

## Synthesis and Characterization of Nanocrystalline Gd Doped CeO<sub>2</sub>

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Nano-sized gadolinia doped ceria prepared by combustion method lowers sintering temperature. The dopant concentration dependent lattice distortion is correlated with the electrical properties and grain size. The linear thermal expansion coefficient study suggests enhancement in it by doping.

**Key Words:** Solid electrolyte, X-ray powder diffraction, Solid oxide fuel cells

### INTRODUCTION

Ceria based solid solutions have been regarded as the most promising solid electrolytes for intermediate temperature solid oxide fuel cells (IT-SOFC) due to their ionic conductivity higher than YSZ<sup>1</sup>. Amongst various cations *viz.* Ca<sup>2+</sup>, Sr<sup>2+</sup>, Y<sup>3+</sup>, La<sup>3+</sup>, Gd<sup>3+</sup>, and Sm<sup>3+</sup> doped ceria the gadolinia and the samaria doped ones have emerged as promising solid electrolytes.

In fact, according to literature densification of ceria-based ceramics below 1600°C has been difficult<sup>2, 3</sup>. The severe sintering conditions make it difficult to co-fire with other components of SOFC thereby expensive manufacturing of SOFCs<sup>4, 5</sup>. Generally, the reduction in particle size facilitates obtaining requisite dense ceramic at considerably low sintering temperatures. The present study was focused on grain size effect on packing density and conductivity.

### EXPERIMENTAL

The solid solutions Gd<sub>x</sub>Ce<sub>(1-x)</sub>O<sub>2</sub>, where  $x = 0.05$  and  $0.1$ , were prepared by combustion route<sup>6</sup>. An appropriate molecular stoichiometric amount of cerium, samarium and gadolinium in the form of hexahydrated nitrates (99.99% pure, Sigma USA) along with glycine fuel were dissolved in the distilled water and charred at 550°C. The foamy, pale yellow in color, residue was crushed and sintered at 800°C for 7 hrs in air. The pellets of dimensions 9mm diameter and 1-2 mm thickness were sintered at various temperatures in the range from 800 to 1300°C for 7 hours.

The samples were characterized by the X-ray powder diffraction. The complex impedance in the temperature and frequency ranges 100–600°C and 10mHz to 1MHz, respectively was measured using Solartron 1255B FRA. The details of

measurement procedure have been described elsewhere<sup>7</sup>. The sintered density was determined following Archimedes principle.

## RESULTS AND DISCUSSION

The X-ray powder diffraction patterns (XRD) of  $\text{Gd}_{0.05}\text{Ce}_{(0.95)}\text{O}_2$  and  $\text{Gd}_{0.1}\text{Ce}_{(0.90)}\text{O}_2$  are depicted in Figs. 1a and 1b, respectively. All the potential characteristic lines in XRD patterns match well with the standard JCPDS data corresponding to  $\text{CeO}_2$ . Absence of line(s) corresponding to oxides/nitrites of Gd and Ce confirms the formation of  $\text{Gd}_x\text{Ce}_{(1-x)}\text{O}_2$  solid solutions. The diffraction

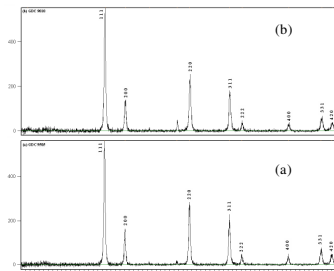


Fig.1: XRD of (a)  $\text{Gd}_{0.05}\text{Ce}_{(0.95)}\text{O}_2$  and (b)  $\text{Gd}_{0.10}\text{Ce}_{(0.90)}\text{O}_2$  sintered at  $800^\circ\text{C}$  for 7 hrs.

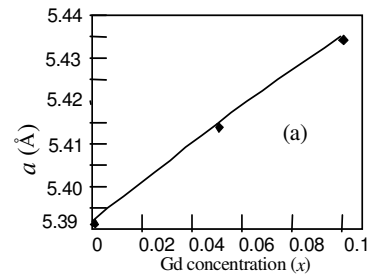


Fig. 2: Variation of lattice cell constants,  $a$ , with dopant concentration.

line broadening is due to the small crystallite size. The lattice cell constant,  $a$ , seen to increase linearly with dopant concentration (Fig.2a). A linear relationship between  $a$  and  $x$  represented by Eq. 1 is in good agreement with Vegard's rule.

$$a(x) = 5.372 + 0.002x \quad (1)$$

As seen from the Fig. 3a the crystallite size, obtained from x-ray powder diffraction data, initially increases linearly with and later shows the tendency of saturation. The average crystallite size is found  $\approx 20$  nm, which grows to 600 nm after sintering. The packing density increases rapidly (Fig. h rise in

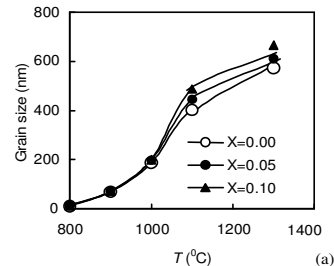
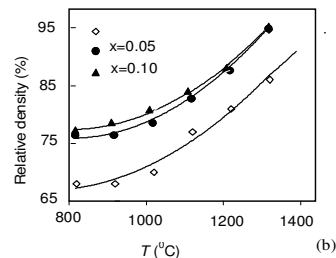


Fig. 3: Variation of (a) grain size and (b) relative packing density with sintering temperature.

sintering temperature 3b) due to sintering above 1000°C. Moreover, doping with Gd enhances the packing density of CeO<sub>2</sub>. Sintering at 1300°C gives 95% dens materials.

The gadolinium doping accelerates grain growth and densification, however, densification retards at  $x = 0.20$ . The inhibition effect of dopants on grain growth has previously also been observed in other materials<sup>8</sup>. Guo *et al* attributed inhibition phenomenon to the decrease in space charge potential with increasing dopant content<sup>9</sup>. In nanoscale range, since a comparatively larger grain diffuses much faster, the densification is accelerated by dopant content. Sudden reduction in densification, in spite of grain growth in case of  $x = 0.20$ , is attributed to retarding defect interaction.

The Gd doping introduces additional oxygen vacancies into the host CeO<sub>2</sub> lattice so as to achieve the charge neutrality. The  $Gd'_{Ce}$  and  $V''_O$  point defects tend to cluster due to electrostatic attraction, and the tendency further increases with increasing dopant concentration. Subsequently, it leads to the formation of large ( $Gd'_{Ce} - V''_O$ ) pair defect aggregated clusters. It eventually slows down the mobility of cations thereby decreases densification.

The variations of lattice cell constant,  $a$ , with temperature is depicted in Fig 4. Evidently  $a$  increases linearly with the increase in temperature. Furthermore, volume expansion coefficient also increases with dopant concentration i.e.  $\alpha_{Gd0.05}$  (0.0046)  $<$   $\alpha_{Gd0.1}$  (0.0051). The mismatch in ionic size and valence of guest Gd for host Ce introduces lattice strain and vacancies that leads to the increase in anharmonicity in the crystal lattice vibration, thereby, the thermal expansion coefficient.

It is worth to mention here that the complex impedance data revealed the oxygen reactivity; the bulk conductivity, excluding electrode effect as well as

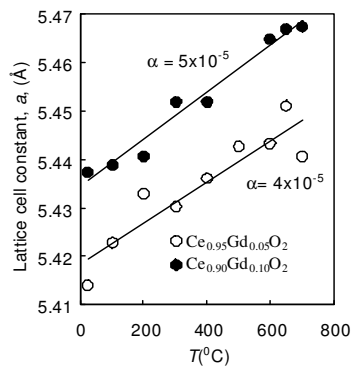


Fig.4:Variation of lattice cell constant,  $a$ , with temperature

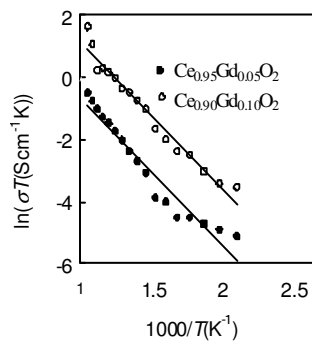


Fig.5. Arrhenius plots for  $Gd_xCe_{1-x}O_2$  ( $x=0.05$  and  $0.1$ )

displacement current, was obtained from detailed complex impedance analysis<sup>7</sup>.

The temperature dependent bulk conductivity for  $\text{Gd}_{0.05}\text{Ce}_{(0.95)}\text{O}_2$  and  $\text{Gd}_{0.1}\text{Ce}_{(0.90)}\text{O}_2$ , depicted in Fig.5, are seen to obey Arrhenius law within the temperature range of measurements. It is also evident from Fig.5 that the doping with Gd not only increases the ionic conductivity but also reduces the activation enthalpy of ion conduction.

The partial substitution of Gd in  $\text{CeO}_2$  gives additional/extrinsic oxygen vacancies so as to achieve electro-neutrality in the host lattice. The platinum porous film on the flat surfaces of electrolyte acts as catalyst to promote the reaction,



The free oxygen ions migrate through  $\text{Gd}_x\text{Ce}_{(1-x)}\text{O}_2$  lattice leading to the ionic conductivity. The increase in conductivity and reduction in activation enthalpy with Gd content is consequential of both the additional/extrinsic vacancies and the lattice strain.

## Conclusions

Nano-sized Gd doped ceria,  $\text{Gd}_x\text{Ce}_{(1-x)}\text{O}_2$ , prepared by glycine-nitrate combustion method reduces the sintering temperature. Dense sintered materials provide high oxygen conductivity. The thermal expansion coefficient of ceria increases with Gd doping.

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