HYDRATION THERMODYNAMICS OF PROTON-CONDUCTING PEROVSKITE $\text{Ba}_4\text{Ca}_2\text{Nb}_2\text{O}_{11}$

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The oxygen nonstoichiometry index $\delta$, i.e. number of oxygen vacancies per formula unit, in perovskite-type $\text{BaCa}_{(1+y)/3}\text{Nb}_{(2-y)/3}\text{O}_3-\delta$ (BCNy) oxides can be tailored by varying the Ca–Nb ratio $y$, and equals $\delta = y/2$. These oxygen vacancies can be hydrated under humid atmosphere, providing nonstoichiometric BCNy oxides with good proton conductivity. It makes them promising materials for proton-conducting solid oxide fuel cell (SOFC) electrolytes and high-temperature humidity sensors. The present work aimed to partly address the lack of fundamental thermodynamic studies on BCNy by investigating the heat of low-temperature hydration-induced phase transition as well as the higher-temperature thermodynamics of hydration and related defect chemistry of BCN50 oxide.

BCN50 oxide was prepared via the standard ceramic technique from the high-purity $\text{BaCO}_3$, $\text{CaCO}_3$ and $\text{Nb}_2\text{O}_5$. Phase-purity of the as-obtained BCN50 powder was confirmed by means of X-ray diffraction (XRD) with 7000S diffractometer (Shimadzu, Japan) using Cu Kα radiation. Calorimetric measurements were performed with an original heat-flux differential scanning calorimeter (DSC). Temperature-dependent equilibrium water content in BCN50 samples in dry ($\log(p_{H_2O}/atm) \leq -3.5$) and wet ($\log(p_{H_2O}/atm) = -1.67$) air was measured by thermogravimetry (TG) using CI Precision (UK) microbalances.

The defect structure model for BCN50 based on the single reaction of water uptake was discussed and successfully verified using the proton content dependencies, $x(T, p_{H_2O})$, at 623–773 K [1]. The values of the hydration enthalpy of cubic ($\text{Fm}\overline{3}\text{m}$) BCN50, either measured directly or evaluated using the equilibrium $p_{H_2O} = T - x$ data [1], were shown to be close to each other. The enthalpy of the cubic→monoclinic phase transition for $\text{Ba}_4\text{Ca}_2\text{Nb}_2\text{O}_{11} \cdot 0.92\text{H}_2\text{O}$ was calculated using calorimetrically measured low-temperature heat of hydration. As this transition introduces a degree of disorder, lowering the crystal lattice symmetry, its entropy, $\Delta S^0_{tr} = \Delta H^0_{tr}/T_{tr}$, where $T_{tr}$ is the phase transition temperature, should be positive, making the phase transformation enthalpy $\Delta H^0_{tr}$ endothermic.

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