Oral presentation

Incommensurate structures in organic-inorganic metal-halides

A. Gągor, D. Drozdowski

Institute of Low Temperatues and Struture Research Polish Academy of Science, Wrocław, Poland
a.gagor@intibs.pl

Organic-inorganic hybris based on protonated polar molecules and complex metal-halide units possess remarkable and tuneable properties that make them suitable for variety of applications including solar cells, light-emitting diodes, detectors, sensors, scintillators or nonlinear optical devices [1-2]. The functional properties like photoluminescence, ferroelectricity, second harmonic generation (SHG) are often strongly temperature dependent and appear in a sequence of polymorphic phase transitions. In this wealth of various phases also appear modulated crystal structure arrangements.

Incommensurately modulated structures may be induced either by temperature or chemical substitutions. They may appear as intermediate phases adopting temporary molecular arrangements or maintain the non-periodic order in a wide range of temperatures. The incommensurate crystal packing arises from the interplay between stabilizing role of hydrogen-bonding interactions and thermally activated movements of the soft, organic part of the structure. These two factors affect the inorganic units by the change of metal-halide bonds, distortions of metal coordination and altering the spacing between all components building the crystal structure. Here, basing on the single-crystal x-ray diffraction data processed in *Jana2020* [3], we present the incommensurate structures in three hybrids: (1) the incommensurate low-temperature (LT) polymorph in $FASbCl_4$ of *Pnma(0,β,0)00s* symmetry and **q**~0.41**b***, see **Fig 1;**
(2) phase transitions in MHy_2PbCl_4 leading to stabilization of intermediate incommensurate *Pmmn(00γ)s00* phase with **q**~0.25**c*** between centrosymmetric and LT polar $P2_1$ phase [4]; (3) compositionally driven incommensurate structure in $MHy_2Pb(I/Br)_4$ of *Pnma*(00*γ*)0*s*0 superspace group and **q**~0.45**c*** which appears only for high iodine concentration [5]. In these materials suppressed cations dynamics, whether it's due to temperature or chemical pressure, lead to ordered modulated atomic arrangements.

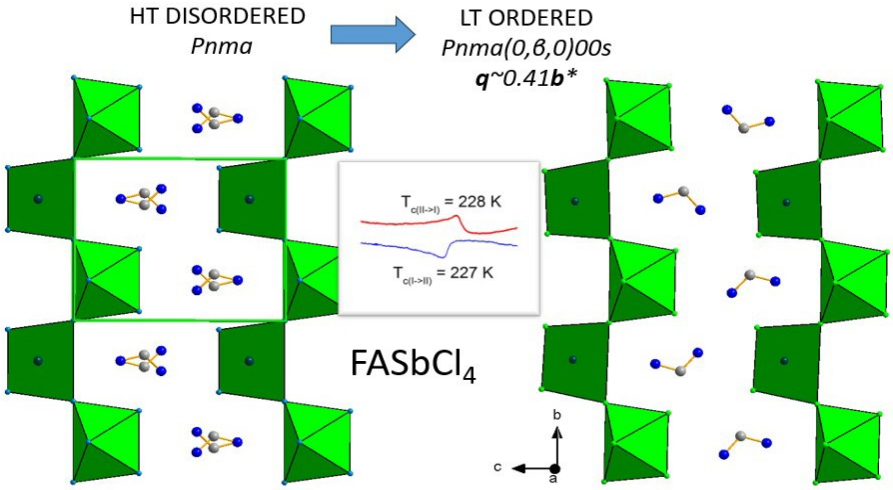

Figure 1. Phase transition in $FASbCl_4$, hydrogen atoms in formamidynium (FA) are omitted for clarity.

[1] Saparov, B.; Mitzi, D.B. (2016) Chem. Rev. **116**, 4558−4596.

[2] Han, Y.; Yue, S.; Cui, B.B. (2021) Adv. Sci. **8**, 2004805.

[3] Petříček, V.; Palatinus, L.; Plášil, J.; Dušek, M. (2023) Zeitschrift fur Krist. - Cryst. Mater. **238** (7–8), 271–282.

[4] Fedoruk, K.; Drozdowski, D.; Mączka, M.; Zaręba, J. K.; Stefańska, D.; Gagor, A.; Sieradzki, A. (2022) Inorg. Chem. **61**, 15520–15531.

[5] Drozdowski, D.; Kabański, A.; Stefańska, D.; Ptak, M.; Mączka, M.; Gagor, A. (2024) J. Mater. Chem. C DOI: 10.1039/d4tc00865k

The research was supported by the National Science Centre as part of the OPUS 22 project (No. 2021/43/B/ST5/01172) and OPUS 18 (No. 2019/35/B/ST5/00043).