

A high pressure Raman study of ThO₂ 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 ThO₂ 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 ThO₂ and CeO₂ exhibit similar Raman features and from this it is believed that the two structures are the same, and have the PbCl₂-type structure. The pressure dependence $d\omega/dP$ of the observed phonons and their mode Grüneisen parameters are similar to the isostructural CeO₂. The observed second-order Raman features are also identified from the calculated phonon dispersion curves for ThO₂.

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 (SiO₂), 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, PrO₂, CeO₂, TbO₂, UO₂ and ZrO₂ 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 SiO₂ (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 (PbCl₂ 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 PbF₂ (Kessler *et al* 1974; Kourouklis and Anastassakis, 1987) and phase transitions to the PbCl₂ structure have been reported. We recently investigated CeO₂ by high pressure Raman spectroscopy (Kourouklis *et al* 1987) and found a pressure-induced phase

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transformation at 31 GPa. The high pressure phase was metastable over a 20 GPa range, but reverted suddenly below 11 GPa, to the fluorite phase. By comparing the new Raman spectrum of CeO_2 with the high pressure phases of alkaline earth difluorides we (Kourouklis *et al* 1987) concluded that the high pressure phase of CeO_2 is very likely to be the PbCl_2 type.

In view of the close similarity in physical properties between CeO_2 and ThO_2 , we felt that it would be worthwhile investigating ThO_2 under high pressure by Raman spectroscopy. We find that the fluorite phase of ThO_2 also transforms near 30 GPa to another phase, as evidenced by the appearance of new Raman peaks in the spectrum. We observed two features in the second-order spectrum of ThO_2 in the diamond cell and were able to record the effect of pressure on them up to 7 GPa. These results are presented and discussed in this paper.

2. Experiment

Flux grown single crystals of ThO_2 (3–4 mm in linear dimensions and 0.5 mm in thickness) were available. The crystals were very clear but had a light brownish colour. For mounting inside the diamond cell, small platelets of about 30 to 100 μ in linear dimensions and about 30 to 50 microns in thickness could easily be obtained, for the crystals easily cleavable.

Pressure was generated using a gasketed diamond anvil cell (Jayaraman 1986) and measured using the well-known ruby fluorescence technique (Barnett *et al* 1973). The diamonds had 0.6 mm flats and we used full-hard tempered stainless steel 301 indented gaskets with a 150–200 μ diameter hole, and an indented thickness of 75 μ . With well-centered gasket hole, pressures close to 40 GPa could be reached. For pressure medium 4:1 methanol-ethanol mixture was used in some loadings, while in others high pressure (2 kbar) argon gas was loaded into the cell to serve as the pressure medium for the higher pressure range. The results obtained with the two pressure media in the region of overlap were consistent.

The Raman measurements were carried out with a Spex double monochromator provided with conventional photon counting system. For excitation the 488 nm laser line from an Ar^+ laser was used at power levels, ranging from 30–40 mW for recording the first-order, and 100–150 mW to record the second-order spectrum. We also tried the 514.5 nm line, but found that the sample exhibited several fluorescence bands in the second-order region. However, with 488 nm excitation this problem did not exist.

3. Results

The fluorite Raman peak and the two features observed in the second-order Raman spectral region are shown in figure 1 for three different pressures. The fluorite Raman peak is at 465 cm^{-1} at 1 atmosphere pressure and increases in frequency at the rate of $d\omega/dP = 3.3 \text{ cm}^{-1}/\text{GPa}$. The two second-order features shown also shift to higher frequency with pressure. The pressure dependence of the first-order Raman peak (fluorite-peak) as well as the observed second-order peaks is plotted in figure 2.

Up to 30 GPa, only the fluorite Raman peak is observed. At higher pressures several weak Raman features appear, indicating a phase transition. These additional Raman

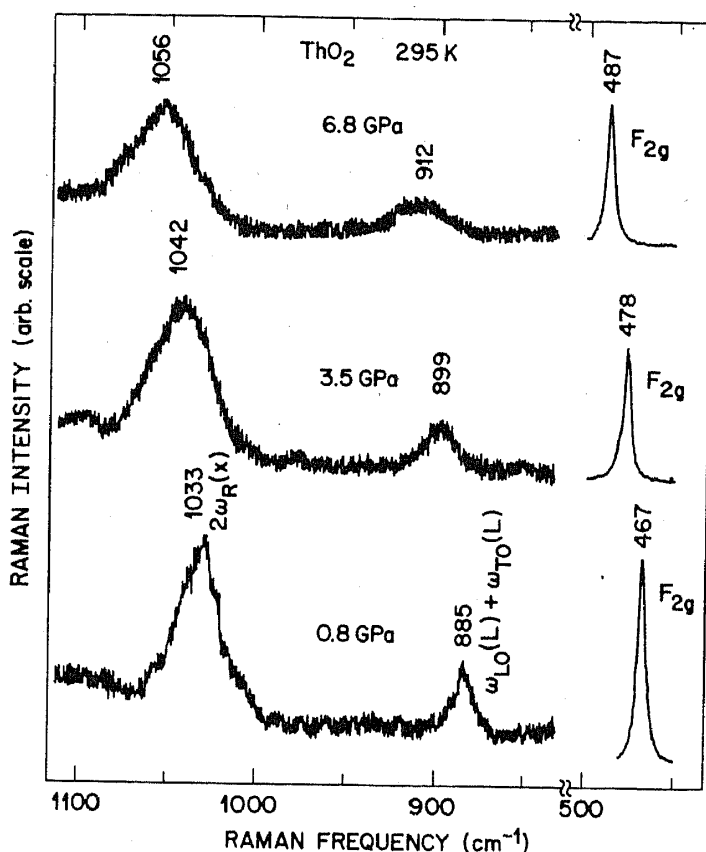


Figure 1. Raman spectrum of ThO_2 at three pressures. The sharp peaks to the extreme right are the fluorite-phase Raman peaks and the peaks to the left are the observed second-order Raman peaks which we label as $\sim 1030 \text{ cm}^{-1} 2\omega_R(x)$ and $\sim 880 \omega_{LO}(L) + \omega_{TO}(L)$.

peaks appear to gain in intensity at higher pressures, evidently due to the growth of the high pressure phase out of the fluorite phase. On releasing pressure, the Raman peaks of the high pressure phase persist down to 10 GPa, whereupon they suddenly disappear; only the fluorite Raman peak is observed below 10 GPa. The effect of pressure on the Raman spectra of ThO_2 is presented in figure 3, in which the open circles are the data points obtained on the increasing pressure cycle, and the filled circles on the decreasing pressure cycle. The dashed line marks the transition pressure from the fluorite phase.

4. Discussion

Thorium dioxide, ThO_2 , crystallizes in the cubic fluorite-type lattice (Linares 1967) and belongs to the space group O_h^5 ($\text{Fm}\bar{3}\text{m}$). Group theory predicts one triply degenerate Raman active optical phonon of Γ_{25} symmetry (F_{2g}) and two infrared active phonons of Γ_{15} symmetry (F_{1u}) corresponding to the LO and TO modes. Therefore, the first-order Raman spectrum of ThO_2 is very simple and consists of only one Raman line. To interpret the second-order Raman spectrum it is necessary to have the dispersion curves of the ThO_2 crystal. This has been calculated (Ishigame and Kojima 1976) using the Born-von Karman model and the experimentally

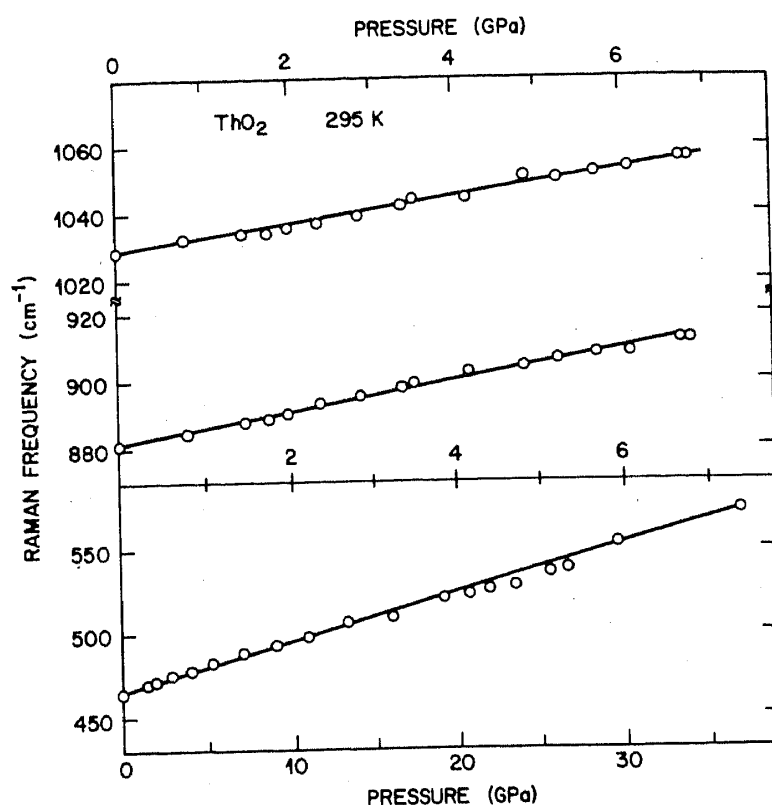


Figure 2. Pressure dependence of the first-order fluorite Raman peak (bottom) and the two second order peaks (top-two curves). Note the different pressure scales.

determined elastic constants (Anderson 1970), and the three vibrational frequencies ω_R , ω_{T0} and ω_{L0} (Axe and Pettit 1966). In the second-order Raman spectrum, overtones of these frequencies and of the zone boundary phonons, as well as combination and difference frequencies at each wave vector q are allowed. With nine phonon branches there are 45 two-phonon modes possible. Assuming that most of the critical points are at the high symmetry points of the Brillouin zone, the two-phonon dispersion curves have been constructed and presented by Ishigame and Kojima (1976). The latter authors have recorded the second-order spectrum of ThO₂ and have assigned the features in this spectra with the help of calculated frequencies of Raman active combinations and overtones, at the three symmetry points Γ , M and L points in the Brillouin Zone, and selection rules for the Raman process.

Ishigame and Kojima (1976) were able to see half a dozen features in their second-order spectra, of which the three prominent ones were near 1136 cm^{-1} , 934 cm^{-1} and 558 cm^{-1} . These were assigned to $2\omega_{L0}$, $2\omega_R$ and $2\omega_{T0}$. We had hoped to see these phonons in the diamond cell, but the two phonons we have observed are at 880 cm^{-1} and 1030 cm^{-1} . These would correspond to $2M_5$ ($2\omega_R(X)$) and $L_1 + L_3$ ($\omega_{L0}(L) + \omega_{T0}(L)$) according to Ishigame and Kojima (1976) and Kojima's assignment. Surprisingly, we were not successful in recording the $2\omega_{L0}$ or the $2\omega_R$ which appear strongly in the second-order spectra of the latter authors. The pressure dependence of the two observed features is shown in figure 2 and given in table 1.

In the same table the pressure Raman data for ThO₂ are compared with CeO₂. In fact the pressure dependence of the ω_R for the two materials is almost identical.

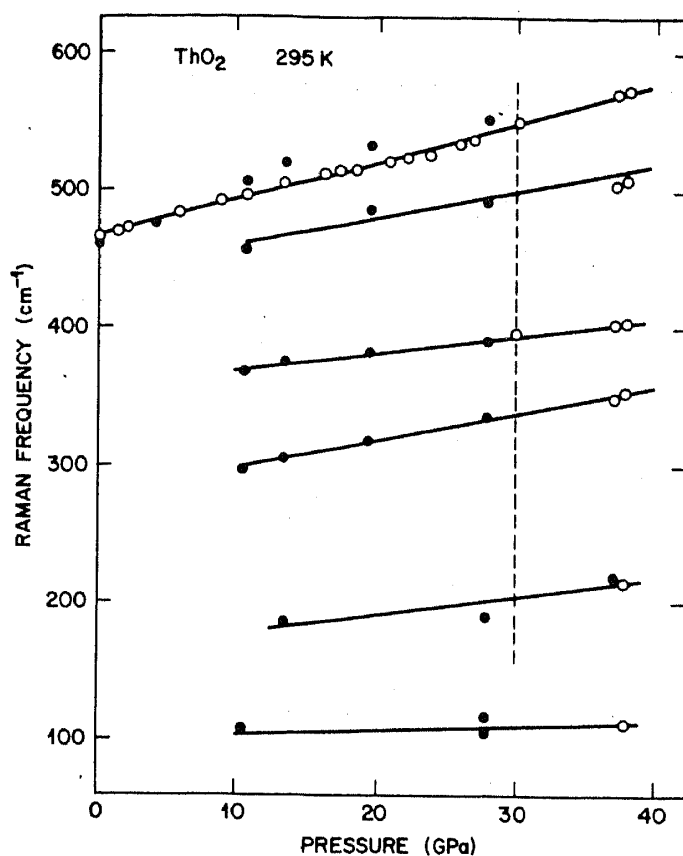


Figure 3. Effect of pressure on the Raman peaks of the fluorite phase and the high pressure phase. Phase transition near 30 GPa is marked by the dashed vertical line; open circles represent data taken on the increasing pressure cycle and filled circles are data for decreasing pressure cycle. Note the large region of metastability for the high pressure phase.

In evaluating the Grüneisen parameter for CeO₂ we had assumed the bulk modulus B of ThO₂, which was obtained from the elastic constant data (Anderson 1970). If the strong similarity in the behaviour of the F_{2g} phonon (ω_R) between the two materials is extended to the F_{1u} phonons (ω_{L0} and ω_{T0}) the same pressure behaviour as that of CeO₂ could be assumed for ThO₂ for the latter two phonons.

Table 1. A comparison of the effect of pressure on the first- and second-order phonons in ThO₂ and CeO₂.

| First-order | | | | Second-order | | |
|------------------|---------------------------------|---|----------|---------------------------------|---|------|
| | ω (cm ⁻¹) | $d\omega/dP$ (cm ⁻¹ /GPa) | γ | ω (cm ⁻¹) | $d\omega/dP$ (cm ⁻¹ /GPa) | |
| ThO ₂ | 465(ω_R) | 3.33 | 1.46 | ~ 1030 | $2\omega_R(X)$ | 3.75 |
| | 567(ω_{L0}) | — | — | ~ 880 | $\omega_{L0}(L) + \omega_{T0}(L)$ | 4.68 |
| | 279(ω_{T0}) | — | — | | | |
| CeO ₂ | 466(ω_R) | 3.29 | 1.44 | 580 | $\omega_{T0}(X) + LA(X)$ | 5.4 |
| | 585(ω_{L0}) | 4.2 | 1.5 | 660 | $\omega_R(X) + LA(X)$ | 7 |
| | 275(ω_{T0}) | — | — | 880 | $\omega_{L0} + \omega_{T0}$ | 5 |
| | | | | 1030 | $2\omega_R(X)$ | 4.6 |
| | | | | 1160 | $2\omega_{L0}$ | 12 |

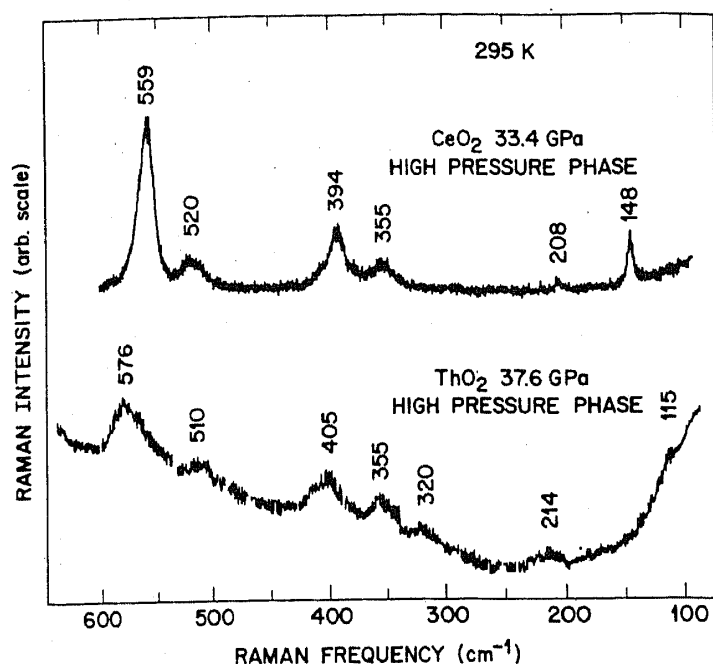


Figure 4. The Raman spectrum of the high pressure phases of ThO_2 (bottom) and CeO_2 (top) compared.

4.1 Phase transition

The one-peak fluorite-phase Raman spectrum of ThO_2 becomes complex at pressures above 30 GPa and we ascribe this to a pressure-induced structural phase transition. The Raman spectrum of the high pressure phases of CeO_2 and ThO_2 is compared in figure 4 and the similarities are quite striking. We therefore believe that the two high pressure phases have a similar structure.

From an X-ray diffraction study of the ThO_2 quenched from high pressure-high temperature conditions, Liu (1980) has suggested a phase transition from the fluorite to an orthorhombic phase. Further, the latter author (Liu 1980) has proposed the Ni_2Si type structure for this phase; in Ni_2Si , Si is ten-fold coordinated and hence it would be a coordination increase from eight to ten-fold. However, our view is that the high pressure phases of CeO_2 and ThO_2 are similar and suggest the PbCl_2 type structure as the most likely phase for both of them. It is possible that the quenched material has a structure different from that of the structure at high pressure. Again, an insitu high pressure X-ray diffraction study may be expected to give a definitive answer on this point.

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