

**THERMODYNAMIC PROPERTIES
OF TERNARY CESIUM LEAD HALIDES**

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Ternary halides CsPbX_3 , CsPb_2X_5 , and Cs_4PbX_6 ($\text{X} = \text{Cl}, \text{Br}$) are promising semiconductor materials due to their potential applications in optoelectronics and photovoltaics. Stability of these compounds under real operating conditions, both in relation to decomposition into constituent components and in relation to the effects of oxygen, carbon dioxide and water vapor present in the air, is a current issue. The main aim of this work was to determine standard enthalpies of formation from binary halides and isobaric heat capacities of these substances.

CsPbX_3 and Cs_4PbX_6 samples were synthesized via melt crystallization and solid-state sintering, respectively. Cesium and lead halides (CsX and PbX_2 ; $\text{X} = \text{Cl}, \text{Br}$) were used as the precursors. The stoichiometric mixtures of the starting materials were carefully ground in an agate mortar and placed in evacuated and hermetically sealed glass ampules. The ampules with Cs_4PbX_6 were heated in a furnace at 300 °C for 24 h and then cooled to room temperature at a rate of 2 °C/h. This procedure was repeated 3 times with intermediate regrinding of the reacting mixture. The ampules with CsPbX_3 were heated in a furnace at 630 °C for 12 h and then cooled to room temperature at the same rate. CsPb_2X_5 were prepared by dissolving $(\text{CH}_3\text{COO})_2\text{Pb} \cdot 3\text{H}_2\text{O}$ in hot HX ($\text{X} = \text{Cl}, \text{Br}$) solution and subsequent adding of CsX powder. The precipitates were separated from cooled solutions on a glass filter, washed with ethanol, and dried at 70 °C for 1 h.

The standard enthalpies of formation from binary halides were determined using solution calorimetry. The obtained values for all studied samples are negative, of the order of $-20 \text{ kJ} \cdot \text{mol}^{-1}$. This fact indicates the thermodynamic stability of these substances at $T = 25 \text{ }^\circ\text{C}$.

Temperature dependencies of the isobaric heat capacity were measured using adiabatic calorimetry (from 77 K to 350 K) and differential scanning calorimetry (from 350 K to temperatures near the melting points). Based on the analysis of captured data, a number of phase transitions in CsPbX_3 samples were obtained, their enthalpies and entropies were estimated. Additionally, temperature dependencies of the enthalpy increments from 373 K to temperatures near the melting points were determined for all synthesized samples using drop calorimetry.