CHAPTER 4

STUDY OF ELECTRICAL CONDUCTIVITY
CHANGES AND PHASE TRANSITIONS IN
$\text{Pb}_3\text{O}_4$ DOPED $\text{ZrO}_2$.

*The work present in this chapter has been accepted for publication in
CHAPTER 4

4.1. Introduction

In early twentieth century pure zirconia (ZrO$_2$) was of very limited interest as a structural or engineering ceramic, and its use was restricted to refractory applications. ZrO$_2$ has other intrinsic physical and chemical properties, including hardness, chemical inertness, ionic conductivity, electrical properties and high melting temperature, that make it attractive as an engineering material and the focus of continued effort to understand and improve its mechanical behavior [1-2].

At ambient pressure, pure ZrO$_2$ exists in three basic polymorphs: cubic (Fm$ar{3}$m fluorite), tetragonal (P$_4$2$_1$/nlc, distorted fluorite) high temperature phases and a monoclinic (P2$_1$/c) phase stable at room temperature. ZrO$_2$ doped with lower valent cations are technologically important, e.g., with respect to its high ionic conductivity [3-5].

Anionic conductivity of ZrO$_2$ arises from oxygen exchange jumps into neighboring empty sites. Although pure ZrO$_2$ does not show high oxide-ion conductivity, divalent or trivalent oxide - doping enhances the conductivity, because of the increase in the oxide-ion vacancy concentration in the fluorite structure [6, 7]. Several attempts have been made to explain this nonmonotonic behavior of the conductivity in doped
zirconia's in terms of ordering and clustering tendencies between vacancies, oxygen ions, and dopant ions [8].

Trilead tetroxide Pb₃O₄ is a bright orange red compound, which occurs naturally as the mineral, minium. Pb₃O₄ has been used in batteries and ceramics and is also widely used in corrosion resistant oil based paints [9]. Pb₃O₄ (called red lead) has the metal in II and IV oxidation states and behaves as a mixture of 2PbO + PbO₂ [10, 11].

This chapter presents the study of variation of electrical conductivity of ZrO₂ doped with Pb₃O₄ as a function of temperature and compositional variation for a sample series. The phase relationships and doping effect were also examined by DTA and X-ray powder diffraction.

4.2. Experimental

4.2.1. Sample preparation

ZrO₂ (Aldrich, 99.99 % pure) was doped with 1, 2, 3, 4, 5 and 6-mol% of Pb₃O₄ (Pb₃O₄ was prepared along with the prescription as given in ref. [12]). 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 hydraulic press (Spectralab Model SL-89) to prepare the pellets having diameter of 2.4cm and thickness 0.1cm. The pellets were then annealed in a muffle furnace at 850°C for 28 hours.
4.2.2. Conductivity measurements

The a.c. conductivity measurements were performed in the temperature range 40-800°C using a GENRAD 1659RLC Digibridge at different frequencies (10 kHz, 1 kHz, 120 Hz, 100 Hz) by means of the two-probe method. The rate of heating was maintained at 1°C/min.

4.2.3. Differential thermal analysis

Differential thermal analysis was recorded on Perkin Elmer Pyris Diamond TG/DTA in air, and the heating rate was 20°C/min.

4.2.4. 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.

4.3. Results and discussion

4.3.1. Conductivity studies

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

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

\[ = n e^2 \lambda^2 v y / k T \exp(\Delta S^*/k-\Delta H^*/kT), \]  

where \( n \) is the number of ions per unit volume, \( e \) the ionic charge, \( \lambda \) the distance between two jump positions, \( v \) the jump frequency, \( y \) the
intersite geometry constant and $\Delta G^*$, $\Delta S^*$ and $\Delta H^*$ are the activation free energy, entropy and enthalpy terms respectively. The equation can be written in a simpler form as

\[ \sigma T = \sigma_0 \exp(-Ea/kT) \] (4.3)

$\sigma_0$ being equal to $n e^2 \lambda^2 v y / k \exp (\Delta S^*/k)$ and $\Delta H^* = Ea$; the activation enthalpy equals experimental activation energy for ionic motion [13].

Doping of ZrO$_2$ is achieved by substitution of the host cation by lesser valent Pb$^{2+}$ and this leads to creation of anionic vacancies. Creation of vacancies give rise to migration of vacancies and thus result in higher conductivity [14]. Moreover, the conductivity also rises due to ‘lattice loosening effect’ [15-17]. The introduction of larger Pb$^{2+}$ ion ($r_{\text{Pb}}^{2+} = 1.20 \text{ Å}$ 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. This is why the Pb$_3$O$_4$-doped-ZrO$_2$ possesses a higher conductivity prior to phase transition than the pure ZrO$_2$. Increasing the Pb$_3$O$_4$ concentration leads to the introduction of more anionic vacancies in the lattice, and hence, results in increase in the electrical conductivity. Figure 4.1 shows the rise in isothermal conductivity measured at 10 kHz as the level of substitution increases at room temperature.
Figure 4.1. Compositional variation of room temperature conductivity of Pb$_3$O$_4$–ZrO$_2$ system.
The variations in conductivity with temperature at 10 kHz for ZrO$_2$, Pb$_3$O$_4$ and various doped samples (1, 2, 3, 4, 5 and 6-mol% of Pb$_3$O$_4$) are shown in Figure 4.2. From the figure it can be observed that all the compositions exhibit similar electrical conductivity behavior. The conductivity of the doped samples increases with rise in temperature, attains a maximum at 180°C and then decreases. The initial increase in conductivity with rise in temperature arises due to increase in rate of hopping of oxygen and migration of vacancies.

The drop in conductivity beyond 180°C is due to collapse of the fluorite framework, since on cooling, the higher conductivity is regained and no hysteresis is observed (Figure 4.3). 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 [17-19].

The electrical conductivity of ZrO$_2$ shows a second rise at 460°C due to its phase transition from monoclinic to tetragonal form, which starts around 460°C and is completed around 1160°C. All the doped samples studied by us, also show a second rise in conductivity due to phase transition of ZrO$_2$ but at temperatures above 460°C. This shift in transition
Figure 4.2. The temperature dependence of electrical conductivity of Pb$_3$O$_4$-ZrO$_2$ system.
Figure 4.3. The temperature dependence of electrical conductivity of Pb₃O₄-ZrO₂ system in heating and cooling mode with 5 % Pb₃O₄.
temperature increases with rise in Pb$_3$O$_4$ concentration. It is therefore concluded that in the doped samples phase transition of ZrO$_2$ is shifted to higher temperatures due to interaction between Pb$_3$O$_4$ and ZrO$_2$.

Conductivity variations with temperature for all the samples have 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 $E_{a1}$ and $E_{a2}$ for the temperature ranges 120°C – 180°C and 500°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 phase is higher because of defect formation enthalpy contribution [20].
Table 1
Activation energies for various molar ratios at different temperature ranges

<table>
<thead>
<tr>
<th>mol % of Pb$_3$O$_4$</th>
<th>$E_{a1}$ (120°C - 180°C)</th>
<th>$E_{a2}$ (500°C - 720°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.28</td>
<td>0.79</td>
</tr>
<tr>
<td>2</td>
<td>0.26</td>
<td>0.88</td>
</tr>
<tr>
<td>3</td>
<td>0.32</td>
<td>0.89</td>
</tr>
<tr>
<td>4</td>
<td>0.33</td>
<td>1.05</td>
</tr>
<tr>
<td>5</td>
<td>0.37</td>
<td>1.08</td>
</tr>
<tr>
<td>6</td>
<td>0.37</td>
<td>1.08</td>
</tr>
</tbody>
</table>

4.3.2. Differential Thermal Analysis

DTA curves are illustrated in Figure 4.4. DTA curve of pure ZrO$_2$ shows a sharp exothermic peak at 460°C since the phase transition of ZrO$_2$ from monoclinic to tetragonal form starts at 460°C and is completed at 1160°C [21, 22]. However, it is of interest to see the influence of Pb$_3$O$_4$ on the crystallization of ZrO$_2$ from monoclinic to tetragonal phase. Figure 4.4 shows that the exothermic peak due to the phase transition in pure ZrO$_2$ appears at 460°C, while for Pb$_3$O$_4$-doped-ZrO$_2$ samples it shifts to higher temperatures because of interaction between Pb$_3$O$_4$ and ZrO$_2$. The shift increases with increasing Pb$_3$O$_4$ content. Consequently, the exothermic peaks appear at 500, 588, 609, 610, 611 and 618°C for 1, 2, 3, 4, 5 and 6-mol% of Pb$_3$O$_4$ respectively.
Figure 4.4. DTA curves for Pb$_3$O$_4$-ZrO$_2$ system.
4.3.3. X-Ray Powder Diffraction

The Pb$_3$O$_4$-ZrO$_2$ system annealed at 850°C consists of a mixture of two phases: tetragonal and monoclinic, as it can be inferred from the presence of three diffraction peaks in the region 26°C to 32°C (Figure 4.5). These XRD lines are attributed to the tetragonal phase and the monoclinic phase [23]. The intensity of the peak for tetragonal ZrO$_2$ is low in pure ZrO$_2$, but on doping with Pb$_3$O$_4$, it increases significantly. This is due to the fact that the tetragonal phase is known to be retained at low temperatures on doping [24]. The new peaks, which appear in the doped samples, show the presence of Pb$_3$O$_4$ in samples. It may be therefore concluded that the phase composition is not only influenced by the temperature but also by the presence of dopants.

4.4. Conclusion

Electrical conductivity of Pb$_3$O$_4$ doped ZrO$_2$ rises initially with increase in Pb$_3$O$_4$ concentration due to creation and migration of oxide ion vacancies. The phase transition of ZrO$_2$ from monoclinic to tetragonal at ~ 460°C is confirmed by a 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 Pb$_3$O$_4$. 
Figure 4.5. X-ray diffraction patterns for Pb$_3$O$_4$-ZrO$_2$ system at room temperature after annealing.
References


