Abstract. The Rare-Earth sesquioxides (RE$_2$O$_3$) exhibit interesting physical and chemical properties. Some of these oxides have tremendous technological applications. At ambient conditions, the RE$_2$O$_3$ systems exist in three polymorphic forms, namely: hexagonal A-type, monoclinic B-type, and cubic C-type. The structural stability of three RE$_2$O$_3$ systems: RE = Gd, Ho, Tm and the Tb$_4$O$_7$ system have been studied under high pressure. All the four systems exhibited interesting pressure induced phase transitions. Gd$_2$O$_3$ exhibited C-A transition at ~ 12 GPa, whereas Ho$_2$O$_3$ and Tm$_2$O$_3$ exhibited C-B transition at pressures of 9.5 and 7 GPa respectively. Tb$_4$O$_7$ transformed from its cubic fluorite structure to probably the cotunnite phase at a relatively higher pressure of 27 GPa. The unusual large pressure stability of Tb$_4$O$_7$ was attributed to the presence of Tb$^{4+}$ ions. The bulk moduli show systematic increase with higher cations, probably due to the enhanced influence of the $4f$ electron states and increased nature of covalency. However, the mechanisms of the structural transitions C-B-A with increased pressure and increased cation radii are yet to be understood.

1. Introduction
The Rare-Earth sesquioxides (RE$_2$O$_3$) exhibit interesting structural, physical and chemical properties and also have important technological applications [1]. Some of these oxides have potential application as nuclear waste host materials[2]. Therefore, it is crucial to understand their structural stability at extreme conditions of pressure and temperature. At ambient conditions, the RE$_2$O$_3$ systems exist in three polymorphic forms, namely: hexagonal A-type with space group SG: P-3m1 and Z=1, monoclinic B-type with SG: C2/m and Z=6, and cubic C-type with SG: Ia-3 and Z=16 [3]. The lighter RE$_2$O$_3$ systems with larger cation sizes (La-Pm) exist in A-type structure. The cubic structure is characteristic of heavier RE$_2$O$_3$ with smaller cation sizes (Tb-Lu). The RE$_2$O$_3$ systems with medium cation radii (Sm-Gd) may exist in both B and C type structures. Thus the RE$_2$O$_3$ systems adopt the structural sequence A-B-C with the increasing atomic number or decreasing ionic radii. Two more high temperature polymorphs, the cubic X (SG: Im-3 m) and hexagonal H (SG: P6$_3$/mmc) phases also have been reported above 2000°C [4]. The molar volumes of these compounds decrease with increasing cation coordination in the sequence C-B-A [4,5]. Hence, the phase transition sequence of C-B-A is usually expected for most of the RE$_2$O$_3$ systems under pressure [4-6].
In this investigation, the structural stability of three RE$_2$O$_3$ systems: RE=Gd, Ho, Tm and the Tb$_4$O$_7$ system have been studied under high pressure using X-ray diffraction (XRD) and laser Raman. The systematic structural transition data have been compared and contrasted with the results available for other RE$_2$O$_3$ systems and plausible reasons have been suggested for the observed trends.

2. Experimental Details
All the oxide samples of purity 99.99% were characterised by XRD using a high precision Guinier diffractometer and were found to be in single phase. High pressure X-ray diffraction (HPXRD) experiments were carried out in the angle dispersive mode by using a Mao-Bell type Diamond Anvil Cell (DAC). Either the PSD based Guinier diffractometer [7] or image plate based mar345dtb diffractometer was used for carrying out the HPXRD experiments. A mixture of methanol, ethanol and water (MEW) in the volume ratio 16:3:1 was used as the pressure transmitting medium. Either the equation of state (EOS) of Ag [8] or the ruby fluorescence method [9] was employed for determining the sample pressure. The incident Mo X-ray was obtained from Rigaku 18 kW rotating anode X-ray generator. The incident X-ray was monochromatised by a curved crystal monochromator in the case of Guinier diffractometer and a flat graphite monochromator in the case of mar345dtb diffractometer. Some samples in their high pressure metastable phase were laser heated using the LHDAC facility developed in our laboratory [10] to check the reversibility of the high pressure phase.

3. Results and Discussion
HPXRD experiments on the three RE$_2$O$_3$ systems (RE=Gd, Ho and Tm) and the Tb$_4$O$_7$ were carried out up to the maximum pressures of 25, 17, 30 and 35 GPa respectively [11-14]. All the four systems exhibited interesting pressure induced structural transitions. Gd$_2$O$_3$ transformed from its C-type cubic structure to the A-type hexagonal structure at ~ 12 GPa with a 13% volume collapse (Figure 1)[11]. On releasing the pressure from 25 GPa, the daughter phase was retained at ambient. The pressure quenched sample at NTP was laser heated to about 500°C using the LHDAC facility[10] to check the reversibility of the above transition. Although a small fraction of the cubic phase reappeared, the structure remained mostly hexagonal indicating the irreversible nature of the transition. A recent study on Er-doped Gd$_2$O$_3$ up to ~40 GPa indicated the C→A transition at 8.57-12.5 GPa [15]. However, it

![Figure 1](image.png)

**Figure 1.** High pressure XRD patterns of Gd$_2$O$_3$ showing the C-A transition above 12 GPa. The top pattern is at 0.1MPa after return cycle[11].
transformed to the B phase during the return cycle. Similar results have been observed by other investigators in nano-crystalline Eu-doped Gd_{2}O_{3} [16] and pure Gd_{2}O_{3} [17,18]. The differences in the phase transition behaviour during the return cycle may be due to the difference in the sample quality and the thermal history. The P–V data up to 12 GPa were fitted to the Birch–Murnaghan equation of state [19] and the bulk modulus and its pressure derivative were found to be: B_{0} = 118 ± 21 GPa and B_{0}' = 13.9 ± 7.7 respectively [11]. This value of bulk modulus is smaller compared to the reported values of 164, 134 and 188 GPa [15,17,18] with B_{0}' fixed at 4. These values of the bulk moduli are comparable with those reported for other RE_{2}O_{3} systems [4, 20-22].

Ho_{2}O_{3} on the other hand transformed from the C-type cubic phase to B-type monoclinic phase at 9.5 GPa [12]. The high pressure B-phase remained stable up to 17 GPa. High pressure Raman studies on Ho_{2}O_{3} indicated a Ho–O stretching vibration peak at wave number 372 cm\(^{-1}\). This peak slowly broadened and moved towards higher wave number on compression, and finally disappeared above 7 GPa, signifying the above phase transition. A recent study on Ho_{2}O_{3} up to 63 GPa indicated C→B transition at 8.9 GPa and B→A at 14.8 GPa [23]. During the return cycle, it transformed to the B phase. In our experiment, since the B-phase was stable up to 17 GPa, the same B-phase was obtained on releasing the pressure. In case of Tm_{2}O_{3}, the irreversible C-B transition was observed at 7 GPa [13]. The P–V data for Ho_{2}O_{3} up to 9.5 GPa and that of Tm_{2}O_{3} up to 7 GPa were fitted to the Birch–Murnaghan equation of state [19] and the values of the bulk modulus and its pressure derivative obtained from the above fit were: B_{0} = 178 ± 7 GPa, B_{0}' = 4 and B_{0} = 154.5 ± 7.5 GPa, B_{0}' = 4 respectively. The B_{0} and B_{0}' values for Ho_{2}O_{3} reported by Jiang et al [23] are 206 GPa and 4.8 respectively.

Figure 2. High pressure XRD patterns of Tb_{4}O_{7} showing the structural transition above 27 GPa [14].

Terbium oxide Tb_{4}O_{7} transformed from its fluorite cubic structure to probably cotunnite type (orthorhombic) structure at ~27 GPa (Figure 2) [14]. The large structural stability of the compound under pressure is thus unusual, when compared with other RE_{2}O_{3} systems. The P–V data was fitted to the Birch–Murnaghan equation of state [19]. The bulk modulus and its pressure derivative of the cubic phase were found to be B_{0} = 195.7 ± 3.8 GPa and B_{0}' = 4 respectively. This bulk modulus is comparable to that observed in other rare earth oxides [18, 20, 21, 23]. However, the transition pressure of 27 GPa for Tb_{4}O_{7} is much higher than that generally found in other rare-Earth oxide systems (<15 GPa) [18, 20-24]. This has been attributed to the presence of Tb\(^{3+}\) ions in Tb_{4}O_{7}. The
XPS spectra on the sample confirm the presence of Tb$^{4+}$ ions [14]. In Tb$_2$O$_3$, the different cation sites in the fluorite lattice are occupied by trivalent and tetravalent Tb ions, which are coordinated by 6 and 8 oxygen anions respectively. X-ray absorption spectroscopy studies reveal that the $f^8$ 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. The remaining seven-$4f$ electrons of the cation remain localized. This indicates that the last $f$ electron participates in a partial type covalent bonding [25]. In other sesquioxides, the bonding is mostly ionic in nature with the cations in the $3^+$ state. Since our sample mostly consisted of Tb$^{4+}$ ions due to the presence of Tb$_2$O$_3$, this may probably be one of the reasons for the large structural stability seen here.

The summary of our phase transition data along with that reported in literature are shown in figure 3. It can be seen that the C-A transition pressure increases with increasing Z of the cation [20,24]. The bulk moduli of these systems along with that of the other C-type RE$_2$O$_3$ systems reported in the literature [18, 20-24] are shown in figure 4. The increase in B$_0$ with increasing atomic number Z of the cation can be clearly seen. These anomalous phase transition and compressibility behaviour of the RE$_2$O$_3$ systems have to be understood in terms of their electronic structure.

In the C-type structure, the cations have 6 fold coordination, that is each cation is surrounded by 6 anions. There are two types of cation sites- 3/4th in 24d and 1/4th 8a positions. In the B-type structure, 2/3rd cations are surrounded by 7 anions and 1/3rd by 6 anions. In A-type structure, each cation is surrounded by 7 anions. Although the cation radii increase in the sequence C-B-A, the molar volumes decrease (density increase) and the cation coordination numbers increase in the same sequence[4, 5, 20, 26]. This contrasting behaviour can be understood from the following arguments. The RE$_2$O$_3$ systems mostly exhibit ionic bonding with the cations mostly in the 3$^+$ state and the $4f$ electrons localized [4,20, 21, 26]. Cations with 4$^+$ state, in which one $4f$-electron participates in bonding, have tendency to form higher oxides like REO$_2$ [20]. Electronic structure calculations have clearly indicated that the nature of covalency between the O-p and RE-p$\text{d}$ as well as the influence of $4f$ states increase in the sequence A-B-C [4,20,26]. The increased nature of directional covalent bonding keep the ions apart leading to their higher molar volume and lower cation coordination, and hence the increased molar volume in the sequence A-B-C. Considering the molar volume difference, the structural sequence C-B-A is expected under high pressure.
Further, the free energy difference between C and B type phases are very large compared to that of the A and B phases [18, 20, 21,26]. The C→B transitions are accompanied with large scale rearrangement of atoms, breaking of bonds and large volume collapse (≈10%) [4,5,18, 27]. That is why the C→B transitions are reconstructive type and irreversible. The B→A transitions involve minor displacement of atoms, small volume collapse (≈2-5%), displacive in nature and are reversible [4, 6, 18, 21, 28]. Depending on the sample history and the experimental conditions (such as hydrostaticity, rate of pressurization, temperature, etc.), either the sequence C → B → A (Sm2O3, Yb2O3, Ho2O3, Lu2O3) or direct C → A (Gd2O3, Dy2O3, Er2O3) transitions are observed [4-6, 18, 21, 23, 28, 29]. Considering the very small free energy difference between the B and A phases[21], missing of the intermediate B phase during the C→A transition is not surprising. However, during the return cycle, the systems mostly land up in the B phase (Dy2O3, Ho2O3, Er2O3,Yb2O3). This is due to the fact that there is a large kinetic barrier in the reconstructive type transition from B→C, whereas the A→B displacive transition proceeds without any hindrance.

Now returning to the compressibility behaviour, the bulk moduli of these systems along with that of the other C-type RE2O3 systems reported in the literature [18,20-24] are shown in figure 4. The increase in B0 with increasing atomic number Z of the cation can be clearly seen. The theoretical estimated values of bulk moduli show very little difference between the A and C type RE2O3 systems [20]. Thus it can be safely stated that the lighter RE2O3 systems (with lower molar volume and higher density) have lower bulk moduli compared to that of the heavier RE2O3 systems (with higher molar volume and lower density). Considering the higher density (lower molar volume) of the lighter RE2O3 systems, the bulk moduli of these are expected to be higher than that of the heavier RE2O3 systems. However, as can be seen from figure 4, the observation is just the opposite, that is, the heavier sesquioxides show higher bulk moduli compared to that of the lighter sesquioxides. This behaviour again can be understood from the increased covalent bonding in the heavier sesquioxides compared to the mostly ionic bonding in the lighter sesquioxides [20,26].

In summary, the RE2O3 systems exhibit the same structure sequence C-B-A on increasing cation radii as well as increasing pressure. The origin of this strange structural behavior may be due to the steric effects. A systematic structural study has to be carried out to understand this behaviour. For this purpose, systematic high resolution synchrotron based X-ray diffraction experiments and Rietveld analysis along with micro-Raman studies have to be carried out. The compressibility behaviour may be attributed to the increased covalent bonding in the heavier sesquioxides (less compressible) compared to the mostly ionic bonding in the lighter sesquioxides (more compressible).

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