

Accepted Manuscript

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PII: S0254-0584(16)30598-3

DOI: [10.1016/j.matchemphys.2016.07.066](https://doi.org/10.1016/j.matchemphys.2016.07.066)

Reference: MAC 19090

To appear in: *Materials Chemistry and Physics*

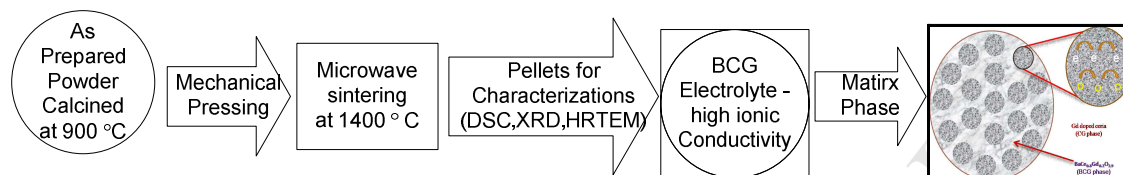
Received Date: 12 January 2016

Revised Date: 9 July 2016

Accepted Date: 31 July 2016

Please cite this article as: A.S. Kumar, R. Balaji, S. Jayakumar, C. Pradeep, Microwave assisted sintering of gadolinium doped barium cerate electrolyte for intermediate temperature solid oxide fuel cells, *Materials Chemistry and Physics* (2016), doi: 10.1016/j.matchemphys.2016.07.066.

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Graphical Abstract:

**MICROWAVE ASSISTED SINTERING OF GADOLINIUM DOPED BARIUM
CERATE ELECTROLYTE FOR INTERMEDIATE TEMPERATURE
SOLID OXIDE FUEL CELLS**

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Abstract:

In Solid Oxide Fuel Cell, 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. The calcination temperature for the as-prepared powder was identified using Differential Scanning Calorimetry. The crystal structure of the sample was found to exhibit its orthorhombic perovskite structure. The particle size was determined using High-Resolution Transmission Electron Microscope with uniform in shape and size, match with XRD results and confirmed from structural analysis. Thus, the sample prepared via co-precipitation and the electrolyte sintered through microwave can be a promising one for fuel cells operated at lower temperature.

Keywords: Co-Precipitation, composite materials, nanostructures, Microwave processing, Solid Oxide Fuel cells

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1. INTRODUCTION:

Solid oxide fuel cells (SOFCs) have attracted a great deal of consideration among the promising systems for electrical power generation [1], high efficiency energy conversion [2] and friendly environment nature.[3] The most commonly studied electrolyte material with high ionic conductivity was yttrium-stabilized zirconia (8%YSZ), a polycrystalline ceramic added with zirconia as dopant exhibited good stability in both oxidizing and reducing atmospheres. However, YSZ electrolyte supported solid oxide fuel cells have shown higher ionic conductivity at higher operating temperature and faced a lot of problems during elevated temperature operation such as thermal degradation, thermal expansion mismatch between the interconnectors and interfacial reaction between the electrodes-electrolyte were became a great deal of challenge for such electrolyte material used in the fuel cell for energy conversion [4].In order to overcome those problems, the operating temperature of fuel cell much be reduced below 800°C and to achieve the total conductivity of 0.1 Scm^{-1} . By reducing the operating temperature will ultimately improve the stability performance of the electrolyte materials and the interconnecting ceramic materials can be replaced by stainless steel, a cost effective one to avoid corrosion for fuel cell environment. Hence, it became an essential need to show the sturdy impetus to develop the suitable oxide ion conducting electrolyte for the solid oxide fuel cells operated at intermediate temperature (400°C- 700°C) [5]. Cerium oxide (CeO_2) doped with aliovalent cation was considered as one of the most studied material with the cubic fluorite structure of Fm3m space group and have shown high ionic conductivity when compared with YSZ at 1000°C [6]. But these ceria systems are not been considered as the best electrolyte for lower temperature operation because the undoped ceria system have no defects formation in their crystal structure and the creation of oxygen vacancies are very negligible. Whereas, doped ceria with aliovalent cations like Gd^{3+} and Sm^{3+} ions, creates the oxygen vacancies which aggressively increases the ionic conductivity of doped ceria systems for intermediate temperature operation [7,8,9,10]. However, at lower oxygen partial pressure this doped ceria will undergo the reduction process of cerium from Ce^{4+} ions to Ce^{3+} ions, leads to undesired electronic conduction [11]. To achieve high ionic and lower electronic conductivity, it is necessary to go for composite materials. In composites, one phase will increase the ionic conductivity and another phase suppresses the electronic conductivity. Hence a strong motivation is required to develop the composite electrolyte for reducing the reduction mechanism by suppressing the electronic conduction through one phase of a solid electrolyte and to improve the migration of oxide ions through the other phase in the composite matrix, favors mixed ionic conduction (H^+ , O_2^-) may result in higher open cell voltage for fuel cells [12,27].

Ceria as well as barium cerate based electrolytes were usually prepared by using its water soluble salts, such as oxalates, nitrates, and acetates. These doped ceria based electrolytes samples was processed and synthesized by different techniques such as spin coating method [2], conventional solid-state method[9],pechini method[10],carbonate co-precipitation[14],citrate

complexation method[15], precipitation[16], oxalic co-precipitation [17], freeze drying [18], combustion [19] gel-casting process [20], hydrothermal method [21] co-precipitation [22] and glycine-nitrate process [23] as reported in the literatures, particularly on Gd^{3+} ion doped ceria system. Among the various methods of research groups, a very little work have been carried out to prepare barium cerate electrolyte through wet chemical route and the microwave assistance for reducing the sintering temperature of solid electrolyte was not studied in detail so far. In order to synthesis composite electrolyte, a chemical route is followed to achieve nanoparticles of BCG-CG matrix phases with less agglomeration. The nanosized particle helps to uniformly distribute the individual phase. Otherwise, a channel of single phase may form and affects the ionic conductivity and increases the electronic conduction in the composite electrolyte [24]. The composite electrolyte prepared through solid state method leads to segregation of phases which subsequently results in increasing the electronic conductivity and decreases the OCV of the fuel cells. So the chemical route was followed to synthesis composite electrolyte [1,24]. In addition, the wet chemical method has been considered as one of the well established and widely adopted synthesis techniques of low cost and has more promising advantages in preparing the well-defined nanoparticles for good densification of solid ceramics [15].

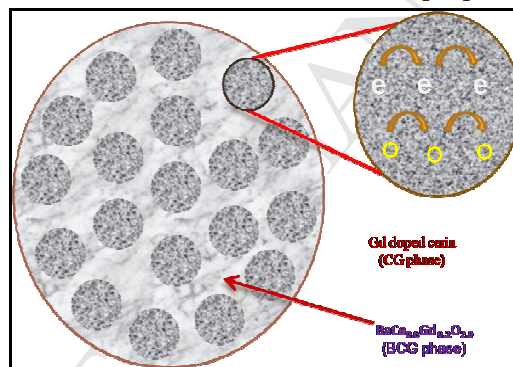


Figure.1.CG-BCG Composite Matrix Phase Prediction.

Microwave sintering method was adopted to reduce the sintering temperature of electrolyte and to prevent the phase segregation in composites matrix effectively by heating the solid electrolyte very rapidly. The development of matrix phase in composite will acts as a productive (or) blocking layer to suppress the electronic conductivity in CG phase and increase ionic conduction in BCG phase as shown in Figure.1. The necessity for fast sintering of the pellets is to reduce the evaporation of Barium content from the composition of the electrolyte at high temperature and to avoid the barium loss, the sintering process is carried out using microwave furnace at a heating rate of $45^{\circ}\text{C}/\text{min}$ and soaking time of 20 minutes at 1400°C . In microwave sintering (MS), the material gets heated directly due to energy conversion process taking place at the molecular level [25,26]. The transformation the heat energy to the materials is mainly due to the interaction of electromagnetic wave taking place very rapidly, results in the reduction of sintering temperature of electrolyte and decreases the energy consumption significantly. Whereas, in conventional sintering the energy transferred from heating element of the furnace to

the sample surface and the longer soaking time of the electrolyte may lead to the formation of cracks on the surface of the solid electrolyte [26]. Chemical stability of electrolyte in CO_2 atmosphere and mechanical strength of solid ceramic can be improved by increasing the formation of matrix phase in composite for fuel cell operated at lower temperature [27]. Moreover, barium cerate composites have attracted its choices as an electrolyte with increased ionic conductivity at a higher operating temperature and therefore it is very crucial need to reduce the operating temperature of barium cerate based electrolyte operated at the intermediate temperature for SOFC application. [13,14].

Hence, the objective of the present work is to prepare gadolinium doped barium cerate powder by means of co-precipitation technique and to develop the composite matrix by sintering the solid electrolyte very rapidly through microwave sintering technique. The as-prepared powder was calcined and pellets were sintered using microwave furnace followed by its characterization using DSC, TG-DTA, XRD and HRTEM techniques and results were presented.

2. EXPERIMENTAL WORK:

2.1 Powder synthesis:

The Gadolinium doped barium cerate (BCG) powder has been synthesized via chemical route (Co-precipitation technique). Barium nitrate (99.5% pure) purchased from Sigma–Aldrich, Italy) and Cerium nitrate hexahydrate (99.5%), Sigma–Aldrich, Italy) were taken separately and get dissolved in distilled water. Gadolinium oxide (99.9%, Sigma–Aldrich, Italy) was dissolved in conc. nitric acid by heating in a separate beaker and stirred well until the powder gets completely dissolved. These two solutions were then slowly mixed together and then added with PEG (Poly Ethylene Glycol) acts as excipient (fillers) to the mixture. Ammonium Hydroxide was added gradually in to the mixture to maintain the pH >10 and the precipitant was kept in a beaker for 24hr aging, followed by drying in hot air oven at 90°C for about 8-9 hours [28, 29]. The flakes obtained from the mixture were calcined at 300°C and 600°C for 4 hours to obtain the dry powder. DSC was carried out with the help of TA Instruments for its phase confirmation and XRD using a PW 1729 X-ray diffractometer for determining the crystallinity and the purity of the as-prepared dry powder.

2.2 Pellet Preparation:

Green pellets were obtained by uniaxial pressing the as-prepared powder at 14.7 MPa, using a steel die of 12 mm diameter. Polyvinyl alcohol (PVA) was added with the precursor powder as a binder to increase the green strength of the pellets for good compaction [1] and the percentage of PVA addition was limited to 3% to avoid cracks and to have proper bonding with oxide ions during microwave sintering [26,29]. The pressed pellets were taken in alumina boat for fast sintering using microwave furnace at 1400°C for 20 minutes in air with the heating rate of 45°C per minutes to form a dense pellet and to reduce the loss of barium content [30]. When

compared with the earlier work reported by venkat.etal [1], sintering temperature of the pressed pellets was reduced from 1550°C to 1400°C by means of microwave heating in the less soaking time of 20 minutes. The pellets Ba10CG and BCG15 were prepared with the following chemical compositions (Table-1) and further undergone characterization.

Sample	BaO (mol fraction)	CeO ₂ (mol fraction)	GdO _{1.5} (mol fraction)
Ba10CG	0.10	0.80	0.20
BCG15	1.00	0.85	0.15

Table 1: Chemical compositions ratios for BCG15 and Ba10CG samples.

2.3 Density measurement:

The relative density of Ba10CG and BCG15 samples sintered through microwave furnace were measured using Archimedes principle by liquid displacement method. Higher densification of 93% was observed for BCG15 pellet sintered at 1400°C reveals that the complete precipitation of gadolinium in ceria lattice with the formation of perovskite structure, whereas Ba10CG have shown 89% of densification with minimum porosity (figure not shown).

3. RESULTS AND DISCUSSIONS:

3.1. Thermal Analysis - DSC Analysis:

DSC phase analysis was carried out with the help of TA Instruments for Ba10CG electrolyte for the temperature range from 30 °C to 450°C at a constant heating rate of 5°C per min. The analysis was carried out twice for the same sample and the second run patterns are shown in Figure.2. In the first run, multiple broad peaks accompanied by a sharp exothermic and endothermic peak were observed at different temperatures specifically below 280°C. The presence of sharp exothermic peak may be due to the decomposition of the organic component such as ethylene glycol and the broad endothermic peaks were due to the continuous evaporation of organic compound. The sharp endothermic peak was observed at 270°C with a change in enthalpy of 4.85 J/g, it was attributed to the formation of GDC phase in which gadolinia is fully dissolved into the ceria fluorite structure. [22,23].

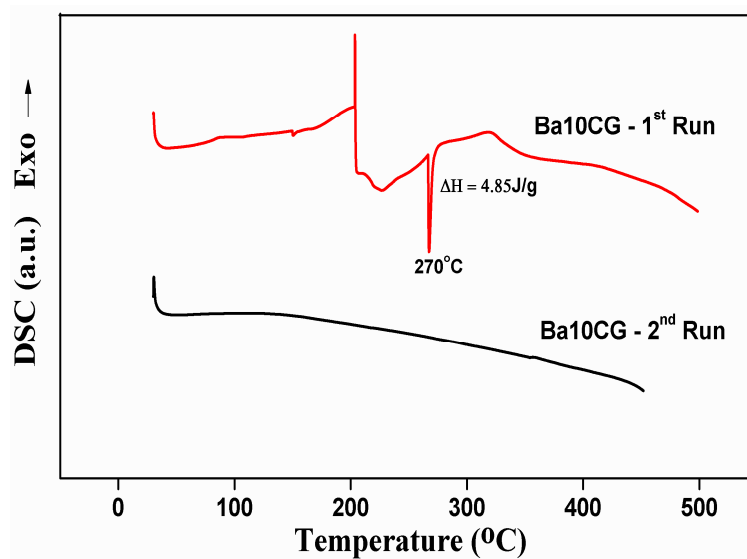


Figure.2. DSC patterns for Ba10CG powder sample.

Noteworthy to understand that the complete phase formation was identified within the five-degree interval, even though the heating rate was kept at 5°C per min. For the same sample, a second run was carried out to confirm the completion of phase formation. As expected, the pattern exhibits no sign of peak except the slight drift in the baseline. Based on this DSC results, calcination temperature was identified and further works were carried out for all the samples at 300°C for a period of 4 hrs using a programmable high-temperature furnace at a heating rate of 10°C per min.

3.2. TG/DTA Analysis:

The collective Thermal analyses (Differential Scanning Calorimetry-DSC and Thermogravimetric Analysis-TGA) were carried for all barium doped GDC powders to determine most favorable sintering parameters. The DSC/TGA thermogram were recorded using the module DSC-TGA Standard instruments (SDT Q600 V8.3 Build 101) under a nitrogen atmosphere at an invariable heating rate of 10°C per minute from room temperature to 1005°C. DSC curves have been drawn to study the percentage of barium loss in both the samples as shown in Figure.3. The sign of major three peaks corresponding to the change in energy and weight loss in the precursor has been observed. The first exothermic peak for desorption of physisorbed (surface) water and organic solvent loss were observed in the first region at 102°C. The second endothermic peak region from 481°C to 550°C reveals the combustion of residual organic species. In the third stage of an exothermic region where barium carbonate which gets decomposed at the temperature ranging from 550°C to 800°C after which, there's no weight loss observed, which indicates the formation of the single phase.

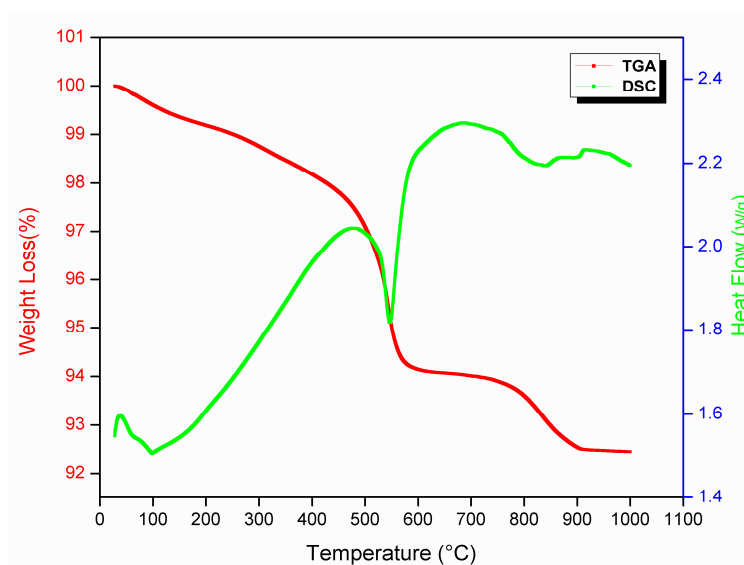


Figure.3. TG/DTA for Ba10CG sample.

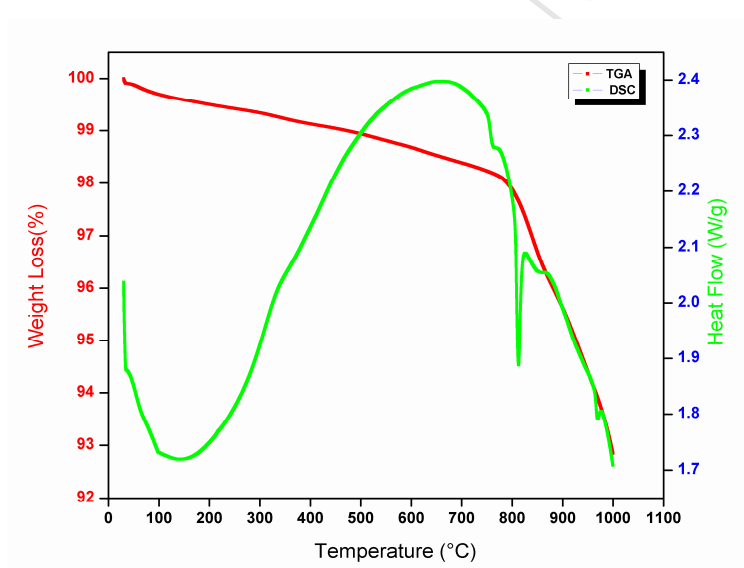


Figure.4. TG/DTA for BCG15 sample.

Figure.4. shows DSC curves for BCG15 sample sintered at 1400°C. Sign of three major peaks was observed. First exothermic peaks at 105°C reveals that all the water content in the sample were get observed and the organic species were get evaporated. The second endothermic region one started at 812°C shows that the combustion organic species takes place. Decomposition of barium carbonate saturated at 812°C and get completed at 825°C, which shows that the formation of the single phase in the samples with no weight loss. Therefore, from

this thermal analysis, reveals that the single phase formation was observed for both the samples. The phase formation for the powder sample is further verified by XRD analysis.

3.3. XRD Studies for Powder samples:

Structural analysis was carried out using a PW 1729 X-ray diffractometer to obtain XRD pattern for the as-prepared powder samples such as Ba10CG and BCG15. XRD pattern for Ba10CG powder calcined at 300°C, BCG15 calcined at 300 °C and 600°C were shown in Figure.5. The diffraction pattern for Ba10CG is in excellent agreement with that of Gd-doped Ceria in JCPDS Reference code: 01-075-0162 and the crystal structure of Ba10CG belongs to fluorite family. The peaks are identified and indexed accordingly. The XRD study for Ba10CG clearly shows that the planes are highly oriented in (111) plane due to the loss of barium content in GDC phase [1]. As mentioned in DSC studies, XRD analysis confirmed the phase formation at 300°C. Hence, the sharp endothermic peak obtained in DSC pattern was due to the formation of Gd-doped ceria phase [29]. From both the study, it is understood that 4.85J/g of heat energy is required to form a GDC phase. On the other hand, the same calcination temperature i.e. 300°C was not sufficient for the BCG15 to form the required perovskite phase, evident in XRD pattern. Hence the calcination temperature for BCG15 was increased to 600°C [8, 16]. At this temperature, the phase was completely formed and also in excellent agreement with the JCPDS (ref no: 082-2373) [1].

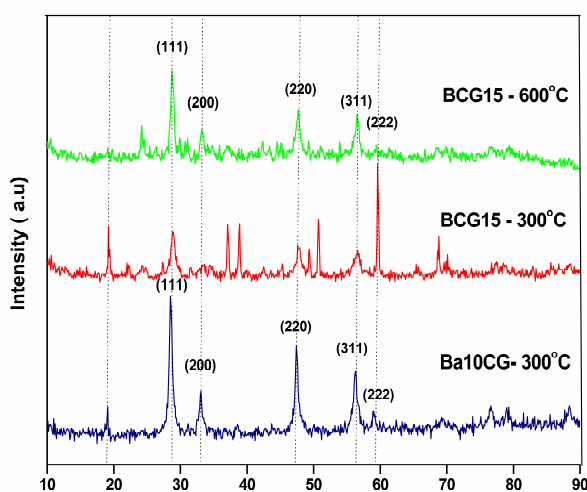


Figure. 5. XRD pattern for Ba10CG, BCG15 calcined at 300 °C and 600 °C.

In contrast, orthorhombic perovskite phase was not observed in both Ba10CG and BCG15. The orthorhombic phase was highly expected in BCG15 because of 50 mol% of barium oxide was added along with Gadolinium oxide and Cerium oxide. Interestingly, most of the strong peaks of barium cerate plunge in the position of GDC. The absence of orthorhombic phase may be due to the insufficient amount of energy and lower calcination temperature for Ba10CG

and BCG15. The crystallite sizes for both the samples were calculated from equation (1) with 2θ value from XRD main reflection (111) plane using Scherer's formula [31].

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

where D is crystallite size in nm, λ is the radiation wavelength (for Cu $K\alpha$ radiation, $\lambda = 1.5406 \text{ \AA}$), θ is the diffraction peak angle and β is the broadening of the line ("half width") measured at half its maximum intensity (in radians). The particle size of the Ba10CG and BCG15 were calculated to be around 10 to 15 nm which is nearly equal to the value reported earlier [22, 29, 32]

3.4 XRD studies for sintered pellets:

XRD pattern for Ba10CG and BCG15 pellets sintered at 1400°C for 20 minutes in air with the programmed heating rate of 45°C per minute and cooling rate of 10°C per minute using the microwave furnace were shown Figure.6. It was noted that sintering temperature for the pellets was found to be reduced from 1550°C to 1400°C , the work carried out by Venkat.etal [1] and diffraction patterns of Ba10CG and BCG15 match with that of fluorite (JCPDS reference code: 01-075-0162) and orthorhombic perovskite structure (JCPDS reference code: 01-082-2373) respectively[29].

The diffraction pattern clearly shows that the formation of two-phase matrix in the sintered samples using microwave furnace. One phase matches with Fluorite, $\text{Ce}_x\text{Gd}_{(1-x)}\text{O}_{2(x/2)}$ (GDC) and other one matches with orthorhombic Perovskite $\text{BaCe}_y\text{Gd}_{(1-y)}\text{O}_{3(y/2)}$ (BCG) [1]. The two major advantage of these CG-BCG phases are the enhancement of ionic conductivity at gadolinium doped barium cerate phase (BCG phase) and decrease in electronic conduction at gadolinium doped ceria phase (GDC phase) as predicted in figure.1 [26,27].

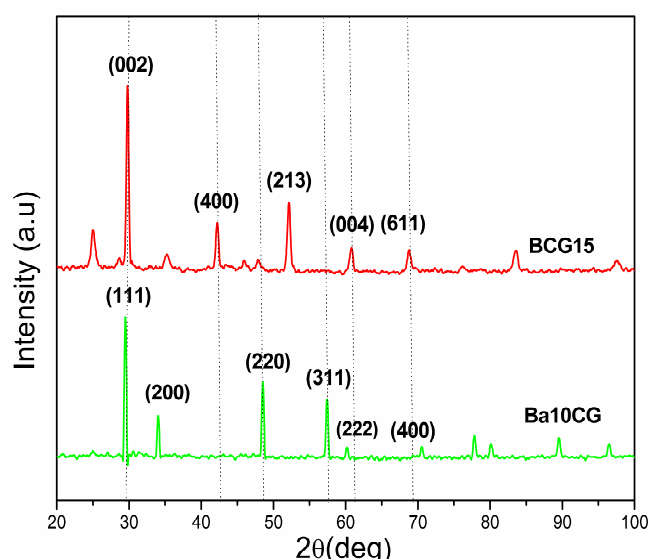


Figure.6. XRD patterns for Ba10CG and BCG15 sintered pellets at 1400°C .

Table.2 shows the lattice constants for the different composition of the prepared samples. The lattice constant for BCG15 and Ba10CG samples were calculated and found to be in the match with lattice constants as reported in the work of A. Venkata Subramanian.et.al [1].

Sample	a(Å)	b(Å)	c(Å)
BCG15	8.576	4.3908	6.004
Ba10CG	5.273	--	--

Table 2: Lattice constants for BCG15 and Ba10CG samples.

3.5. HRTEM Studies:

The HRTEM images of as-synthesized Ba10CG and BCG15 nanoparticles shows typical degrees of agglomeration and poly disparity [33] obtained through co-precipitation process were shown in Figure.7a and Figure.8a. Typical nanoparticles are agglomerates of several primary particles. The agglomerates are termed as secondary particles. They formed when primary particles are held together by weak surfaces forces (soft agglomerates) such as van der Waals or capillary forces or by strong chemical bonds (hard agglomerates). The approximate particle size obtained for both Ba10CG and BCG15 are around 50nm. However, the calculated crystallite size from XRD is around 15nm for both the compositions as reported earlier [22,29]. The correlation between size obtained by XRD and TEM are due to the fact that the XRD size usually equals or smaller than the size obtained by TEM analysis. When the particles are delineated by well-defined boundary or loose nano particles of ceramic materials, XRD and TEM values are in good agreement with each other. On the other hand, in nanocrystalline materials, the term grain is used interchangeably with crystallite to refer to the smallest single-phase and crystallized regions separated by grain boundaries [23].

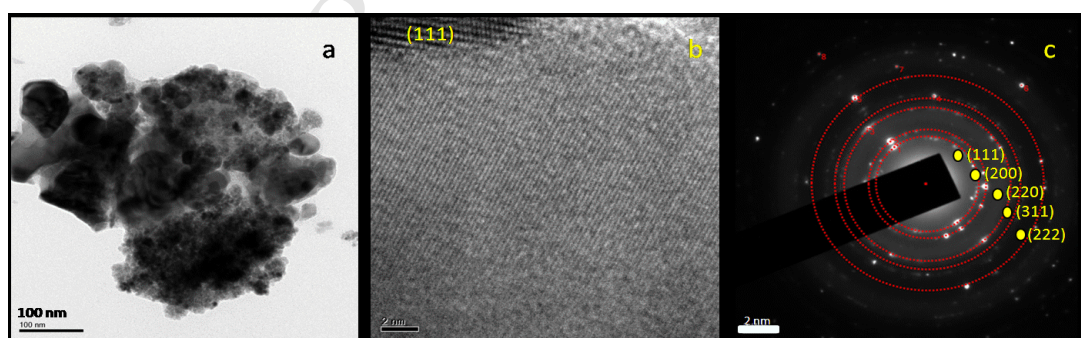


Figure.7.High resolution TEM images (a) Particle size (b) Nano scale and (c) SAED pattern of Ba10CG.

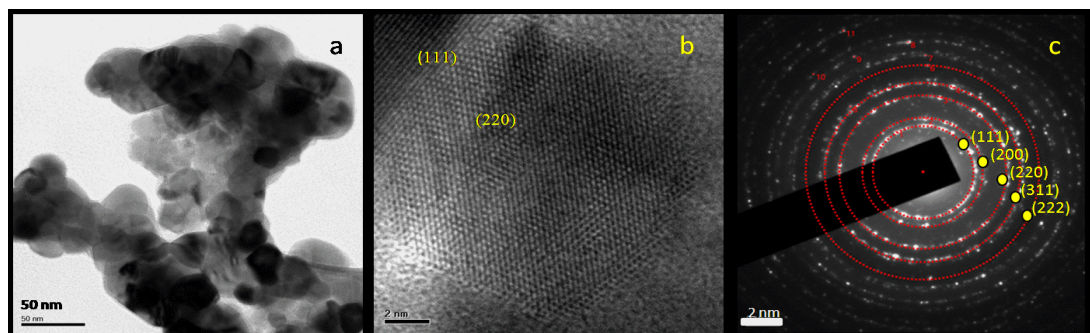


Figure.8. High resolution TEM images (a) Particle size (b) Nano scale and SAED pattern of BCG15.

Figure.7b and Figure.8b show atomic resolution images of Ba10CG and BCG15 recorded using The JEOL JEM 2100 High-Resolution Transmission Electron Microscope (HRTEM). The arrangements of atoms can be clearly seen in both the images. A further insight can be obtained by image processing of HRTEM images to obtain d spacing. The corresponding plane for the obtained d-spacing was shown in respective images. Figure.7c and Figure.8c shows the SAED pattern for Ba10CG and BCG15, respectively confirm the presence of crystalline nanoparticles [15, 16]. The lattice parameters have been calculated and indexed from SAED patterns accordingly and are in excellent agreement with XRD pattern.

The Energy dispersive spectrum (EDS) of Ba10CG and BCG15 samples were shown in Figure.9. The spectrum analysis the weight and atomic percentage of all the elements present in the compound [34].

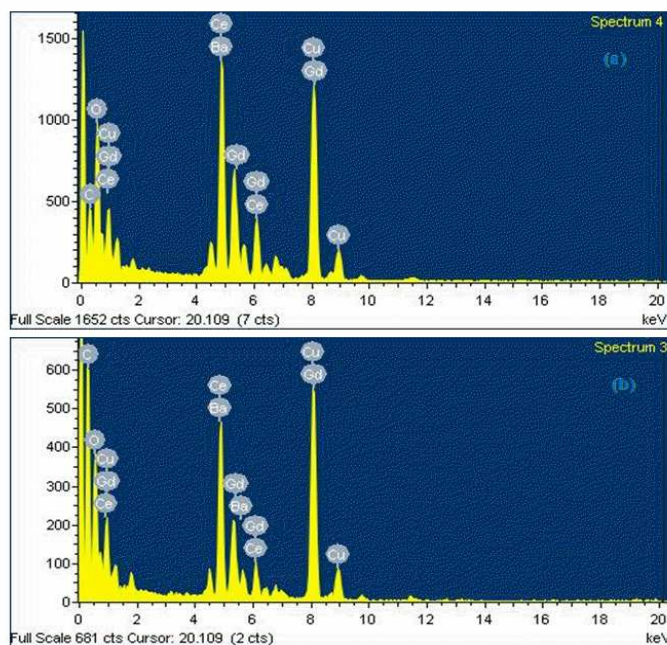


Figure.9. Energy dispersive spectrum for (a) Ba10CG and (b) BCG15.

The solid solution prepared through this co-precipitation method which lead to the complete precipitation of Gd^{3+} ions in $BaCeO_3$ phase. EDS analysis was carried out to check qualitatively the presence of all elements like Gadolinium, Cerium, barium, oxygen and any other foreign materials in the compound.

4. CONCLUSIONS:

Gadolinium-doped barium cerate composite electrolyte was successfully synthesized via co-precipitation technique and prepared samples were sintered using microwave furnace at reduced temperature. The presence of the sharp endothermic peak at 270°C in DSC thermogram confirms the orthorhombic BCG phase formation. The grain size for both Ba10CG and BCG15 were found to be around 15nm. From XRD and DSC study it was understood that 4.85J/g of heat energy required to form a BCG composite phase and from HRTEM results the growth of nanoparticles for both the samples were observed and found to be around 50nm in size. Hence, microwave assisted sintering of BCG electrolyte synthesized by means of co-precipitation method has advantages to form perovskite phase at 600°C during calcination and the sintering temperature of the solid electrolyte was reduced from 1550°C to 1400°C in less soaking time of 20 minutes using microwave and relatively a simple technique for synthesis of nanocomposite electrolyte for solid oxide fuel cell application.

5. ACKNOWLEDGEMENT

The authors would like to thank the Management, Principal, and TEQIP II, PSG College of Technology for their support extended towards this research work and the special gratitude to UGC, New Delhi for generous financial support (Grant No/F.No: 39-863/2010(SR)).

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- To synthesis the composite electrolyte by chemical method and sinter using microwave.
- To reduce the temperature of electrolyte for high ionic conductivity in SOFC's.
- To study the phase purity and to develop nanocomposite at reduced temperature.