

# Chemical Precipitation of $\text{BaCeO}_3$ – $\text{CeO}_2$ Based Nano-ceramic Composite Oxide Materials and Their Physical Characterization

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## Abstract:

*In order to reduce the operating temperature of solid oxide fuel cells (SOFCs), novel electrolyte materials based on  $\text{CeO}_2$  and  $\text{BaCeO}_3$  are being developed in the scientific realm. In this context, we propose a new methodology for preparing the nano-ceramic composite materials such as  $\text{BaCe}_{0.9}\text{Gd}_{0.9}\text{O}_{3-\delta}$  –  $\text{Ce}_{0.9}\text{Gd}_{0.9}\text{O}_{2-\delta}$  (BCGO–CGO) and  $\text{BaCe}_{0.8}\text{Sm}_{0.2}\text{O}_{3-\delta}$  –  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$  (BCSO – CSO) as possible electrolytes for SOFC using a simple low temperature chemical precipitation method. The precursor materials used in this preparation were barium nitrate, cerium nitrate and gadolinium nitrate / samarium nitrate (as basic materials), sodium hydroxide (as a precipitator material) and poly vinyl pyrrolidone (as surfactant). In a typical experiment, the aqueous solution containing  $\text{Ba}^{2+}$ ,  $\text{Ce}^{3+}$  and  $\text{Gd}^{3+}/\text{Sm}^{3+}$  ions was mixed with the solution of alkali in a magnetic stirrer and then the required percentage of surfactant was added. The formed hydroxides of Ba, Ce and Gd/Sm were washed with water and ethyl alcohol and dried at 50–100°C for 24 hours. The dried powder was then heat treated for 2 h each at 300, 450 and 600°C respectively and then cooled down to room temperature. It was found that the orthorhombic structure could be formed after being calcined at 600°C for 2 h, and the powders were mainly composed of nano-size particles. Characterization by TGA-DTA, XRD, particle size measurements & SEM are presented to evaluate the fundamental physical properties of the proposed nano-composite materials.*

**Keywords:** Nano-ceramic composite powders, Synthesis, Chemical precipitation, Characterization

## 1. INTRODUCTION

Ceria-based materials have been previously developed as functional electrolytes for high performance intermediate temperature solid oxide fuel cell (ITSOFC) applications. To improve the electrolyte performance in SOFC, composite electrolyte materials based on  $\text{CeO}_2$  with other oxide materials are being developed worldwide [1, 2]. The nanocomposite approach is based on the fact that in the nano-scale the materials become conductive though they are non-conductive in

normal (mm) scale. In this case, the particle bulk nature is not anymore dominant but the effects of the boundaries and interfaces among the particles turn to determinable factor for the material property and conductivity. The second phase particles can be introduced to form the composites in order to adjust and optimize the interfacial effects to the maximum. This is the basic principle of the nanocomposites. Typical examples are various ceria–oxide composites, e.g.  $\text{CeO}_2$ – $\text{SiO}_2$ ,  $\text{CeO}_2$ – $\text{La}_2\text{O}_3$ , doped ceria–doped  $\text{BaCeO}_3$  (perovskite  $\text{H}^+$  conducting oxide) and ceria–salt composites as well as corresponding thin film materials. The

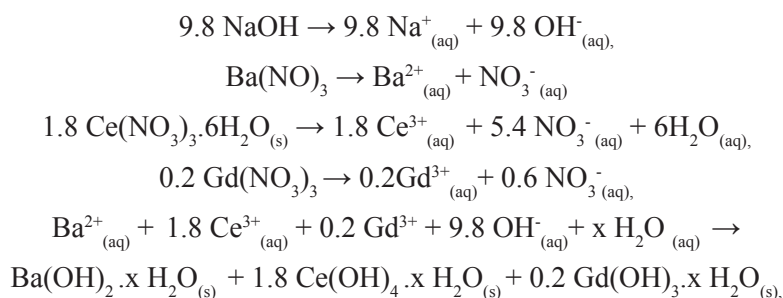
nanocomposite approach uses the two-phase interfacial mechanisms to Create new material functions neither limited by nor changing the single-phase bulk structure, which can be an efficient tool to Create advanced materials and devices by optimizing and developing the interfacial functions that each individual phase/component does not possess.

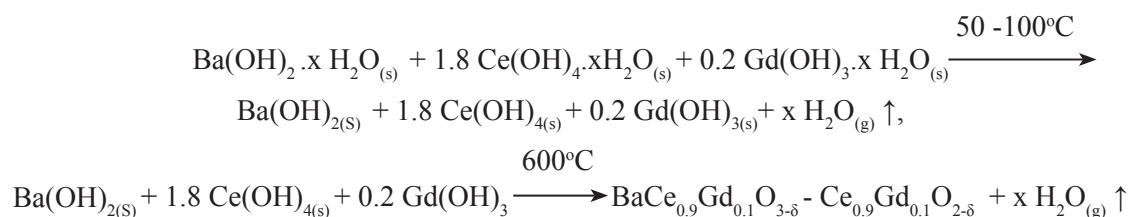
The ceria based composite electrolytes (usually containing two phases) and their successful Low Temperature SOFC (LTSOFC) applications have shown great performance improvements that have demonstrated a breakthrough in fuel cell R&D [3,4]. New research achievements on the ceria based electrolyte materials showed superionic and dual or hybrid H<sup>+</sup>/O<sup>2-</sup> conduction with a conductivity of 10<sup>4</sup>S cm<sup>-1</sup> below 600°C [5]. Currently joint industrial developments on the ceria based composite electrolytes have been scaled up for production, to manufacture the prototype LTSOFCs. Bin Zhu et.al have prepared BaCe<sub>0.8</sub>Y<sub>0.2</sub>O<sub>3-δ</sub> (BCY20) – samarium doped CeO<sub>2</sub> (CSO) composites via sol–gel and co-precipitation processes and used as electrolytes in SOFC<sup>1</sup>. These composites displayed hybrid proton and oxygen ion conduction. Jang et.al have prepared yttria doped ceria (YDC) and gadolinia doped ceria (GDC) composite electrolytes by polymeric sol process and used as electrolyte in LTSOFC [6]. In this study, we focus our attention on the synthesis and characterization of nano-ceramic composite materials namely BaCe<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>3-δ</sub> - Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>2-δ</sub> (BCGO-CGO) and BaCe<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>3-δ</sub> - Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>2-δ</sub> (BCSO – CSO) by a simple chemical precipitation process in presence of a precipitant sodium hydroxide and a surfactant PVP (polyvinyl pyrrolidone).

## 2. EXPERIMENTAL

### 2.1. Preparation of BaCe<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>3-δ</sub> - Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>2-δ</sub> (BCGO–CGO) nano-ceramic composite material by chemical precipitation process

High purity Ba(NO<sub>3</sub>)<sub>2</sub>, Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Gd<sub>2</sub>O<sub>3</sub>, nitric acid, sodium hydroxide and poly vinyl pyrrolidone were used in the preparation of BaCe<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>3-δ</sub> - Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>2-δ</sub> nano-ceramic composite material. Initially, 0.25 M of Ba(NO<sub>3</sub>)<sub>2</sub> (6.5335 g of Ba(NO<sub>3</sub>)<sub>2</sub> in 100 ml, 0.45 M of Ce(NO<sub>3</sub>)<sub>3</sub> (19.539 g of Ce(NO<sub>3</sub>)<sub>3</sub> in 100 ml of water), 0.05 M of Gd(NO<sub>3</sub>)<sub>3</sub> (0.9062 g of Gd<sub>2</sub>O<sub>3</sub> is dissolved in 10 ml HNO<sub>3</sub> and made upto 100 ml with water) and 2.45 M of sodium hydroxide (9.8 g of sodium hydroxide in 100 ml of water) were prepared. Initially 2 ml of 10 % PVP was added slowly to the sodium hydroxide solution. To this mixture, Ba(NO<sub>3</sub>)<sub>2</sub>, Ce(NO<sub>3</sub>)<sub>3</sub> and Gd(NO<sub>3</sub>)<sub>3</sub> and solutions were added consequently drop wise. They were mixed perfectly by a magnetic stirring apparatus (1000 rpm) at room temperature for 1 hour. Throughout the experiment, pH was maintained as greater than 9 by the addition of alkali. The resultant yellow coloured precipitate [Ba(OH)<sub>2</sub> + Ce(OH)<sub>4</sub> + Gd(OH)<sub>3</sub>] was filtered, and then washed with deionized water and ethanol for 5 – 10 times. It was dried at 50 – 100°C for 24 hours. Then, the calcination was carried out at 300°C, 450°C and 600°C for 2 hours each. During calcination at high temperature, the surfactant was removed and phase pure yellow coloured BaCe<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>3-δ</sub> - Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>2-δ</sub> nano-ceramic composite material was formed. Figure 1 shows a schematic illustration of the synthesis of BaCe<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>3-δ</sub> - Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>2-δ</sub> nano-ceramic composite material by chemical precipitation process. Main reactions occur during the experimental procedure can be written briefly as follows:

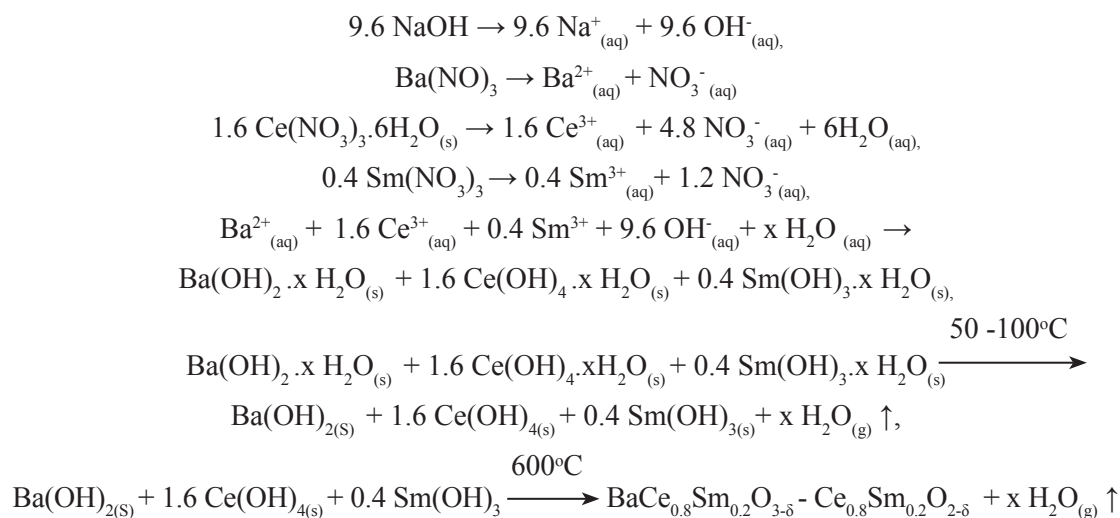


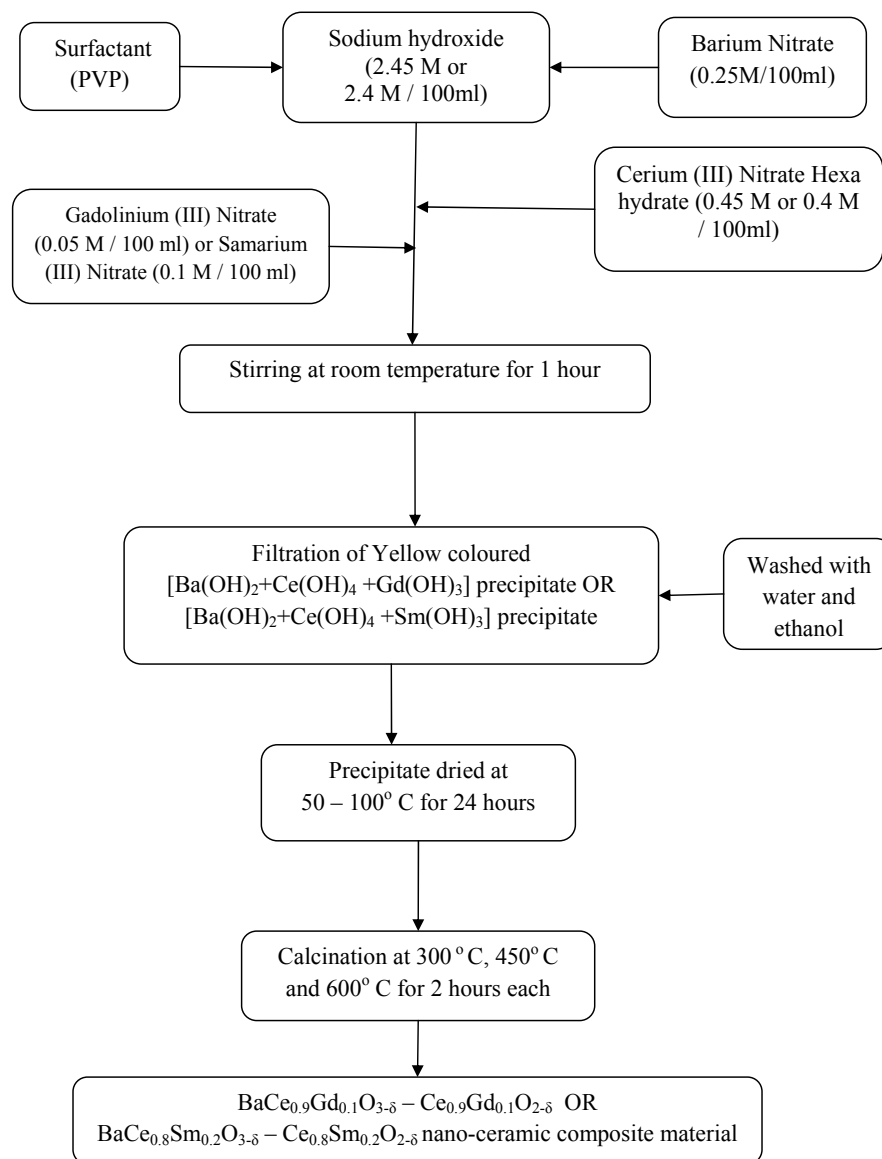


## 2.2. Preparation of BaCe<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>3-δ</sub> - Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>2-δ</sub> (BCSO–CSO) nano-ceramic composite material by chemical precipitation process

High purity Ba(NO<sub>3</sub>)<sub>2</sub>, Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Sm<sub>2</sub>O<sub>3</sub>, nitric acid, sodium hydroxide and poly vinyl pyrrolidone were used in the preparation of BaCe<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>3-δ</sub> - Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>2-δ</sub> nano-ceramic composite material. Initially, 0.25 M of Ba(NO<sub>3</sub>)<sub>3</sub> (6.5335 g of Ba(NO<sub>3</sub>)<sub>3</sub> in 100 ml, 0.4 M of Ce(NO<sub>3</sub>)<sub>3</sub> (13.0456 g of Ce(NO<sub>3</sub>)<sub>3</sub> in 100 ml of water), 0.1 M of Sm(NO<sub>3</sub>)<sub>3</sub> (1.7436 g of Sm<sub>2</sub>O<sub>3</sub> is dissolved in 10 ml HNO<sub>3</sub> and made upto 100 ml with water) and 2.4 M of sodium hydroxide (9.6 g of sodium hydroxide in 100 ml of water) were prepared. In this preparation also, initially 2 ml of 10% PVP was added slowly to the sodium hydroxide solution. To this mixture, Ba(NO<sub>3</sub>)<sub>2</sub>, Ce(NO<sub>3</sub>)<sub>3</sub> and Sm(NO<sub>3</sub>)<sub>3</sub> solutions were added consequently drop wise. They were mixed

perfectly by a magnetic stirring apparatus (1000 rpm) at room temperature for 1 hour. Throughout the experiment the pH was maintained as greater than 9 by the addition of alkali. The resultant yellow coloured precipitate [Ba(OH)<sub>2</sub> + Ce(OH)<sub>4</sub> + Sm(OH)<sub>3</sub>] was filtered, and then washed with deionized water and ethanol for 5–10 times. It was dried at 50–100°C for 24 hours. Then, the calcination was carried out at 300°C, 450°C and 600°C for 2 hours each. During calcination at high temperature, the surfactant was removed and phase pure yellow coloured BaCe<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>3-δ</sub> - Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>2-δ</sub> nano-ceramic composite material was formed. Figure 1 shows a schematic illustration of the synthesis of BaCe<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>3-δ</sub> - Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>2-δ</sub> nano-ceramic composite material by chemical precipitation process. Main reactions occur during the experimental procedure can be written briefly as follows:



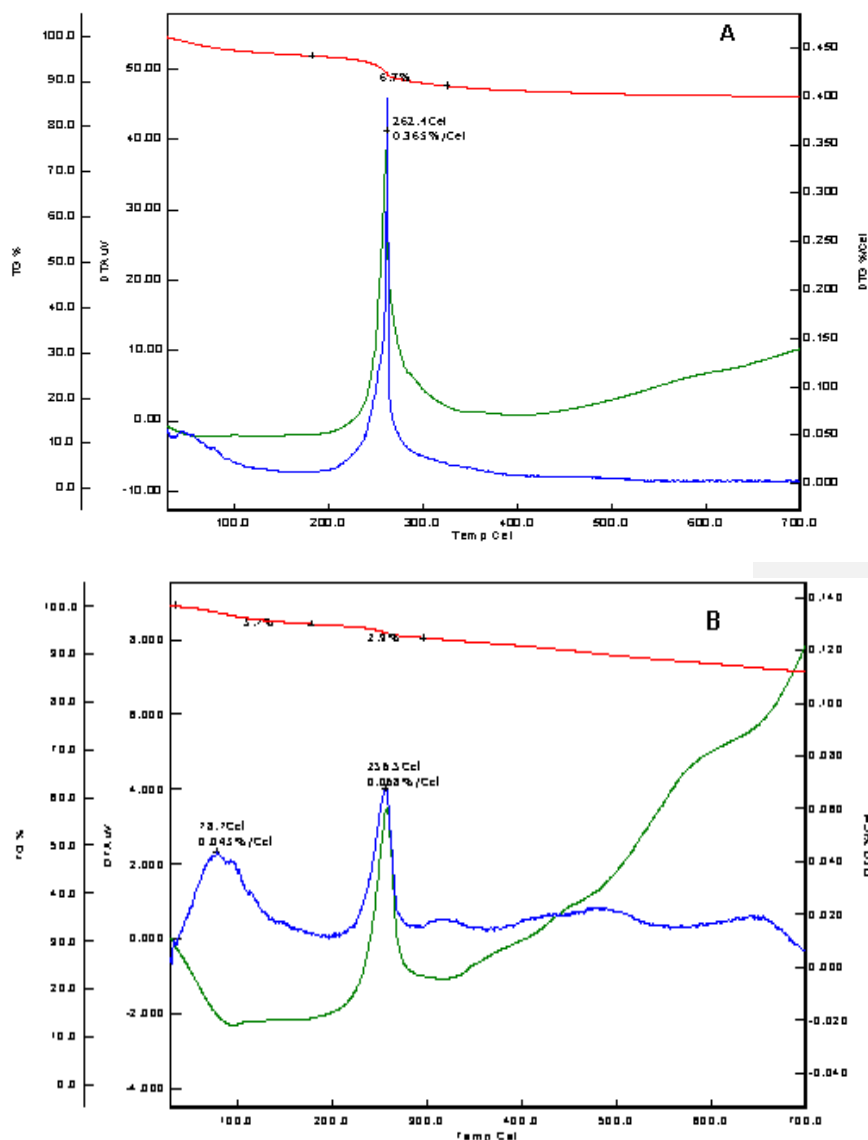


**Figure 1:** Schematic illustration of the synthesis of  $BaCe_{0.9}Gd_{0.1}O_{3-\delta} - Ce_{0.9}Gd_{0.1}O_{2-\delta}$  (BCGO – CGO) and  $BaCe_{0.8}Sm_{0.2}O_{3-\delta} - Ce_{0.8}Sm_{0.2}O_{2-\delta}$  (BCSO – CSO) nano-ceramic composite materials by chemical precipitation process

### 2.3. Characterization of the nano-ceramic composite powder

Thermal analysis of the precursor material were performed with SI EXSTAR 6000 TG/DTA 6300 instrument between 25 and 700°C in nitrogen atmosphere. The powder XRD studies were carried out using Shimadzu XRD6000 X-ray diffractometer at a scan speed of 5 deg/min using

CuK $\alpha$  radiation. The lattice parameters were calculated by least square fitting method using DOS computer programming. The theoretical densities of the powders were calculated with the obtained XRD data. The crystallite sizes of the powder were calculated by Scherrer's formula. Bruker IFS 66V FT-IR spectrometer was employed to record the FTIR spectra of doped BaCeO<sub>3</sub> powder in the



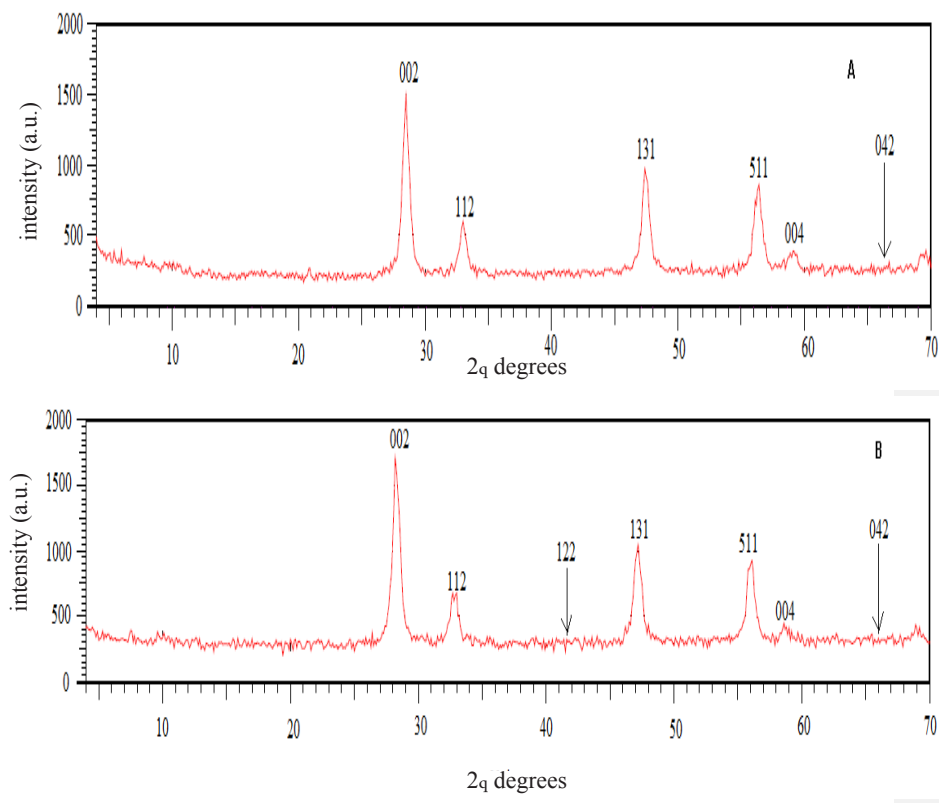
**Figure 2:** DTA/TGA spectrum obtained on precursor materials  
 (a)  $[\text{Ba}(\text{OH})_2 + \text{Ce}(\text{OH})_4 + \text{Gd}(\text{OH})_3 + \text{PVP}]$   
 (b)  $[\text{Ba}(\text{OH})_2 + \text{Ce}(\text{OH})_4 + \text{Sm}(\text{OH})_3 + \text{PVP}]$

range of  $4000 - 400 \text{ cm}^{-1}$ . The crystallite sizes of the ceramic powders were calculated by Scherrer's formula. The particle size of the powder was measured using Malvern Particle Size Analyzer using triple distilled water as medium. The surface morphology of the particles was studied by means of JEOL Model JSM-6360 scanning electron microscope.

### 3. RESULTS AND DISCUSSION

#### 3.1. Thermogravimetry / differential thermal analysis (TGA/DTA) of precursor materials

The TGA/DTA spectrums obtained with the precursor materials  $[(\text{Ba}(\text{OH})_2 + \text{Ce}(\text{OH})_4 + \text{Gd}(\text{OH})_3 + \text{PVP})$  and  $(\text{Ba}(\text{OH})_2 + \text{Ce}(\text{OH})_4 +$



**Figure 3:** XRD pattern obtained on nano-ceramic composite materials

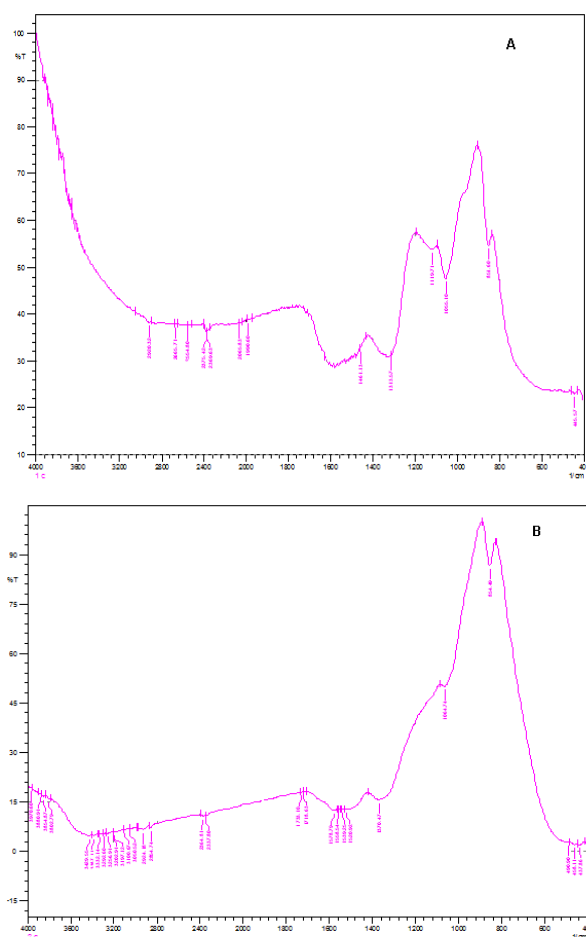
(a)  $BaCe_{0.9}Gd_{0.1}O_{3-\delta} - Ce_{0.9}Gd_{0.1}O_{2-\delta}$  (BCGO – CGO)

(b)  $BaCe_{0.8}Sm_{0.2}O_{3-\delta} - Ce_{0.8}Sm_{0.2}O_{2-\delta}$  (BCSO – CSO)

Sm(OH)<sub>3</sub> + PVP] are indicated in Figures 2 (a) & 2 (b). The DTA peaks closely corresponding to the weight changes observed on the TGA curves. From Figure 2 (a), the total weight loss from the temperature of 25 to 700°C was found to be 11.0%. Initial weight loss of about 3% is observed at around 100°C, which is due to the removal water molecule from the water sample. Then, the total weight loss of 5.7 % is observed at 262°C which is attributed to the removal of oxides of carbon and nitrogen present in the sample. This is confirmed with an exothermic peak around 262°C in the DTA curve. The further weight loss present in the sample until 700°C is due to the decomposition of remaining organics present in the sample. After 300°C, the weight loss from the sample is gradual which is attributed to the slow removal organics present in the sample. From Figure 2 (b), it is inferred that major weight loss is observed at 2 places. The weight loss of about 2 % is found at

78°C which is confirmed with an exothermic peak and probably which is attributed to the starting of water removal from the sample. The second weight loss is observed at 256°C, similar to the previous case may be due to the removal of oxides of carbon and nitrogen present in the sample. This removal of gases is also confirmed with a strong exothermic peak in the sample. The total weight loss of this sample at 700°C is found to be 12%. The removal of organics and other volatile compounds from both the samples is completed at around 700°C. From the observation, it was understood that the phase pure compound can be prepared at 700°C.

### 3.2. Structural determination of $BaCe_{0.9}Gd_{0.1}O_{3-\delta} - Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (BCGO – CGO)/ $BaCe_{0.8}Sm_{0.2}O_{3-\delta} - Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (BCSO – CSO) nano-ceramic composite materials by XRD



**Figure 4:** FTIR spectrum obtained on nano-ceramic composite materials

- (a)  $BaCe_{0.9}Gd_{0.1}O_{3-\delta}-Ce_{0.9}Gd_{0.1}O_{2-\delta}$  (BCGO-CGO)  
 (b)  $BaCe_{0.8}Sm_{0.2}O_{3-\delta}-Ce_{0.8}Sm_{0.2}O_{2-\delta}$  (BCSO-CSO)

Venkatasubramanian et.al [7] have synthesized a composite electrolyte based on  $BaO-CeO_2-GdO_{1.5}$  ternary system through conventional solid state reaction route. They confirmed the presence of two phase microstructure by X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM) studies. It is reported that  $BaCeO_3$  doped with 10 mol% Gd / Y was indexed as orthorhombic geometry [8]. It is reported that the crystal structure of  $Ce_{0.8}Sm_{0.2}O_{2-\delta}$  (SDC) prepared by spray pyrolysis is found to be cubic [9]. 20% Gd-doped  $CeO_2$  films in the cubic phase were investigated using x-ray diffraction XRD [10]. However, noClear reported data available in the literature for the structural elucidation of

$BaCe_{0.9}Gd_{0.1}O_{3-\delta}-Ce_{0.9}Gd_{0.1}O_{2-\delta}$  (BCGO-CGO) and  $BaCe_{0.8}Sm_{0.2}O_{3-\delta}-Ce_{0.8}Sm_{0.2}O_{2-\delta}$  (BCSO-CSO) nanocomposite electrolytes for application in SOFC systems. Wang et.al [11] have studied the structural properties of  $BaCe_{0.94}Y_{0.06}O_{2.84}$  and reported its crystal structure as orthorhombic crystal geometry with unit cell parameters  $a = 8.7817 \text{ \AA}$ ,  $b = 6.2360 \text{ \AA}$  and  $c = 6.2190 \text{ \AA}$  with unit cell volume,  $V = 340.5 \text{ \AA}^3$ . Zhang and Yang have prepared proton conducting electrolyte  $BaCe_{0.9}Gd_{0.1}O_{3-\delta}$  over  $Ce_{0.9}Gd_{0.1}O_{2-\delta}$  substrates by dry pressing method as suitable electrolyte for SOFC application. The XRD data of the above sample revealed that no other evident phases apart from  $BaCe_{0.9}Gd_{0.1}O_{3-\delta}$  phase in the sample [12].

In this work, the structural properties of  $BaCe_{0.9}Gd_{0.1}O_{3-\delta}-Ce_{0.9}Gd_{0.1}O_{2-\delta}$  (BCGO - CGO) and  $BaCe_{0.8}Sm_{0.2}O_{3-\delta}-Ce_{0.8}Sm_{0.2}O_{2-\delta}$  (BCSO - CSO) synthesized by chemical precipitation technique are investigated. The as-synthesized powders were yellow in colour. The observed XRD patterns of the composite materials are shown in Figures 3 (a) and 3 (b). The obtained XRD pattern of the materials was matched with the standard data for  $BaCeO_3$  (JCPDS card No. 22-74) as standard JCPDS data for  $BaCeO_3 - CeO_2$  is not available for our nano-ceramic composite materials. Interestingly, the XRD analysis confirmed the presence of single phase compound with orthorhombic structure for both the materials. The diffraction patterns of the  $BaCe_{0.9}Gd_{0.1}O_{3-\delta}-Ce_{0.9}Gd_{0.1}O_{2-\delta}$  (BCGO - CGO) and  $BaCe_{0.8}Sm_{0.2}O_{3-\delta}-Ce_{0.8}Sm_{0.2}O_{2-\delta}$  (BCSO - CSO) are similar to that of reported  $BaCeO_3$  except for slight shifts in the diffraction angles. The lattice parameters are calculated from  $2\theta$  values in the X-ray diffraction patterns. The unit cell volume, crystallite size and theoretical density values are calculated for these samples. The crystallographic properties of the prepared nano-ceramic composite materials are in line with the reported data for parent perovskite ( $BaCeO_3$ ) [11]. The obtained crystal structure and unit cell parameters are reported in Tables 1 & 2. From the XRD data, it was understood that chemical precipitation method is a good method to prepare phase pure nano-ceramic composite materials for any application.

**Table 1:** XRD data obtained on  $BaCe_{0.9}Gd_{0.1}O_{3-\delta} - Ce_{0.9}Gd_{0.1}O_{2-\delta}$  (BCGO – CGO) nano-ceramic composite powder

Properties	Standard XRD data for $BaCeO_3$ powder (JCPDS N0.22-74)	Obtained XRD data for BCGO – CGO powder
Crystal structure	Orthorhombic	Orthorhombic
Unit cell lattice parameters (Å)	a = 8.779	a = 8.80342
	b = 6.214	b = 6.20351
	c = 6.236	c = 6.26707
Unit cell volume (Å <sup>3</sup> )	340.1906	342.2578
Theoretical density (g/cc)	6.3533	9.6824
Crystallite size (nm)	---	9.3007

**Table 2:** XRD data obtained on  $BaCe_{0.8}Sm_{0.2}O_{3-\delta} - Ce_{0.8}Sm_{0.2}O_{2-\delta}$  (BCSO – CSO) nano-ceramic composite powder

Properties	Standard XRD data for $BaCeO_3$ powder (JCPDS N0.22-74)	Obtained XRD data for BCSO–CSO powder
Crystal structure	Orthorhombic	Orthorhombic
Unit cell lattice parameters (Å)	a = 8.779	a = 8.84625
	b = 6.214	b = 6.22316
	c = 6.236	c = 6.29121
Unit cell volume (Å <sup>3</sup> )	340.1906	346.3413
Theoretical density (g/cc)	6.3533	9.5583
Crystallite size (nm)	---	9.6172

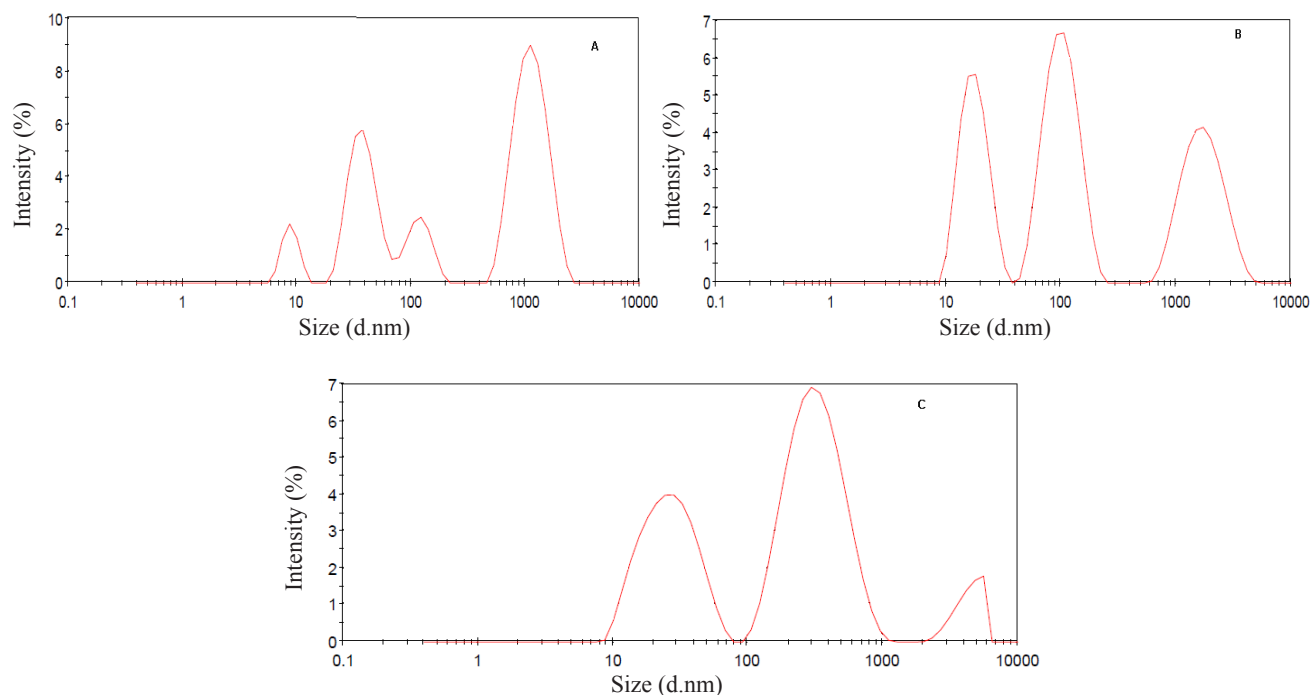
**Table 3:** Particle characteristics data (based on intensity) obtained on  $BaCe_{0.9}Gd_{0.1}O_{3-\delta} - Ce_{0.9}Gd_{0.1}O_{2-\delta}$  (BCGO – CGO) nano-ceramic composite powder

	Trial	Peak 1		Peak 2		Peak 3		Average particle size (d.nm)
		% intensity	Diameter (nm)	% intensity	Diameter (nm)	% intensity	Diameter (nm)	
Based on intensity	Trial – 1	53.5	1157	28.3	38.89	11.6	116.5	73.53
	Trial – 2	41.2	104.9	30.6	18.05	28.2	18.06	50.78
	Trial – 3	58.5	343.3	34.5	27.86	7.0	4382	65.58
Based on volume	Trial – 1	92	8.343	6.6	33.27	1.5	1254	73.53
	Trial – 2	1.1	81.95	2.0	2133	97	14.91	50.78
	Trial – 3	0.9	432.3	96.8	16.64	2.3	4731	65.58

**Table 4:** Particle characteristics data (based on intensity) obtained on  $BaCe_{0.8}Sm_{0.2}O_{3-\delta} - Ce_{0.8}Sm_{0.2}O_{2-\delta}$  (BCSO – CSO) nano-ceramic composite powder

	Trial	Peak 1		Peak 2		Peak 3		Average particle size (d.nm)
		% intensity	Diameter (nm)	% intensity	Diameter (nm)	% intensity	Diameter (nm)	
Based on intensity	Trial – 1	53.7	587.9	28.3	3933	18.0	44.32	216.9
	Trial – 2	53.6	400.8	43.7	63.09	2.7	5051	121.4
	Trial – 3	56.2	69.83	43.8	1242	--	--	127.2
Based on volume	Trial – 1	10.7	673.2	56.2	4416	33.1	43.23	216.9
	Trial – 2	12.0	464.3	71.9	55.51	16.1	5192	121.4
	Trial – 3	56.2	69.83	43.8	1242	--	--	127.2





**Figure 5 (a-c):** Particle size distribution patterns (based on intensity) obtained on  $BaCe_{0.9}Gd_{0.1}O_{3-\delta} - Ce_{0.9}Gd_{0.1}O_{2-\delta}$  (BCGO – CGO) nano-ceramic composite powder

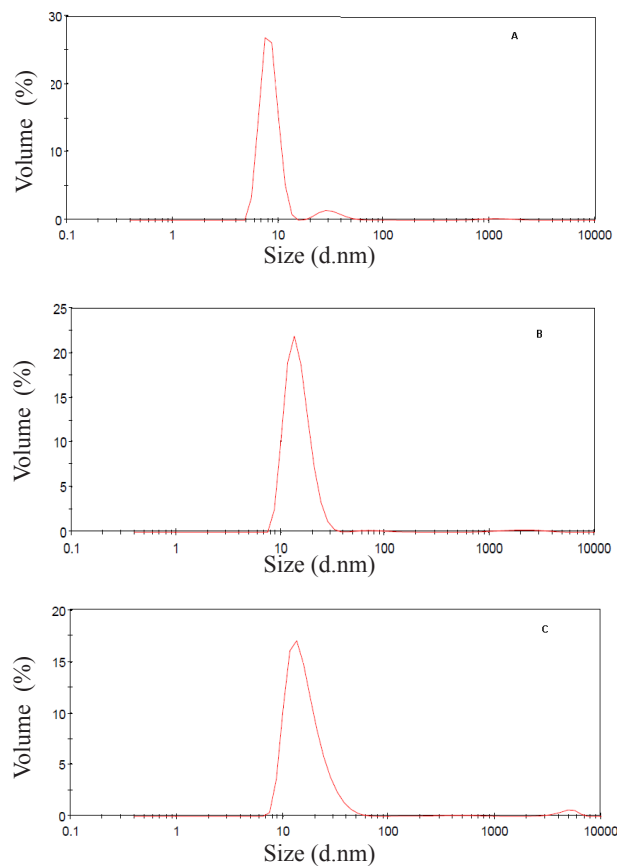
### 3.3. Fourier transform infrared (FTIR) spectroscopic studies of $BaCe_{0.9}Gd_{0.1}O_{3-\delta} - Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (BCGO – CGO) / $BaCe_{0.8}Sm_{0.2}O_{3-\delta} - Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (BCSO – CSO) nano-ceramic composite powders

Figures 4 (a) and 4 (b) show the FTIR spectrums obtained on  $BaCe_{0.9}Gd_{0.1}O_{3-\delta} - Ce_{0.9}Gd_{0.1}O_{2-\delta}$  (BCGO – CGO) /  $BaCe_{0.8}Sm_{0.2}O_{3-\delta} - Ce_{0.8}Sm_{0.2}O_{2-\delta}$  (BCSO – CSO) nano-ceramic composite powders synthesized by chemical precipitation technique. FTIR measurements were done using KBr method at RT. The wide absorption bands appeared at  $3429\text{ cm}^{-1}$  in BCSO - CSO is attributed to the stretching vibration of H-O bond of water(moisture) [13]. However, this particular absorption band is not found in BCGO –CGO sample. The peaks appeared at  $1313\text{ cm}^{-1}$  in BCGO-CGO and  $1371\text{ cm}^{-1}$  in BCSO – CSO are attributed to the Ce-O in the sample as reported [14]. Both spectra present a large absorption band located at around  $500\text{ cm}^{-1}$ , which cannot be completely observed on the graph. This absorption band can be attributed to the Ce–O

stretching vibration present in the sample [15]. The bands located at around  $1055\text{ cm}^{-1}$  in BCGO – CGO and  $1054$  in BCSO – CSO have been attributed to the  $CO_2$  asymmetric stretching vibration as reported<sup>15</sup>. Also, the bands appeared at around  $2500\text{ cm}^{-1}$  in both the samples are attributed to the presence of atmospheric  $CO_2$  in the sample [16]. It is reported the  $CeO_2$  based nanoparticles can absorb atmospheric  $CO_2$  [15]. The FTIR data revealed the spectral resemblance present in the two samples and also which confirmed the formation of single phase in both the samples.

### 3.4. Particle size measurements obtained on of $BaCe_{0.9}Gd_{0.1}O_{3-\delta} - Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (BCGO – CGO) / $BaCe_{0.8}Sm_{0.2}O_{3-\delta} - Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (BCSO – CSO) nano-ceramic composite powders

The prepared materials were subjected to particle size measurements using Malvern particle size analyzer with triple distilled water as medium. For all the measurements, 0.20 g of sample was taken and

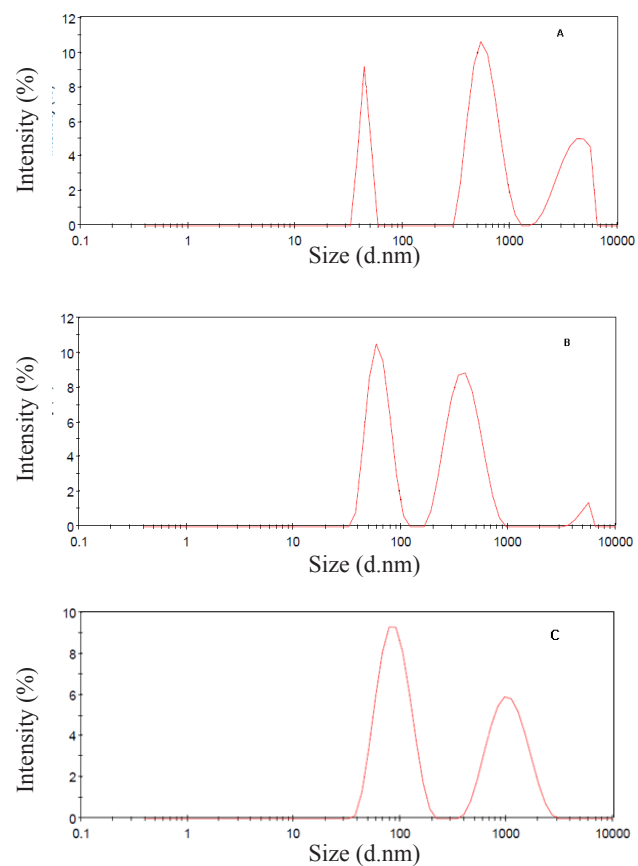


**Figure 6 (a-c):** Particle size distribution patterns (based on volume) obtained on  $BaCe_{0.9}Gd_{0.1}O_{3-\delta} - Ce_{0.9}Gd_{0.1}O_{2-\delta}$  (BCGO – CGO) nano-ceramic composite powder

sonicated in 200 ml triple distilled water for about 5 minutes and then the sample was subjected for particle size analysis. The particle size distribution curves of doped are shown in Figures 5 - 8.

#### 3.4.1. Particle size distribution data of $BaCe_{0.9}Gd_{0.1}O_{3-\delta} - Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (BCGO – CGO) powder

The particle size distribution curves obtained with BCGO-CGO powder prepared by chemical precipitation method are shown in Figures 5 and 6. The particle characteristics obtained on BCGO-CGO power are indicated in Table 3. From the Figures 5 and 6 and the particle characteristics data

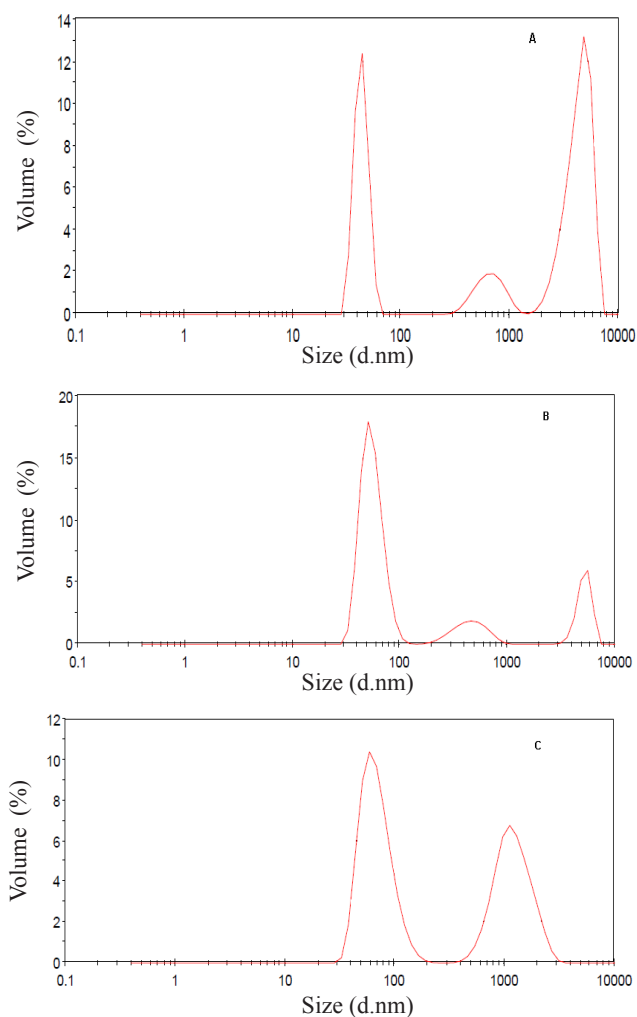


**Figure 7 (a-c):** Particle size distribution patterns (based on intensity) obtained on  $BaCe_{0.8}Sm_{0.2}O_{3-\delta} - Ce_{0.8}Sm_{0.2}O_{2-\delta}$  (BCSO – CSO) nano-ceramic composite powder

(Table 3), it was understood that the average particle size of BCGO-CGO powder prepared by chemical precipitation method is found to be around in the range 50 - 73 nm. The bigger particles present in the sample may be due to the particle agglomeration during high temperature heat treatment.

#### 3.4.2. Particle size distribution data of $BaCe_{0.8}Sm_{0.2}O_{3-\delta} - Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (BCSO – CSO) powder

The particle size distribution curves obtained with BCSO-CSO powder prepared by chemical precipitation method are shown in Figures 7 and 8. The particle characteristics obtained on BCSO power

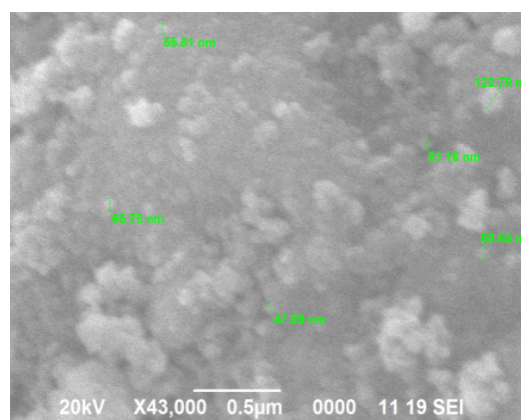


**Figure 8 (a-c):** Particle size distribution patterns (based on volume) obtained on  $BaCe_{0.8}Sm_{0.2}O_{3-\delta} - Ce_{0.8}Sm_{0.2}O_{2-\delta}$  (BCSO – CSO) nano-ceramic composite powder

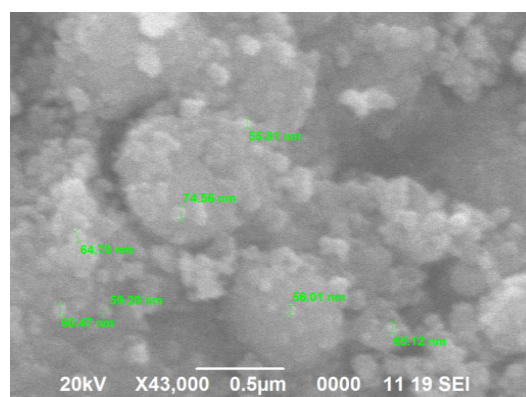
are indicated in Table 4. From the Figures 10 and 11 and the particle characteristics data (Table 4), it was understood that the average particle size of BCSO powder prepared by chemical precipitation method is found to be around in the range 121.4- 216.9 nm, which is higher the particle size data obtained for the previous sample. The bigger particle size found in the sample is due to the particle agglomeration at high temperature calcination.

### 3.5 Scanning Electron Microscopic (SEM) studies of $BaCe_{0.9}Gd_{0.1}O_{3-\delta} - Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (BCGO – CGO) / $BaCe_{0.8}Sm_{0.2}O_{3-\delta} - Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (BCSO – CSO) nano-ceramic composite powders

The SEM photographs of the BCGO-CGO powder prepared by chemical precipitation method are indicated in Figure 9 (a). From the micrograph, it was understood that the surface is rough. Bigger particles are also seen in the micrograph. The average grain size is found to be in the range 45 – 120 nm. The SEM photographs of the BCSO-CSO powder prepared by chemical precipitation



(a)



(b)

**Figure 9:** SEM Photographs obtained on calcined (a)  $BaCe_{0.9}Gd_{0.1}O_{3-\delta} - Ce_{0.9}Gd_{0.1}O_{2-\delta}$  (BCGO – CGO) nano-ceramic composite powder; (b)  $BaCe_{0.8}Sm_{0.2}O_{3-\delta} - Ce_{0.8}Sm_{0.2}O_{2-\delta}$  (BCSO – CSO) nano-ceramic composite powder

method are indicated in Figure 9 (b). In this micrograph, bigger particles are seen which may be due to the linking of smaller particles together. Also, the surface is not smooth and the grain size is varied from 56 to 74 nm. The bigger particles found in the sample may be due to high temperature treatment process.

#### 4. CONCLUSIONS

Chemical precipitation of  $\text{BaCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\delta}$  –  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$  (BCGO – CGO) /  $\text{BaCe}_{0.8}\text{Sm}_{0.2}\text{O}_{3-\delta}$  –  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$  (BCSO – CSO) nano-ceramic composite powders using barium nitrate, cerium nitrate hexa hydrate,  $\text{Gd}_2\text{O}_3$ ,  $\text{Sm}_2\text{O}_3$ , nitric acid, sodium hydroxide and surfactant (PVP) is dealt with. The TGA/ DTA studies carried out to find out the optimum temperature needed for getting a phase pure compound. The powder XRD data obtained on nano-ceramic composite powders is in good agreement with the standard reported JCPDS data for  $\text{BaCeO}_3$ . From the FTIR data, it is understood that the Ce-O absorption band is present in both the samples. The particulate properties obtained on composite powder suggest that the particles are present in nano diameter range. From the SEM photographs, it is confirmed that the particles were present in the range of 45 – 120 nm in the samples.

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#### REFERENCES

1. B. Zhu, X. Liu, T. Schober, *Electrochem. Comm.* 6 (2004): 378.
2. T. Kawada, H. Yokokawa, M. Dokiya, N. Sakai, T. Horita, J. V. Herle, K. Sasaki, *J. Electroceram.* 1 (1997): 155.
3. B. Zhu, *J. Power Sources*, 93 (2001): 82.
4. B. Zhu, *J. New Mater. Electrochem. System* 4 (2001): 239.
5. T. Schober, *Electrochem. Solid State Lett.* 8 (2005): A199.
6. W. S. Jan, S. H. Hyun, S. G. Kim, *J. Mater. Sci.* 37 (2002): 2535.
7. A. Venkatasubramanian, P. Gopalan, T.R.S. Prasanna, *Int. J. Hydrogen Energy* 35 (2010): 4597.
8. S. Yamaguchi, N. Yamada, *Solid State Ionics* 162-163 (2003): 23.
9. B. B. Patil, S. H. Pawar, *App. Sur. Sci.* 253 (2007): 4994.
10. S. Toshi, K. Igor P. Vladimir, A. Harlan U, *J. App. Phy.* 91 (2002): 2308.
11. W. Wang-Ng, Z. Yang, L. P. Cook, Q. Huange, J. A. Kaduk, J. Frank, *Solid State Sci.* 7 (2005): 1333.
12. L. Zhang, W. Yang, *J. Power Sources* 179 (2008): 92.
13. X. Chao, Z. Junwu, Y. Xujie, L. Lude, W. Xin, *J. Rare Earths*, 26 (2008): 51.
14. *Inorganics IR Grating Spectra* [M]. Sadtler Research Laboratories Inc., 1965.
15. L. Truffault, M. Ta, T. Devers, K. Konstantinov, V. Harel, C. Simmonard, C. Andreazza, I. P. Nevirkovets, A. Pineau, O. Veron, J. Blondeau, *Mat. Res. Bull.* 45 (2010): 527.
16. A. C. Tas, P. J. Majewski, F. Aldinger, *J. Am. Ceram. Soc.* 83 (2000): 2954.