This paper describes the effect of 8 mole% yttria stabilized zirconia (8YSZ) additions on \((\text{CeO}_2)_\text{x}(\text{Gd}_2\text{O}_3)_\text{x}\) between 0 and 20 mole% 8YSZ, on the ionic conductivity. For all samples examined with XRD, a single cubic-phase was observed, stable between room temperature and 800°C. Whereas, Raman spectroscopy showed a mixed composition. Between 1 and 5 mole% 8YSZ, the ionic conductivity was very similar to \((\text{CeO}_2)_\text{x}(\text{Gd}_2\text{O}_3)_\text{x}\) with no YSZ additions. However, the ionic domain increased from \(P_{O_2} = 10^{15}\) atms. to \(10^{17}\) atms., showing greater stability of the system containing YSZ.

**INTRODUCTION**

\((\text{CeO}_2)_\text{x}(\text{Gd}_2\text{O}_3)_\text{x}\) are possible candidates as medium temperature (500 - 750°C) solid oxide fuel cell (SOFC) electrolyte materials (1-2). The lower temperatures, over traditional yttria stabilized zirconia (YSZ) based SOFC systems, would provide a number of benefits including: use of metallic bi-polar plates, lower degradation problems, less thermal mismatch of components, and the ease of sealing for the planar design. \((\text{CeO}_2)_\text{x}(\text{Gd}_2\text{O}_3)_\text{x}\) has been extensively studied (1-3), and has been found to have relatively high oxygen ion conductivity at these temperatures, although it is relatively unstable in reducing environments (4-5), and also inherently weak (6).

At low partial pressures, however, CeO\(_2\) is prone to developing electronic conductivity, where the Ce\(^{4+}\) ion can be reduced to Ce\(^{3+}\), and hence limits its use as an electrolyte. Much work has been undertaken to reduce this phenomena. Yahiro et al. (4) and Mehta et al. (5) have deposited thin layers of YSZ onto doped CeO\(_2\) and successfully suppressed the electronic current. The reaction between YSZ and CeO\(_2\) has also been examined, and has been shown to form a solid solution of 10 mole% YSZ in CeO\(_2\) (7).

X-ray diffraction is typically used for the determination of phase composition and cell parameters of crystalline materials. However, the complementary technique, Raman spectroscopy, is being used more frequently to characterize electrolyte materials, particularly in conjunction with XRD.

This paper will describe the fabrication and microstructure of \((\text{CeO}_2)_\text{x}(\text{Gd}_2\text{O}_3)_\text{x}\) / yttria stabilized zirconia (YSZ) materials, and will relate the microstructure and phase composition to the electrical properties.
EXPERIMENTAL

\((\text{CeO}_2)_{0.8}(\text{GdO}_{1.5})_{0.2}\) was synthesized using a reverse strike co-precipitation technique. \(\text{Ce(NO}_3)_3\) (99.5% Janssen), and \(\text{Gd(NO}_3)_3\) (99.9% Aldrich) were dissolved in the correct stoichiometric proportions in distilled water. A solution of 0.05M oxalic acid was used as the precipitant, and the precipitation reaction was carried out by adding the nitrate solution to the precipitant, which was adjusted to pH 6.7 to 6.9, using ammonia solution, during the whole of the reaction. The precipitant was continually stirred at 750 rpm. The precipitate was filtered, washed in triply distilled water and ethanol, and dried at 50°C in an oven, followed by calcining at 700°C/1h.

\(((\text{CeO}_2)_{0.8}(\text{GdO}_{1.5})_{0.2})_x(\text{YSZ})_x\ (x = 0.01 - 0.2)\) samples were synthesized by weighing, in the correct stoichiometric proportions, the calcined \((\text{CeO}_2)_{0.8}(\text{GdO}_{1.5})_{0.2}\) material and 8 mole % yttria stabilized zirconia (Toysio 8YSZ). The mixture was mixed in isopropyl alcohol, and milled, using YSZ milling media, for 24h. The mixed powders were dried, and re-milled for a further 24h. After drying (50°C/1h), the powders were pressed into pellets at 30MPa using an uniaxial die-press, and at 200MPa using a Stanstead FP2347 isostatic press. The samples were then sintered at 1600°C/10h with a heating and cooling rate of 3°C/min.

The relative density of the sintered ceramic samples was measured using the standard Archimedes method, and related to the powder x-ray diffraction pattern.

Powder x-ray diffraction analysis was carried out on polished samples using a Philips X-Pert system, with CuK\(_\alpha\) radiation. High temperature powder x-ray diffraction was obtained in air using an Anton Paar HTK high temperature furnace mounted on the goniometer, automated by an IBM micro-computer.

Raman spectroscopy was performed on samples using a Spex 1403 0.84 m double beam pass spectrometer equipped with a Spectra Physics 164 argon-ion laser and a water cooled Hammamtsu R943-02 photomultiplier tube. Spectra were obtained using a 514 nm laser line at an incident power of ca. 40 mW. The scanning rate used to collect the spectra was kept at 0.5 cm\(^{-1}\)s\(^{-1}\). The spectrometer was interfaced to a DM1B computer to provide scans and data manipulation. The fired samples were scanned as polished discs oriented at approximately 45° to the incident beam.

AC conductivity measurements were performed on the pellets, from 0.1 Hz to 10 MHz, using a Solatron SI 1260 impedance/gain phase analyzer, interfaced to a personal computer, and run through a lab-view program; 10 points were taken per decade of frequency. The impedance measurements were made from 200 - 800°C in air, using a non-inductively wound furnace, with a controlled heating and cooling rate. Pt paste (Degussa) was painted onto either side of the pellet, and fired at 1000°C/1h, to act as electrodes. The pellet was placed into an alumina holder using a spring-clip arrangement between Pt electrode connections. Sample temperatures were taken using a Pt/Rh thermocouple mounted close to the sample. The effect of oxygen partial pressure (1 - 10\(^{-20}\) atm.) on the sample, at 800°C, was obtained using \(\text{N}_2/\text{O}\), and \(\text{CO}/\text{CO}_2\) gas mixtures. The gases were mixed using Platon flow meters, and the oxygen partial pressure was measured with a yttria-stabilized zirconia oxygen gas sensor mounted in a separate furnace.
RESULTS AND DISCUSSION

Fig. 1 shows the percentage theoretical density of \((\text{CeO}_2)_{0.8}(\text{GdO}_{0.5})_2\cdot(x \cdot \text{8YSZ})\) at \(x = 0\) to \(x = 0.2\). Theoretical densities of over 97% were attainable for the samples sintered at 1600°C/10h. Fig. 1 also shows the theoretical density of all the samples examined in this work. Due to the smaller size of the Zr\(^{4+}\) ionic radii, compared to the Ce\(^{4+}\) ionic radii, as \(x\) was increased, the theoretical density decreased.

Fig. 2 shows typical room temperature powder x-ray diffraction plots for the \((\text{CeO}_2)_{0.8}(\text{GdO}_{0.5})_2\cdot(x \cdot \text{8YSZ})\) sample at \(x = 0.2\). For all the samples \((x = 0-0.2)\), a single cubic-ZrO\(_2\) structure was formed (9), with very sharp reflection peaks, indicative of a compositionally homogeneous sample. Our previous work (7) has shown that no reaction takes place between YSZ and CeO\(_2\) at temperatures as high as 1300°C. Above 1300°C, however, a solid solution occurs, as observed in this work, for samples sintered at 1600°C. Each powder x-ray diffraction peak was also noted as having doublets, due to K\(\alpha_1\) and K\(\alpha_2\). As the value of \(x\) was increased the peaks shifted towards higher 2\(\theta\) values. This can again be explained by the larger Ce\(^{4+}\) ionic radii compared to the Zr\(^{4+}\) ionic radii. The lattice parameters were calculated from the powder x-ray diffraction data, and are given in Table 1. As the YSZ \((x)\) content increased, the lattice parameter decreased, this is also indicative of the formation of a compositionally homogeneous solid solution. The values are in accordance with the work of Hong and Virkar (3) for \((\text{CeO}_2)_{0.8}(\text{ZrO}_2)_{0.2}\). The values given by Yashima et al. (9) for \((\text{CeO}_2)_{1-x}(\text{ZrO}_2)_x\), \((x = 0.1\) and 0.2\) are also given in Table 1 for comparison.

High temperature powder x-ray diffraction was performed on the samples at between room temperature and 800°C. No second phases, nor phase changes, were observed at temperatures up to 800°C, nor during any heating and cooling regimes performed (room temperature, heated to 800°C, and cooled back to room temperature). In fact, the samples remained a single cubic-phase, even after 200h at 800°C.

| \(x\) | 8YSZ lattice parameter (Å) |
|------|---------------------------|
| 0    | 5.417                     |
| 0.01 | 5.407                     |
| 0.02 | 5.405                     |
| 0.05 | 5.394                     |
| 0.1  | 5.379 (5.37)              |
| 0.15 | 5.356                     |
| 0.2  | 5.331 (5.36)              |

Fig. 3 shows the comparison Raman spectra of \((\text{CeO}_2)_{0.8}(\text{GdO}_{0.5})_2\cdot(x \cdot \text{8YSZ})\), at \(x = 0, 0.01, 0.02\) and 0.05 8YSZ at room temperature (ca. 20°C). Several features are apparent. Firstly, the major band at 464 cm\(^{-1}\) corresponds to the F\(_{2g}\) mode for ceria (10). At 20 mole% 8YSZ, this band has shifted to 475 cm\(^{-1}\), likely due to either distortion of the fluorite cell of the doped ceria if increase in band position indicates a decrease in bond length, as indicated by XRD cell parameters, or a shift due to the overlap with the
spectrum of 8YSZ. With increase in mole% 8YSZ there is an increase in intensity of bands at 295, 575, 974 and 1043 cm⁻¹, seen clearly in fig. 6(f). These bands correlate with the bands observed for pure 8YSZ at 320, 600, 950 and 1000 cm⁻¹. Bands at wavenumbers > 950 cm⁻¹ for YSZ have been attributed to fluorescence bands arising from the presence of rare-earth impurities. The spectrum of gadolinia-doped ceria, fig. 3(a), shows evidence of many bands in the fluorescent/luminescent region, i.e., 980, 1037, 1082, 1137, 1159, 1195, 1274, 1319 and 1380 cm⁻¹. Bands at 974 and 1043 cm⁻¹ correspond to fluorescent bands reported for 8YSZ at 950 and 1000 cm⁻¹ (8).

Thus, the Raman spectra indicate that the composition of the these materials, \((\text{CeO}_2)_{0.8}(\text{GdO}_{1.5})_{0.2}\), \(x (8\text{YSZ})_x\), at \(x = 0\) to 0.2, contain a mixture of the two materials, unlike XRD patterns which show a single cubic phase for all compositions studied. Moreover, Raman spectroscopy appears to resolve more information about the composition, whereas, x-ray analysis indicates no significant change in the crystal planes.

The ionic conductivity of \((\text{CeO}_2)_{0.8}(\text{GdO}_{1.5})_{0.2}\), \(x (8\text{YSZ})_x\), for \(x = 0.01\) to 0.2, versus temperature in air, is shown in fig. 4. Only one mechanism is observed for the sample; for \(x = 0.01\) to 0.05, the change in slope is due to the system polarization at high frequency and high temperature, and occurs at approximately 800°C. As the value of \(x\) was increased, the ionic conductivity was found to decrease. At \(x = 0\), or \((\text{CeO}_2)_{0.8}(\text{GdO}_{1.5})_{0.2}\), the ionic conductivity at 750°C was 0.22 S/cm, which is similar to that found in the literature (1). With increasing \(x\), the ionic conductivity was found to decrease; the ionic conductivity of the samples containing \(x = 0.01\) and \(x = 0.02\) were very similar to \((\text{CeO}_2)_{0.8}(\text{GdO}_{1.5})_{0.2}\) at comparable temperatures.

It is interesting to note that the samples containing greater than \(x = 0.1\), showed ionic conductivities lower than 8 mole% YSZ. The large drop in the ionic conductivity at \(x > 0.05\) is postulated as being due to the large deformation of the ceria lattice, as described in Table 1.

The activation energy of the samples is shown in Table 2, from 450°C to 750°C. As the value of \(x\) increased, the activation energy was found to increase; the value for 8 mole% YSZ is given for comparative purposes.

Fig. 5 shows a plot of total conductivity at 800°C as a function of oxygen partial pressure (\(P_{O_2}\)), for \((\text{CeO}_2)_{0.8}(\text{GdO}_{1.5})_{0.2}\), \(x (8\text{YSZ})_x\), at \(x = 0, 0.01, 0.02\) and 0.05 8YSZ. Two major regions are observed, a high oxygen partial pressure region, where the conductivity is independent of \(P_{O_2}\), and a low oxygen partial pressure region, where the conductivity increases with decreasing \(P_{O_2}\). The slope of approximately 1/4 seen in fig. 5, and also observed by Arai et al. (11) for \((\text{CeO}_2)_{0.8}(\text{GdO}_{1.5})_{0.2}\), can be predicted by the following rationale.

At low oxygen partial pressures, associated with the anodic conditions found, \(Ce^{4+}\) ions are reduced to \(Ce^{3+}\), ions, according to equation (1).

\[
O_6^+ \leftrightarrow \frac{1}{2}O_2 + V_0 + 2e^-
\]  

where \(e\) is equivalent to \(Ce^{3+}\), and \(V_0\) is an oxygen vacancy.
For CeO$_2$ doped with Gd$_2$O$_3$, the defect reaction can be described by reaction 2.

$$\text{Gd}_2\text{O}_3 \leftrightarrow 2\text{Gd}_{\text{Ce}}^+ + \text{Vo} + 3\text{O}_2^*$$ \[2\]

Thus, the equilibrium constant ($K_{\text{red}}$) for the reduction reaction is given by equation 3.

$$K_{\text{red}} = n^2 [\text{Vo}]\text{Po}_2^{1/2}$$ \[3\]

The condition for $n$, the number of electrons, being « [Gd$_{\text{Ce}}$], yields the equation (4)

$$n = \frac{K_{\text{red}}^{1/2}}{[\text{Gd}_{\text{Ce}}^-]}\text{Po}_2^{-1/4}$$ \[4\]

Table 2 The activation energy of ((CeO$_2$)$_{0.8}$(GdO$_{1.3}$)$_{0.2}$)$_{1-x}$(8YSZ)$_x$ for $x = 0$ to 0.2.

| $x$  | Activation energy (eV) for 8YSZ |
|------|--------------------------------|
| 0    | 0.49                           |
| 0.01 | 0.492                          |
| 0.02 | 0.530                          |
| 0.05 | 0.643                          |
| 0.1  | 0.780                          |
| 0.15 | 0.811                          |
| 0.2  | 0.932                          |
| 1    | 0.925                          |

Hence, the conductivity is proportional to $\text{Po}_2^{-1/4}$, as shown in fig. 5, except at the highest YSZ levels ($x = 0.05$), where the slope is slightly more shallow possibly due to the higher dopant concentrations (12), although this was not examined in any detail.

The ionic domain (the $\text{Po}_2$ value at which the electronic conductivity equals the ionic conductivity, given by a change in slope of the graph), for the (CeO$_2$)$_{0.8}$(GdO$_{1.3}$)$_{0.2}$ was found to be approximately $10^{15}$ atms., while at increasing values of $x$, the ionic domain was found to increase to lower partial pressures. For example, at $x = 0.01$, the ionic domain was found to be approximately $10^{16}$ to $10^{17}$ atms., while at $x = 0.05$, the ionic domain was lower than $10^{17}$ atms.
CONCLUSIONS

Single cubic-phase \((\text{CeO}_2)_{0.8}(\text{GdO}_2)_{0.2}(\text{YSZ})\), can be formed from \(x = 0\) to 0.2, and is stable from room temperature to 800°C, although Raman spectroscopy indicates a mixed composition. The ionic conductivity of the material decreased as \(x\) increased, although only a small decrease was observed between \(x = 0\) and \(x = 0.05\). At \(x > 0.05\), a large drop in conductivity was observed which is indicative of a large lattice deformation. With increasing \(x\), the ionic domain was found to increase to lower \(\text{PO}_2\) values; \(\text{PO}_2 = 10^{-15}\) atm. for \(x = 0\), and \(\text{PO}_2 = 10^{-17}\) atm. for \(x = 0.05\).

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Fig. 1 Percentage theoretical density and actual theoretical density (from powder x-ray diffraction data) for \((\text{CeO}_2)_{0.8}(\text{GdO}_{1.5})_{0.2} \cdot (8\text{YSZ})_x\) for \(x = 0\) to 0.2.

Fig. 2 Room temperature powder x-ray diffraction data for \((\text{CeO}_2)_{0.8}(\text{GdO}_{1.5})_{0.2} \cdot (8\text{YSZ})_0\).

Fig. 3 Comparison of the room temperature Raman spectra of \((\text{CeO}_2)_{0.8}(\text{GdO}_{1.5})_{0.2} \cdot (8\text{YSZ})_x\) at \(x = 0\) (a), 0.01 (b), 0.02 (c), 0.05 (d), 0.10 (e), 0.15 (f) and 0.20 (g).
Fig. 4 The ionic conductivity of $\left(\text{CeO}_2\right)_{0.8}\left(\text{GdO}_1.5\right)_{0.2}x\left(\text{YSZ}\right)_y$, as a function of temperature.

Fig. 5 The conductivity of $\left(\text{CeO}_2\right)_{0.8}\left(\text{GdO}_1.5\right)_{0.2}x\left(\text{YSZ}\right)_y$, at $x = 0$ to 0.05, as a function of oxygen partial pressure, at 800°C.