CHAPTER 3

OPTICAL AND HIGH PRESSURE STUDIES OF Sn-DOPED CeO$_2$ NANOPARTICLES

3.1 INTRODUCTION

Cerium dioxide (CeO$_2$) is an oxide of the rare-earth metal cerium (chemical symbol Ce), which belongs to the lanthanide group. Cerium, named after the planet Ceres, can relatively often be found in nature in minerals like cerite, monazite or bastnaesite (ranked 28th in elemental abundance). In combination with oxygen it is easily converted into CeO$_2$. Apart from CeO$_2$ cerium forms the oxides Ce$_2$O$_3$ and Ce$_3$O$_4$ Normally cerium dioxide is the result of the oxidation of cerium hydroxide and cerium carbonate. Technical grade CeO$_2$ is generally present as micro or nanoscale white to light yellow powder.

Over the last two decades cerium oxide (CeO$_2$) based materials have been extensively studied and employed in various applications including fast ion conductors, oxygen storage capacitors, catalysts, UV blockers and polishing materials. Nano-structured cerium dioxide, among other things, is used as an oxygen-storing diesel additive in vehicle exhaust catalysts. It still oxidizes carbon monoxide and excess hydrocarbons into CO$_2$ when there is a temporary lack of oxygen in the exhaust mixture. During that process, CeO$_2$ is reduced to Ce$_2$O$_3$ that is re-oxidized later as soon as there is enough oxygen again in the exhaust gases. Aside from its role in exhaust catalysts where it mainly supports the much more active but also more expensive platinum, there is also a direct addition to the fuel intended. “The basis of the electron
theory of metals, with special reference to the Transition Metals” (Mott 1949).

Figure 3.1 Crystal structure of CeO$_2$

An iron-grey, shiny and soft metal

Atomic Number: 58; Atomic Weight: 140.116; Melting point: 1071 K;

Boiling Point: 3743 K; Oxidation States: 4+ and 3+;

Electron Configuration: [Xe] 4f$^1$ 5d$^1$ 6s$^2$
N. F. Mott theorized that in some materials it was precisely the opposite. It was these interactions, or “correlations”, between the electrons themselves which dominated the electronic properties in the solid. This interaction is really nothing more than the well known coulomb interaction but has far-reaching implications for the transport properties of some materials. If strong enough, these correlations can turn a simple material like NiO into an insulator. These materials, for which strong electron correlations exist, became known as Mott insulators. One exciting prediction born out of Mott’s work was the existence of a transition between two regimes; one where electron correlation dictates the materials properties and another where the kinetic energy of the system can override the strong correlations. This become known as a Mott transition and was originally predicted for the transition metal oxides NiO, FeO, MnO and CoO, the prototypical insulators used to illustrate Mott’s ideas. He described an energy E required to remove an electron from one site to another, as in metallic conduction. He theorized that the application of pressure would reduce E by bringing the ions closer together. At a critical distance the materials would undergo a sharp transition to the metallic state. It has since been shown that some of the most technologically important materials derive their properties from electron correlations. Another phenomenon which involves changes in electron correlation occurs in the elemental rare-earth metal Ce.

At a pressure of 7 k bar, trivalent Cerium undergoes a dramatic 15% change in volume (Zachariasen and Ellinger 1977). This volume collapse occurs abruptly, i.e., first order. What is more interesting is that it occurs without a change in crystal structure. All materials become denser with pressure and, in general, transform to more closely packed structures. And, these transitions are very often accompanied by large volume changes. However, the $\gamma$-$\alpha$ transition in Ce was isostructural and must therefore occur due to changes at the atomic level. It was later discovered that many of the
other 4\textit{f} metals undergo similar volume collapse transitions (VCTs) at high pressure. Although Cerium’s is the only isostructural VCT, the physical mechanism underlying all these transitions is thought to be the same. It is generally believed that these VCT transitions are the result of changes in the degree of 4\textit{f} correlation at high pressures. The promotional model was the first, and most straightforward, scenario proposed to describe the isostructural volume-collapse phenomenon in Ce.

Most of the lanthanides are trivalent, with the exception of Eu and Yb which each steal one valence electron to make a half-filled and filled 4\textit{f} orbital, respectively. This leaves Ce with an electron configuration of 4\textit{f}, despite it being the second of the lanthanide series. In 1968, Coqblin et al. hypothesized that the volume-collapse was the result of a promotion of this single single 4\textit{f} electron into the valence orbitals (Coqblin and Blandin 1968). One commonality between the rare earth metals, post-collapse (with the exception of Ce), is their low symmetry crystal structures. These structures are in contrast to the high symmetry, cubic structures that occurs pre-collapse at low pressures. These low-symmetry structures are similar to those found in the 5\textit{f} metals (the actinides) and are characteristic of \textit{f}-electron bonding. This fact led physicist B. Johansson to believe that the \textit{\alpha}-\textit{\gamma} transition in Ce was the result of a “metallization” of the 4\textit{f} electrons by band broadening, i.e. a change in the \textit{f}-\textit{f} correlation resulting in a Mott transition within 4\textit{f} orbitals (Johanssen 1974). The delocalized \textit{f} electrons would then be able to participate in bonding, causing the very low symmetry structures seen post-collapse. In this chapter, Sn-doped with CeO\textsubscript{2} nanoparticles were prepared and the structural, optical and high pressure induced electrical resistivity studies were investigated.
3.2 EXPERIMENTAL DETAILS

This chapter describes the synthesis, optical and high pressure studies of Tin (Sn) doped CeO$_2$ nanoparticles. It possesses many unique chemical, electronic and optical properties. It is advantageous in several applications, such as solar cells, catalysis and gas-sensing applications (Vaishanv et al 2006). The samples were prepared through simple precipitation method. The associated structural, optical, and high pressure electrical resistivity studies of the nanoparticles as a function of dopant concentrations have been systematically studied. X-ray powder diffraction reveals that all samples have the FCC crystal system of CeO$_2$ and the lattice parameter analysis indicated the dopant ions may be substitute into the lattice position of the parent atom. In addition of the dopant atoms result the enhanced optical and high pressure electrical resistivity studies.

The cerium oxide ultrafine particles were prepared by a method which comprises the steps of mixing, stirring and calcination. An aqueous solution of Cerium nitrate hexa hydrate Ce(NO$_3$)$_3$.6H$_2$O prepared. Few drops of ammonia solution were added to the base and its pH is maintained at 10. The solution was stirred well until precipitation occurs. The precipitates were washed, dried and the resulting mixture is heated up to a temperature of 100°C for 24 h. The mixture was refined using pestle and motar and it is calcinated at 600°C for 5 h to promote the crystallization.

The Sn-doped CeO$_2$ nanoparticles were prepared in three compositions via of 4, 6 and 8mol% by dissolving Cerium nitrate hexahydrate Ce(NO$_3$)$_3$.6H$_2$O and SnCl$_2$2H$_2$O in de-ionised water and the resulting mixture is stirred by adding a few drops of ammonia till precipitation occurs. The above process was carried out at room temperature and the pH value was maintained at 10. The resultant precipitates were washed, dried and heated to a temperature of 100°C for 12 h. The obtained
powders were thoroughly refined using pestle and mortar. These powders were calcined as reported above.

3.3 RESULTS AND DISCUSSION

3.3.1 Structural Analysis

Figure 3.2 shows the XRD patterns of the pure and Sn-doped Cerium oxide nanoparticles with larger broadening of peaks, which in turn leads to a small particle size. All the peaks indexed to a pure cubic fluorite structure (JCPDS 34-394) of CeO$_2$ with lattice constant ‘a’ = 5.411 Å. The intensive diffraction peak is located at 2θ=28.66, 33.07, 47.48 and 56.34º, corresponding to (111), (200), (220) and (311) lattice planes respectively. They are well matched with the peaks of face centered cubic crystal structure (Santos et al 2008 and Gulicovski 2009). No impurity peaks are observed in the patterns indicating a complete reaction between cerium nitrate and ammonia to form cerium oxide. Due to the Sn$^{2+}$ doping the crystallinity of the CeO$_2$ was considerably decreases when compared to pure CeO$_2$. It can be seen from the well defined peak broadening in the XRD pattern of the doped samples as in Figure 1 (b-d). In addition to the above all the peaks are shifted towards lower angle indicates the decrease in volume of the crystal. The average crystallite size and lattice parameter of the pure and Sn doped CeO$_2$ nanoparticles are given in table 3.1. The mean diameters of the nanoparticles were calculated using Scherrer’s equation (Sujana et al 2008),

$$D = \frac{0.9\lambda}{(\beta \cos \theta)}$$

(3.1)

Where $\beta$ is the full width at half maximum value of maximum intensity peak,
$\theta$ - Diffraction angle and

$\lambda$ – Wavelength of the X-rays (1.5408 Å).

Figure 3.2 X-ray powder diffraction patterns of pure and Sn-doped CeO$_2$ nanoparticles.

The increase of lattice parameter in the nanoparticles with decreasing particle size is called a lattice relaxation (Leoni et al 2004). The lattice relaxation accompanied with decreasing particle size is of great
importance and would strongly affect the properties of CeO$_2$ nanoparticles (Perebeinos et al 2002).

Table 3.1 Summary of Pure and Sn-doped CeO$_2$ nanoparticles calcined at 600 ° C

<table>
<thead>
<tr>
<th>Composition / 600° C</th>
<th>Lattice Parameter ‘a’ (Å)</th>
<th>Unit Cell volume ‘a$^3$’ (Å$^3$)</th>
<th>Mean Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>5.365</td>
<td>154.42</td>
<td>25.56</td>
</tr>
<tr>
<td>4mol% Sn-CeO$_2$</td>
<td>5.349</td>
<td>153.04</td>
<td>25.48</td>
</tr>
<tr>
<td>6mol% Sn-CeO$_2$</td>
<td>5.346</td>
<td>152.78</td>
<td>21.20</td>
</tr>
<tr>
<td>8mol% Sn-CeO$_2$</td>
<td>5.269</td>
<td>148.32</td>
<td>17.14</td>
</tr>
</tbody>
</table>

Figure 3.3 show the FT-IR spectra of pure and Sn-doped CeO$_2$ samples. The spectra clearly show the three intense bands positioned at 3420, 1614 cm$^{-1}$ and below 700 cm$^{-1}$. The broad absorption bands at 3420 and 1614 cm$^{-1}$ associated to the symmetric stretching (ν OH) and bending modes of (δ OH) internally bonded water molecules respectively. The more intense band was observed at 2380 cm$^{-1}$ for 6% Sn doped CeO$_2$ when compared to pure CeO$_2$. This confirms the additional CO$_2$ was absorbed at CeO$_2$ surface with the addition of Sn. Furthermore the O-C-O stretching band also observed in the 1300-1600 cm$^{-1}$ region. The bending mode of Ce–O–C (δ) was observed at well below 700 cm$^{-1}$ affirms the formation CeO$_2$ without impurities (Sujana et al 2008 and Dos Santos 2008). The peak positioned at 450 to 550 cm$^{-1}$ attributed to the O-Ce-O stretching mode of vibration (Finocchio et al 1999 and Zawadzki 2008). This FT-IR study fairly agrees with the XRD results.
Figure 3.3 FT-IR spectra of pure and Sn-doped CeO$_2$ nanoparticles

Figure 3.4 (a) shows the Raman spectrum of pure CeO$_2$ nanoparticles. Ceria a cubic fluorite structure-metal dioxide has a single Raman mode at 464 cm$^{-1}$ (Dos Santos et al. 2008). This peak confirms the cubic nature of the sample, which has F$_{2g}$ symmetry and can be viewed as a symmetric breathing mode of O atoms around each cation. Since only the O atoms move, the vibrational mode is nearly independent of cation mass. At ambient conditions, apart from this primary peak, some weak peaks are also visible at 498, 517, 559, 670, and 917 cm$^{-1}$. The peaks occurring at 559, 670, and 917 cm$^{-1}$ may be ascribed to the second-order Raman transitions of CeO$_2$. 
In case of 6 mol % Sn-doped CeO$_2$ shows the Raman line is found to shift slightly to lower frequency (by a few cm$^{-1}$) as the particle size decreases as shown in the Figure 3.4 (b). The peak 630 cm$^{-1}$ show the strong impression of Sn content in Ce host (Wang et al 2002).

Figure 3.4 (a) Raman spectrum of pure CeO$_2$
3.3.2 Morphological Analysis

The SEM images of pure and Sn-doped CeO₂ nanoparticles are shown in the figure 3.5 (a) and (b). It is clearly seen that the particles were highly aggregated emerged in porous nature (Chanjira and Sukon 2009). Both the samples were shows in identical surface morphology. In the case of 6 mol % Sn²⁺ doping more agglomeration was observed. This confirms the reduction in crystalline size significantly by adding Sn ions to CeO₂ host. The quantitative elemental analysis was performed using EDX. The observed EDX spectrum of pure and 6 mol% Sn²⁺ doped CeO₂ was shown in Figure 3.6 (a) and (b). From the spectrum it can be seen that the cerium and tin
absorption was strongly observed, which confirms the stochiometric concentration of the elements.

Figure 3.5  (a) SEM micrographs of Pure CeO$_2$ nanoparticles with different magnifications
Figure 3.5  (b) SEM micrographs of 6 mol% of Sn-doped CeO$_2$ nanoparticles with different magnification
Figure 3.6 (a) EDX spectrum of pure CeO$_2$ nanoparticles.

Figure 3.6 (b) EDX spectrum of 6 mol% of Sn-doped CeO$_2$ nanoparticles.
3.3.3 Optical Absorption Analysis

UV-vis absorption spectra of pure and Sn-doped CeO$_2$ were shown in figure 3.7 (a). It indicates the strong absorption peaks at 300 nm and 310 nm for pure and doped CeO$_2$ nanoparticles. The absorbance peak slightly shifted towards lower wavelength side due to Sn incorporation into Ce. The observed UV region absorption band confirms the direct electron transition between Ce$^{4+}$ and O$^{2-}$ in CeO$_2$. Direct optical Energy band gap is determined using the Kubelka-Munk function (Karthik et al 2010),

$$F(R) = \frac{(1-R)^2}{2R}$$  \hspace{1cm} (3.2)

Linearly extrapolated absorption curves at real axis gives the band gap energy $E_g$ as shown in figure 3.7 (b). The obtained $E_g$ values of the pure and 6 mol % Sn doped CeO$_2$ are 4.85 eV and 5.04 eV respectively. This $E_g$ values are quite high when compared to earlier reports (Sahoo et al 2010 and Debnath et al 2007). In our case, the Sn doped sample shows large $E_g$ than the pure CeO$_2$. It indicates the size dependent quantum confinement of the nanoparticles (Hui Wang et al 2002). For the doped cerium oxide shows the shift in energy band concludes that the large number of electron-hole confinement. This may be due to the presence of Sn$^{2+}$ in Ce$^{4+}$ site which provides additional holes for trapping process. This leads to the reduction in electrical resistivity gradually with respect to the Sn concentration under high pressure.
Figure 3.7  (a) UV-vis absorption spectra of pure and Sn-doped CeO$_2$ nanoparticles

Figure 3.7  (b) Energy band gap Plots of pure and 6 mol% of Sn- doped CeO$_2$ nanoparticles
3.3.4 High Pressure Electrical Resistivity

Electronic phase change of the semiconducting materials is one of the major facts to their potential applications. Various methods have been followed to study the phase transition of CeO$_2$. Only limited number of reports were published elsewhere towards high pressure induced electronic phase transition on CeO$_2$. Under high pressure the structural deviation of nanocrystals can change the physical properties such as cell volume and lattice constant. In addition to the above the electrical resistivity of the pure and Sn doped CeO$_2$ also noted with respect to pressure. Electrical resistivity of these materials were measured by passing 15µ A current through a test sample with two probes, and thereby measuring the voltage developed across two separate voltage probes contacting the sample.

Figure 3.8 (a) High Pressure induced electrical resistivity of pure CeO$_2$ nanoparticles
Resistance measurements were made for increasing pressure with respect to the pre-calibrated Bi-curves. The change in relative resistivity with increasing pressure was shown in Figure 3.8 (a, b). According to Dmitriev et al by increasing pressure from 0 to 8 GPa, there is possible to an iso-structural FCC $\gamma \rightarrow$ FCC $\alpha$ electronic phase transitions occur due to the $f$ band electron in the cerium electron shell (Dmitriev et al 2004). In controversy to the above result, Ge et al reports up to 28 GPa they were not found any phase change in pure CeO$_2$. But they were studied the particle size of the CeO$_2$ is as well below 10 nm (Ge et al 2008). This result well agrees with the Ge et al which means, there is no any phase transition due to pressure induced internal volume change. It further confirms the presence of Sn in the Ce matrix prevent the structural modification during under pressurization. This may be due to the presence of low ionic radius Sn in Ce site could form the strong covalent bond with oxygen. The doping of Sn$^{2+}$ can provide the additional holes to conduction which may reduce the electrical resistivity of the sample under high pressure. Otherwise, due to the high pressure the oxygen defects can be increases which enhance the electrical conductivity significantly. The systematic decrease of relative resistivity was observed with increase of pressure and tin concentration.

Figure 3.8 (b) shows at 8 mol% of Sn-doped CeO$_2$ nanoparticles shows abrupt decrease in relative resistivity upto 1 GPa and further decreases almost linearly with increasing pressure to 7.8 GPa. It indicates that the high concentration of Sn could involve more electron – hole trapping process under high pressure, this resulting that low relative resistivity even at low pressure. It indicates that increasing the dopant level of Sn, the relative resistivity decreases with the increase of pressure. It is moreover, that the materials behave a metallic property in increasing the pressure.
Figure 3.8  (b) High Pressure induced electrical resistivity of pure and Sn-doped CeO$_2$ nanoparticles

3.4 CONCLUSION

Ultrafine Sn doped and undoped Cerium oxide nanoparticles were successfully synthesized using simple chemical precipitation method. From the XRD and FT-IR analysis, we found that the obtained nanopowders were in single phase cubic structure with an average particle size in the range 25-17 nm for the pure and doped samples. Laser Raman spectra confirms the cubic nature of the sample. The SEM observation clearly reveals that the particles are strongly aggregated and appeared in porous morphology. UV-vis spectra concludes that both the pure and Sn doped particles absorption occurs at the
UV region. The obtained band gap value ascribes the most probable electron-hole confinement which leads to the high conductivity. The pressure induced electrical resistivity measurement strongly evidences that there is no electronic phase transition in CeO$_2$ nanoparticles under high pressure due to the change in pressure induced internal volume. It further confirms the gradual decrease of relative resistivity with increasing pressure and doping concentration shows metallic character.