ELECTRICAL AND DIELECTRIC PROPERTIES OF SCANDIA AND CERIA STABILIZED ZIRCONIA

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ABSTRACT

Scandia stabilized zirconia sample, containing 1mole % CeO_2, (1Ce9Sc sample) was prepared by using chemical polymeric precursor route called pichini method. Two zirconia samples doped with 10 and 15 mole % CeO_2 (10Ce and 15Ce samples) were prepared by using the same method for comparison. Co-doping zirconia with 1 mole % of CeO_2 and 9 mole % of Sc_2O_3 suppressed the undesired rhombohedral phase and fully stabilized this sample in the cubic phase. Addition of 15 mole % of CeO_2 fully stabilized zirconia in the tetragonal phase. The dielectric and electrical properties of all the prepared samples were investigated in the frequency range from 10 kHz to 5MHz in the temperature range from 25°C to about 325°C. At temperature range from 125 to 325°C, 1Ce9Sc sample has the highest conductivity. For all the prepared samples, as the frequency increases both the dielectric constant and dielectric loss decreases.

Keywords: Co-doped scandia stabilized zirconia, ceria stabilized zirconia, electrical properties, dielectric properties.

INTRODUCTION

Undoped zirconia and stabilized zirconia have wide range of applications. In recent years, a major thrust of applied development in the semiconductor industry has been the search for materials that could replace SiO_2 as the gate dielectric in complementary metal–oxide–semiconductor (CMOS) technology. Among the most promising materials are ZrO_2 and HfO_2, which do have much higher dielectric constants and some other positive features as well (e.g., chemical stability) (Wilk *et al*., 2001; Yeo *et al*., 2002; Zhao *et al*., 2005).

For ceria stabilized zirconia system**,** zirconia-rich compositions, $Ce_xZr_{1-x}O_2$ (x < 0.3) find applications as ceramic materials and ionic conductors whereas ceria-rich oxides (x > 0.3) are exploited above all as catalytic materials (Kaspar *et al*., 1999; Trovelli *et al*., 1997; Trovelli, 1996).

Scandia stabilized zirconia (ScSZ) is one of the candidates that could be used as electrolyte in the intermediate temperature in the solid oxide fuel cells (Badwal, 1987; Badwal *et al*., 2000; Ruh *et al*., 1977; Arachi *et al*., 1999; Yamamoto *et al*., 1995)**.** Abbas *et al*. (2010) prepared scandia stabilized zirconia containing 10 mole % Sc_2O_3 and up to 1 mole % of Gd_2O_3, CaO, or CeO_2 to investigate the influence of the co-doping with various cations on the ionic conductivity and on the phase transition at low temperature. Wang *et al*. (2005**)** studied

the structural and the impedance of zirconia doped with 10 mole % Sc_2O_3 and different amounts of CeO_2.

The study of dielectric properties of the oxide ion conductors can produce valuable information about oxide ion conduction (Biswas, 2010). Dielectric relaxations due to ionic displacement induced by the migration of oxygen vacancies have been reported in some oxygen ionic conductors (Iguchi *et al*., 2003**;** Kurumada *et al*., 2005).

A variety of factors, such as degree of crystallinity, roughness, chemical homogeneity, and stoichiometry can affect the dielectric properties and leakage currents across the dielectric layers (Wilk *et al*., 2001)**.** There have been many reports on the electrical properties of zirconia films, but detailed reports on microstructural characterization along with electrical characteristics are scarce (Ramanthan *et al*., 2002).

Thompson *et al*. (1992) studied the effect of different dopants with different cations (Mg, Ca, Ce) on the dielectric properties of zirconia. Sayan *et al*. (2005) investigated the permittivity of ZrO_2 thin film**.** Biswas (2009) investigated the dielectric relaxation and ac conductivity behavior for yttria stabilized zirconia (YSZ) compounds with yttria concentration varying from 8 to 12 mol%. Kumar and Manna (2008) measured the frequency and temperature-dependent conductivities and impedance in range of 50 Hz–1MHz and 300–900 K for a solid solution of 8 mol% of scandia-stabilized cubic-zirconia

(8ScSZ) prepared by the co-precipitation technique. From the above mentioned literature, it is clear that there is no systematic work done for investigation of the electrical and dielectric properties of zirconia co-doped with CeO_2 and Sc_2O_3 at different temperature and frequency to reach the best conditions.

This paper aims to study the effect of co-doping of zirconia with 9mole % of Sc_2O_3 and 1mole % of CeO_2 on the electrical and the dielectric properties (which is not widely studied) to continue the previous work done for this system (Abbas *et al.*, 2010).10Ce and 15Ce samples were used for comparison. Moreover, the effect of CeO_2 content on electrical conductivity and the dielectric properties of zirconia were studied. The correlation of the crystal structure on the dielectric properties for all the prepared samples will be investigated.

MATERIALS AND METHODS

$(ZrO_2)_{1-x}$-$(CeO_2)_x$ and $(ZrO_2)_{90}$-$(CeO_2)_y$-$(Sc_2O_3)_{10-y}$ systems were prepared using polymeric precursors chemical route based on Pechini method (Pechini, 1967) mentioned in our previous work (Abbas *et al.*, 2008) from the solution of the metal nitrates using citric acid as complexing agent and ethylene glycol as gel former where x=0.1, 0.15 and y=1. For the conductivity measurements, ceramic powders were compacted using direct uniaxial pressing into cylindrical pellets with 8 mm diameter and 2 mm thickness under a pressure of 400 MPa and were sintered at 1500°C for 5h. Then the sintered samples were coated with platinum paste on both sides. The heating rate was 2°C/min, 4 h holding at 1000°C. The electrical properties and the dielectric properties (dielectric constant and dielectric loss) were measured in the temperature range from 25°C to about 325 °C every 25°C in the frequency range from 10 kHz to 5MHz using Hioki 3532 LCR Hi – Tester.

RESULTS AND DISCUSSION

Table1 shows the nomenclature and the composition of all samples used in this work. From XRD analysis from our previous work (Abbas *et al.*, 2008; Abbas *et al.*, 2010) it was found that, 10Ce sample has mixture of monoclinic and tetragonal phase structure and 15Ce sample is fully stabilized in the tetragonal phase. 1Ce9Sc sample is fully stabilized in the cubic phase. The monoclinic, tetragonal, and cubic phases were matched to PDF numbers 37-1484 (McMurdie *et al.*, 1986), 42-1164 (Teufer, 1962), 27-0997 (Katz, 1997). The tetragonal unit cell volume increases with increasing CeO_2 concentration. The unit cell volume for the cubic phase (for 1Ce9Sc sample) is lower than that of the tetragonal phase (for 10 and 15Ce samples) which in turn is lower than that of the

monoclinic phase (10Ce sample). The unit cell volume decreases in the direction of increasing the symmetry where the cubic phase has higher symmetry than the tetragonal phase which in turn has higher symmetry than the monoclinic phase (Figs. 1 and 2).

Table 1. The nomenclature and the composition of all samples used in this work.

Nomenclature	Composition (mole %)
10Ce	$10 CeO_2 + 90 ZrO_2$
15Ce	$15 CeO_2 + 85 ZrO_2$
1Ce9Sc	$1 CeO_2 + 9 Sc_2O_3 + 90 ZrO_2$

Figure 3 represents the variation of the electrical conductivity for the prepared samples as a function of temperature in the range of room temperature up to about 325ºC. It is clear for all the samples that the curves are divided into three parts. The first part at low temperature and up to 100ºC and the other two parts start above 100ºC. In the low temperature part the conductivity decreases as the temperature increases till 100ºC indicating that the samples loss water at this temperature range and above 100ºC, the conductivity increases with increasing of temperature.

Above 100ºC, 10Ce sample has higher conductivity than 15Ce sample. This might be due to above 10 mole % CeO_2; complex associate is formed between Ce^{3+} ion and the oxygen vacancy. This result is in agreement to that obtained by Abbas *et al.* (2009). At temperature range from about 125 to 325ºC, the 1Ce9Sc sample has higher conductivity than ZrO_2-CeO_2 system. This might be due to the fact that the ionic radius of Sc^{3+} ion in 1Ce9Sc system is 87 pm (Shanon, 1976) which is close to that of Zr^{4+} ion (84pm) and lower than that of Ce^{3+} ion (1.14pm) in the ZrO_2-CeO_2 system. This may lead to that the Zr^{4+} ion can be substituted by Sc^{3+} ion easier than by Ce^{3+} ion. Thus the charge carrier mobility in case of 1Ce9Sc system is higher than that in case of ZrO_2-CeO_2 system.

For ZrO_2-CeO_2 system, the conductivity curves show change in the slope at 250ºC. Moreover, the conductivity above 100ºC is frequency independent and is associated with very low activation enthalpy. This might be due to the conduction arises from hopping of charge carriers between localized states. This behavior of conductivity is similar to that detected by Tcheliebou *et al.* (1996) below 300 ºC for ZrO_2-CeO_2 system.

Glushkova *et al.* (2006) found that for ZrO_2-12mole%CeO_2, the electronic transport of the hopping type as a result of electron exchange between adjacent cations Ce^{3+} and Ce^{4+} should occur over boundaries of solid solution grains containing cerium cations in different charge states.
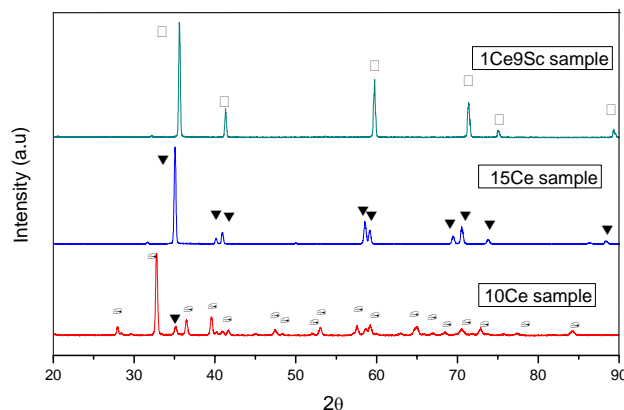
Fig. 1. X-ray diffraction pattern of the sintered samples, obtained at room temperature (Abbas, 2009) where □ represents the cubic peaks, ● represents the monoclinic peaks and ▼ represents the tetragonal peaks.
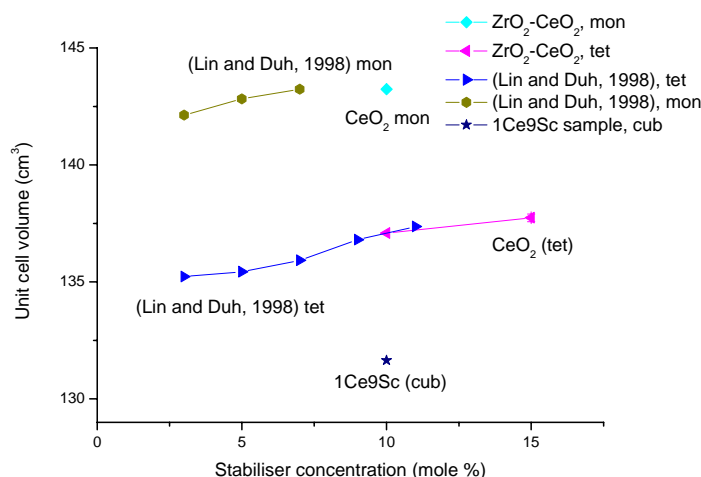

Fig. 2. Unit cell volume for the prepared samples as a function of the dopants concentration (Abbas, 2009) and those from references (Lin and Duh, 1998).

Figures 4 and 5 shows the dielectric constant as a function of frequency and temperature for 10Ce sample. As the frequency increases, the dielectric constant slightly decreases in the low temperature range and up to 250ºC. The decrease in the dielectric constant becomes larger at higher frequency range due to dielectric dispersion in this temperature range. For 10Ce sample at 10 kHz (Fig. 5), as the temperature increases the dielectric constant decreases up to 100ºC and above 150ºC it slightly increases till 250 ºC and above this temperature it rapidly increases. This result is in harmony with that obtained from the conductivity figure of this sample (Fig. 3). Increasing of temperature results always in increasing the dielectric constant due to decrease in the density of packing and increase in dipole freedom in electric field as can be shown in figures 4 and 5.

For ZrO_2-CeO_2 system, the dielectric constant of 15Ce sample is higher than that of 10Ce sample (Table 2). This might be due to the following: as detected from the XRD part (Figs.1 and 2), 10Ce sample has mixture of monoclinic and tetragonal phases whereas 15Ce sample is fully stabilized in the tetragonal phase. Increasing the CeO_2 content transform the monoclinic phase to tetragonal phase and this leads to a large increase in the dielectric constant values. This might be due to the sudden decrease in the unit cell volume from the monoclinic to tetragonal phase. The change in the dielectric constant results from changes in the polarizability of the unit cell and also because of the more ionic character nature of the tetragonal compared to the monoclinic phase. This result is in agreement to that obtained by Thompson *et al*. (1992) for yttria-zirconia system.

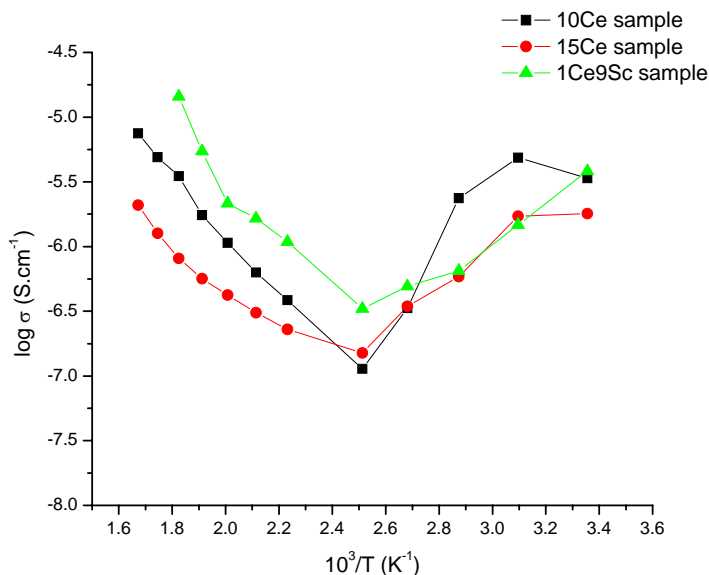Figure 6 shows that for 1Ce9Sc sample, as the

Fig. 3. The conductivity of the prepared samples as a function of temperature.
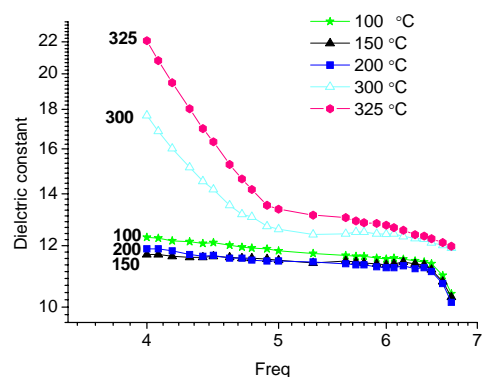

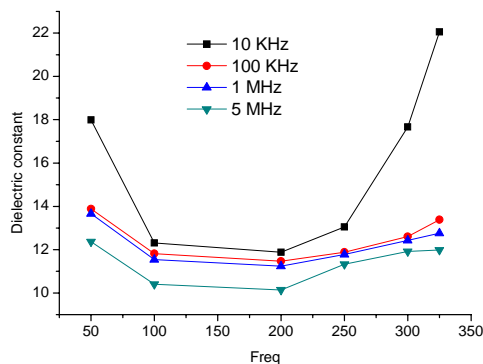Fig. 4. The dielectric constant of 10Ce sample as a function of frequency.

Fig. 5. The dielectric constant of 10Ce sample as a function of temperature.

Table 2. The dielectric constant at 10MHz for ZrO_2-CeO_2 system as function of temperature.

Sample	50 °C	100 °C	150 °C	200 °C	250 °C
10Ce	17.99	12.31	11.69	11.89	13.05
15Ce	49.24	40.39	40.75	41.53	42.37

temperature increase the dielectric constant slightly increase till 200ºC, and above this temperature the dielectric constant rapidly increases which is in harmony with the result observed from conductivity curve also of this sample (Fig. 3). The large increase in the dielectric constant above 200ºC might be due to phase transformation. As the frequency increases the dielectric constant slightly decreases in the temperature range from 50 to 200ºC whereas it rapidly decreases at 250ºC. In the

temperature range (50-250ºC) the decrease in the dielectric constant becomes larger at higher frequency. Dielectric constant almost decreases by increasing frequency (dielectric dispersion) and is indicated clearly at higher frequencies and temperatures.

Table 3 summarizes the crystal structure, the density, relative density, molar volume obtained from our previous work (Abbas *et al*., 2008, 2010) and the dielectric
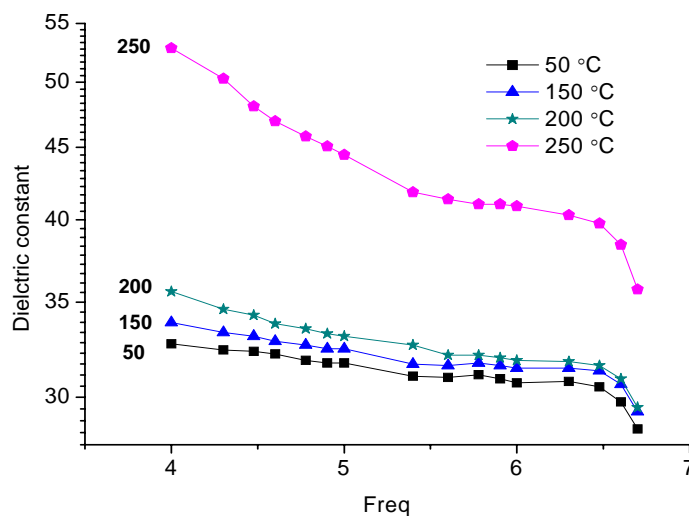
Fig. 6. The dielectric constant of 1Ce9Sc sample as a function of frequency.

Table 3. The crystal structure, density, relative density, molar volume and the dielectric constant for 10Ce and 1Ce9Sc samples at 10MHz. M denotes the monoclinic phase, T denotes the tetragonal phase, and C denotes the cubic phase.

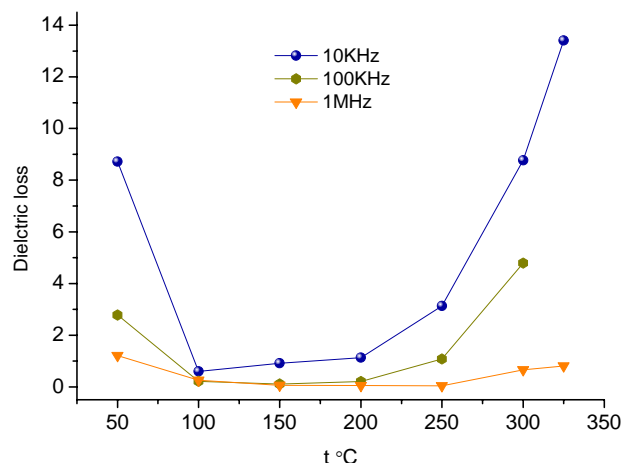| Sample	Crystal structure	Density (g/ cm^3)	Relative density	Molar volume (cm^3)	Dielectric constant at 10MHz at 150 °C
10Ce	M+T	5.44	---	21.30	11.69
1Ce9Sc	C	5.27	91	19.92	31.45

Fig. 7. The dielectric loss of 10Ce sample as a function of temperature.

constant for the prepared samples. 1Ce9Sc sample has higher dielectric constant than that of 10Ce sample at 10MHz at 150ºC. The values of the dielectric constants for the prepared samples are close to that from the literature (Balog *et al*., 1777; Houssa *et al*., 2000; Cho *et al*., 2002) which vary from 18 to 35 for ZrO$_2$. The dielectric constant value of 10Ce sample at 10MHz is close to that obtained by Mogensen *et al*. (2000) in the frequency range from 0.5 to 50MHz.

Table 3 shows the crystal structure, density, relative density, molar volume and the dielectric constant for 10Ce and 1Ce9Sc samples at 10MHz. M denotes the monoclinic phase, T denotes the tetragonal phase, and C
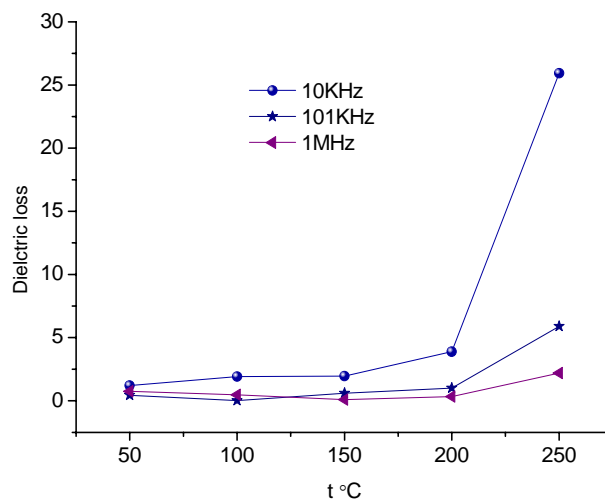
Fig. 8. The dielectric loss of 1Ce9Sc sample as a function of temperature.

denotes the cubic phase.

For ZrO_2-CeO_2 system, there were no indications of a maximum of dielectric loss in the range of the frequency of investigation. This result is in agreement to that obtained by Tcheliebou *et al.*, 1996 for ZrO_2-CeO_2 in the CeO_2 content range (8-36 mole %). Figure 7 shows that for 10Ce sample, at low temperature range below 100ºC, the dielectric loss decreases and above this temperature it slightly increases up to 250ºC then rapidly increases. The increase of dielectric loss denoted more dipole freedom as can be seen by higher values of dielectric loss as the increases of frequency and temperature.

Figure 8 shows that for 1Ce9Sc sample, at low temperature range below 100ºC, the dielectric loss decreases and above this temperature it slightly increases up to 200ºC then rapidly increases. This is also in a harmony with the results obtained from the conductivity figure of this sample (Fig. 3). For 1Ce9Sc sample, there were no indications of a maximum of dielectric loss in the range of the frequency of investigation. From figures 7-8, it is clear that the dielectric loss of 1Ce9Sc sample is higher than that of 10Ce sample in the investigated range of temperature and frequency.

CONCLUSION

We have investigated the electrical and dielectric properties of scandia stabilized zirconia sample, containing 1mole % CeO_2 (1Ce9Sc) and ZrO_2-CeO_2 systems. For ZrO_2-CeO_2 system, there is a change in the slope of the Arrhenius plot at 250°C. Moreover, increasing the CeO_2 content leads to decrease of the conductivity. The dielectric constant and dielectric loss is dependent on the crystal structure. 1Ce9Sc sample has

higher conductivity, dielectric constant and dielectric loss above 100°C than that of 10Ce sample. For 1Ce9Sc sample, there is a change in the slope of the Arrhenius plot and large changes in the dielectric constant and dielectric loss above 200°C. For all the investigated samples, there were no indications of a maximum of dielectric loss in the range of the frequency of investigation.

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