



Nd-doped Ba(Ce,Zr)O_{3-δ} proton conductors for application in conversion of CO₂ into liquid fuels

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ABSTRACT

The paper presents crystal structure, transport properties, chemical stability in CO₂ atmosphere and thin film membrane preparation for materials from the Ba(Ce_{1-x}Zr_x)_{0.9}Nd_{0.1}O_{2.95} ($x = 0, 0.25, 0.5, 0.75, 1$) group of perovskite-type structure oxides. Transformation of crystal structure from orthorhombic Pnma to orthorhombic Imma and cubic Pm3m with increasing x_{Zr} was observed along with linear decrease of pseudo-cubic unit cell volume and free lattice volume. Electrical conductivity of bulk and grain boundary was determined in dry air, as well as in air humidified with H₂O or D₂O. The highest proton conductivity was observed for material with $x_{Zr} = 0.25$. Further increase of Zr content led to decrease of conductivity as high as 2 orders of magnitude. This effect was coupled with bell-shape dependence of activation energy and pre-exponential term. Such behavior was explained as superimposed effects of high proton mobility for zirconium-rich materials due to cubic symmetry and cerium-rich materials due to softness of oxygen–oxygen separation distance, along with high proton concentration for cerium-rich perovskites. The deteriorating effect of grain boundaries on total electrical conductivity was far more pronounced for Zr-rich materials than in the case of Ce-rich ones. Declining grain boundary conductivity was attributed to both increase of number of grain boundaries and decrease of inherent grain boundary conductivity for Zr-rich samples. The highest chemical stability in CO₂ atmosphere was achieved for high-Zr content materials, on the contrary, for BaCe_{0.9}Nd_{0.1}O_{2.95} in CO₂ atmosphere, the decomposition onset temperature was below 500 °C. 2 μm thin film membrane of Ba(Ce_{0.75}Zr_{0.25})_{0.9}Nd_{0.1}O_{2.95} was successfully prepared on c-plane sapphire and fused silica substrates. Film's crystal structure matched that of the bulk material. The electrical conductivity of thermally treated film obtained on c-plane sapphire in wet air was $3.7 \times 10^{-4} \text{ S cm}^{-1}$ at 600 °C.

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1. Introduction

Nowadays, oxides with perovskite-type structure exhibiting proton conductivity are attracting considerable interest, since they can find numerous applications, such as electrolytes for solid oxide fuel cells, gas sensors and gas separation membranes [1–3]. They have been also proposed for membrane reactors, e.g., for electrochemical reduction of CO₂ in proton conducting solid oxide electrolysis cell (SOEC) [4,5]. Nevertheless, materials for proton conducting membranes are still not sufficiently developed, and therefore extensive investigations of proton absorption and migration mechanisms, as well as further application tests are needed.

Wide interest in ABO₃ perovskites exhibiting proton conductivity stems from Iwahara's works in early 1980s [6]. Since then, most attention was paid to the family of B-site rare earth doped barium and strontium cerates and zirconates [7–14]. Among the most

important features of proton-conducting oxides, in context of their application, is value of ionic conductivity, which depends on both proton concentration and proton mobility. Another crucial parameter is chemical stability in operating conditions. Incorporation of protons into acceptor-doped perovskite-structure oxides follows reaction (1) written in Kröger–Vink notation,



Number of protons incorporated into the oxide at given temperature is determined by water vapor partial pressure in surrounding atmosphere, level of acceptor doping, which controls concentration of oxygen vacancies, as well as by enthalpy and entropy changes during the reaction (1). From point of view of selection of appropriate materials, most crucial among the above-mentioned parameters seem to be change of enthalpy and entropy. Norby et al. [7] correlated empirically enthalpy of hydration with the weighted difference of Alfred-Rochow electronegativities between B- and A-site cations in ABO₃ perovskite – the smaller the difference, the more negative enthalpy of hydration. On the other hand, changes of protons' mobility not

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necessarily follows proton concentration. Kreuer [8,15] pointed out that it is the “softness of the oxygen separation coordinate,” which controls the proton mobility and as such depends on atomic bond stiffness.

In this work materials from $\text{Ba}(\text{Ce}_{1-x}\text{Zr}_x)_{0.9}\text{Nd}_{0.1}\text{O}_{2.95}$ ($x = 0, 0.25, 0.5, 0.75$ and 1) group with gradually changing chemical, structural and transport properties are examined. Neodymium was selected as a dopant because of its deteriorating tendency for partitioning into A-site lattice positions, which was described for $\text{BaCe}_{1-x}\text{Nd}_x\text{O}_{3-x/2}$ perovskites [16,17], however, which is not fully recognized in BaCeO_3 – BaZrO_3 solid solutions. Discussion in this work is based on parameters such as pseudo-cubic cell volume, lattice free volume, tolerance factor, lattice distortion angle, and difference between B- and A-site atom electronegativity. Results of bulk and grain boundary proton conductivity impedance spectroscopy measurements in dry air, as well as in air humidified with H_2O or D_2O are given. A material with highest proton conductivity, $\text{Ba}(\text{Ce}_{0.75}\text{Zr}_{0.25})_{0.9}\text{Nd}_{0.1}\text{O}_{2.95}$, was selected for preliminary studies of preparation of thin film membranes using PLD method on standard substrates: Si(100), fused silica and c-plane sapphire.

Comparing to previous works on similar group of materials [18,19], this paper focuses on crystal structure–proton conductivity correlation and provides data on isotope effect in proton conductivity measurements. Additionally, the present work brings detailed description of procedure of preparation and properties of thin film membranes prepared by PLD method from the selected material with optimized composition.

2. Experimental

All samples were prepared by high temperature solid state synthesis with relevant oxides and carbonates as substrates: BaCO_3 (Chempur, 99%), ZrO_2 (Aldrich 99%), CeO_2 (Aldrich, 99.9%) and Nd_2O_3 (Aldrich, 99.9%). Thoroughly milled reactants were calcined at 1200°C for 24 h. After subsequent milling powders were uniaxially pressed at 100 MPa and then sintered at 1500°C for $\text{BaCe}_{0.9}\text{Nd}_{0.1}\text{O}_{2.95}$ and at 1550°C all other compositions. Crystal structure of the obtained materials was investigated using X-ray diffraction (XRD) method with Philips X'Pert Pro diffractometer equipped with $\text{Cu K}\alpha$ radiation source. Diffraction data were refined using GSAS/EXPGUI Rietveld software package [20,21]. Scanning electron microscopy investigations were carried out with FEI Nova Nano 200 microscope. Density of sinters was determined on the basis of their mass and dimensions. Electrical conductivity was measured by means of impedance spectroscopy method using Solartron 1260 frequency response analyzer with sinusoidal excitation voltage equal 0.2 V. For calculation of specific conductivity, sample's porosity was taken into account according to Bruggeman's effective medium approximation [22]. Stability of materials in CO_2 atmosphere was examined using thermogravimetry (TG) technique on TA Instruments Q5000IR thermobalance in flowing CO_2 with heating rate $5^\circ\text{C}/\text{min}$.

Material with nominal composition of $\text{Ba}(\text{Ce}_{0.75}\text{Zr}_{0.25})_{0.9}\text{Nd}_{0.1}\text{O}_{2.95}$ was chosen to be used as a target for thin film preparation by pulsed laser deposition (PLD). The $\text{Ba}(\text{Ce}_{0.75}\text{Zr}_{0.25})_{0.9}\text{Nd}_{0.1}\text{O}_{2.95}$ films were deposited using SURFACE™ PLD setup equipped with KrF excimer laser (Compex PRO, deposition parameters $\lambda = 248\text{ nm}$, 7 Hz , 1.9 J cm^{-2}). The c-plane sapphire, Si(001) and fused silica wafers were used as substrates. During deposition the oxygen background pressure was 0.1 mbar, the target-to-substrate distance was 7.5 cm and the substrate temperature was 700°C . The thickness of the films was $2\ \mu\text{m}$. Additionally, after the deposition selected films were annealed in air at 500°C for 5 h in order to improve their crystallinity. For electrical measurements, the 200 nm thick rectangular Au electrodes with dimensions $20\text{ mm} \times 2\text{ mm}$ were deposited by the e-beam technique using a shadow mask.

Thin film X-ray diffraction (XRD) measurements were carried out with a Diff8 Bruker fitted with a Göbel mirror to obtain a parallel beam of the $\text{Cu K}\alpha$ radiation source (40 kV and 40 mA). Surface images and the chemical composition were examined using Scanning Electron Microscope FEI Quanta 200 FEG-ESEM with EDAX/EDS. Electrical conductivity of thin films was measured in a Probostat measurement cell (Norecs, Norway) by impedance spectroscopy technique using a Novocontrol Alpha-A spectrometer in the frequency range $100\text{--}10^6\text{ Hz}$, with an excitation voltage of 0.050 V.

3. Results and discussion

All samples obtained after sintering turned out to be single-phased and perovskite-type structure, however, varying with lattice distortion: XRD pattern of $\text{BaZr}_{0.9}\text{Nd}_{0.1}\text{O}_{2.95}$ was successfully refined with $Pm\bar{3}m$ cubic space group, all $\text{Ba}(\text{Ce,Zr})_{0.9}\text{Nd}_{0.1}\text{O}_{2.95}$ solid solutions needed Imma orthorhombic symmetry to achieve acceptable refinement, and finally, $\text{BaCe}_{0.9}\text{Nd}_{0.1}\text{O}_{2.95}$ belonged to Pmcn orthorhombic space group. The detected structural evolution is driven mainly by the difference in radius between cerium and zirconium ions – substitution of Ce^{4+} ($0.87\ \text{\AA}$ in octahedral coordination) by Zr^{4+} ($0.72\ \text{\AA}$) [23] resulted in increase of crystal's symmetry manifested as increase of tolerance factor and decrease of octahedrons tilting (B–O₁–B and B–O₂–B-angles) (Fig. 1). This behavior is expected and can be justified as follows: in the case of $\text{BaZr}_{0.9}\text{Nd}_{0.1}\text{O}_{2.95}$ A- and B-site cations (in ABO_3 perovskite) match each other forming cubic perovskite structure with tolerance factor, defined as $t = (r_A + r_O) / (\sqrt{2}(r_B + r_O))$, equal 1. Ba and O ions are arranged in the cubic close-packed manner with zirconium ions fitting well to the octahedral hole in the center of the unit cell. Larger neodymium ions ($0.983\ \text{\AA}$ [23]) seem not to disturb this arrangement, however, their presence leads to mentioned above effect of partitioning between B- and A-sites. Fig. 1 also shows that substitution of zirconium with larger cerium results in lattice swelling (linear increase of pseudo-cubic cell volume (V_{p-c})). Along with the increase of volume of atoms (V_{at}) within the unit cell, and increasing structural distortion, free lattice volume, defined as $(V_{p-c} - V_{at})/V_{p-c}$, rose as well. Weighted differences of Allred-Rochow electronegativities between B- and A-site cations (ΔX_{B-A}) for the considered group of materials were presented for comparison in Fig. 1. Linear dependence of ΔX_{B-A} as a function of Zr content, with the lowest value for $\text{BaCe}_{0.9}\text{Nd}_{0.1}\text{O}_{2.95}$ and the highest for $\text{BaZr}_{0.9}\text{Nd}_{0.1}\text{O}_{2.95}$, suggests, according to Norby et al. [7], linear increase of negative value of hydration enthalpy, and, as a consequence, higher proton concentration for a given temperature, pressure, and level of doping.

Changes in chemical composition of the examined materials led to considerable variation of sintered samples' microstructure. Fig. 2 shows exemplary SEM image of $\text{Ba}(\text{Ce}_{0.75}\text{Zr}_{0.25})_{0.9}\text{Nd}_{0.1}\text{O}_{2.95}$ cross-section, whereas relative density of the pellets as a function of Zr content is depicted in Fig. 3. Together with rising zirconium content, relative density of the pellets diminished monotonically from 99% for $\text{BaCe}_{0.9}\text{Nd}_{0.1}\text{O}_{2.95}$ to 76% for $\text{BaZr}_{0.9}\text{Nd}_{0.1}\text{O}_{2.95}$. The decrease of relative density was coupled with decrease of the materials' average grain size. In general, development of more sophisticated preparation procedure may result in higher relative density of the samples, however, presented results point to increasing difficulty of preparation of dense membranes with growing Zr content.

Set of impedance spectra of materials from the $\text{Ba}(\text{Ce}_{1-x}\text{Zr}_x)_{0.9}\text{Nd}_{0.1}\text{O}_{2.95}$ group, measured at around 300°C in dry air and in air humidified with 3 vol% of H_2O or D_2O , is presented in Fig. 4. The spectra of Zr-rich materials are composed of two easily distinguishable semicircles, from which the high-frequency one can be attributed to charge transport in grain interior and the low frequency semicircle to charge transport along grain boundaries [24]. Electrical parameters of samples were derived from spectra using equivalent circuit model, $(R_{\text{bulk}}Q_{\text{bulk}}) - (R_{\text{gb}}Q_{\text{gb}})$, where R denotes resistance

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