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# Structural and electrical properties of CGO10 thin films prepared using spray pyrolysis technique

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***Abstract***

*Solid electrolyte for intermediate temperature solid oxide fuel cell (IT-SOFC) is a challenge for material researchers. However, Gd doped ceria (CGO) found to be a promising electrolyte among the other competitive materials. In the present investigation, we report the structural and electrical properties of CGO thin films prepared by spray pyrolysis technique. The process parameters were optimized for synthesizing $Ce_{0.9}Gd_{0.1}O_{1.95}$ (CGO10) films. Films were characterized by XRD and EDS and are observed to be phase pure. The SEM showed the dense and uniform film growth. The dc conductivity measured is of the order of 0.5S/cm at 623K.*

## INTRODUCTION

Gadolinium doped ceria are known to be good oxygen ion conductors (OICs) with applications in solid oxide fuel cells (SOFCs), oxygen sensors, oxygen pump and in methane to syngas conversions [1]. The use of thin film OICs as an electrolyte in SOFC keeps the ohmic losses at minimum level and allows to operate at intermediate temperatures. Further, less expensive materials may be used to fabricate the device.

Several methods to fabricate CGO in bulk [2-4] as well as in thin film form [5, 6] have been reported. The spray pyrolysis method is simple, cost effective and has been widely applied for the deposition of oxide thin films [7, 8]. Recently, spray pyrolysis synthesis technique has been used for the preparation of SOFC electrolyte thin films [9]. Spray pyrolysis method offers a great promise of depositing the dense and thin electrolyte suitable for IT-SOFC [10]. In the present work, CGO10 thin films by spray pyrolysis method is fabricated and characterized for their structural, morphological and electrical properties.

## EXPERIMENTAL

An aqueous solution of cerium nitrate ($Ce(NO_3)_3.6H_2O$, 99.9% Pure; ALFA AESAR) and gadolinium nitrate ($Gd(NO_3)_3.6H_2O$, 99.9% Pure; ALFA AESAR) was prepared according to the stoichiometry of the desired phase i.e. CGO10. The solution was sprayed using glass nozzle with air as carrier gas on preheated ultrasonically cleaned glass substrates. The crystallization of material was achieved by subsequent annealing at 450°C for 2h in air. Thermogravimetric and differential thermal analysis (TG-DTA) was carried out using a Perkin-Elmer TGA-DTA-DSC instrument to determine the decomposition temperature. The prepared films were characterized for their structural (using X-ray diffractometer, PHILIPS-PW-3710), morphological (using scanning electron microscope, JEOL-JSM-6360 with EDS unit) and electrical properties (using two probe technique).

## RESULTS AND DISCUSSION

Thermogravimetric measurement was performed in oxygen atmosphere to know the decomposition temperature of host material i.e. cerium nitrate (figure 1). The possible chemical reaction during thermal decomposition predicted from weight loss calculation is,

$$Ce(NO_3)_3.6H_2O \rightarrow CeO_2 + 3NO_2 + 6H_2O + 1/2\,O_2$$

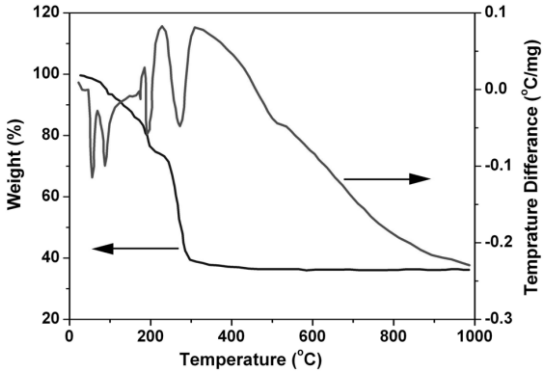


**Fig 1**: TG-DTA of precursor chemical-$Ce(NO_3)_3.6H_2O$.

According to the reaction, weight loss would be 60.36% and experimentally it is observed to be 59.86 %. An evaporation of water and nitrate from the material is also seen in the DTA profile of cerium nitrate. From the figure 1, it is observed that the decomposition is almost complete at 290°C and hence spray depositions were carried out at the substrate temperature of 300°C. The concentration of the precursor solution was optimized to 0.04M. The film thickness was in the range of 0.5–3.3µm. All films were annealed at 450°C in air for 3h.

**Structural and morphological properties**

Fig 2 shows XRD patterns of CGO films. The reflection peaks observed in fig 2 are labeled according to JCPDS (PDF No. 75-0161), which confirms the fluorite type crystal structure of the films. Films showed the presence of (111), (200), (220), (311), (222), (400), (331), (420), and (422) diffraction peaks without any presence of impurity peaks, confirming the single phase of compound. The lattice parameter, '***a***', is ~ 5.421Å, which is comparable to our earlier reported value [11]. The crystallite size calculated from line broadening method was 110–120 nm.

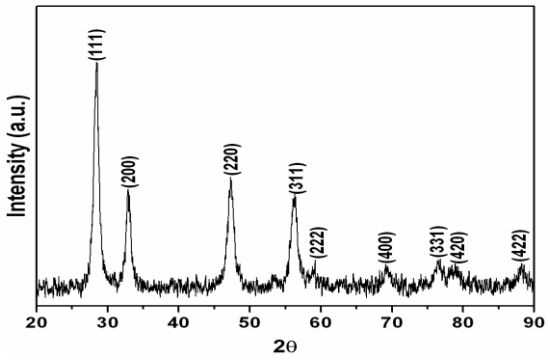


**Fig 2:** XRD of CGO10 film (annealed).

The elemental analysis of the film was carried out using energy dispersive spectrometer (EDS). The estimated atomic ratio is in good agreement with that of the precursor solution, which was 9: 1 for Ce: Gd. Fig 3 shows the SEM of CGO film. SEM clearly shows grain growth is of micron size with uniform and dense surface.

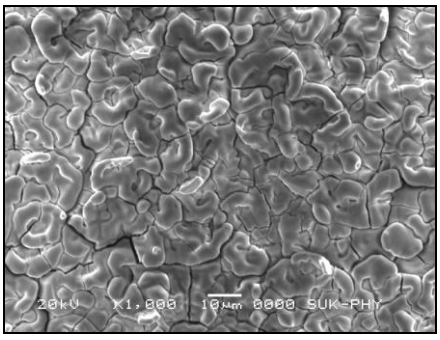


**Fig 3:** SEM of CGO10 film (annealed).

**Electrical properties of CGO10 films**

The dc conductivity of films was measured using conventional two probe technique. Typical variations of ln(σT) with 1000/T for CGO10 films are shown in fig 4. The conductivity of films at 623K is of the order of 0.5S/cm, which is greater than that of reported for the bulk CGO10 at 1073K (~0.12 S/cm) [11]. Observation showed that dc conductivity decreases with thickness. The change in slope at 533K (in fig 4) is attributed to initiation of ionic diffusion in films [12].

Activation energies were calculated by fitting the conductivity data to Arrhenius relation for thermally activated conduction, which is given as,

$$\sigma = (\sigma_0 / T).\exp(E_a / KT) \quad \ldots \textbf{(1)}$$

where, $E_a$ is the activation energy for conduction, T the absolute temperature, K the Boltzmann constant and $\sigma_o$ the pre-exponential factor. The $E_a$, decreases from 0.70 eV for 3.3μm film to 0.40 eV for 0.5μm film.

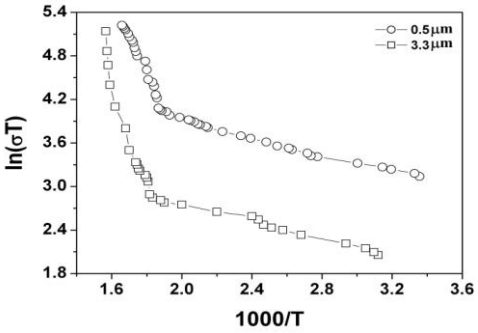


**Fig 4:** Variation of ln(σT) with 1000/T**.**

**CONCLUSIONS**

In conclusion, dense, phase pure CGO films can be prepared by spray pyrolysis technique (SPT) with well monitored thickness. The CGO films, synthesized in the present work, showed the phase pure fluorite structure with lattice parameter, ***a*** ~ 5.421Å. The films are dense with uniform grain growth. The dc conductivity is of the order of 0.5S/cm at 623K and decreases with increase in CGO10 film thickness. The ability of SPT to control thickness of the film of CGO10 layers can enable the OIC based device operation at relatively low temperatures.

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**REFERENCES**

1. S. Skinner and J. Kilner, "Oxygen Ion Conductors: Review", Materials Today, **30**, March 2003.
2. M. Hirano and E. Kato, Commun. Am. Ceram. Soc. **79** (1996) 777.
3. S. Zha, Q. Fu, Y. Lang, C. Xia and G.Y. Meng, Mater. Lett. **47** (2001) 351.
4. C. Xia and M. Liu, J. Am. Ceram. Soc. **84** (2001) 1903.
5. M. Lang, R. Henne, S. Schaper and G. Schiller, J. Therm. Spray Technol. **10** (2001) 618.
6. T. Nguyen, K. Kobayashi, T. Honda, Y. Iimura, K. Kato, A. Neghisi, K. Nozaki, F. Tappero, K. Sasaki, H. Shirahama, K. Ota, M. Dokiya and T. Kato, Solid State Ionics **174** (2004) 163.
7. S.K. Pawar and S.H. Pawar. Mat. Res. Bull. **18** (1983) 211.
8. P. S. Patil, Mater. Chem. Phys. **59** (1999) 185
9. D. Perednis and L.J. Gauckler, Solid State Ionics **166** (2004) 229.
10. J. Rupp, T. Drobek, A. Rossi and L. Gauckler, Chem. Mater. **19** (2007) 1134.
11. L.D. Jadhav, S.H. Pawar and M.G. Chourashiya, Bull. Mater. Sci. **2** (2007) 97.
12. S. Zha, C. Xia and G. Meng, J. Power Sources **115** (2003) 44.