High pressure phase transition in Nd$_2$O$_3$

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Abstract. High pressure structural and spectroscopic investigations have been carried out on rare-earth sesquioxide, Nd$_2$O$_3$, using energy dispersive x-ray diffraction and Raman scattering techniques. Our measurements show that ambient hexagonal structure of Nd$_2$O$_3$ is stable up to 27 GPa. Beyond this pressure, it undergoes a structural phase transition to a lower symmetry phase. On release of pressure, it reversibly transforms back to the hexagonal phase suggesting the nature of phase transition to be of displacive kind.

1. Introduction
Rare-Earth (RE) sesquioxides (R$_2$O$_3$-R-rare earth element) are important materials, both scientifically as well as technologically due to their existence in various polymorphic forms and wide variety of applications such as laser rods, phosphors, refractory and abrasive materials etc.$^1$ Like the RE metals, the physical properties of the RE sesquioxides are also affected by the partial filling of their inner 4f-electron shells leading to the well known effect, lanthanide contraction.$^2$ However 4f electrons do not participate in bonding and are core like in nature. The s and d valence electrons thus dominate in bonding and leave their respective atomic cores$^3$ in a trivalent state except for Eu, Yb, Ce, and Pr where divalent and tetravalent states are also observed. The screening of the 4f electrons by the Xe core serves to leave the bulk properties of the lanthanides relatively unchanged as electrons are added to the 4f shell. It is because of this reason that the properties of the trivalent lanthanides are expected to vary in a gradual manner as one traverse the series. As a consequence, depending on RE$^{3+}$ cation radii, there exist three polymorphic modifications of RE sesquioxide under ambient conditions viz. hexagonal (A-type), monoclinic (B-type) and cubic structures (C-type).$^3$ The rare earth sesquioxides were first investigated systematically by Goldschmidt and his co-workers in 1925.$^4$ His original designations for the phases (A,B and C) are still in use today. Larger RE$^{3+}$ cation radii sesquioxides are found to be stabilized in hexagonal structure whereas for smaller ones, cubic structure is more stable. In-between sesquioxides (viz. Sm, Eu, Gd) are found to have monoclinic structure at elevated temperatures.$^5$ The hexagonal phase (A-type) has been found to be denser than the monoclinic as well as cubic phase. It has been observed that pressure also affects the stability of various polymorphs in RE sesquioxides. This is also corroborated by the fact that molar volumes of hexagonal and monoclinic phases are relatively lower than that of cubic phase. As a consequence, under high pressures B-type structure is favored over the C-type and the hexagonal (A) type over both of the other structure types. Pressure is also known to enhance the stability regime of monoclinic phase as a function of lanthanide atomic number at elevated temperatures. Under ambient temperature, cubic and monoclinic structured sesquioxides are known to undergo polymorphous transition to hexagonal at under high pressures. However, the role of high pressure on hexagonal structured sesquioxide is relatively less studied. Since high pressure should lead 4f electrons to become more delocalized or
hybridized, it would be interesting to investigate high pressure behavior of some partially 4f filled rare-earth sexquioxide. With this motivation we have investigated high pressure behavior of Nd$_2$O$_3$ using energy dispersive x-ray diffraction (EDXRD) and Raman scattering techniques.

2. Experimental details
High pressure EDXRD measurements were carried out on Nd$_2$O$_3$ up to 40 GPa at BL-11 (EDXRD beam line) of Indian synchrotron source, INDUS-II (RRCAT, Indore). A- type Nd$_2$O$_3$ was obtained commercially from Sigma-Aldrich and had a stated purity of 99.999%. Since Nd$_2$O$_3$ is highly hygroscopic, several milligrams of sample were annealed in inert environment at ~700°C for about 24 hours prior to measurements in order to get rid of carbonate and hydroxide impurities. Mao-bell kind of diamond anvil cell (DAC) was used for high pressure measurements. Sample was loaded in ~100 µm hole in pre-indent tungsten gasket. For hydrostatic compression, 1:1 pentane iso-pentane mixture was used as pressure transmitting medium. It also helped in getting rid of any type of contamination of sample during experiments. Since diffraction peaks of standard elements, generally used as pressure calibrants e.g. gold, copper etc. are nuisance in diffraction measurements, ruby chip (~20 µm) was used as pressure calibrant in diamond anvil cell (DAC). Pressure calibration at different pressures was carried out using offline ruby pressure measurement setup configured around Ocean optics Maya2000 spectrometer. Further, to avoid diffraction peaks of gasket material in EDXRD measurements, we used collimated white beam of synchrotron radiation cut down to a size of ~50 µm. Raman spectroscopic measurements were carried out in a similar manner using Mao-bell kind of DAC on our laboratory based micro-focus confocal Raman setup up to 47 GPa. 532 nm frequency doubled Nd:YAG diode pumped solid state laser was used as an excitation source. Same setup was used for pressure calibration using ruby chip which was also loaded along with sample and 1:1 pentane iso-pentane mixture.

3. Results and discussion
EDXRD measurements (Fig. 1a) show that the ambient phase of Nd$_2$O$_3$ has the symmetry of A –type hexagonal phase. Most of the prominent peaks viz. 100,011,110 112 etc. of hexagonal phase are visible even at the highest measured pressure (40.1 GPa). Assuming hexagonal phase to be stable up to the highest measured pressure we have determined $a$ and $c$ axis at each measured pressure.

![Figure 1](image_url)

Figure 1. (a) EDXRD data at representative pressures, (b) lattice parameter as function of pressure
As shown in Fig. 1b, $c$ axis has been found to be more compressible than the $a$ axis and $c/a$ ratio changes from 1.57 to 1.48 at the highest pressure of our measurement. However we observed enhanced compressibility of $c$ axis beyond 25.5 GPa. This is also concomitant with the emergence of a few additional diffraction peaks between 011 and 012 peaks (Fig. 1a). This is suggestive of a structural phase transition to a lower symmetry phase. Other diffraction peaks present earlier have been found to broaden beyond 25.5 GPa. Since the diffraction pattern has not changed much except a few additional peaks, the transformed phase might be structurally very close to the initial phase and the diffraction peaks of new phase are appearing at similar positions to that of initial phase.

![Figure 2. $A_{1g}$ Raman mode as a function of pressure](image)

Our Raman scattering measurements show that the most intense $A_{1g}$ mode at 440 cm$^{-1}$ splits with pressure (Fig. 2a). J. P. McClure has explained this splitting in his thesis work$^6$ in terms of asymmetric change in the bond lengths of Ln cation (in present study Ln is Nd) and O atoms along the $c$ axis which introduces addition Raman mode. The gap widens as a function of pressure. However, there is $d\omega/dp$ slop change above 27 GPa (Fig. 2b). This reduced stiffening of Raman modes suggests structural relaxation above this pressure as this change is concomitant with the emergence of new diffraction peaks in EDXRD measurements. On release of pressure, the hexagonal phase (A-type) reappears suggesting the phase transition to be of displacive kind. This new phase could have been similar to the novel hexagonal type super lattice structure observed in La$_2$O$_3$ obtained by cell doubling along $c$ axis.$^6$ However; we did not observe any super-lattice peak in our diffraction measurements.

This new phase also seems to be different from monoclinic (B-type) structure of Nd$_2$O$_3$. Even though the known monoclinic phase has diffraction peaks between the (002) and (012) peaks of hexagonal phase (A type), there are other prominent diffraction peaks of monoclinic phase which are absent in our measurements. In order to get the symmetry of new phase we considered all the diffraction peaks observed at 31.5 GPa and analysed using CRISFIRE and Chekcell software. Our analysis shows the best solution to be a monoclinic phase with $P2_1/m$ (space group: 11)
Table 1. Lattice parameter of the monoclinic phase using CRISFIRE and Chekcell software

| Lattice parameter | Value   |
|-------------------|---------|
| $a$(Å)            | 6.922   |
| $b$(Å)            | 6.286   |
| $c$(Å)            | 5.003   |
| $\beta$(Degree)  | 113.91° |

It is interesting to note that the high pressure phase transition in A-type La$_2$O$_3$ was reported to be at ~18 GPa whereas our investigation shows phase transition in case of Nd$_2$O$_3$ takes place at ~27 GPa. The bulk modulus of the hexagonal phase of Nd$_2$O$_3$ has been found to be 135.6 GPa using Birch-Murnaghan equation of state (Fig. 3) which is also higher than that of La$_2$O$_3$ (113 GPa). This suggests that the stability region of hexagonal phase increases with the increasing Ln atomic number or in other words with decreasing cation radii. This observation is similar to the behaviour of cubic to hexagonal phase transition observed in other rare-earth sesquioxides with further smaller cation radii.

Figure 3. EOS of hexagonal (Type-A) phase of Nd2O3

4. Conclusion
Our EDXRD and Raman measurements show that Nd$_2$O$_3$ transforms to a lower symmetry phase at ~27 GPa. As observed in La$_2$O$_3$ this could be due to the relatively different bond length compressibility of the two RE-O bonds in the hexagonal structure. However the high pressure structure may not be similar to the superlattice hexagonal structure conjectured in case of La$_2$O$_3$. Our structural analysis suggests the high pressure phase of Nd$_2$O$_3$ to be of monoclinic symmetry. Further high pressure experiments based on high resolution angle dispersive x-ray diffraction measurements might give further insight into the new phase of Nd$_2$O$_3$.

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