CHAPTER 3

STUDY OF ELECTRICAL CONDUCTIVITY CHANGES AND PHASE TRANSITIONS IN CuO DOPED ZrO$_2$.

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3.1. Introduction

Zirconia and ZrO$_2$ containing materials find a wide range of application in foundry refractories, ceramics, abrasives and paint pigments. Tough, wear resistant, zirconia has been developed for applications such as extrusion dies, piston caps, and machinery wear parts amongst others [1]. Due to their excellent mechanical properties [2, 3] and high sinterability, yttria doped tetragonal zirconia polycrystalline materials are often preferred in structural applications. At 2680°C it is cubic phase which crystallizes from the melt and transforms to a tetragonal phase at 2300°C which in turn transforms to the monoclinic form between 950 and 1150°C [4]. The insertion of Y$_2$O$_3$, CaO, MgO or Ce$_2$O$_3$ into the crystal structure is known to stabilize the high temperature phases of zirconia even at low temperatures [5, 6].

Presences of aliovalent ions (impurities and dopants) change the concentration of defects. Dissolution of CuO in the fluorite phase of ZrO$_2$ leads to Cu$^{2+}$ ions occupying Zr$^{4+}$ sites, and an, effectively positively charged oxygen vacancy is created for each Cu$^{2+}$ ion present in order to preserve electroneutrality. The defect equation can be written in the Kroger-Vink notation as:
CuO → Cu"Zr + O° + V°° (3.1)

This chapter presents the study of variation of electrical conductivity as a function of temperature in ZrO₂ doped with different mol % of CuO. The phase relationships of sample series of doped and undoped materials were also examined by DTA, X-ray powder diffraction and FT-IR spectral studies.

3.2. Experimental

3.2.1. Sample preparation

ZrO₂ (Aldrich, purity 99.99%) and CuO (Aldrich, purity 99.999%) were mixed in an agate mortar in various compositions (1, 2, 3, 4 and 5-mol% of CuO) in an agate mortar. Pellets of above compositions were prepared by applying a pressure of 0.49GPa with the help of a hydraulic press (Spectralab Model SL-89). The pellets of diameter 2.4cm and thickness 0.1cm were annealed in air at 1000°C for 25 hours.

3.2.2. Conductivity measurements

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

3.2.3. Differential thermal analysis

Differential thermal analysis was performed by 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.

3.2.4. X-ray powder diffraction

X-ray studies were recorded using Bragg – Bretano Siemens D 5000 diffractometer; using Ni- filtered CuKα radiation (λ = 1.54060 Å) with monochromatic beam.

3.2.5. Fourier- transform infrared spectroscopic studies

IR spectra were recorded in transmittance mode on Magna 550 series Nicolat USA spectrophotometer. Samples were diluted (1% by weight) in dry KBr and scanned over range 4000-600 cm⁻¹.

3.3. Results and discussion

3.3.1. Conductivity studies

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

\[ \sigma = n e^2 \lambda^2 vy/kT \exp (-\Delta G^*/kT) \]  \hspace{1cm} (3.2)

\[ = n e^2 \lambda^2 vy/kT \exp (\Delta S^*/k-\Delta H^*/kT) \]  \hspace{1cm} (3.3)
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 the activation free energy, entropy and enthalpy terms respectively. The equation can be written in a simpler form as,

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

(3.4)

\( \sigma_0 \) being equal to \( ne^2\lambda^2vy/k\exp(\Delta S^*/k) \) and \( \Delta H^* = E_a \); the activation enthalpy equals the experimental activation energy for ionic motion [7].

Doping of \( \text{ZrO}_2 \) is achieved by substitution of the host cation by lesser valent \( \text{Cu}^{2+} \) and this leads to creation of anionic vacancies. Creation of more and more vacancies give rise to increased vacancy migration and thus result in higher conductivity [8]. Figure 3.1 shows the rise in isothermal conductivity at room temperature as the level of substitution increases.

The size of \( \text{Cu}^{2+} \) and \( \text{Zr}^{4+} \) are 0.74 Å and 0.79Å respectively. It has been shown that the good oxygen ion conductors are highly desirable when the lattice is as undisturbed as possible, and this is possible when the sizes of host and dopant ions are very close [4].

The variations in conductivity with temperature at 10 kHz for \( \text{ZrO}_2 \), \( \text{CuO} \) and the various doped samples are shown in Figure 3.2. It may be
Figure 3.1. Compositional variation of room temperature conductivity of CuO-ZrO$_2$ system.
seen that the conductivity variations for the various compositions follow a uniform pattern. As is evident from the figure, all compositions show initial gradual increase in conductivity with rise in temperature till 220°C and thereafter show a decreasing trend. This increase in conductivity with rise in temperature is due to increase in rate of vacancy migration. The drop in conductivity beyond 220°C is due to collapse of the fluorite framework, since on cooling, the higher conductivity is regained and no hysteresis is observed (Figure 3.3). This supported the argument of lattice collapse and its subsequent recovery on cooling, employing restructuring of the sublattice. Such type of decrease in conductivity has been reported earlier [10 – 12].

Pure ZrO₂ is found to show a rise in conductivity from about 460°C, due to the gradual transition of monoclinic phase to tetragonal phase (ZrO₂ is reported to undergo a phase transition which starts at about 460°C from monoclinic to tetragonal [6, 13]). The doped samples also show a second rise in conductivity but at temperatures beyond 460°C. We therefore conclude, that, this second rise in conductivity in the doped samples is also due to the phase transition of ZrO₂.

Conductivity variation with temperature for all the samples has also been studied at 1 kHz, 120 Hz and 100 Hz as well, and it was
Figure 3.2. The temperature dependence of electrical conductivity of CuO-ZrO$_2$ system.
Figure 3.3. The temperature dependence of electrical conductivity of CuO-ZrO₂ system in heating and cooling mode with higher dopant content (5% CuO).
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 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 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 [9].

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

<table>
<thead>
<tr>
<th>mol% of CuO</th>
<th>Activation Energy (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{a1}$ (500°C - 640°C)</td>
</tr>
<tr>
<td>0</td>
<td>0.57</td>
</tr>
<tr>
<td>1</td>
<td>0.62</td>
</tr>
<tr>
<td>2</td>
<td>0.62</td>
</tr>
<tr>
<td>3</td>
<td>0.65</td>
</tr>
<tr>
<td>4</td>
<td>0.69</td>
</tr>
<tr>
<td>5</td>
<td>0.70</td>
</tr>
</tbody>
</table>

3.3.2. Differential thermal analysis

The results of DTA (Figure 3.4) support the above argument. For pure ZrO$_2$, it shows an exothermic peak at 460°C, which is a
confirmation of the phase transition in ZrO₂ from monoclinic phase to
tetragonal phase, reported earlier [14]. DTA curves of all the doped
samples show a slight shift in the exothermic peak towards higher
temperatures side, which suggests a shifting of the transition
temperature to higher side in the doped samples.

3.3.3. X-ray powder diffraction

The X-ray data recorded at room temperature, of CuO doped ZrO₂
after annealing at 800°C is shown in Figure 3.5. The data could not be
adequately modeled on the monoclinic (marked by m) structure of ZrO₂
[15], as the high temperature phases are said to be retained at lower
temperature by doping with lower valent cations [16].

3.3.4. Fourier-transform infrared spectroscopic studies

FT-IR spectra of ZrO₂, CuO and doped samples having 1, 3, and
5-mol% of CuO are given in Figure 3.6. The doped samples clearly
indicate the presence of ZrO₂ characterized by the absorption bands
759, 1156 and 3426cm⁻¹ which has been earlier reported [17]. These
bands coincide well with characteristic wave numbers of ZrO₂. The peak
at 3426cm⁻¹, characteristic of ZrO₂, is also found in the doped samples,
but with reduced intensity. However, in 3% and 5% CuO samples this
Figure 3.4. DTA curves for CuO - ZrO₂ system.
Figure 3.5. X-ray diffraction patterns for CuO–ZrO$_2$ at room temperature after annealing.
Figure 3.6. FT-IR spectra for CuO - ZrO₂ system.
peak is more significant as compared to that in 1% CuO, due to higher concentration of CuO (CuO is found to give a peak in this region). The 1634 cm\(^{-1}\) peak of CuO is present in 5% CuO but absent in 1% and 3% CuO samples, due to lower concentration of CuO. The ZrO\(_2\) peaks at 1156, 759 and 579 are also found in the doped samples but with decreased intensities.

3.4. Conclusion

On doping with CuO, the electrical conductivity of ZrO\(_2\) is found to be enhanced considerably between 40\(^\circ\)C and 300\(^\circ\)C, due to creation of oxygen ion vacancies and hopping of oxygen ions into neighboring vacancies. At room temperature the electrical conductivity rise with increase in CuO but at higher temperatures maximum conductivity is observed for 1% CuO. Phase transition of ZrO\(_2\) from monoclinic to tetragonal form which starts at 460\(^\circ\)C is confirmed by a sharp rise in conductivity and by an exothermic peak in DTA curves. But in the doped samples, ZrO\(_2\) is found to undergo this phase transition above 460\(^\circ\)C. No effect of change in frequency was observed on the electrical conductivity behavior. The activation energy is also found to increase with rise in concentration of CuO.
References