INTRODUCTION

Though high-temperature protonic conduction was discovered in doped strontium cerate \( \text{SrCeO}_3 \) [1–3], that in materials based on barium cerate is much higher [4]. Studying protonic solid electrolytes based on barium cerate is due to both a purely scientific interest in the phenomenon of protonic conduction in oxides and their application in electrochemical devices [5].

The overall and ionic conduction in air of doped barium cerates \( \text{BaCe}_{1-x}\text{R}_x\text{O}_{3-\delta} \) (BCR), where \( \text{R} \) is a rare-earth element, has been described comprehensively enough [6–17], but protonic conduction in air is barely studied. Attention was focused mainly on BCR doped with Nd, Gd, or Y at \( x \) of 0.05 or 0.10. As most studies were done on BCN, these compounds may be viewed as model ones.

Measurements of electroconductance and transport numbers for ions (\( t_i \)) and protons in \( \text{BaCeO}_3 \) doped with neodymium in the cerium sublattice (0–16%) are measured in moist air (\( \text{pH}_2\text{O} = 2.6 \text{kPa} \)) at 550–1000°C. Partial (by protons, oxygen, and holes) conductances and appropriate effective activation energies are determined. Literature sources are reviewed.

THEORY IN BRIEF

The emergence of hydrogen defects and corresponding charge transfer in oxides is due to reactions of hydrogen-containing components of the gas phase with crystal-chemical lattice defects [22]. Doping barium cerate with cations of rare-earth elements \( \text{R}^{3+} \) gives rise to substitutional defects \( \text{R}_\text{Ce}^\prime \) (Kroeger–Vink notation [23]). The compensating defects are positively charged oxygen vacancies \( \text{V}_\text{O}^- \) [24, 25]:

\[
\text{R}^{3+} \rightarrow \text{R}_\text{Ce}^\prime + 1/2\text{V}_\text{O}^- + \text{O}_\text{O}^\times,
\]

\[
\text{Ce}^{4+} \rightarrow \text{Ce}^\prime + \text{O}_\text{O}^\times,
\]

with ions \( \text{R}_\text{Ce}^\prime \) being capable of forming stable neutral complexes \( \text{R}_\text{Ce}^\prime \text{V}_\text{O}^- \) or \( \text{R}_\text{Ce}^\prime \text{V}_\text{O}^- \text{R}_\text{Ce}^\prime \) [26, 27]. In oxidative media oxygen vacancies \( \text{V}^- \) interact with oxygen of the gas phase to bring about electronic holes \( h^- \) and, consequently, hole conduction [24, 28–30] in the reaction

\[
1/2\text{O}_2 + \text{V}^- = 2h^- + \text{O}_\text{O}^\times
\]

whose equilibrium constant is

\[
K_2 = \frac{[h^-]^2}{[\text{V}^-]([\text{pO}_2]^{1/2})}.
\]

The loss of oxygen by the oxide in reducing media leads to the appearance of electrons \( e^- \) and electronic conduction [25] through the reaction

\[
\text{O}_\text{O}^\times = 1/2\text{O}_2 + \text{V}^- + 2e^-.
\]

Characteristics of Proton-Conducting Electrolytes

\( \text{BaCe}_{1-x}\text{Nd}_x\text{O}_{3-\delta} \) (0 ≤ \( x \) ≤ 0.16) in Moist Air

N. V. Sharova* and V. P. Gorelov

Institute of High-Temperature Electrochemistry, Ural Division, Russian Academy of Sciences, ul. S. Kovalevskoi 22, Yekaterinburg, 620219 Russia

Received December 15, 2004

Abstract—Electroconductance, overall transport number for ions, and transport number for protons in \( \text{BaCeO}_3 \) doped with neodymium in the cerium sublattice (0–16%) are measured in moist air (\( \text{pH}_2\text{O} = 2.6 \text{kPa} \)) at 550–1000°C. Partial (by protons, oxygen, and holes) conductances and appropriate effective activation energies are determined. Literature sources are reviewed.

Key words: barium cerate, transport numbers for ions, protonic conduction

* Corresponding author, e-mail: n.sharova@ihte.uran.ru
which was confirmed by magnetic measurements [25, 26]. Barium cerate can contain up to 15% Ce$^{3+}$ [29]. The interaction of oxygen vacancies with water vapor leads to the emergence of interstitial protons $H^+_i$ in the oxide [24, 28–32]

$$\text{H}_2\text{O} + V'_0 = 2H^+_i + O^\times_0,$$

(5)

Thus, reactions (1), (2), and (5) produce four types of charged defects, whose concentrations are interconnected through the condition of the crystal’s electroneutrality [24]

$$[\text{RCe}] = p + 2[V'_0] + [H^+_i]$$

(7)

Here, $p$ is the concentration of holes $h^-$. If humidity is high and $p\text{O}_2$ is low, at temperatures that are not too high, the concentration of holes and oxygen vacancies in oxides based on barium cerate may be ignored. Then (7) simplifies to

$$[\text{RCe}] \approx [H^+_i],$$

(8)

whence it follows that, under these conditions, the concentration of hydrogen is nearly the same as that of dopant R$^{3+}$ [28, 33]. However, the dissolved-hydrogen amount (4 ± 1 at. % H) in undoped barium cerate is also considerable. Possibly, this is connected with hydration of the oxide surface.

Proton is a positively charged elementary particle whose size is vanishingly small as compared with other lattice ions. In the lattice of oxides, the proton is localized near an oxygen ion [24, 25, 33–35]; moreover, it insert itself in the electron sheath of the oxygen ion [36]. Thus, an interstitial proton may be represented as an $\text{OH}^-$ group that occupies an oxygen point, i.e. $\text{(OH)}^\times_0$ [37], albeit this defect is not transferred as a whole

$$\text{H}_2\text{O} + V'_0 + O^\times_0 = 2\text{(OH)}^\times_0,$$

(9)

$$K_3 = \frac{[\text{(OH)}^\times_0]^2}{[V'_0]p\text{H}_2\text{O}}.$$

(10)

Investigating $\text{BaCe}_{1-x}\text{Nd}_x\text{O}_{3-\delta}$ by an isotope exchange method, the authors of [38] established that hydrogen and oxygen possess different diffusion coefficients and concluded that the proton is transferred as an individual particle. The authors of [37, 39] came to the same conclusion.

Some authors explored the isotope effect in protonic conductors [40–42]. The proton was found to hop from one equilibrium position into another as a result of an activation process, practically without a quantum effect (tunneling). The authors of [42] also deny the existence of the equipage mechanism of proton transfer, i.e. proton transfer together with the migration oxygen ion.

**EXPERIMENTAL**

The source materials for synthesizing samples via a ceramics technology were $\text{BaCO}_3$ (ultra-high purity grade 7-4, for optical glass making), $\text{CeO}_2$ (TseO-L), and $\text{NdO}_1.5$ (HO–CC). The initial reactants were mixed in appropriate proportions and, after preliminary synthesis at 1150°C (1 h) in air pressed were bars of size 4 by 4 by 17 mm for measuring electroconductance and rings with an outside diameter of 14 mm, for measuring transport numbers of ions and protons. The pressed samples were sintered in air at 1450°C for 2 h. The through (open) porosity was determined by soaking in kerosine.