‘Breathing’ 2D Hybrid Double Halide Perovskites consisting of non-toxic elements

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Lead halide perovskites AMX_3 (A^+ = Cs, CH_3NH_3 or HC$(NH_2)_2$, M^{+2} = Pb, Sn or Ge and X- = Cl, Br or I) have taken the semiconductor field by storm in the last decade, guided by the immense development of efficient photovoltaics that have reached power-conversion efficiencies >25%.[1] A notable class among them is dimensionally reduced two-dimensional (2D) perovskites that offer much greater sensitivity to moisture that boosts the devices’ performance, in addition to the exotic photo physics they possess relative to their stable excitonic features at room temperature. Further branching out in the class of 2D perovskites, recent reports have shown that it is possible to stabilize double 2D perovskites consisting of two metal ions in an ordered periodic arrangement.[2] These compositions due to the absence of lead atoms have demonstrated a variety of interesting physical qualities which in combination with their low toxicity make them an alternative direction towards the discovery of novel inorganic semiconductors.

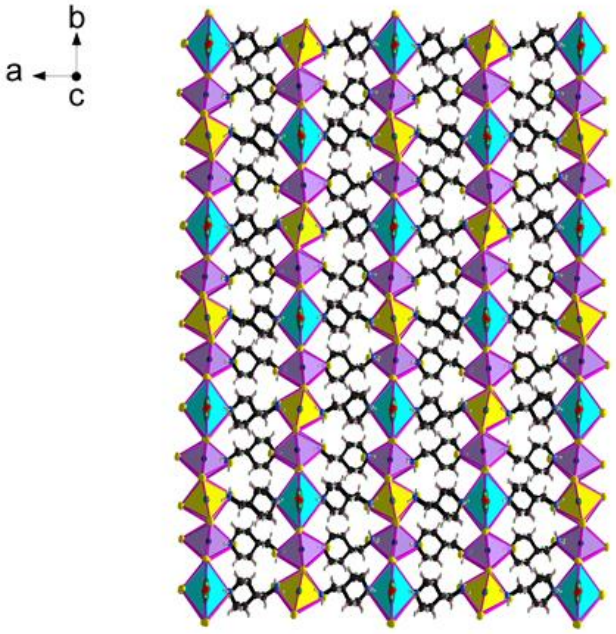

Figure 1: Representative layer stacking of a hybrid 2D double halide perovskite $(4AMP)_2AgM^{III}Br_8.0.5H_2O$. Yellow octahedra are Ag-atom centered, blue ones are disordered Ag atom centered and purple polyhedra consists are M(III)-atom centered. The organic cations interdigitate between the two-dimensional sheets in quintuple conformation ordering

In this work, we demonstrate that 2D hybrid double halide perovskites based on mixed metal Ag-In, Ag-Bi and Ag-Sb compositions, with a general chemical formula $(4AMP)_2AgM^{III}Br_8.0.5H_2O$, ($4AMP^{2+}$ is the dication of 4-aminomehtyl piperidine, M^{III} is In, Sb or Bi), can be obtained in good yield and high chemical purity using low-temperature wet chemistry. The new compounds, which possess the Ruddlesden-Popper structure-type, have been characterized by single-crystal and powder X-ray diffraction and their optical properties at room temperature were determined (Figure 1). The compounds possess a strong optical absorption in the visible likely deriving from a slightly indirect band gap transition. Another feature that these compounds possess, is that they are ‘’breathing’’. All three compounds contain 0.5 H_2O molecules in the unit cell, and can be dehydrated reversibly with thermal treatment and water vapor exposure, respectively. Solid solutions with a combination of three different metals, Ag-Sb-Bi, have also been obtained and characterized. The above properties render these mixed-metal 2D hybrid halide perovskites suitable for integration so much into environmentally friendly optoelectronic devices, as much in small molecule sensing in their dehydrated form.

1. Aryal, U.K., et al., *2D materials for organic and perovskite photovoltaics.* Nano Energy, 2022. **94**: p. 106833.
2. Li, X., et al., *Bismuth/Silver-Based Two-Dimensional Iodide Double and One-Dimensional Bi Perovskites: Interplay between Structural and Electronic Dimensions.* Chemistry of Materials, 2021. **33**(15): p. 6206-6216.