

## Phase progression via phonon modes in lanthanide dioxides under pressure

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### ABSTRACT

The present paper reports the phase progression in nano-crystalline oxides PrO<sub>2</sub> and CeO<sub>2</sub> up to pressures of 49 GPa and 35 GPa, respectively, investigated via in situ Raman spectroscopy at room temperature. The samples were characterized at ambient conditions using X-ray diffraction (XRD), AFM, and Raman spectroscopy and were found to be cubic with fluorite structure. With an increase in applied pressure the cubic bands were seen to steadily shift to higher wavenumbers for both the samples. However, we observed the appearance of a number of new peaks around a pressure of about 34.7 GPa in CeO<sub>2</sub> and 33 GPa in PrO<sub>2</sub> which were characteristic of an orthorhombic  $\alpha$ -PbCl<sub>2</sub> type structure. The mode Gruneisen parameters for both the phases were obtained from the pressure dependence of frequency shifts. On decompression, the high pressure phase existed down to a total release of pressure.

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### 1. Introduction

Among the lanthanide dioxides, the rare earth oxide CeO<sub>2</sub> or ceria, has been the subject of intense theoretical and experimental study. Ceria is a hard material with a relatively high dielectric constant ( $\epsilon = 26$ ) and a wide band gap. It is widely applied in glass, ceramics and catalyst manufacture [1–3]. Similarly, PrO<sub>2</sub> is an insulator, isostructural with UO<sub>2</sub> and has an anomalously small ordered moment in the anti-ferromagnetic phase [4]. It is one of the key materials in the investigation of intermediate valence state and for high energy spectroscopic studies of PrBCO and related materials [5]. For microelectronics, oxides on single crystalline silicon systems are considered as highly functional buffer oxide structures to achieve the global integration of alternative semiconductors on Si engineered silicon wafers, e.g. Ge/PrO<sub>2</sub> [6], InP/Gd<sub>2</sub>O<sub>3</sub> [7].

Further, due to perfect match in crystal lattice with that of a Si single crystal, CeO<sub>2</sub> has also been studied as a promising candidate to act as a crystalline insulator layer in the silicon-on-insulator structure (SOI) epitaxial structures [8–10]. Cerium is known for its oxygen storage capacity, i.e. it can easily take up and release oxygen under oxidizing and reducing conditions, respectively [11]. Cerium doped glass is used to block out UV light for medical glass ware and

aerospace windows and also to prevent polymers from darkening in sunlight. It is applied to optical components to improve performance. Nano crystalline cerium oxide has applications in coating technology, e.g. wood coating industry. CeO<sub>2</sub> nano-particles are very effective in terms of UV filtration. Recently it has been discovered that its nanoparticles are also useful in Glaucoma treatment.

These lanthanide dioxides, LnO<sub>2</sub>, have a cubic fluorite structure at ambient conditions. Generally cubic calcium fluorite (CaF<sub>2</sub>) with space group  $Fm\bar{3}m$  ( $O_h^5$ ) and  $\alpha$ -PbCl<sub>2</sub> orthorhombic phase with space group  $Pnma$  ( $D_{2h}^{16}$ ) are two different phases of these lanthanide dioxides [12–14]. They are primarily perceived in (CaF<sub>2</sub>) structure with four praseodymium/cerium and eight oxygen atoms per unit cell. The structure consists of a simple cubic oxygen sub-lattice with the Ce/Pr ions occupying alternate cube centres. Normally, the oxygen ions have a formal charge of  $-2$ ; the anions are tetrahedrally coordinated to the Ce/Pr ions and octahedrally coordinated to the surrounding oxygen atoms. The Ce/Pr ions have a charge of  $+4$ .

Recently, the crystallographic data for the high pressure phase of PrO<sub>2</sub> has been reported [15]. In the orthorhombic structure the Ce/Pr ions are ninefold coordinated and the oxygen ions show either tetrahedral or square pyramidal coordination spheres.

The dynamics of Pr/CeO<sub>2</sub> under pressure are interesting because they can be related to the systematics of the high pressure behaviour of the lanthanides and actinide dioxides/fluorite type compounds. High pressure Raman study on alkaline-earth difluorides (CaF<sub>2</sub>, SrF<sub>2</sub> and BaF<sub>2</sub>) has shown that they undergo a cubic

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to orthorhombic phase transformation at elevated pressures, i.e. at 8.3, 5.0, and 2.3 GPa, respectively [16–18]. Cerium oxide has the same type of structure as the difluorite and has been found to transform into the orthorhombic  $\alpha$ -PbCl<sub>2</sub> type structure (space group  $Pnma$  ( $D_{2h}^{16}$ )) at elevated pressures [14,19–22]. The high pressure Raman studies on CeO<sub>2</sub> [19] have indicated that a distinct pressure induced phase transition occurs at around 31 GPa and the high pressure spectra are consistent with the lower symmetry  $\alpha$ -PbCl<sub>2</sub> structure [22].

High pressure studies on various nano-oxides have been shown to indicate that a decrease in particle size significantly changes the transition pressure and compressibility. In addition, novel properties of nanosized materials make for an interesting study of their high pressure behaviour. A large variation in the transition pressure has been reported while going from micro to nano-size in various materials. Previous studies on nano-CeO<sub>2</sub> also indicate a decrease in phase transformation pressure to 22–26 GPa [2,3,21]. Further, the results reported indicate that the transformation is kinetically hindered and therefore sluggish and completes several GPa above the starting transition pressure. On the contrary, Ge et al. did not observe phase transition up to about 28 GPa in 5–6 nm nano-CeO<sub>2</sub> [22]. However, very limited high pressure experimental work has been conducted on PrO<sub>2</sub> [12,23,24]. High pressure phase transitions of PrO<sub>2</sub> and some other iso-structural fluorite type dioxide have been studied using the diamond anvil cell and laser heating [23], and pressure induced structural phase transition from cubic fluorite phase to an orthorhombic phase similar to that of ThO<sub>2</sub> has been reported.

In this context, we have carried out a high pressure Raman study of nano-crystalline CeO<sub>2</sub> and PrO<sub>2</sub> to investigate the range of pressure for the onset of the phase transition for these nano-crystalline materials. The high pressure Raman data for PrO<sub>2</sub> has not been reported previously to the best of our knowledge. Previously, ab-initio band structure calculations were also carried out using TB-LMTO calculations within local density approximation, to find the pressure-induced structural transitions and the stability of PrO<sub>2</sub> and CeO<sub>2</sub> in cubic and orthorhombic phases [25,26]. Theoretically, the cubic to orthorhombic transition was shown to occur at 41 GPa in PrO<sub>2</sub> and 47 GPa in CeO<sub>2</sub>.

## 2. Materials and methods

The PrO<sub>2</sub> and CeO<sub>2</sub> powders used in the present study were commercially prepared samples from Johnson Matthey Rare Earth Products, UK. The powders were used for the present study in the as-received state and not subjected to any pre-treatment and, as per the manufacturer claims, the common metal impurities are in ppm level.

The sample was characterized at ambient conditions using X-ray diffraction, atomic force microscopy, and Raman spectroscopy. The XRD of samples was carried out by Bruker Axs, Germany, D-8 Advance powder X-Ray Diffractometer using Cu K $\alpha$  ( $\lambda = 1.5404 \text{ \AA}$ ) radiation. A slow  $2\theta$  scan of 0.025 per second was done. Atomic force microscope (AFM) image of sample was obtained from a digital instrument of Veeco Metrology Group, Nanoscope IIIa under ambient conditions. The measurement was done in the tapping mode at a scanning rate of around 1 Hz using the standard silicon probe.

The Raman studies were carried out using an Ar<sup>+</sup> ion laser having wavelength of 514.5 nm, Model Innova 70, from Coherent, USA. The laser power on sample was kept at about 100 mW. The signal was attained using a single stage Jobin Yvon-Spex monochromator through an optical fibre cable. At the end of the monochromator a water cooled photomultiplier tube (PMT) is coupled for detecting the Raman signal. The obtained Raman spectrum was deconvoluted using Voigt fit.

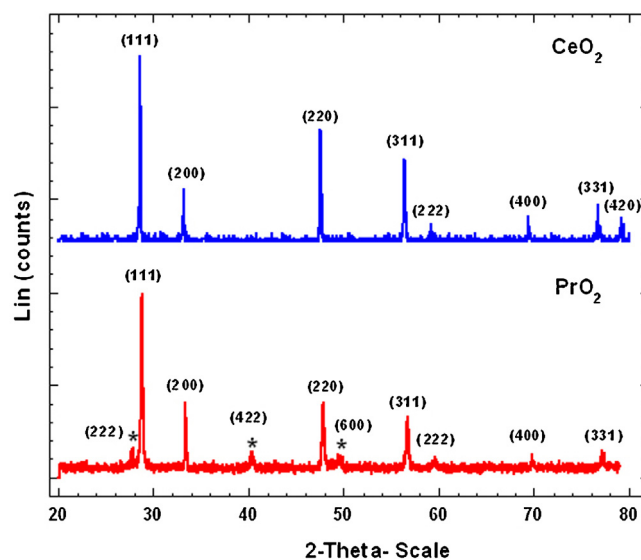


Fig. 1. X-ray diffraction patterns of CeO<sub>2</sub> and PrO<sub>2</sub> samples under study.

A Mao-Bell type diamond anvil cell DAC (Diacell Products, UK, Model B-05) with octagonal flats having about 400  $\mu\text{m}$  diameter culets was used to generate high pressure. The sample was loaded in the drilled gasket hole along with a few small ruby chips (5–10  $\mu\text{m}$ ) for monitoring the pressure in Raman experiments, from the wavelength shifts of its fluorescence peaks. The pressure transmitting medium used was methanol:ethanol in the ratio of 4:1.

## 3. Results at ambient conditions

The cubic fluorite structure for these samples was confirmed by X-ray diffraction and the particle size analysis was done in conjunction with AFM. The X-ray diffraction patterns in Fig. 1 show that both the samples have a cubic structure with space group  $Fm\bar{3}m$  (no. 225). The observed diffractions peaks for CeO<sub>2</sub> agree very well with the JCPDS data card no. 34-0394 while those of PrO<sub>2</sub> shown in Fig. 1 agree with the JCPDS data card no. 24-1006. However, a few additional peaks were also observed in PrO<sub>2</sub> which showed that the sample also had Pr<sub>4</sub>O<sub>7</sub> or PrO<sub>1.75</sub> in small quantities. The particle size was estimated using the X-ray diffraction data and the Debye Scherrer relation. The average particle size was thus estimated to be about 36 nm for CeO<sub>2</sub> and about 60 nm for PrO<sub>2</sub>.

Fig. 2(a and b) shows the 3-D atomic force micrographs of the samples i.e. CeO<sub>2</sub> and PrO<sub>2</sub> respectively. The average particle size was estimated to be  $32 \pm 10 \text{ nm}$  and  $71 \pm 10 \text{ nm}$  respectively for CeO<sub>2</sub> and PrO<sub>2</sub>. Hence it is clearly established that the samples under study are nano-crystalline in nature. The difference in the particle size estimated by XRD and AFM come about as XRD gives an overall average effect while AFM calculation are usually based on averaging over a small area of the sample. In addition the difference also incorporates the uncertainty of the measurement using AFM.

Fig. 3 shows the Raman spectrum at ambient conditions for CeO<sub>2</sub> and PrO<sub>2</sub>. The Raman spectrum of CeO<sub>2</sub> at ambient conditions is cubic in nature and an intense first order Raman peak [27,28] (fluorite peak – F<sub>2g</sub> mode) occurs at  $465 \text{ cm}^{-1}$ . In Ceria the first order Raman active mode is the triply degenerate symmetrical stretching vibration of the CeO<sub>8</sub> vibrational unit at  $\sim 465 \text{ cm}^{-1}$ . Only the oxygen atoms move in this mode, which is therefore very sensitive to the oxygen sub-lattice disorder resulting from processing and/or grain-size-induced non-stoichiometry. Group theory predicts the triply degenerate Raman active optical phonon of  $\Gamma_{25}$  symmetry,

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