

Thermochemical properties of hybrid two-dimensional lead halide perovskites based on bulky aromatic spacer cations

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Hybrid halide perovskites have been studied extensively in the last decade given their remarkable photophysical properties. Nevertheless, these relatively new class of solid materials continues to surprise with the wealth of unconventional properties they possess, including a remarkable thermal expansion/contraction they possess that can be compared with those of viscous liquids [1]. The interest in the thermal properties of the material has been reinvigorated following the recent discovery that a certain variety of two-dimensional (2D) lead halide perovskites can undergo a reversible glass/crystalline transition upon moderate heating [2]. Because of this unique property, materials of this type have acquired a distinct research interest, targeting switchable phase change materials, towards volatile memory applications.

The purpose of this work towards this end was to synthesize a variety of 2D materials with bulky, asymmetric organic cations that are difficult to interdigitate between the inorganic perovskite sheets, as an attempt to trigger a potential glass-crystal transition in the solids. Thus, materials of the general formula A_2PbX_4 ($X = \text{Br, I}$ and $A = 2\text{-Phenethylamine (PEA)}$, $2\text{-(1-Naphthyl)ethylamine (1-NEA)}$, $2\text{-(2-Naphthyl)ethylamine (2-NEA)}$ and $2\text{-(4-Biphenyl)ethylamine (BPEA)}$) were synthesized and structurally characterized by Single-Crystal and X-ray diffraction and their thermal properties were recorded via Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). We find that the so much the conformation, as much as number of aromatic rings incorporated in the organic carbon chain strongly impact the thermal properties of the materials, either by manipulating the thermal stability of the materials or by shifting the temperature of the corresponding structural phase transition. Despite the fact that no clear glass-crystal transition was observed in the selected collection of halide perovskites, certain trends relating to the order of the phase transitions and the transition temperature range could be deduced by a careful analysis of the thermodynamic quantities, in comparison with those of the linear aliphatic spacer ammonium cations [3]. Moving forward, we propose a design of new ammonium cation that can be used to moderate the transition temperature and, ideally, inhibit the crystal-crystal transition in favor of a glass-crystal modifications, suitable for application in rewritable memory devices.

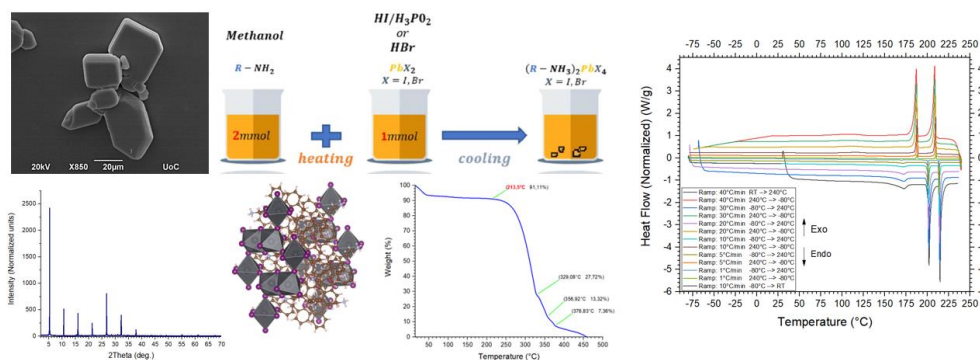


Figure 1. Design illustration of the synthetic process together with the SEM analysis, the powder and single – crystal XRD characterizations and the thermogravimetric analysis of the DSC and TGA data of the iodine and bromide perovskite compounds used in the above study.

References

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