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Electrical and sensing properties of indium-doped barium cerate

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Abstract

Systematic analysis of electrical characteristics of $BaCe_{0.75}In_{0.25}O_{3-\delta}$ (BCI25) sintered sample was performed in a dry and a wet argon atmosphere in the 250 °C – 700 °C temperature range. The water vapor sensing properties of BCI25 porous film and its response and recovery times were investigated under different conditions of temperature and water vapor concentration. The 30 μm thick film obtained from the powder calcined at 1050 °C exhibited sensitivity comparable to that of the sintered sample with a significantly shorter response and recovery times. While the sensitivity of the film gradually decreased with a decrease in partial pressure of water vapor ($p(H_2O)$), a noticeable sensitivity was still

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observed at $p(H_2O)$ of 200 Pa. Decrease in conductivity depended logarithmically on the partial pressure of water with the slope of 0.52 that is close to the theoretical value. After several cycles, the reusability test proved an almost unchanged ratio between the impedance value in the dry and the wet Ar atmosphere ($p(H_2O) = 2.34$ kPa), which implied that BCI25, having good stability and sensitivity, is a promising high-temperature humidity sensor.

Keywords: C. Ionic conductivity; D. Perovskites; E. Sensors; $BaCeO_3$.

1. Introduction

Mixed oxide perovskites with ABO_3 general formula have various potential applications as catalysts [1], photocatalysts [2], gas sensors [3], materials for the construction of fuel cells [4], etc. Within this group of materials, acceptor-doped perovskites with large lattice constants (such as $BaCeO_3$, $SrCeO_3$, and $BaZrO_3$) have been known as fast proton conductors. They are used as electrolytes for proton-conducting fuel cells [5, 6]. In addition, they can be used for humidity detection in a high-temperature environment, which is essential for industrial processes [7, 8]. The thermal stability and mechanical durability of these ceramic materials under high-temperature conditions make them a good choice for high-temperature humidity sensors.

The ability of doped perovskite oxide materials to conduct both protons and oxygen ions at high temperatures has been studied since the beginning of the 1980s [9, 10]. The structure of mixed oxide perovskite materials consists of A^{2+} cations surrounded by twelve

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oxygen anions and B^{4+} surrounded by six oxygen anions in an octahedral environment. Doping of such structure with a cation of lower valence at the B-site causes the formation of oxygen vacancies ($V_O^{\bullet\bullet}$). Vacancies facilitate oxygen ion transport through the material at elevated temperatures. Besides, in a humid environment, water molecules dissociate, producing the hydroxyl ion occupying the vacancy, and H^+ bonds with the oxygen ion from the lattice. This process results in the formation of protonic defects ($OH_O^{\bullet}$), obeying the electroneutrality condition expressed by Equation (1):

$$[OH_O^{\bullet}] + 2[V_O^{\bullet\bullet}] = \left[In_{Ce}^{'}\right] = \text{const.} \tag{1}$$

These defects are responsible for the high-temperature conductivity at 450 °C – 700 °C [11], while proton conductivity ($\sigma_{OH_o^{\bullet}}$) is dependent on partial vapor pressure ($p(H_2O)$) according to Equation (2):

$$\sigma_{OH_o^{\bullet}} \sim p(H_2O)^{1/2} \tag{2}$$

The unique property of doped perovskite mixed oxides to dissolve water molecules and conduct both oxygen anions and protons can be used as a sensing mechanism for detecting water molecules since the creation of the protonic defects increases the total electric conductivity of the material. According to the model proposed by Wang et al. [12], the concentration of water dissolved in a proton conductor is a function of partial pressure of H_2O in the atmosphere surrounding the sensor, enabling the determination of water concentration. Moreover, proton-conducting perovskites respond selectively to water vapor in the presence of other gasses, such as NH_3, NO_2, H_2, and O_2 [13].

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Several attempts have been made to construct high-temperature humidity sensors based on doped mixed oxide perovskites. Bulk tubular and thick film sensors of Nd- and Yb-doped $SrCeO_3$ showed a response in the 200 °C – 400 °C range [14], while $Ba_3Ca_{1.18}Nb_{1.82}O_9$ responded to wet air by an increase of conductivity in the 500 °C – 700 °C range [12]. The In-doped $CaZrO_3$ ceramics impedance decreased in the presence of H_2O under a nitrogen atmosphere in the 400 °C – 700 °C range [15]. Thin films of Y-doped $BaZrO_3$ produced by sputter deposition and pulsed laser deposition were tested at 400 °C and 500 °C – 650 °C, respectively. They showed increased conductivity when exposed to the wet N_2 atmosphere [13, 16, 17]. All these examples indicate the high sensitivity of the investigated materials, regardless of their form and processing conditions, and are characterized by an immediate drop in resistivity in the presence of water vapor.

Despite a very high proton conductivity of doped $BaCeO_3$, its main drawback is chemical instability in CO_2 and wet atmospheres. As a trivalent medium-sized ion with amphoteric character, indium can replace yttrium in $BaCe_{1-x}Y_xO_{3-\delta}$ and serve as a point defect source and inhibit deterioration in the CO_2 atmosphere due to its high electronegativity (1.78) compared with cerium (1.12) and yttrium (1.22). It was confirmed by recent investigations that doping with In^{3+} significantly improved the stability of the material, with some adverse effects on the conductivity [18]. Thus, a certain drop in conductivity compared with $BaCe_{1-x}Y_xO_{3-\delta}$ can be ascribed to the relatively high electronegativity of In and reduced lattice symmetry because of its smaller ionic radius. It was found that around 25 mol% of In^{3+} provides the maximal ionic conductivity within doping concentrations up to 40 mol%. In this study, the systematic electrical

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characterization of $BaCe_{0.75}In_{0.25}O_{3-\delta}$ ceramics was carried out in dry and wet argon

atmospheres as a basis for investigating the sensing properties of the porous film made of

this material by varying parameters such as temperature and humidity conditions.

2. Experimental section

$BaCe_{0.75}In_{0.25}O_{3-\delta}$ (BCI25) powder was synthesized by the auto-combustion reaction

method using barium(II) nitrate (Fluka, min. 99.0 %), cerium(III) nitrate hexahydrate

(Fluka, min. 99.0 %), indium(III) nitrate pentahydrate (Aldrich, 99.99 %) and citric acid

monohydrate (Fluka, 99 %) as starting reagents. An aqueous solution containing

stoichiometric quantities of metallic nitrates and citric acid was prepared using a citric

acid/metal ions molar ratio of 2:1. The pH value of the solution was adjusted to ~7 by the

addition of 25 % aqueous ammonia solution (around 15 ml). The resulting mixture was

heated at ~80 °C until the resinous product was obtained. The temperature was gradually

increased over 200 °C until the combustion reaction was initiated and the voluminous ash

product was formed. As-obtained precursor powder was calcined at 1050 °C.

Dense ceramic pellets were produced by uniaxial pressing of the powder at 150

MPa in a cylindrical die of 8 mm in diameter, followed by sintering in an air atmosphere at

1400 °C for 5 h. XRD analysis of the calcined powder and pulverized sintered sample of

BCI25 was performed on a RIGAKU Ultima IV X-ray diffractometer using CuK_α radiation

($\lambda_{CuK\alpha} = 1.54178 \times 10^{-10}$ m). The data for BCI25 powder were collected from 20° to 90° 2Θ

with a step size of 0.02° and a counting time of 3 s. The solutions of the unit cell

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parameters were estimated by a trial-and-error method using Dicvol [19] program for indexing powder diffraction patterns. The best solutions were further tested, and unit cell parameters were refined by Le Bail full pattern profile fitting method [20] using the FullProf software suite [21].

The specific surface area was determined by measuring N_2 adsorption/desorption isotherms at 77 K with a NOVA 600BET surface area and porosity analyzer (Anton Paar, Austria). Before the measurements, the samples were treated at 250 °C for 5 h in a vacuum to remove moisture and physisorbed gases. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) equation.

The electrical characterization of the sintered BCI25 pellet was investigated by a Hioki IM3536 impedance analyzer within the temperature range of 250 °C – 700 °C in dry and wet argon atmospheres. The applied frequency range was 10 Hz – 5 MHz. The wet argon atmosphere ($p(H_2O) = 2.34$ kPa) was provided by introducing the gas through a gas washer filled with distilled water at room temperature. The argon flow rate through the system was kept at 100 cm^3/min using a digital mass flow controller and meter (MKS PR 4000B-F).

To investigate BCI25 sensing properties, the porous film was prepared by applying the BCI25 paste of the powder calcined at 1050 °C. The paste was prepared by mixing the BCI25 powders with a vehicle consisting of 95 wt% terpineol and 5 wt% of polyvinyl butyral (PVB) in a 1:1 ratio. The paste was applied by the doctor blade method onto an alumina substrate with interdigitated Pd/Ag electrodes. In this case, possible diffusion of

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Pd/Ag into the sensing layer is minimized. DSC-TGA analysis of the BCI25 paste was performed on a simultaneous thermal analyzer 6000 ("Perkin Elmer"). The porous films were obtained after thermal treatment in a chamber furnace at 800 °C for 5 h. Morphology and possible compositional differences in the samples were analyzed by back-scattered electron imaging using a TESCAN Vega TS5130MM scanning electron microscope. ImageJ software was used for the grain size analysis of the pellet. The particle size of the porous film was analyzed by a high-resolution scanning electron microscope (Jeol 6300).

The water vapor sensing properties of BCI25 were investigated using in-house built testing equipment consisting of a quartz tube inserted into the tube furnace. Argon, with a 200 cm^3/min flow rate, was passed through a water bath at 25 °C before entering the quartz tube containing the BCI25 thick film sensor. Different H_2O concentrations were provided by diluting humid Ar with dry Ar in a corresponding volume ratio. The impedance measurements of the samples were performed using the Hioki IM3536 impedance analyzer at 100 Hz. The reusability test of the selected film was conducted by an alternate flow of dry Ar and Ar saturated with water vapor ($p(H_2O) = 2.34$ kPa) at 500 °C. This process was repeated several times to check the recovery behavior of the sensor. A schematic representation of the experimental setup for measuring sensing properties is shown in Figure 1.

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3. Results and discussion

The XRD patterns of BCI25 powder calcined at 1050 °C and pulverized ceramics sintered at 1400 °C are presented in Figures 2a and 2b. The main reflections were indexed and referred to a perovskite structure with orthorhombic symmetry (space group *Pmcn*). The small peaks at ~23.9° and ~30.5° in the calcined sample indicated the presence of a small amount of $BaCO_3$ and In_2O_3 as secondary phases. These peaks diminished during the sintering process at 1400 °C. The refinement results showed that all unit cell parameters decreased after sintering at 1400 °C and accordingly, the unit cell volume decreased from 335.70(2) $Å^3$ for the BCI25 powder calcined at 1050 °C to 330.09(2) $Å^3$ for the pulverized BCI25 pellet sintered at 1400 °C. This indicates the reincorporation of In_2O_3 into the perovskite lattice, considering that the ionic radius of In^{3+} (0.80 Å) is smaller than that of Ce^{4+} (0.87 Å). Also, the BSE image of the BCI25 pellet confirmed no presence of any secondary phase. Although the density of the BCI25 sample can almost reach its theoretical value after sintering at 1300 °C, traces of In_2O_3 were still observed at this temperature [18]. As confirmed in our previous study, traces of In_2O_3 as a secondary phase did not deteriorate electrical properties and stability in CO_2 of BCI25. In this study, the BCI25 sample sintered at 1400 °C also reached 98 % of the theoretical value, implying that significant bulk density improvements cannot be achieved by increasing the sintering temperature. As for the microstructure, the average grain size remarkably increased from 1.5 μm at 1300 °C [18] to 2.8 μm at 1400 °C (Figure 2c), indicating that the higher sintering temperature enhanced the grain growth. The grain size distribution is rather multimodal, as seen in Figure 2d, where roughly 90 % of the grains were between 1 μm and 4 μm. These values are notably

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higher than for the vast majority of the doped barium cerates sintered at 1400 °C and at even higher temperatures [22–26], which thus makes In beneficial for the sintering of $BaCeO_3$.

To evaluate the influence of the temperature and humidity on the electrical characteristics of BCI25, impedance spectra of the BCI25 pellet sintered at 1400 °C were recorded in the 250 °C – 700 °C temperature range under the dry Ar and wet Ar atmospheres. The shape of the spectra varied gradually with temperature and depended on the atmosphere. Therefore, several circuit models were proposed for the fitting of the spectra. In the 250 °C – 375 °C temperature range, the impedance spectra were fitted with a circuit consisting of two resistors (*R1* and *R2*) in parallel with two constant phase elements (*CPE1* and *CPE2*) and a Warburg element (*W1*). Typical spectra are presented in Figure 3. The effective capacitances were calculated from the formula $C = (Q \cdot R)^{(1/n)}/R$, where *Q* and *n* represent constants of *CPE*. The effective capacitances for *CPE1* elements in this temperature range were ~10^{-11} F/cm, suggesting that *R1* and *CPE1* are related to the grain bulk and grain boundary [27, 28]. According to the calculated values for *CPE2* (~10^{-7} F/cm), *R2* and *CPE2* represent processes at the electrode, while the grain boundary contribution could not be identified in both cases. The absence of a semicircle representing the grain boundary contribution in the middle-frequency range and the low effective capacitance (~10^{-11} F/cm) is rather an indication of the negligible effect of the grain boundaries on the conduction mechanism. This assumption is corroborated by the existence of relatively large grains and, consequently, a lower number of grain boundaries present in the bulk material. Warburg element represents diffusion processes at the electrode at low

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frequencies [29, 30]. These spectra can also be optionally fitted with an additional

inductance element (*L1*). At the same time, at temperatures above 400 °C, it was necessary

to represent stray inductance that became dominant at higher frequencies, making the

fitting of the spectra difficult above 500 °C. Therefore, only the total conductivities (grain

bulk and boundary) were determined for the investigated temperature interval.

The total electrical conductivities vs. temperature were presented in the form of

Arrhenius plots (Figure 4). Under the dry Ar atmosphere, the calculated activation energy is

0.58 eV for the whole temperature range. This value is characteristic of the conduction

mechanism provided by oxygen vacancies ($V_O^{\bullet\bullet}$) that enable the mobility of the oxygen ions

through the perovskite structure. For comparison, the activation energy of 0.66 eV was

reported for $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ in dry Ar [22]. Under wet Ar, however, two regions could be

distinguished. In the first one, below 450 °C, the constant difference between the

conductivities in dry and wet Ar suggests that all the vacancies are saturated with protons

under the wet Ar atmospheres. The activation energy of 0.53 eV below 450 °C is higher

than the theoretical values for the proton conductivity. Similarly, Amsif et al. reported the

value of 0.53 eV for La-doped $BaCeO_3$ in the temperature range of 150 °C – 250 °C in a

wet-5% H_2–Ar atmosphere [23]. This can be ascribed to the trapping effect or as a

consequence of high proton concentrations [31]. Additionally, some deviation from

Arrhenius law in the dry Ar atmosphere may occur due to the phase transitions that the

$BaCeO_3$ lattice undergoes in the observed temperature range [32]. Above 450 °C

concentration of the protonic defects decreases with the temperature increase, causing the

conductivity to increase at a lower rate and gradually approach the conductivity values

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under dry Ar [33]. Consequently, the activation energy decreases to 0.39 eV in this region

which is comparable with the literature values of 0.36 eV – 0.44 eV for Nb- and Ta-doped

$BaCe_{0.9}Y_{0.1}O_{3-\delta}$ in wet Ar and 550 °C – 750 °C temperature range [24, 34].

According to the Arrhenius plots, the ratio between the impedance in dry Ar and

wet Ar ($|Z|_{dryAr}/|Z|_{wetAr}$) as a measure of material's sensitivity becomes higher below

450 °C. However, dense sintered samples exhibited very long response and recovery times

at 500 °C and (11 min, and 33 min, respectively, for 80 μm thick sample) and this trend

was more pronounced at lower temperatures. On the other hand, impedance variations with

slight temperature changes tend to increase at lower temperatures. Therefore, it was more

appropriate to examine these properties of BCI25 in the form of a porous film by lowering

the conductivities of the sample and thus making variations in temperature less significant

at the observed temperature. Also, response and recovery times are significantly shorter in

porous materials than in dense ones due to a slow diffusion process of gas molecules

through a dense solid bulk. Thus, the porous film formed from the powder obtained by the

auto-combustion synthesis method was chosen because the as-obtained ceramic powders

possess higher specific surface area, unlike those obtained by other synthesis methods, such

as the classical solid-state synthesis method [35, 36]. The powder was calcined at 1050 °C

and its BET-specific surface area was 2.076 m^2/g. For comparison, the specific surface area

decreased to 0.394 m^2/g after calcination at 1400 °C. Apparently, the calcination at 1400 °C

leads to excessive particle agglomeration and results in a much lower specific surface area.

Therefore, the thermal treatment of the ceramic paste applied onto the alumina substrate

was carried out at the lowest temperature possible. TG analysis of BCI25 paste was

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performed in the 200 °C – 900 °C temperature range (Figure 5a). It showed that a total

mass loss of approximately 5 %, corresponding to the amount of organic component of the

paste, occurred at around 800 °C. Additionally, the back-scattered image revealed that the

film's surface was rather uniform in composition, without carbonates as a possible

secondary phase (Figure 5b). The film contained particles ~100 nm in size (Figure 5c) and

scattered agglomerates of several micrometers, while its porosity was about 59 %. Thus the

film retained the high specific surface area and small particles (in the submicron range) as

the active places necessary for good sensitivity and fast response.

Yet, there was a limiting factor for investigating the sensing properties of the porous

film at temperatures lower than 450 °C due to their large impedances both in wet and dry

argon and their variation with slight temperature changes. The morphology of the porous

film containing smaller particles and pores induced a significant decrease in the electrical

conductivity compared with the dense samples. Therefore, it was optimal to study sensing

properties at temperatures around 500 °C, whereas a still relatively high $|Z|_{dryAr}/|Z|_{wetAr}$

ratio can provide good sensitivity and the impedances are not too high. Thus, humidity

sensing tests were performed on a 30 μm thick sample under various partial pressures of

water vapor. First, the appropriate sensing temperature and frequency were optimized for

the film. The impedance was measured under the alternate flow of dry and wet Ar at 450

°C, 500 °C, 550 °C, and 600 °C. The ratio between the impedance values in the dry and wet

atmospheres decreased with the increase in temperature, which is consistent with the

differences in activation energy values derived from the Arrhenius plot for the sintered

sample of BCI25. Besides, the sensitivity of the investigated porous film did not deviate

significantly from that of the pellet sintered at 1400 °C throughout the 450 °C – 600 °C

temperature range (Figure 6a). On the other hand, the impedance values measured in the

wet and dry atmospheres slowly decreased and were almost invariant of frequency up to

10^6 Hz (Figure 6a), and the frequency of 100 Hz was chosen for further investigation. In

comparison with the sintered sample, the thick porous film exhibited shorter response and

recovery times under the same temperature and humidity conditions (Figure 6b). It can be

explained by the higher surface area of the porous film that facilitates the diffusion of the

charge carriers.

The sensing mechanism can be presented by Equations (3) and (4) using Kröger-

Vink notation:

$$2BaO + In_2O_3 \rightarrow 2Ba_{Ba}^{\times} + 2In_{Ce}' + 5O_O^{\times} + V_O^{\bullet\bullet} \tag{3}$$

$$H_2O + V_O^{\bullet\bullet} + O_O^{\times} \rightleftarrows 2OH_O^{\bullet} \ (\Delta H < 0, \ \sigma \propto [OH_O^{\bullet}]) \tag{4}$$

Doping of BaCeO$_3$ with a cation of lower valence, such as indium, results in the

formation of an oxygen-deficient material containing vacancies at the oxygen site ($V_O^{\bullet\bullet}$) [9].

In contact with the humid atmosphere, water molecules penetrate the film and enter the

crystal lattice occupying oxygen vacancies. At the same time, one of the protons from the

water molecule gets transferred to another oxygen atom creating two OH$^+$ ions ($OH_O^{\bullet}$).

These protons can hop from one O atom to another, and their mobility enables the

emergence of proton conductivity, resulting in a quick increase in the total conductivity.

After the reintroduction of the dry atmosphere, a sensing material recovers by releasing the

water molecules and returns to the starting conductivity values. Introducing the humidity

into the dry Ar atmosphere leads to an immediate decrease in the observed value of the

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impedance (a few seconds) and saturation time of about 1 min. At the same time, the

recovery takes several minutes upon reintroducing the dry Ar atmosphere. Similar behavior

was found in other perovskite materials such as $Ba_3Ca_{1.18}Nb_{1.82}O_9$ [12], while for the Y-

doped barium zirconate thin films (< 500 nm), the recovery time was shorter [13, 17].

Reusability and the influence of water vapor concentration on its sensing properties

were investigated on the porous film (Figure 7). After several measurements of the

impedance by an alternating flow of dry Ar and Ar saturated with water vapor ($p(H_2O)$ =

2.34 kPa) at 500 °C, the resulting cycles were presented in Figure 7a, characterized by the

hysteresis that represents the change in the impedance between the initial value and value in

the succeeding cycle(s). The hysteresis for the sensor output in dry Ar was ~3 % between

the first two pairs of cycles and without further change. In the saturated wet Ar atmosphere,

the hysteresis amounted to 0.6 % between the first two cycles, while no change in value

was observed between the second and the third cycle. These values are similar and

somewhat smaller than those found in the literature [13, 17], indicating the high stability of

the sensor.

The sensing response of the film for different concentrations of water vapor is

presented in Figure 7b, showing that sensitivity, expressed as $|Z|_{dryAr}/|Z|_{wetAr}$ ratio,

gradually decreased with water vapor partial pressure from 3.92 (2.34 kPa) to 3.53 (1.17

kPa), 2.43 (0.468 kPa) and 1.88 (0.234 kPa). The dependence of the conductivity change

(σ_{wet} - σ_{dry}) on the partial pressure of water $p(H_2O)$ is presented as a logarithmic plot in

Figure 8. The calculated slope of the linear fit is 0.52, which is very close to the theoretical

value of 1/2 [12]. While the response time increased with the decrease in water vapor

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partial pressure from 1.0 min, 2.5 min, 4.2 min, and 4.7 min, the opposite trend was observed for the recovery times: 11.0 min, 10.5 min, 6.8 min, and 6.0 min. As can be seen from Figure 7b, by comparing the intensity of the first peak ($p(H_2O) = 0.234$ kPa) and last peak ($p(H_2O) = 2.34$ kPa), the recovery, when 90 % of water vapor is removed, is relatively quick and amounts only about 10 s. This finding indicates the very high sensitivity of the BCI25 to water vapor and the ability to recover relatively fast.

4. Conclusions

The electrical characterization of the BCI25 sintered sample under the dry and wet Ar atmospheres was performed in the 250 °C – 700 °C temperature range. The decrease in impedance was observed when the sample was exposed to the humid Ar atmosphere suggesting that this material has the potential for application as a humidity-sensing material. According to the Arrhenius plots, the $|Z|_{dryAr}/|Z|_{wetAr}$ ratio is favorable for sensing properties at lower temperatures, but 500 °C was chosen as the optimal temperature due to very high impedances and unreliable measurements for the porous film at lower temperatures. The sensing properties of the porous BCI25 film were studied under various water vapor concentrations. The film exhibited sensitivity to water vapor expressed as $|Z|_{dryAr}/|Z|_{wetAr}$ ratio that did not deviate significantly from that of the densely sintered sample. On the other hand, the response and recovery times for the porous film were much shorter. The film's sensitivity decreased with the partial pressure of water vapor, while noticeable sensitivity was detected even at 230 Pa. The impedance hysteresis in dry Ar was ~3 %, and in the saturated wet Ar atmosphere amounted to 0.6 % between the first two

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cycles, all of which proved good stability, reusability, and sensitivity of BCI25 as a high-temperature humidity sensor. Although this material has the potential for humidity sensing at temperatures below 500 °C, much attention should be paid to decreasing the impedance of the porous films at lower temperatures.

References

[1]   S. Tasleem, M. Tahir, Recent progress in structural development and band engineering of perovskites materials for photocatalytic solar hydrogen production: A review, Int. J. Hydrogen Energy. 45 (2020) 19078–19111. https://doi.org/10.1016/j.ijhydene.2020.05.090.

[2]   J. Zhu, H. Li, L. Zhong, P. Xiao, X. Xu, X. Yang, Z. Zhao, J. Li, Perovskite oxides: Preparation, characterizations, and applications in heterogeneous catalysis, ACS Catal. 4 (2014) 2917–2940. https://doi.org/10.1021/cs500606g.

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[3] J.W. Fergus, Perovskite oxides for semiconductor-based gas sensors, Sensors Actuators B Chem. 123 (2007) 1169–1179. https://doi.org/10.1016/j.snb.2006.10.051.

[4] M. Bilal Hanif, M. Motola, S. Qayyum, S. Rauf, A. Khalid, C.-J. Li, C.-X. Li, Recent advancements, doping strategies and the future perspective of perovskite-based solid oxide fuel cells for energy conversion, Chem. Eng. J. 428 (2022) 132603. https://doi.org/10.1016/j.cej.2021.132603.

[5] D.A. Medvedev, J.G. Lyagaeva, E.V. Gorbova, A.K. Demin, P. Tsiakaras, Advanced materials for SOFC application: Strategies for the development of highly conductive and stable solid oxide proton electrolytes, Prog. Mater. Sci. 75 (2016) 38–79. https://doi.org/10.1016/j.pmatsci.2015.08.001.

[6] N.L.R.M. Rashid, A.A. Samat, A.A. Jais, M.R. Somalu, A. Muchtar, N.A. Baharuddin, W.N.R. Wan Isahak, Review on zirconate-cerate-based electrolytes for proton-conducting solid oxide fuel cell, Ceram. Int. 45 (2019) 6605–6615. https://doi.org/10.1016/j.ceramint.2019.01.045.

[7] I.C. Kemp, Humidity Effects in Solids Drying Processes, Meas. Control. 40 (2007) 268–271. https://doi.org/10.1177/002029400704000901.

[8] S.C. Okoro, M. Montgomery, F.J. Frandsen, K. Pantleon, Effect of water vapor on high-temperature corrosion under conditions mimicking biomass firing, Energy & Fuels. 29 (2015) 5802–5815. https://doi.org/10.1021/acs.energyfuels.5b01045.

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[9]   H. Iwahara, T. Esaka, H. Uchida, N. Maeda, Proton conduction in sintered oxides and its application to steam electrolysis for hydrogen production, Solid State Ionics. 3–4 (1981) 359–363. https://doi.org/10.1016/0167-2738(81)90113-2.

[10]   H. Uchida, N. Maeda, H. Iwahara, Relation between proton and hole conduction in $SrCeO_3$-based solid electrolytes under water-containing atmospheres at high temperatures, Solid State Ionics. 11 (1983) 117–124. https://doi.org/10.1016/0167-2738(83)90048-6.

[11]   H. Iwahara, H. Uchida, K. Ono, K. Ogaki, Proton conduction in sintered oxides based on $BaCeO_3$, J. Electrochem. Soc. 135 (1988) 529–533. https://doi.org/10.1149/1.2095649.

[12]   W. Wang, A.V. Virkar, A conductimetric humidity sensor based on proton conducting perovskite oxides, Sensors Actuators B Chem. 98 (2004) 282–290. https://doi.org/10.1016/j.snb.2003.10.035.

[13]   X. Chen, L. Rieth, M.S. Miller, F. Solzbacher, Pulsed laser deposited Y-doped $BaZrO_3$ thin films for high temperature humidity sensors, Sensors Actuators B Chem. 142 (2009) 166–174. https://doi.org/10.1016/j.snb.2009.07.041.

[14]   M.A. Hassen, A.G. Clarke, M.A. Swetnam, R.V. Kumar, D.J. Fray, High temperature humidity monitoring using doped strontium cerate sensors, Sensors Actuators B Chem. 69 (2000) 138–143. https://doi.org/10.1016/S0925-4005(00)00530-X.

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[15] M. Zhou, A. Ahmad, Sol–gel processing of In-doped CaZrO$_3$ solid electrolyte and the impedimetric sensing characteristics of humidity and hydrogen, Sensors Actuators B Chem. 129 (2008) 285–291. https://doi.org/10.1016/j.snb.2007.08.022.

[16] X. Chen, L. Rieth, M.S. Miller, F. Solzbacher, Comparison of Y-doped BaZrO$_3$ thin films for high temperature humidity sensors by RF sputtering and pulsed laser deposition, Sensors Actuators B Chem. 148 (2010) 173–180. https://doi.org/10.1016/j.snb.2010.03.074.

[17] X. Chen, L. Rieth, M.S. Miller, F. Solzbacher, High temperature humidity sensors based on sputtered Y-doped BaZrO$_3$ thin films, Sensors Actuators B Chem. 137 (2009) 578–585. https://doi.org/10.1016/j.snb.2009.01.024.

[18] A. Malešević, A. Radojković, M. Žunić, A. Dapčević, S. Perać, Z. Branković, G. Branković, Evaluation of stability and functionality of BaCe$_{1-x}$In$_x$O$_{3-\delta}$ electrolyte in a wider range of indium concentration, J. Adv. Ceram. 11 (2022) 443–453. https://doi.org/10.1007/s40145-021-0547-1.

[19] A. Boultif, D. Louër, Powder pattern indexing with the dichotomy method, J. Appl. Crystallogr. 37 (2004) 724–731. https://doi.org/10.1107/S0021889804014876.

[20] A. Le Bail, H. Duroy, J.L. Fourquet, Ab-initio structure determination of LiSbWO$_6$ by X-ray powder diffraction, Mat. Res. Bull. 23 (1988) 447–452. https://doi.org/10.1016/0025-5408(88)90019-0

[21] J. Rodríguez-Carvajal, Recent advances in magnetic structure determination by

19

neutron powder diffraction, Phys. B Condens. Matter. 192 (1993) 55–69.

https://doi.org/10.1016/0921-4526(93)90108-I.

[22]   M. Amsif, D. Marrero-López, A. Magrasó, J. Peña-Martínez, J.C. Ruiz-Morales, P.

Núñez, Synthesis and characterisation of $BaCeO_3$-based proton conductors obtained

from freeze-dried precursors, J. Eur. Ceram. Soc. 29 (2009) 131–138.

https://doi.org/10.1016/j.jeurceramsoc.2008.06.001.

[23]   M. Amsif, D. Marrero-Lopez, J.C. Ruiz-Morales, S.N. Savvin, M. Gabás, P. Nunez,

Influence of rare-earth doping on the microstructure and conductivity of

$BaCe_{0.9}Ln_{0.1}O_{3-\delta}$ proton conductors, J. Power Sources. 196 (2011) 3461–3469.

https://doi.org/10.1016/j.jpowsour.2010.11.120.

[24]   A. Radojković, M. Žunić, S.M. Savić, G. Branković, Z. Branković, Enhanced

stability in CO_2 of Ta doped $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ electrolyte for intermediate temperature

SOFCs, Ceram. Int. 39 (2013) 2631–2637.

https://doi.org/10.1016/j.ceramint.2012.09.028.

[25]   A. Radojković, M. Žunić, S.M. Savić, G. Branković, Z. Branković, Chemical

stability and electrical properties of Nb doped $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ as a high temperature

proton conducting electrolyte for IT-SOFC, Ceram. Int. 39 (2013) 307–313.

https://doi.org/10.1016/j.ceramint.2012.06.026.

[26]   A. Radojković, M. Žunić, S.M. Savić, S. Perać, D.L. Golić, Z. Branković, G.

Branković, Co-doping as a strategy for tailoring the electrolyte properties of

$BaCe_{0.9}Y_{0.1}O_{3-\delta}$, Ceram. Int. 45 (2019) 8279–8285.

20

https://doi.org/10.1016/j.ceramint.2019.01.134.

[27] M. Amsif, D. Marrero-López, J.C. Ruiz-Morales, S.N. Savvin, P. Núñez, Effect of sintering aids on the conductivity of $BaCe_{0.9}Ln_{0.1}O_{3-\delta}$, J. Power Sources. 196 (2011) 9154–9163. https://doi.org/10.1016/j.jpowsour.2011.06.086.

[28] D. Marrero-López, J. Canales-Vázquez, J. Ruiz-Morales, A. Rodríguez, J. Irvine, P. Núñez, Synthesis, sinterability and ionic conductivity of nanocrystalline LaMoO powders, Solid State Ionics. 176 (2005) 1807–1816. https://doi.org/10.1016/j.ssi.2005.05.005.

[29] S. Hossain, A.M. Abdalla, N. Radenahmad, A.K.M. Zakaria, J.H. Zaini, S.M.H. Rahman, S.G. Eriksson, J.T.S. Irvine, A.K. Azad, Highly dense and chemically stable proton conducting electrolyte sintered at 1200 °C, Int. J. Hydrogen Energy. 43 (2018) 894–907. https://doi.org/10.1016/j.ijhydene.2017.11.111.

[30] M. Jebli, C. Rayssi, S. Bouzidi, J. Dhahri, M. Ben Henda, N. Zaidi, Effect of Nb substitution on the structural, dielectric and modulus character of $Ba_{0.97}La_{0.02}TiO_3$ ceramics, Inorg. Chem. Commun. 129 (2021) 108628. https://doi.org/10.1016/j.inoche.2021.108628.

[31] Y.-C. Jeong, B.-K. Kim, Y.-C. Kim, Proton migration in bulk orthorhombic barium cerate using density functional theory, Solid State Ionics. 259 (2014) 1–8. https://doi.org/10.1016/j.ssi.2014.02.010.

[32] F.W. Bezerra Lopes, M. Arab, H.P. Macedo, C.P. de Souza, J.F. de Souza, J.R.

Gavarri, High temperature conduction and methane conversion capability of $BaCeO_3$ perovskite, Powder Technol. 219 (2012) 186–192. https://doi.org/10.1016/j.powtec.2011.12.039.

[33]   T. Norby. N. Christiansen, Proton conduction in Ca- and Sr-substituted $LaPO_4$, Solid State Ionics. 77 (1995) 240–243. https://doi.org/10.1016/0167-2738(94)00274-V.

[34] A. Radojković, S.M. Savić, S. Pršić, Z. Branković, G. Branković, Improved electrical properties of Nb doped $BaCe_{0.9}Y_{0.1}O_{2.95}$ electrolyte for intermediate temperature SOFCs obtained by autocombustion method, J. Alloys Compd. 583 (2014) 278–284. http://dx.doi.org/10.1016/j.jallcom.2013.08.189.

[35]   M. Žunić, L. Chevallier, A. Radojković, G. Branković, Z. Branković, E. Di Bartolomeo, Influence of the ratio between Ni and $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ on microstructural and electrical properties of proton conducting Ni–$BaCe_{0.9}Y_{0.1}O_{3-\delta}$ anodes, J. Alloys Compd. 509 (2011) 1157–1162. https://doi.org/10.1016/j.jallcom.2010.09.144.

[36]   X. Meng, N. Yang, J. Song, X. Tan, Z.-F. Ma, K. Li, Synthesis and characterization of terbium doped barium cerates as a proton conducting SOFC electrolyte, Int. J. Hydrogen Energy. 36 (2011) 13067–13072. https://doi.org/10.1016/j.ijhydene.2011.07.075.

Figure 1. Schematic representation of the experimental setup used for humidity sensing analysis.

Figure 2. Le-Bail fitting profile of the powder diffraction pattern of BCI25 powders calcined at 1050 °C (a) and pulverized ceramics sintered at 1400 °C (b), BSE image (c) and grain size distribution of the BCI25 sample sintered at 1400 °C (d).

Figure 3. Impedance spectra of sintered samples of BCI25 at 300 °C and 325 °C in dry (a) and wet (b) Ar and 400 °C and 425 °C in dry (c) and wet (d) Ar.

Figure 4. Arrhenius plots for the BCI25 sample sintered at 1400 °C in wet and dry argon atmospheres in the 250 °C – 700 °C temperature range.

Figure 5. TG/DTA curves of the BCI25 paste (a), BSE image (b), and high-resolution SEM image (c) of the surface of the film produced from BCI25 powder calcined at 1050 °C.

Figure 6. Dependence of $|Z|_{dryAr}/|Z|_{wetAr}$ ratio on temperature with the dependence of impedance on frequency under wet and dry Ar (a) and response and recovery times and $|Z|_{dryAr}/|Z|_{wetAr}$ values of the porous film and sintered pellet at 500 °C (b).

Figure 7. Humidity response of porous film at 500 °C to wet Ar (a) and humidity response of porous film at 500 °C to gas mixtures with different partial pressures of water (b).

Figure 8. Logarithmic plot of the conductivity difference in wet and dry argon vs. water partial pressure.

Figure 1

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Figure 3

Figure 3

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Figure 7

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