

## A study on ultrafine powders of gadolinia doped ceria prepared by gel-combustion method

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Manuscript received 19 February 2010, revised 04 June 2010, accepted 21 June 2010

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**Abstract :** In this paper ultrafine powder of gadolinia doped ceria was prepared by a combustion synthesis method using metal nitrates, both as a precursor and oxidizer and glycine as fuel for combustion. The influence of glycine to metal molar ratio on the characteristics of the powders has been studied. Characterization of the powder samples was performed using, FTIR spectroscopy, TG/DTA analysis, X-ray diffractometry, Small angle X-ray scattering (SAXS) technique and scanning electron microscopy. The ultrafine powders prepared by glycine to metal ratio 1.2 gives the best powder properties. The indexing of diffraction pattern shows that the gadolinia doped ceria powders have face centered cubic symmetry.

**Keywords :** Doped ceria, gel-combustion method, nanomaterials, X-ray diffraction, SAXS, IT-SOFC.

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### Introduction

Solid oxide fuel cells (SOFCs) have drawn a great deal of interest in recent years as potential sources of electrical energy because of their higher efficiencies and environmental friendly nature<sup>1,2</sup> and also due to increase in the petroleum fuel price. A major barrier in the commercialization of SOFCs is its high cost due to its high temperature operation which requires expensive interconnects and sealing materials and high processing cost. This problem can be solved by lowering the operating temperature of SOFCs to 600–800°C<sup>3</sup>. This will also increase the life-span of SOFCs three times<sup>4,5</sup>. The conventionally used electrolyte in SOFCs is yttria-stabilized zirconia<sup>6</sup> (YSZ), which requires cell operation at around 1000°C but it has very poor ionic conductivity in the temperature range of 600–800°C. So extensive research has been carried out to find new fluorite type materials, which have higher conductivity values than those of zirconia based electrolytes<sup>7–12</sup> in the temperature range of 600–800°C.

Ceria doped with rare-earth oxides have been considered as one of the most promising class of materials for intermediate temperature-solid oxide fuel cells because of their much higher oxygen ion conductivity at lower temperature<sup>13,14</sup>. Cerium dioxide CeO<sub>2</sub>, has fluorite structure (CaF<sub>2</sub> type), in which each cerium atom is surrounded

by eight oxygen atoms and gadolinium sesquioxide Gd<sub>2</sub>O<sub>3</sub>, has C-type structure (Mn<sub>2</sub>O<sub>3</sub> type) in which oxygen coordination number for each Gd atom is six. From the structure of ceria it is clear that the simple way to enhance the path for migration of oxygen ion is to replace the cations in the mother lattice with polarizable cations. Big cations are chosen for this purpose because the polarizability of an ion increases with its radius. Although, in the case of fluorite structure it is necessary that the ratio between cation and the anion must be close to 0.70 otherwise it will not be stable. On the basis of an oxide ion radius of 0.138 nm, the optimum cation size is close to 0.1 nm, which best suits with the radius of lanthanide elements<sup>15</sup>. On the basis of this theory cerium based solid solutions are being investigated.

Nanoparticles of metals, semiconductors and oxides have distinguished physical and chemical properties due to quantum size effects and have been studied by many research groups<sup>16–18</sup>.

Combustion synthesis is an important powder processing technique generally used to produce nanocrystalline complex oxide ceramics<sup>19,20</sup>. This process is found to be very useful due to its high energy efficiency, fast heating rates, short reaction times and high reaction temperature. The synthesized powders are nanosized, homogeneous, have fewer impurities and have higher surface areas as

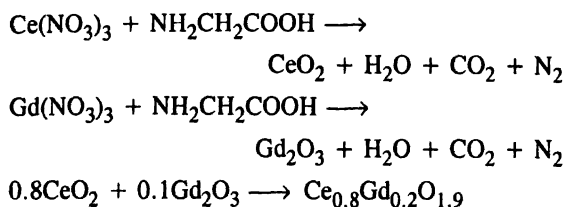
than the powders prepared by conventional solid state methods. The combustion synthesized powders can be sintered to high densities at lower temperature. The processes such as co-precipitation, sol-gel, hydrothermal are not able to produce the final products directly. These methods require many tedious and time taking intermediate steps. Repeated grindings and calcinations are required in solid state method<sup>21</sup>. Washing, drying and calcinations of the precursors are necessary in co-precipitation and hydrothermal methods<sup>22,23</sup>. Sol-gel method requires higher calcinations temperature<sup>24</sup>.

Glycine is found to be suitable fuel in the combustion synthesis because it is readily available, does not react violently and contains least amount of carbon contents<sup>25</sup>. In addition it does not produce toxic gases and its heat of combustion at 25°C (-3.24 kcal/g) is more negative in comparison to urea (-2.98 kcal/g) or citric acid (-2.76 kcal/g).

This work examines the feasibility of glycine as fuel in the gel combustion process and effect of glycine to metal molar ratio on the nature of combustion reaction and the characteristics of the product obtained.

## Results and discussion

The glycine molecule contains a carboxylic acid group at one end and an amine group at the other end, both of which participate in the complexation of metal ions. This "zwitterionic" character allows effective complexation with metal cations of varying ionic size. Thus, glycine first forms complexes with metal cations, which increases their solubility and prevents selective precipitation as water is evaporated and later it serves as fuel for the combustion reaction being oxidized by the nitrate ions. The combustion process is an exothermic redox reaction. The flame temperature can reach 1100 to 1400°C which is affected by the ratio of glycine to metal and reach maximum at the proper ratio. Assuming that the sole gaseous products of combustion were H<sub>2</sub>O, CO<sub>2</sub> and N<sub>2</sub> with all glycine fuel stoichiometrically oxidized by nitrates, the reaction can be expressed as follows :



The large volume of gases generated during such type of auto-ignition process quickly cools the powder formed which leads to nucleation of crystallites without further growth. From the FTIR spectra, the characteristics groups were assigned to different frequencies. FTIR spectrum of glycine was recorded to see the completion of the combustion reaction by comparing it with the spectra of precursors formed after the combustion reaction. The comparison of the spectra (Fig. 1) shows that glycine have been destroyed completely in all the samples prepared, during the combustion process, since no characteristics peaks of glycine was found in the samples prepared by combustion method. However a broad peak appeared, around 3400 cm<sup>-1</sup> due to O-H stretching vibration of water molecule. Dissolved CO<sub>2</sub> was indicated by the small band located at around 2350 cm<sup>-1</sup>. A band around 1600 cm<sup>-1</sup> occurred in all the samples which is due to bending vibration of water molecule. A band around 1400 cm<sup>-1</sup> is due to trace amount of nitrate ions. The band around 500-750 cm<sup>-1</sup> indicated a bond between metal and oxygen.

The TG/DTA results of GDC20 precursor is shown in Fig. 2. From the TGA results we see that major weight loss occurs between 40-200°C which is due to loss of adsorbed water in the samples. Weight loss above 200°C is due to decomposition of precursors to oxides with the evolution of O<sub>2</sub>, NO<sub>2</sub>, NH<sub>3</sub> and H<sub>2</sub>O. From the DTA plots we see a broad endothermic peak around 100°C which is due to loss of water in the samples. An exothermic peak in DTA result around 280°C is due to formation of solid solution of Gd<sub>2</sub>O<sub>3</sub> doped ceria which is also supported by XRD results.

The XRD patterns of the products obtained from different glycine to metals molar ratio are shown in Fig. 3. All the patterns show that the phase pure, nanocrystalline powders of GDC20 with cubic fluorite structure have been formed. There were no other peaks of other phase. The powders obtained from glycine to metal molar ratio 1.2 have average crystallite size of 20 nm with high degree of crystallinity. The powders obtained from glycine to metal ratio 0.7 have the average crystallite size of 16 nm, while the average crystallite size of powders obtained from the glycine to metals ratio 2.0 was 28 nm. The synthesized powders obtained from glycine to metal ratio 1.2 were calcined in air at various temperatures to investigate the evolution of crystalline phases. The XRD

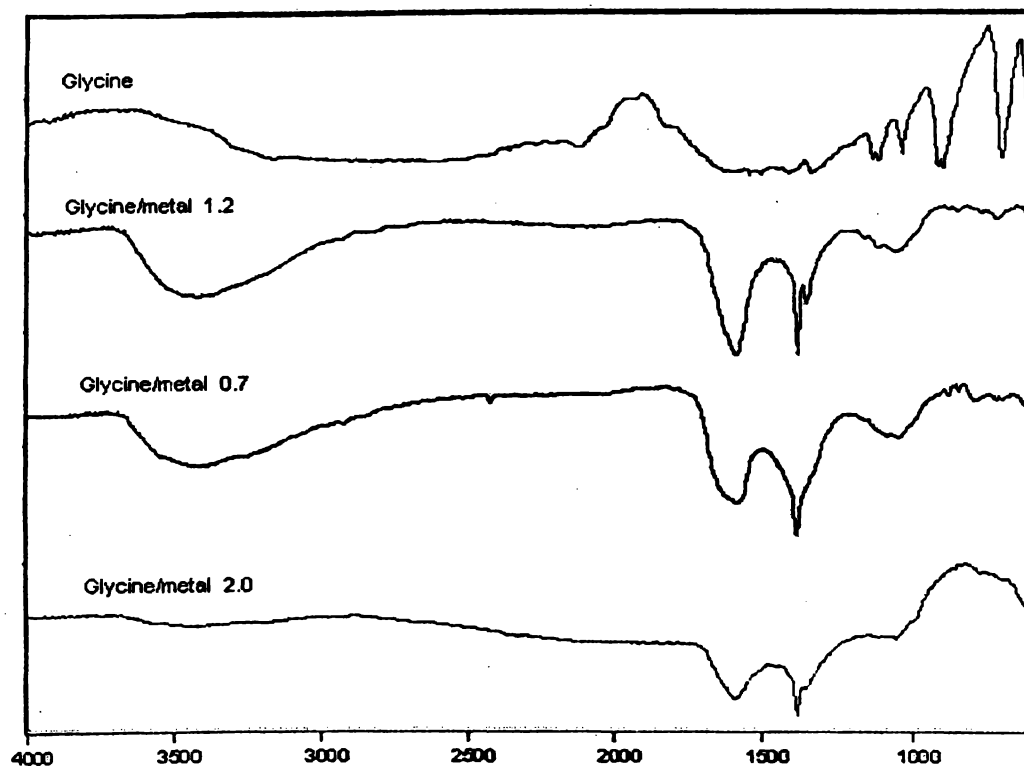


Fig. 1. FTIR spectra of GDC20 precursors.

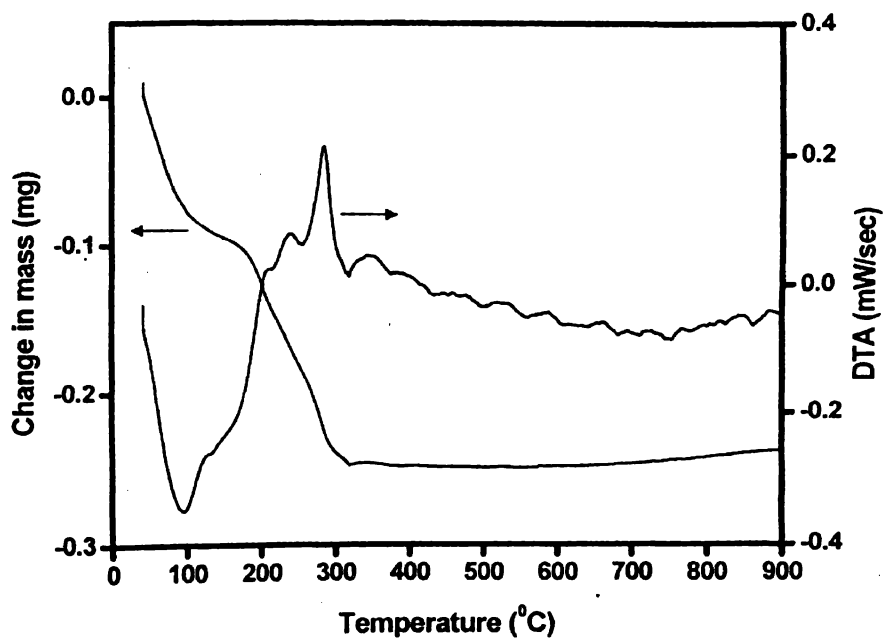


Fig. 2. TG/DTA pattern of GDC20 precursor.

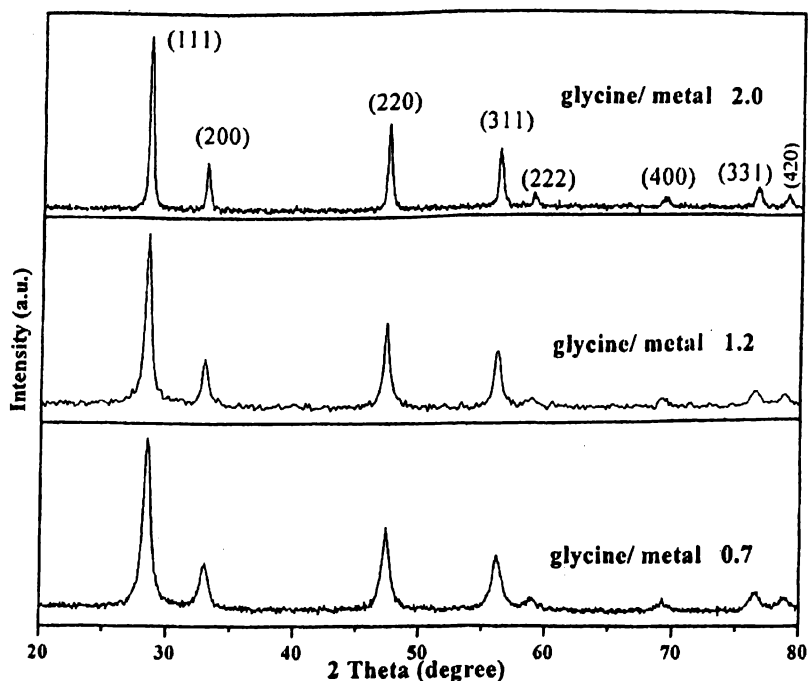


Fig. 3. XRD spectra of GDC20 samples obtained from different ratio of glycine to metal.

pattern of the sample obtained from glycine to metal molar ratio 1.2 and after heating at different temperatures is shown in Fig. 4. It can be seen that the width of the XRD peaks gradually decreases with the increase in calcinations temperature. After heating the synthesized powder, obtained from glycine to metal molar ratio 1.2, at 700°C for 5 h we see little effect on peak width and intensity indicating little change in crystallite size. The average crystallite size of this powder was 20 nm and after heating at 700°C for 5 h the size increases to 24 nm and it goes to 48 nm after heating at 1200°C.

Lattice parameters of  $\text{Ce}_{1.8}\text{Gd}_{0.2}\text{O}_{1.9}$  sample prepared with different glycine to metal ratio and after calcinations at higher temperature is shown in Tables 1 and 2. After calcinations in air at different temperatures up to 1200°C, GDC20 samples were single phase and face centered cubic crystal system (space group  $\text{Fm}\bar{3}\text{m}$ ) with lattice parameters  $a = b = c = 5.4224 \text{ \AA}$  (ICDD, PDF = 340394). The theoretical density of the GDC20 specimens was determined to be  $7.282 \text{ g cm}^{-3}$  with the lattice parameters calculated from the XRD measurements. The direct formation of GDC20 during the auto ignition of

Table 1. Lattice parameters of  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$  sample prepared by gel-combustion method with different glycine to metal ratio

Glycine to metal ratio	Structure	Lattice parameters <sup>a</sup> $a$ (Å)	Cell volume <sup>b</sup> $V$ (Å) <sup>3</sup>
0.7	Cubic	5.4242	159.59
1.2	Cubic	5.4291	160.02
2.0	Cubic	5.4244	159.61

<sup>a</sup> ± 0.0002.  
<sup>b</sup> ± 0.1.

Table 2. Lattice parameters of  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$  sample prepared by gel-combustion method with glycine to metal ratio 1.2 and calcined at different temperatures

Calcination temperature	Structure	Lattice parameter <sup>a</sup> $a$ (Å)	Cell volume <sup>b</sup> $V$ (Å) <sup>3</sup>
As synthesized	Cubic	5.4291	160.02
700°C	Cubic	5.4309	160.19
1200°C	Cubic	5.4224	159.44

<sup>a</sup> ± 0.0002.  
<sup>b</sup> ± 0.1.

the gel shows the intimate contact of the homogeneously distributed metal ions in the gel matrix. XRD patterns also shows that a single solid solution of gadolinium doped ceria is formed after annealing as there are only peaks of

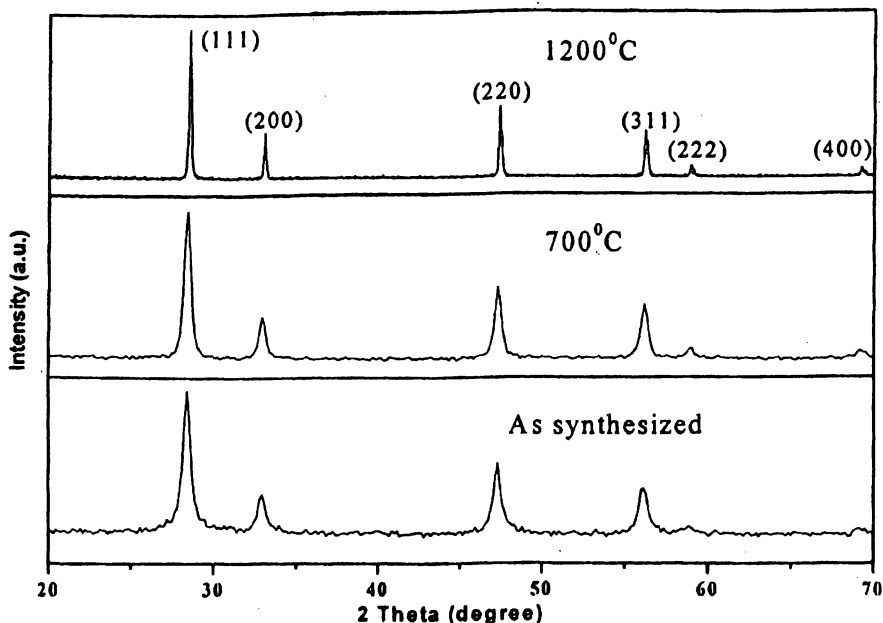


Fig. 4. XRD spectra of GDC20 sample prepared by using glycine to metal ratio 1.2 and calcined at different temperature.

$\text{CeO}_2$ . GDC20 samples retained the cubic symmetry of  $\text{CeO}_2$  ( $a_0 = 5.4117 \text{ \AA}$ ) as the ionic radii of Gd ( $0.938 \text{ \AA}$ ) is closer to that of Ce ( $0.87 \text{ \AA}$ ). Thus, ceria fluorite structure dissolves 20 mol% gadolinium oxide.

Small angle X-ray scattering (SAXS) is ideal technique for studying the sizes and shapes of nanoparticles. The experiment involves scattering of a monochromatic beam of X-rays from the sample and measuring the elastically scattered photon intensity as a function of the scattering angle. The particle size distribution results obtained from SAXS study are shown in Fig. 5. The shapes of particles were found to be nearly spherical. Particle size of GDC20 samples prepared by gel combustion method is between 3–32 nm. Scanning electron microscope was used to observe the morphology of a sample at higher magnification, higher resolution and with depth of focus. SEM micrograph of GDC20 sample prepared by gel-combustion method using glycine to metals molar ratio 2 is shown in Fig. 7. It shows that agglomeration has taken place which is supposed due to high *in situ* combustion temperature. The particles are bonded together by weak van der Waals forces and it can be easily broken by mini-

um mechanical milling. SEM micrograph shows that the particles are nearly spherical shape.

### Experimental

**Sample preparation :** To prepare  $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$  (GDC20) powders by glycine-nitrate process (GNP), stoichiometric amount of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (CDH, Bombay) were dissolved in distilled water to produce the transparent mixed metal-nitrate solution. Glycine ( $\text{NH}_2\text{CH}_2\text{COOH}$ ) (Loba Chemie, Bombay), which is able to bind the metal ions and acts as a fuel in combustion reaction was then added to the mixed metal-nitrate solution. The molar ratio of glycine to metal was set from 0.7 to 2. The transparent aqueous solution containing metal nitrates and glycine was heated in a beaker on a hot plate at  $\approx 90^\circ\text{C}$  under stirring and converted to a viscous gel due to thermal dehydration. As soon as viscous gel was formed, the temperature of the hot plate was increased to  $200^\circ\text{C}$ . At this stage, the viscous gel swelled and auto-ignited with flame, resulting in fine powder of pale yellow in color with evolution of large volume of gases. The time for which the auto-ignition exists was very small ( $< 8 \text{ s}$ ). The powder was calcined at  $700^\circ\text{C}$  to

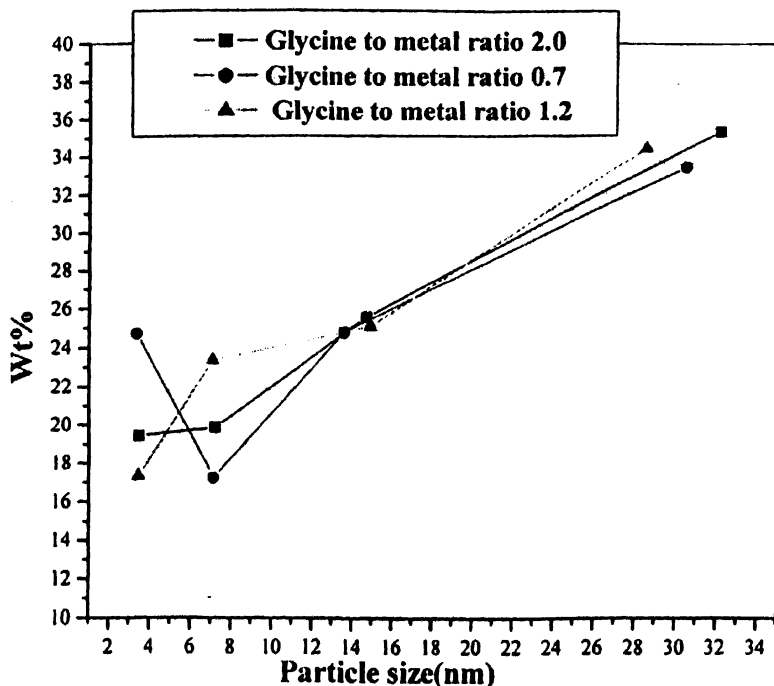


Fig. 5. Particle size distribution of GDC20 samples prepared by gel combustion method with different glycine to metal molar ratio.

remove any carbon residues remaining in the powder and to form a well crystalline structure. Flow chart for combustion synthesis of GDC20 sample using glycine is shown in Fig. 6.

*Physicochemical characterization* : Fourier Transform Infrared (FTIR) spectra were recorded at room temperature using a spectrometer (FTLA, 2000, Make : ABB Ltd.) with a resolution of  $4\text{ cm}^{-1}$ . Pellets were prepared with 13 mm KBr die set by compressing an intimate mixture obtained by grinding 1 mg of the substance in 100



Fig. 7. SEM micrograph of GDC20 sample prepared by gel-combustion method using glycine to metal molar ratio 2.

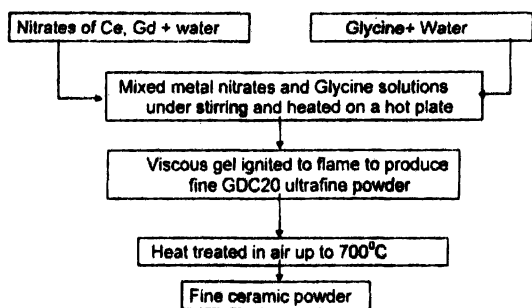


Fig. 6. Flow chart for combustion synthesis of GDC20 samples.

mg of KBr with mortar and pestle and applying an optimum pressure of 9 Ton using a 15 Ton hydraulic pellet press (Kimaya Engineeres, Thane). While preparing the pellets necessary precautions were taken to avoid moistures. The instrument calibration was confirmed by re-

ording the spectra of standard polystyrene film. Powder X-ray diffraction data for the samples were collected on a Rigaku D-max 2000/JADE 6.0 copper rotating anode X-ray diffractometer using Cu- K $\alpha$ 1 radiation (1.54056 Å) and using silicon as an external standard. The data were collected at a scanning rate of 1° per min. The patterns were indexed to generate their lattice parameters using POWD program (Version 2.2). The average crystallite size, *D* of the calcined powders was estimated from the broadening of XRD reflections using the Scherrer relation :

$$D = 0.9 \lambda / \beta \cos \theta_B \quad (1)$$

where  $\lambda$  is the wavelength of the radiation used,  $\beta$  is the full width at half maximum (in radian) on two theta scale and  $\theta_B$  is the Bragg's angle. High grade silicon powder was used as standard to account for instrument broadening correction. Thermal analysis was done on TG/DTA Equipment (SETRAM model 92-16.18) in air from room temperature to 900°C with a heating rate of 5°C/min. Al<sub>2</sub>O<sub>3</sub> was used as a reference material and the sample was kept in cylindrical platinum crucible. For particle size distribution, Small Angle X-ray Scattering (SAXS) experiments were performed on Rigaku RINTPC2000 using rotating anode X-ray generator operated at 40 kV and 40 mA in transmission geometry using radiation with wavelength of 1.54056 Å in the region of small angle scattering 0.02–5°. The microstructure of powder samples was studied using both Optical microscope (GETNER SD-2PL) and Scanning Electron Microscopy (SEM), Philips ESEM model XL 30.

#### Conclusion :

In the current study ultrafine powders of gadolinia doped ceria were synthesized at a very low temperature (~200°C) by employing glycine-nitrate auto ignition process. The best powder properties were observed for the powders with glycine to metals molar ratio 1.2. The success of this technique is due to intimate blending among the constituents using suitable fuel (glycine) in an aqueous medium followed by an exothermic redox reaction between the fuel and an oxidizer (nitrates). It is a simple,

quick and inexpensive method involving a single step reaction and does not require any complicated experimental setup.

#### Acknowledgement

The authors gratefully acknowledge Nanophosphor Application Centre, University of Allahabad, Allahabad for providing characterization facilities. One of the authors is also thankful to Mr. Preyas Ankit for his help in recording FTIR spectra.

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