EXPERIMENTAL THERMOCHEMICAL VERIFICATION OF TRENDS IN THERMODYNAMIC STABILITY OF HYBRID PEROVSKITE-TYPE ORGANIC-INORGANIC HALIDS

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Hybrid perovskite-type methylammonium lead halides have received great attention in recent years due to high conversion efficiency obtained in solar cells based on such materials. Since the time of the first demonstration photovoltaic devices based on the hybrid perovskites $CH_3NH_3PbX_3$ (X = Cl, Br, I) have showed huge progress in increase of conversion efficiency reaching currently 20.1%. However, despite very promising achievements fundamental chemistry and physics of hybrid organic-inorganic (HOIP) perovskites is far from being completely understood. In particular it is true for thermodynamic properties of HOIP perovskite-type halides ABX_3 and A_2BX_4 (A=CH_3NH_3, formamidinium, Cs, Rb, etc; B=Sn, Pb, 3d-element; X = Cl, Br, I). Moreover, reported results of DFT calculations aiming at estimating the stability of these materials often give controversial results. In addition, some of the HOIP perovskites (for example, $CH_3NH_3PbX_3$ (X = Cl, Br, I)) are known to be entropy-stabilized phases. Therefore experimental verification of the stability trends in HOIP perovskite-type halide systems is strongly required. This is especially important for assessment of the stability of these materials under particular working conditions. Therefore, the main aim of this work was to study the thermodynamics of formation of HOIP perovskite-type halides ABX_3 and A_2BX_4 (A=CH_3NH_3, formamidinium, Cs, Rb, etc; B=Sn, Pb, 3d-element; X = Cl, Br, I). Their standard formation enthalpy at 298 K was measured by solution calorimetry. Heat capacity was measured in the temperature range 2-298 K using PPMS system. Standard entropy was obtained by integration of the Cp/T vs T curve. Standard Gibbs free energy of ABX_3 and A_2BX_4 (A=CH_3NH_3, formamidinium, Cs, Rb, etc; B=Sn, Pb, 3d-element; X = Cl, Br, I) was evaluated using measured formation enthalpy and entropy. Trends in variation of the thermodynamic functions with chemical composition and crystal structure of HOIP perovskite-type halides were analyzed and compared with available results of DFT calculations.

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