CHAPTER 3

HIGH PRESSURE X-RAY DIFFRACTION STUDIES ON GADOLINIUM AND TERBIUM OXIDES

3.1 INTRODUCTION

The polymorphism and other properties of rare-earth (RE) sesquioxides (\(\text{R}_2\text{O}_3\); R=Rare earth element) have been studied extensively owing to the fact that these compounds are quite important, scientifically as well as technologically. When doped with other RE elements and transition-metal ions, they are used as lasers of various wavelengths (Petermann et al 2002) and as phosphors (Antic Fidancev et al 2002, Justel et al 2001). They are also used as refractory and abrasive materials and have a wide range of other applications (Laversenne et al 2001).

Recently, there have been several studies in the area of radiation damage effects on a variety of rare earth oxides, due to their potential application as nuclear waste host materials (Falca et al 2003). Among other requirements, the nuclear waste host materials should be resistant to crystalline to amorphous transitions induced by self-radiation damage and extreme pressure and temperature environment. Therefore, it is quite interesting to study the structural changes that occur in these oxides when subjected to high pressure.
There is a recent review on the thermodynamics of the rare earth sesquioxides by Zinkevich (2007) where in, they have described the classification of the polymorphic forms of these oxides. Hoekstra et al (1964) initially studied the high pressure-high temperature quenched oxide samples and have found that most of the $R_2O_3$ transform into other polymorphic forms below a pressure of ~ 4 GPa and ~ 1273 K. However, researchers have reported the in-situ compression behavior of $R_2O_3$ - Chen et al (1994), Meyer et al (1995), Chen Hai young et al (2007), Qixun Guo et al (2008). Recently, Gd$_2$O$_3$ and Sm$_2$O$_3$ have been studied under pressure using X-ray diffraction technique, both showing a phase transition from the cubic to the hexagonal ‘A’ phases at around 12 GPa and 7.5 GPa respectively. The range and existence of each phase depends on the ionic radius of the RE and the temperature. Above 2273 K, the X and H phases are stable, while below this temperature, the A, B and C phases are commonly observed.

Gadolinium oxide, or gadolinia Gd$_2$O$_3$, has a variety of interesting and important applications. It has a neutron absorption cross-section that is much higher than other compounds (Falca et al 2003) and a high refractive index (Bhattacharya, Biswas and Sahoo 2004), which makes it a very useful material in optics. It is used as a contrast agent in clinical MRI on account of its paramagnetic nature. Owing to its thermal stability and refractory properties, it is used as protective and corrosion-resistant coatings. It is also an ultraviolet-transmitting material and is used in lasers. Since Gd$_2$O$_3$ may be subjected to extreme conditions in applications such as control rods in nuclear reactors and hence it is very important to understand the structural changes that occur under extreme pressure and temperature conditions.

There was an earlier report on high-pressure energy-dispersive X-ray diffraction (HPXRD) studies of Gd$_2$O$_3$, which revealed a phase transition from the cubic to a possible hexagonal phase at around 10.9 GPa (Hai-Yong
et al 2007). Raman study by Nita et al (2007) on cubic nano crystalline Gd$_2$O$_3$ revealed a phase transition at 12.62 GPa. However, the high pressure phase was not described in detail, and the bulk moduli of the phases were not given. After our studies were published, Zhang et al (2008) had studied Gd$_2$O$_3$ up to 43 GPa using a synchrotron source and had observed a transition from the C to the A type structure and they have confirmed the high pressure structure as the hexagonal A-type structure.

The rare earth sesquioxide Tb$_2$O$_3$ crystallizes in the cubic bixbyte structure at ambient conditions. Earlier, by the application of high pressure and high temperature simultaneously, pure Tb$_2$O$_3$ (quenched) was found to transform to the monoclinic B type phase at around 0.25 GPa and 1173 K (Hoekstra et al 1964). The results of high pressure studies done on terbium oxide (having Tb$^{3+}$ and Tb$^{4+}$) are presented in the latter part of this chapter.

### 3.2 EXPERIMENTAL DETAILS

#### 3.2.1 Gadolinium oxide

Gadolinium oxide, 99.9% (REO), obtained from M/S Johnson and Matthey, was characterized by XRD technique using a high-resolution Guinier diffractometer with a scintillation detector having an overall resolution of $\delta d/d = 0.005$. The in-situ HPXRD was carried out using a Mao–Bell-type diamond-anvil cell (DAC) in the angle dispersive mode. Micro samples were loaded into a 250 mm hole drilled into a pre-indenteted stainless-steel gasket. A ruby chip was placed alongside the sample for pressure calibration by the ruby fluorescence method. The ruby was excited with an argon laser of wavelength 514.5 nm. A mixture of methanol, ethanol and water in the volume ratio 16: 3: 1 was used as the pressure-transmitting medium.
3.2.2 Terbium oxide

Terbium oxide, 99.9% (REO) was obtained from M/S Johnson and Matthey and characterized by X-ray diffraction technique using a high-resolution Guinier diffractometer with a scintillation detector having an overall resolution of $\delta d/d=0.001$. XPS measurements were carried out in a SPECS make spectrometer using Al K$_\alpha$ at 1486.74 eV as a probe. The X-ray source power was set at 300W. Argon ion beam with energy of 5KV and current of 50 $\mu$A was employed for sputtering the samples. The Spectrometer, which has a resolution of 0.6 eV, was calibrated with a standard specimen.

The in-situ high-pressure X-ray diffraction was carried out with a Mao-Bell type diamond anvil cell (DAC) in the angle dispersive mode using the high-pressure Guinier diffractometer. The powdered sample was loaded into a 250 $\mu$m hole drilled into a pre-indentied stainless steel gasket of the DAC. A ruby chip was loaded along with the sample for pressure calibration by ruby fluorescence method. The ruby excitation was done with an argon laser of wavelength 514.5 nm. A mixture of methanol, ethanol and water in the volume ratio 16:3:1 was used as the pressure-transmitting medium.

3.3 RESULTS AND DISCUSSIONS

3.3.1 Gadolinium Oxide

The high-pressure XRD pattern (Figure 3.1) of Gd$_2$O$_3$ revealed that the sample has a cubic structure with lattice parameter $a = 10.843\pm0.002\text{Å}$ and space-group $Ia\bar{3}$ (206) at ambient pressure. At around 12.4 GPa new peaks emerge which is a clear indication of structural phase transition. The most prominent peak appears at $\theta = 7.27^\circ$ which emerges between the (222) peak at $\theta = 6.4^\circ$ and (400) peak at $\theta = 7.57^\circ$ of the parent phase. Another prominent new peak appears at $\theta = 10.75^\circ$. The high pressure phase remained
stable up to 25 GPa. There was no indication of a reversal of the phase as the pressure was lowered to ambient. Further, the sample was laser heated around 773 K using the laser heated diamond anvil cell facility, to check for reversibility of the above transition. However, the transition was found to be irreversible even after laser heating at 773 K.

Figure 3.1 Angle dispersive XRD patterns for Gd$_2$O$_3$ for various pressures indicating the structural transition at 12 GPa

Out of the five different polymorphic forms of the rare earth sesquioxides, the hexagonal structure was the likely candidate for the high-pressure phase, with regard to the decreasing order of symmetry. The earlier reported pressure induced transition for the nano sized Gd$_2$O$_3$ is to the monoclinic structure. The high-pressure phase was fitted to various structures, for example, the Sm$_2$O$_3$ type structure (which is the B form of Gd$_2$O$_3$ a =
14.061 Å, b = 3.566 Å, c = 8.710 Å) and the Bi$_2$O$_3$ structure (which is a tetragonal distortion of a simple cubic form with a = 10.93 Å, c = 5.62 Å). Most of the lines were not indexed in both cases. Therefore, both the structures were not a proper fit. In early 1980, a sophisticated computer program for data entry and review was developed at the National Bureau of Standards (now the National Institute of Standards and Technology) under the name NBS*AIDS83. This program was designed to evaluate data for both the Powder Diffraction File and for Crystal Data. A standardized procedure is followed which checks many aspects of the data as allowed by the information available. The d-spacings are evaluated by figures of merit (Smith and Snyder, 1979) where unit cells are provided by the authors. These figures of merit are based on the average error in the observed diffraction angle compared to the calculated value from the refined unit cell and are used to assign the quality indicator for the data set. Crystallographic conditions are compared with the symmetry assignment provided by the author. The program also checks the consistency of the chemical formula by determining the formula weights and the density for comparison with measured values. The NBSAIDS83 software was used here and the Figure of merit obtained was around 5.19. For indexing the high-pressure pattern, we have considered four lines at theta values 6.42°, 7.27°, 9.47°, 10.75° at 12.4 GPa which could not be indexed to the above two structures.

After fitting various possible structures to the high-pressure phase, the best fit was found to be with the La$_2$O$_3$ type structure with lattice parameters: a = 3.741 Å, c = 5.709 Å, c/a = 1.54, and space group P3m1 (No.164) with Z = 1. The analysis was done using the NBS AIDS83 program. (Mighell et al 1981). Table 3.1 shows the various structures that were fitted to the high pressure phase. The P-V data for Gd$_2$O$_3$ is shown in Figure 3.2. The graph shows a volume collapse of about 13% across the structural transition. The P-V data was fitted to the Birch - Murnaghan
equation (Birch 1947) for both the parent phase and the daughter phase separately.

Table 3.1  The various structures that were fitted to the high pressure phase

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Monoclinic (Sm$_2$O$_3$)</th>
<th>Orthorhombic (B$_2$O$_3$)</th>
<th>Tetragonal (Bi$_2$O$_3$)</th>
<th>Hexagonal (La$_2$O$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>C2/m</td>
<td>Ccm21</td>
<td>C42b</td>
<td>P3m1</td>
</tr>
<tr>
<td>Lattice parameter(Å)</td>
<td>a=14.06</td>
<td>a=4.61</td>
<td>a=10.93</td>
<td>a=3.74</td>
</tr>
<tr>
<td></td>
<td>b=3.56</td>
<td>b=7.80</td>
<td>c=5.62</td>
<td>c=5.7</td>
</tr>
<tr>
<td></td>
<td>c=8.710</td>
<td>c=4.129</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume (Å)$^3$</td>
<td>448.39</td>
<td>134.12</td>
<td>672.41</td>
<td>69.20</td>
</tr>
<tr>
<td>Number of lines matched</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Figure of merit</td>
<td>0.62</td>
<td>0.29</td>
<td>2.42</td>
<td>5.19</td>
</tr>
</tbody>
</table>

Figure 3.2  The pressure versus V/Vo values fitted to the Birch - Murnaghan Equation of state
Table 3.2 The observed and calculated d-spacing for the parent cubic phase at 1 atm and the hexagonal high pressure phase at 12 GPa

<table>
<thead>
<tr>
<th>Cubic (1 atm)</th>
<th>Hexagonal (~12 GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-obs   d-cal</td>
<td>d-obs   d-cal</td>
</tr>
<tr>
<td>h   k    l</td>
<td>h   k   l</td>
</tr>
<tr>
<td>4.4333 4.4346 2 1 1</td>
<td>1.8531 1.8629 5 3 0</td>
</tr>
<tr>
<td>3.1231 3.1375 2 2 2</td>
<td>1.8104 1.7917 6 0 0</td>
</tr>
<tr>
<td>2.7037 2.7156 4 0 0</td>
<td>1.7612 1.7621 6 1 1</td>
</tr>
<tr>
<td>2.5561 2.5603 3 3 0</td>
<td>1.6708 1.6761 5 4 1</td>
</tr>
<tr>
<td>2.3123 2.3159 3 3 2</td>
<td>1.6376 1.6398 6 2 2</td>
</tr>
<tr>
<td>2.1241 2.1303 5 1 0</td>
<td></td>
</tr>
<tr>
<td>1.9132 1.9202 4 4 0</td>
<td></td>
</tr>
</tbody>
</table>

The bulk modulus values obtained from the above fitting are: 

\[ B_o = 117.621 \pm 21.20 \text{ GPa}; \quad B_o' = 13.89 \pm 7.761 \text{ and } B_{12} = 142.1 \pm 13.6 \text{ GPa}; \quad B_{12}' = 6.1 \pm 4.2 \]

for the parent cubic and daughter hexagonal phase respectively. The values of the bulk modulus are comparable to that observed in other rare earth sesquioxides (Mikami and Nakamura 2006). Table 3.2 gives the d-values for both the parent and the daughter phases. The values are a guide to the theta positions and not to the intensities. Figure 3.3 shows the variation of different interplanar spacing for parent and the daughter phase as a function of pressure. The interplanar spacing show monotonic decrease with pressure.

The theoretically obtained value for volume (Petit et al 2005) of the A type structure matched well with the experimental observations. The large
volume collapse across the structural transition and the wide difference between the total energies of the two phases (Petit et al 2007) suggest that the phase transition may be of the reconstructive type. The transition occurs with an increase in the co-ordination number from six to seven with an increase in density and decrease in symmetry (Brazhkin 2007) which is expected during high-pressure transitions. Furthermore, it has been reported that these transformations might not be reversible at temperatures below 1473 K - 1673 K, where the metal atom mobility is small (Eyring 1978).

Figure 3.3  The variation of the d- spacing with different values of pressure for the two different phases.
3.3.2 Terbium Oxide

The high pressure X-ray diffraction patterns up to 35GPa are shown in Figures 3.5 and 3.6. The parent phase was found to be of fluorite structure having lattice parameter a=5.31 ± 0.001 Å and (space-group Fm̅3m No.225) at STP. All the d (h k l) values were in good match with the PDF no. 13-0387 of ICDD (International Centre for Diffraction Data, USA). Most of the rare earth elements form sesquioxides at STP, however, some like Ce, Pr and Tb, form compounds with larger oxygen coordination number. In terbium, the extra electron above the half filled shell is also less tightly bound and therefore this element frequently shows a valence greater than 3⁺. Terbium oxide normally occurs as Tb₄O₇ and it is reported that Tb₂O₃ is prepared by reducing oxygen from Tb₄O₇, and when the reduction is complete, the material is pure white in color. However, even a slight amount of Tb⁴⁺ will lead to charge transfer absorption and coloration (Gregory McCarthy, 1971). Since our sample was of slight buff color, we tried matching the observed d values with the ICDD (International Centre for Diffraction Data, USA) files for Tb₄O₇, viz: 13-0387 and 32-1286. In order to check the genuineness of the space group assignment in the ICDD file 13-0387, we took the atom positions from the Pearson’s handbook (Villars and Calvart 1985) for the structure type Cu₇S₄ (space group Fm̅3m) and generated a theoretical pattern using LAZY PULVERIX program (Yvon et al 1977).

The generated pattern was found to be very different from what is given in the ICDD file. In the case of ICDD no: 32-1286, the intensities were also not matching properly. Moreover, an experimental diffraction pattern for Tb₄O₇ is not available for comparison. Observations by Baenziger et al, (1961) points out that the TbO₁.₇₁₅ (i.e. ~Tb₄O₇) phase has XRD patterns very similar to that of the fluorite – type phase, except that some of the diffraction lines have split into doublets or triplets and a few additional weak lines occur.
However, we observed sharp diffraction lines characteristic of a cubic phase. Hence, we believe that our sample is mainly Tb$_4$O$_7$ with some amounts of Tb$_2$O$_3$. In order to investigate the oxidation state of Tb, XPS studies were done. The Tb 4d spectra in Figure 3.4 shows that along with the hump at 148.52 eV for Tb$^{3+}$, there is a good intensity for the Tb$^{4+}$ ions at around 150.59 eV (Moulder et al 1995). The peaks are very broad around this area and cannot be further resolved and for clarity, a UPS study will have to be done on the sample.

![Tb 4d region](image.png)

**Figure 3.4** Terbium 4d spectrum showing a broad peak near the Tb$^{3+}$(148.52 eV) and Tb$^{4+}$(150.59 eV) which indicates the presence of both.

In Figure. 3.5, the four prominent peaks: (111), (200), (220) and (311) of the parent fluorite phase are indexed. Above 27GPa, as seen in Figure 3.6, the signature peaks of the parent fluorite phase slowly start to broaden out and split, indicating a phase transition, probably to the cotunnite phase, which is the high pressure phase of fluorite structure.
Figure 3.5 X-ray diffractogram for Tb$_4$O$_7$ for pressures up to ~4GPa

Figure 3.6 X-ray diffractogram for Tb$_4$O$_7$ at pressures up to 35 GPa along with the return cycle pattern at 0.1 MPa. Large broadening and splitting of the first two diffraction peaks indicate emergence of a cluster of several peaks.
The P-V data for the parent cubic phase of Tb₄O₇ up to around 5 GPa is shown in Figure 3.7. The P-V data was fitted to the Birch-Murnaghan equation of state. The bulk modulus of the cubic phase is found to be $B_0 = 195.7 \text{ GPa} \pm 3.81$ and $B_0' = 4$. This bulk modulus is comparable to that observed in other rare earth oxides (Mikami and Nakamura 2006).

![Graph showing P-V data for Tb₄O₇ up to 5 GPa fitted to the Birch-Murnaghan Equation of state.](image)

**Figure 3.7** P-V data for Tb₄O₇ up to 5 GPa fitted to the Birch-Murnaghan Equation of state

Analyzing the crystal structure of a high-pressure phase is not a trivial task. The high pressure XRD patterns generally have limited ‘d’ range due to mechanical constraints of the DAC and have several artifacts like broadening of peaks, disproportionate intensities due to preferred orientation, interfering gasket peaks etc, which make the task of solving the crystal structure very difficult. One has to use trial and error methods and make some intelligent analysis to obtain the ionic positions at high pressures. The peaks
of the high pressure phase obtained in this study are too broad to be considered for any meaningful analysis. The broad peaks may be due to a cluster of peaks and cannot be distinguished due to the limited resolution of the instrument. This structural transition was found to be irreversible in nature, as can be seen from the XRD pattern of the return cycle at 0.1 MPa in Figure 3.7.

The transition pressure of 27 GPa for terbium oxide is much higher than that generally found in other oxides (<15 GPa). In Tb₄O₇, the different cation sites in the fluorite lattice are occupied by trivalent and tetravalent Tb ions, which are coordinated by 6 and 8 oxygen atoms respectively. X-ray absorption spectroscopy studies reveal that the f⁸ ground state configuration of Tb is well localized in the trivalent oxide while in the case of tetravalent oxide, the last 4f electron delocalizes in the valence band and the remaining seven-4f electrons remain localized. This indicates that the last f electron participates in a partial type covalent bonding (Esteva et al 1986). As our sample mostly consists of 

\[ \text{Tb}^{4+} \]
ions due to the presence of \( \text{Tb}_4\text{O}_7 \) as discussed earlier, this may probably be one of the reasons for the large stability seen here. The reported transition pressures for the other oxides at room temperature are all below 15 GPa, as in most of the cases the bonding is ionic in nature.

### 3.4 CONCLUSIONS

A structural transition with a volume collapse of \( \sim 13\% \) was observed at \( \sim 12 \) GPa for \( \text{Gd}_2\text{O}_3 \). The structure of the high-pressure phase is identified as the A-type hexagonal (\( \text{La}_2\text{O}_3 \) type). The phase transition is irreversible in nature and does not revert to the parent phase even after laser heating at \( \sim 500^0\text{C} \).
The large structural stability of terbium oxide under pressure compared with other rare earth oxides is rather unusual and has been attributed to the presence of Tb$^{4+}$ ions. The large structural stability and high bulk modulus make the oxide an ideal choice for the nuclear waste immobilization. The phase transition is irreversible in nature and does not revert to the parent phase on releasing the pressure to 0.1MPa. However, the tendency of the oxide to transform to other higher oxides on exposure to air could be a deterrent and should be examined more carefully.