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Abstract of the doctoral dissertation entitled: *Polymorphism in lead halides comprising protonated methylhydrazine: hybrid organic-inorganic compounds with tunable structural and optoelectronic properties* (pol. *Polimorfizm w halogenkach ołowiu zawierających protonowaną metylohydrazynę: organiczno-nieorganiczne związki hybrydowe o przestrajalnych właściwościach strukturalnych i optoelektronicznych*).

In recent years hybrid organic-inorganic perovskites (HOIPs) based on lead halides gained substantial interest in materials science and industry due to exceptional properties, such as high power conversion and quantum efficiencies, long carrier diffusion lengths, etc. combined with costly efficient synthesis. However, their potential for applications is limited by several factors, including high vulnerability to moisture or chemicals, resulting in rapid degradation. As the unique properties of molecular lead halides arise directly from the intermolecular interactions and depend on the crystal composition, the attention of researchers is increasingly directed toward new analogs by substituting the A- B-, and X- sites in the perovskite ABX_3 structure.

The family of lead halide HOIPs has been recently expanded with compounds comprising methylhydrazinium (MHy^+) cation. The crystal structure of $MHyPbX_3$ perovskites (X = Br, Cl) consists of a three-dimensional (**3D**) network of corner-sharing PbX_6 octahedra, which are heavily distorted due to interactions with MHy^+ cations situated within the voids. Unlike their counterparts, $MHyPbX_3$ crystallize in noncentrosymmetric, polar space groups, thus opening the possibilities for observations of nonlinear optical and ferroic features. MHy^+ has also been found to act as a spacer in MHy_2PbX_4 (X = Br, I) two-dimensional (**2D**) HOIPs. The current state of the art on MHy-based lead halide hybrids calls for developing new compounds using the A- and X-site compositional engineering.

The effects of substitution and alloying of the A and X sites on crystal structure and selected optoelectronic properties are described in six articles (**D1** – **D6**). In **D1**, halide-alloying introduced to $MHyPbBr_xCl_{3-x}$ **3D** HOIPs prompts the stabilization of both high-temperature polymorphs of single-halide analogs and enables tuning of bandgap value, ionic conductivity, and the characteristics of photoluminescence bands. The same approach is used in **D2** for $MHy_2PbBr_{4-x}I_x$ **2D** HOIPs, inducing a rich polymorphism driven by the temperature and halides contribution. In **D3**, layered MHy_2PbCl_4 is characterized. This compound shows a unique sequence of temperature-induced polymorphs, starting from high-temperature centrosymmetric, intermediate modulated, and low-temperature polar phase. The concurrence

of MHy^+ and imidazolium cation in **D4** promotes a formation of **2D** perovskites with (110)-oriented layers, featuring a profound tilting arising from interactions with organic cations. Finally, articles **D5** and **D6** describe the hybrid compounds of lower dimensionality of octahedra connections, i.e., $MHyPbI_3$ **1D** compound with parallel double-chains, and $Cs_2MHy_2PbX_6$ (X = Br, I) **0D** analog with isolated octahedra, respectively.