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Ionic conductivity studies on Mg stabilized zirconia by impedance spectroscopy

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Abstract

The high ionic conductivity of stabilized zirconia by substitutional doping of lower valent metal oxides (MgO, CaO, Y_2O_3, Sc_2O_3 etc.) found applications in fuel cells, gas sensors etc. The Mg stabilized zirconia has been synthesized by co-precipitation method. The formation of the compound has been confirmed by X-ray diffractogram (XRD) analysis. The electrical characterization is carried out using the impedance spectroscopy method in the frequency range of 50–5 MHz. The conductivity isotherm of the conductance spectra is falling onto one master curve, which suggests a temperature independent relaxation mechanism. The impedance analysis shows depressed semicircles, due to the bulk and grain boundary effects. The bulk and grain boundary resistance of the material has been extracted from the impedance analysis and it is found to be $7.3 \times 10^4\,\Omega\,\mathrm{cm}^{-1}$ and $2 \times 10^5\,\Omega\,\mathrm{cm}^{-1}$, respectively, at 773 K. The modulus peak maximum shifts to higher frequency with increase in temperature and broad nature of the peaks indicate the non-Debye nature of the material.

Keywords: Stabilized zirconia; Conductance master plot; Impedance analysis; Modulus analysis

1. Introduction

High temperature tetragonal and cubic polymorphs of ZrO_2 can be stabilized at room temperature by adding the stabilizing agents like MgO, CaO, and Y_2O_3 with appropriate proportions [1]. Mg-partially stabilized zirconias are favored for technological applications because of their better mechanical properties [2]. Relatively few investigations have dealt with their electrical properties above 1000 °C [3,4]. It was reported that below 1000 °C stabilized zirconia exists as a mixture of different crystallographic phases: cubic (c), tetragonal (t), monoclinic (m), and orthorhombic (o) [5]. But only the cubic phase of zirconia is found to have high ionic conductivity. In the present study, pure ZrO_2, 18 and 22 mol% of Mg stabilized zirconia have been synthesized by co-precipitation method. A cubic phase of stabilized zirconia along with traces of tetragonal phase has been formed for 22 mol%-ZrO_2. The electrical properties using impedance spectroscopy are studied at 500 °C with special significance given to conductance spectra. The literature survey reveals that for crystalline ionic conductors the discussions of conductance master plot which gives the details about the relaxation mechanism are very rare [6]. Hence in the present study an attempt has been made to analyze the relaxation mechanism in stabilized ZrO_2 materials from scaling properties of conductance spectra.

2. Experimental

The samples pure ZrO_2, 18 and 22 mol% Mg 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 precipitation solution was washed thoroughly with water and dried in an oven at 120 °C for 5 h. The resultant agglomerates were ground into fine powder using the mortar

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and pestle. The fine powder has been calcined at 650 °C. For the preparation of the 18 and 22 mol% of Mg stabilized zirconia the appropriate amount of precursors $ZrOCl_2{\cdot}8H_2O$ and $MgCl_2$ has been added to the distilled water and the same procedure mentioned above is followed. The 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 with desired phase, 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 and 500 °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 of all the samples are shown in Fig. 1. Pure ZrO_2 is dominated by monoclinic crystal structure. The 18 mol% Mg stabilized ZrO_2 shows the presence of cubic and tetragonal phases along with the monoclinic phase of ZrO_2. The presence of monoclinic phase may be due to the presence of unreacted ZrO_2 in this sample. However 22 mol% Mg stabilized ZrO_2 has only cubic and tetragonal phases. The formation of multiple phases may be due to the slow diffusion of magnesium atoms in to the host material [7]. The unit cell parameters and the particle size for all the three samples have been reported elsewhere [8]. The particle sizes for all the samples are in the order of nm which confirms the formation of nano crystalline phases in the present samples.

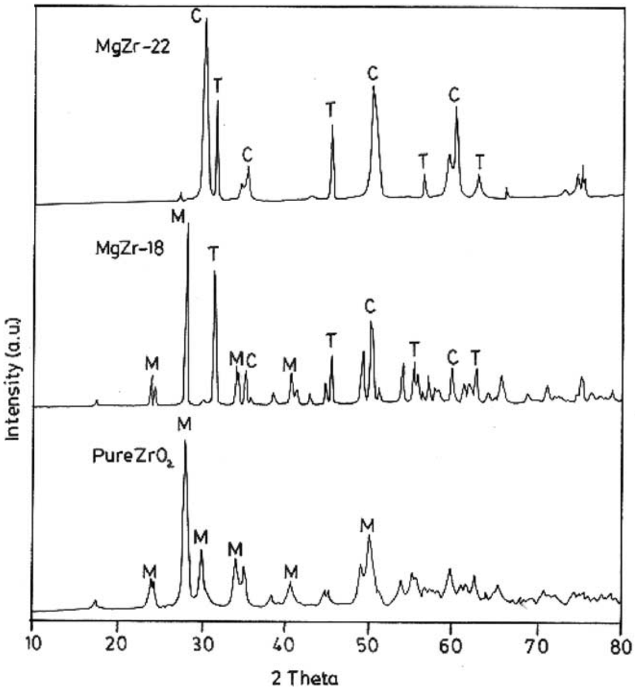

Fig. 1. XRD pattern for all the samples at room temperature (M: monoclinic; C: cubic; T: tetragonal).

3.2. Conductivity spectra analysis

The frequency and temperature dependant conductivity spectra obey the time temperature superposition principle. This means that for a given material, the conductivity isotherms can be collapsed to a master curve upon appropriate scaling of the conductivity and frequency axes. Recently, Roling et al. [9] reported that separation of strong and weak electrolytes concerns how the ionic relaxation mechanism depends on the total ionic concentration. This indirectly indicates the dependence of relaxation mechanism on temperature [10]. It has also been reported that appropriate scaling mechanism of conductance spectra and modulus spectra results in a master curve suggesting a temperature independent relaxation mechanism. The importance of scaling both the axes for glassy ion conductors has been reported by Funke et al. [11]. It has been reported that the scaling relationships are not restricted to ion conducting glasses, but has also found in the case of amorphous semiconductors and crystalline ionic conductors [9]. However, in the present study, the time temperature superposition principle using the conductivity master plot alone is discussed. Fig. 2 shows the normal conductivity spectra for 22 mol% Mg stabilized zirconia.

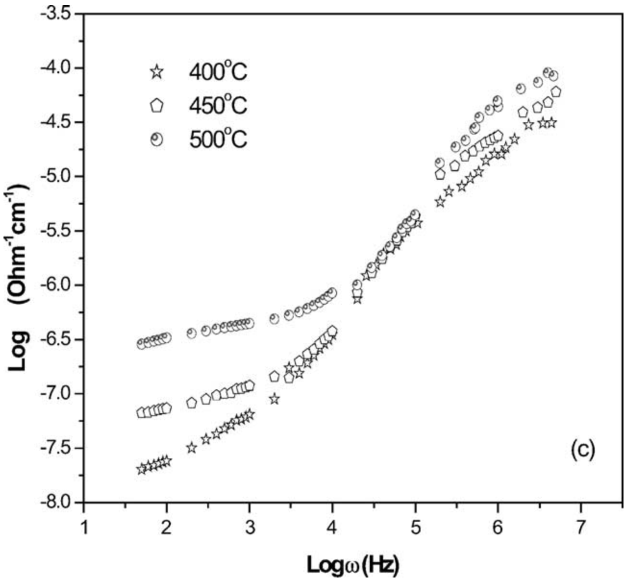

Fig. 2. Conductivity spectra at various temperatures for 22 mol% Mg–ZrO_2.

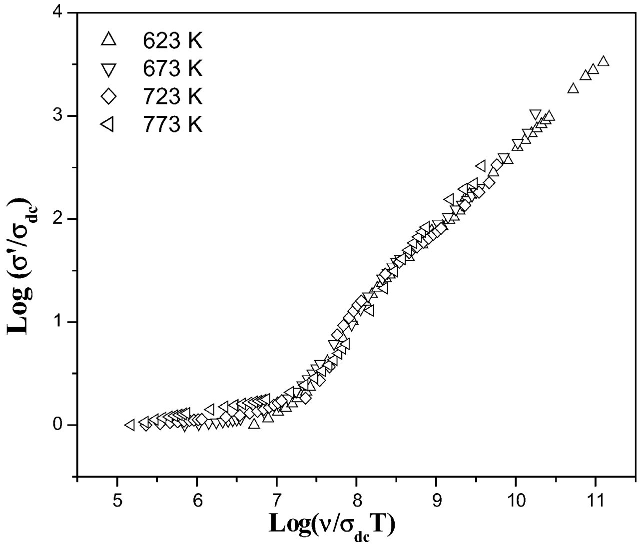

Fig. 3. Conductivity master curves at various temperatures for 22 mol% Mg–ZrO_2.

The frequency dependence of the real part of the conductivity (σ'), shows a low frequency plateau, which corresponds to the dc conductivity of the bulk material, and a dispersive region at high frequency, which corresponds to the ac conductivity. This response is similar for all the three samples. The cross-over frequency from dc to ac conductivity is defined as

$$\sigma'(\nu) = 2\sigma_{\mathrm{dc}} \tag{1}$$

With increasing temperature the cross-over regime from the dc to dispersive conductivity shifts to higher frequencies while the dc conductivity increases by the same amount. In order to analyze the relaxation mechanism of the present samples master plot has been drawn for all the samples. The cross-over frequencies are connected, a straight line with a slope of one has been obtained, and the scaling has been done by shifting the conductivity isotherms along the straight line of slope of one i.e. by scaling both the axis with the factor $\sigma_{\mathrm{dc}}T$. The resulting scaling plot is shown in Fig. 3. The master plot for pure ZrO_2 shows that the individual curves are shifted to higher values of $\nu/\sigma_{\mathrm{dc}}T$ as temperature increases. This confirms that the relaxation mechanism is temperature dependant and it obeys weak electrolyte theory. For 18 and 22 mol% Mg stabilized zirconia it has been observed that all the isotherms falling onto one master curve. This confirms that the time temperature superposition principle is fulfilled suggesting a temperature independent relaxation mechanism and also it indicates that both the samples 18 and 22 mol% Mg stabilized zirconia obeys the strong electrolyte theory.

3.3. Impedance analysis

Fig. 4 shows the complex impedance diagram for all the samples at 500 °C. The impedance data shows depressed semicircles, due to the bulk and grain boundary effects. The circular fitting of the complex impedance plot has been done by using the programme EQ developed by Boukamp [12,13] yields the value of n and it is used to find the depression angle from the formula $(1-n)$ $(\pi/2)$. The off axis angles are of the order of 14 and 19°, respectively, for the high and low frequency semicircles. The depressed semicircle indicates the non-Debye nature of the material. The associated capacitance value for the two semicircles has been calculated using the formula $\omega RC = 1$. The capacitance value is found to be in the order of pF & nF and therefore they have been attributed to a conduction process through the bulk and the grain boundary of the material [14]. The large difference in time constants allows the grain interior resistance semicircle to be clearly separated from that of the grain boundary curve. The bulk and grain boundary resistance of the material 22 mol% Mg–ZrO_2 it is found to be $7.3\times10^4\ \Omega\,\mathrm{cm}^{-1}$ and $2\times10^5\ \Omega\,\mathrm{cm}^{-1}$, respectively, at 773 K. The bulk resistance is found to decrease with increase in Mg doping.

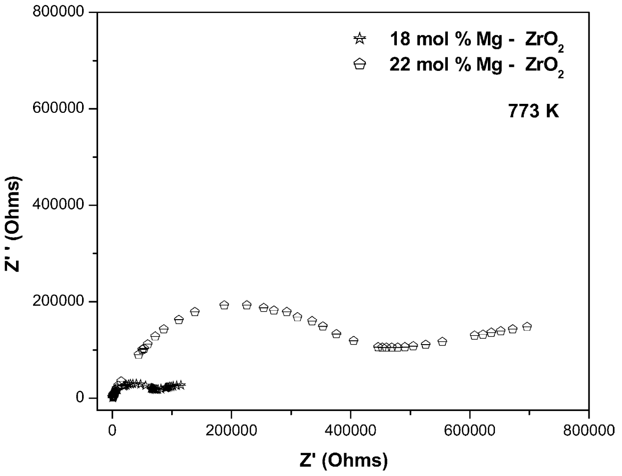

Fig. 4. Cole–cole plot at 500 °C for 18 and 22 mol% Mg–ZrO_2.

3.4. Modulus analysis

The ion transport process in ionic conductors has been studied in terms of electrical modulus spectra as well as conductivity spectra. The modulus formalism in which an electric modulus M^* is defined in terms of the reciprocal of the complex relative permittivity ε^*

$$M^* = \frac{1}{\varepsilon^*} = M' + j\,M'' \tag{2}$$

Well defined asymmetric peaks are observed for all the samples and the peak position shifts towards higher frequency with increasing in temperature. The broad nature of the peaks indicates the non-Debye nature of the material. Fig. 5. shows the modulus master plot. The non-exponential conductivity relaxation can be described by a Kohlrausch Williams Watt (KWW) function $\phi(t)$, which represents the distribution of

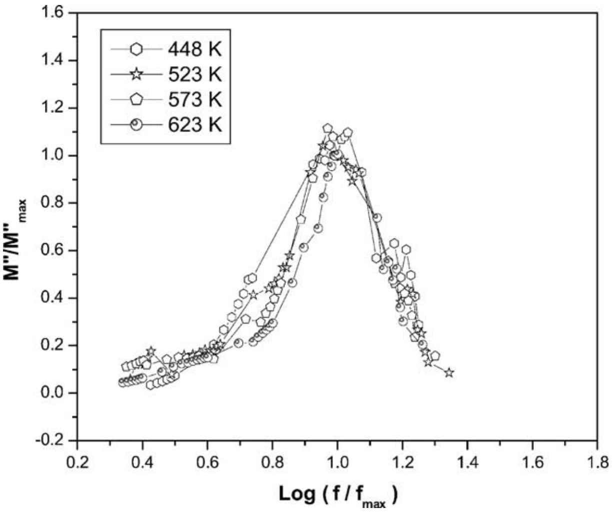

Fig. 5. Plots of $M''/M''_{\max}$ vs. log $(f/f_{\max})$ for 22 mol% Mg–ZrO$_2$.

relaxation time in ion conducting materials [15].The electric modulus can be represented as

$$M^* = M_\infty \left[1 - \int_0^\infty \mathrm{d}t \exp(-\varpi t)\frac{\mathrm{d}\phi}{\mathrm{d}t}\right] \qquad (3)$$

and,

$$\phi = \phi_0 \exp\left[-\left(\frac{t}{\tau_0}\right)^\beta\right] \qquad (4)$$

where, τ_0 is conductivity relaxation time and β is Kohlrausch exponent. The smaller the value of β, the greater the deviation with respect to Debye-type relaxation. The β parameter corresponding to the studied samples was established for each composition as a function of temperature using modulus formalism. Using the modulus formalism, i.e. M'' spectrum, the corresponding full-width-half-height (FWHH) is wider than the breadth of the Debye peak (1.14 decades) and thus results in a value of $\beta = 1.14/\mathrm{FWHH}$. The modulus peaks are fitted by using the software PEAKFIT and the full-width-half-height values are extracted and the corresponding β values have been calculated. The β parameter does not depend on the temperature in the range studied. The value of β decreases with increase in Mg doping. The β parameter for all the samples shows the same trend. This indicates the increase of charge carrier concentration and more non-Debye nature to the host material. The resulting high ionic conductivity for 22 mol% Mg stabilized zirconia may be due to the high charge carrier concentration and the behavior of the sample as strong electrolyte. Since in strong electrolytes where most if not all the anions or cations are mobile. This fact is also confirmed from the conductance spectra as already discussed.

4. Conclusion

The Mg stabilized zirconia has been prepared by co-precipitation method. The formation of the mixed cubic and tetragonal face has been confirmed from X-ray diffractogram studies. The relaxation mechanism in stabilized ZrO$_2$ materials from scaling properties of conductance spectra indicates that 22 mol% Mg–ZrO$_2$ obeys the time temperature superposition principle. The impedance analysis gives the details about the bulk and grain boundary resistance. The modulus spectrum indicates the increase of non-Debye nature with increase in Mg doping.

References

[1] R. Muccillo, R.C.B. Netto, E.N.S. Muccillo, Synthesis and characterization of calcia fully stabilized zirconia solid electrolytes, Mater. Lett. 49 (2001) 197–201.

[2] R.H.J. Hannnik, R.C. Garvie, Sub-eutectoid aged Mg-PSZ alloy with enhanced thermal up-shock resistance, J. Mater. Sci. 17 (1982) 2637–2643.

[3] T.L. Wen, N.X. Li, C. Kuo, W. Weppner, Conductivity of MgO-doped ZrO$_2$, Solid State Ionics 18/19 (1986) 715–719.

[4] F.W. Poulsen, J.B.B. Sorensen, K.G. Ahari, G.G. Knab, M. Hartmanova, Oxygen ion conduction in ternary zirconia mixtures: effect of SrO on MgSZ, Solid State Ionics 40/41 (1990) 947–951.

[5] E.N.S. Mucillo, M. Kleitz, Ionic conductivity of fully stabilized ZrO$_2$: MgO and blocking effects, J. Eur. Ceram. Soc. 16 (1996) 453–465.

[6] B. Roling, What do electrical conductivity and electrical modulus spectra tell us about the mechanism of ion transport process in melts, glasses and crystals? J. Non-Cryst. Solids 244 (1999) 34–43.

[7] P. Bohac, A. Orliukas, K. Sasaki, L.J. Gauckler, The effect of the second phase precipitation on the ionic conductivity of Zr$_{0.82}$Mg$_{0.15}$O$_{1.85}$, in: B.V.R. Chowdri, et al. (Eds.), Proceedings of the Fourth Asian Conference on Solid State Ionics, World Scientific Company, Singapore, 1994, pp. 55–160.

[8] M. Vijayakumar, S. Selvasekarapandian, M.S. Bhuvaneswari, G.H. Kumar, G. Ramprasad, R. Subramanian, P.C. Angelo, Synthesis and ion dynamics studies on nano crystalline Mg stabilized zirconia, Physica B 334 (2003) 390–397.

[9] B. Roling, A. Happe, K. Funke, M.D. Ingram, Carrier concentrations and relaxation spectroscopy: new information from scaling properties of conductivity spectra in ionically conducting glasses, Phys. Rev. Lett. 78 (1997) 2160–2163.

[10] D.P. Almond, G.K. Duncan, A.R. West, The determination of hopping rates and carrier concentrations in ionic conductors by a new analysis of ac conductivity, Solid State Ionics 8 (1983) 159–164.

[11] K. Funke, B. Roling, M. Lange, Dynamics of mobile ions in crystals, Solid State Ionics 105 (1998) 195–208.

[12] B.A. Boukamp, A nonlinear least squares fit procedure for analysis of immittance data of electrochemical systems, Solid State Ionics 20 (1986) 31–44.

[13] B.A. Boukamp, A package for impedance/admittance data analysis, Solid State Ionics 18 and 19 (1986) 136–140.

[14] X. Guo, Z. Zhang, Grain size dependent grain boundary defect structure: case of doped zirconia, Acta Mater. 51 (2003) 2539–2547.

[15] S. Selvasekarapandian, M. Vijayakumar, AC impedance spectroscopy studies on LiDyO$_2$, Mater. Chem. Phys. 9720 (2002) 1–5.