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Journal of the European Ceramic Society 25 (2005) 2573–2575

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A comparative study on ionic conductivity of Sr and Mg stabilized zirconia by impedance spectroscopy

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Abstract

The high ionic conductivity of stabilized zirconia materials by substitutional doping of lower valent metal oxides (MgO, SrO, CaO, Y_2O_3, Sc_2O_3, etc.) are materials of outstanding technological importance. The Mg and Sr stabilized zirconia have been synthesized by co-precipitation method. The formation of the compound has been confirmed from XRD analysis. The particle size has been calculated from the XRD analysis and are found to be in the order of nm. The electrical characterization is carried out using the impedance spectroscopy method in the frequency range of 50 Hz–5 MHz. The conductance spectra show the dc plateau and dispersive region. The dispersive region suggests the correlated hopping motion of ions. The charge carrier concentration is found to be higher for Sr stabilized zirconia rather than for Mg stabilized zirconia. The bulk resistance for Sr and Mg stabilized zirconia have been found to be in the order of $3.47 \times 10^7\ \Omega\,\text{cm}^{-1}$ and $5.05 \times 10^5\ \Omega\,\text{cm}^{-1}$.

Keywords: Stabilized zirconia; Ionic conductivity

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1. Introduction

Stabilized zirconias are materials of outstanding technological importance, because of their use as electrolytes in high temperature fuel cells.[1,2] While some researchers focus on the development of SOFCs for operation at high temperatures of 900–1000 °C, it becomes increasingly important to reduce the operation temperature of the fuel cells down to the range of 400–800 °C, in order to substantially increase the life of SOFC, widen the selection of electrode, and to reduce the cost of the materials processing and cell fabrication.[3,4] So in order to reduce the operating temperature of SOFCs the operating temperature of the corresponding electrolyte plays an important role.[5] The stabilized zirconias with tetragonal and cubic polymorphs are found to have an operating temperature in the range of 600–800 °C.[4] The high temperature tetragonal and cubic polymorphs of zirconia can be stabilized at room temperature provided a nonometric grain size is maintained and/or different binary oxide systems such as CaO, SrO, MgO, etc., are added.[6,7] Numerous reports have been published on the ionic conductivity of Mg–ZrO_2.[5–8] We had already reported that 18 mol% and 22 mol% of Mg–ZrO_2 were found to have high ionic conductivity compared to pure ZrO_2.[8] In the present study a comparative analysis of pure ZrO_2, 18 mol% of Mg and Sr stabilized zirconia has been reported. The Ac impedance technique is a powerful tool to analyze the electrical properties of ceramic ionic conductors. So far no report has been published on the Impedance analysis of Sr stabilized zirconia. Hence, in the present study Ion dynamics analysis of Sr stabilized zirconia has been reported and compared with Mg stabilized zirconia.

2. Expérimental

The samples pure ZrO_2, 18 mol% Mg and Sr stabilized zirconia have been prepared by co-precipitation method. The raw material $ZrOCl_2\cdot 8H_2O$ (>99% purity), was dissolved in distilled water and stirred well. Precipitation of the powder was done using aqueous NaOH as the hydrolyzing agent. The

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doi:10.1016/j.jeurceramsoc.2005.03.104

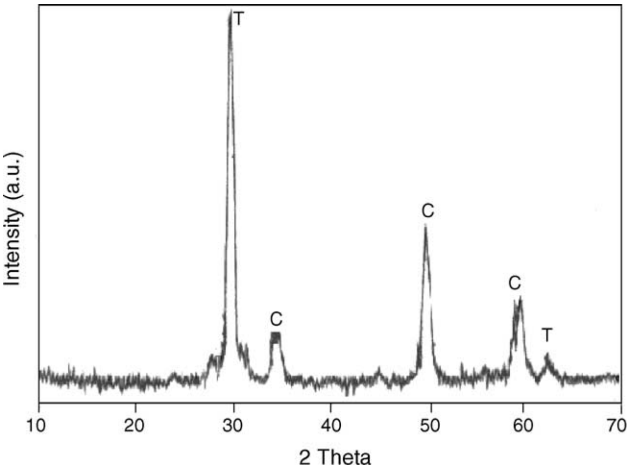

Fig. 1. XRD pattern for Sr stabilized zirconia at room temperature.

detailed preparation procedure for pure ZrO_2 and 18 mol% Mg stabilized zirconia have been reported elsewhere.[8] The same procedure has been adopted to prepare 18 mol% Sr stabilized zirconia. The prepared samples are annealed at 800 °C for 24 h in open-air atmosphere. X-ray diffractogram (XRD) has been taken to confirm the formation of samples by using Philips X-ray diffractometer PW 1830. The annealed samples are crushed into fine powder and sprayed in a die. A pressure around 4000 kg cm^{-2} is applied to form pellets with 0.1 cm thickness and 1.0 cm diameter. Aluminum has been coated on both sides of the pellet by thermal evaporation method using HINDHIVAC 12 AD coating unit. The ac impedance measurements are made in the temperature range of 100–400 °C. The impedance analyzer HIOKI 3532 controlled by a computer is used to obtain the electrical measurements in the frequency range of 50 Hz–5 MHz.

3. Results and discussions

3.1. XRD analysis

The X-ray diffraction patterns (Fig. 1), the unit cell parameters of pure and 18 mol% Mg stabilized zirconia have been reported elsewhere.[8] Fig. 1 shows the XRD pattern for Sr stabilized zirconia. The particle size (*D*) are estimated using the Debye Scherrer's formula:

$$D = \frac{0.94\lambda}{\beta_{2\theta}\cos\theta} \qquad (1)$$

where λ is the wavelength of the X-ray and $\beta_{2\theta}$ is the full width at half maximum of the corresponding peak of the XRD pattern. The particle size for Sr and Mg stabilized zirconia have been found to be 23 and 32 nm, respectively. This indicates the formation of nano crystalline phases in the present sample. The XRD analysis reveals that Sr stabilized zirconia has found to have mixture of tetragonal and the cubic fluorite structure. But in literature[9] it has been reported that there are no solid solutions with the fluorite structure in the ZrO_2–MO (M = Be, Sr, Ba) at temperatures below 1500 °C. But in the present study the cubic fluorite structure has been observed for Sr stabilized zirconia. This has been due to the presence of nano sized particles in the sample, which in turn stabilizes the desired phase. Since it has been already been reported by Ramamoorthy et al. that the cubic phase in Y_2O_3–ZrO_2 system has fully been stabilized due to the smallness of the crystallite site.[10]

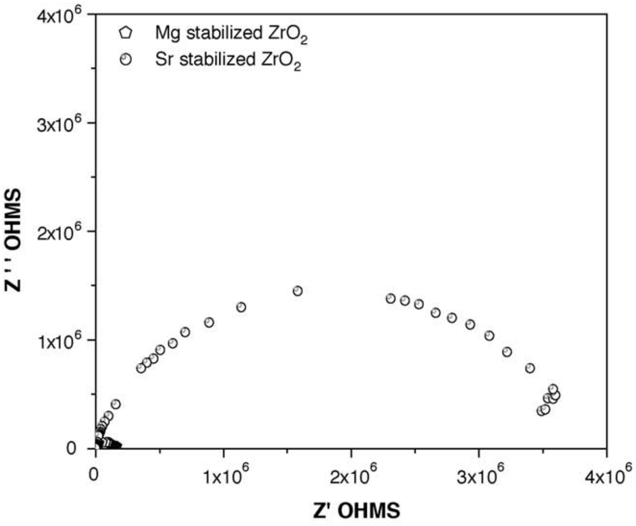

Fig. 2. Cole–Cole plot for Sr and Mg stabilized zirconia at 400 °C.

3.2. Impedance analysis

Fig. 2 shows the Cole–Cole plot of impedance for Mg and Sr stabilized zirconia at 400 °C. The data fall on a single semicircle whose center lies below the real axis at high frequencies indicating the non-debye nature of the material. The associated capacitance of the semicircle has been calculated from the relation $\omega RC = 1$ at the arc maximum and it is found to be in the order of pF, that is attributed to a conduction process through the bulk of the material.[11] The bulk resistance of the sample at various temperatures has been calculated from the low frequency interception of real axis. The bulk resistance of Sr stabilized zirconia has found to be low compared to the pure ZrO_2. The bulk resistance of the material for Sr and Mg stabilized zirconia are found to be $3.47 \times 10^7\ \Omega\ cm^{-1}$ and $5.05 \times 10^5\ \Omega\ cm^{-1}$ at 400 °C. The bulk resistance is found to be decreasing with increase in temperature for both the samples. The bulk resistance value of both the samples indicates the high ionic conductivity for the sample Mg stabilized zirconia.

3.3. Conductivity spectra analysis

Fig. 3 shows the conductance spectra for Sr and Mg stabilized zirconia at 400 °C. Each curve displays a low frequency plateau, which corresponds to the dc conductivity of the bulk

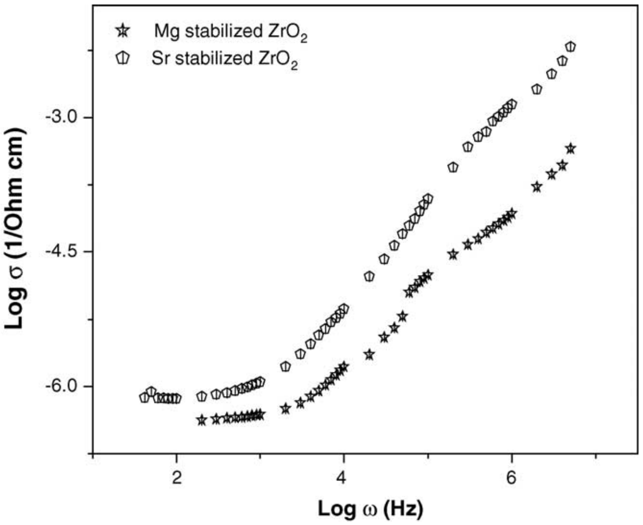

Fig. 3. Conductivity spectra for Sr and Mg stabilized zirconia at 400 °C.

material, and a dispersive region at high frequency, which corresponds to the ac conductivity. The existence of such a dispersive regime in the conductivity rules out the possibility that mobile ions perform a random hopping and reveals that the ionic motion is somehow correlated. The dc conductivity estimated from the conductivity spectra can be represented as,[12]

$$\sigma_{\mathrm{dc}} = \left(\frac{N\mathrm{e}^2 d^2 \gamma}{6}\right)\left(\frac{\omega_{\mathrm{H}}}{kT}\right) \qquad (2)$$

where, N and e are the carrier concentration and charge, d and ω_{H} are the characteristic hopping distance and frequency and γ is a geometrical factor. In the case of stabilized zirconia samples the product of geometrical factor and hopping distance can be taken as $d^2\gamma = 0.35a^2$ with $a = 0.516$ nm being the structural parameter.[8] The hopping frequency has been extracted from the almond and West formalism.[8]

$$\omega_{\mathrm{H}} = \left(\frac{\sigma_{\mathrm{dc}}}{A}\right)^{1/n} \qquad (3)$$

The charge carrier concentration (N) has been calculated for all the samples using the above values by substituting in Eq. (1). The charge carrier concentration calculated from the Eq. (1) for Sr stabilized zirconia and for Mg are in the order of 10^{25} and $10^{24}$and are found to be constant over the temperature range studied. This implies that all the ions responsible for the conductivity are in mobile state and it supports the strong electrolyte theory. It has been observed that even though the charge carrier concentration has found to be higher for Sr stabilized zirconia rather than for Mg stabilized zirconia, the conductivity has found to be very high for Mg stabilized zirconia. This may be due to the high ionic size of Sr compared to Mg. It has already been reported that Mg–ZrO_2 has attracted considerable attention, as the low radius of the magnesium cations gives high ionic conductivity.[9] The high ionic radius of Sr may block the oxide ions mobility resulting in decrease of ionic conductivity.

4. Conclusion

The samples have been prepared by co-precipitation technique. The XRD analysis reveals the nano crystalline phase of both the samples which in turn stabilizes the cubic phase and the particle size of the samples. The impedance analysis reveals that the sample Mg–ZrO_2 has found to have high ionic conductivity compared to Sr–ZrO_2. The conductance spectra reveal that the charge carrier concentration of Sr–ZrO_2 has found to be one order higher than for the sample Mg–ZrO_2.

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