonium (HA), and octylammonium (OA). Analysis showed the successful formation of phase-pure layered structures in the case of the BA cations for n = 1 and 2, as well as changes in optoelectronic properties depending on the number of layers. It should be emphasized that obtaining these compound by mechanochemical synthesis has not been previously reported in the literature.

The presented dissertation addresses topics in the field of materials chemistry, with a particular focus on the development of solvent-free synthesis methods for perovskite materials, as well as on their structural and optoelectronic properties. These studies contribute to expanding

knowledge about the relationships between the composition, structure, and properties of perovskites, which paves the way for the more rational design of their desired optoelectronic characteristics and for the future development of this class of compounds toward modern technologies.