IMPORTANCE OF DEFECT CHEMISTRY FOR UNDERSTANDING THE THERMODYNAMIC PROPERTIES OF OXIDES WITH AND WITHOUT OXYGEN EXCHANGE

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Only thermodynamic analysis can unambiguously determine the compounds' stability and compatibility under particular conditions. However, such analysis requires the knowledge of temperature-depended Gibbs free energies, which can be derived from the enthalpy of formation and heat capacity data. Drop calorimetry is currently the most widely used techniques for the heat capacity measurements above room temperature. This technique is suitable nonstoichiometric oxides that exhibit oxygen exchange since the sample has enough time to reach equilibrium with environment at the measurement temperature.

For such oxides, the enthalpy increments should be recalculated so as to correspond to constant oxygen content by subtracting the enthalpy of oxygen exchange, which in turn is estimated using the defect structure model. The as obtained enthalpy increments of the constant-composition oxides are then fitted with the integrated $C_p(T)$ functions. The latter depends strongly on the composition of an oxide with respect to metals since they can undergo spin transition and charge disproportionation as it occur in cobalt-contained both cubic [1] and double perovskites [2].

For the oxides that do not exhibit the spin state transition above room temperature, $C_p(T)$ can be taken as equal to the sum of Einstein term, modified by taking into account the anharmonicity of atomic vibrations, and charge disproportionation contribution. The noticeable value of the latter highlights the seldom mentioned importance of defect chemistry for discussing the thermal properties of oxides, especially those containing cations that can change their oxidation state, even in the absence of oxygen exchange.

1. R.E. Yagovitin et al. Thermodynamics of advanced $Pr_{1-x}Ba_xCoO_{3-\delta}$ ceramics: enthalpy increments and heat capacity // Ceramics International. 2026. Vol. 52, P. 6215–6222. https://doi.org/10.1016/j.ceramint.2025.12.380

2. R.E. Yagovitin et al. Thermodynamics of Formation and Disordering of $YBaCo_2O_{6-\delta}$ Double Perovskite as a base for Novel Dense Ceramic Membrane Materials. Membranes 2023, 13, 10. https://doi.org/10.3390/membranes13010010