

Microwave induced combustion Synthesis of Nano-Codoped Ceria and their electrical properties

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In this work, $Ce_{0.75}Gd_{0.1}Ca_{0.15}O_{1.8}$ nanopowders are successfully synthesized by a Glycine-nitrate combustion process under the microwave irradiation. Then calcination was carried out at 700 °C. Calcined powders identified by room temperature X-ray diffraction were single phase and had a crystallite size between 16 to 24 nm (based on Schererr formula). Scanning electron microscopy (SEM) was employed to characterize the morphology of powder. We also studied the effect of fuel to nitrate ratio on the amount of released energy and on the crystallite size and compositional homogeneity of the resulting powders. Finally electrical properties of obtained powder were studied.

Keywords: Solid oxide fuel cell; Doped ceria; Microwave; Combustion synthesis

1. INTRODUCTION

Solid oxide fuel cell (SOFC) has attracted much attention in recent years because of its high-energy conversion efficiency and environmental friendship. Conventional SOFCs which use yttria-stabilized zirconia (YSZ) as an electrolyte are operated at around 1273K. However, such high temperatures often lead to some problems such as solid-state reactions between the components, thermal degradation and thermal expansion mismatch. It becomes increasingly important to reduce the operating temperature of the SOFC.

Doped ceria is a potential electrolyte material for ITSOFCs because it shows much higher oxygen ionic conductivity than YSZ [1-2]. Ceria itself is not a good ionic conductor, but ionic conductivity increases significantly with the introduction of oxygen vacancies caused by the doping of aliovalent cation into the ceria lattice. In fact two approaches have been used to improve the ionic conductivity of the electrolytes: one is to enhance the grain boundary conductivity utilizing additives to scavenge the impurity phase in the grain boundaries [3,4] but the exact role of the additives is still debatable. The other is to dope ceria with two or more components at the same time [5-7] and the research results showed that complex doping with several rare earth or/and alkali earth elements was an effective method to improve the ionic conductivity of the electrolyte.

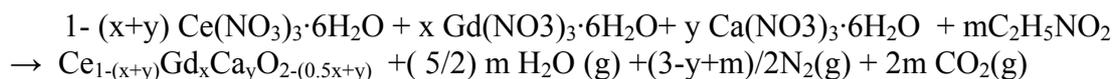
In the past few years, combustion synthesis of multi component ceramic oxides has been gaining reputation as a straightforward preparation process to produce homogeneous, very fine, crystalline and unagglomerated powders, without the intermediate decomposition and or calcining step [8, 9] The basis of the combustion synthesis technique comes from the thermo chemical concepts used in the field of propellants and explosives [10]. In the present work, we used the glycine–nitrate solution combustion synthesis technique to obtain nanocrystalline $Ce_{1-(x+y)}Gd_xCa_yO_{2-(0.5x+y)}$ powder. We also investigated the role of fuel-to-oxidant ratio, dopant concentration on combustion process and properties of resulted nanopowders.

2. EXPERIMENTAL

The synthesis process is started by the combustion of a redox mixture, in which metal nitrate acted as an oxidizing reactant and glycine as a reducing one. According to this concept, the valences of some elements and ions are as follows: C = +4, H = +1, O = -2, divalent metal ions = -2 and trivalent metal ions = -3 [11]. The valence of nitrogen is considered to be zero. Accordingly, the oxidizing and reducing valences of the compounds used in the combustion mixture can be calculated. So the oxidizing valency of cerium nitrate and gadolinium nitrate is -15 and that of calcium nitrate is -10 and also the reducing valency of glycine is +9. Therefore based on the propellant chemistry [12], the stoichiometry of the mixture can be determined using the total ratio of the oxidizing to the reducing valences as a numerical coefficient which can be defined as the Elemental stoichiometry coefficient (Φ) which is shown following.

$$\text{Elemental stoichiometry coefficient } (\Phi) = \frac{\sum (x_i * v_R)}{\sum (y_i * v_O)}$$

which x and y are stoichiometry coefficient of fuel and oxidant (nitrate) respectively, v_o and v_R are the oxidizing and reducing valences respectively. Based on this concept, the theoretical amount of glycine which can react with nitrate completely, was calculated by $\Phi = 1$ in the above equation. Thus, for reaching to 1 mol of $\text{Ce}_{1-(x+y)}\text{Gd}_x\text{Ca}_y\text{O}_{2-(0.5x+y)}$ is needed to $(15-5y)/9$ mol of glycine. The formation of solid solution may be presented by the following reaction:



To start the synthesis process, the metal nitrates and glycine were dissolved in double distilled water and then, pH value of solution was adjusted at 8 by adding ammonium hydroxide. The solution containing nitrates and glycine was added to a crucible. Now there is two ways in order to heat the mixture, by hot plate as a conventional method and using microwave as a novel method with a lot of advantages. In both of the two ways, for first the solution boiled and underwent dehydration followed by decomposition with the evolution of large amounts of gases. After the solution reached the point of spontaneous combustion, it began burning, the auto-ignition gave out large volume of gases and afterward the voluminous powder was produced. During the ignition, the container was covered with a fine-mesh sieve to prevent the powder from flying out of its container.

In order to investigate the effect of fuel to oxidant ratio on the properties of obtained powder by microwave induced combustion synthesis, we prepared four samples through the above method by the combustion of solutions which had different Elemental stoichiometry coefficients (Φ) in the following three ranges:

- 1) Fuel-deficient region $\Phi = 0.6, 0.8$ and 0.9
- 2) Stoichiometry region $\Phi = 1.0$
- 3) Fuel-rich region $\Phi = 1.2$

Then calcination of the powders was carried out at 700°C for 3h to remove any traces of fuel and to obtain phase pure powder. Obtained powder samples through microwave-induced combustion process were pelletized and sintered at 1100°C for 4h. The bulk densities of all sintered samples were greater than 93% of the theoretical densities in all specimens.

The crystalline phases were identified by X-ray diffraction analysis (XRD) by using an X-ray diffractometer (Siemens D5000) and $\text{Cu K}\beta$ radiation ($\lambda = 0.15418 \text{ nm}$). The average crystallite size, D, was estimated by using the Scherrer formula: $D = (0.9\lambda)/(\beta \cos \theta)$ [13] Which, β is the line broadening measured at half of height of peak, θ is the angle of reflection and λ is the wavelength of radiation. The lattice parameters were calculated by using formula that is shown in below:

$$1/d_{hkl}^2 = h^2/a^2 + k^2/b^2 + l^2/c^2 \quad [14]$$

which, d is the interplanar distance, (h, k, l) are the miller indices for the corresponding d -spacing and a, b, c are the lattice parameters. Scanning electron microscopy (Philips SEM) was used to morphological studies. Chemical composition of the resulted powder was obtained from EDAX analysis and the electrical properties were studied by using an impedance analyzer (Zahner, IM6E). Pt paint was used to fabricate the electrodes.

3. RESULTS AND DISCUSSION

3.1. Xray diffraction (XRD) studies

3.1.1. Phase structure

Fig. 1 shows the XRD pattern of the calcined powders at 700 °C in which $\Phi = 1$ and indicates the presence of a single phase with cubic fluorite structure. No peaks of un-reacted CaO and Gd₂O₃ are observed, suggesting in-situ solid solution formation. The calculated lattice parameter was 5.42 Å, which is in well agreement with the reported values. It was also observed that the calcination of the powder at 700 °C is not showing a significant change in the crystallite size. The formation of nanocrystalline structure indicated by XRD was further supported by SEM studies.

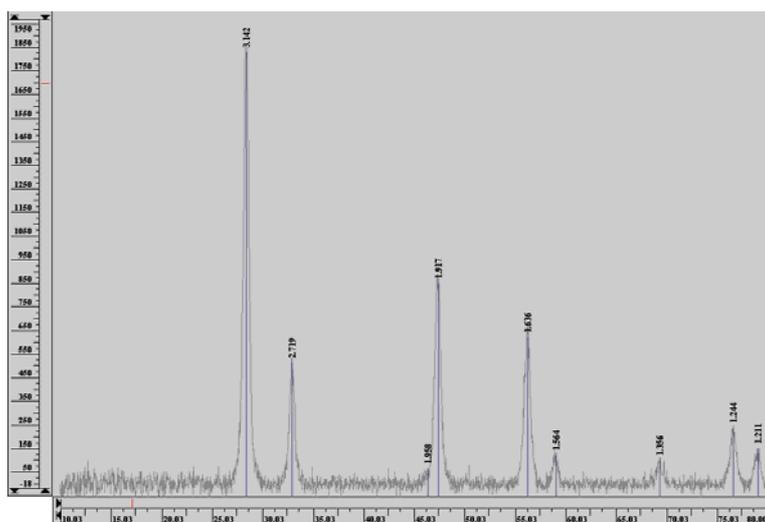


Fig. 1. XRD pattern of the calcined powders at 700 °C in which $\Phi = 1$.

3.1.2. The effect of fuel to oxidant ratio on the crystallite size

Fig. 2a and b show crystallite sizes of four synthesized powder's samples through combustion of different fuel to oxidant ratios by hot plate and microwave irradiation. As can be seen in Fig. 2a maximum crystallite size is related to deficient fuel ratio. ($\Phi = 0.9$) It is probably due to thermal decomposition of some nitrates at 250 °C that causes to decreasing amount of oxidant at the moment of combustion. Thus, when we use conventional heat sources such as hot plate, the most energy and largest crystallites are obtained through combustion with deficient fuel ratio.

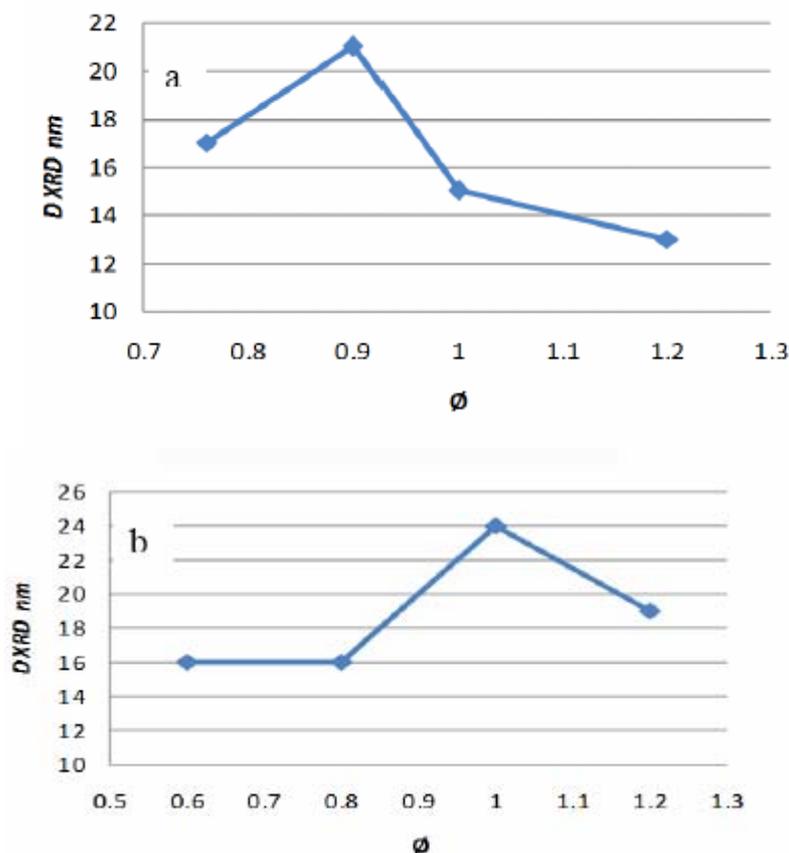


Fig. 2. Crystallite sizes of synthesized powder through a) combustion of solution with different Φ by hot plate b) microwave induced combustion of solution with different Φ .

But when we use microwave irradiation as heat sources, unlike the conventional heating methods, due to the very fast combustion process thermal decomposition of nitrates is not occurred, therefore in Fig. 2b the most released energy and thus the maximum crystallite sizes is observed through combustion of equal ratio of fuel and oxidant.

Table 1. The result of EDAX analysis (C_{real}) of the calcined powders, the primary designed composition (C_{ideal}) and total differences between them (D).

$D = \sum C_{ideal} - C_{real} $	primary designed composition (C_{ideal})			EDAX analysis result (C_{real})			Φ
	Ce mol%	Gd mol%	Ca mol%	Ce mol%	Gd mol%	Ca mol%	
$13+0+13=26$	75	10	15	88	10	2.0	0.6
$8+2+10=20$	75	10	15	83	12	5.0	0.8

3.1.2.2. The effect of fuel to oxidant ratio on the compositional homogeneity

Table 1 shows the result of EDAX analysis (C_{real}) of the calcined powders, the primary designed composition (C_{ideal}) and total differences between them (D). It can be seen, as Φ increases the composition of related powder is more near to the primary designed composition and it shows compositional homogeneity increases due to increase amount of glycine as fuel. It is probably

because of glycine's ability to form metal ion complexes which helps in preventing ions selective precipitation and therefore in maintaining the compositional homogeneity of the resulted powder [15-21].

3.2. Morphological studies

Fig. 3 and 4 Show the SEM micrograph of calcined powder's sample through combustion process by microwave and hot plate respectively. Both of them indicate the particles with spherical shape but, the particles in Fig. 3 are smaller and more uniform than Fig4. (Average particle size in fig.3 is 30 nm but for fig. 4 is 45 nm) This issue indicates the effect of uniform microwave radiation to reach particle size uniformity and to reduce the agglomerates.

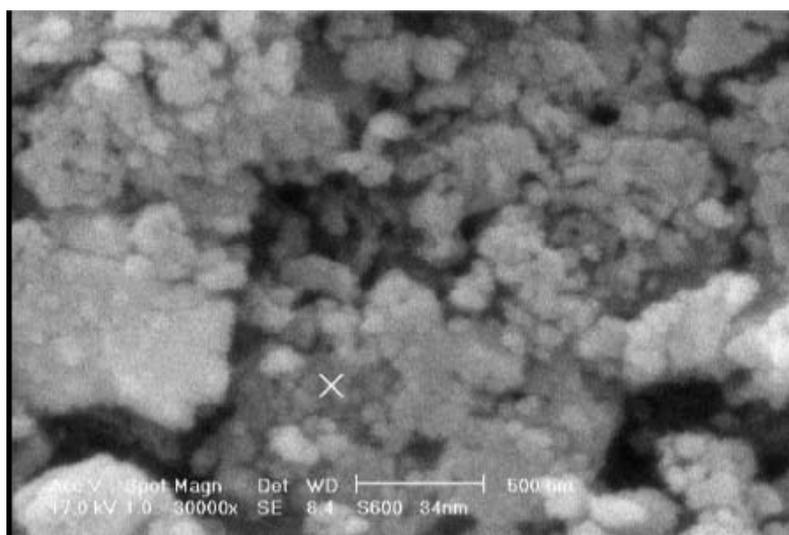


Fig. 3. SEM micrograph of calcined powder's sample combustion by microwave.

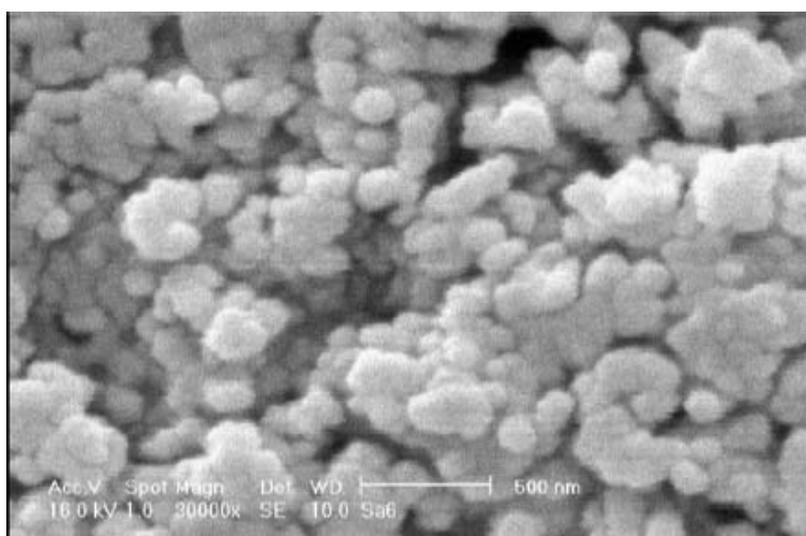


Fig. 4. SEM micrograph of calcined powder's sample through combustion by hotplate

3.4. Electrical properties

The impedance spectra of $\text{Ce}_{0.75}\text{Gd}_{0.1}\text{Ca}_{0.15}\text{O}_{1.8}$ electrolyte at 300 °C is shown in Fig. 5. The frequency increases from the right to the left across the plot. In the ideal case, the ac impedance of an ionic conductor contains the contributions from the grain, the grain boundaries and the

electrolyte-electrode interface, which can be reflected in a complex plane by three successive semi-circles.

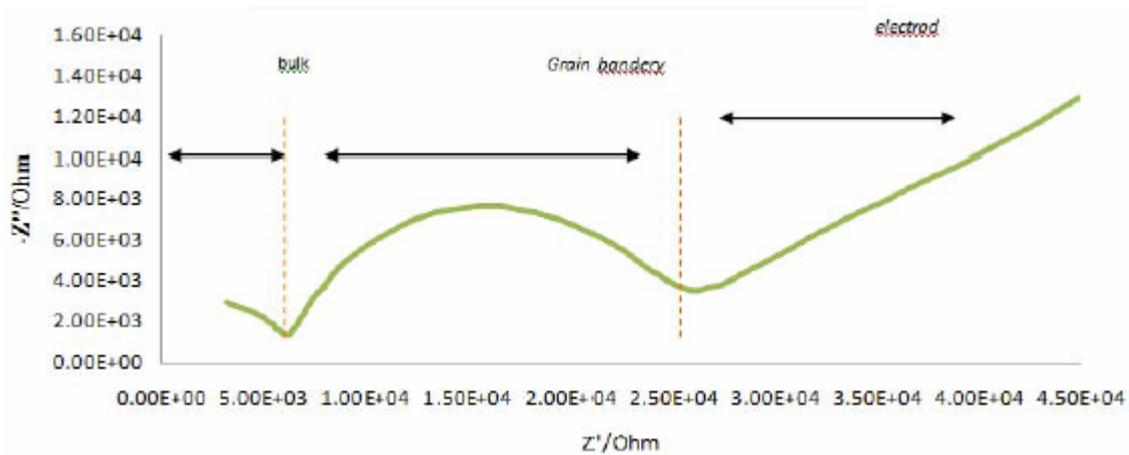


Fig. 5. Impedance spectra of Ce_{0.75}Gd_{0.1}Ca_{0.15}O_{1.8} electrolyte at 300 °C.

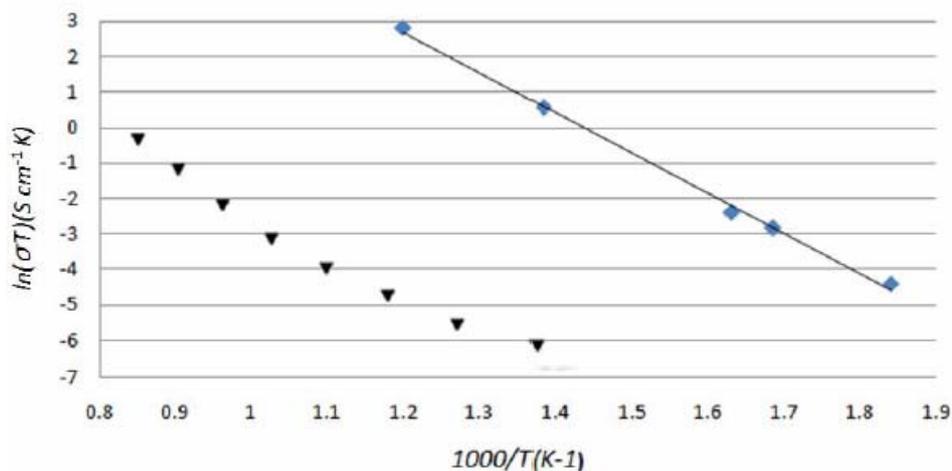


Fig. 6. The Arrhenius plots of ■ the doped sample and ▼ reported result of pure ceria [24].

In Fig. 5 three main features can be observed: two distinct arcs at high frequency and one incomplete depressed arc at low frequency. The intercept of the high-frequency arc at the real axis represents the grain resistance (R_g), the intercept of the intermediate frequency arc is the grain boundary resistance (R_{gb}) and the intercept of the low-frequency arc is the electrode polarization resistance. Therefore, the resistance data for sample at different temperatures can be obtained and then converted to the grain conductivity (σ_g), grain boundary conductivity (σ_{gb}) and total conductivity (σ_t), using the relation [22]:

$$\begin{aligned} \sigma_g &= (1/R_g) \cdot (L/S) \\ \sigma_{gb} &= (1/R_{gb}) \cdot (L/S) \\ \sigma_t &= (1/R_t) \cdot (L/S) \\ R_t &= R_g + R_{gb} \end{aligned}$$

where L is the sample thickness and S is the electrode area on the sample surface. Fig. 6 presents the Arrhenius plots of the best our sample and reported result of pure ceria [23] in the temperature range of 250-550 °C. It could be seen that co-doping with a proper ratio of Gd and Ca could enhance the conductivity of ceria electrolytes. The electrical conductivity of the co-doped Ce_{0.75}Gd_{0.1}Ca_{0.15}O_{1.8} ceramics at 550 was 19.9E-3 while that of pure ceria has reported much

smaller than it, about $1.4E-5$ according to Fig. 5 $\{\ln(\sigma T) = 4.8\}$. As can be seen, the codoping effect was more apparent in the lower temperature region than in the higher temperature region.

4. CONCLUSION

In this work, we successfully synthesized four samples of $Ce_{0.75}Gd_{0.1}Ca_{0.15}O_{0.8}$ through microwave induced combustion of solutions which had different Elemental stoichiometry coefficients (Φ) in following three ranges:

- 1) Fuel-deficient region $\Phi = 0.6, 0.8$ and 0.9
- 2) Stoichiometry region $\Phi = 1.0$
- 3) Fuel-rich region $\Phi = 1.2$

XRD results indicated the presence of a single phase with cubic fluorite structure and the calculated lattice parameter was 5.42 \AA . It was observed that, because of glycine's ability to form metal ions complexes which helps in preventing ion selective precipitation, as the amount of glycine increases, the compositional homogeneity of the resulted powder increases. The effect of uniform microwave radiation led to particle size uniformity and reduce agglomerates and also high speed combustion caused to preventing thermal decomposition of nitrates at $250 \text{ }^\circ\text{C}$, thus unlike the conventional heating method it was observed that when we use microwave irradiation as the heating source, the most released energy and the maximum crystallite sizes can be obtained through combustion of equal ratio of fuel and oxidant. Finally it was shown that, co-doping with a proper ratio of Ca and Gd could enhance the conductivity of ceria electrolytes well.

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