

MS13 Structural Characterization of Functional Materials

MS13.1-02

The cation-dependent structural, optical, and magnetic properties of molecular hypophosphite perovskites
A. Gagor¹, M. Mączka¹, D. Stefańska¹, A. Pikul¹

¹*Institute of Low Temperature and Structure Research, Polish Academy of Sciences - Wrocław (Poland)*

Abstract

Organic-inorganic hybrids that crystallize in a perovskite architecture of a general formula ABX_3 are perspective multifunctional materials showing ferroelectric, multiferroic photovoltaic, photoluminescent (PL), and barocaloric properties [1]. The crystal structure of these compounds is built of B-metal centres (usually Pb^{2+} , Sn^{2+} , Mn^{2+} , Cd^{2+} , Zn^{2+} etc.) coordinated octahedrally by X-molecular units (halide, formate, azide, cyanate, dicyanamide, or hypophosphite ions $H_2PO_2^-$) which also act as bridging-ligands. Organic A-site molecular cations, which in contrast to inorganic perovskites have a non-spherical shape and often possess a dipole moment, occupy the large voids and interact via hydrogen bonds with the metal-ligand framework having the potential to strongly modify it [2].

The multiatomic, extended X-site ligands, like hypophosphite ions, produce unconventional octahedral tilts, columnar shifts, and unprecedented off-centre shifts of organic cations that are absent in inorganic perovskites. This high tendency for symmetry breaking was expected to favour improper ferroelectricity or other functional properties but, starting from 2017 when the first hypophosphite perovskite was reported up to now, all reported hypophosphite perovskites had centrosymmetric structures.

Herein we report the crystal structures, magnetic and photoluminescent properties of new hypophosphites based on imidazolium, pyrrolidinium, and guanidinium. We show that replacing Mn^{2+} with Cd^{2+} and Co^{2+} tunes the physical properties. The Co-based analogues are weak ferromagnets with a stronger ferromagnetic response and higher ordering temperatures compared to manganese counterparts. The Cd analogues have broadband emission correlated with distortion of the cadmium-hypophosphite framework. The most interesting discovery in this family, however, is the polar symmetry of pyrrolidinium-based cadmium hypophosphite. The non-centrosymmetric structure hasn't been reported for any known hybrid hypophosphite. The new hypophosphites exhibiting magnetic or polar order, and photoluminescent properties show that hypophosphite perovskites are a promising platform for the creation of new functional materials, including light-emitting, ferroelectric, and multiferroic.

This research was supported by the National Science Centre (Narodowe Centrum Nauki) in Poland under project no. 2018/31/B/ST5/00455

References

- [1] B. Saparov and D. B. Mitzi; Organic-Inorganic Perovskites: Structural Versatility for Functional Materials Design, *Chem. Rev.*, 2016, 116, 4558—4596;
[2] Boström, Hanna L. B.; Senn, Mark S.; Goodwin, Andrew; L. 2018; Recipes for improper ferroelectricity in molecular perovskites, *Nature Communications*, 2380, 9, 1