MS13-2-1 Two-dimensional methylhydrazinium lead chloride perovskites with temperature-controlled centrosymmetric, modulated and polar crystal phases
#MS13-2-1

D. Drozdowski [1], A. Gągor [1]
[1]**Institute of Low Temperature and Structure Research, Polish Academy of Sciences - Wroclaw (Poland)**

Abstract
In the last few years one of the most compelling themes in materials science is the synthesis and physicochemical studies of hybrid organic-inorganic perovskites (HOIPs). The three-dimensional (3D) HOIPs, which consist of corner-sharing PbX_6 octahedra (X = Cl, Br, I) network with voids filled by small organic cations (e.g., methylammonium or formamidinium), have been described already as a breakthrough in optoelectronics, especially in photovoltaic technology [1]. These structures, however, possess meaningful drawbacks in the terms of possible applications, i.e., poor resistance to moisture and chemicals. One of the keys to overcoming these issues is to reduce structural dimensionality to the two-dimensional (2D) HOIPs, where the octahedra layers are separated by organic cations. This approach allows not only to improve stability and certain properties (e.g., photoluminescence quantum yield [2]), but also to incorporate larger organic cations, as the geometric limitations, coming from the 3D inorganic linkage, are no longer a blockage.
Indeed, our group effectively enriches the HOIPs family with the structures comprising methylhydrazinium (MHy^+) cation. It is worth noting that the MHy^+ is small enough to maintain 3D alignment (see $MHyPbBr_3$ and $MHyPbCl_3$ [3, 4]), and simultaneously sufficiently large to separate the 2D perovskite layers. We have already reported two 2D HOIPs with MHy^+ – MHy_2PbI_4 and MHy_2PbBr_4 [5, 6]. Herein, description of these newcomers will be limited to the phase transition (PT) mechanism. HT phase of MHy_2PbI_4 adopts *Pmmn* symmetry and undergoes a PT to *Pccn* at 298 K, and later to *P*-1 at 233 K on cooling. MHy_2PbBr_4 possesses HT phase isostructural to the iodide analogue but undergoes a PT at 368 K to modulated *Pmmn*, and eventually, at 343 K, to polar $Pmn2_1$ space group. This observation suggests that the halide substitution leads to formation of different crystal phases in 2D MHy lead halide HOIPs, which determine their properties.
Continuation of the halide substitution approach in the MHy_2PbX_4 (X = halide) 2D HOIPs has led to development of another representative, i.e., MHy_2PbCl_4. Unlike the counterparts described above, MHy_2PbCl_4 crystallizes at room temperature in a modulated *Pmmn*(00α)*s*00 superspace group. While the HT phase, stabilized at 332 K (338 K) on cooling (heating), is isostructural to the Br- and I- analogues, cooling down to 205 K induces a PT to polar $P2_1$ symmetry. Origins of such interesting crystal phases sequence will be discussed, with expected influence on the optical and dielectric properties.

References
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Fragments of MHy+ cations alignment in MHy2PbCl4,