Wet Chemical Synthesis and Characterisation of $Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3-\delta}$ Proton Conductor

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ABSTRACT

$Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3-\delta}$ (BSCZGY) proton conducting electrolyte material for intermediate temperature solid oxide fuel cells (IT-SOFCs) has been synthesized by a sol-gel modified Pechini process and its sinterability, thermal expansion, microstructure, ionic conductivity and chemical stability have been investigated. Ionic conductivity at 700 ºC was measured to be ~ 8 x 10^{-3} S cm^{-1} in wet 5 vol% H_2/Ar atmospheres. Chemical stability test in pure CO_2 up to 1200 ºC shows that the material is highly stable; better than the stability of $BaZr_{0.3}Ce_{0.5}Y_{0.1}Yb_{0.1}O_{3-\delta}$.

Key words: Sol-gel modified pechini process, sinterability, ionic conductivity, chemical stability

Introduction

Solid oxide fuel cells (SOFCs) due to high efficiency (up to 60%), fuel flexibility and low pollution emission, are considered promising alternative sources of energy production. However, its high operation temperature in the range 800 – 1000 ºC which is dictated by the choice of electrolyte material (Oxide-ion conductors) such as YSZ, put several challenges like high cost and long-term stability issues [1]. To avoid the issues associated to high temperature operation, there is growing interest in SOFCs based on proton conducting electrolyte materials which can operate in intermediate temperature (400 – 700 ºC) range due to lower activation energy required for protonic conduction [1, 2]. Tremendous advantages result from its employment including cheaper interconnect materials, shorter start-up and shut-down time, easier and more reliable sealing, less chances of materials and performance degradation. Also as water in formed at the cathode side, hence fuel dilution is avoided which results in higher fuel utilization efficiency and in higher OCV values [2, 3].

Mostly perovskite (ABO_3) type oxides are employed as electrolyte materials presenting proton conduction, among them being doped barium cerates and doped barium zirconates, which are widely investigated in the literature [4 – 9]. Doped barium-$BaCeO_3$, especially with 15 or 20 mol% of Y, possesses high ionic conductivity in the operating temperature range and aliovalent co-doped $BaCeO_3$ shows even better ionic conductivity than Y-doped $BaCeO_3$ [10 – 14]. However, its poor resistance to carbonation in CO_2 containing atmospheres, as well as the instability in water vapours are big challenges. On the contrary, doped-$BaZrO_3$ e.g. $BaZr_{0.8}Y_{0.2}O_{3-\delta}$, possesses very high chemical stability in CO_2 and H_2O containing atmospheres due to high covalence of the Zr – O bond [1, 9, 15]. However, though it has high symmetry (cubic) as compared to cerates (orthorhombic) it still shows lower ionic conductivity than the latter, due to high grain boundary contributions, limiting its practical applications [16]. It has also a refractory nature and a lot of variation exist in the reported conductivity values. It's typical sintering temperature is also very high, generally ~ 1700 ºC which makes the development of electrode supported cells quite difficult [1].

To find a balance between ionic conductivity and chemical stability, solid solutions between $BaCeO_3$ and $BaZrO_3$ has been suggested and investigated in the literature [17 - 24]. One well-known solid solution, $Ba(Zr_{0.1}Ce_{0.7}Y_{0.2})O_{3-\delta}$ (BZCY), the most widely used proton conducting electrolyte material to date, was reported to possess the highest ionic conductivity of 9×10^{-3} S cm^{-1} at 500 ºC as well as high chemical stability and there was no evidence of any carbonation or change in structure after exposing it to an atmosphere containing 2% CO_2 and 15% H_2O at 500 ºC for one week [25]. However, later it has been reported that BZCY was unstable when it was kept in 3% (balanced with air) CO_2 at 600 ºC for 24 hours and diffraction peaks corresponding to $BaCO_3$ and CeO_2 were observed in XRD [26]. Aliovalent Y + Yb co-doped BCZY showed better performance than BZCY and higher ionic conductivity of 14×10^{-3} S cm^{-1} at 500 ºC [27, 28]. However, though initially $BaZr_{0.1}Ce_{0.7}Y_{0.2}Yb_{0.1}O_{3-\delta}$ (BZCYYb) was reported to be stable in CO_2 atmospheres, later it was found to be unstable when heated up to 800 ºC in CO_2/N_2 (1:2 ratio) atmosphere [29].

To improve chemical stability of $BaCeO_3$ – $BaZrO_3$ solid solutions, the ratio of zirconia needs to be increased. However, this causes a drop in ionic conductivity as well as in sinterability and its stability is uncertain. Fabbri et al. while investigating $Ba(Ce_{0.8-x}Zr_x)Y_{0.2}O_{3-\delta}$ system found there was carbonation even for $x = 0.5$ i.e. $BaCe_{0.3}Zr_{0.5}Y_{0.2}O_{3-\delta}$ after exposure to CO_2 at 900 ºC for 3 hours [30]. Also after sintering at 1600 ºC for 8 hours, the relative density was < 90%. The search for a chemically stable electrolyte materials was continuous and very recently a novel composition $Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3-\delta}$ (BSCZGY) with 50 mol% Sr doping at the A site and Y + Gd co-doping at the B site showed very high stability in CO_2 and H_2O containing atmospheres [31]. There was no evidence of carbonation when kept in flowing pure CO_2 at 800 ºC for 24 hours and conductivity of 4×10^{-3} S cm^{-1} at 600 ºC was measured, which is good enough for practical applications [31]. It showed a better densification as well and a relative density of ~ 95% after firing 1450 ºC, when processed via solid state reaction method; while for BZCY and BZCYYb, a sintering temperature 1550 ºC in required for getting a densification > 90% when processed by solid state reaction method [25, 27].

Wet chemical synthesis has several advantages over conventional solid state reaction method. Nanosized particles can be obtained which promote sintering at lower temperatures and hence a gas-tightness of the samples for various applications can be achieved at low temperatures. Various wet chemical routes including sol-gel (polymeric-precursor), solution combustion synthesis, co-precipitation process has been reported for proton conducting barium cerate-zirconate oxides [30, 32 – 38]. Modified Pechini synthesis in which ethylene di-amino tetra-acetic acid (EDTA) is used a chelating agent and citric acid as complexing agent attracts great interest for getting fine crystalline and has been reported by many researchers for the synthesis of barium based proton conducting electrolyte materials [39 – 45].

Here BSCZGY, a promising potential electrolyte material, has been processed by a modified Pechini process and the influence of resultant powder morphology and specific processing conditions upon material properties and stability were investigated.

2. Experimental

2.1. Sample Preparation

Stoichiometric amounts of $Ba(NO_3)_2$ (Alfa Aesar), $Sr(NO_3)_2$, $Ce(NO_3)_3.6H_2O$, $Zr(NO_3)_3.xH_2O$, $Gd(NO_3)_3.6H_2O$ and $Y(NO_3)_3.6H_2O$ (all Sigma Aldrich) were dissolved in deionised water. Before dissolution, the number of water molecules of crystallization in Zr salt $\{Zr(NO_3)_3.xH_2O\}$ was determined to be 5 from thermogravimetric analysis (TGA). Ethylene diamine tetraacetic acid

(EDTA, Sigma Aldrich) and citric acid (Fisher) were employed as chelating and complexing agents respectively. EDTA was mixed in de-ionized water and ammonia solution was added to improve its solubility in de-ionized water. The solution of metal nitrate precursors was poured into EDTA solution while it was stirring. Finally, citric acid was added such that the ratio of nitrate precursors to EDTA and citric acid in molar ratio = 1:1:1.5 respectively. The pH of the solution was adjusted in the range 5 - 6 with the help of nitric acid. The resultant solution was stirred for 24 hours and then it was dried on hot plate at about 100 °C until a dark coloured gel was obtained. The obtained gel was ignited at about 300 °C and then it was calcined at 1000 °C and 1100 °C for 5 hours. To break the agglomerates, the calcined sample was milled for 24 hours in ethanol using zirconia as a milling media and then it was dried at about 80 °C on hot plate.

$BaCe_{0.3}Zr_{0.5}Y_{0.1}Yb_{0.1}O_{3-\delta}$ sample for the comparison of chemical stability, was processed via conventional solid state reaction method. Stoichiometric amounts of $BaCO_3$ (Analar), CeO_2 (Acros Organics), Y_2O_3 (Aldrich) and Zr_2O_3 (Alfa Aesar) were mixed in ethanol and ball milled for 24 hours. After milling, the mixture was dried at 80 °C, pelletized by uniaxial press and then calcined at 1400 °C for 10 hours. After calcination, the sample was ball milled for 2 – 3 hours to break the agglomerates and then dried at 80 °C. The calcination cycle was repeated for the 2nd time to get a pure single phase.

2.2. Characterization

Phase analysis of the calcined and sintered samples of BSCZGY was performed using PANalytical Empyrean Diffractometer. The high resolution XRD patterns of the sintered sample at 1400 °C for 3 hours were analysed through the Rietveld method by using the Fullprof software.

Crystallite size of the calcined powder was calculated via Scherrer equation,

$$D = \frac{0.9\lambda}{\beta cos\theta} \qquad (1)$$

where D is the particle size, λ is the X-Ray wavelength, θ is the angle of XRD peak and $\boldsymbol{\beta}$ (in radians) is the difference of full width half maximum (FWHM) of the sample to that of that standard Si peak.

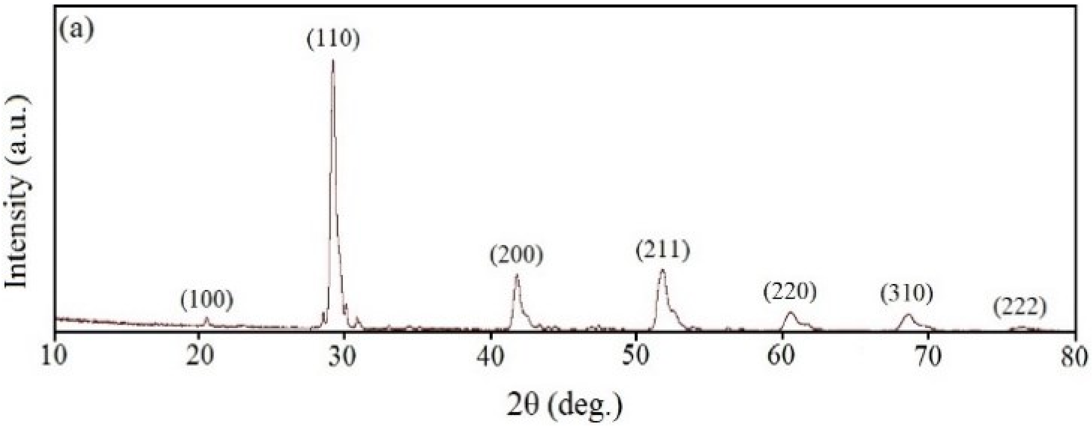
Sinterability and thermal expansion of BSCZGY sample were studied with the help of dilatometry. BSCZGY powders were pressed into pellets with the help of a uniaxial press and then it was placed in dilatometer and heated up to about 1470 °C in air with a heating rate of 3 °C/min, isothermally held for 30 minutes and then cooled down at the same rate of 3 °C/min. Sinterability was studied from the heating curve and thermal expansion co-efficient was determined from the cooling curve. For microstructure studies, the pellets were pressed by uniaxial press, sintered at 1400 °C for 3 hours with a heating rate of 3 °C/min and the its microstructures was studied with the help of JEOL 5600 SEM. Densification of the sintered pellet was measured with a helium gas pycnometer. The ionic conductivity of the sample was measured using a Solartron impedance spectrometer. The sintered pellets of BSCZGY fired at 1400 °C for 3 hours, were polished on sand paper, silver painted, dried in the oven and then fired at 600 °C for 30 minutes. An amplitude of 50 mA was applied and the impedance was measured in the frequency range of 1MHz - 10mHz. Thermogravimetric analysis (TGA) was performed to study the chemical stability. The sintered pellets of BSCZGY and BZ3C5YYb, both fired at 1400C for 3 hours, were ground via mortar and pestle and then TGA of the powdered sample was performed in pure CO_2 with a heating rate of 3 °C/min up to 1200 °C flow rate, held isothermally for 30 minutes and then cooled down with 3 °C/min. The flow rate of CO_2 was 40ml/min.

3. Results and Discussion

3.1. Phase Analysis

X-Ray micrograph of $Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3-\delta}$ (BSCZGY) sample after calcination at 1000 ºC for 5 hours is shown in Fig. 1 (a). There is no peak corresponding to $BaCO_3$ which shows that decomposition is complete and hence phase formation at a low temperature of 1000 ºC. The peaks are quite broad and for crystalline size calculation using Scherrer equation (Eq. 1), the peak with highest intensity i.e. (110) was taken. **β**, the difference of full width of half maximum (FWHF) of the sample (110) peak from the FWHM of standard Si peak (in radians), was put in Eq. 1. The crystallite size was measured to be ~ 31nm; similar grain sizes were reported in the literature when using solution preparation methods, e.g. 30 nm for $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb) [38] or 26 – 42 nm for $Ba(Zr_{0.8-x}Ce_xY_{0.2})O_{2.9}$ system, [33]. An increase in crystalline size was observed with increasing calcination temperature, and after calcination at 1100 ºC, the crystallite size was ~ 50nm. For further application, the calcined sample at 1000 ºC was used. Hence Pechini preparation process favoured formation of fine powders and single phase at much lower temperatures than solid state synthesis. However, in XRD pattern collected after calcination at 1000 ºC there are some minor extra peaks in the pattern, due to incomplete reaction, that are disappearing after sintering at high temperatures. Also, some of the peaks, especially at high diffraction angles, are doubled, suggesting the possible co-existence of two intermediate phases with similar symmetry that are becoming single phase after sintering.

The sample calcined at 1000 ºC, after ball milling for 24 hours, was sintered at 1400 ºC for 3 hours shows a pure phase and good crystallinity (X-Ray micrograph is shown in Fig. 1 b). Rietveld refinement was performed using Fullprof software and the lattice was found to possess cubic structure with space group Pm3m (221), which is consistent with that reported Kannan et al. [31]. The lattice parameter was a = 4.2983(3)Å, with unit cell volume V = 79.4152Å^3 as shown in Table. 1. The slight variation in the lattice parameter compared to the previously reported one (a = 4.282Å [31]) is due to the different preparation conditions. This might be since in the reported one [31] there were two minor peaks near to 2θ of 30º, while here is pure phase and those minor doesn't exist. The theoretical density from lattice parameters was measured to 5.626 g/cc.



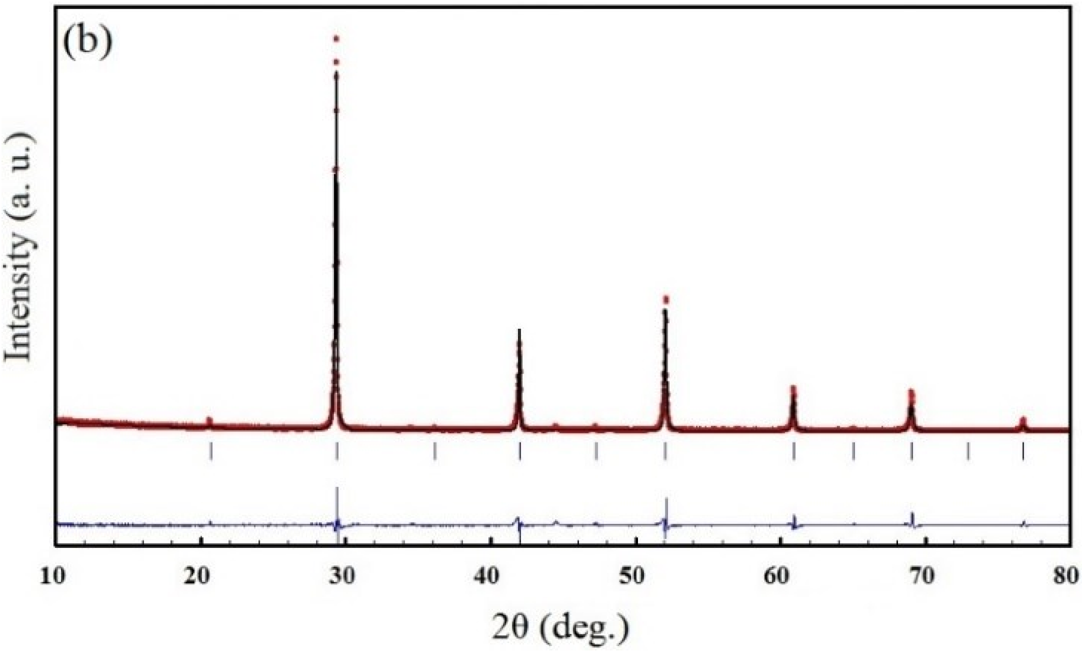


Fig. 1 (a) XRD patterns of $Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3-\delta}$ powders after calcination at 1000 ºC for 5 hours and (b) Rietveld refinement profile of XRD data after sintering at 1450 ºC for 3 hours.

Table 1. Summary of Reitveld refinement for $Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3-\delta}$, processed a modified Pechini method, sintered at 1400 ºC for 3 hours.

Parameters	Rietveld Refinement
a(Å)	4.2983(3)
b(Å)	4.2983(3)
c(Å)	4.2983(3)
V(Å^3)	79.4152(3)
R_p(%)	8.65
R_{wp}(%)	11.8
R_{exp}(%)	6.38
χ^2	3.43

3.2. Sinterability

It is an important requirement that the SOFCs electrolyte is gas tight, therefore, the densification process needs to be studied. Wet chemical route is a useful processing route for obtaining fine crystallites with good sinterability at lower temperature as compared to conventional solid state route.

Sinterability of BSCZGY sample was studied by putting a green pellet in dilatometer and was heated up to about 1470 ºC in air. The sinterability curve is shown in Fig. 2 with first derivative of sinterability curve shown by dotted line to know the temperature of the maximum shrinkage rate (dL/dt). The shrinkage starts at about 758.0 ºC and reaches to its maximum value at 1363.40 ºC. A quite significant shrinkage of 23.56% was measured which is, again, close to the reported shrinkage of ~23% shrinkage reported for $BaZr_{0.7}Pr_{0.1}Y_{0.2}O_{3-\delta}$ (BZPY) [35]. It is higher than the reported shrinkage for $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$(BZCY) and BZCYYb which were 18% and 19.4%, respectively [34, 38]. The significant shrinkage is most likely due to small crystallite size of the powder obtained by this preparation route.

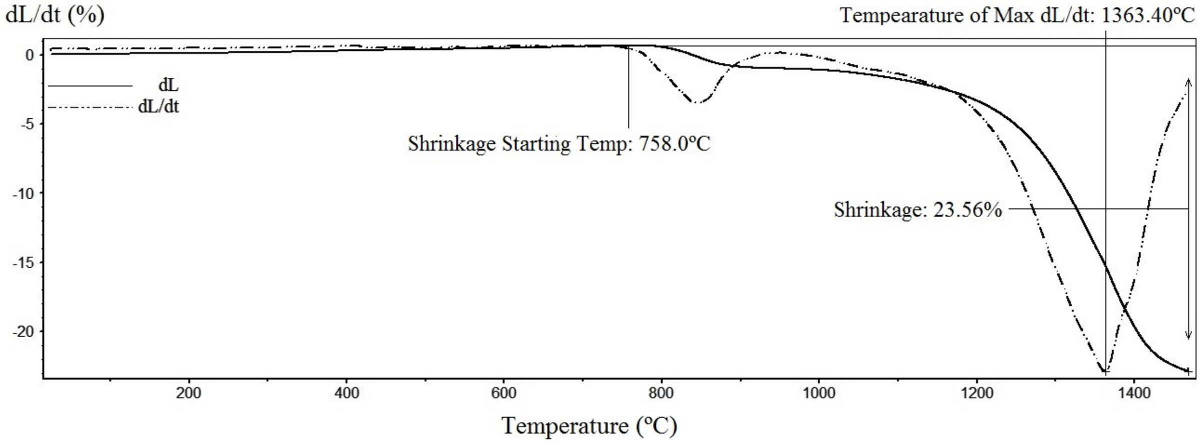


Fig. 2. Sinterability Studies of $Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3-\delta}$ in dilatometry up to 1470 ºC with a heating rate of 3 ºC/min in air.

3.3. Thermal Expansion

Matching thermal expansion of all SOFCs components i.e. anode, cathode and electrolyte is vital to minimize thermal stresses of components during its operation. An average value of 10.45 x 10^{-6} K^{-1} was measured for the thermal expansion co-efficient (TEC) of BSCZGY in the temperature range 50 – 1000 ºC in air. This is a bit higher than the thermal expansion value for BZCYYb which was measured to be 9.1 – 9.8 x 10^{-6} K^{-1} in the temperature range 25 – 1200 ºC in air [45]. This TEC value BSCZGY is close to the thermal expansion coefficient of Pr based cathode materials when measured in the temperature range 30 – 1000 ºC in air and Pr-based cathode materials can be employed [46]. This match can offer good prospects for producing complete electrochemical cells based on proton conducting electrolyte.

3.4. Microstructure

Surface morphology was studied via JEOL 5600 SEM. Fig. 3 shows the SEM images of BSCZGY sample. The microstructure was found quite dense and a relative density of ~ 98% was achieved after firing at 1400 ºC for 3 hours which is comparable to the relative density of BZPY or BZCYYb samples fired between 1400 and 1600 ºC for 8 hours [35], [37]. For a composition with same Zr ratio i.e. 20 mol%, $BaCe_{0.65}Zr_{0.20}Y_{0.15}O_{3-\delta}$, a densification of 93% was achieved after firing at 1400 ºC for 10 hours [40]. The same material i.e. BSCZGY when processed via solid state method, a densification of 95% was achieved after firing 1450 ºC for a long dwelling time of 24 hours. It seems the beneficial role of the smaller crystallite size processed via a wet chemical route (modified Pechini method).

The grain size distribution is relatively uniform in the range 2 – 8µm which is very close to the grain size for $BaCe_{0.5}Zr_{0.3}Y_{0.2}O_{3-\delta}$ when fired at 1600 ºC for 8 hours [30]. The average grain size ~ 4 µm can be seen from Fig. 4, which is comparable to the reported grain size for BZCY and BZCYYb which were 5µm and 3µm after firing at 1400 ºC for 6, 6 hours [47]. It is bigger than for the grain size BZPY which was 1.7µm after firing at 1600 ºC for 8 hours or than the grain size reported for BZCYYb which was about 1.0µm after firing at 1400 ºC for 5 hours [45]. So, wet chemical method is beneficial not only in good densification but in grain growth as well.

Some sub-micron light-coloured crystals on the top surface of the grains were observed in SEM images and one such a large crystal is shown in Fig. 3 (b). From EDX it was found that such crystals have similar ratio of elements as in the grains. The presence of any extra phase was also below the detection limit in the XRD. Since crystallite size was small, this might due to some loose particles left on the surface of the green pellet after pressing. This is not surprising as the raw surface of the samples might contain such defects.

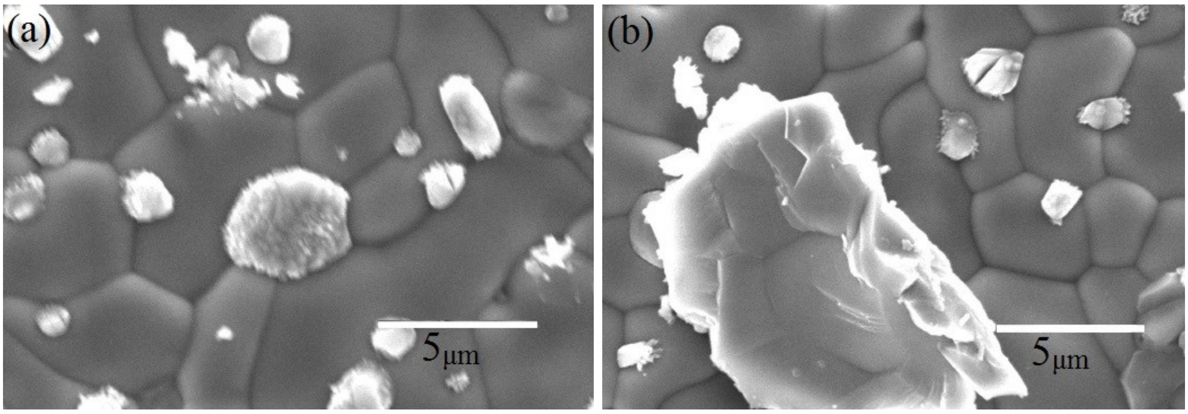


Fig.3. SEM images of $Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3-\delta}$ fired at 1400 ºC for 3 hours in air.

3.5. Ionic Conductivity

An ionic conductivity in the range $10^{-2} – 10^{-3}$ S cm^{-1} at 600 ºC is considered suitable for practical applications of proton conducting oxides. Electrical conductivity was measured in humidified (3vol %) 5 % H_2/Ar atmosphere and Arrhenius plots of electrical conductivity for BSCZGY is shown in Fig. 4.

The measured value of ionic conductivity at 700 ºC is ~ 8 x 10^{-3} S cm^{-1} which is comparable to the reported ionic conductivity values for $Ba(Ce_{0.8-x}Zr_x)Y_{0.2}O_{3-\delta}$ system by Fabbri et al. [30] or to the $BaZr_{0.3}Ce_{0.5}Y_{0.2-x}Yb_{0.1}O_{3-\delta}$ system [48]. This comparison is interesting since one typical composition (BZ3C5YYb) from the system has been compared in stability studies as shown in Fig. 5 (a). The value of conductivity is almost double than the reported conductivity for $BaCe_{0.6}Zr_{0.3}Y_{0.1}O_{3-\delta}$ which was ~ 2.33 x 10^{-3} S cm^{-1} at 600 ºC under the same conditions [49].

The value of ionic conductivity for BSCZGY was measured to be 4.50 x 10^{-3} S cm^{-1} at 600 ºC, higher than the reported value of maximum ionic conductivity of 4.0 x 10^{-3} S cm^{-1} at 600ºC under the same conditions. This slight increase might be due to better densification of 98% as compared 95% in the reported [31]. There is an increase in grain size and it might also be contribution due to bigger grain size. The activation energy for BSCZGY was measured to be 0.558 eV which agrees with the reported value i.e. 0.57 eV (55 kJ/mole) and is in the range of typical activation energy values for proton conducting electrolytes which is 0.4 – 0.6 eV [31]. For example, an activation energy of 0.51eV was reported for $BaZr_{0.7}Pr_{0.1}Y_{0.2}O_{3-\delta}$ and 0.60eV for BZCY in wet 5 % H_2/Ar atmosphere [35, 38].

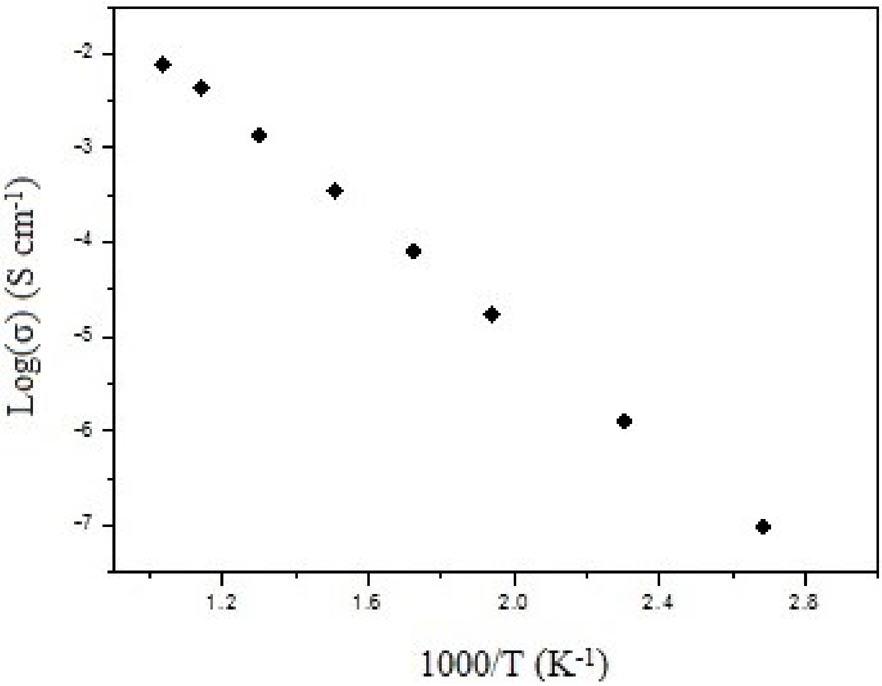


Fig. 4. Arrhenius plots of electrical conductivity for $Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3-\delta}$ in wet 5 vol% H_2/Ar.

3.6. Chemical Stability

One of the main challenge of cerium-based proton conducting electrolyte materials is its stability issues in CO_2 containing atmosphere [10 – 14]. $BaCeO_3$ react with CO_2 and forms $BaCO_3$ and CeO_2 as shown in Eqn. (2),

$$BaCeO_3 + CO_2 \rightarrow BaCO_3 + CeO_2 \tag{2}$$

The chemical reaction in Eqn. (1) has been reported to occurs at 1141 ºC [22], so both samples i.e. BSCZGY and BZ3C5YYb for comparison were heated up to 1200 ºC in pure CO_2 with a flow rate of 40 ml/min, held isothermally for 30 minutes and then cooled down with the same rate of 3 ºC/min. The heat treatment in CO_2 up 1200 ˚C or a bit higher has already been reported by many in the literature [14, 35, 40, 49, 50]. Fig. 5 (a) shows thermogravimetric analysis (TGA) curves for BSCZGY and $BaZr_{0.3}Ce_{0.5}Y_{0.2}Yb_{0.1}O_{3-\delta}$, (BZ3C5YYb). BSCZGY was found relatively much more stable than BZ3C5YYb, however still some minor peaks corresponding to CeO_2 were observed, represented by the symbol "*" as shown in Fig. 5 (b). The original structure is still maintained and the crystallinity is reduced as shown in Fig. 5 (b). There is a small weight gain of about 0.3% after stability test as can be seen from curve 1 (Fig 5 a) which is much smaller than weight gain of 1.79% for BZ3C5YYb. The weight gain is comparable to the weight gained for a composition with higher Zr content of 70 mol% at the B site i.e. $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-\delta}$, which was roughly 0.3 – 0.4%, when heated in pure CO_2 up to 1250 ºC with a heating/cooling rate of 2 ºC/min [49]. For composition with 30 mol% of Zr at the B site i.e. $BaC_{0.6}Zr_{0.3}Y_{0.1}O_{3-\delta}$, the weight gain was about 2% under the same conditions as for 70 mol% of zirconia, up to 1250 ºC in pure CO_2 [49]. In case of BZCYYb, when heated to 1200 C in pure CO_2 with a heating/cooling rate of 10 ºC/min, the weight gain was 7.7%. Similarly, for $BaCe_{0.5}Zr_{0.3}Y_{0.2}O_{3-\delta}$, when heated up to 1200 ⁰C with a heating/cooling rate of 5 ºC/min, the weight gain was > 9% [50]. Hence, though there are some peaks corresponding to CeO_2, it relatively is quite significant.

BSCZGY has recently been reported to possess high stability in pure CO_2 at 800 ºC and there was no evidence of carbonation after it was kept for 24 hours in pure CO_2 at 800 ºC with a flow rate of 10 ml/min; however here it found not to be so stable when heated up to 1200 ºC in pure CO_2 [31]. The reason might be that Kannan et al. stability test was performed only up to 800 ºC in pure CO_2, which is much lower than temperature at which chemical reaction between $BaCeO_3$ and CO_2 occurs i.e. 1141 ºC [22, 31]. Hence heating a proton conducting electrolyte material below the carbonation say up to 800 ºC in CO_2 is not a good representative for testing its chemical stability and that's why some well-known proton conducting electrolyte materials like BZCY and BZCYYb were initially reported to be stable in CO_2, but later were found to be unstable when tested at higher temperatures [25 – 27, 29, 31]. Hence it is vital to test chemical stability in CO_2 up to 1200 ºC. Nevertheless, the relative is still quite high than for practical applications. There is a weight gain of only 0.3% after stability test for BSCZGY sample.

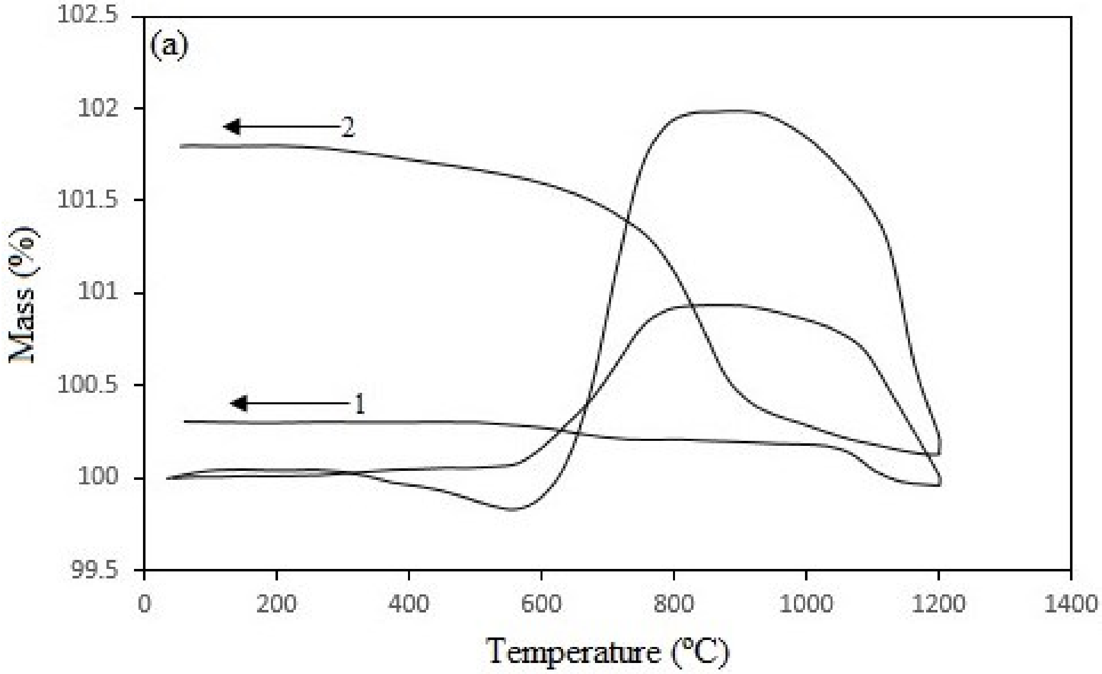


Fig. 5 (a) Thermogravimetric analysis of (1) $Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3-\delta}$ and (2) $BaZr_{0.3}Ce_{0.5}Y_{0.1}Yb_{0.1}O_{3-\delta}$ heated up to 1200 ºC in pure CO_2 with a flow rate of 40 ml/min and with a heating/cooling rate of 3 ºC/min.

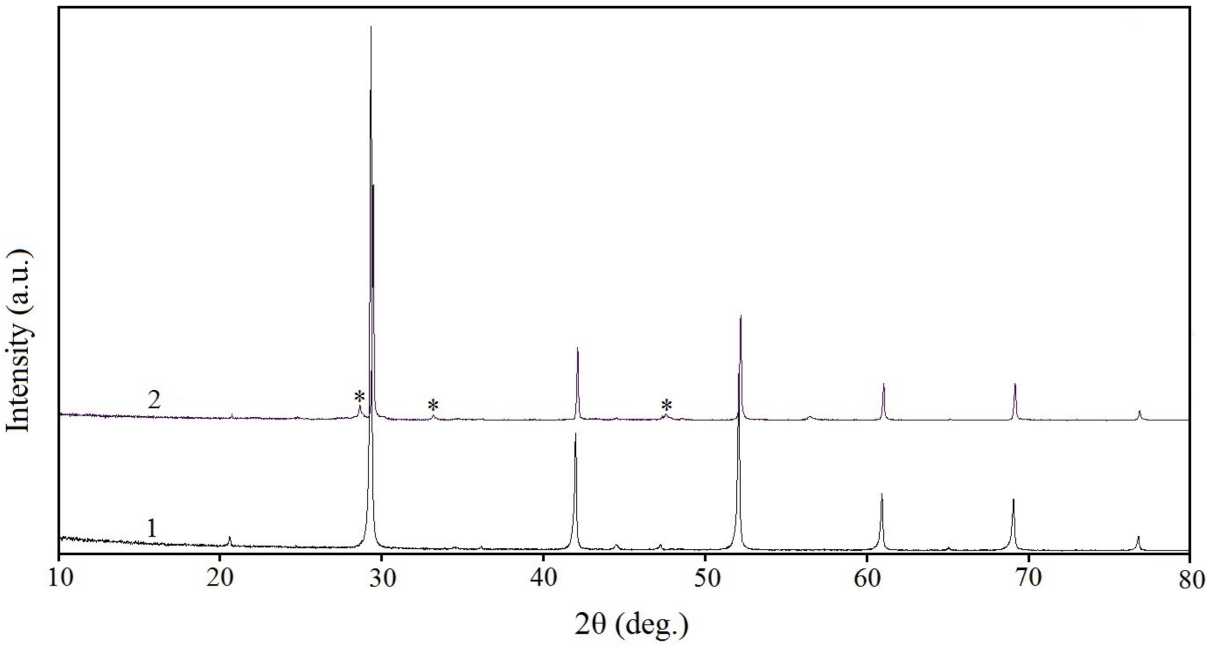


Fig. 5 (b). Curve 1, XRD pattern of $Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3-\delta}$ (BSCZGY) powder before (1) and after stability test (b) in pure CO_2 up to 1200ºC.

Conclusion

Proton conducting $Ba_{0.5}Sr_{0.5}Ce_{0.6}Zr_{0.2}Gd_{0.1}Y_{0.1}O_{3-\delta}$ electrolyte material, processed by modified pechini process has a good sinterability and a densification of ~ 98% was achieved after sintering at 1400 ºC for 3 hours. The proton conductivity is 8×10^{-3} S cm^{-1} at 700 ºC, higher than the value measured for the sample of the same composition but prepared by solid state method or other similar composition. This proton conductivity value, together with the good stability in CO_2 makes the material suitable for practical applications and is related to the specific preparation route for the sample.

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