Abstract. The specimen of $\text{BaCe}_{0.7} \text{Zr}_{0.1} \text{Y}_{0.05} \text{Zn}_{0.15} \text{O}_3$, a perovskite-type electrolyte, has been synthesized for application in an anode-supported protonic solid oxide fuel cell by the conventional solid state reaction in air at 1200°C for 12 hours. Structural and thermal characterization has been performed using room temperature X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA). Rietveld analysis of the XRD data has been analyzed by FullProf program and confirmed the single phase of the sample with an orthorhombic crystal structure in the Pbnm space group. To understand the temperature dependent behaviour TG/DTA scan of the precursor was recorded. The TG/DTA scan was performed under constant flow of Argon which exhibits a gradual weight loss up to 900°C. The SEM image of the pellet surface of the sample shows that the sample sintered at 1200°C was dense and suitable to use as electrolyte in solid oxide fuel cells (SOFCs).

1. Introduction
Solid-oxide fuel cells (SOFCs) operate at intermediate-temperature have attracted tremendous attention globally because of their potential long-term stability and economic competitiveness for many (including housing and automotive) applications [1]–[5]. To date, the best available electrolyte material appears to be doped ceria, which potentially meets most of the requirements for fuel-cell operation below 600 °C [6]. Some significant issues still remain, however, including electronic conductivity and undefined mechanical integrity under fuel-cell operating conditions. The finding of a new solid electrolyte for low-temperature SOFCs is a great challenge for the SOFC community. Proton conductors show potential candidates as electrolytes for low-temperature SOFCs because of their low activation energy of protons conduction. Many perovskite-type oxides show high proton conductivity in a reducing atmosphere [7]–[9]. One of the most important challenges for this type of proton conductor is a proper compromise between conductivity and chemical stability [10]–[12]. As for example, doped BaCeO3 has sufficiently high ionic conductivity, but the chemical stability in a CO$_2$ and H$_2$O containing atmosphere is inadequate for fuel-cell applications.

Because BaCeO$_3$ and BaZrO$_3$ easily form solid solutions, it is possible to replace a desired fraction of Ce in BaCeO$_3$ with Zr to form a solid solution that exhibits both adequate proton conductivity as well as sufficient thermal and chemical stability over a large range of circumstances relevant to fuel cell operation [7], [13]–[15]. Compared with doped cerates, doped zirconates possess enhanced chemical stability but lower conductivity. The stability of doped barium cerates is improved by the introduction of Zr at B site in order to accomplish high proton conductivity, as well as adequate chemical and...
thermal stability in a broad range of conditions referring to the fuel-cell operation. However, it is complicated to get the electrolyte with high density and high sintering temperatures are always required for it. In order to improve sinterability, Babilo and Haile [16] and Tao and Irvine [17] introduced Zn into Y and Zr doped BaCeO$_3$. Another report [18] showed the stable proton-conducting electrolyte BaCe$_{0.7}$Zr$_{0.1}$Y$_{0.05}$Zn$_{0.15}$O$_{3-\delta}$ by co-doping of Zr and Zn in the lattice could be sintered densely at lower temperatures and the chemical stability was also improved. Here, we report a new composition, BaCe$_{0.7}$Zr$_{0.1}$Y$_{0.05}$Zn$_{0.15}$O$_3$ (BZCYZ), where cerium is substituted by zirconium, yttrium and zinc. The composition was prepared as a single phase perovskite at a lower temperature comparing with the other works in the literatures and investigated the structural and thermal properties.

The proton conductivity of the electrolyte is mainly dependent on the concentration of oxygen vacancies in the perovskites oxides. The oxygen vacancies in these oxides can be significantly increased by acceptor doping, i.e., doping at the B-site by lower valance elements (LVE), typically yttrium or other rare earth metals [19].

During the synthesis and the SOFC cell operation following two reactions can occur in the presence of oxygen:

$$2\text{Ce}_x\text{O}_y + \text{M}_2\text{O}_3 \rightarrow 2\text{M}_x\text{Ce}_y + \text{V}_o + 2\text{CeO}_2$$  \hspace{1cm} (1)

$$\frac{1}{2} \text{O}_2 + \text{V}_o \rightarrow \text{O}_x + 2\text{h}$$ \hspace{1cm} (2)

The following mechanism has been proposed for the incorporation of protons in a hydrogen or water rich atmosphere and their conduction [20]–[22],

$$\text{H}_2\text{O}(g) + \text{V}_o + \text{O}_x \rightarrow 2\text{OH}_o$$ \hspace{1cm} (3)

The significance of this research project is to developing intermediate-temperature (500-700°C) ceramic proton conductor as an anode support and electrolyte with a lower temperature and for adequate proton conductivity to meet the commercial target of reversible SOFCs and finding compatible electrodes with optimized functionality for dual-mode operation of reversible SOFCs.

A set of tasks and associated performance objectives have been identified to meet the research goal as follows: Investigate and use solid state and wet chemical fabrication routes for BaCe$_{0.7}$Zr$_{0.1}$Y$_{0.05}$Zn$_{0.15}$O$_3$ ceramic proton conductors and associated electrode materials in glycine nitrate, sol-gel, and co-precipitation processes; in later case Y can be replaced by some other target materials to look at the performances.

In this work solid state reaction method was adopted to synthesis the sample since it is commonly adopted for the preparation of ceramic compounds because of its low manufacturing cost and simplicity. Many investigators have employed solid-state reactions to synthesize oxides pertinent to IT-SOFCs [17], [23].

2. Experimental

The sample was carefully synthesized as possible to avoid any of the chemical contamination and have done the other experiments with the instruments of precise conditions.

2.1. Synthesis of BCZYZ

The perovskite sample of BaCe$_{0.7}$Zr$_{0.1}$Y$_{0.05}$Zn$_{0.15}$O$_3$ of total amount 10 g was synthesized by the conventional solid state reaction in air at 1200°C for 12 hours inside a muffle furnace (box furnace, Model: ST-1700 MX-III) using the ingredients chemicals supplied from the company Sigma Aldrich. Powders of (purity more than 99.95%) BaCO$_3$, CeO$_2$, ZrO$_2$, Y$_2$O$_3$ and ZnO were used as initial chemicals in precise stoichiometric ratios. The powders were weighed individually using a precise digital micro balance (Model: AND, GR-200) and then thoroughly mixed in an agate mortar (made up of fine stone) for one hour. The sample was then milled intimately using a ball-mill machine (Paul O. Abbe Inc., Model 202421) for about 4 hours with appropriate amount of ethanol and then was dried on a magnetic heater (Stuart, Model: SB 162) with stirring. Disc-shaped pellets of 2 g were made into a
13 mm dia stainless steel die under a Hydraulic press (Hydraulic Bench Press, Kennedy, Model: HBP 010) with a pressure of 4 ton. The pellets were then fired at 900°C for 12 hours inside the muffle furnace with a heating and cooling rate of 5°C/min. Then the calcinated sample was ground in a mortar pestle for one hour and then mixed with a small amount of poly vinyl alcohol (PVA) as a binder and then ground again for about 20 minutes and finally pressed into the pellets of 2 g of 13 mm dia under the hydraulic press of 5 ton pressure. The pellets of the sample were finally sintered at 1200°C for 14 hours inside the furnace.

2.2. Structural analysis
The X-ray diffraction experiment was performed on the sample using D8 Advanced Bruker XRD system with CuK\(\alpha1\) radiation of wavelength \(\lambda = 1.5406 \text{ Å}\) in the angular range of \(\theta = 20^\circ\) to \(80^\circ\) with a step size of 0.02\(^\circ\) at room temperature.

The programs TREOR90 [24] and Checkcell [25] were used for indexing and refinement of the lattice parameters. The XRD data were analyzed using FullProf [26] suite program.

2.3. Thermal analysis
Thermogravimetric analysis (TGA) data were collected using a SETARAM TG-DTA/DSC thermogravimetric analyzer. The samples were heated up to 900 °C in the TG furnace at a heating rate of 10 °C/ min in dry argon. TGA in pure Ar was carried out on at 10 °C/ min from 20 to 900 °C, held isothermally for 90 min, and then cooled down to 20 °C at the same rate, with flowing the same gas.

2.4. Microstructural analysis
Scanning Electron Microscopy (SEM) experiments were carried out with a high resolution SEM machine (Model: JSM-7610F, OXFORD); with SEI DETECTOR and ACCEL Voltage 5.00 Volt and the images were taken in different magnifications for getting better fracture images.

3. Results and discussion

3.1. XRD pattern analysis
Figure 1 shows the Rietveld analysis XRD spectra of BaCe\(_{0.7}\)Zr\(_{0.1}\)Y\(_{0.05}\)Zn\(_{0.15}\)O\(_3\) at room temperature after sintering at 1200°C. The Rietveld analysis of the X-ray diffraction pattern confirmed the single phase perovskite structure for the sample of BaCe\(_{0.7}\)Zr\(_{0.1}\)Y\(_{0.05}\)Zn\(_{0.15}\)O\(_3\) in which the peaks are identical with the BCZYZ in the literature [18]. In this XRD pattern it is shown the observed, calculated, difference between the observed and calculated data and the Bragg positions respectively.

![Figure 1. Rietveld analysis profile of X-ray diffraction pattern of as-prepare BaCe\(_{0.7}\)Zr\(_{0.1}\)Y\(_{0.05}\)Zn\(_{0.15}\)O\(_3\) at room temperature.](image)
The structure of BaCe$_{0.7}$Zr$_{0.1}$Y$_{0.05}$Zn$_{0.15}$O$_3$ exhibits the orthorhombic structure with the space group Pbnm and this space group has been used finally in the data refinement process for generating the calculated diffraction profiles after justified with some other crystals structures and space groups.

The refinement parameters are listed in Table 1. Figure 2 shows the schematic 3D ball and stick diagram of the material.

![Figure 2. Schematic 3D ball and stick diagram of BaCe$_{0.7}$Zr$_{0.1}$Y$_{0.05}$Zn$_{0.15}$O$_3$.](image)

**Table 1.** Crystallographic information from Rietveld analysis of the XRD data.

| Quantity                  | Results                                                                 |
|---------------------------|-------------------------------------------------------------------------|
| Unit cell parameters (Å)  | $a = 6.098(9)$, $b = 6.102(7)$, $c = 8.666(3)$ and $\alpha = \beta = \gamma = 90^\circ$ |
| Space group               | Pbnm                                                                    |
| Atomic fractional coordinates | Ba (0.511, 0.0120, 0.250); Ce/Zr/Y/Zn (0, 0, 0); O1 (0.155, 0.156, 0.250) and O2 (0.582, 0.081, 0.0004) |
| Oxygen occupancy          | 98%                                                                     |
| R-factors (%)             | $R_p$: 11.4, $R_{wp}$: 16.1, $R_{exp}$: 7.64, Chi$^2$: 4.45            |

3.2. **Scanning Electron Microscopy (SEM)**

Figure 3 demonstrates the SEM of a) BaCe$_{0.7}$Zr$_{0.1}$Y$_{0.05}$Zn$_{0.15}$O$_3$ and b) the literature sample BCZY-Z within the magnifications indicated to the bottom of the pictures. The SEM micrograph of the fracture surfaces of our reported sample a) shows that the sample sintered at 1200$^\circ$C were dense sample without obvious pores and crakes.

![Figure 3.](image)

(a) (b)
From the SEM image 3 a) it is clear that the grain size of the pure BCZY had bimodal microstructures consisting of two sizes of grains; the larger grains and other smaller grains.

The sizes of the bigger grains are 0.7-0.8 μm and smaller 0.25-0.30 μm respectively. On zinc substitution the grain size was found to be uniform. The average grain size for ceria rich compositions was larger than that for Zr rich compositions. This indicates that the nature of dopant influences the overall grain size distribution. The larger grain size of the sample offers less overall grain boundary resistance. The smaller grain size of the sample gives high overall grain boundary resistance.

Figure 3 b) represents the cross-sectional micrograph of the fracture surfaces of BCZY-Z pellets after sintering 1320°C of literature [27] which stated that the SEM of the sample confirmed a high degree of compaction, was quite dense without obvious pores and crakes. But our reported sample sintered at 1200°C shows that it is highly dense without any pores and crakes.

3.3. Thermo gravimetric analysis (TGA)

In the Figure 4 we see two curves, the blue curve shows the heat flow versus temperature graph which indicates that the heat flow was almost constant through the rising and falling during the experiment and the red one is for the weight change versus temperature which is also explained separately in Figure 5. From the Figure 5 we observe that mass is gradually decreases during the heating process and almost unchanged during the cooling of BaCe$_{0.7}$Zr$_{0.1}$Y$_{0.05}$Zn$_{0.15}$O$_3$ under the argon gas environment.

The TGA measurement shows a two stages weight loss. In the case of argon, the initial weight loss takes place in between 100 and 200° C and the second weight loss was in between 300 and 900° C. The weight losses are related to the lattice oxygen loss from the structure. The loss of lattice oxygen at high temperature or in a reducing atmosphere provides oxygen vacancies for possible oxygen migration.

4. Conclusions

The X-ray diffraction pattern demonstrates that the BaCe$_{0.7}$Zr$_{0.1}$Y$_{0.05}$Zn$_{0.15}$O$_3$ perovskite prepared in the solid state ceramic method at a lower temperature comparative to other in literatures and are of single phase orthorhombic structure with Pbnm space group. The SEM profile picture of the specimen shows highly dense in nature which indicates that this sample can be the good electrolyte material as the proton conductor. The TG/DTA analysis of the sample indicates that the sample prepared in the solid state reactions successfully completed at this temperature which has been sintered.
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References
[1] Fabbri E, Pergolesi D and Traversa E 2010 Chem. Soc. Rev. 39 no. 11 4355–4369
[2] Duan C, Tong J, Shang M, Nikodemski S, Sanders M, Ricote S, Almansoori A and O’Hayre R 2015 Sci. 349 no. 1321–1326
[3] De Souza E C C and Muccillo R 2010 Mater. Res. 13 no. 6254 1321–1326
[4] Haugsrud R and Norby T 2006 Nat. Mater. 5 no. 3 193–196
[5] Karnik R N 2014 Nature 516 no. 7530 173–175
[6] Shi Z, Sun W and Liu W 2014 J. Power Sources 245 953–957
[7] Katahira K, Kohchi Y, Shimura T and Iwahara H 2000 Solid State Ionics 138 no. 1–2 91–98
[8] Azad A K and Irvine J T S 2008 Solid State Ionics 179 no. 19–20 678–682
[9] Kannan R, Singh K, Gill S, Fürstenhaupt T and Thangadurai V 2013 Sci. Rep. 3 2138
[10] Lv J, Wang L, Lei D, Guo H and Kumar R V 2009 J. Alloys Compd. 467 no. 1–2 376–382
[11] Azad A K and Irvine J T S 2007 Solid State Ionics 178 no. 7–10 635–640
[12] Sawant P, Varma S, Wani B N and Bharadwaj S R 2012 Int. J. Hydrogen Energy 37 no. 4 3848–3856
[13] Stevenson D A, Jiang N, Buchanan R M and Henn F E G 1993 Solid State Ionics 62 no. 3–4 279–285
[14] Azad A K, Kruth A and Irvine J T S 2014 Int. J. Hydrogen Energy 39 no. 24 12804–12811
[15] Azad A K, Setsoafia D D Y, Ming L C and Petra P M I 2015 Adv. Mater. Res. 1098 104–109
[16] Babili P and Haile S M 2005 J. Am. Ceram. Soc. 88 no. 9 2362–2368
[17] Tao S and Irvine J T S 2006 Adv. Mater. 18 no. 12 1581–1584
[18] Lu X, Ding Y and Chen Y 2009 J. Alloys Compd. 484 no. 1–2 856–859
[19] Bonanos N 2001 Solid State Ionics 145 no. 1–4 265–274
[20] Glöckner R, Islam M S and Norby T 1999 Solid State Ionics 122 no. 1–4 145–156
[21] Ahmed I, Knee C S, Karlsson M, Eriksson S G, Henry P F, Matic A, Engberg D and Börjesson L 2008 J. Alloys Compd. 450 no. 1–2 103–110
[22] Azad A K and Irvine J T S 2009 Chem. Mater. 21 no. 2 215–222
[23] Ahmed I, Karlsson M, Eriksson S G, Ahlberg E, Knee C S, Larsson K, Azad A K, Matic A and Börjesson L 2008 J. Am. Ceram. Soc. 91 no. 9 3039–3044
[24] Werner P E, Eriksson L and Westdah M 1985 J. Appl. Crystallogr. 18 367–370
[25] Lougier J and Bochu B Checkcell: Graphical Powder Diffraction Indexing Cell and Space Group Assignment Software.
[26] Rodriguez-Carvajal J 1993 Phys. B Condens. Matter. 192 no. 1–2 55–69
[27] Li Y, Guo R, Wang C, Liu Y, Shao Z, An J and Liu C 2013 Electrochim. Acta 95 95–101