Hydration thermodynamics of proton-conducting perovskite Ba$_4$Ca$_2$Nb$_2$O$_{11}$

Vladimir Sereda *, Dmitry Malyshkin, Dmitry Tsvetkov, Andrey Zuev

Institute of Natural Sciences and Mathematics, Ural Federal University, 620002, 19 Mira St., Yekaterinburg, Russia

ABSTRACT

The defect structure model based on the single reaction of water incorporation, involving structural oxygen vacancies, was discussed and successfully verified using existing $p_{H_2O} - T - x$ data for cubic Ba$_4$Ca$_2$Nb$_2$O$_{11}$·xH$_2$O – a promising electrolyte material for proton-conducting solid oxide fuel cells. As a result, the enthalpy of hydration (ΔH^0_{hydr}) was obtained. It was found to be close to the partial molar enthalpy of water in Ba$_4$Ca$_2$Nb$_2$O$_{11}$·xH$_2$O as well as to the calorimetrically measured value of $\Delta H^0_{hydr} = -107.9 \pm 14.4$ kJ/mol of H$_2$O. Using ΔH^0_{hydr} and the value of low-temperature heat of hydration, the enthalpy of the hydration-induced cubic→monoclinic phase transition in Ba$_4$Ca$_2$Nb$_2$O$_{11}$·0.92H$_2$O was calculated as 63.9 ± 14.2 kJ/mol of Ba$_4$Ca$_2$Nb$_2$O$_{11}$.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

The oxygen nonstoichiometry index δ, i.e. the 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 [1–5]. It makes them promising materials for proton-conducting solid oxide fuel cell (SOFC) electrolytes and high-temperature humidity sensors. Among the BCNy compounds, Ba$_4$Ca$_2$Nb$_2$O$_{11}$ (BCN50) stands out clearly because of its large theoretical water uptake, up to $x = 1.0$ in Ba$_4$Ca$_2$Nb$_2$O$_{11}$·xH$_2$O, and its fully 1:1-ordered structure [1]. Besides, in contrast with the other BCNy, the crystal structure of highly hydrated BCN50 is known to differ from that of the "dry" sample. At lower temperature ($T < 573$ K) under humid atmospheres (water partial pressure $p_{H_2O} > 10^{-1.8}$ atm), when x is close to 1.0, BCN50 was found to be monoclinic with either $C2/m$ [4,6] or $P2_1/n$ [7] space group assigned. Partially hydrated BCN50 (at higher temperatures and/or in less humid environment) is cubic ($Fm\bar{3}m$) [4,6–8].

Despite a number of works on the crystal structure [1], water content [2,3] and other properties of various BCNy compounds, including BCN50 [4–9], there is a lack of fundamental thermodynamic studies on these materials, and the defect chemistry of BCN50 was discussed only qualitatively [5,7,9]. Therefore, the present work aimed to partly address these issues 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.

2. Experimental

BCN50 oxide was prepared via the standard ceramic technique from the high-purity BaCO$_3$, CaCO$_3$ and Nb$_2$O$_5$. Stoichiometric quantities of precursors were calcined in air at 1073–1473 K with 100 K step for 8 h at each temperature with intermediate regrindings. Finally, the powder was uniaxially pressed into pellets, annealed in air at 1773 K for 8 h and subsequently slowly (100 K/h) cooled to room temperature. The pellets prepared in this way were then crushed in an agate mortar. 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 (see Fig. 1).

Calorimetric measurements were performed with an original heat-flux differential scanning calorimeter (DSC). The calorimetric cell consisted of two identical alumina crucibles with a thermopile in the form of 16 (8 on each crucible) K-type thermocouple junctions rigidly mounted on crucibles' sides. Two aluminum crucibles, one of which empty and another one containing around 0.5 g of BCN50 powder, were inserted into the alumina ones. The calorimetric cell was then placed in a furnace and held at a given
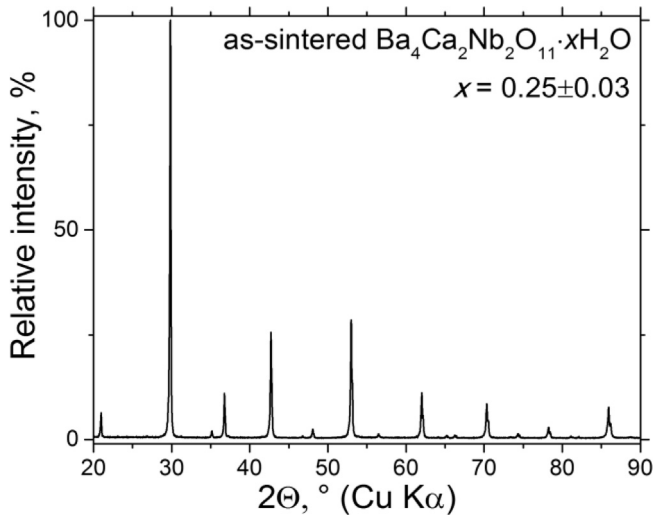
Fig. 1. XRD pattern for as-sintered BCN50.

temperature in 50 ml/min flow of dry ($\log\left(p_{H_2O}/atm\right) \leq -3.5$) air for at least 48 h to achieve equilibrium water content in the sample. The inlet air was dried by passing it through the column with pre-annealed zeolites. After that, the air flow was redirected abruptly so as to bubble it through the flask with a saturated solution of KBr ($\log\left(p_{H_2O}/atm\right) = -1.67$), and the corresponding heat effects resulting from the sample hydration were recorded. The DSC hydration experiment was repeated, at least, 3 times at each temperature. The heat sensitivity of DSC setup was calibrated using standard metals' heats of fusion in scanning mode with various heating rates, and the sensitivity coefficient extrapolated to zero heating rate was used to calculate the heat of hydration.

Temperature-dependent equilibrium water content in BCN50 samples in dry ($\log\left(p_{H_2O}/atm\right) \leq -3.5$) and wet ($\log\left(p_{H_2O}/atm\right) = -1.67$) air was measured by thermogravimetry (TG) using CI Precision (UK) microbalances.

3. Results and discussion

Let us discuss first the defect reactions accompanying the hydration of cubic ($Fm\bar{3}m$) BCN50 at higher temperatures ($T = 623–773$ K). It was shown previously [1,7,9] that BCN50 is a perovskite-type oxide with 1:1 ordered structure, where Ca and Nb ions are placed on alternate (1 1 1) planes. The intrinsic oxygen vacancy concentration in dehydrated BCN50 is determined by the Ca:Nb ratio, i.e. the electroneutrality conditions, and equals 1 mol of structural vacancies per mole of the $Ba_4Ca_2Nb_2O_{11}$. Taking into account that the oxygen vacancies in BCN50 are of a structural nature [7,9], the water uptake by the sample can be written in Kröger-Vink notation as

$$2O_O^\times + V_O^\times + H_2O \rightleftarrows 2OH_O^\cdot + O_V''$$ (1)

provided that $Ba_4Ca_2Nb_2O_{11}$ with 1 structural vacancy, $V_O^\times$, per formula unit is chosen as a reference crystal. The oxygen from the water molecule fills the structural vacancy resulting in negatively charged defect O_V''.

For simplicity, we assume that the defect chemistry of BCN50 at $T = 623–773$ K and $\log\left(p_{H_2O}/atm\right) < -1.6$ is governed solely by the reaction (1). Corresponding set of equations comprising the

equilibrium constant of reaction (1), mass and charge balances is expressed as

$$\begin{cases} K_1 = \dfrac{[O_V''][OH_O^\cdot]^2}{[V_O^\times][O_O^\times]^2 p_{H_2O}} = \exp\left(-\dfrac{\Delta H_1^0}{RT} + \dfrac{\Delta S_1^0}{R}\right) \\ [OH_O^\cdot] = 2[O_V''] \\ [O_O^\times] + [OH_O^\cdot] + [O_V''] = 11 + x \\ [V_O^\times] = 1 - x \\ [OH_O^\cdot] = 2x \end{cases}$$ (2)

where x is the amount of water in hydrated BCN50 ($Ba_4Ca_2Nb_2O_{11}\cdot xH_2O$). The analytical solution of the set (2) with respect to p_{H_2O} yields

$$p_{H_2O} = -\frac{4x^3}{4x^3 - 48x^2 + 165x - 121}\exp\left(\frac{\Delta H_1^0}{RT} - \frac{\Delta S_1^0}{R}\right)$$ (3)

According to Eq. (3), the slope of $\log x = f\left(\log p_{H_2O}, T\right)$ dependencies should be close to 1/3 at low level of hydration in agreement with the qualitative assessment of the defect chemistry of BCN50 made by Animitsa et al. [5,7,9].

Standard enthalpy, ΔH_1^0, and entropy, ΔS_1^0, of reaction (1) were obtained as a result of nonlinear fitting of Eq. (3) to the equilibrium $p_{H_2O} - T - x$ data for BCN50 reported by Animitsa and Kochetova [7]. The results of such fitting are presented in Fig. 2a and Table 1. A good agreement between the calculated surface and the experimental data, as seen in Fig. 2a, is confirmed by close to unity coefficient of determination $R^2 = 0.98$.

In principle, the other defect equilibria, such as those expressed by Eq. (4) or Eq. (5):

$$O_O^\times + V_O^\times \rightleftarrows V_O^{\cdot\cdot} + O_V''$$ (4)

$$O_O^\times + OH_V' \rightleftarrows OH_O^\cdot + O_V''$$ (5)

could influence the defect chemistry of BCN50. However, it is implied in Eqs. (4) and (5) that there are different sites occupied by protons (OH_V' and $OH_O^\cdot$) and oxide ions ($O_O^\times$ and O_V''). In order to affect the hydration thermodynamics of BCN50, these sites should be regarded as crystallographically and energetically nonequivalent. Otherwise, the said reactions would describe the defect exchange between the equal positions, being essentially meaningless.

However, nonequivalent crystallographic positions of oxygen were found only in fully hydrated monoclinic ($P2_1/n$) BCN50 at lower (less than 573 K) temperatures [4,7] but not in the cubic ($Fm\bar{3}m$) BCN50 that is the focus of the present discussion. In addition, the reaction (4) is unlikely to proceed at $T \leq 773$ K, because of the insufficient mobility of oxygen at such a low temperature. Besides, the introduction of either Eq. (4) or Eq. (5) into the defect structure model does not improve the results of the model verification (fitting). Consequently, one can assume that the equilibria (4) and (5) affect the defect chemistry of BCN50 insignificantly, at least, under the conditions discussed in the present work ($T = 623–773$ K and $\log\left(p_{H_2O}/atm\right) < -1.6$).

Partial molar enthalpy, Δh, and entropy, Δs, of water, calculated using $p_{H_2O} - T - x$ data [7], are shown in Fig. 2b and c, respectively. It is seen that, while Δs increases slightly with water content increase, Δh in BCN50 is almost composition-independent. The average value of Δh, Δh_{avg} (see Table 1), is in good agreement with ΔH_1^0, reinforcing our assumption that the defect structure model based on reaction (1) describes the uptake of water by BCN50 quite well.