

# Microwave and conventional sintering of gadolinium doped barium cerate: a comparative study

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Ceria based solid electrolyte have been successfully synthesized by solid state route. Precursor powder was milled for 6h, 8h, 12h using ball milling technique with the help of zirconia ball. The calcination was carried out at 600°C to form the required phase formation and confirmed from XRD results. Sintering was carried out at two different techniques such as microwave and conventional sintering for the prepared samples. The results were compared with XRD, SEM and electrical conductivity measurements and reported.

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## 1. Introduction:

Solid oxide fuel cell technology has become one of the most powerful sources for future electrical power generation which can convert chemical energy of fuel into electrical energy with higher efficiency and gives out low environmental pollution [1]. Usually SOFC are operated at higher temperature with hard ceramic materials. Traditional YSZ have been studied as one of the most promising electrolyte material for high temperature operation, because of its higher oxygen ion conductivity. This high temperature operation may lead to thermal variance between the electrodes and electrolyte, mechanical instability of the materials which results in failure of SOFC's lifetime [2]. In order to overcome these problems the operating temperature of electrolyte must be reduced to lower operating temperature called intermediate temperature (500-800°C) [3,4]. This could be achieved or done by doping the aliovalent cations with CeO<sub>2</sub> or by reducing the particle size to nanometre range which acts as the driving force for sintering [5].

When compared with YSZ, doped ceria with Gd or Sm is to be considered as one of the mostly studied electrolyte for SOFC application to get high ionic conductivity at relatively low operating temperature [6,7,8]. From the discussions of earlier researchers, this doped ceria gives higher oxygen ion conductivity even at 800°C when compared with the value of YSZ at 1000°C [9,10,11]. Gadolinium doped barium cerate electrolyte have also attracted its choices with higher ionic conductivity under reduced atmosphere below 650°C to meet the commercial requirement of IT SOFC [12,13,14].

Present work is aimed to prepare the barium cerate electrolyte and compare its results by means of two sintering techniques such as conventional sintering and microwave sintering respectively. Solid state method, a cost effective and simple method have been chosen and adopted to prepare the powder sample with its required phase

formation at low temperature having high oxygen ion conductivity with lower electronic conduction [13]. In addition to these solid state method various synthesis and processing methods have been investigated and reported such as precipitation method [6], polyol method [9], hydrothermal [15, 16, 17], mechanochemical [18], pechini method [19], and gel-casting process [20]. Among all these methods, sintering aids is not discussed and compared by means of any parameters. So the outcome of the results for this barium cerate electrolyte will give the comparable statement and were examined from the XRD, SEM and impedance analysis.

## 2. Experimental method:

### 2.1 Samples preparation and characterization

The Gadolinium doped barium cerate powder has been synthesized by means of solid state route. Stoichiometric amount of BaCO<sub>3</sub> (99.95%, Alfa Aesar, USA), CeO<sub>2</sub> (99.9%, Sigma Aldrich, USA) and Gd<sub>2</sub>O<sub>3</sub> (99.9%, Alfa Aesar, USA) were ball milled in Zirconia containers with ethyl alcohol for 6hrs. YSZ balls were used as grinding medium. The milled powders were dried in a hot air oven at 120°C for 1h, ground in an agate mortar and calcined at 1200°C for 6 h, followed by this calcination the precursor powder were divided into three equal units and the each samples were then undergone 6, 12 and 18hrs of ball milling respectively. Green pellets were obtained by uniaxial pressing at 100 MPa, using a steel die of 12 mm diameter. Polyvinyl alcohol (PVA) was added as a binder to increase the green strength of the pellets and to avoid agglomeration during synthesis [21, 22]. The pellets were densified at 1550°C for 8 h in air by conventional sintering and 20 min in microwave sintering. In both the case sintering was carried out at a controlled heating and cooling rate of 5°C min<sup>-1</sup>. After sintering, the surface in contact with

alumina plate was polished with 400 grit silicon carbide (SiC) paper to remove the interfacial reaction products.

The different mole fraction of  $Ba_xO$  ( $x=0.1, 0.2, 0.3, 0.4$  mol) in Gadolinium Doped Ceria in which 0.8 mol fraction of Cerium Oxide and 0.2 mol fraction of Gadolinium oxide ( $0.8CeO_2 - 0.2GdO_{1.5}$ ) were studied and the maximum density was achieved for the composition having 0.2 mol fraction of BaO and named as BCG20 for further discussion. Hence, this composition is chosen for the present study and compared with microwave sintered BCG20 at  $1550^\circ C$  for 20 min. Powders after calcinations as well as the sintered samples were characterized by XRD technique using a PW 1729 X-ray diffractometer. Sintered samples were polished and cleaned with acetone. Thermal etching of polished samples was carried out at  $1350^\circ C$  for 4 h. Samples were coated with carbon to prevent charge accumulation during SEM studies. Hitachi S3400N SEM was used for obtaining Secondary Electron (SE) images. Frequency dependent AC conductivity of composite electrolyte was measured from 1 to  $10^5$  Hz and the temperature range of 500 to  $800^\circ C$  and reported.

### 3. Results and discussion

#### 3.1 Phase analysis

XRD patterns of calcined powder of BCG20, conventionally sintered BCG20 and microwave sintered BCG20 were shown in Fig. 1. The diffraction patterns clearly show the existence of two phases in all the samples [23]. One phase matches with Fluorite GDC (JCPDS Reference code: 01-075-0162) and other one matches with Orthorhombic Perovskite BCG (JCPDS Reference code: 01-082-2373) [24].

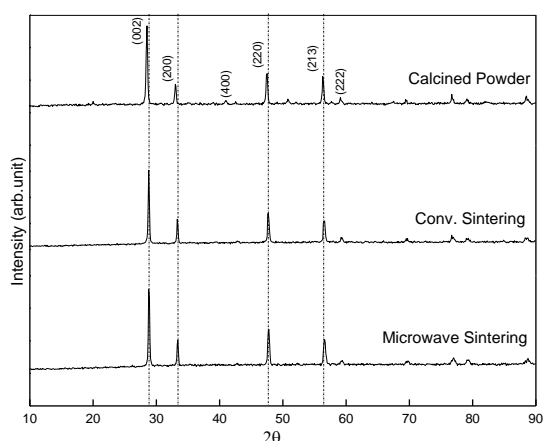


Fig. 1. XRD patterns for calcined, microwave sintered and conventionally sintered BCG sample.

Lattice parameters for both the phases of all the samples are shown in Table 1. The table clearly indicates that there is no significant difference in lattice parameters between conventional and microwave sintered BCG20.

Lattice parameter is increased with dopant concentration to 0.2 mole fraction confirms the dissolution of gadolinium oxide in fluorite structure of cerium oxide [25]. The lattice constants for both BCG20 samples were calculated and found to be in match with lattice constants as reported in the work of A. Venkatasubramanian et al [23].

Table 1. Lattice parameters of BCG20.

Samples	BCG20 Phase			GDC Phase
	a/Å	b/Å	c/Å	c/Å
BCG - Calcined	8.761	6.242	6.211	5.391
BCG-Conv. Sintered	8.798	6.232	6.208	5.420
BCG-Microwave Sintered	8.801	6.230	6.206	5.422

#### 3.2 Microstructural analysis

Scanning electron microscopy was taken for microwave sintered BCG20 and conventionally sintered BCG20 to observe the morphological features and elemental distribution [9]. SE images do not show such a contrast, indicating contrast arises due to mean atomic number of elements present in the grain.

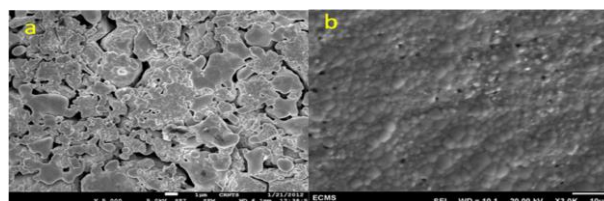


Fig. 2. SEM micrograph for (a) microwave sintered BCG and (b) Conventionally sintered BCG.

Elemental Dispersive spectrum (EDS) analysis (Fig. 2) shows the presence of elements Ce, Gd and O in certain regions and elements Ba, Ce, Gd and O in certain regions of both the samples. Further, Ba concentration observed in conventionally sintered BCG20 is very small when compared to microwave sintered BCG20. The loss is because of evaporation of barium content when it is taken for prolonged heating. On the other hand, microwave sintered BCG suffocates high porosity that may hinder the motion of the anion.

#### 3.3 Electrical measurements

Frequency dependent conductivity spectra obtained for conventional and microwave sintered BCG20 composite electrolytes at various temperatures is shown in Fig. 3. The frequency dependent conductivity plots show independent plateau region at all the measured frequency range. The high frequency dispersion is predominant at lower temperatures and with increase in temperature it shifts

towards the high frequency region (not shown). The high frequency dispersion region disappears at higher temperatures, since the hopping frequency of the charge carriers increases with temperature. The dc plateau and the extended conductivity dispersion at higher frequencies usually follow Jonschers power law:

$$\sigma(\omega) = \sigma_0 + A\omega^n$$

where,  $\sigma(\omega)$  is the conductivity at a particular frequency,  $\sigma_0$  the dc conductivity of the sample at zero frequency,  $A$  and  $n$  are weakly temperature dependent parameters and  $n$  is the power law exponent that varies from zero to one ( $0 < n < 1$ ). The DC conductivity obtained for microwave and conventionally sintered BCG at 800°C are  $1 \times 10^{-2}$  S/cm and  $3 \times 10^{-2}$  S/cm, respectively.

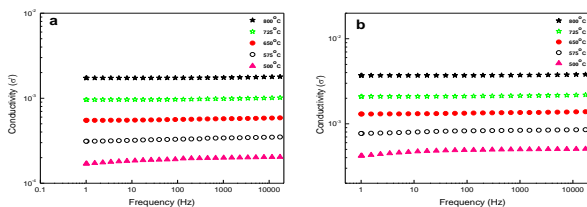


Fig. 3. Frequency dependent conductivity for (a) microwave and (b) Conventionally sintered BCG sample.

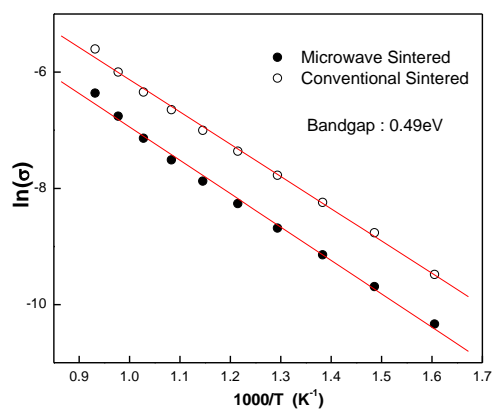


Fig. 4. Arrhenius plot for (a) microwave and (b) Conventionally sintered BCG sample.

The variation with temperature of the dc conductivity (obtained from the Jonschers power law) of the composite electrolytes are shown in the Arrhenius plot of Fig. 4. The activation energy of the ions is determined from the Arrhenius equation:

$$\sigma = \sigma_0 \exp(-E_a/KT)$$

The activation energy of both the composites is found to be 0.49 eV.

## 4. Conclusions

Gadolinium doped Barium cerate electrolyte have been successfully prepared by Solid state method. Both conventional and microwave sintered BCG20 shows two phase system and are in excellent agreement. Lattice parameter was found increased with increase in barium dopant concentration. Loss of barium content is observed in conventional sintering due to higher soaking time at 1500°C. Porous morphology was observed in microwave sintered BCG micro structure. The DC conductivity of the conventionally sintered BCG exhibits three times higher than the microwave sintered BCG at 800°C. The activation energy of both the composites holds the similar value. Hence BCG can acts as a good electrolyte material for solid oxide fuel cell applications.

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