CHAPTER 5

STUDY OF ELECTRICAL CONDUCTIVITY
CHANGES AND PHASE TRANSITIONS IN
PHO DOPED ZrO$_2$. 
5.1. Introduction

Zirconia, ZrO₂, has attracted much interest since it has proven useful as refractory material, structural ceramics, high temperature solid electrodes and optical materials. Pure ZrO₂ crystallizes in the so-called baddeleyite structure monoclinic (P2₁/c) under ambient conditions. At high temperatures, it transforms to a tetragonal (P4₂/nmc), and then to a cubic fluorite structure (Fm₃m). The tetragonal and cubic phases of ZrO₂ are stabilized by doping with other oxides like CaO, MgO and Y₂O₃[1-5].

Anionic conductivity of ZrO₂ arises from migration of vacancies. Although pure ZrO₂ does not show high oxide-ion conductivity, divalent or trivalent oxide - doping enhances the conductivity, because of the increase of the oxide-ion vacancy concentration in the fluorite structure [6, 7].

Dissolution of PbO in the fluorite phase of ZrO₂ leads to Pb²⁺ ions occupying Zr⁴⁺ sites, and an effectively positively charged oxygen vacancy is created for each Pb²⁺ ion present to preserve electroneutrality. The defect equation can be written in the Kröger-Vink notation as:

\[
PbO \leftrightarrow Pb''_{Zr} + O'_{O} + V'_{O}
\] (5.1)
Although the number of vacancies increases monotonically with dopant concentration, ionic conductivity in the doped zirconia always exhibits a maximum for some critical dopant composition, with significantly decreased conductivity for lower and higher dopant levels. Several attempts have been made to explain this nonmonotonic behavior of conductivity in the doped zirconias in terms of ordering and clustering tendencies between vacancies, oxygen ions and dopant ions [8].

This chapter presents the study of variation of electrical conductivity of ZrO$_2$ doped with PbO as a function of temperature and composition for a sample series. The phase relationships of sample series of doped and undoped materials were also examined by DTA and X-ray powder diffraction.

5.2. Experimental

5.2.1. Sample preparation

ZrO$_2$ (Aldrich, purity 99.99 %) was doped with 1, 2, 3, 4, 5 and 6 mol % of PbO (Aldrich, 99.999% pure). Pellets of above molar compositions were prepared by applying a pressure of 0.49GPa with the help of a hydraulic press (Spectra Lab Model SL-89). The pellets of diameter 2.4cm and thickness 0.1cm were annealed in a muffle furnace at 950°C for 24 hours.
5.2.2. Conductivity measurements

The a.c. conductivity measurements were carried out by the two-probe method in the temperature range 40-800°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.

5.2.3. Differential thermal analysis

Thermal analysis was recorded on Perkin Elmer Pyris Diamond TG/DTA in air and the heating rate was 20°C per minute. For each experiment, 10 ~ 15 mg of sample was used.

5.2.4. X-ray powder diffraction

X-ray studies were recorded using Stoe Powder Diffraction System, using CuKα radiation (λ = 1.54060 Å). The X-ray powder diffraction studies were carried out for confirming new phases and crystal structures.

5.3. Results and Discussion

5.3.1. Conductivity studies

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

\[ \sigma = n e^2 \lambda^2 \nu_y / k T \exp(-\Delta G^*/kT) \]

\[ = n e^2 \lambda^2 \nu_y / k T \exp(\Delta S^*/k - \Delta H^*/kT) \]
where \( n \) is the number of ions per unit volume, \( e \) the ionic charge, \( \lambda \) the distance between two jump positions, \( \nu \) 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,

\[
\sigma \Gamma = \sigma_0 \exp \left( -\frac{E_a}{kT} \right)
\]

(5.4)

\( \sigma_0 \) being equal to \( ne^2\lambda^2\nu y/k \exp (\Delta S^*/k) \) and \( \Delta H^* = E_a \); the activation enthalpy equals the experimental activation energy for ionic motion [9].

Doping of ZrO\(_2\) is achieved by substitution of the host cation by lesser valent Pb\(^{2+}\) 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 [10]. Moreover, the conductivity may also rise due to ‘lattice loosening effect’. The introduction of larger Pb\(^{2+}\) ion (viz. \( r_{\text{Pb}}^{2+} = 1.20 \text{ Å} \) and \( r_{\text{Zr}}^{4+} = 0.79 \text{ Å} \)) generates additional free volume and weakens the lattice bonding forces, which permit greater facility to oxygen mobility [11 - 13]. This is why the PbO doped ZrO\(_2\) possesses a higher conductivity prior to phase transition than the pure ZrO\(_2\). Increasing the PbO concentration leads to the introduction of more anionic vacancies in the lattice, and hence, results in increase in the electrical conductivity. Figure 5.1 shows the
Figure 5.1. Compositional variation of room temperature conductivity of PbO-ZrO$_2$ system.
rise in isothermal conductivity as the level of substitution increases, at room temperature at 10 kHz.

The variations in conductivity with temperature at 10 kHz for ZrO₂, PbO and ZrO₂ doped with 1, 2, 3, 4, 5 and 6 mol % of PbO are shown in Figure 5.2. The figure exhibits similar electrical conductivity behavior for all the compositions. The conductivity of the doped samples increases sharply with temperature, attains a maximum at 163°C and then decreases. The initial increase in conductivity with temperature arises due to increase in rate of migration of vacancies [10].

The drop in conductivity above 163°C is due to collapse of the fluorite framework, since on cooling, the higher conductivity is regained and no hysteresis is observed (Figure 5.3). This supported the argument of lattice collapse, and its subsequent recovery on cooling, employing restructuring of the sublattice. Such type of decrease in the conductivity has been reported earlier [13–15]. The second rise in conductivity in pure ZrO₂ observed around 460°C is due to its phase transition from monoclinic to tetragonal which starts around 460°C and is completed around 1160°C [16,17]. The second rise in conductivity observed in the doped samples beyond 460°C is also due to phase transition of ZrO₂. It is observed that this phase transition takes place at higher and higher
Figure 5.2. The temperature dependence of electrical conductivity of PbO-ZrO$_2$ system.
Figure 5.3. The temperature dependence of electrical conductivity of PbO-ZrO$_2$ system in heating and cooling mode with 6mol %. 
temperatures as the percentage of PbO increases. Conductivity variations with temperature for all the samples has been studied at 10 kHz, 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 $E_{a1}$ and $E_{a2}$ for the temperature ranges 80°C – 140°C and 460°C – 720°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 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 range is higher because of defect formation enthalpy contribution [18].

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

<table>
<thead>
<tr>
<th>mol% of PbO</th>
<th>Activation Energy (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{a1}$</td>
</tr>
<tr>
<td>0</td>
<td>0.19</td>
</tr>
<tr>
<td>1</td>
<td>0.32</td>
</tr>
<tr>
<td>2</td>
<td>0.39</td>
</tr>
<tr>
<td>3</td>
<td>0.43</td>
</tr>
<tr>
<td>4</td>
<td>0.45</td>
</tr>
<tr>
<td>5</td>
<td>0.46</td>
</tr>
<tr>
<td>6</td>
<td>0.48</td>
</tr>
</tbody>
</table>
5.3.2. Differential thermal analysis

DTA was carried out for ZrO₂ and PbO doped ZrO₂ samples in Figure 5.4. Phase transition of pure ZrO₂ from monoclinic to tetragonal is confirmed by an exothermic peak at 460°C in agreement with earlier works [19, 20]. In the doped samples also, we get an exothermic peak due to phase transition of ZrO₂ from monoclinic to tetragonal but at higher temperatures. The exothermic peaks for 1, 3 and 5 mol% of PbO are obtained at 490, 514 and 548°C respectively. Thus this phase transition shifts to higher and higher temperatures as the PbO concentration increases.

5.3.3. X-ray powder diffraction

The X-ray data recorded at room temperature, of ZrO₂, PbO and PbO doped ZrO₂ after annealing at 950°C is depicted in Figure 5.5. The data could not be adequately modelled on the monoclinic structure of ZrO₂ and was found to contain a small amount of the tetragonal form also [21], as the high temperatures phases are said to be retained at lesser temperatures by doping with lesser valent cation [22].

5.4. Conclusion

Electrical conductivity of ZrO₂ is remarkably increased on doping with PbO in the temperature range 80°C-380°C. Electrical conductivity of PbO
Figure 5.4. DTA curves for PbO- ZrO$_2$ system.
Figure 5.5. X-ray diffraction patterns for PbO-ZrO$_2$ system after annealing.
doped ZrO$_2$ increases with increase in PbO concentration till 163°C due to creation of oxide ion vacancies and hopping of oxide ions into neighboring vacancies. With rise in temperature rate of hopping increases, which results in rise in conductivity. The phase transition in PbO doped ZrO$_2$ from monoclinic to tetragonal between 480°C-548°C, is confirmed by a sharp rise in conductivity as well as by an exothermic peak in DTA. No effect of change in frequency was observed on the electrical conductivity behavior. The Activation energy is also found to increase with increase in concentration of PbO.
References