Synthesis and Characterisation of Ceramic Proton Conducting Perovskite-type Multi-element -Doped Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO_{3- δ} (0 < x < 0.5; y = 0, 0.1, 0.15; z = 0.1, 0.2)

Kalpana Singh, Ramaiyan Kannan, and Venkataraman Thangadurai*

Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, AB, T2N 1N4, Canada. E-mail: <u>vthangad@ucalgary.ca</u>; Fax: +1 (403) 289 9488; Tel: +1 (403) 210 8649

Abstract

This study addresses the influence of A-and B-site co-doping on the chemical and electrical properties of perovskite-type Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO_{3- δ} (0 < x < 0.5; y = 0, 0.1, 0.15; z = 0.1, 0.2). The powders synthesised at 1450 °C through solid state (ceramic) reaction showed relative density greater than 94 % by Archimedes method, and is supported by dense microstructure by scanning electron microscopy images. The effect of doping electronegative elements on the A-and B-site on chemical stability is exemplified by dopant dependent chemical stability under CO₂ and water vapour. Thermogravimetric analysis (TGA) of the powdered samples under CO₂: N₂ (1:1) showed variation in weight gain with respect to doping element concentration in Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO_{3- δ}, revealing the improved chemical stability of Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3-δ} and Ba_{0.5}Sr_{0.5}Ce_{0.5}Zr_{0.3}Gd_{0.1}Y_{0.1}O_{3-δ}. Excellent chemical stability under water vapour at 90 °C for 24 h was observed for all the investigated compositions. However, extended exposure time of 168 h lead to the appearance of a small amount of Ba(OH)₂, as observed from powder X-ray diffraction patterns and TGA analysis after stability tests. The electrical conductivity measurements by ac impedance spectroscopy under dry and humid atmospheres revealed conductivity. the proton Among the samples investigated in this work. $Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3-\delta}$ (BSCZGY3) showed the highest conductivity of ~10⁻³ S/cm at 700 °C in air/3% H_2O and $H_2/3%$ H_2O .

Keywords: Perovskites; Proton conducting oxides; Chemical stability; Doping, Electronegativity; Impedance spectroscopy.

Introduction

Iwahara *et al.* demonstrated the existence of proton (H⁺) conductivity (~10⁻² S/cm) under humid conditions in the perovskite-type acceptor-doped ABO₃ (A = Sr, Ba; B = Ce, Zr) at 500-700 °C [1, 2]. BaCeO₃ and BaZrO₃ have been extensively studied as electrolytes for proton-conducting solid oxide fuel cells (H-SOFCs) owing to their high H⁺ conductivity [3]. However, BaCeO₃ decompose under water vapor and CO₂ conditions (Equation 1 and 2) [4-9]. BaCeO₃ is thermodynamically unstable under CO₂ atmosphere below ~ 1040 °C and under water vapour (P_{H2O} = 0:5 atm) below ~ 404 °C (equation 1) [7-9]. Also, Gd- and La-doped BaCeO₃ was found to be unstable in boiling water and humid air [10]. Wu and Liu showed that Gd-doped BaCeO₃ was stable at 600 and 700 °C for 1000 h under water vapour, whereas it decomposed at a much lower temperature of 85 °C (equation 2) [11]. As H-SOFCs will be subjected to many heating and cooling cycles during operation, low temperature instability in H₂O-containing atmospheres is a concern for BaCeO₃ based electrolytes.

$$BaCeO_3 + CO_2 \to BaCO_3 + CeO_2 \tag{1}$$

$$BaCeO_3 + H_2O \to Ba(OH)_2 + CeO_2 \tag{2}$$

On the other hand, BaZrO₃ exhibit excellent chemical stability under CO₂ and humidity but lower H⁺ conductivity compared to BaCeO₃ [3, 12-14]. Though, Gibbs free energy of formation of BaZrO₃ is higher than Gibbs free energy of formation of carbonate between 600-800 K, it might be kinetically slow to cause major instability [15-17]. In order to obtain dense ceramic, high temperature (>1500 °C) and prolonged sintering times are needed, which lead to high grain boundary resistance in BaZrO₃ system [18, 19]. Higher electronegativity of Zr makes BaZrO₃ more stable in CO₂ and H₂Ocontaining atmospheres than BaCeO₃ [3]. Thus, a solid solution of BaCeO₃ and BaZrO₃ has been investigated in order to achieve good H⁺ conductivity and chemical stability under CO₂ and humidity [20-28]. Fabbri *et al.* exposed Zr-doped BaCe_{0.8-x}Zr_xY_{0.2}O_{3- δ} (0.0 \leq x \leq 0.8) to 100 % CO₂ at 900 °C for 3 h, and observed that the sample with x = 0.5 showed good chemical stability and good H⁺ conductivity [25]. Ryu and Haile found that Zr-doped BaCe_{0.7}Zr_{0.1}Nd_{0.1}O₃ and BaCe_{0.5}Zr_{0.4}Gd_{0.1}O₃ compromise chemical stability under CO₂ against their H⁺ conductivity [21].

Taniguchi et al. subjected BaCe_{0.2}Zr_{0.6}Gd_{0.2}O_{3-δ} to boiling water for 200 h and found it to be stable by monitoring variation in pH of surrounding water [28]. They also investigated the influence of moisture on the surface of BaCe_{0.4}Zr_{0.4}In_{0.2}O_{3- δ} by exposure to 85% relative humidity for 4000 h at 85 °C and found no deposits on its surface through SEM [28]. Though these reports have shown improved chemical stability for Zr-doped BaCeO₃; few reports have also shown that stability is still an issue for a lower doping level of Zr. For example, Ba_{0.98}Ce_{0.6}Zr_{0.2}Y_{0.2}O_{3-δ} (BCZY) decomposed to BaCO₃, Ba(OH)₂ and Ce0:75Zr0:25O2 after exposing to humid air for 24 h at 200 °C and soaking in boiling water for 3 h [29]. 10 mol % Zr-doped BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-δ} formed BaCO₃ under CO₂ as seen through a weight gain of 7.7 % in TGA [30]. Also, the addition of Zr requires high sintering temperature of ~1550 °C, although wet-chemistry preparation routes and sintering aids can help in overcoming this problem [24, 31]. In addition, Zr-doping in BaCeO₃ lead to increase in activation energy for H⁺ transport [13, 21, 27, 32]. Literature studies have suggested that with increasing electronegativity of B-site elements in perovskites, the chemical stability increases in the following order: cerate \rightarrow zirconate \rightarrow stannate \rightarrow niobate \rightarrow titanate [3]. It has also been reported that smaller the difference between the electronegativity of B-site and A-site cations, larger is the stability of protonic defects [33]. Thermodynamically, SrCeO₃ is more stable towards CO₂ than BaCeO₃ and Sr- doping on the A-site has shown to improve the chemical stability of BaCeO₃ under water [34, 35].

Based on ionic radius and electronegativity, Zr, Y, and Gd seem to be ideal dopants for the Cesites in BaCeO₃ (Table 1). Additionally, computational studies by Glöckner and Islam showed that Y and Gd both had the "lowest solution energy" for doping on the Ce-site [37]. Also, Sr doping on the Basite was explored in order to improve chemical stability under water at low temperature [38]. Recently, we have shown that Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Y_{0.1}Gd_{0.1}O₃₋₆ exhibited good chemical stability under water vapour and CO₂ conditions [38, 39]. However, the role of dopants and their concentrations were not fully understood with relation to chemical stability and conductivity. Thus, the principle objective of this work is to study systematically the influence of dopants and their concentrations on the chemical stability of doped-BaCeO₃ under H₂O (specifically at low temperature) and CO₂-containing atmospheres and on ionic conductivity. Co-doping approach on both A-and B-sites in particular with higher electronegative dopants was explored. As both the chemical stability and conductivity is affected by dopants and their concentrations, several compositions of the chemical formula Ba_{0.5}Sr_{0.5}Ce_{1-x-y-} $_zZr_xGd_yY_zO_{3-\delta}$ (x = 0 < x < 0.5; y = 0.1, 0.2, z = 0, 0.1, 0.15) were prepared and investigated for their chemical stability and electrical properties using state-of-the-art solid state experimental methods.

Experimental methods

Synthesis

Perovskites of the nominal compositions $Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO_{3-\delta}$ (0 < x < 0.5; y = 0, 0.1, 0.15; z = 0.1, 0.2) were prepared by solid state (ceramic) method in an ambient atmosphere at elevated temperature. Starting materials barium carbonate, strontium carbonate, cerium oxide, zirconium oxide, gadolinium oxide and yttrium oxide (99.9%, Alfa Aesar) were mixed in stoichiometric amounts, and ball milled at 200 rpm for 6 h using iso-propanol as a solvent. After milling, the iso-propanol was evaporated in an oven and then the mixture was heated for 24 h at 1050 °C. After cooling, dried powder was ball milled again for 6 h. After milling and drying for the second time, the powder was pressed into pellets (~2 cm x 1 cm) by using an isotactic press for 3 minutes at a pressure of 200 MPa. The pellets were covered with parent powder in order to suppress potential Ba evaporation and then subjected to

final sintering at 1450 °C for 24 h in an ambient atmosphere. The process of final sintering at 1450 °C was repeated to get single-phase perovskite-type structure.

Characterization techniques

After sintering at 1450 °C, the pellet was crushed, and the powder was subjected for phase characterisation at room temperature using powder X-ray diffractometer (PXRD) (Bruker D8 with Cu K α radiation) with a 0.01° step size and a counting time of 3s per step from 10° to 120°. Lattice constants (*a*) were obtained through the WinCSD software [40]. The relative density (equation 3) of assistered pellets (~1 cm diameter, ~2 mm thickness) was determined by Archimedes method and then compared with theoretical density (equation 4) based on lattice constant and crystal parameters obtained from PXRD analysis.

$$\rho_{rel} = \frac{\rho_{solv} \times M}{M_1 - M_2} \tag{3}$$

where ρ_{solv} is the density of water, M is the dry weight of pellet in the air; M₁ is the saturated weight of pellet after removal of excess water from the surface and M₂ is the suspended weight of pellet in the water after immersion in the boiling water.

$$\rho_{theor} = \frac{ZM}{V \times N_A} \tag{4}$$

where Z is the number of atoms per unit cell, M is the molar mass; V is the unit cell volume ($Å^3$), and N_A is the Avogadro's constant.

TGA at the heating and cooling rate of 10 $^{\circ}$ C min⁻¹ was performed on powders after chemical stability tests using Mettler Toledo TGA/DSC/HT1600. *In-situ* TGA was also performed under flowing CO₂/N₂ (1:1) gas mixture. Ex-situ chemical stability under water vapour was conducted by hanging

powdered samples at 90 °C for 24 h and 168 h. *Ex-situ* chemical stability under CO_2 was performed by flowing pure CO_2 at 800 °C for 24 h over powder kept inside the quartz tube.

For electrical conductivity measurements, pellets were cut into smaller disks of ~1cm in diameter and 0.2 cm in thickness and brushed painted by Pt paste (current collector) on both sides and cured at 800 °C for 2 h. Electrical conductivity measurements were performed in the temperature range of 300– 750 °C in air, air/3% H₂O, N₂/3% H₂O, N₂/3% D₂O and H₂/3% H₂O, using an AC impedance analyzer (Solartron SI 1260) over the 10⁻¹ to 10⁶ Hz frequency range and with an applied voltage of 100 mV. In order to confirm that H⁺ are major charge carriers in humid conditions, electrical measurements were performed under D₂O and H₂O by flowing N₂ through H₂O/D₂O at room temperature. 3% H₂O condition was achieved by bubbling the carrier gas through water at 25 °C. Before conductivity measurement at different temperatures, samples were kept at a temperature of measurement for at least 45 minutes to several hours to attain thermal stability. Zview® modeling software (Scribner Associates, Inc.) was used to analyze the AC impedance spectra.

Results and discussion

Phase and morphology analysis of calcined powders and pellets

Fig. 1(a) shows the PXRD patterns of $Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO_{3-\delta}$ (0 < x < 0.5; y = 0, 0.1, 0.15; z = 0.1, 0.2) ($Ba_{0.5}Sr_{0.5}Ce_{0.8}Gd_{0.1}Y_{0.1}O_{3-\delta}$ (BSCGY 1); $Ba_{0.5}Sr_{0.5}Ce_{0.7}Zr_{0.1}Gd_{0.1}Y_{0.1}O_{3-\delta}$ (BSCZGY2); $Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3-\delta}$ (BSCZGY3); $Ba_{0.5}Sr_{0.5}Ce_{0.5}Zr_{0.3}Gd_{0.1}Y_{0.1}O_{3-\delta}$ (BSCZGY4); $Ba_{0.5}Sr_{0.5}Ce_{0.35}Zr_{0.4}Gd_{0.15}Y_{0.1}O_{3-\delta}$ (BSCZGY5); $Ba_{0.5}Sr_{0.5}Ce_{0.4}Zr_{0.4}Gd_{0.1}Y_{0.1}O_{3-\delta}$ (BSCZGY6); $Ba_{0.5}Sr_{0.5}Ce_{0.7}Zr_{0.1}Y_{0.2}O_{3-\delta}$ (BSCZY7) and $Ba_{0.5}Sr_{0.5}Ce_{0.5}Zr_{0.5}O_{3-\delta}$ (BSCZ8)) samples prepared at 1450 °C in air for 24 h. Single-phase perovskite was obtained for all compositions, except for BSCZGY6 and BSCZGY8. PXRD patterns of BSCGY1 and BSCZY7 showed splitting of peaks and were indexed in the *Pnma* space group for an orthorhombic crystal system. BSCGY1 and BSCZY7 show additional diffraction peak at $2\theta = 34.4^{\circ}$ (*hkl* = 112) corresponding to orthorhombic phase (Figure 1(b)). Rest of the investigated perovskite compositions were indexed on a cubic space group *Pm3m* (BSCZGY2-BSCZGY6 and BSCZ8). For the BSCZGY6, additional peaks for secondary phases were observed at $2\theta = 28.8^{\circ}$, 30.9° , 31.9° and 33.4° corresponding to ZrO₂ (inorganic crystal structure database (ICSD) # 89426), Ba(OH)₂ (Alfa Aesar commercial powder), and doped CeO₂ (powder diffraction file (PDF) # 000500204), respectively. BSCZGY8 showed highly intense peaks corresponding to secondary phases of ZrO₂ (ICSD # 89426), doped CeO₂ (PDF # 000500204), and BaCO₃ (PDF # 000410373) along with diffraction peaks for cubic perovskite phase. The presence of secondary phases in BSCZGY6 and BSCZGY8 indicates the need for high sintering temperature for a high doping level of Zr in Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO₃₋₈ [21, 41, 42].

Fig. 1(b) shows that diffraction peaks have been shifted to higher 20 angles for all the BSCZGY phases compared to un-doped BaCeO₃. As the Zr content increased from 10 to 40 mol% (BSCZGY2 to BSCZGY6), the diffraction peaks shifted to higher angles, indicating substitution of smaller Zr⁴⁺ (0.72 Å) into Ce⁴⁺ (0.87 Å) sites [36]. The lattice constant was found to decrease with the increase in Zr content from BSCZGY2 to BSCZGY6 (Table 2). The presence of secondary phase of ZrO₂ (ICSD # 89426) in BSCZGY6 indicates that not all Zr substituted Ce-sites, which anticipated to the higher value of lattice constant of 4.273 Å than BSCZGY5 (4.236 Å). The same trend was also seen in the average ionic radii of B-sites, which decreased from BSCZGY1 to BSCZGY 8 (Table 2). Even though tolerance factor for BSCGY1 and BSCZY7 is 0.91 and 0.95, the reason for orthorhombic distortion in these cases is not yet clear. For comparison, Table 2 also shows the pseudo-cubic lattice (*a*₀) constant values for the orthorhombic BSCGY1 (4.404 Å) and BSCZY7 (4.398 Å) phases. The *a*₀ was calculated using the equation: $\sqrt[3]{0.25abc}$ (where *a*, *b* and *c* represent orthorhombic cell constant) [43]. The higher *a*₀ in

BSCGY1 is expected due to doping of larger size Y^{3+} and Gd^{3+} on the Ce^{4+} site ($Y^{3+} = 0.9$ Å, $Gd^{3+} = 0.938$ Å) [36]. Fig. 2 shows the variation of lattice constant and tolerance factor, as a function of the average ionic radius of B-site cations in single-phase $Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO_{3-\delta}$. As expected, the increase in average ionic radius leads to increase in lattice constant and a decrease in tolerance factor.

Densities $\geq 94\%$ were obtained for all single-phase Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO_{3-δ} compositions from Archimedes method. The density was found to decrease with increasing Zr content in Ba_{0.5}Sr_{0.5}Ce_{1x-y-z}Zr_xGd_yY_zO_{3-δ}. BaZr_{0.85}Y_{0.15}O_{3-δ} prepared by ceramic method showed relative density in the range of 75–80% [21]. Fig. 3 shows typical SEM micrographs of polished pellet surfaces after final sintering and reveals the dense nature of the investigated perovskites. The average grain-size decreased with increasing Zr content. The smaller grain-size in high Zr content samples is consistent with the refractory nature of Zr samples, as they have slower grain growths.

Chemical stability of $Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO_{3-\delta}$ powders towards CO_2 and H_2O -containing atmospheres

Achieving chemical stability under water vapour at low temperatures (< 400 °C) is critical for proton conducting doped-BaCeO₃ [10, 44] and thus, the chemical stability of investigated perovskites under high water content (69%) was performed at 90 °C for 24 h and 168 h. PXRD of water treated samples show mainly peaks due to perovskite-type phase and no additional peak for Ba(OH)₂ impurity (Fig. 4(a)). However, extending the treatment time to 168 h showed small diffraction peaks for Ba(OH)₂ (Alfa Aesar commercial powder) and ZrO₂ (ICSD # 89426) (Fig. 4(b)). As opposed to water vapour stability, the CO₂ stability of these compositions varies with compositional change and exhibit lower chemical stability. Fig. 5 reveals that BSCZGY3, BSCZGY4, and BSCZGY5 have better chemical stability under CO₂ than other compositions. In BSCZGY6, the intensity for secondary phase ZrO₂ (ICSD # 89426) and doped CeO₂ (PDF # 000500204) increased, and the additional peak of BaCO₃ (PDF # 000410373) appeared after CO₂ exposure. BSCGY1, BSCZGY2, and BSCZY7 were decomposed completely, suggesting that Zr substitution is critical to improve the chemical stability of the doped BaCeO₃ under CO₂ and water vapour atmospheres at elevated temperature.

TGA curves obtained after water vapour exposure for 24 h and 168 h are shown in Figs. 6(a) and (b), respectively. As the water vapour exposure period was extended to 168 h, there was an increase in weight loss for all the investigated compositions. Among the BSCZGY samples studied, BSCZY7 showed the maximum weight loss (~1.4 wt. %) for 24 h and BSCZGY5 (~3.5 wt. %) for 168 h. Weight loss in TGA curves can be attributed to formation of Ba(OH)₂ (equation 2), incorporation of water molecules in the oxide ion vacancies in Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO_{3-δ} (equation 5), and excess water adsorbed at grain-boundaries and or surfaces [38]. For the second case, one mole of acceptor dopant (M³⁺) leads to the formation of 0.5 moles of oxygen vacancies, thus, in theory, ~0.6 and 0.8% weight loss should be observed for 20 and 25 mol% doped Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO_{3-δ}, assuming that water has filled all oxide ion vacancies in the structure.

Tanner *et.al* [45] and Bhide *et.al* [10] have shown that the decomposition of doped-BaCeO₃ under water vapour conditions occur in two steps, and shows bulk-type decomposition mechanism. The first step is water dissolution into the oxygen lattice (O_o^x) (which requires oxide ion vacancy $(V_o^{\bullet\bullet})$, equation 5), and the second step is decomposition reaction (equation 2) [10, 45].

$$H_{2}O(g) + V_{0}^{\bullet\bullet} + O_{0}^{x} \leftrightarrow 2OH_{0}^{\bullet}$$
(5)

Since oxide ion vacancy is higher in the case of BSCZGY5, the decomposition is expected to be higher after exposure to water vapour for 168 h. Thus, 25 mol % doping in BSCZGY5 leads to greater weight loss for 168 h exposure to water vapour, as seen in Fig. 6(b). The improved stability under water vapor conditions due to Sr-doping is seen compared to previous studies on $BaCe_{0.84}Zr_{0.01}Sm_{0.15}O_{3-\delta}$ and

BaCe_{0.8-x}Zr_xGd_{0.15}Pr_{0.05}O_{3- δ} (x = 0.01, 0.05, 0.1, 0.2 and 0.3) [46, 47]. BaCe_{0.84}Zr_{0.01}Sm_{0.15}O_{3- δ} and BaCe_{0.8-x}Zr_xGd_{0.15}Pr_{0.05}O_{3- δ} showed a weight loss >8% and >10 %, respectively in TGA analysis due to the formation of Ba(OH)₂ under similar conditions, and showed the presence of CeO₂ in PXRD patterns [46, 47].

Fig. 6(c) shows the TG curves under CO_2/N_2 (1:1) for all $Ba_{0.5}Sr_{0.5}Ce_{1-x-v-z}Zr_xGd_vY_zO_{3-\delta}$ compositions. The initial weight loss can be attributed to sample dehydration and gradual weight gain above 400 °C, and 600 °C indicates the formation of BaCO₃. BSCZGY6 did not show any weight gain owing to high Zr content (0.4) (higher covalency of Zr-O bond compared to Ce-O bond) and found to chemically stable under CO₂. Moreover, the decomposition reaction temperature increased with increasing Zr in Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO_{3-δ}. Though BSCZGY6 and BSCZGY5 have same Zr content, BSCZGY5 showed small weight gain (0.4 wt. %) might be due to the presence of more Gd [18]. Among the samples investigated, the high weight gain was observed for BSCZGY1, BSCZGY2, and BSCZY7 (Fig. 6(c)), however, literature studies have shown weight increase of up to 7.5 wt. % for un-doped BaCeO₃ [48]. In addition, Zr doping of x = 0.5 was needed to achieve considerable chemical stability and $x \ge 0.8$ was needed to achieve complete stability under CO₂ [12, 20, 49]. Fig. 6(d) shows the percentage conversion to BaCO₃ as a function of Zr content in Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO_{3-δ} and confirms the positive influence of Zr- doping in suppressing BaCO₃ formation. These results show that adding more electronegative elements seems to help in improving chemical stability under CO₂. It is also worth to mention that the chemical stability of sintered pellets will be greater than powder samples as CO₂ reacts with perovskite phase at solid/gas interface and cannot dissolve in the perovskite lattice [50].

Electrical conductivity of $Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO_{3-\delta}$

Typical Nyquist plots of Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO_{3-δ} (0 < x < 0.5; y = 0, 0.1, 0.15; z = 0.1, 0.2) obtained in air, air/3% H₂O, N₂/3% H₂O, N₂/3% D₂O and H₂/3% H₂O at 600 °C are shown in Fig. 7. At low temperatures, semicircles due to bulk, grain-boundary and electrode contributions (electrode– electrolyte interface phenomena) were observed, while contribution due to grain-boundary disappeared at high temperatures (>600 °C). For all the investigated compositions, the lowest resistance was seen under H₂/3% H₂O and the highest resistance under N₂/3% D₂O (Fig. 8). Also, samples showed slightly lower resistance in air/3% H₂O compared to dry air. Variation of total (bulk + grain-boundary + electrode) conductivity as a function of temperature for all compositions under different atmospheres is shown in Figs. 8(a)-(f). Significantly higher conductivity and lower activation energy values under H₂/3% H₂O confirms potential H⁺ conducting nature in all compositions (Fig.8 and Table 3). Also, the reduction in total conductivity and increased activation energy under N₂/3% D₂O shows the isotope effect, which supports the above statement. These results indicate the contribution of H⁺ towards conductivity under humid conditions and it can be described using the defect equilibrium reaction (equations 5 and 6) [3]:

$$H_2(\mathbf{g}) + 2h^{\bullet} + 2O_0^x \leftrightarrow 2OH_0^{\bullet} \tag{6}$$

The H⁺ transport mechanism in acceptor-doped perovskites can be explained by Grotthuss mechanism, as proposed by Kreuer [3]. Grotthuss mechanism involves the rotational diffusion of the protonic defect (hydroxyl group, OH_0^{\bullet}) around oxygen, and then the transfer/jump of proton (H⁺) between nearest lattice oxygen. Figure 8 (e) shows the Arrhenius plot under H₂/3% H₂O for all compositions and reveals slightly higher conductivity for BSCZGY3 [38] and BSCZGY5. The low total conductivity of Ba_{0.5}Sr_{0.5}Ce_{0.5}Zr_{0.3} Gd_{0.1}Y_{0.1}O_{3- $\delta}$} (BSCZGY4) is due to high Zr content, which leads to a low rate of grain growth in the ceramics, and hence high grain-boundary resistance [12, 21, 32, 51].

Ba_{0.5}Sr_{0.5}Ce_{0.4}Zr_{0.4}Gd_{0.1}Y_{0.1}O_{3- δ} (BSCZGY6) exhibits the lowest conductivity due to high Zr content and secondary phases, which can segregate along the grain-boundaries and thus lead to increase in grain-boundary resistance. SEM measurements show that with increase in Zr content, the grain size decreases and leads to large grain-boundary resistance, and hence lower electrical conductivity [12, 21, 32, 51] The activation energy in the wet air was slightly larger than in wet N₂ (Table 3). On comparing total conductivity (bulk + grain-boundary) values of BSCZGY3 and BSCZGY5 in wet H₂ with the literature studies (Figure 8 (f)), the significant lower conductivity of current compositions is quite evident. However, it is worth to mention that the samples in literature studies were prepared by sol-gel, citrate-nitrate, and solid state reacting sintering methods, which lead to large-grained ceramics [12, 52-55]. For example, Yamazaki et al. [52] prepared BaZr_{0.8}Y_{0.2}O_{3- δ} (BZY20) employed the sol-gel method and reactive sintering method in order to achieve large-grained (~1 µm) ceramic which ultimately lead to high conductivity (~1 x 10⁻² Scm⁻¹ at 450 °C). In addition, BaCe_{0.5}Zr_{0.3}Y_{0.2}O_{3- δ} decomposed under CO₂ condition within 3h at 900 °C into BaCO₃ and CeO₂ [9]. The lower conductivity of current samples can be improved if synthesised through soft chemistry route and solid state reactive sintering methods.

Conclusions

Solid solution Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO_{3- δ} (0 < x < 0.5; y = 0, 0.1, 0.15; z = 0.1, 0.2) was studied in order to find an optimal composition with good chemical stability and high ionic (proton) conductivity for SOFCs. Single-phase, perovskite-type oxides were obtained through solid state synthesis route after final sintering at 1450 °C. The lattice constants decreased with increase in Zr content in Ba_{0.5}Sr_{0.5}Ce_{1-x-y-} _zZr_xGd_yY_zO_{3- δ} due to its smaller Zr⁴⁺ ionic radii than Ce⁴⁺. Relative densities of ≥94% were obtained for all prepared compositions. The purpose of achieving better chemical stability against water vapour through co-doping more electronegative dopants into the A-and B-site of BaCeO₃ structure at low temperature (90 °C) was successful for 24 h period of the test. With the increase in Zr-doping level at the B-site, the chemical stability against CO₂ increased, however it was accompanied by decrease in proton conductivity, where BSCZGY6 showed the lowest electrical conductivity. Though Zr-doping enhanced the chemical stability towards CO₂ to some extent; it was not able to stop decomposition reaction entirely. The proton conducting nature of compositions was seen through increased conductivity in humid atmospheres (air/3% H₂O, N₂/3% H₂O, and H₂/3% H₂O). Among the samples studied in this work, Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3-δ} (BSCZGY3) seems to be the optimal composition with lower weight gain under CO₂, and highest conductivity (0.003 S/cm, 700 °C) under H₂/3% H₂O.

Acknowledgements

This work was supported by the Natural Science and Engineering Research Council of Canada (NSERC)'s Discovery Grants program. The authors are again grateful to NSERC for providing funding through the Research Tools and Instruments and Infrastructure grants (RTI) program.

References

- Iwahara H, Esaka T, Uchida H, Maeda N. Proton conduction in sintered oxides and its application to steam electrolysis for hydrogen production. Solid State Ionics 1981; 3 /4:359-363.
- Iwahara H, Uchida H, Ono K, Ogaki K. Proton conduction in sintered oxides based on BaCeO₃. J. Electrochem. Soc. 1988; 135 (2):529-533.
- 3) Kreuer KD. Proton-conducting oxides. Annu. Rev. Mater. Res. 2003; 33:333-359.
- Bhella SS, Fürstenhaupt T, Paul R, Thangadurai V. Synthesis, structure, chemical stability, and electrical properties of Nb-, Zr-, and Nb-co-doped BaCeO₃ perovskites. Inorg. Chem. 2010; 50:6493-6499.

- 5) Sneha BR, Thangadurai V. Synthesis of nano-sized crystalline oxide ion conducting fluorite-type Y₂O₃-doped CeO₂ using perovskite-like BaCe_{0.9}Y_{0.1}O_{2.95} (BCY) and study of CO₂ capture properties of BCY. J. Solid State Chem. 2007; **180**:2661-2669.
- Trobec F, Thangadurai V. Transformation of proton-conducting perovskite-type into fluorite-type fast oxide ion electrolytes using a CO₂ capture technique and their electrical properties. Inorg. Chem. 2008; 47:8972-8984.
- Gopalan S, Virkar AV. Thermodynamic stabilities of SrCeO₃ and BaCeO₃ using a molten salt method and galvanic cells. J. Electrochem. Soc. 1993; 140 (4):1060-1065.
- Scholten MJ, Schoonman J. Synthesis of strontium and barium cerate and their reaction with carbon dioxide. Solid State Ionics 1993; 61:83-91.
- Bonanos N, Knight KS, Ellis B. Perovskite solid electrolytes: Structure, transport properties and fuel cell applications. Solid State Ionics 1995; 79:161-170.
- Bhide SV, Virkar AV. Stability of BaCeO₃-based proton conductors in water-containing atmospheres. J. Electrochem. Soc. 1999; 146 (6):2038-2044.
- Wu Z, Liu M. Stability of BaCe_{0.8}Gd_{0.2}O₃ in a H₂O -containing atmosphere at intermediate temperatures. J. Electrochem. Soc. 1997; **144 (6)**:2170-2175.
- 12) Fabbri E, D'Epifanio A, Di Bartolomeo E, Licoccia S, Traversa E. Tailoring the chemical stability of Ba(Ce_{0.8-x}Zr_x)Y_{0.2}O_{3-δ} protonic conductors for intermediate temperature solid oxide fuel cells (IT-SOFCs). Solid State Ionics 2008; **179**:558–564.
- K. Katahira K, Y. Kohchi Y, T. Shimura T, Iwahara H. Protonic conduction in Zr-substituted BaCeO₃. Solid State Ionics 2000; **138**:91–98.
- Snijkers FMM, Buekenhoudt A, Cooymans J, Luyten JJ. Proton conductivity and phase composition in BaZr_{0.9}Y_{0.1}O_{3-δ}. Scr. Mater. 2004; **50**:655–659.

- Uda T, Babilo P, Haile SM. Thermodynamic analysis and conductivity of yttrium doped barium zirconate. 207th ECS Meeting Abstract, 2005 Quebec City, Canada.
- Jacob KT, Waseda Y. Potentiometric determination of the Gibbs energies of formation of SrZrO₃ and BaZrO₃. Metall Mater Trans B 1995; 26B:775-781.
- Cordfunke EHP, Booij AS, Huntelaar ME. The thermochemical properties of BaCeO₃(s) and SrCeO₃(s) from T= (5 to 1500) K. J. Chem. Thermodynamics 1998; **30**:437-447.
- 18) Iguchi F, Sata N, Tsurui T, Yugami H. Microstructures and grain boundary conductivity of BaZr₁. $_xY_xO_3$ (x = 0.05, 0.10, 0.15) ceramics. Solid State Ionics 2007; **178**:691–695.
- Iguchi F, Yamada T, Sata N, Tsurui T, Yugami H. The influence of grain structures on the electrical conductivity of a BaZr_{0.95}Y_{0.05}O₃ proton conductor. Solid State Ionics 2006; 177:2381–2384.
- 20) Zuo BC, Zha S, Liu M, Hatano M, Uchiyama M. Ba $(Zr_{0.1}Ce_{0.7}Y_{0.2})O_{3-\delta}$ as an electrolyte for low-temperature solid-oxide fuel cells. Adv. Mater. 2006; **18**:3318–3320.
- Ryu KH, Haile SM. Ba(Zr_{0.1}Ce_{0.7}Y_{0.2})O_{3-δ} as an electrolyte for low-temperature solid-oxide fuel cells. Solid State Ionics 1999; **125**:355–367.
- 22) Sawant P, Varma S, Wani BN, Bharadwaj SR. Synthesis, stability and conductivity of BaCe_{0.8-} _xZr_xY_{0.2}O_{3-δ} as electrolyte for proton conducting SOFC. Int. J. Hydrogen Energy 2012; 37:3848– 3856.
- 23) Zuo C, Dorris SE, Balachandran U, Liu M. Effect of Zr-doping on the chemical stability and hydrogen permeation of the Ni–BaCe_{0.8}Y_{0.2}O_{3-δ} mixed protonic–electronic conductor. Chem. Mater. 2006; 18:4647-4650.
- 24) Barison S, Battagliarin M, Cavallin T, Doubova L, Fabrizio M, Mortalò C, Boldrini S, Malavasic L, Gerbas R. High conductivity and chemical stability of BaCe_{1-x-y}Zr_xYyO_{3-δ} proton conductors prepared by a sol–gel method. J. Mater. Chem. 2008; 18:5120-5128.

- 25) Fabbri E, D'Epifanio A, Di Bartolomeo E, Licoccia S, Traversa E. Tailoring the chemical stability of Ba(Ce_{0.8-x}Zr_x)Y_{0.2}O_{3-δ} protonic conductors for intermediate temperature solid oxide fuel cells (IT-SOFCs). Solid State Ionics 2008; **179**:558–564.
- 26) Chien RR, Tu CS, Schmidt VH, Lee SC, Huang CC. Synthesis and characterization of protonconducting Ba(Zr_{0.8-x}Ce_xY_{0.2})O_{2.9} ceramics. Solid State Ionics 2010; **181**:1251-1257.
- Zhong ZM. Stability and conductivity study of the BaCe_{0.9-x}Zr_xY_{0.1}O_{2.95} systems. Solid State Ionics 2007; **178**:213–220.
- Taniguchi N, Nishimura C, Kato J. Endurance against moisture for protonic conductors of perovskite-type ceramics and preparation of practical conductors. Solid State Ionics 2001; 145:349– 355.
- 29) Yoo Y, Lim N. Performance and stability of proton conducting solid oxide fuel cells based on yttrium-doped barium cerate-zirconate thin-film electrolyte. J. Power Sources 2013; **229**:48-57.
- 30) Fabbri E, Bi L, Tanaka H, Pergolesi D, Traversa E. Chemically stable Pr and Y co-doped barium zirconate electrolytes with high proton conductivity for intermediate-temperature solid oxide fuel cells. Adv. Funct. Mater. 2011; 21:158-166.
- 31) Guo Y, Ran R, Shao Z. Optimizing the modification method of zinc-enhanced sintering of BaZr_{0.4}Ce_{0.4}Y_{0.2}O_{3-δ}-based electrolytes for application in an anode-supported protonic solid oxide fuel cell. Int. J. Hydrogen Energy 2010; **35**:5611–5620.
- 32) Haile SM, Staneff G, Ryu KH. Non-stoichiometry, grain boundary transport and chemical stability of proton conducting perovskites. J. Mater. Sci. 2001; **36**:1149-1160.
- 33) Norby T, Widerøe M, Glöckner R, Larring Y. Hydrogen in oxides. Dalton Trans. 2004; 19:3012– 3018.

- 34) Lu J, Wang L, Fan L, Li Y, Dai L, Guo H. Chemical stability of doped BaCeO₃-BaZrO₃ solid solutions in different atmospheres. J. Rare Earth 2008; 26:505-510.
- 35) Hung IM, Peng HW, Zheng SL, Lin CP, Wu JS. Phase stability and conductivity of Ba_{1-y}Sr_yCe_{1-x}Y_xO_{3-δ} solid oxide fuel cell electrolyte. J. Power Sources 2009; **193**:155–159.
- 36) Shannon RD. Revised effective ionic radii and systematic studies of interatomic distances in halides and chaleogenides. Acta. Cryst. 1976; A32:751-767.
- Glöckner R, Islam MS, Norby T. Protons and other defects in BaCeO₃: a computational study. Solid State Ionics 1999; **122**:145–156.
- 38) Kannan R, Singh K, Gill S, Fürstenhaupt T, Thangadurai V. Chemically stable proton conducting doped BaCeO₃ -no more fear to SOFC wastes. Sci. Reports 2013; 3:2138.
- 39) Singh K, Baral AK, Thangadurai V. Grain boundary space charge effect and proton dynamics in chemically stable perovskite-type Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3-δ} (BSCZGY): a case study on effect of sintering temperature. J. Am Ceram. Soc. 2016; **99**:866-875.
- 40) Akselrud L, Grin Yu. WinCSD: software package for crystallographic calculations (Version 4). J. Appl. Crystallogr. 2014; 47.
- 41) Azad AK, Irvine JTS. Synthesis, chemical stability and proton conductivity of the perovksites Ba(Ce, Zr)_{1-x}Sc_xO_{3-δ}. Solid State Ionics 2007; **178**:635–640.
- Ricotea S, Bonanos N. Caboche G. Water vapour solubility and conductivity study of the proton conductor BaCe_{0.9-x}Zr_xY_{0.1}O_{3-δ}. Solid State Ionics 2009; **180**:990–997.
- 43) Ubic R. Revised method for the prediction of lattice constants in cubic and pseudocubic perovskites.J. Am. Ceram. Soc. 2007; **90** [10]:3326–3330.

- 44) Matsumoto H, Kawasaki Y, Ito N, Enoki M, Ishihara T. Relation between electrical conductivity and chemical stability of BaCeO₃-based proton conductors with different trivalent dopants. Electrochem. Solid-State Lett. 2007; 10:B77–B80.
- 45) Tanner CW, Virkar AV. Instability of BoCeO₃ in H₂O-containing atmospheres. J. Electrochem.
 Soc. 1996; 143:1386-1389.
- 46) Kannan R, Gill S, Maffei N, Thangadurai V. BaCe_{0.85-x}Zr_xSm_{0.15}O_{3-δ} (0.01 < x < 0.3) (BCZS): Effect of Zr content in BCZS on chemical stability in CO₂ and H₂O vapour, and proton conductivity. J. Electrochem. Soc. 2013; 160:F18–F26.
- 47) Gill S, Kannan R, Maffei N, Thangadurai V. Effect of Zr substitution for Ce in BaCe_{0.8}Gd_{0.15}Pr_{0.05}O_{3-δ} on the chemical stability in CO₂ and water, and electrical conductivity. RSC Adv. 2013; **3**:3599–3605.
- 48) Babilo P, Haile SM. Enhanced sintering of yttrium-doped barium zirconate by addition of ZnO. J.Am. Ceram. Soc. 2005; 88 [9]:2362–2368.
- 49) Yang L, Wang S, Blinn K, Liu M, Liu Z, Cheng Z, Liu M. Enhanced sulfur and coking tolerance of a mixed ion conductor for SOFCs: BaZr_{0.1}Ce_{0.7}Y_{0.2-x}Yb_xO3-δ. Science 2009; **326**:126–129
- 50) Chen F, Sørensen OT, Meng G, Peng D. Chemical stability study of BaCe_{0.9}Nd_{0.1}O_{3-δ} high-temperature proton-conducting ceramic. J. Mater. Chem. 1997; **7(3)**: 481-485.
- Babilo P, Uda T, Haile SM. Processing of yttrium-doped barium zirconate for high proton conductivity. J. Mater. Res. 2007; 22:1322-1330.
- Yamazaki Y, Sanchez RH, Haile SM. High total proton conductivity in large-grained yttrium-doped barium zirconate. Chem. Mater. 2009; 21:2755–2762.

- 53) Shi Z, Sun W, Wang Z, Qian J, Liu W. Samarium and yttrium co-doped BaCeO₃ proton conductor with improved sinterability and higher electrical conductivity. ACS Appl. Mater. Interfaces 2014;
 6:5175–5182.
- 54) Yang L, Zuo C, Liu M. High-performance anode-supported solid oxide fuel cells based on Ba(Zr_{0.1}Ce_{0.7}Y_{0.2})O_{3-δ} (BZCY) fabricated by a modified co-pressing process. J. Power Sources 2010; **195**:1845–1848.
- 55) Suksamai W, Metcalfe IS. Measurement of proton and oxide ion fluxes in a working Y-doped BaCeO₃ SOFC. Solid State Ionics 2007; **178**:627–634.

Electronegativity (χ) (eV), Pauling	Ionic radii (Å)
0.89	1.35
0.95	1.18
1.12	0.87
1.33	0.72
1.22	0.90
1.20	0.938
1.13	0.99
1.10	0.868
1.17	0.958
3.50	1.40
	Electronegativity (χ) (eV), Pauling 0.89 0.95 1.12 1.33 1.22 1.20 1.13 1.10 1.17 3.50

Table 1 -Electronegativities and Shannon ionic radii of the host cations and their dopants [36].

Table 2-Variation of average ionic radius (AIR) (Å), tolerance factor (*t*), calculated [43] and experimental lattice constants (Å) for $Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO_{3-\delta}$ (0 < x < 0.5; y = 0, 0.1, 0.15; z = 0.1, 0.2) and $BaCeO_3$.

Composition	AIR (Å)	t	a _{calc} (Å)	$a_{exp}(\text{\AA})^{\pm}$	Relative density
	(B-site)				(%)
BaCeO ₃	0.87	0.94	4.348	4.397	
BSCGY1	0.88	0.91	4.404*	<i>a</i> = 6.23 (2)	99.8
				<i>b</i> = 8.71 (6)	
				c = 6.21(3)	
BSCZGY2	0.86	0.91	4.299	4.316 (2)	96.8
BSCZGY3	0.85	0.92	4.280	4.298 (9)	95.0
BSCZGY4	0.84	0.93	4.261	4.271 (2)	94.2
BSCZGY5	0.82	0.93	4.246	4.236 (5)	95.6
BSCZGY6	0.82	0.93	4.241	4.273 (6)	96.6
BSCZY7	0.77	0.95	4.398*	<i>a</i> = 6.22 (3)	
				<i>b</i> = 8.76 (5)	
				c = 6.23(2)	
BSCZ8	0.80	0.94	4.2094	4.340 (6)	

[±]The numbers in parentheses for lattice constant values are the uncertainty in the last digit.

* Pseudo-cubic lattice constant (a_o) .

Table 3-Activation Energies (eV) for Total Conductivity (E_a) (300-750 °C) for Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z} Zr_xGd_yY_zO_{3- δ} (0 < x < 0.5; y = 0, 0.1, 0.15; z = 0.1, 0.2) in (A) Air, (B) Air/3% H₂O, (C) N₂/3% H₂O, (D) N₂/3% D₂O, and (E) H₂/3% H₂O.

Sample	Α	В	С	D	Ε
BSCGY1	0.91	1.01	0.86	0.95	0.50
BSCZGY2	0.94		1.10	1.11	0.63
BSCZGY3	0.65	0.73	1.04	1.05	0.55
BSCZGY4	0.90	0.84	0.91		0.59
BSCZGY5	0.86	0.96	0.91		0.51
BSCZGY6	1.03	0.81	0.84	0.87	0.66
BSCZY7	1.03	1.13		1.04	0.58

Figure Captions

Fig. 1. PXRD patterns for the (a) as-prepared Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO_{3- δ} (0 < x < 0.5; y = 0, 0.1, 0.15; *z* = 0.1, 0.2) powders sintered at 1450 °C for 24 h in air, and (b) selected area PXRD showing 20 shift and splitting of high intensity peak around 20 = 29 degrees (dotted vertical lines in (b) refer to the orthorhombic phase). For comparison, simulated PXRD pattern of cubic BaCeO₃ (space group *Pm3m*, ICSD # 1500893) is also included in the figure. Unreacted precursors present in the product are marked as • = ZrO₂ (ICSD # 89426), * = Ba(OH)₂ (Alfa Aesar commercial powder), • = doped CeO₂ (PDF # 000500204), and • = BaCO₃ (PDF # 000410373). For comparison, a result on recently investigated Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3- δ} is also included [38].

Fig. 2. The plot of experimental lattice constants (Å) (left ordinate) calculated from PXRD data for single- phase $Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO_{3-\delta}$ and tolerance (right ordinate) as a function of the average ionic radius of B-site.

Fig. 3. Typical SEM image obtained on the polished pellets of the as-prepared Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z} $Zr_xGd_yY_zO_{3-\delta}$ (a) BSCZGY3; (b) BSCZGY4; (c) BSCZGY5; and (d) BSCZGY6.

Fig. 4. PXRD patterns of Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO_{3-δ} (0 < x < 0.5; y = 0, 0.1, 0.15; z = 0.1, 0.2) powders after exposure to water vapor at 90 °C for (a) 24 h and (b) 168 h. Secondary phases present the reaction product are marked as • = ZrO₂ (ICSD # 89426), * = Ba(OH)₂ (Alfa Aesar commercial powder), • = doped CeO₂ (PDF # 000500204), and • = BaCO₃ (PDF # 000410373), and • = SrCO₃ (ICSD # 202793). For comparison, simulated PXRD pattern of cubic BaCeO₃ (space group *Pm3m*, ICSD #1500893) is also included in the figure. For comparison, a result on recently investigated Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3-δ} is also included [38].

Fig. 5. PXRD patterns of Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO_{3- $\delta}$} (0 < x < 0.5; y = 0, 0.1, 0.15; z = 0.1, 0.2) powders after exposure to pure CO₂ at 800 °C for 24 h. Secondary phases in the reaction products are marked as • = ZrO₂ (ICSD # 89426), * = Ba(OH)₂ (Alfa Aesar commercial powder), • = doped CeO₂ (PDF # 000500204), and • = BaCO₃ (PDF # 000410373), and • = Y₂O₃ (ICSD # 77081). For comparison, simulated PXRD pattern of cubic BaCeO₃ (space group *Pm3m*, ICSD #1500893) is also included in the figure. For comparison, a result on recently investigated Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3- δ} is also included [38].

Fig. 6. TGA curve obtained for $Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO_{3-\delta}$ (0 < x < 0.5; y = 0, 0.1, 0.15; z = 0.1, 0.2) powders after exposure to water vapour at 90 °C for (a) 24 h, (b) 168 h, (c) *in-situ* TGA under CO₂/N₂ (1:1), and (d) estimated % conversion to BaCO₃ as a function of Zr in $Ba_{0.5}Sr_{0.5}Ce_{1-y_{1-y_{2-}}}$ _{y3}Zr_{y1}Gd_{y2}Y_{y3}O_{3- δ} from TGA curve (c). For comparison, a result on recently investigated $Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3-\delta}$ is also included [38].

Fig. 7. Typical AC impedance plots obtained at 600 °C under different atmospheres for (a) BSCGY1; (b) BSCZGY2; (c) BSCZGY3; (d) BSCZGY4; (e) BSCZGY5; (f) BSCZGY6; and (g) BSCZY7. For comparison, a result on recently investigated Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3-δ} is also included [38].

Fig. 8. Arrhenius plot of Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO_{3- δ} (0 < x < 0.5; y = 0, 0.1, 0.15; z = 0.1, 0.2) in air, air/3% H₂O, N₂/3% H₂O, N₂/3% D₂O and H₂/3% H₂O. (a) BSCGY1; (b) BSCZGY3; (c) BSCZGY4; (d) BSCZGY6; and (e) comparison of electrical conductivity in H₂/3% H₂O for samples BSCGY1-BSCZY7, and (f) comparison of total electrical conductivity in H₂/3% H₂O for BSCZGY3 and BSCZGY 5 with literature studies on acceptor-doped BaCeO₃ and BaZrO₃ [12, 52-55].





Fig. 1. PXRD patterns for the (a) as-prepared $Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO_{3-\delta}$ (0 < x < 0.5; y = 0, 0.1, 0.15; z = 0.1, 0.2) powders sintered at 1450 °C for 24 h in air, and (b) selected area PXRD showing 20 shift and splitting of high intensity peak around 20 = 29 degrees (dotted vertical lines in (b) refer to the orthorhombic phase). For comparison, simulated PXRD pattern of cubic BaCeO₃ (space group *Pm3m*, ICSD # 1500893) is also included in the figure. Unreacted precursors present in the product are marked as • = ZrO₂ (ICSD # 89426), * = Ba(OH)₂ (Alfa Aesar commercial powder), • = doped CeO₂ (PDF # 000500204), and • = BaCO₃ (PDF # 000410373). For comparison, a result on recently investigated Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3-\delta} is also included [38].



Fig. 2. The plot of experimental lattice constants (Å) (left ordinate) calculated from PXRD data for single- phase $Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO_{3-\delta}$ and tolerance (right ordinate) as a function of the average ionic radius of B-site.



Fig. 3. Typical SEM image obtained on the polished pellets of the as-prepared $Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}T_xGd_yY_zO_{3-\delta}$ (a) BSCZGY3; (b) BSCZGY4; (c) BSCZGY5; and (d) BSCZGY6.





Fig. 4. PXRD patterns of Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO_{3- δ} (0 < x < 0.5; y = 0, 0.1, 0.15; z = 0.1, 0.2) powders after exposure to water vapor at 90 °C for (a) 24 h and (b) 168 h. Secondary phases present the reaction product are marked as • = ZrO₂ (ICSD # 89426), * = Ba(OH)₂ (Alfa Aesar commercial powder), • = doped CeO₂ (PDF # 000500204), and • = BaCO₃ (PDF # 000410373), and • = SrCO₃ (ICSD # 202793). For comparison, simulated PXRD pattern of cubic BaCeO₃ (space group *Pm3m*, ICSD #1500893) is also included in the figure. For comparison, a result on recently investigated Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3- δ} is also included [38].



Fig. 5. PXRD patterns of Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO_{3- $\delta}$} (0 < x < 0.5; y = 0, 0.1, 0.15; z = 0.1, 0.2) powders after exposure to pure CO₂ at 800 °C for 24 h. Secondary phases in the reaction products are marked as • = ZrO₂ (ICSD # 89426), * = Ba(OH)₂ (Alfa Aesar commercial powder), • = doped CeO₂ (PDF # 000500204), and • = BaCO₃ (PDF # 000410373), and • = Y₂O₃ (ICSD # 77081). For comparison, simulated PXRD pattern of cubic BaCeO₃ (space group *Pm3m*, ICSD #1500893) is also included in the figure. For comparison, a result on recently investigated Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3- δ} is also included [38].



Fig. 6. TGA curve obtained for $Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO_{3-\delta}$ (0 < x < 0.5; y = 0, 0.1, 0.15; z = 0.1, 0.2) powders after exposure to water vapor at 90 °C for (a) 24 h, (b) 168 h, (c) *in-situ* TGA under CO₂/N₂ (1:1), and (d) estimated % conversion to BaCO₃ as a function of Zr in $Ba_{0.5}Sr_{0.5}Ce_{1-y1-y2-y3}Zr_{y1}Gd_{y2}Y_{y3}O_{3-\delta}$ from TGA curve (c). For comparison, a result on recently investigated $Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3-\delta}$ is also included [38].





Fig. 7. Typical AC impedance plots obtained at 600 °C under different atmospheres for (a) BSCGY1; (b) BSCZGY2; (c) BSCZGY3; (d) BSCZGY4; (e) BSCZGY5; (f) BSCZGY6; and (g) BSCZY7. For comparison, a result on recently investigated $Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3-\delta}$ is also included [38].





Fig. 8. Arrhenius plot of $Ba_{0.5}Sr_{0.5}Ce_{1-x-y-z}Zr_xGd_yY_zO_{3-\delta}$ (0 < x < 0.5; y = 0, 0.1, 0.15; z = 0.1, 0.2) in air, air/3% H₂O, N₂/3% H₂O, N₂/3% D₂O and H₂/3% H₂O. (a) BSCGY1; (b) BSCZGY3; (c) BSCZGY4; (d) BSCZGY6; and (e) comparison of electrical conductivity in H₂/3% H₂O for samples BSCGY1-BSCZY7, and (f) comparison of total electrical conductivity in H₂/3% H₂O for BSCZGY3 and BSCZGY 5 with literature studies on acceptor-doped BaCeO₃ and BaZrO₃ [12, 52-55].