HYDRATION THERMODYNAMICS OF PROTON-CONDUCTING PEROVSKITE $Ba_4Ca_2Nb_2O_{11}$

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The oxygen nonstoichiometry index δ, i.e. number of oxygen vacancies per formula unit, in perovskite-type $BaCa_{(1+y)/3}Nb_{(2-y)/3}O_{3-\delta}$ (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 $BaCO_3$, $CaCO_3$ and Nb_2O_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 ($\log(p_{H_2O}/\mathrm{atm}) \leq -3.5$) and wet ($\log(p_{H_2O}/\mathrm{atm}) = -1.67$) air was measured by thermogravimetry (TG) using CI Precision (UK) microbalances.

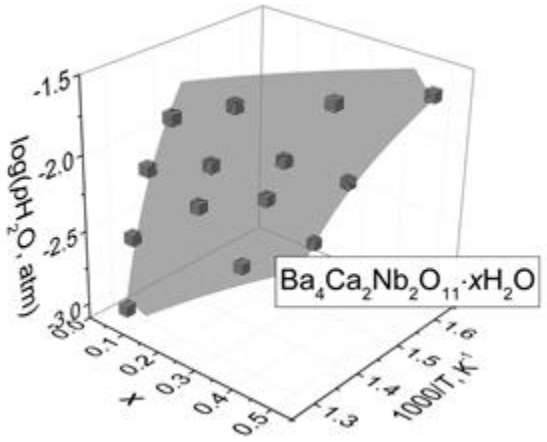

Figure 1 – The results of model analysis: points – experimental data [1]*, surface – fitted model*

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 ($Fm\bar{3}m$) 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 $Ba_4Ca_2Nb_2O_{11}\cdot 0.92H_2O$ 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 ΔH^0_{tr} endothermic.

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1. Animitsa I.E., Kochetova N.A. Chimica Techno Acta 3(1) (2016) 5-13.