

# Investigation on structural and electrical property of gadolinium doped barium cerate electrolyte for SOFCs

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Solid oxide fuel cells (SOFCs) have attracted a great deal of consideration among the promising fuel cell systems for energy conversion. In SOFC, electrolyte plays a vital role to increase the energy conversion efficiency. The main hurdle is its higher operating temperature (1000°C) which results in design limitation and higher fabrication cost. In this work, Gadolinium Doped barium cerate (BCG) composite electrolyte was successfully synthesized to operate at intermediate temperature (600–800°C) by co-precipitation technique. The structure of BCG was identified as orthorhombic perovskite and the crystallite size was found to be around 30 nm. From TEM, the particle size was found to be 32nm and is in good agreement with XRD results. Further, the particles sizes were found to be uniform in size and shape. From the above results it is understood that the obtained particle is a single crystallite which indicates the absence of agglomeration. The formations of BCG nanoparticles were resulted in reduced sintering temperature of the electrolyte. By lowering the sintering temperature, the barium loss was successfully reduced in order to get the required orthorhombic perovskite phase. The lower activation energy was found for BCG composite electrolyte, which can acts as a best electrolyte for at intermediate temperature applications.

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## 1. Introduction

Solid oxide fuel cells (SOFC) play an important role as a power sources invented for the direct conversion of chemical energy into electrical energy. SOFC systems provides environmental friendly nature with free from pollutions. In SOFCs, chemically stable electrolyte acts as the central component in the conversion of oxide ion by the process of reduction of oxidant at cathode and oxidation of fuel in the anode side. The yttrium stabilized zirconia has been considered as a state of art as oxide ion electrolytes which operates at higher temperature (800°C to 1000°C) for energy conversion with higher ionic conductivity and efficiency too [1]. This higher temperature operation may leads to several problems for fuel cells such as high materials cost, low performance of the fuel cell and thermal mismatch between the interconnects during fabrication. In order to overcome these problems, the operating temperature of the fuel cell must be reduced to intermediate temperature (500–700°C) by choosing the suitable electrolyte materials with high ionic conductivity [2,3]. The other oxygen ion conducting electrolytes are doped bismuth oxide, lanthanum galleite, doped ceria. Among this gadolinium doped barium cerate with perovskite structure of  $ABO_3$  group have been considered as a one of the good choice of candidate with high ionic conductivity for solid oxide fuel cell application due to the fast migration of oxide ions at lower operating temperature [4, 5, 6, 7, 18].

In the present research work gadolinium doped barium cerate electrolyte was prepared by wet chemical method. The compact disc shaped pellet was sintered using a modern microwave technique in less processing time to have higher ionic conductivity with less electronic conduction at intermediate operating temperature (500°C–700°C) [7,8]. The as prepared powder sample was characterized using DSC for identifying the calcination temperature, followed by calcination, the powder sample was studied through XRD analysis to identify the phase purity and subsequently pressed into pellet with 14.7 MPa for sintering at 1400°C in microwave furnace. Structural investigation was carried out with the help of SEM and HRTEM and the conductivity measurement was carried out using impedance analyzer and presented.

## 2. Experimental work

The Gadolinium doped barium cerate (BCG) powder was synthesized via chemical route (Co-precipitation technique). Barium nitrate (99.5% pure) purchased from Sigma-Aldrich, Italy and Cerium nitrate hexa hydrate (99.5%), Sigma-Aldrich, Italy were taken separately and get dissolved in 30 ml of distilled water. On the other hand, Gadolinium oxide (99.9%, Sigma-Aldrich, Italy) was dissolved in 5ml of Conc. Nitric acid by heating in a separate beaker and stirred well until the powder get completely dissolved into gadolinium nitrate. The

individual nitrate solutions were then slowly mixed together and added with Ammonium Hydroxide to precipitate out with  $\text{pH} > 10$  and continuously stirred well with 1000 rpm in a magnetic stirrer for about 30 minutes. PEG (Poly Ethylene Glycol of 10%) was added to the mixer as excipient (fillers) and to reduce the formation of agglomeration. The mixture was kept in a water bath for drying after stirring for 30 minutes. The obtained precipitant solution was filtered with watt man filter paper and again kept for drying in hot air oven at  $80^\circ\text{C}$  for about 8-9 hours [7,8, 9]. The flakes obtained from the mixture was then calcinated at  $900^\circ\text{C}$  for 4 hours to obtain the dry porous powder and named as BCG for further discussions. DSC studies was carried out with the help of TA Instruments to identify the calcination temperature and XRD study was carried out for the identification and determination of its phase, crystallinity and the purity of the as-prepared green powder.

Green pellets were obtained by uniaxial pressing at 14.7 MPa, using a steel die of 12 mm diameter. Polyvinyl alcohol (PVA) was added as a binder to the powder to increase the green strength of the pellet [7,8]. The prepared pellet was taken in alumina boat for sintering in microwave furnace at  $1400^\circ\text{C}$  for 20 minutes in air. The sintered pellet was then characterized using XRD, SEM, HRTEM, EDS and Impedance analysis.

### 3. Results and discussions

DSC curve (Fig. 1) shows that the BCG phase formation completed at  $900^\circ\text{C}$ , where the as prepared powder is crystallized into perovskite structure. From DSC curve it is to understood the up to  $400^\circ\text{C}$  there is a linear decrease in weight loss can be attributed as desorption of physisorbed (surface) water and organic solvent loss in the first region at  $102^\circ\text{C}$ . The sign of two sharp weight loss peak are observed at  $550^\circ\text{C}$  and  $760^\circ\text{C}$ . The first down peak may be due the combustion of residual organic species with 5.87% weight loss and the second plateau is due to the decomposition of barium carbonate with 1.68% weight loss, after which there is no sign of any loss from  $900^\circ\text{C}$  which indicates that the BCG phase completion of barium cerate electrolyte [9]. Based on this DSC analysis the calcination temperature was identified for the powder sample and further calcined at  $900^\circ\text{C}$  for 4 hours to get dry porous powder for further studies [18].

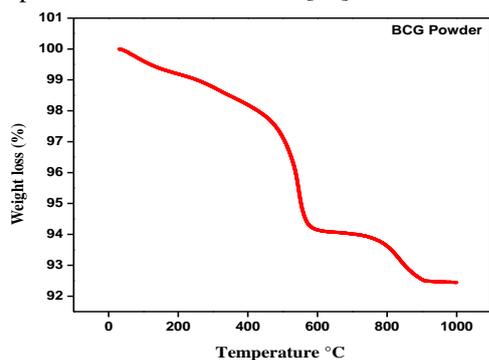


Fig. 1. DSC-TGA Curve for BCG calcined at  $900^\circ\text{C}$

XRD pattern for the as prepared BCG powder sample (a) calcined at  $900^\circ\text{C}$  and (b) pellet sintered at  $1400^\circ\text{C}$  have been shown in Fig. 2. All the major diffraction peaks are indexed accordingly for the calcined powder with orthorhombic perovskite structure and found to match with the JCPDS file No: 082-2373. In the XRD pattern of the calcined powder, some of the peaks values are not shown because of insufficient energy to form its phase and may be due to lower calcination temperature [6]. But in contrast XRD for the pellet shows all the major reflection peaks of orthorhombic perovskite structure. The phase was identified as orthorhombic perovskite structure for both powder and pellet. From the XRD pattern of calcined powder, it was clearly seen that the peaks are very sharp and highly intense in nature. This confirms the complete phase formation occurs at  $900^\circ\text{C}$ , the calcination temperature is much lesser than the earlier reported values and the sintering temperature have also been reduced from the earlier reported work [8] and is in well agreement with all results obtained [9]. The crystallite size of the BCG powder sample was calculated from Debye Scherer method using the equation (1) and the value found to be around 30 nm [10,11]

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

where  $D$  is crystallite size in nm,  $\lambda$  is the radiation wavelength (for  $\text{Cu K}\alpha$  radiation,  $\lambda = 1.5418 \text{ \AA}$ ),  $\theta$  is the diffraction peak angle and  $\beta$  is the peak broadening measured at half its maximum intensity (in radians). The crystallite size value was found to be nearly equal to the value reported earlier [12, 13, 18]

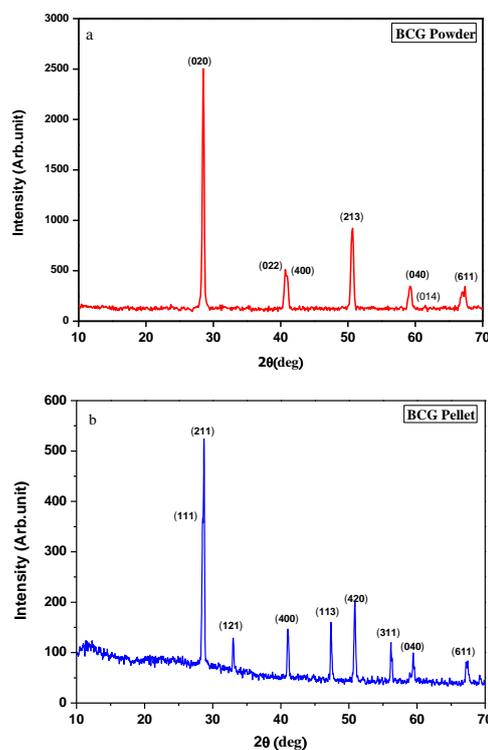


Fig. 2. XRD Pattern for BCG powder (a) Calcined at  $900^\circ\text{C}$  and (b) pellet sintered at  $1400^\circ\text{C}$

HRTEM image of the powder sample calcined at 900°C was shown in Fig. 3 and it was well observed that the particle size of BCG powder is very small in nature and found to be around 30nm. The crystalline nano particles are observed for the as prepared powder samples. The crystallite size from XRD is found to be much closer and in good agreement with this HRTEM results (Fig. 3b). The entire image shows the development of the spherical structured nano particles with high crystallinity [11, 18]

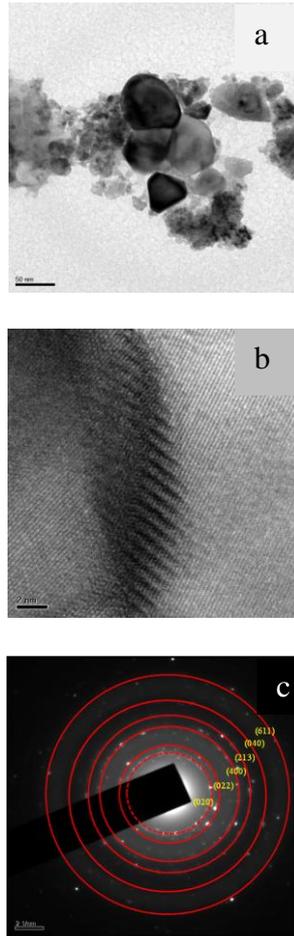


Fig. 3. High resolution TEM images (a) Particle size (b) Nano scale and (c) SAED pattern of BCG

SAED pattern depicts the formation of perovskite phase with all its major reflection peaks (Fig. 3c). The crystalline plane are indexed in SAED pattern and found to match exactly with XRD pattern with all major reflection peaks [14]. The Stoichiometric composition of Ba, Ce, Gd are identified qualitatively and confirmed through EDS analysis (Fig. 4). The solid solution prepared through co precipitation method leads to the complete precipitation of  $Gd^{3+}$  ions in  $BaCeO_3$  phase. The presence of Cu in EDS may be due to grid used in TEM analyzer [18].

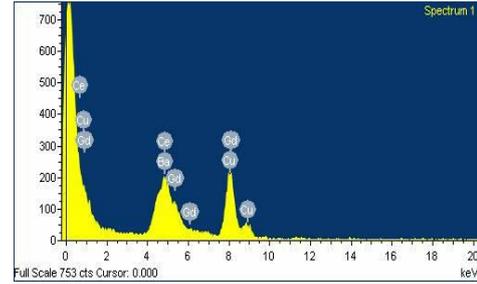


Fig. 4. Energy dispersion spectra of BCG powder calcined at 900 °C

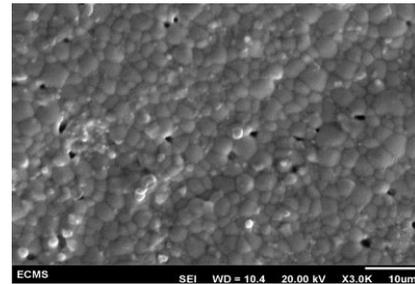


Fig. 5. SEM image for BCG pellet sintered at 1400 °C

The microstructural analysis of BCG was studied through SEM analysis. From this SEM results (Fig.5) the average grain size was found to be around 1 $\mu$ m. The sintered sample shows a well developed nano grains with less porosity and the formation of uniform grain size with closely packed at boundary which result in lower grain boundary resistance in the dense electrolyte and also to have high ionic conductivity. As reported from Venkatasubramanian et.al [8] the area of dark region increases with BCG phase mole fraction and are compared with XRD results. A very few enclosed pores are also absorbed on the surface of the pellet.

The electrochemical response for BCG composite electrolyte sintered at 1400°C was carried out through conductivity measurement. The real and imaginary parts from impedance spectra are calculated for the sample to obtain the Nyquist plots as shown in (Fig. 6). The DC conductivity of the electrolyte was calculated and found to be lesser than one order at 700°C compared with other BCG composite electrolyte sintered through conventional method.

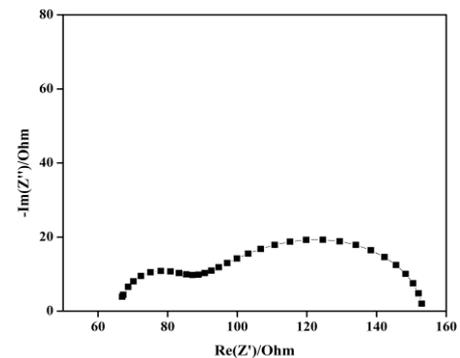


Fig. 6. Cole-Cole Plot for BCG

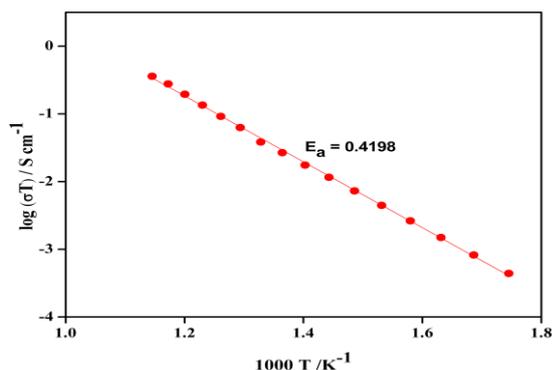


Fig. 7. Arrhenius plot for BCG

The ionic conductivity value for BCG electrolyte was found to increase while sintered through microwave technique, because of the existence of BCG grain in between the voids of grains with minimum barium loss. From the earlier reported values, it was understood that composite matrix phase present in the solid electrolyte can improve the ionic conduction through BCG Phase with minimum activation energy of 0.41eV and prevent the leakage current in doped ceria phase of the solid electrolyte.

The electrical conductivity measurement was taken subsequently in air using Novo control GmbH Alpha A high-resolution analyzer having Platinum electrodes with homemade sample holder for BCG, the high dense electrolyte from 300°C to 800°C and shown in the Arrhenius plot (Fig. 7). The activation energy value has been calculated from the linear fit of the curve for thermally activated conduction using equation (2).

$$\sigma T = A \exp\left(-\frac{E_a}{kT}\right) \quad (2)$$

Where  $E_a$  is the activation energy for conduction,  $T$  is absolute temperature and  $\sigma_0$  is a pre - exponential factor. The values are in well agreement with the values reported earlier [15]. The reduction in sintering temperature through microwave has increased the conduction phenomenon through grains in the solid electrolyte with decreased activation energy [16]. As studied in SEM results, a dense electrolyte with fine microstructure can give high ionic conductivity through interior grains [17].

#### 4. Conclusion

Gadolinium Doped barium cerate (BCG) composite powder was successfully synthesized by co-precipitation technique. BCG nanoparticles can acts as a best electrolyte for intermediate temperature (500–700°C) applications. The structure of BCG was identified and confirmed as orthorhombic perovskite phase with the average crystallite size of 30nm. HRTEM image shows the particle size to be around 32nm and in good agreement with XRD results. Further, the particles size was found to be uniform in size and shape.

The formation of single crystallite BCG nanoparticles indicates the absence of agglomeration at low sintering

temperature. The required orthorhombic perovskite phase was successfully retained at lower sintering temperature with reduced barium loss by means of microwave sintering. The electrical conductivity measurement value shows that the composite electrolyte with lower activation energy can give high ionic conductivity and hence, BCG nanocomposite electrolyte can act as a good candidate for solid oxide fuel cell application.

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