Accepted Manuscript

Thermal, Structural And Electrical Properties Of Samarium Doped Barium Cerate Electrolyte For Sofcs

A. Senthil Kumar, R. Balaji, S. Jayakumar

PII:	S0254-0584(17)30700-9
DOI:	10.1016/j.matchemphys.2017.09.008
Reference:	MAC 19975
To appear in:	Materials Chemistry and Physics
Received Date:	26 April 2017
Revised Date:	30 August 2017
Accepted Date:	03 September 2017

Please cite this article as: A. Senthil Kumar, R. Balaji, S. Jayakumar, Thermal, Structural And Electrical Properties Of Samarium Doped Barium Cerate Electrolyte For Sofcs, *Materials Chemistry and Physics* (2017), doi: 10.1016/j.matchemphys.2017.09.008

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



Highlights

The authors have made an attempt to synthesis samarium doped barium cerate based nanocomposite electrolyte for solid oxide fuel cell application through the novel microwave sintering.

The main aim of the present work carried out are listed below

- To prepare the composite electrolyte by wet chemical method and sintered through microwave furnace.
- To develop a dual phase microstructure in electrolyte for high ionic conductivity in SOFC's.

THERMAL, STRUCTURAL AND ELECTRICAL PROPERTIES OF SAMARIUM DOPED BARIUM CERATE ELECTROLYTE FOR SOFCs

A.Senthil Kumar^{a*}, R.Balaji^a S.Jayakumar^b

^a Ceramic Processing Lab, Department of Physics , PSG College of Technology Coimbatore – 641 004, TN, INDIA.
 ^b Department of Physics, PSG Institute of Technology and applied research , Coimbatore - 641 062

ABSTRACT:

In the present investigation Samarium doped barium cerate electrolyte powder of $(1-x)Ce_{0.8}Sm_{0.2}O_{2-\delta}-xBaCe_{0.8}Sm_{0.2}O_{3-\delta}$ (where x= 0.1 mole fraction) stoichiometry formula is successfully synthesized through wet chemical route. A SDC-BCS nanocomposite electrolyte is premeditated with respect to its thermal, structural, morphological properties and conductivity performance. The crystal structure and microstructure of the SDC-BCS composite is investigated from XRD and SEM analysis. TG analysis reveals that the calcination temperature (900°C) of the as prepared powder sample. The crystal structure of as prepared SDC-BCS composite powder is identified as cubic perovskite with orthorhombic distortions occurred at 900°C. From TEM analysis, the particle size is found to be around 32nm. SEM analysis reveals that the existence of dual phase microstructure in the composite at 1400°C. The preparation of dense SDC-BCS nanocomposite with the development of dual phase microstructure is achieved for the better ionic conductivity in SDC-BCS nanocomposites for SOFC application.

Keywords: Chemical route, Microwave sintering, SDC-BCS nanocomposite, Solid oxide Fuel cell.

Corresponding author: Dr.A.SENTHIL KUMAR ASSISTANT PROFESSOR (Sr.G) DEPARTMENT OF PHYSICS PSG COLLEGE OF TECHNOLOGY COIMBATORE-641004. TAMIL NADU, INDIA Tel: 91-422 2444453, Fax: 91-422 4344453 Corresponding author: senthu.ramp@gmail.com, askinpsg@gmail.com*

1. INTRODUCTION:

In the current research trends, Solid oxide fuel cells (SOFCs) attracted a great deal of consideration among the promising fuel cell systems exist for energy conversion. SOFC consist of three main components, they are anode, cathode and an electrolyte. The solid electrolyte plays a very important role for higher efficiency energy conversion. The main stumbling block for fuel cell is its high temperature operation (1000°C) and results in design limitation with higher fabrication cost. The modern trend in SOFC have attracted the young researcher to develop a suitable oxygen ion conducting solid electrolytes for electrochemical energy conversion for high efficiency, low cost, more sustainable and environmentally friendly nature. In SOFC, electrolyte is considered as a main component for the diffusion of oxide ions to get the required ionic conductivity (0.1S cm⁻¹). Yttria Stabilized Zirconia (YSZ) has been considered as a most promising candidate with high ionic conductivity of 0.015 Scm⁻¹ at 1000°C [1]. YSZ has shown unrelenting ionic conduction in both oxidizing and reducing atmosphere. But the main problem associated with this Zirconia based electrolyte was its high temperature operation leads to thermal mismatch, instability and higher cost fabrication limits its niche commercial requirements.

The above stated problems can be overcome by reducing the operating temperature of solid electrolyte to intermediate temperature (600-800°C) [2, 3]. Ceria based solid electrolytes with fluorite structure have been studied as a possible oxygen ion conducting electrolyte to replace Yttria Stabilized Zirconia (YSZ) with high ionic conductivity at intermediate temperature (600°C-800°C). But, these pure ceria was not a good oxygen ion conductor. Doping with aliovalent cation such as samarium into ceria lattice is an effective approach to facilitate the creation of oxygen vacancies for improving the ionic conductivity. However, these doped ceria materials exhibits its low open cell voltage(OCV) with partially increased electronic conduction and also acts as a n-type conductor due to the reduction of Ce^{4+} to Ce^{3+} [4, 5]. The formation of oxide defect at high temperature results in instability of oxygen partial pressure during fuel cell operation and in turn reduces its OCV [6,7]. Another class of pervoskite type oxide ion conductors with ABO₃ structures such as barium cerate, strontium cerate, barium zirconate are considered as best solid electrolytes [8,9] for getting required high ionic conductivity at intermediate temperature. But the undoped BaCeO₃ Pervoskite structure was instable in CO₂ atmosphere and form BaCO₃, which in turn leads to poor mechanical strength and thus decreases the ionic conductivity of electrolyte.[10,11].

Hence doped barium cerate based materials such as samarium or gadolinium with co-existence of fluorite-pervoskite structured can overcome the above stated individual problems and are highly preferred as solid electrolyte for fuel cell application.[12,13]. The presence of doped barium cerate (BCS) as second phase in composite can prevent the internal leakage caused by the reduction mechanism occurred in first phase called samarium doped ceria phase(SDC) and ultimately improve the open circuit voltage of the fuel cell [14]. In the present research work, samarium doped barium cerate based SDC-BCS composite electrolyte was prepared as nanocomposite electrolyte for high ionic conductivity at BCS phase and low electronic conduction in SDC phase at intermediate operating temperature(600°C-800°C).

2. EXPERIMENTAL MEHTODS:

2.1 SDC-BCS Powder Synthesis and Pellet Preparation:

The Samarium doped barium cerate (SDC-BCS) composite electrolyte powder was successfully synthesized through wet chemical method. Cerium nitrate, samarium nitrate and barium nitrate powders were dissolved in 50 ml of distilled water in a beaker and stirred continuously at 500 rpm in a magnetic stirrer until the salt gets dissolved completely. Ammonium hydroxide solution was added into the mixture to maintain the pH >10. By the addition of NH₄OH, the mixture was precipitated out and again kept on a magnetic stirrer with 1000 rpm for 30 minutes for homogeneity. In order to obtain the gel, the mixture was then added with 10% of PEG (Poly Ethylene Glycol) acts as a complexion agent and again stirred well for about 30 minute to improve the formation of green body solid solution [15]. To dry out the gel, the precipitate was dried in hot air oven maintained at 95°C for 12 hours. The obtained flakes are kept in furnace at 400°C for 2 hr to get the dry powder. The dry powder was grained well and calcined at 900°C to obtain the required SDC-BCS composite matrix with dual phase in the as prepared powder.

The dense SDC-BCS pellets were prepared from the as prepared powder by pressing uniaxially at15MPa using a steel die of 12 mm diameter. Before pressing into pellets, the as prepared powder was mixed well with 1 % of Poly vinyl alcohol (PVA) binder to obtain the well compact disc shaped green pellets. The addition of PVA to the powder can improve the good sintering ability and increases the strength of the pellet. The well compacted pellets are taken in alumina boat for sintering in microwave furnace. In microwave, the sintering was carried out for 20 min at heating rate of 45°C per min. Hence, disc shaped SDC-BCS composites electrolyte was prepared.

2.2 SDC-BCS Composite Materials Characterization:

The as prepared SDC-BCS composite electrolyte powder and pellets were physically characterized. Thermal analysis (TGA) was carried out for the as prepared powder with the help of Netzsch, Germany, NETZSCH STA 449F/3 Instruments to identify the calcination temperature. XRD analysis was carried out to determine the crystallinity and the phase purity of the as-prepared green powder using Shimadzu powder X-ray diffraction analyzer, in nickel filtered Cu-K α ($\lambda = 0.15418$ nm) radiation. The particle size distribution studied through Transmission electron microscopy (TEM, JEM-2010) along with an energy- dispersive X-ray spectroscopy (EDS) system. Scanning electron microscopy (SEM, JEOL JSM-6700F) was employed to examine the surface morphology of the powders and the development of microstructures. Conductivity measurement was carried out for all the composites using Novo control GmbH Alpha-A high-resolution electrochemical impedance analyzer. Impedance measurement was performed to know the electrical behavior of composite electrolyte. The total conductivity of the composite was obtained from the impedance spectra. Platinum electrodes were used with homemade sample holder to measure the impedance response of SDC-BCS composite electrolyte.

3. RESULTS AND DICUSSIONS

3.1 TG Analysis for Ba10CS powder:

The collective Thermogravimetric analysis (TGA) was employed to measure the percentage of weight loss occurred in the powder sample with increase in calcination temperature. TG analysis was mainly used to determine the temperature of phase formation and also to study the rate of decomposition reaction occurred in Ba10CS powder sample. The TGA thermogram was recorded under nitrogen atmosphere at a heating rate of 10°C per minute from room temperature to 1100°C.

The TGA thermograms of as prepared powder with 10 mol% of Ba content are shown in Figure 1. TGA patterns are provided simultaneously to understand the origin of the endothermic peaks and associated weight loss. The loss was clearly noticed in TGA pattern. The percentage of weight loss for all the three samples falls between 4 to 7 wt%. The gradual decrease in weight was observed till 500°C and a steep behavior was observed till 600°C (Figure.1.a, b).



Figure.1 TGA-analysis for SDC-BCS composite powder calcined at 700°C, 800°C and 900°C

The weight loss in this temperature range was mainly due to the loss of organic specious present in the powder. The second endothermic peak present at 550°C was attributed as the decomposition of nitrates between 550 °C to 700°C as studied in previous available literature [14,15]. The presence of third endothermic peak at 870°C indicates the decomposition of left over barium nitrate into BaO and confirms the formation of BCS phase. Figure 1c clearly depicts the minimum percentage of weight loss occurs at 900°C. However, the formation of SDC phase was not known from this study. It was understood from the literature that the formation of SDC phase for micron sized particles can occur at 700°C [16]. In this case, the evidence of formation of SDC phase may be over shadowed by the weight loss at various stages.. In order to determine the phase formation of SDC and ascertain the formation of BCS phase, the as prepared Ba10CS powders was calcined at 700°C, 800°C and 900°C for 4 hours and presented.

3.2 Structural Analysis for Ba10CS powder:

XRD analysis was performed for Ba10CS powder calcined at 700°C, 800°C and 900°C respectively for about 3 hours and shown in Figure.2. The XRD results indicated that Ba10CS powder calcined at 900°C have shown the existence of dual phase with fluorite- pervoskite-type structure. The variation of diffraction pattern in Ba10CS powder was observed with increase in calcination temperature. As the temperature was increased from 700°C to 900°C, more diffraction peaks are emerged and are attributed as the formation of BaO from Ba(NO₃)₂. The characteristics peak position at

23°92' corresponds to BaCO₃ phase entirely disappeared by increasing the calcination temperature and leads to the formation of samarium doped BaCeO₃ phase. The fluorite and perovskite structure was fashionably formed for the calcined at 900°C.



Figure.2 XRD pattern for Ba10CS powder calcined at 700°C, 800°C and 900°C for 4 hours

The diffraction peaks corresponds to SDC phase oriented along (111) plane and BCS phase along (020) plane are clearly observed in the XRD pattern and no impure phases are observed, which indicates that SDC phase has good chemical compatibility with BCS phase [14]. The high intense peak position at 28.42° correspond to SDC phase and 28.68° for BCS phase. The existence of these two phases confirms that most of the grains are oriented at (111) plane and (002) plane of both the SDC and BCS phases respectively. The gradual enhancement in the volume of BCS phases i.e. barium cerate phase was observed as the calcination temperature increases in the step of 100°C.

3.3 HRTEM Analysis for Ba10CS powder:

The JEOL JEM 2100 High Resolution Transmission Electron Microscope (HRTEM)was used to analysis the samples. HRTEM analysis was carried out for Ba10CS powder calcined at 700°C and 900°C respectively for 4 hours to gain the information on particle size distribution, shape, crystal structure and variation of particle size with increase in the calcination temperature of as prepared powder. The HR-TEM image displayed in Figure. 3a(i) and 3b(i) confirms the distribution of particle and the variation of nanocrystalline in the powder prepared through chemical route method. The size of the nanoparticle are found to be around 27nm and are similar to the values observed from XRD results.



Figure:3a High resolution TEM images (i) Particle size (ii) Nano scale and (iii) SAED pattern of Ba10CS powders calcined at 700°C for 4 h



Figure:3b High resolution TEM images (i) Particle size (ii) Nano scale and (iii) SAED pattern of Ba10CS powders calcined at 900°C for 4 h

The lattice spacings of 0.31nm and 0.32 nm shown in Figure 3a(ii) and 3b(ii) corresponds to the (111) and (002) crystalline plane for doped ceria (SDC) and doped barium cerate (BCS) phase respectively. The existence of both the phase confirms the composite nature of the as prepared powder [17]. Figure 3a, 3b clearly shows the development of nano-particles in Ba10CS powder calcined at 700°C and 900°C respectively. Good crystalline state was observed from the SAED patterns of the sample calcined at 900°C, confirms the presence of crystalline nanoparticles in the powder and their nanocrystallinity. Strong and bright reflections were observed from SAED patterns and the ring pattern confirms that the as prepared powder was nanometer in size. From the optical imaging analysis, the average distribution of particle in the SDC-BCS powder was determined qualitatively using the imaging software.

Sample Code	Calcination Temperature (°C)	Particle size (nm)
BallCS	700	20
Baroes	900	32

Table. 1 Variation of particle size with increase in calcination temperature for SDC-BCS powder

The variation of particle size between 20nm to 32nm for SDC-BCS powder was studied from TEM image. The average particle size and the range of size distribution while increasing the calcination temperature was shown in Table.1. The existence of nanoparticle in the form of composite play an important role in the densification behavior of ceramics. As the particle size was lesser then 34 nm, it was expected to have low sintering temperature and time [18].



Figure.4. Energy dispersive spectrum of Ba10CS powder calcined at (a) 700°C and 900°C

Figure 4 shows the Energy dispersive spectrum (EDS) of Ba10CS sample. From the EDS measurement, it was observed that the presence of Samarium, Cerium and barium in the compound with no other impure elements [19]. No evident pattern for residual impurities was observed in the as prepared SDC-BCS powder. The EDS result confirms that the method of process and the calcination temperature of electrolyte powder was are more sufficient to produce the nano composite matrix with dual phase.

3.4 XRD analysis for SDC-BCS Pellet:

Figure.5 shows the XRD pattern for the existence of both SDC phase, BCS phase in the pellet sintered at 1300°C and 1400°C for 20 min through microwave sintering. The structural investigation was carried out to know the effect of sintering temperature. The existences of cubic fluorite structure for SDC phase and orthorhombic perovskite structure for BCS phase was observed and shown Figure 5 (c) & (d). The XRD result confirms the formation of dual phase matrix in the form of composite. The presence of major diffraction planes (020), (400) and (402) confirms that the BCS phase was successfully retained in the composite sintered at 1400°C within the minimum soaking time of 20 min. As the sintering temperature increase, the intensity of the peak pertaining to BCS phase increases and

shows the indications of increase in volume of BCS phase in the composite. The diffraction peaks for both the phases are compared and indexed from JCPDS files No:75-0158 for SDC phase and 85-2155 for BCS phase. In addition, no by-product phases are observed, indicating that there was no superimposition of SDC and BCS phases. The intensity of peak around 28.67° for (020) plane was considered as the predominant peak for samarium doped barium cerate (BCS) phase and found to increase with increase in sintering temperature. The gradual decrease in the peak position at 28.42° of (111) plane correspond to the samarium doped ceria phase was also observed with increase in temperature.



Figure:5 XRD pattern of SDC-BCS pellet sintered at 1300°C and 1400°C for 20mins

The high intense peak present at 28.68° and 28.42° confirms that most of the grains are oriented at (020) plane and (111) plane of both the phases respectively. It can also be observed that the diffraction pattern with the main reflexes are at (020), (400), (402), (040), (420), (611) correspond to the barium cerate phase and the reflected peaks position at (111),(200),(220), (311), (400) corresponds to samarium doped barium cerate. The XRD pattern for SDC-BCS composite depicts that the formation of BaCe_{1-x}Sm_xO_{3-δ} doped barium cerate phase with increase in sintering temperature of the composite by following the reaction mechanism (1,2).

$$BaCO_3 \rightarrow BaO + CO_2^{\uparrow} \tag{1}$$

$$BaO + Ce_{0.8}Sm_{0.2}O_{1.9} \rightarrow BaCe_{1.-x}Sm_xO_{3-\delta}$$
(2)

The formation of BCS phase formation with lattice parameters a = 8.753, b = 6.244, c = 6.231 are in good agreement the values earlier reported [**20,21**]. The Corresponding d-spacing values are calculated from the equation (3).

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

(3)

The crystalline size was calculated from the Scherer's formula (equation.4) for the high intense peak and found to increase from 30nm to 32nm. It was clearly observed that with an increase in sintering temperatures, all the peaks become sharper and this was an indication of increase in particle size [14,28].

$$\mathbf{D} = \frac{\mathbf{0.9\lambda}}{\beta \, \mathbf{Cos} \mathbf{\theta}} \tag{4}$$

Hence, from this structural analysis, it was inferred that the pellet sintered at 1400°C can influence the formation of composite structure with existence of SDC and BCS phase, co fired by means of microwave sintering.

Table:2 Unit cell parameters for Ba10CS pellets sintered at 1400° C for 20 mins.

Method of	Temperature of	Type of	Unit cell parameters			Unit	Ref
synthesis	Synthesis (K)	structure	a	b	с	volume	Rei.
BaCe _{0.9} Gd _{0.1} O ₃	1600-1650	orthorhombic	8.770	6.221	6.244	340.66	[18]
BaCe _{0.8} Gd _{0.2} O ₂	1500	orthorhombic	8.816	6.233	6.180	338.8	[19]
Ba10CG	1500-1550	orthorhombic	8.791	6.242	6.212	340.8	[15]
Ba40CG	1550-1550	orthorhombic	8.774	6.244	6.203	339.8	[15]
Ba10CS	1400	orthorhombic	8.753	6.244	6.231	340.94	This Work
Ba10CS	1300	orthorhombic	8.796	6.239	6.212	340.54	This

			Work

The lattice parameter and unit cell volume for both the phases was calculated from XRD data. The corresponding lattice parameters, unit cell volume of Ba10CS pellet was calculated from equation (3) and are listed in Table-2 with comparison to the earlier reported values and found to match exactly noteworthy at lower sintering temperature, which reveals that these SDC-BCS phase was successfully retained at 1400°. All the major peak, d-spacing values are in well agreement with the JCPDS data of Reference code: 85-2155 [13]. Density values for both the samples are measured to be 92% and 96% respectively using the normal geometric calculations (not shown).

3.5 Microstructural Analysis for SDC-BCS Pellet:

SEM analysis was carried out to know the development of morphology in SDC-BCS composite electrolytes sintered at 1300°C and 1400°C. As expected, the composite electrolyte exhibited uniform distribution of SDC and BCS grains. The observed morphology was mainly recognized as SDC- BCS grains in the form of composite matrix. The average grain size of 2-4 µm and are quite dense in nature without having any connected pores [22]. The SEM image shows no porosities, thus avoiding the possible effect on the impedance response of the composites. Figure 6(a) and 6(b) exhibits the distribution of two types of grain size. The observed grain size are in micron and submicron range. The micron size grain was continuous and acts as matrix. The presence of grain boundary was well defined between the microns sized grains. The grains are almost uniform in size and perfectly packed. The mean grain sizes of the pellet sintered at 1300°C and 1400°C are approximately 2µm and 4µm, respectively. The pellet sintered at 1400°C shows homogeneous distribution of submicron sized grain within the matrix and acts as reinforcement in the composites. The submicron grains are present in between the voids of micron sized grains and increasing the density of the composites [23].

The volume of BCS phase was found to increase and in consistent with the XRD results. The presence of SDC grain in composite acts as a protective layer for BCS crystalline grains as predicted [14]. The increase in grain size and the decrease in grain boundary was observed as the sintering temperature increased from 1300°C to 1400°C and this behavior can enhance the ionic conductivity in SDC- BCS composite. When compared with the chemical stability of individual SDC and BCS phase, the presence of two phase microstructure in SDC-BCS composites can apparently improve the

chemical stability of electrolyte operated at high temperature. Thus, the existence of SDC and BCS grains are acting as a protective layer for each other [24].



Figure.6 SEM image for SDC-BCS pellet sintered at (a) 1300°C and (b) 1400°C

Hence, from this SEM analysis it was understood that the high dense pellet of two phase microstructures are grown in equal size while increasing the sintering temperature of the solid ceramic using microwave furnace in less soaking time.

3.6 Conductivity studies for SDC-BCS Pellet:

The Impedance measurement was carried out for Ba10CS composite electrolyte sintered at 1300°C and 1400°C respectively over the frequency range from 1Hz to 1MHz, with an applied potential of 0.1V in the temperature range between 300°C-800°C. In addition to understand the electrical behavior of SDC-BCS composite, the electrochemical property of the pellet was studied by EIS at an Open Circuit Voltage condition. The equivalent circuit was used to fit the data using EC lab Software.

The Nyquist plots are fitted between the real and imaginary parts of the impedance. Figure.7 shows the Nyquist plots for SDC-BCS composite recorded at 700°C. This plots are usually appears in the form of two semicircles, represent the different conduction mechanism occurred in the materials. The resistances measured at intermediate frequency semicircle are generally ascribed to grain boundary effect. The resistance of the pellet sintered at 1300°C was higher than the pellet sintered at 1400°C. The variation in resistance phenomenon was mainly due to the difference in microstructure of the composite and the effect of grain boundary diffusions [25].



Figure.7 EI Spectrum for SDC-BCS composite measured under open circuit conditions at 700°C,

The change in resistance with raise in temperature was mainly due to decrease in bulk resistance of the electrolyte materials and thus inferred that there was an increase in the conductivity of the composite materials. Figure 8. shows the Arrhenius plot for both the composites with increase in sintering temperature. It was well understood that the increase in BCS pervoskite phase can ultimately decrease the activation energy at low temperature.

Hence the co existence of fluorite and pervoskite phase in SDC-BCS composite electrolyte can effectively block the leakage of electronic current through SDC phase and ultimately improves the mobility of oxygen ions through BCS phase [26]. The bulk conductivities and activation energies values are calculated using the following equations (5).

$$\sigma = \frac{L}{SR}$$
(5)

where σ is the conductivity, L is the thickness of the electrolyte, S is the tested electrolyte area, R is the corresponding resistance of the electrolyte, and the activation energy corresponds to the conductivity of the electrolyte was calculated from the linear fit of the Arrhenius curves using the following Arrhenius equation.

$$\sigma T = A \exp\left(-\frac{E_a}{kT}\right) \tag{6}$$

T is the temperature in Kelvin, A is the pre-exponential factor, Ea is the activation energy and k is the Boltzmann constant. Here to be noticed that we considered only the total conductivity of the electrolyte at 700°C.

Table.3 Variation of conductivity and activation energy of SDC-BCS composite with increase in sintering temperature



Figure.8. The Arrhenius plot of SDC-BCS composite electrolyte

The total conductivity for SDC-BCS composites electrolytes was the sum of the conductivity of SDC-BCS grains, grain boundary between BCS, grain boundary between SDC and grain boundary between SDC and BCS grains. The total ionic conductivity of the composites was extracted from the equivalent circuit fitted over the respective Nyquist plot. The total ionic conductivity and activation energy as a function of temperature for (1-x) Ce_{0.8}Sm_{0.2}O_{3-δ}-xBa Ce_{0.8}Sm_{0.2}O_{3-δ} (x=0.1mole fraction)

measured under open circuit condition at 700°C was shown in Table.3. The highest conductivity of 1.19x10-3 Scm⁻¹ was observed for the composite sintered at 1400°C for 20 minutes using microwave techniques.

Hence microwave sintering can be an effective technique for the development of dual phase SDC-BCS microstructure in Ba10CS composite in less processing time. Hence, SDC-BCS composite electrolyte with dual matrix can be a good choice of electrolyte give the required ionic conductivity operated at intermediate temperature for solid oxide fuel cell applications [27,28].

4. Conclusions:

Samarium doped barium cerate composite electrolyte powder was synthesized through chemical route and the pellets were sintered using microwave techniques. The calcination temperature of 900C was identified from TG analysis. The coexistence of SDC-BCS phase with cubic – pervoskite was identified from structural analysis. SEM analysis confirms the homogenous distribution of two phase microstructure. The high ionic conductivity was observed for the composite electrolyte sintered at 1400C with a minimum soaking time of 20 minutes. The increase in conductivity was due to the diffusion of oxygen ion preferred to migrate through the continuous channel of samarium doped barium cerate phase. Hence, the SDC-BCS composite with dual phase microstructure can acts as a best choice of electrolyte for the energy conversion in solid oxide fuel cell application.

Reference:

- [1]. B.C.H. Steele, Appraisal of Ce 1- y Gd y O 2- y/2 electrolytes for IT-SOFC operation at 500 C. Solid State Ionics 129 (2000) 95-110.
- [2]. A. Venkatasubramanian, P. Gopalan*, T.R.S. Prasanna: 'Synthesis and characterization of electrolytes based on BaO–CeO2–GdO1.5 system for Intermediate Temperature Solid Oxide Fuel Cells', International Journal of Hydrogen energy., 35 (2010),4597-4605.
- [3]. K.C. Anjaneya, G.P. Nayaka, J. Manjanna, V.M. Ashwin Kumar, G. Govindaraj, K.N. Ganesha: Investigation on the Sr-doped ceria Ce1-xSrxO2-□□(x = 0.05–0.2) as an electrolyte for intermediate temperature SOFC Journal of Alloys and Compounds', 598 (2014), 33–40.
- [4]. S.U. Dubal, A.P. Jamale, S.T. Jadhav, S.P. Patil, C.H. Bhosale, L.D. Jadhav. Yttrium doped BaCeO3 thin films by spray pyrolysis technique for application in solid oxide fuel cell. Journal of

Alloys and Compounds, 587 (2014) 664-669.

- [5] A.J.Jacobson, B.T.Tofield, B E F Fender, The structures of BaCeO3, BaPrO3 and BaTbO3 by neutron diffraction: lattice parameter relations and ionic radii in O-perovskites, Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry, 28(1972) 956-961.
- [6]. S.T.Jadhav, V.R.Puri, L.D. Jadhav, NiO-GDC-BCY composites as an anode for SOFC, Journal of Alloys and Compounds, 685(2016) 626-632.
- [7]. W.Sun, W. Liu, A novel ceria-based solid oxide fuel cell free from internal short circuit, Journal of Power Sources, 217 (2012)114-119.
- [8]. T. Takahashi, H. Iwahra, Ionic conduction in perovskite-type oxide solid solution and its application to the solid electrolyte fuel cell, Energy Conversion 11 (1971) 105-111.
- [9]. S.C. Singhal, Advances in solid oxide fuel cell technology. Solid state ionics 135.1 (2000)305-313.
- [10]. Shima, D., and S. M. Haile. "The influence of cation non-stoichiometry on the properties of undoped and gadolinia-doped barium cerate." Solid State Ionics 97.1 (1997): 443-455.
- [11]. Li, J G, Wang, Y, Ikegami, T, Mori, T & Ishigaki, T, Reactive 10mol% RE2O3 (RE= Gd and Sm) doped CeO2 nanopowders: Synthesis, characterization, and low-temperature sintering into dense ceramics", Materials Science and Engineering: B, 121(2005) 54-59.
- [12]. H.Wang, L.Zhang, X.Liu, H.Bi, S.Yu, F.Han, L.Pei, Electrochemical study on Ce0.85Sm0.15O1.925-BaCe0.83Y0.17O3-δ composite electrolyte, Journal of Alloys and Compounds, 632(2015) 686-694.
- [13]. J. Luo, R. J. Ball, R. Stevens, Gadolinia doped ceria/yttria stabilised zirconia electrolytes for solid oxide fuel cell applications, Journal of Materials Science 39 (2004) 235–240.
- [14]. W.Sun, Y.Jiang, Y Wang, S.Fang, Z. Zhu, W.Liu, A novel electronic current-blocked stable mixed ionic conductor for solid oxide fuel cells, Journal of Power Sources, 196 (2011) 62-68.
- [15]. Haile, Sossina M. "Fuel cell materials and components." Acta Materialia 51.19 (2003): 5981-6000.
- [16]. J. Garcia-Barriocanal, A. Rivera-Calzada, M. Varela, Z. Sefroui, E. Iborra, C. Leon, S.J.Pennycook, J.Santamaria, Colossal ionic conductivity at interfaces of epitaxial ZrO2: Y2O3/SrTiO3 heterostructures, Science 321 (2008) 676-680.
- [17]. D.J.L. Brett, A. Atkinson, N.P. Brandon, S.J. Skinner, Intermediate temperature solid oxide fuel cells Chem. Soc. Rev. 37 (2008) 1568-1578.
- [18]. M. Goedickemeier, L.J. Gauckler, Engineering of Solid Oxide Fuel Cells with Ceria-Based

Electrolytes. Journal of The Electrochemical Society 145 (1998) 414-421.

- [19]. H. Kato, T. Kudo, H. Naito, H. Yugami, Electrical conductivity of Al-doped La1-xSrxScO3 perovskite-type oxides as electrolyte materials for low-temperature SOFC, Soild State Ionics 159 (2003) 217-222.
- [20]. Kreuer, K. D. "On the development of proton conducting materials for technological applications." Solid state ionics 97.1 (1997): 1-15.
- [21] T. Mahata, G. Das, R.K. Mishra, B.P. Sharma: 'Combustion synthesis of gadolinia doped ceria powder', Journal of Alloys and Compounds, 391 (2005), 129-135.
- [22].C.J.Bardwell, R.I.Bickley, S.Poulston, M.V.Twigg, Thermal decomposition of bulk and supported barium nitrate, Thermochimica Acta, 613(2015) 94-99.
- [23]. T.S.Zhang, J.Ma, L.B.Kong, P.Hing, J.A.Kilner, Preparation and mechanical properties of dense Ce0.8Gd0.2O2–δ ceramics, Solid State Ionics, 167(2004)191-196.
- [24].K.S.Knight, Structural phase transitions in BaCeO3, Solid State Ionics, 74.3-4 (1994) 109-117.
- [25]. S.M.Haile, D.L.West, J.Campbell, The role of microstructure and processing on the proton conducting properties of gadolinium-doped barium cerate, Journal of materials research, 13 (1998)1576-1595.
- [26]. Q.X.Fu, S.W.Zha, W.Zhang, D.K.Peng, G.Y.Meng, B.Zhu, Intermediate temperature fuel cells based on doped ceria–LiCl–SrCl 2 composite electrolyte, Journal of power sources, 104(1) (2002) 73-78.
- [27] Kumar AS, Balaji R, Jayakumar S, Pradeep C, Microwave assisted sintering of gadolinium doped barium cerate electrolyte for intermediate temperature solid oxide fuel cells, Journal of Materials Chemistry and Physics 182 (2016) 520-525.
- [28]. J.Maier, Nanoionics: ion transport and electrochemical storage in confined systems, Nature materials, 4(11) (2005) 805-815.

3

THERMAL, STRUCTURAL AND ELECTRICAL PROPERTIES OF SAMARIUM DOPED BARIUM CERATE ELECTROLYTE FOR SOFCs

A.Senthil Kumar^{a*}, R.Balaji^a

^a Department of Physics, PSG College of Technology Coimbatore – 641 004, TN, INDIA

