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IONIC CONDUCTIVITY MEASUREMENTS IN GADOLINIA DOPED CERIA

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ABSTRACT

Gadolinia doped ceria (5, 10, 15 mol% of Gd) powders sintered at 1823 K have been studied using x-ray diffraction, microhardness and ac impedance spectroscopy techniques. It has been observed that there was an increase in lattice parameter and hardness with increasing addition of gadolinia. The electrical conductivity measurements indicated that the conductivity is mainly due to ionic diffusion with an activation energy of 1.01eV and 0.87 eV for 5 and 10 mol% doped ceria respectively. The extent of grain boundary contribution to the conductivity was found to reduce with increasing temperature of measurement.

Key words : doped ceria, sintering, x-ray diffraction, conductivity

1. INTRODUCTION

Ionic conductors have provided a fascinating interdisciplinary field of study in the area of clean energy sources, sensors and high energy density batteries. In oxygen ion conductors, current flow occurs by the movement of oxygen ions through the crystal lattice as a result of thermally activated hopping of the oxygen ions moving from a crystal lattice site to another crystal lattice site. The ionic conductivity is consequently strongly temperature dependent and at high temperatures, it can approach values close to 1 S/cm comparable to the levels of ionic conductivity found in liquid electrolytes[1]. Yttria–stabilised zirconia (YSZ) is a typical electrolyte material which requires a high operation temperature (1073-1273K) to provide sufficient oxygen ion conductivity [2]. But the high operating temperatures with YSZ as an electrolyte can lead to complex materials problems such as electrode sintering, interfacial diffusion between electrolyte and electrodes, and mechanical stress due to different thermal expansion coefficients. Great efforts thus have been made to reduce the operating temperature by adapting either new electrolyte with high ionic conductivity or by reducing the electrolyte thickness or both. gadolinia doped ceria (GDC) based solid electrolytes, with oxygen deficient fluorite structure [3-5] and Sr- and Mg-doped $LaGaO_3$ based oxide with perovskite structures [6-8] are key candidates since both structures allow oxide-ion conductivity at low operating temperatures (873-1073K).

Ceria based solid solutions have been acknowledged to be the most promising electrolytes for intermediate temperature solid oxide fuel cells (SOFCs), since their ionic conductivity is higher than YSZ at the intermediate temperature range. The ionic conductivity of ceria based electrolytes, doped with various dopants (e.g. Ca^{2+}, Sr^{2+}, Y^{3+}, La^{3+}, Gd^{3+} and Sm^{3+}) at different dopant concentrations, has been extensively investigated [9-13] . Of these Gd^{3+} or Sm^{3+} doped ceria ceramics have the highest conductivity due to the smallest association enthalpy between the dopant cation and the oxygen vacancy in the fluorite lattice [14,15] . The crystal structure of gadolinia doped ceria possesses the same fluorite structure as the stabilized zirconia. Gd^{3+} and Ce^{4+} ions occupy the alternate body centers and the mobile oxygen vacancies are introduced by substituting Ce^{+4} with trivalent rare earth ions such as Gd. Also the conductivity of the doped ceria depends on the kind of dopant and its concentration. Ceria based ion conductors are reported to have purely ionic conductivity at high oxygen pressures. At lower oxygen partial pressures, these materials become partially reduced.

High bulk density pellets are desirable for many applications such as ionic conductivity measurements, bulk thermal expansion, and thermal conductivity studies. To develop electrolytes for SOFC applications, studies of the sintering and microstructure of electrolytes are important for obtaining dense materials with higher ionic conductivity. It is noted that the sintering and densification behaviour of ceria –based electrolytes rely strongly on the characteristics of the raw powders [16,17]. In our effort to produce sintered targets for pulsed laser ablation, a series of doped ceria pellets were studied. Ceria doped with varying contents of Gd were prepared by solid state reaction from high purity powders of Gd_2O_3 and CeO_2. The variation of hardness, lattice parameter and ionic conductivities of the doped ceria as a function of dopant concentration is investigated.

2. EXPERIMENTAL PROCEDURE

Sintered targets of doped ceria pellets with varying Gd mole fractions (5, 10, 15 mole%) were prepared by solid state reaction from high purity powders of Gd_2O_3 and CeO_2. The mixed powders were pressed into pellets uniaxially at 4 tons/square inch of pressure and the pellets were calcined at 1623-1723K for 4 h and reground in an alumina mortar with a pestle. The reground powders were subsequently pressed uniaxially at 4 tons /sq. inch with a heating and cooling rate of about 10 K/min. Pressed compacts were sintered in an alumina boat for 6 h in air at 1823 K. Surface morphology and composition of the sintered pellets were analyzed with XL30 ESEM Philips scanning electron microscope (SEM) fitted with x-ray energy dispersive analyzer (EDAX)). SEM was used to check for the presence of porosity and grain structure . The density of the pellets was evaluated from the measurements of weight and dimension. X-ray diffractograms (XRD) were recorded for characterising the crystalline phases present (PW1730 Philips, $CuK_{\propto}$ radiation). The conductivities of GDC pellets were measured by AC-impedance spectroscopy by supplying a voltage of 50 mV to the sample at frequencies ranging from 0.01 Hz to 32 MHz using a Solartron frequency response analyser. The conductivity measurements were carried out on samples that were at least 92% dense. The samples were heated in a home-built muffle furnace in flowing oxygen, and the thermocouple was placed very close to the sample so as to minimise the temperature measurement errors.

3. RESULTS AND DISCUSSION

The particles size of the ceria and gadolinia powders had a strong influence on the sintering characteristics of the pellets. It was observed that larger sized particles (>5um) did not sinter well. Initial trials on sintering of the doped ceria indicated that the densities were quite lower than 80% of the theoretical density when they were sintered at temperatures less than 1673 K. All the pellets were finally sintered at 1823 K and their densities were in the range 90-92% and are in agreement with values reported in the literature[18]. It has been observed from scanning electron microscopy that the grains are in the sub-mircon range and containing a small amount of porosity (figure not shown). However, no other secondary phases were observed after the final sintering. The microhardness measurements indicated a rapid increase in the hardness from 350 VHN to about 1000 VHN with the addition of Gd (Fig. 1). Since, Gd has a tendency for suppressing the grain growth and solid solution hardening, addition of Gd increases the hardness of the doped ceria. However, the increase in the hardness due to solid solution is predominant at concentration of 5 mole % doped GDC and only a slight increase in the hardness 10-15mole% GDC pellets.

To begin with, samples were sintered at 1623 K for different duration. It was noticed that the full width at half maximum and intensity of the f.c.c reflections of the GDC increased with increasing sintering temperature. However, trace amounts of impurity phases were noticed. Fig.2a shows powder XRD patterns for GDC samples containing 5, 10, 15 mol% of Gd at a sintering temperature of 1823 K for 6 h. These patterns were recorded from a small amount of the sintered pellet which was crushed into powder. The XRD patterns clearly revealed no secondary or impurity phases except for a small shift towards lower 2θ position. The data on peak positions, peak widths and relative peak intensity were fitted using a peak-fitting program, which calculated a theoretical data curve from the original data assuming a symmetrical peak shape. A Lorentzian function gave the best fit to the experimental data. Lattice parameters were then refined from the fitted data using a least square fitting procedure with an error of about1%. Fig.2b shows an increase in the lattice parameter from 5.409Å to 5.419Å with the increasing dopant concentration from 5mole% to 15 mole%. This increase in the lattice parameter has been attributed to a slightly larger radius of the dopant Gd^{3+} (1.053 Å) compared to that of the host ion Ce^{4+} (0.97 Å). Though no systematic study of lattice parameter variation as a function of sintering temperature was carried out, it was noticed that there is an increase in the lattice parameter with sintering temperature and a saturation in the lattice parameter was seen beyond1773 K. This also suggests that for the given doping concentration of gadolinia, the sintering temperature of 1823 K is sufficiently high enough to ensure the dissolution of gadolinia into ceria.

The technique of AC impedance is well suited for the measurement of electrical conductivities of solid ionic conductive materials [12,19]. In addition to the overall conductivity, one can also obtain information about electrode processes, and in the case of polycrystalline materials, the separate contributions of the bulk crystal lattice (grain interior) and grain boundaries. The real (Z') and imaginary components (z") of the impedance (z) were determined by measuring the amplitude and phase angle(θ) of the current. By plotting –Z" versus Z', one obtains Nyquist plot, where each arc in the plot represents a distinct process whose time constant is sufficiently separated from the others over the range of measurement frequencies. At higher temperatures, the time constants associated with the bulk and grain boundary impedances are much lower than those associated with the electrode interface. As a result, impedance spectra of samples at higher temperatures show only a single arc which results from the electrode interfacial processes. The left most x-intercept of the arc is the resistance of the sample, from which conductivity values can be determined. The typical plots obtained for 5 and 10 mol% of GDC measured at various temperatures are shown in Fig. 4 and Fig. 5 respectively. The samples showed two semicircular arcs in the plot between real and imaginary impedance. However, these two arcs tend to overlap at higher temperatures for GDC with 5 mole% than with 10mole % doped GDC. The first arc at higher frequency (left) is attributed to the contribution from grain interior and the second one (right) to the grain boundary. The impedances were found out from the individual semicircles and the grain interior and the total conductivity (grain interior and grain boundary) were evaluated.

The temperature dependence of conductivity is given by the Arrhenius equation

$$\sigma = \sigma_0 \exp^{-\frac{Ea}{KT}}$$

$$\ln \sigma = \ln \sigma_0 + \left(-\frac{E_a}{K} \right) . \frac{1}{T}$$

Where σ and σ_0 are the electrical conductivity and pre exponential factor respectively. E_a, K and T are the activation energy, Boltzman`s constant and temperature respectively. The above equation gives a straight line between lnσ and T, the slope of which is $\left(-\frac{E_a}{K}\right)$. A typical plot between logarithmic conductivity and temperature of the GDC pellets with 5 and 10mole% of Gd are shown in Fig.6.

The conductivities from the grain interior and the grain boundaries were calculated based on the impedances measured at various temperatures. Though the conductivities increase with increasing temperature, the contribution from the grain boundary decreases with increasing temperature. This is more evident with 5mol% GDC (Fig. 4) than 10 mole%. GDC. For example, the activation energies measured for the grain interior and grain boundary for 5mole% doped ceria are found to be 1.27eV and 0.94 eV respectively. Typical total conductivity is found to increase from 0.128S/cm to 0.199S/cm at 1023 K with increasing dopant concentration from 5 mole % to 10 mole % Gd. The activation energy for the total conductivity is found to decrease from 1.01eV for 5mole %GDC to 0.87eV for 10mole% GDC. Similar measurements on GDC with 15 mole% shows an increased conductivity than those of the other GDCs. These results are in good agreement with the literature[12] and suggest that the conduction is mainly due to ionic diffusion. At high temperature range, the contribution from the grain boundary conductivity to the total conductivity is expected to be relatively small because the activation energy associated with oxygen-ion migration within ceria lattice is much lower than that for the grain boundary conductivity. In this way, the role of the grain boundary or the impurity phases (if present) becomes more critical in the low temperature range. The conductivity measurements are also influenced by sintering characteristics and the processing conditions. For, example density and amount of porosity of the pellet may also alter the measurements of conductivity. It is also observed that the densification is better with the increased amounts of Gd doping because of the larger mobility of oxygen, although grain growth is lower[16]. It is also possible to achieve higher conductivities if the contribution of the grain boundaries to the total resistance to ionic diffusion is minimised.

4. CONCLUSIONS

This study was undertaken to prepare sintered pellets to use them as targets for the pulsed laser ablation of thin films of GDC on desired substrates. Some of the important conclusions of the present study are the following:

(i) The hardness of the pellets sintered at 1823 K, 6h was found to increase with increasing dopant concentration. A large increase in the hardness was noticed even with 5mole% addition of Gd. The increase in hardness is attributed to solid solution strengthening and suppression of grain growth with increase in the addition of Gd.

(ii) An increase in the lattice parameter with increase in the dopant concentration is noticed. This is attributed to the influence of Gd with larger ionic radius than that of the ceria.

(iii) AC impedance spectroscopy showed an increase in the conductivites for 10 mole% Gd doped ceria than those of the 5mole% doped ceria. In contrast to the 5 mole% Gd doped ceria, 10 mole% doped ceria showed grain boundary contribution even at temperatures like 773K. This could be attributed to the dominance of the granularity of the sample retained with the increasing addition of Gd.

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FIGURES

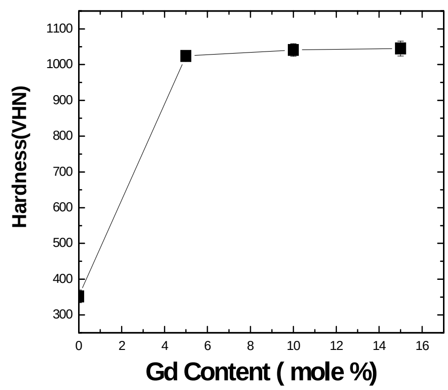


Fig.1 Microhardness versus Gd concentration of the pellets sintered at 1823K, 6 h.

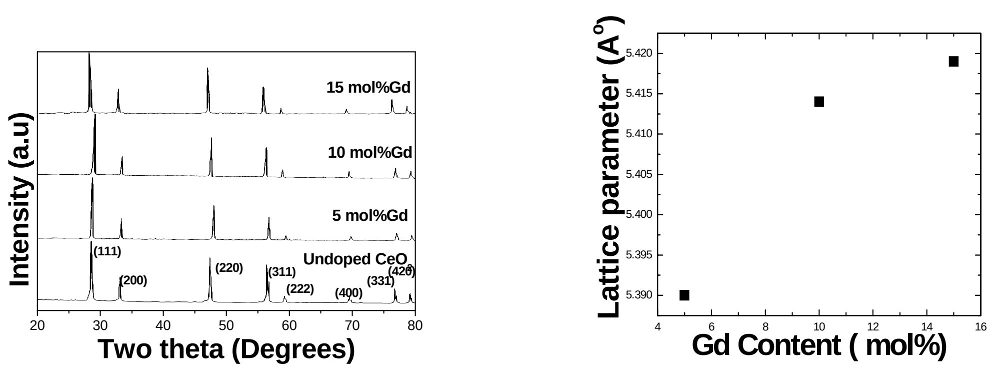


Fig. 2 (a) XRD patterns of the doped ceria with 5,10 and 15mole% of Gd sintered at1823K, 6 h. and (b) Lattice parameter variation as a function of dopant concentration for the samples sintered at1823K, 6h.

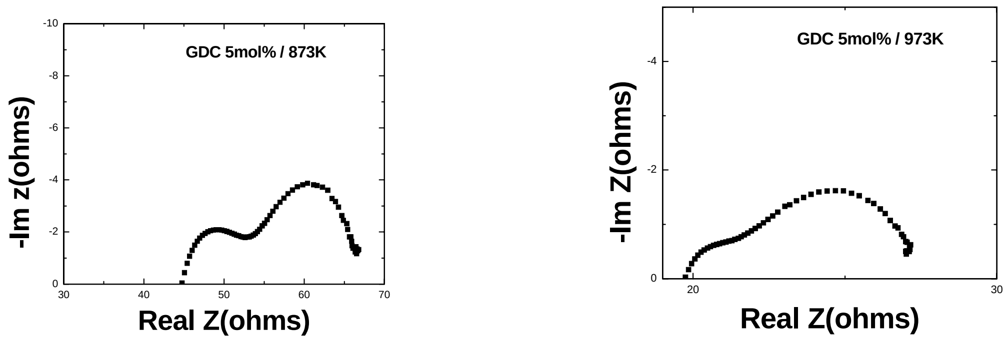


Fig. 4 Typical Complex impedance plots between imaginary impedance (Z’’) and real impedance(Z’) of GDC-5mol% pellets measured at (a) 873K and (b) 973K.

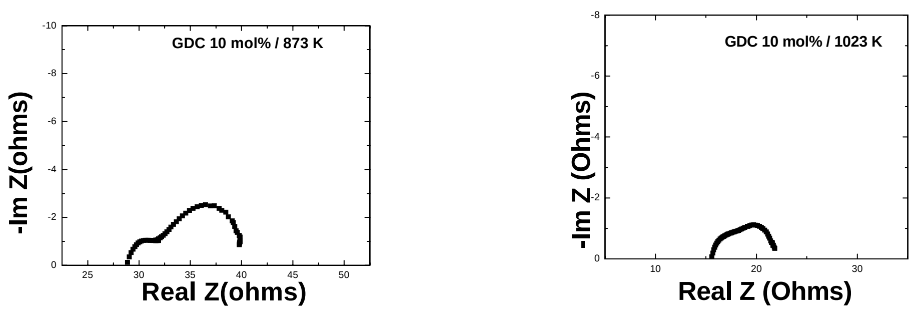
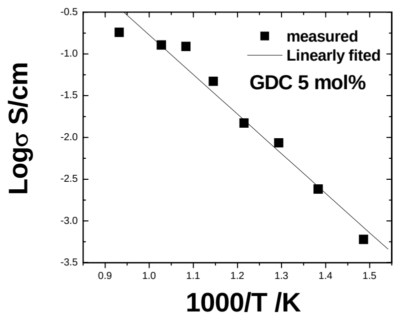


Fig.5 Typical Complex impedance plots between imaginary impedance(Z’’) and real impedance(Z’) of GDC-10mol% pellets ;(a) 873K and (b) 1023 K.



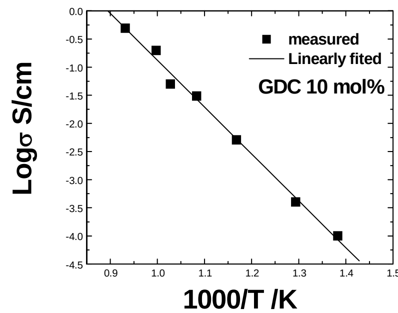


Fig.6 Conductivity as function of temperatures. (a) 5mole% GDC and (b) 10mole% GDC.