

## A high pressure Raman study of ThO<sub>2</sub> to 40 GPa and pressure-induced phase transition from fluorite structure

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**Abstract.** The pressure dependence of the first-order Raman peak and two second-order Raman features of ThO<sub>2</sub> crystallizing in the fluorite-type structure is investigated using a diamond anvil cell, up to 40 GPa. A phase transition from the fluorite phase is observed near 30 GPa as evidenced by the appearance of seven new Raman peaks. The high pressure phases of ThO<sub>2</sub> and CeO<sub>2</sub> exhibit similar Raman features and from this it is believed that the two structures are the same, and have the PbCl<sub>2</sub>-type structure. The pressure dependence  $d\omega/dP$  of the observed phonons and their mode Grüneisen parameters are similar to the isostructural CeO<sub>2</sub>. The observed second-order Raman features are also identified from the calculated phonon dispersion curves for ThO<sub>2</sub>.

**Keywords.** High pressure Raman spectra; pressure-induced phase transition; thorium dioxide; fluorite structure.

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### 1. Introduction

Several transition and rare earth metal dioxides crystallize in the cubic fluorite structure (Linares 1967). Their stability and behaviour at high pressure are of much interest not only to materials science but also are relevant to geophysical aspects of high pressure research (Liu 1980). Silicon dioxide (SiO<sub>2</sub>), an important constituent of the earth's interior, is expected to undergo a transition to the fluorite structure, and then on to denser phases at the high pressure and temperature conditions prevailing in the lower mantle region (Syono and Akimoto 1968; Liu 1979). In fact, PrO<sub>2</sub>, CeO<sub>2</sub>, TbO<sub>2</sub>, UO<sub>2</sub> and ZrO<sub>2</sub> have all been subjected to a few hundred kbar pressure and high temperature in the neighborhood of 1000°C in laser-heated diamond anvil cell, as cases relevant to an understanding of the high pressure polymorphism of SiO<sub>2</sub> (Liu 1980). X-ray diffraction studies on these oxides quenched from high pressure-high temperature conditions have indicated phase transitions, and it has been suggested (Liu 1980) that the high pressure phases may have the so-called cottunite (PbCl<sub>2</sub> type), or a distorted cottunite structure.

The stability of fluorite-type (cubic) structure against pressure has been investigated by high pressure Raman spectroscopy in alkaline earth difluorides and PbF<sub>2</sub> (Kessler *et al* 1974; Kourouklis and Anastassakis, 1987) and phase transitions to the PbCl<sub>2</sub> structure have been reported. We recently investigated CeO<sub>2</sub> by high pressure Raman spectroscopy (Kourouklis *et al* 1987) and found a pressure-induced phase

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