

# EFFECT OF GLYCINE - NITRATE RATIO ON SDC NANO-POWDER SYNTHESIZED BY GLYCINE - NITRATE COMBUSTION SYNTHESIS

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**ABSTRACT:** Nano-crystalline SDC powder was synthesized by glycine nitrate combustion process (GNP). Effect of variation of glycine to nitrate molar ratio on the powder properties were studied. Molar ratios of glycine/nitrate (g/n) were varied as 0.87 (fuel lean), 0.46 (fuel rich), and 0.60 (stoichiometric). Optimized (g/n) ratio is 0.85. Powder synthesized by using g/n as 0.85 is smooth lime-yellow in color and has 35 m<sup>2</sup>/g surface area as observed from BET studies. From XRD calculation crystallite size of as synthesized powder was found to be 11 nm for fuel lean composition. All the powders are found to be highly porous. Porosity also found to depend on the g/n ratio. From EDS mapping of the powder it is seen that, all the elements are distributed uniformly over the powder. A.C. conductivity is found to be high as 0.0300 and 0.61 S-cm<sup>-1</sup> at 700 °C for the pellet sintered at 1100 °C and 1300 °C respectively. This investigation shows that, the glycine nitrate combustion technique is inexpensive, rapid method to synthesize nano-crystalline oxide powders within short time.

**Keywords:** Fuel cells, oxide materials, chemical synthesis, crystal structure, atomic force microscopy (AFM).

## 1. INTRODUCTION

Eight mol % Ytria-Stabilized Zirconia (YSZ) is widely used as electrolyte materials in solid oxide fuel cells (SOFCs) as it possesses high ionic conductivity at high temperatures [1,2]. There is increasing interest in decreasing operating temperature of solid oxide fuel cells (SOFCs) from 1000°C to the intermediate to low temperature range of 400-800 °C [3]. Samarium doped ceria have the highest electrical conductivity because of the close ionic radius of Sm<sup>3+</sup> compared to the radius of Ce<sup>4+</sup> [4]. Hence Samaria doped ceria (SDC) is reported as potential candidate as electrolyte material for intermediate temperature- SOFC. Several synthesis methods are investigated to prepare nano - crystalline SDC powder such as combustion synthesis [5], co-precipitation route [6], hydrothermal synthesis [7], and acrylamide polymerization process [8]. Earlier SDC powders have been synthesized successfully by the combustion synthesis using different complexing agents/ fuels such as glycine [9], urea [10], and citric acid [11]. The synthesized powders are generally more homogeneous, have fewer impurities and have higher surface area than powders prepared by conventional solid state methods [12]. Also it is inexpensive method and takes short time as compared to sol gel method [13]. In this study the, work is reported on the study of effect of glycine to nitrate ratio on the powder properties such as color, crystallite size, electrochemical surface area of SDC powder. The work also reports the enhancement in the ionic conductivity of SDC material than the earlier reported values.

## 2. EXPERIMENTAL

### 2.1 Powder Synthesis

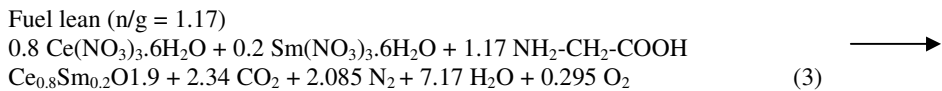
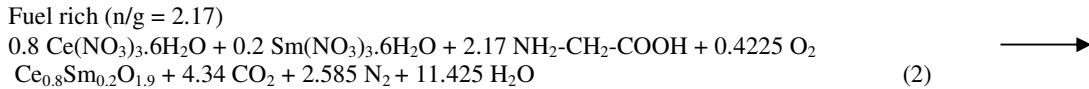
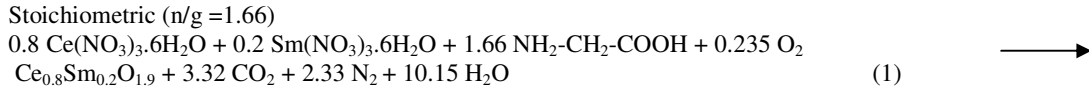
A glycine nitrate combustion synthesis method was used to synthesize the nano sized powder of Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9</sub> (SDC). High purity reagents Ce (NO<sub>3</sub>)<sub>3</sub> .6H<sub>2</sub>O, Sm (NO<sub>3</sub>)<sub>3</sub> .6H<sub>2</sub>O and glycine (NH<sub>2</sub>CH<sub>2</sub>COOH) (99.99 % pure, Alfa Aesar, India) were dissolved in double distilled water, Ce: Sm was selected as 8:2 in order to have high conductivity [14]. Glycine was dissolved in double distilled water. In order to study effect of g/n ratio on powder characteristics, glycine/nitrate (g/n) ratios were varied as 0.87 (fuel lean), 0.46 (fuel rich), and 0.60 (stoichiometric). Glycine and metal nitrate solutions were mixed thoroughly, to ensure molecular level mixing, to form a clear, homogeneous solution. After homogenization the solution was heated on hot plate at 80 °C. Then the temperature of the hot plate was raised to 180-250 °C. It results in to the formation of foamy, highly porous milky white color powder. The ash was sintered at 600 °C for 2h then grounded in agate mortar for 5-10 min and cold pressed at a 16 Mpa to obtain green compact pellets with thickness about 1mm and diameter of 13 mm. The pellets were sintered in air at 1100 °C, and 1300 °C for 4 h with a heating rate 3 °C /min and then used for conductivity measurements.

**2.2 Powder Characterization**

Thermo-gravimetry and derivative thermo-gravimetry (TG-DTG) of as synthesized powders were carried out by using TG instrument (TG 209 F3 Tarsus). The phase identification of synthesized powders was made with the powder X-ray diffraction (XRD) technique using Phillips PW-1710 diffractometer. The micro-structural and compositional analysis of the synthesized powders was conducted with scanning electron microscope (2ELSS EVO series, model EVO 50), BET surface area of the as formed powders heated at 600 °C for 2 h was measured with Micromeritics Gemini, model 2375. AC conductivity of the pellets sintered at 1100, and 1300 °C for 4 h was obtained from two probe impedance spectroscopy.

**3. RESULTS AND DISCUSSION**

In the case of glycine nitrate combustion synthesis the g/n ratio for complete oxidation is called as stoichiometric [2], here it is 0.60. Below and above the glycine to nitrate molar ratio of 0.60 is called a fuel lean and fuel rich ratio respectively. Here selected fuel lean and rich ratios are 0.87 and 0.46 respectively. Redox reactions during combustion involving these ratios are given by equation (1, 2 and 3).



**3.1. TG -DTG Study**

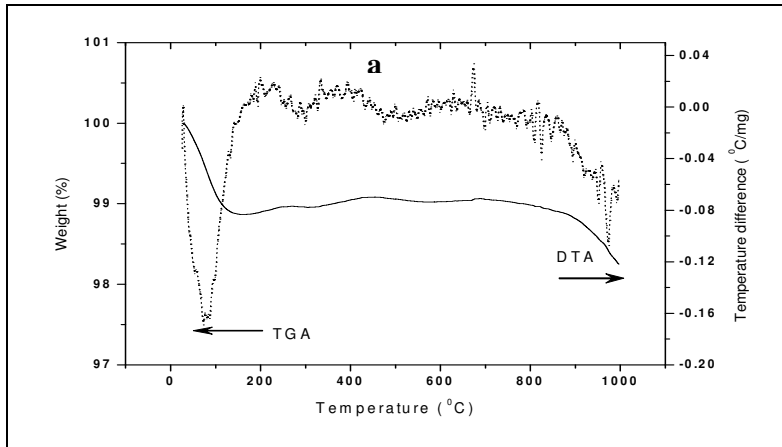


Fig.1 Simultaneous TG-DTG plots of SDC powder synthesized with g/n ratio 0.85 and heat treated at 600 °C for 2h.

Fig.1 shows the simultaneous thermo-gravimetry and derivative thermogravimetry (TG/DTG) plots of SDC powder with g/n = 0.85 and heat treated at 600 °C. From Fig. 1 it is seen that the weight loss of about 2.5 % was observed till 100 °C, this is due to the removal of water content from the powder. A continuous increase in the weight of the powder after heating it in air environment, above 100 °C was observed. It suggests that some amount of un-reacted glycine and nitrates left behind and react with each other during further heating in air environment. Also sample showed a sharp endothermic peak at about 980 °C showing the complete formation of the desired product. This suggests that the SDC has been crystallized almost perfectly at this temperature.

**3.2 XRD Analysis**

In GNP, different g/n ratios as fuel lean (0.85); stoichiometric (0.60) and fuel rich (0.46) strongly affect the powder characteristics. Fig. 2 shows the comparison of the XRD plots obtained for the powder synthesized by using these ratios. All peaks have been identified and indexed from the known patterns of the standard data files

[15]. XRD patterns of all powders shows the peaks (111), (002), (022), (113), (222), (044), (133), (024), (224) corresponding to only cubic phase of  $Ce_{0.8}Sm_{0.2}O_{1.9}$ , confirming their single phase and polycrystalline nature. The average values of the lattice parameters 'a' for fuel lean, stoichiometric and fuel rich compositions are found to be 5.4446 Å, 5.4276 Å, 5.4516Å, for cubic SDC, respectively. The calculated 'a' matches well with the reported values [16-19]. For each powder (111) peak corresponding to the cubic fluorite SDC phase is most intense one. Hence it is further analyzed to yield the crystallite size of the material by using the Scherrer's formula [20].

$$d = 0.9\lambda / \beta \cos \theta \quad (4)$$

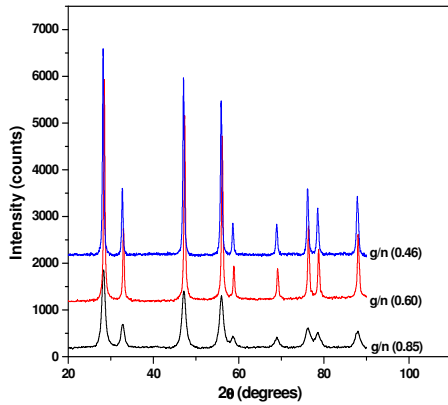


Fig 2

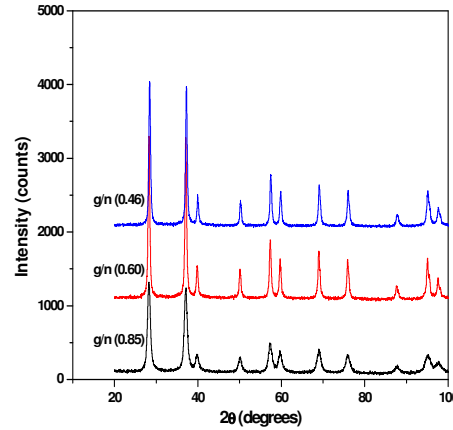


Fig 3

Fig.2 XRD patterns of SDC powder synthesized at different g/n ratios as Fuel lean (0.85), Stoichiometric (0.60) and Fuel rich (0.46).

Fig.3 XRD patterns of SDC powder synthesized at different g/n ratios as Fuel lean (0.85), Stoichiometric (0.60) and Fuel rich (0.46) and heat treated at 600 °C

where, d is crystallite size of the powder,  $\lambda$  is the wavelength of the X-ray radiation,  $\beta$  = full width at half maxima and  $\theta$  is angle of diffraction. Corresponding crystallite sizes are given in Table 1.

Fig. 3. shows the XRD patterns of the powders synthesized with different g/n ratios and heat treated at 600 °C for 2 h. All powders are showing separate peaks corresponding to cubic fluorite SDC phases (111), (002), (022), (113), (222), (004), (133), (024), (224). The average values of the lattice parameters 'a' for fuel lean, stoichiometric and fuel rich compositions are found to be 5.4468 Å, 5.4449 Å, 5.4362 Å, for cubic SDC, respectively. Similar to previous one the calculated 'a' matches well with the reported values [16-19]. From Figs 2 and 3 it is concluded that the as synthesized powders are less crystalline as compared to the heated ones. And hence simultaneous growing and narrowing of the peaks were observed due to the better crystallization and enhanced crystallite size in case of heated powders. Crystallite size of these different powders is calculated by using Scherrer's formula and these values are mentioned in Table 1.

Table 1 Effect of g/n molar ratio on SDC powder properties.

g/n molar ratio	Color of the as synthesized powder	Crystallite size (from XRD(as synthesized powder) nm	Crystallite size (from XRD (powder heated at 600 °C for 2h )
0.85	Lime yellow	8.46	11.23
0.60	Milky white	18.77	17.69
0.46	Milky white	22.22	18.39

From Table 1 it is seen that the powders prepared from fuel lean ratio are having small crystallite size as compared to the stoichiometric and fuel rich compositions. This is due to the less amount of heat evolved during the combustion of fuel lean ratio as compared to others. Since nano-crystalline ceramics have superior powder

properties such as large surface area, better sinterability, higher conductivity [21], hence we have optimized fuel lean ratio (0.85) for further studies.

Crystallite size of the powder is found to increase with the increase in the quantity of the glycine. But overall powder synthesized by using glycine nitrate combustion synthesis is ultra fine with nanometer size grains. The reason for nano-crystalline nature may be due to atomic and molecular level mixing of reagents during combustion synthesis process. From Tables 1 it is concluded that the *g/n* ratio plays important role on the powder properties, powder color and hardness. Due to nano-crystalline nature the powder synthesized from fuel lean ratio is lime yellow in color than that of synthesized from stoichiometric and fuel rich ratio (milky white). Similar observations were reported by R. D. Purohit et. al in case of  $CeO_2$  by combustion synthesis [16].

### 3.3 SEM Analysis

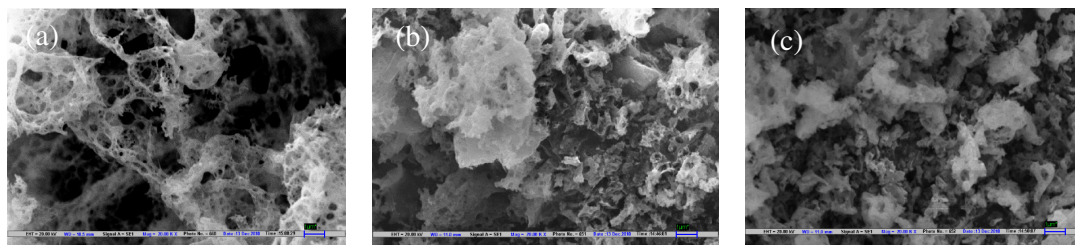
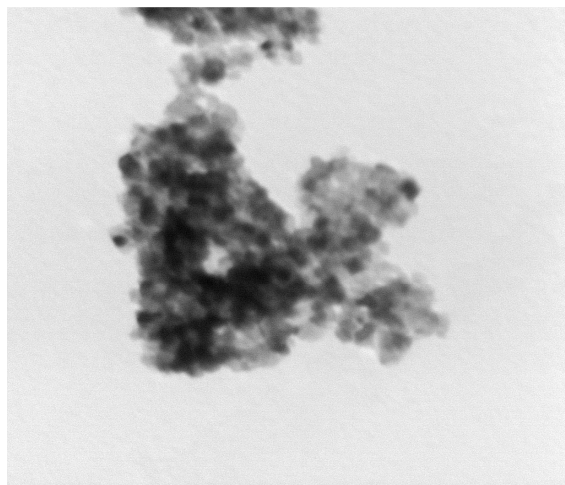


Fig. 4 SEM images of as synthesized SDC powders with (a) *g/n* ratio 0.60 (b) *g/n* ratio 0.85 (c) *g/n* ratios 0.46.

Fig. 4 shows SEM images of as synthesized SDC powders with (a) *g/n* ratio 0.60 (b) *g/n* ratio 0.85 (c) *g/n* ratio 0.46 respectively and heat treated at 600°C for 2 h. (Here powders corresponding to fuel rich and lean ratios are crushed). During combustion synthesis exothermic reaction takes place and large amount of gases evolved which makes the powders highly porous hence all the powders are found to be highly porous. Porosity also found to depend on the *g/n* ratio. From Fig 4 it is seen that fuel rich (*g/n* = 0.46) composition shows increase in the crystallite size of the powder and hence decrease the surface area due to local sintering of the powder particles. This is due to large amount of heat evolved during combustion of fuel rich composition [16].

### 3.4 TEM Analysis

Fig. 5 shows the TEM images of the SDC powder with fuel lean (*g/n* = 0.85) ratio. TEM images reveals the

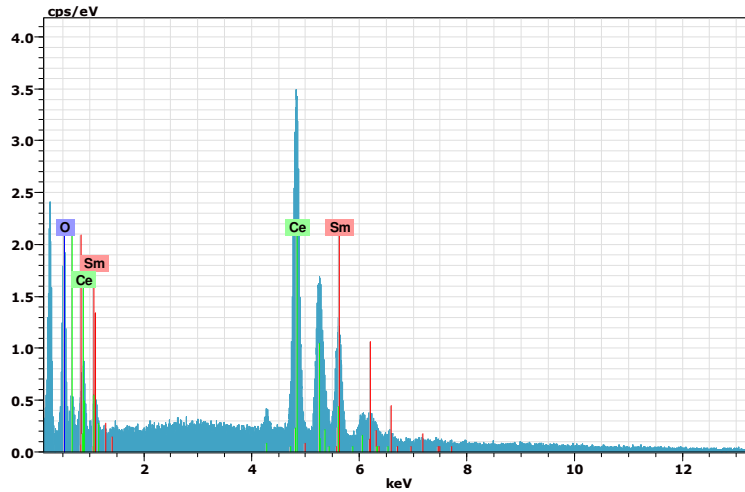


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Fig. 5 TEM micrographs of SDC powder synthesized with *g/n* ratio 0.85 heat treated at 600 °C for 2h.

nano-crystalline nature of the synthesized powders. The powders are found to be agglomerated. The average particle size of the powders was found to be about 5 nm and is in agreement with the average crystallite size calculated from the XRD.

### 3.5 EDAX Analysis



**Fig.6 EDAX images of SDC powders synthesized with g/n ratio (a) 0.85 and heat treated at 600 °C for 2h.**

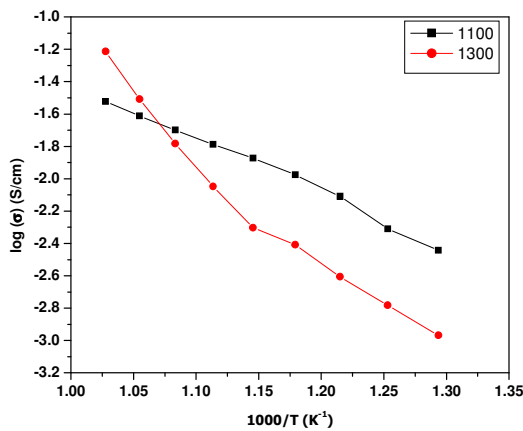
The EDS analysis of the powder with glycine to nitrate fuel lean ( $g/n = 0.85$ ) and heat treated at 600 °C for 2 h is shown in Fig. 6. Synthesized powder shows peaks corresponding to the elements Ce, Sm and O. No other peaks were observed showing the formation of phase pure SDC powder. The composition of the powder agrees with the theoretical value, showing the formation of  $Ce_{0.8}Sm_{0.2}O_{1.9}$  powder. All the elements are distributed uniformly over the powder.

### 3.6 BET Analysis

It is observed that the powder synthesized from the fuel lean ratio has high surface area ( $35 \text{ m}^2/\text{g}$ ) as compared to the powder synthesized from the stoichiometric ( $24.6 \text{ m}^2/\text{g}$ ) and fuel rich compositions ( $22.6 \text{ m}^2/\text{g}$ ) is found to affect the powder characteristics adversely. This results into the increase in the crystallite size, premature partial local sintering among the active primary particles produced during combustion, thereby reducing the surface area [46, 61]. BET results are in accordance to the XRD results.

### 3.7 Electrical Properties

In order to study the effect of sintering temperature on the electrical conductivity of the SDC pellets the conductivity of the pellets sintered at 1100, and 1300 °C was measured in the temperature range 300-700 °C in air environment.



**Fig.7. Variation of log of conductivity vs 1000/T of the pellets sintered at 1100, and 1300 °C for 4h.**

Conductivity was estimated by,

$$\sigma = L/RA \quad (5)$$

where, L is the thickness of the pellet, A is the electrode area and R is the resistance as determined with the impedance spectroscopy. The plot of  $\log(\sigma)$  vs  $1000/T$  (Fig. 7) was plotted and activation energy was calculated by using,

$$\sigma T = \sigma^{\circ} \exp(-E_a/kT) \quad (6)$$

where,  $E_a$  is the activation energy for conduction, T the absolute temperature, and  $\sigma^{\circ}$  is a pre-exponential factor [22].

From Fig. 7 it is seen that Overall conductivity of the both the pellets increase with the increase in temperature showing semi-conductor behavior. It is seen that the conductivity of the pellets increases with the sintering temperature. As sintering temperature increases the grain size of the material increases and porosity decreases, which intern increase the connectivity of the material and the conductivity increases. A.C. conductivity is found to be high as 0.0300 and 0.61 S-cm<sup>-1</sup> at 700 °C for the pellet sintered at 1100 °C and 1300 °C respectively and are better than that reported for SDC [5,9].

Activation energies were found to be 0.62 eV for the pellets sintered at 1100 °C for 4 h and are found to be lower than that reported for SDC [5, 9]. When the grain size decreases from a few micrometers to the nano level, the grain boundaries show unusually high conductivity. [23-24]. This is due to the fact that in nano-crystalline materials grain boundaries have high defect densities and the atoms there have high mobility. Hence, the ionic conductivity may be significantly enhanced in nano-crystalline materials compared to the microcrystalline ones [23], same has been observed in the present work.

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