THERMODYNAMIC PROPERTIES OF COMPOSITIONALLY COMPLEX (HIGH-ENTROPY) OXIDES WITH PEROVSKITE AND ROCK-SALT STRUCTURES

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Compositionally complex oxides (also called “high-entropy oxides” or HEOs) have become a popular subject of scientific investigation over the past decade. These oxides usually have five or more cations mixed in equimolar proportions within one sublattice. The random cation distribution results in high configurational entropy, which compensates for the enthalpy of mixing and allegedly stabilizes the structure. Furthermore, this new material design approach provides vast possibilities for fine-tuning the chemical composition and, therefore, the properties.

However, up until very recently [1,2], experimental investigations into thermodynamics of HEOs have been quite limited, and so the understanding of their stability and stabilization issues had mostly been based on indirect or speculative evidence.

This work focuses on the synthesis and thermodynamic properties of selected compositionally complex A-site mixed rare-earth perovskite cobaltites and rock-salt oxides. All the studied cobaltites were synthesized via the standard glycerol-nitrate technique, while the rock-salt oxides were prepared via the solid-state reaction method. The crystal structure and elemental composition of the samples were characterized using X-ray diffraction (XRD) and scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS), respectively. In this study, several thermochemical techniques were employed, including high-temperature oxide melt solution calorimetry (to determine enthalpies of formation), adiabatic and drop calorimetry (to measure heat capacity and enthalpy increments), as well as differential scanning calorimetry and thermogravimetry (to measure heat capacity and investigate thermal stability).

Based on experimental and literature data, the standard enthalpies of formation and the temperature dependencies of heat capacity were determined for all studied oxides. For $Co_{0.2}Cu_{0.2}Mg_{0.2}Ni_{0.2}Zn_{0.2}O$, the first oxide designated in the literature as a HEO, the temperature dependence of the Gibbs energy was obtained over a wide temperature range. This study provides an experimental basis for discussing the factors affecting the thermodynamic stability of “high-entropy” cobaltites and highlights the contributions of both configurational and non-configurational entropy to the stabilization of $Co_{0.2}Cu_{0.2}Mg_{0.2}Ni_{0.2}Zn_{0.2}O$.

1. Sereda V. V., Tsvetkov D. S., Sereda A. V. et al. Thermodynamics of compositionally complex (“high-entropy”) oxides – A-site mixed $(5R_{0.2})CoO_{3-\delta}$ (R = rare-earth element) perovskite-type cobaltites // Acta Materialia. – 2026. – Vol. 306, № 121943

2. Sereda V. V., Tsvetkov D. S., Sereda A. V. et al. Experimental thermodynamic study of the “high-entropy” oxide $(MgCoNiCuZn)_{0.2}O$: entropic stabilization confirmed, but is it all that matters? // J. Mater. Chem. A. – 2026. – Vol. 14, № 9, P. 5419-5441