MS13-1-1 Structure-properties correlation in metal halide perovskites containing diammonium cations #MS13-1-1

M. Morana [1], R. Chiara [1], L. Malavasi [1]
[1]University of Pavia - Pavia (Italy)

Abstract
Metal halide perovskites (MHPs) are materials of great interest that have been proposed for manifold applications. However, the classic perovskite structure, corresponding to the ABX3 formula (where A = small cation, B = metal and X = halide) shows a low stability to air and humidity limiting the actual application. On the other hand, layered perovskites, whose structure is made of alternating layers of organic cations and metal-halide octahedra, are gaining the spotlight thanks to their improved stability. Two main structure types are commonly formed Ruddlesden–Popper (RP) or Dion–Jacobson (DJ) perovskites. The former is characterized by staggered perovskite layers, whereas in DJ perovskites the layers are eclipsed, i.e. stacked without relative displacement [1]. In particular, ditopic ligands such as diammonium cations usually give DJ perovskites with formula A′An–1BnX3n+1 where A′ and A are organic cations, and n represents the number of inorganic layers. Correlating structural distortions and optical properties in layered perovskites is of key importance to modulate their properties and design novel and optimized materials. Thanks to the vast work performed on perovskites including monoammonium cations, well-defined parameters, such as the B-X bond distance and the B-X-B angle, have been defined and a careful materials design is now possible [2]. On the other hand, such kind of correlation is still partially missing on perovskites including a diammonium cations. In order to further enlarge the family of layered perovskites containing diammonium cations, a systematic and rationale investigation was performed, in particular the four diammonium cations represented in Figure 1 namely 1,3-phenylenediammonium (1,3-PDA), 1,3-xylylenediamimonium (1,3-XDA), 1,4-phenylenediammonium (1,4-PDA), and 1,4-xylylenediamimonium (1,4-XDA). We also explored the effect of different halides characterizing the structures and properties of Pb-Br and Pb-Cl layered perovskites. The structural data obtained from single-crystal XRD have been coupled to optical spectroscopy (absorbance and photoluminescence) investigation, allowing to highlight peculiar behaviours templated by the nature of the diammonium cation, such as broadband or narrowband emission.

References
[1] Huang, P.; Kazim, S.; Wang, M.; Ahmad, S. Toward Phase Stability: Dion-Jacobson Layered Perovskite for Solar Cells. ACS Energy Lett. 2019, 4, 2960– 2974, DOI: 10.1021/acsenergylett.9b02063

[2] Li, X.; Hoffman, J. M.; Kanatzidis, M. G. The 2D Halide Perovskite Rulebook: How the Spacer Influences Everything from the Structure to Optoelectronic Device Efficiency. Chem. Rev. 2021, 121 (4), 2230–2291. https://doi.org/10.1021/acs.chemrev.0c01006.

Starting diamines used for the synthesis