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Effect of sintering on the structural and morphological properties of barium cerate based electrolyte for IT-SOFCs application

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Abstract

The present work aims to study the variation of structural properties of solid electrolyte sintered through microwave sintering and conventional sintering techniques. X-ray diffraction analysis was performed upon the as burned powder calcined at 600°C and 900°C for phase identification, HRTEM results reveals the particles size are in nano scale order for the powder synthesized through co precipitation method. XRD and SEM studies were carried out for the pellets sintered through these two techniques. It was observed that the sample sintered in microwave oven form the phase pure crystallinity, good densification, uniform microstructure and also gives higher ionic conductivity than conventionally sintered one. Hence, the solid ceramic sintered in short duration through microwave can give high dense nanocomposite solid electrolyte for electrochemical conversion in solid oxide fuel cell.

1. Introduction

In the recent decades, electrochemical conversion devices were identified as the most needed for the conversion of electric power directly. Among those conversion systems, solid oxide fuel cell (SOFC) is considere as one of the most attractive choice for the conversion of such energy with low environmental pollution and higher output efficiency. The main components of SOFC's are anode, cathode, electrolyte and the interconnects. In SOFC's, solid electrolyte plays an important role in the conversion of energy by means of electrochemical process. Most recently rare earth doped barium cerate based electrolytes have received its significant attention as a choice of an alternative electrolytes to replace the state of art Yttria-stabilized zirconia (YSZ) for energy conversion in a solid oxide fuel cell. In order to have higher efficient energy conversion, the solid electrolyte must be a denser one to meet its commercial requirements with high mechanical strength and stability. Sintering also become one of the most important processes to densify the solid electrolyte. The sintering of solid ceramics at this high temperature may results in the formation of cracks and being a great deal of challenges to improve the chemical stability and mechanical strength of electrolyte [1]. So it's an essential need to identify the most favorable/convenient method to sinter the solid electrolyte at very low temperature (500°C to 800°C). Very few research works have focussed to find out an alternate sintering method for the reduction of temperature and soaking time of the solid electrolyte.

The microwave processing is relatively a new method for the development of ceramics and composite materials and fundamentally different from the conventional heating process. In microwave sintering (MS), the material gets heated by means of direct transformation of heat energy to the materials at molecular level by the interaction of electromagnetic wave and results in reducing the energy consumption drastically. Whereas in case of conventional sintering method, the energy transferred from heating element to the sample surface [2, 3]. When compared with conventional sintering (CS), these microwave techniques include following advantages such as reduction in sintering temperature and soaking time, heating occurs uniformly throughout the materials, lower environmental hazards, time and energy saving, higher production rate, controlled grain growth, improved crystalline nature, reduced surface defects and uniform microstructures enhancement [4,5-8]. Very recently, researchers have devoted their special interest to increase the reaction rate rapidly by using microwave sintering technique and also to dig up the high dense solid electrolyte especially for SOFC applications [9, 10]. Because of rapid heating occurred in electrolyte through microwave, the formation of cracks in the materials was reduced and samples shows higher mechanical properties than that of conventionally sintered one [11, 12]. Rapid heating crop up in the material was mainly due to internal and volumetric heating mechanism and thereto reduces thermal gradient by providing the uniform heating environment to the solid electrolyte [13, 14].

Materials processed by using microwave energy in the frequency range from 300Hz to 300GHz are mainly employed in oxide and nonoxides ceramic materials [15.16]. D.E. Clark et.al studied the benefits of microwave processing and summarized the major research outcome with fundamental features of microwave method[17]. The synthesis processes of ceramic/composite materials can be promoted with the help of this most perspective sintering technique. The high dense solid electrolyte can be obtained at reduced sintering temperature and time, when compared with that of the conventionally sintered ceramics [2]. Oh et. al have clearly pointed out the advantages of this technique such as reduction in soaking time and the sintering temperature of gadolinium doped ceria (GDC) based electrolyte material [9]. Chemical stability of GDC based electrolyte has shown its appreciable results in the presence of H_2O and CO_2 atmosphere. But these doped ceria systems are plagued by the problem of exhibiting electronic conductivity under low oxygen partial pressure. A ceria-based solid electrolyte sintered at high temperature may tend to release oxygen by the reduction of cerium from Ce^{4+} ions to Ce^{3+} ions as shown in Figure.1a. This reduction of Ce^{4+} ions causes a pinhole effect with the expansion of microcracks in the solid electrolyte which ultimately reduces the open circuit voltage (OCV) and in turn decreases the output efficiency of fuel cell [18–20]. In order to suppress this reduction process in solid ceramic, new approaches have been adopted through microwave sintering. The existence of dual matrix phase in composite electrolyte can successfully retained in barium cerate based (BCG) materials and resolved the existing problems [7.21,22]. But, in such composite electrolytes, acceptor doped $BaCeO_3$ as second phase have shown its chemical instability at high temperature and readily undergoes decomposition and /or react with H_2O and CO_2 atmosphere, limits their practical application as an electrolyte in IT-SOFC's (Figure.1b). However, the presence of BCG as second phase in composite will prevent the internal leakage of electrons caused by the reduction mechanism in first phase called doped ceria phase and ultimately improve the open circuit voltage of the fuel cell [21-23].

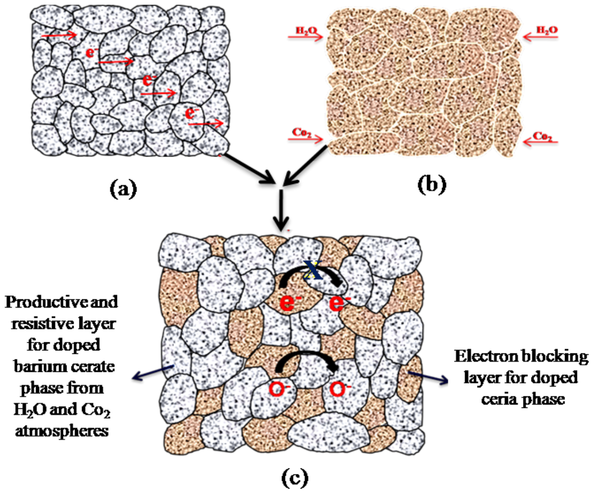

Figure:1 *Composite Matrix prediction for a) GDC Grains, b) BCG Grains and c) GDC-BCG Composite*

The existence of either GDC or BCG single phase was inaccessible to reach the high open cell voltage at lower operating temperature and commercial requirement individually. A matrix phase of GDC-BCG with the superposition of fluorite and orthorhombic structure can improve the open cell voltage in barium cerate based electrolyte by limiting the practical drawbacks of individual GDC and BCG phase are shown in Figure.1c respectively. From the available literature it was understood that in composite electrolytes made Gd-doped ceria (GDC Phase) acts as oxygen ionic conducting phase ($Ce_{0.8}Gd_{0.2}O_{2-\delta}$) and Gd-doped barium cerate (BCG Phase) acts as proton conducting phase ($BaCe_{0.8}Gd_{0.2}O_{2-\delta}$). The presence of two phase in a composites exhibits higher open cell voltage (OCV) only at high temperature [25,27]. The subsistence of GDC phase in the composite matrix acts as protective layer for BCG grains from reacting with H_2O and CO_2 atmosphere and in turn improves the chemical stability of the composite electrolyte. On the other hand the presence of BCG phase in the matrix is highly useful to reduce the reduction mechanism at GDC grains and improve the mechanical strength of the composite electrolyte by means of perculation effect as shown in Figure.1c.[23]. When compared with doped ceria based materials, composite electrolytes with dual matrix phase have shown their special interest at reduced sintering temperature [24,25,27]. Hence, it becomes very essential need to identify an alternate method to reduce the sintering temperature and soaking time for the existence of dual matrix phase in such composites electrolytes with tailored features to get higher open cell voltage. Electrolytes materials processed through microwave method have shown a remarkable energy and time saving one [24]. Borrell et.al has successfully sintered the high dense and homogeneous solid ceramic with average grain size of 225nm through microwave sintering comparatively at lower temperature (1400°C) with high ionic conductivity. Hence, the reduction in temperature by using microwave sintering technique will ultimately result in reducing the materials cost and improve the stability performance of the electrolyte materials for fuel cell environment [6]. The composites electrolytes sintered through this method can also prevent the phase segregation and block electronic conduction very effectively [7]. The ionic conductivity of electrolyte can be enhanced by the fast migration of oxide ions through the composite matrix and ultimately results in higher open cell voltage in the fuel cell operated at lower temperature [25].

The present work aims to study the variation of structural properties of gadolinium doped barium cerate composite (GDC-BCG) electrolyte processed through microwave and conventional sintering technique and the characteristic results have been compared respectively. The results from XRD, SEM, HRTEM and electrical studies have confirmed the better choice of choosing the ultimate method for the development of fine grains microstructure in the solid electrolyte. The GDC-BCG matrix phase nano composite have been processed at lower sintering temperature for the suitability of the material used as an electrolyte for SOFC applications.

2. Experimental details:

2.1 Powder Synthesis and characterization:

The gadolinium doped barium cerate electrolyte was synthesized by wet chemical method. Cerium nitrate and barium nitrate (99.5% pure) were purchased from Sigma–Aldrich, Italy, dissolved in 50 ml of distilled water into a beaker and Gadolinium oxide (99.9%, Sigma–Aldrich, Italy) was dissolved in 5ml of nitric acid and heated until the salt gets dissolved completely to forms the respective nitrate. The Stoichiometric mixture was dissolved in 50 ml of distilled water separately. Three solutions were poured into a burette one by one and added together into a beaker drop-by-drop slowly with continuous stirring with 500 rpm using magnetic stirrer. Ammonium hydroxide solution was added to the mixture to maintain the value of pH >10. By the addition NH4OH, the mixture gets precipitated out as hydroxides of Cerium, Barium, Gadolinium and kept on a magnetic stirrer with 1000 rpm for 30 minutes. The mixture was then added with 10% of PEG (Poly Ethylene Glycol) acts as a dispersant/binder to the mixture and again stirred for about 30 minutes in a magnetic stirrer to improve gelatinization [25]. To dry out the gel, the precipitate was then dried in hot air oven at 95°C for 12 hours. The obtained gel compound was kept in the furnace at 400°C for 2 hr to get the porous powder. The dry powder was grounded well in mortar and pestle for 30 minutes and undergone calcinations at 600°C and 900°C for 6 hours to ensure the removal of all volatile matters from the as burned powder and also to confirm the temperature at which required phase was formed. X-ray diffractometric analysis was carried out for the as burned powder sample calcined at 600°C and 900°C for the confirmation of phase purity of the sample and high crystallinity using CuKα radiation. JEOL JEM 2100 High-Resolution Transmission Electron Microscope (HRTEM) was used to analyze the variation of particle size with increase in calcination temperature of the as burned powder from 600°C and 900°C respectively. HRTEM results have confirmed the formation of nano size crystal at 900°C and in consistent with XRD results.

2.2 Pellet Preparation:

The high dense pellets were obtained by pressing the as prepared powder uniaxially at 15MPa using a steel die of 12 mm diameter. Before pressing them into pellet, the as-prepared powder was mixed well with 1 % of Poly vinyl alcohol (PVA). PVA acts as a binder or fillers for granulation and to get the high dense pellet. The addition of PVA to the precursor powder will enhance the sintering kinetics of ceramic and in turn increase the green strength of the pellet. In microwave sintering process, the pellet was taken in an alumina boat and covered with alumina –zirconia insulator to minimize the heat loss and to have volumetric heating for the intensification of unique micro structure in the solid electrolyte [26]. The whole sintering procedure was carried out for 20 min with the heating rate of 45°C per min from room temperature to 1400°C using microwave furnace. The temperature was monitored using infrared pyrometer located at the top of the system through a cavity. In case of conventional sintering, high dense ceramics were taken in an alumina crucible and undergone sintering in an electric furnace at 1400°C with the heating rate of 5°C /min for the dwell time of 6 hrs and controlled cooling of

10°C /min till 600°C. The sintering temperature of the sample was controlled by controlling the supply of power to the heating element using Eurotherm temperature controller. The well-compacted disc-shaped ceramics were named as MSP for the pellet sintered in microwave and CSP for the pellet sintered in conventional furnace respectively for further discussions

2.3. Pellet Characterization:

As prepared powder samples were made into a compact disc-shaped pellet after calcinations. Both the pellet sintered by means of microwave and conventional methods, were characterized using XRD analysis through PW 1729 X-ray diffractometer. Microwave and conventionally sintered pellets were cleaned well in acetone, polished, coated with gold to prevent charge accumulation during SEM studies. Scanning electron microscopic analysis was performed on the surface of the pellets to know the development of microstructure. Hitachi S3400N SEM analyzer was used for obtaining Secondary Electron (SE) images. Conductivity measurements were carried out for both the MSP and CSP sample using NOVA control impedance analyzer for measuring the impedance as a function of frequency. The electrical conductivity measurement was employed for both the samples and observed that the sample prepared through microwave sintering have shown higher ionic conductivity with less activation energy. Temperature dependant conductivities were measured in ambient air using Probe state sample holder and their activation energy values were reported for better ionic conductivity [25, 27].

2.4 Density measurement:

The density of the pellets was measured by Archimedes principle using deionised water as the immersion medium. The relative density of the MSP and CSP was measured by liquid displacement method. Its shows that the sample sintered in microwave furnace have shown higher densification nature than that of conventionally sintered one. MSP exhibits 94% of relative density, where as CSP has 89% of relative density at 1400°C. From this density measurement results, it was well clear that the pellet sintered through microwave technique was highly densified at lower sintering temperature in minimum soaking time. The high dense electrolyte sintered through microwave furnace have relatively reduced the sintering time and temperature when compared with that of conventionally sintered pellet.

3. Result and discussion:

3.1 XRD Analysis for as prepared powder:

The structural analysis was carried for the as-prepared powder sample calcined at 600°C and 900°C respectively were shown in Figure 2. The powder sample calcined at 900°C shown all the corresponding peaks with the characteristic interplanar spacing between ((002), (400), (131), (402),(313), (004), (611) ,(404),(441) and (420) planes of orthorhombic perovskite structure, whereas the powder calcined at 600°C has shown only the d-spacing values between (111), (200), (113), (511), (222) and (400) corresponds to fluorite structure

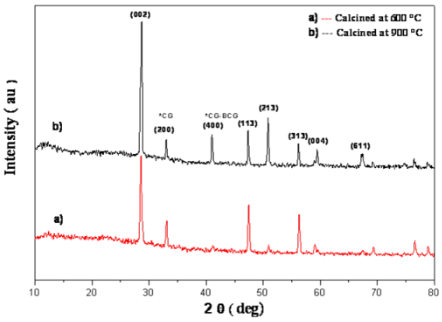

Figure.2. *XRD for powder Calcined at 600°C and 900°C*

The existence of GDC-BCG matrix phase formed at 900°C was the evidence for the formation of barium cerate composite phase with complete precipitation of gadolinium in barium cerate lattice. The formation of $BaCeO_3$ solid solutions was recorded as per JCPDS file no 01-082-2373. The crystallite size of as prepared powder was found to increase form 30nm to 50nm with the increase in calcination temperature with complete crystallization. The crystallite sizes for both the powder sample was calculated from equation (1) with its 2θ value of XRD main reflection (002) plane using Scherrer formula [28,29]:

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

where D is crystallite size in nm, λ is the radiation wavelength (for Cu Kα radiation, λ = 1.5418 Å), 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 diffraction peaks become narrow and sharp which reveals that there is an inference of increase in particle size upon increasing the annealing temperature of the as-prepared powder. The powder sample calcined at higher temperature can be attributed from the sharper peak and the coarsening of nano grains was also observed. In the composite matrix, GDC phase contributes the ionic conduction and BCG phase correspond to both electronic and ionic conduction in the sample[23]. The presence of gadolinium-doped barium cerate phase will increase the ionic conductivity of the electrolyte through the perovskite lattice by decreasing the electronic conductivity in doped ceria phase. The existence of GDC-BCG matrix phase will suppress the grain growth mechanism and also to enhance the total ionic conductivity of the electrolyte through BCG phase by preventing the reduction mechanisms at GDC phase [27]. So, GDC-BCG composite powder with dual matrix phase of orthorhombic perovskite and fluorite structure was able to form in the powder calcined at 900°C. Hence, it can be attributed as the partial substitution/incorporation of gadolinium in barium site by increasing the number of oxygen vacancies for higher ionic conduction in composite electrolyte at fuel cell environment.

3.2. HRTEM Analysis for as prepared powder:

The general morphology of the gadolinium doped barium cerate nanoparticles was observed from TEM analysis and visualized in Figure.3. TEM images were taken using JEOL JEM 2100 High-Resolution Transmission Electron Microscope and shows a homogeneous distribution of polycrystalline nanoparticles in the powder prepared through the wet chemical method. High-resolution TEM image in Figure.3a and 3d clearly indicate the internal crystal lattice formed from high crystalline BCG nanoparticles grown at 900°C. The presence of grain boundary can be seen in Figure 3b and 3e, from TEM image reveals the size and shape of the primary particle. A well-developed nanoparticle of 30nm and 50nm in size has been grown at 600°C and 900°C respectively. The increase in the size of the nanoparticle was observed from TEM results and is in good agreement with the crystallite size measured through XRD analysis.

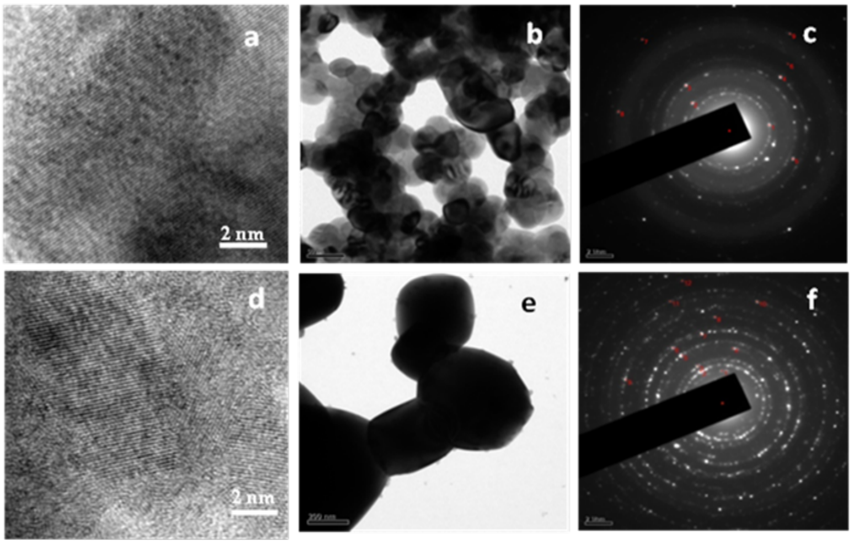

Figure.3. *High resolution TEM images of Powder calcined at 600°C (a-c) and 900°C (d-f)*

The precursor powder calcined at 900°C has good compaction nature and results in formation of high dense pellet, because of loosely agglomerated particles during higher calcination temperature. The powder calcined at high temperature has grown well developed hexagonally shaped nano particles with an average size of 50nm. Lattice fringes are also observed on the surface of the sample with d-spacing of 3.2Å which corresponds to the plane located at 28°32'and are in consistent with the XRD pattern. The particle size distribution confirms the presence of dual matrix GDC-BCG nano phase in the as burnt powder at 900°C and also some degree of agglomeration at higher temperature appear unavoidable [11]. Whereas the powder calcined at lower temperature (600°C) have shown more agglomeration on its surface and exhibited the occurrence of GDC phase only at low sintering temperature. The existence of GDC phase may enhance the leakage of current through matrix phase.

SAED pattern was indexed for the powder samples calcined at 600°C and 900°C respectively shown in Figure 3c and 3f. It was well observed that the powder calcined at 600°C have shown only the presence of fluorite structure with lesser bright spots because of not having the enough temperature for the formation of BCG nano particles with pervoskite structure. The powder calcined at 900°C has formed the polycrystalline GDC-BCG nano particles correspond to the required fluorite-pervoskite structure in less soaking time. The selected area electron diffraction pattern for GDC-BCG nanoparticles exhibits the superimposition of all the bright reflection spots such as (002), (400), (131), (402),(313), (004), (611) ,(404),(441) and (420) corresponds to orthorhombic phase with equal lattice arrangements of the particle. Several research works have been carried out to investigate the dependence of grain size in polycrystalline solid ceramics and observed the highest ionic conductivity in the composite electrolyte with the grain size below 100 nm [30]. In the present investigation, the grain sizes is found to be grown from 30nm to 50nm at high temperature and enhance the conduction mechanism.

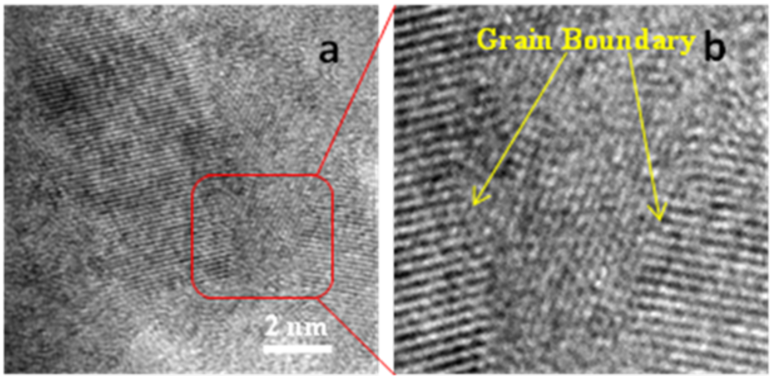

Figure.4. *High resolution TEM images for a) Lattice image of nanoparticles grown at 900°C b) detailed view of an area indicated by red frame.*

From TEM image in Figure.4a, it was observed that there are randomly oriented nano sized fine grains found to grown at 900°C. The development of new crystallographic irregularity has been recognized as the polycrystalline nature of the material. The detailed view image of the lattice in Figure 4b clearly indicates the presence and variation of grain boundary correspond to GDC-BCG dual matrix phase for the nanoparticles grown at higher temperature. These results reveal that gadolinium doped ceria phase was formed at the inter grains of gadolinium doped barium cerate phase and observed in the plane region (400) located at 41°02'. The existence of BCG phase in the matrix will ultimately suppress the growth of GDC phase, results in the enlargement of fine grains. The formation of BCG as second phase in the composite will ultimately reduce the diffusion of charge carrier through the grain boundary and sequentially improves the ionic conduction through larger grains [30]. The variation in grain size and grain boundary density region in the solid electrolyte will easily contribute the transport of oxide ions through grains and reasonably improves the ionic conduction process through solid electrolyte in the fuel cell operated at the lower temperature.

3.3 XRD Analysis for MSP and CSP:

The XRD patterns for the pellets sintered through the microwave and conventional furnace were shown in Figure.5. It was observed that the required fluorite-perovskite structure was formed in the pellet sintered at the lower temperature of 1400^{o}C in the minimum soaking time about 20 min when compared with that of conventionally sintered at 1400^{o}C for 6 hours. Noteworthy to understand that the sintering time of the solid electrolyte was almost using the simple microwave technique due to the faster in reaction rate. The sharpness in both the XRD peaks was inferred with the development of fine grains and the particle size was found to increase for the pellet sintered through microwave technique. The shift in peak towards the right for higher angle 2θ value indicate that there was an increase in grain size and are in good agreement increase in grain size observed in SEM analysis for the pellet sintered through microwave technique.

The diffraction pattern from both the samples were recorded with their main reflection peaks positioned at (002), (400), (131), (402),(313), (004), (611) ,(404), (441) and (420) which correspond to the gadolinium doped barium cerate phase (BCG) of Orthorhombic Perovskite structure (JCPDS Reference code: 01-082-2373) and the reflection peaks at (111), (200), (113), (511), (222) and (400) corresponds to gadolinium doped ceria phase (GDC) with Fluorite (JCPDS Reference code: 01-075-0162). The high-intensity peak for (002) plane depicts the formation of high degree of crystallinity for BCG nanoparticle. The required BCG matrix phase was successfully retained through microwave sintering in a less processing time of 20 min than that of conventionally sintered samples with lattice parameters a=8.753, b= 6.244, c=6.231 and are in good agreement the values reported earlier [31,32]. All the major peak position, d-spacing values are in good agreement with the JCPDS Reference code: 01-082-2373 and found to be in match with lattice constants as reported elsewhere in the work of A.Venkatasubramanian.et.al [21]

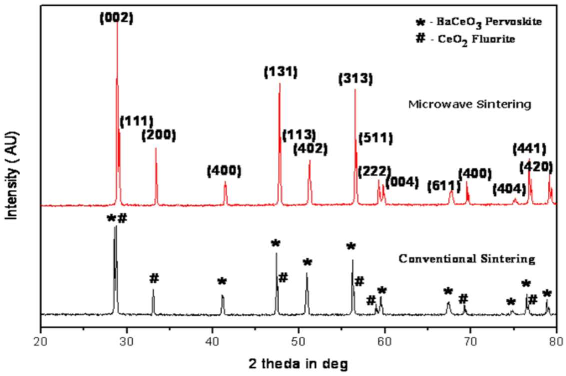

Figure.5 *XRD for MS Pellet sintered at 1400oC and CS Pellet sintered at 1550^{o}C*

From the structural analysis, it was observed that the required orthorhombic pervoskite structure with Pmcn space group of number 62 for composite electrolyte can be synthesized through microwave technique in minimum soaking time. The corresponding lattice parameters, unit cell volume have been calculated using equation (2) and are tabulated (Table.1).

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \qquad (2)$$

Table-1 shows the comparison of methods of sintering, lattice parameter, unit cell volume of the perovskite materials processed through different techniques and the values reported earlier are found to match closer with the present work at lower sintering temperature for increasing the crystal volume of composite to improve the ionic conduction.

XRD Data	Method of Sintering And Temperature	Crystal structure	Unit cell lattice parameters (Å)	Unit cell volume (Å^3)	References
$BaCeO_3$ powder	--	orthorhombic	a = 8.773 b = 6.244 c = 6.221	340.86	(JCPDS N0. 82-2373)
BCG- Microwave	1350-1400	orthorhombic	a =8.796 b =6.239 c =6.212	340.90	This Work
BCG-Conventional	1350-1400	orthorhombic	a =8.753 b =6.244 c =6.231	340.54	This Work
Ba10CG Conventional	1500-1550	orthorhombic	a =8.791 b =6.242 c =6.212	340.8	[24]
Ba40CG Conventional	1550-1550	orthorhombic	a =8.774 b =6.244 c =6.203	339.8	[24]
Conv.Sintering	1620-1670	orthorhombic	a =8.774 b =6.215 c =6.233	339.88	[30]

Table ; 1 Comparison of Unit cell parameters for BCG sintered through different technique

The unit cell volume of 340.90 for $BaCeO_3$ was found to be higher than the unit cell volume available in the literature. This variation in crystal volume may be due to the partial substitution/incorporation of Gd^{3+}ion into Ba-site in $BaCeO_3$ and results in the expansion of the unit cell volume with increase in the number of oxygen vacancies at pervoskite lattice [31]. Any nanocomposite materials sintered at lower temperature will tends to increase the unit cell volume as observed in this work [27,33]. This result reveals that this GDC-BCG nanocomposite electrolyte processed through microwave technique is a suitable electrolyte material for solid oxide fuel cell applications.

3.4 Microstructural Analysis for MS and CS Pellet:

SEM image in Figure.6 a-b shows the comparison of morphology for the pellet sintered through MS and CS techniques. The pellet sintered using the microwave (Figure.6a) have shown a well developed grains, high dense and uniform grain growth than that of conventionally sintered (CS) one (Figure.6b). The average grain size was found to be around 1μm for the pellet sintered through conventional and 2μm for the pellet sintered through Microwave sintering. The variation in grain size may be due to the impact of varied sintering methods. From SEM analysis, it was well attributed that if the sintering time exceeds 60 minutes may results in the loss of barium content and also decreases the density of solid electrolyte by creating some voids. The evaporation of barium may residue out the GDC phase only and results in the reduction of Ce^{4+} ions to Ce^{3+} ions by releasing oxygen from the solid ceramic. [12,34]. Due to this reason doped ceria phase tends to initiate the formation of some cracks and pores on the surface of the sample as seen in Figure.6b. The variation in microstructure in the pellets sintered through both the techniques can be compared with the density values of the pellets measured through Archimedes principle and are in good agreement with each other.

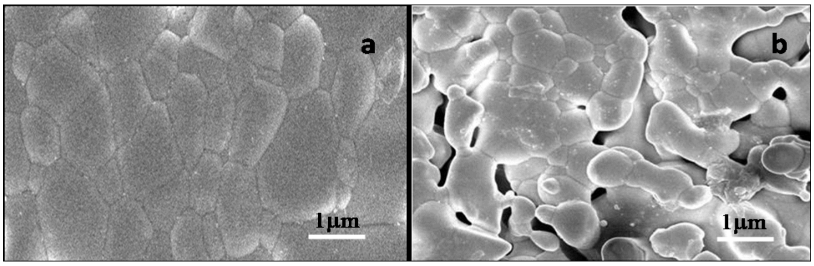

Figure.**6**.*SEM image for pellets a) Microwave sintering and b) Conventional sintering*

In microwave sintering, the material gets heated on the molecular level in lower soaking time, which results in the growth of high dense microstructure. An electrolyte sintered through microwave furnace would have developed controlled grains with the presence of GDC-BCG matrix phase [25, 27]. In this type of composite with dual matrix, the presence of BCG as secondary phase will act as a blocking phase for the leakage current generated by the reduction in doped ceria GDC phase and suppress the release of oxygen ions [12,34]. On the other hand, the presence gadolinium doped barium cerate (BCG) phase can control the growth of gadolinium doped ceria (GDC) phase. The escalation of homogenous BCG nano particles in less processing time will improve the mechanical property and chemical stability of the electrolyte [27, 35-37]. Whereas, in the case of conventional sintering, the heat energy supplied on the surface level of electrolyte for longer duration results in the development of a large number of pores in between the intergrain boundaries. The presence of porosity may be due to the evaporation or the loss of barium ions at high temperature and longer time duration during conventional sintering. Porosity in electrolyte materials increases only at higher sintering temperature and also results in small size grain growth with decreased mechanical strength and durability of the material [36]. The development of smaller grain leads to higher grain boundary resistance and in turn decreases the conduction of oxide ions through the solid electrolyte.

From this SEM analysis, it was emphasized that the samples prepared through microwave sintering method have developed an excellent sintering performance with less porosity in electrolyte. The pellet sintered through microwave have shown the well developed homogenous microstructure with interlocking of grains and grain boundaries than that of the sample sintered through conventional method [37]. The properties of grain and grain boundary for any polycrystalline materials are greatly influenced by the development of microstructures and to study the conductive phenomenon in composite electrolyte. The increase in grain size will ultimately result in increasing the ionic conduction through dense composite electrolyte as studies and predicted in brick layer model [38,39].The presence of larger grains in composite electrolyte with less porosity will increases the ionic conductivity through grain by reducing the grain boundary resistance, which in turn increases the total conductivity of the fuel cell. The composite electrolyte can have high grain conductivity than grain boundary conductivity because of the transport of oxide ions is much faster in grain than that of the grain boundary. So a solid electrolyte sintered by means of microwave can have higher ionic conductivity through grains than grain boundaries, because the grain boundaries are having larger resistance value than the bulk one. The developments of larger grain boundary with smaller grain was observed for the pellet sintered through conventional sintering and are highly porous in nature. The pellets sintered through conventional method are not suitable for high ionic conduction.

Hence, from this SEM analysis it was well clear to understand that the high dense pellet with dual phase microstructure was able to grow in larger size while decreasing the sintering temperature of the solid ceramic through microwave furnace in less processing time and these results are in consistent with the crystallite size measured by XRD analysis. This GDC-BCG dual phase microstructured observation in solid electrolyte holds its good agreement with XRD two-phase predictions as shown in Figure.1.

3.5 Conductivity Measurements:

The electrical conductivity measurement was performed for both the samples sintered through two techniques. From the earlier reported values, it was understood that composite with matrix phase can improve the ionic conduction through BCG Phase with minimum activation energy of 0.4eV and also prevent the leakage current through GDC Phase of solid electrolyte. The activation energy between electrolyte/cathode interface plays an important role to evaluate performance for oxygen diffusion and oxygen ion conductivity. The value of activation energy was calculated from the linear fit curve for thermally activated conduction occurred in composite using equation (3).

$$(3)\ \sigma T = A\exp(-\frac{E_a}{kT})$$

Where Ea is the activation energy for conduction, T is absolute temperature and σ is conductivity. The obtained values are in well agreement with the values reported earlier[40]. As studied in SEM results, a dense electrolyte with fine microstructure can give better ionic conductivity through interior grains present in the composite [41].

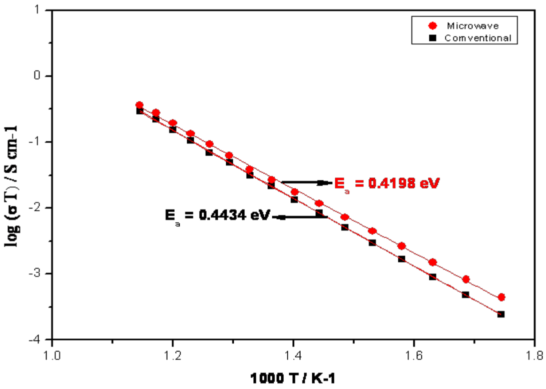

Figure.7. *The Arrhenius plot of MS and CS Pellet*

BCG nano powder was made into disc shaped pellet and sintered at 1400°C for 20 min in microwave furnace and 1400°C for 6 hours in conventional furnace respectively. The electrical conductivity measurement was subsequently recorded in air for both the dense electrolytes at the temperature ranging from 300°C to 800°C, shown in the Arrhenius plot Figure.7. The activation energy for both the pellets sintered in Microwave and Conventional methods was measured to be around 0.41eV and 0.44eV respectively from the Arrhenius plot using the least square fitting technique. The reduction in sintering temperature through microwave have increased the grain growth in the composite and the conduction in solid electrolyte was increased with decrease in activation energy [42].So the electrolyte with GDC-BCG matrix phase have influenced the ionic conduction mechanism through BCG phase by suppressing the electronic leakage in GDC phase as predicted by XRD and SEM analysis. Hence from the above discussions, it can be attributed that the solid electrolyte processed through microwave technique has enhanced the growth of uniform grains. When compared with conventionally sintered pellet, microwave sintered pellet have shown much less activation and increased the migration of oxide ion through uniform grains much faster in rate and result in the better ionic conduction.

Conclusions

Gadolinium-doped barium cerate based composite electrolyte was successfully synthesized by wet chemical method. XRD studies have confirmed the occurrence of dual matrix phase for the as burned powder sample calcined at 900°C. The particle sizes are found to be around 50nm nano scale order measured through HRTEM analysis. The SEM results reveal that the development of fine and uniform microstructure with average grain size of 2μm. The unique grain growth was able to be achieved at lower sintering temperature for the sample heated through microwave at 1400°C in less soaking time. The lower activation energy of 0.41eV was measured for the pellet sintered in the microwave and can improve the ionic conductivity through GDC–BCG matrix phase. Hence, microwave technique can be a better choice for sintering the nanocomposite electrolyte used as a component for electrochemical conversion in the solid oxide fuel cell.

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