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**Physicochemical properties and phase transition
mechanisms of lead halides comprising imidazolium cations
in the structure: novel perovskites with tunable
optoelectronic properties**

**Właściwości fizykochemiczne i mechanizmy przemian
fazowych halogenków ołowiu zawierających w strukturze
kationy imidazoliowe: nowe perowskity o przestrajalnych
właściwościach optoelektronicznych**

w formie spójnego tematycznie cyklu artykułów opublikowanych w czasopismach
naukowych

mgr inż. Szymon Smółka

Rozprawa wykonana pod kierunkiem:
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1.1. Streszczenie w języku angielskim

This dissertation addresses hybrid lead halides containing the imidazolium cation (IM^+) and the structure-dynamics-property relationships within this family of materials. The motivation of the work was to demonstrate that even a small organic cation with a rigid, aromatic framework can reproducibly govern the dimensionality of the inorganic sublattice, the mechanisms of phase transitions, and the optical and dielectric response. A central role is assigned to vibrational spectroscopy, which enables simultaneous tracking of deformations of the Pb-X framework and the ordering and dynamics of IM^+ , including the reorganization of the $\text{N-H}\cdots\text{X}$ hydrogen-bond network accompanying phase transitions.

The literature review discusses the fundamentals of the crystal chemistry of ABX_3 -type structures and their low-dimensional derivatives (3D, 2D, 1D, 0D), the role of anion and cation substitutions, and the impact of these modifications on functional properties. Polymorphism and phase-transition mechanisms in hybrid perovskites are also presented, with consideration of the order-disorder component associated with the organic sublattice and the displacive/deformational component of the inorganic framework, as well as the concept of tunability by temperature and pressure. An important element of this chapter is a rationale for why IR and Raman spectroscopies are exceptionally sensitive to subtle symmetry changes, the number of crystallographically non-equivalent units, and the geometry of hydrogen bonds. The review is concluded with a concise summary of the state of knowledge on compounds in which imidazole occurs as a constituent of the crystal structure.

The experimental part comprises materials synthesis and crystallization, X-ray diffraction, temperature-dependent Raman and IR spectroscopy, dielectric measurements, and optical characterization. Temperature-dependent studies were conducted in a correlated manner by combining thermoanalytical and dielectric measurements with the acquisition of vibrational spectra. This approach allowed thermal and dielectric anomalies to be linked with the evolution of vibrational signatures, such as abrupt frequency shifts, band splitting, and changes in bandwidth, which simultaneously reflect orientational ordering of IM^+ and reorganization of the $\text{N-H}\cdots\text{X}$ interactions, as well as changes in the geometry of the inorganic sublattice. High-pressure studies employed a diamond anvil cell, and high-pressure single-crystal X-ray diffraction was combined with high-pressure Raman spectroscopy, enabling unambiguous determination of transition thresholds and correlation of these thresholds with structural rearrangements.

The results are presented as a series of four publications. Publication [P1] compares three imidazolium lead bromides with different PbBr_6 framework topologies, including one pseudo-three-dimensional compound and two chain-type compounds. It was shown that the connectivity of PbBr_6 octahedra governs the dielectric response, the sequence of phase transitions, and optical properties, including broadband photoluminescence.

Publication [P2] focuses on phase-transition mechanisms in two bromides of different architectures, analyzed using temperature-dependent IR and Raman spectra. Transition signatures were identified as changes in low-wavenumber modes and as reorganization of bands associated with IM^+ and N-H

groups, allowing the coupling between cation dynamics and deformations of the inorganic sublattice to be described.

In publication [P3], hydrostatic pressure was applied as an independent stimulus to induce structural transformations. Combining high-pressure single-crystal X-ray diffraction with Raman spectroscopy enabled separation of stages dominated by IM⁺ ordering from stages arising primarily from compression of the Pb–Br framework, as well as assessment of the reversibility of the changes.

Publication [P4] extends the study to chlorides and demonstrates the effect of halide substitution on IM⁺ dynamics and the phase-transition scenario. Two compounds were obtained and characterized: chain-type IM₃PbCl₅ and porous IM₂Pb₃Cl₈·0.5H₂O featuring a three-dimensional network built from PbCl₈ polyhedra. For IM₃PbCl₅, a sequence of multistep temperature-driven phase transitions was determined and linked to IM⁺ ordering and restructuring of N–H···Cl interactions, consistently observed in diffraction data, vibrational spectra, and the dielectric response.

Overall, the dissertation concludes that the phase-transition mechanisms and functional properties of imidazolium lead halides can be consistently interpreted in terms of coupling between (i) deformation and connectivity of the Pb–halide framework and (ii) ordering and dynamics of IM⁺, controlled by the geometry of the crystal space and the hydrogen-bond network. Within this framework, vibrational spectroscopy is a key tool, as it enables parallel monitoring of both components and their mutual coupling as a function of temperature and pressure.