CHAPTER 7

STUDY OF ELECTRICAL CONDUCTIVITY

CHANGES AND PHASE TRANSITIONS IN

CaO DOPED ZrO₂.
CHAPTER 7

7.1. Introduction

A variety of devices use partially stabilized, doped zirconia as electrolyte due to its high oxygen ionic conductivity. CaO is one of the most common dopant present in high concentration in commercial ZrO$_2$ - based electrolytes. For the successful use of some devices, especially of coulombic titration cells, it is very important to appropriately take into account variations in the oxygen content of the electrolyte as a function of temperature and oxygen activity [1].

Dissolution of CaO in the fluorite phase of ZrO$_2$ leads to Ca$^{2+}$ ions occupying Zr$^{4+}$ sites, and an effectively positively charged oxygen vacancy is created for each Ca$^{2+}$ ion present to maintain electroneutrality. The defect equation can be written in the Kröger-Vink notation as:

$$\text{CaO} \leftrightarrow \text{Ca}^{\text{zr}} + \text{O}_0^\text{r} + \text{V}_{\text{o}}^-$$

(7.1)

The best characterized and perhaps the best understood of all the fast oxygen ion conductors, are those based on the doped fluorite oxides; however these materials are not fast – oxygen ion conductors until they are doped with aliovalent cations. The introduction of aliovalent cations into the host lattice, introduces oxygen vacancies [2]. At ambient
pressure, pure ZrO$_2$ exists in three basic polymorphs: cubic ($Fm3m$, fluorite), tetragonal ($P4_2/nmc$, distorted fluorite) high temperature phases and a monoclinic ($P2_1/c$) phase stable at room temperature [3 - 5]. Zirconia is often combined with cationic dopants ($Y_2O_3$, $Cr_2O_3$, MgO, CaO or $La_2O_3$), which contribute to stabilization of the tetragonal phase at low temperatures [6].

This chapter presents the study of variation of electrical conductivity as a function of temperature in ZrO$_2$ doped with different mol% of CaO. The phase relationships of sample series of doped and undoped materials were also examined by DSC and X-ray powder diffraction.

7.2. Experimental

7.2.1. Sample preparation

ZrO$_2$ (Aldrich, 99.99 % pure) was doped with 2, 4, 6, 8, 10, 15 and 20-mol% of CaO (Aldrich, 99.99% pure). The materials in the above ratios were mixed and grinded in an agate mortar and then pressed at a pressure level of 0.49GPa with the help of a hydraulic press (Spectralab Model SL-89) to prepare the samples in the form of pellets having diameter of 2.4cm and thickness 0.1cm. The pellets were then annealed in a muffle furnace at
1000°C for 28 hours.

7.2.2. Conductivity measurements

The a.c. conductivity measurements of the pellets prepared were performed by means of the two-probe method. The conductivity measured in the temperature range 40-900°C using a GENRAD 1659RLC Digibridge at different frequencies (10 kHz, 1 kHz, 120 Hz, 100 Hz). The rate of heating was maintained at 1°C/min.

7.2.3. Differential scanning calorimetry

DSC was recorded using SETARM Labsys TM performed in air and the heating rate was 20°C per minute. For each experiment, 10 ~ 15 mg of sample was used.

7.2.4. X-ray powder diffraction

X-ray studies were recorded using RINT 1200 Rigaku X-ray diffractometer; using Ni- filtered CuKα radiation (λ = 1.54060 Å) with 30 kV, 40 mA current.

7.3. Results and discussion

7.3.1. Conductivity studies

Temperature dependence of the ionic conductivity is expressed by the Arrhenius equation:

\[ \sigma = ne^2 \lambda^2 vy/kT \exp (-\Delta G^*/kT) \]  

(7.2)
\[ = n e^2 \lambda^2 vy/kT \exp (\Delta S^*/k - \Delta H^*/kT) \quad (7.3) \]

where \( n \) is the number of ions per unit volume, \( e \) the ionic charge, \( \lambda \) the
distance between two jump positions, \( v \) the jump frequency, \( y \) the
intersite geometry constant and \( \Delta G^* \), \( \Delta S^* \) and \( \Delta H^* \) are activation free
energy, entropy and enthalpy terms respectively. The equation can be
written in a simpler form as
\[ \sigma T = \sigma_0 \exp (-E_a/kT), \quad (7.4) \]
\( \sigma_0 \) being equal to \( ne^2 \lambda^2 vy/k \exp (\Delta S^*/k) \) and \( \Delta H^* = E_a \), the activation
enthalpy equals experimental activation energy for ionic motion [7].

Figure 7.1 shows the conductivity isotherm of the CaO - ZrO\(_2\) system
at room temperature, as a function of the CaO content. The conductivity
increases with rise in CaO content and reaches a maximum for 10 mol% of CaO. Small decreases in conductivity were observed when the
concentration of CaO was raised to 15-mol% and 20-mol% of CaO.

Doping of ZrO\(_2\) is achieved by substitution of the host cation by lesser
valent Ca\(^{2+}\) and this leads to creation of the anionic vacancies. Creation
of vacancies give rise to hopping of oxygen ions into neighboring vacant
sites and thus result in higher conductivity.
Figure 7.1. Compositional variation of room temperature conductivity of CaO - ZrO$_2$ system.
In the CaO–ZrO$_2$ system the conductivity maximum is reached with 10-mol% of the dopant though the interactions within the defect associates are strong. This is due to the fact that with divalent dopent cations, the dipoles [M$^{n-}$–V$^{n-}$] are neutral, and the tripoles [M$^{n-}$–V$^{n-}$–M$^{n-}$] are twice positively charged [8, 9]. Thus the dipoles already hinder the conductivity, and many tripoles are necessary for an additional decrease in conductivity, i.e. the concentration of dopant is relatively high at the maximum of conductivity [10].

The variations in conductivity with temperature at 10 kHz for ZrO$_2$, CaO and various doped samples, are shown in Figure 7.2. Similar electrical conductivity behavior is exhibited by all the compositions. The conductivity of the doped samples increases sharply with rise in temperature attains a maximum at 160°C and then decreases. The initial increase in conductivity with temperature arises due to increase in the rate of migration of oxygen ions and vacancies [11].

The drop in conductivity beyond 160°C is due to collapse of the fluorite framework, since on cooling, the higher conductivity is regained and no hysteresis is observed (Figure 7.3). This supported the argument
Figure 7.2. The temperature dependence of electrical conductivity of CaO-ZrO$_2$ system.
of lattice collapse, and its subsequent recovery on cooling, employing restructuring of the sublattice. Such type of decrease in the conductivity has been reported for K$^+$ doped Ag$_2$HgI$_4$ [12], Na$_2$SO$_4$ [13] and K$_2$SO$_4$ [14] as well.

Pure ZrO$_2$ is found to show a second rise in conductivity from about 460° C, due to gradual transition of monoclinic phase to tetragonal phase (ZrO$_2$ is reported to undergo a phase transition from monoclinic to tetragonal which starts at about 460° C [15]). All the CaO doped ZrO$_2$ samples studied by us also show a second rise in conductivity but at slightly lower temperatures. We therefore conclude that the second rise in conductivity in the doped samples is also due to the phase transition of ZrO$_2$.

Conductivity variation with temperature for all the samples has been studied at 1 kHz, 120 Hz and 100 Hz as well, and it was found that the change in frequency does not induce any change in the electrical conductivity behavior.

The activation energies Ea$_1$ and Ea$_2$ for the temperature ranges 500° C–640° C and 660° C–880° C have been calculated and shown in Table 1. A commonly accepted method to study the non-linear Arrhenius behavior is to fit the experimental data by two straight lines, one each in
Figure 7.3. The temperature dependence of electrical conductivity of CaO-ZrO$_2$ system in heating and cooling mode with 20 mol% CaO.
the lower and the higher temperature ranges. The low temperature phase has lower activation energy than the high temperature phase. Since $E_a = \Delta H^*_{\text{migration}} + \frac{1}{2} \Delta H^*_{\text{defect formation}}$, the value of $E_a$ in the high temperature phase is higher because of defect formation enthalpy contribution [16].

Table 1
Activation energies for various molar ratios at different temperature ranges

<table>
<thead>
<tr>
<th>mol% of CaO</th>
<th>$E_{a1}$ (500°C - 640°C)</th>
<th>$E_{a2}$ (660°C - 880°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0$</td>
<td>0.57</td>
<td>0.93</td>
</tr>
<tr>
<td>$x = 0.06$</td>
<td>0.64</td>
<td>0.91</td>
</tr>
<tr>
<td>$x = 0.08$</td>
<td>0.64</td>
<td>0.92</td>
</tr>
<tr>
<td>$x = 0.10$</td>
<td>0.66</td>
<td>0.94</td>
</tr>
<tr>
<td>$x = 0.15$</td>
<td>0.69</td>
<td>0.94</td>
</tr>
<tr>
<td>$x = 0.20$</td>
<td>1.03</td>
<td>1.06</td>
</tr>
</tbody>
</table>

7.3.2. Differential scanning calorimetry

The results of DSC are shown in Figure 7.4. For pure ZrO$_2$, the DSC curve shows a sharp exothermic peak at 460°C due to phase transition of ZrO$_2$ from monoclinic to tetragonal [17]. As is evident from the figure, on doping ZrO$_2$ with CaO the exothermic peak shifts to lower temperatures i.e. around 440°C. These results are in good agreement with those of conductivity results described above.
Figure 7.4. DSC curves for CaO-ZrO$_2$ system.
7.3.3. X-ray powder diffraction

The room temperature X-ray powder diffraction pattern of the calica – zirconia system after annealing at 1000°C shown in Figure 7.5 indicates that at least two zirconia phases, monoclinic and tetragonal, are present. The X-ray pattern of pure ZrO₂ shows the presence of monoclinic phase as the major phase, since at room temperature it is the most stable phase and tetragonal as the minor phase since it is known to be unstable at room temperature. This figure suggests that tetragonal zirconia is the major phase and monoclinic zirconia the minor phase, in the doped samples in accordance with the fact that on doping ZrO₂ with lower valent cations, higher temperature phases are said to be retained at room temperature [18].

7.4. Conclusion

The electrical conductivity of ZrO₂ increases remarkably on doping with CaO in the temperature range 60°C -240°C. The electrical conductivity is found to be maximum for 10-mol% of CaO at room temperature but at higher temperatures it is found to increases with increases in CaO concentration.
Figure 7.5. X-ray powder diffraction of CaO-ZrO₂ system after annealing.
References


