High-pressure phase behavior and equations of state of ThO₂ polymorphs

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ABSTRACT

ThO₂ is an important material for understanding the heat budget of Earth’s mantle, as well as the stability of nuclear fuels at extreme conditions. We measured the in situ high-pressure, high-temperature phase behavior of ThO₂ to ~60 GPa and ~2500 K. It undergoes a transition from the cubic fluorite-type structure (thorianite) to the orthorhombic α-PbCl₂ cotunnite-type structure between 20 and 30 GPa at room temperature. Prior to the transition at room temperature, an increase in unit-cell volume is observed, which we interpret as anion sub-lattice disorder or pre-transformation “melting” (Boulfelfel et al. 2006). The thermal equation of state parameters for both thoriumate [\(V₀ = 26.379(7), K₀ = 204(2), a₀K₁ = 0.0035(3)\)] and the high-pressure cotunnite-type phase [\(V₀ = 24.75(6), K₀ = 190(3), a₀K₁ = 0.0037(4)\)] are reported, holding \(K₁\) fixed at 4. The similarity of these parameters suggests that the two phases behave similarly within the deep Earth. The lattice parameter ratios for the cotunnite-type phase change significantly with pressure, suggesting a different structure is stable at higher pressure.

Keywords: XRD data, ThO₂, Raman spectroscopy, ThO₂ phase transition, high-pressure studies, diamond-anvil cell, high-temperature studies, laser-heating

INTRODUCTION

Actinides, specifically U and Th, are important in the Earth as long-lived radioactive heat producing elements. Assuming the refractory lithophile element budget of the bulk silicate Earth is chondritic in composition, these elements produce up to 36% of the total heat fluxed out of the planet’s surface, but their distribution and role within the dynamics of the deepest part of Earth’s mantle is unknown (McDonough and Sun 1995). These elements are highly refractory (ThO₂ has the highest melting temperature of any oxide at ambient pressures at 3663 K) and nominally incompatible in major mantle minerals, meaning they tend to partition into melts or accessory phases, which makes them excellent tracers for chemical reservoirs in the deep Earth as well as within other planetary bodies (Arevalo et al. 2009; Fonseca et al. 2014). Additionally, U and Th and their oxides are increasingly important as nuclear energy sources for our growing population and they are used in thermally resistant ceramics (Cuney 2013). However, stable materials that resist decomposition or amorphization under varying pressure, temperature, and radiation conditions are needed to contain and immobilize the resulting waste from this industrial usage. Actinide-bearing minerals that are stable under various thermodynamic conditions can point to analogous materials that are stable at ambient conditions. Thus, exploring the mineralogy of actinide-bearing minerals at the extreme pressure and temperature conditions of Earth’s mantle (tens of gigapascals and thousands of Kelvin) is universally important. This paper focuses on the high-pressure, high-temperature phase behavior and equations of state of the simplest Th-bearing mineral, ThO₂.

End-member ThO₂ (thorianite) takes the cubic fluorite-type (CaF₂, \(Fm\bar{3}m\)) structure at ambient conditions (Fig. 1a). Room-temperature X-ray diffraction (XRD) studies show that upon compression this material undergoes a reconstructive phase transition to the orthorhombic cotunnite-type structure (\(\alpha\)-PbCl₂, \(Pnma\)) (Fig. 1b) (Dancausse et al. 1990; Idiri et al. 2004; Jayaraman et al. 1988; Olsen et al. 2004). This phase transition results in an increase in coordination number of the Th cation, from eightfold (cubic) in the fluorite-type structure to ninefold in the cotunnite-type structure. At room temperature, this phase transition is kinetically inhibited, with the high-pressure phase first appearing between 30–40 GPa, and coexisting with the metastable low-pressure phase until 55–57 GPa when the transition is observed to be complete. Because of this sluggishness, the precise position of the equilibrium phase boundary is not well constrained.

Materials in the fluorite-type structure, including ThO₂, have been shown to undergo a “superionic” transition at about 80% the melting temperature of the material, whereby a critical concentration of Frenkel defects occur in the crystal, resulting in anion sub-lattice “melting” (Clauset et al. 1989; Kuksin and Smirnova 2014; Kupryazhkin et al. 2011; March et al. 1980; Matveev and Veshchunov 1997). This transition includes an exponential increase in the enthalpy and specific heat of the material. One computational study has suggested that this transition also occurs at ambient temperature under increasing pressure in the type specimen of fluorite, CaF₂ (Boulfelfel et al. 2006). In this case,
**Figure 1.** (a) Fluorite crystal structure. (b) Cotunnite-type crystal structure. Green spheres represent the Th⁴⁺ cations, red spheres represent the O²⁻ anions. (Color online.)

The formation of a Frenkel defect, in which a F⁻ anion shifts from its tetrahedral site to a previously empty octahedral site, allowing another F⁻ anion to take its place, locally expands the lattice and allows the Ca cations to subsequently shift to their new crystallographic position in the cotunnite-type structure at high pressures.

Previous experiments have shown that phase transitions in similar systems, such as some of the rare Earth pyrochlore (A₂Zr₂O₇)-defect-fluorite [(A,Zr)₂O₇] zirconate materials, which often undergo either amorphization or structural transition to the (defect) cotunnite-type structure under pressure, exhibit anomalous volume expansion just prior to the phase transition (Rittman et al. 2017; Zhang et al. 2010). However, this volume expansion has not been recognized universally in other pyrochlore systems (Li et al. 2016; Rittman et al. 2017). It is likely that the anions in these more complicated pyrochlore compounds are undergoing a similar distortion to the one described above for CaF₂, although it may be dependent upon the relative radii of the cations in the A and B sites (Rittman et al. 2017). A recent Raman spectroscopy study on bulk ThO₂ under pressure has suggested that this material also experiences anion sub-lattice disorder at high pressures (Kamali et al. 2017). It was recognized in that study that one Raman mode appeared within the ThO₂ spectrum at ~25 GPa as shoulder on the F₂ₐ mode of fluoride-type ThO₂, approximately 10 GPa lower than the rest of the cotunnite-type modes appeared in the spectrum (~37 GPa). This mode is thought to signal anion disorder since the F₂ₐ mode results from the breathing of O anions around the Th cation, thus it is only sensitive to movements of the O atoms. UO₂ also exhibits shoulders on the F₂ₐ peak, which are thought to be related to anion sub-lattice disorder, but in this case the disorder may be enhanced due to a slight excess of O in the structure (hyperstoichiometry) (Crowhurst et al. 2015).

The thermo-elastic parameters (e.g., bulk modulus, K, and thermal expansion, α) of this material are necessary for describing its thermodynamic behavior at extreme conditions of pressure and temperature. Recent measurements (XRD, ultrasonic) and calculations of the ambient-pressure isothermal bulk modulus (K₀) of pure thorianite at 300 K are consistent around 185–198 GPa with a pressure derivative (dK/dP = K₀′, where relevant) of ~5 (Boettger 2009; Boudjemline et al. 2011; Idiri et al. 2004; Kanchana et al. 2006; Li et al. 2014; Macedo et al. 1964; Olsen et al. 2004; Shein et al. 2007; Wang et al. 2010). Earlier XRD studies resulted in much higher values of K₀ and K₀′ (262 GPa and 6.7, respectively, Dancausse et al. 1990), while an inelastic X-ray scattering experiment and a different series of calculations predicted K₀′ values around 220 GPa (Claussen et al. 1989; Kanchana et al. 2006; Li et al. 2002; Olsen et al. 2004; Sevik and Çağın 2009). These results are summarized in Table 1. To date, no experimental studies have reported on the behavior of this material at simultaneous high pressures and high temperatures or on the equation of state of the high-pressure cotunnite-type

![ThO₂ crystal structure](image)

**Table 1.** Measured and calculated equation of state parameters for the polymorphs of ThO₂

<table>
<thead>
<tr>
<th>V₀ (cm³/mol)</th>
<th>K₀ (GPa)</th>
<th>K₀′</th>
<th>αK₀ (GPa/K)</th>
<th>Reference</th>
<th>Method</th>
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<tr>
<td><strong>Thorianite</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26.37(7)</td>
<td>204 (2)</td>
<td>4</td>
<td>0.0035(3)</td>
<td>This study</td>
<td>LH-DAC</td>
</tr>
<tr>
<td>26.44</td>
<td>198 (2)</td>
<td>4.6 (3)</td>
<td></td>
<td>Idiri et al. 2004</td>
<td>RT-DAC</td>
</tr>
<tr>
<td>26.39</td>
<td>262 (4)</td>
<td>6.7 (5)</td>
<td></td>
<td>Dancausse et al. 1990</td>
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</tr>
<tr>
<td>25.36</td>
<td>195 (2)</td>
<td>5.4 (2)</td>
<td></td>
<td>Olsen et al. 2004</td>
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<td>25.60</td>
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<td>FP-LMTO-LDA</td>
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<td>25.68</td>
<td>189</td>
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<td>28.8</td>
<td>191</td>
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<td>25.32</td>
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<td>26.76</td>
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<td>Kelly and Brooks 1987</td>
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<td>Shein et al. 2007</td>
<td>FLAPW</td>
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<td>24.75(6)</td>
<td>190 (3)</td>
<td>4</td>
<td>0.0037(4)</td>
<td>This study</td>
<td>LH-DAC</td>
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<td>25.07</td>
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<tr>
<td>26.55</td>
<td>163.2</td>
<td>6.19</td>
<td></td>
<td>Boudjemline et al. 2011</td>
<td>GGA</td>
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<tr>
<td><strong>Cotunnite-type ThO₂</strong></td>
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</table>

Notes: Bold values were held fixed in the fitting procedure. LH = laser-heated; RT = room temperature; FP = full potential; PAW = projector-augmented wave method; PBE = Perdew-Burke-Ernzerhof functional; LCGTO-FF = linear combinations of Gaussian type orbitals-fitting function; LMTO = linear muffin-tin orbital method; LDA = local density approximation; GGA = general gradient approximation; ASA = atomic-sphere approximation; INS = inelastic neutron scattering. This table was adapted from Olsen et al. (2004).
phase. Calculations of the elastic parameters of the high-pressure phase are inconsistent, ranging in values between $K'_{\text{T}} = 148–207$ and $K''_{\text{T}} = 4.2–7.8$ (Boettger 2009; Boudjellene et al. 2011; Li et al. 2014; Wang et al. 2010). In this study, we conducted in situ XRD measurements of ThO$_2$ to ~60 GPa and ~2500 K to more precisely define the thorianite–cotunnite-type phase boundary and to measure the thermal equation of state parameters for both the low- and high-pressure phases of this material.

**Synchrotron X-ray Diffraction and Raman Spectroscopy Experiments**

Four synchrotron powder X-ray diffraction (XRD) experiments on ThO$_2$ were conducted in the laser-heated diamond-anvil cell (LH-DAC), with diamond culets of 300 or 250 μm. ThO$_2$ (99.99%) was purchased from Strem Chemical. The ThO$_2$ starting material was characterized by an ambient condition XRD measurement at the University of Chicago using incident radiation of $\lambda = 1.5418 \text{ Å}$ (CuKα) and Si powder (NBS 640a) as an X-ray standard. In high P-T experiments, amorphous Pt (Alfa Aesar, 0.2–1.6 μm, 99.9%) was mixed with the ThO$_2$ as an absorber for laser heating. The ThO$_2$-Pt mixture was loaded as a powder between flakes of KCl (reagent grade, Alfa Aesar) or KBr (scintillation grade, Alfa Aesar), which acted as the pressure medium, thermal insulator and pressure standard in the high-temperature experiments (Dewaele et al. 2012). Sample B12 was measured at room temperature using cryogenically loaded Ar as the pressure medium and pressure standard (Ross et al. 1986). A 3% uncertainty was assigned to the accuracy of the Ar pressure standard.

Following safety regulations for radiogenic samples at the Department of Energy facilities where these measurements were made, experiments used double containment to prevent accidental environmental contamination or dispersal. The gasket and diamonds provided the first layer of containment. For the second layer of containment, the DACs were securely wrapped in Kapton (polyimide) tape around the diameter of the cell. In the laser-heating path, thin (0.5 mm) sapphire windows (6.35 mm diameter, Edmund Optics) were adhered to the outside of the diamond seat by epoxy. The sapphire windows typically resulted in several large and distinctive X-ray diffraction spots on the detector, which were masked during data analysis.

Room-temperature angle-dispersive powder XRD experiments were performed at sector 12.2.2 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, using a monochromatic incident X-ray beam ($\lambda = 0.4959 \text{ Å}$) of ~10 μm in diameter. High-temperature XRD experiments were conducted at sector 13-ID-D (GSE-CARS) of the Advanced Photon Source (APS), Argonne National Laboratory, using a monochromatic incident X-ray ($\lambda = 0.3344 \text{ Å}$) typically measuring ~3 × 4 μm. At both facilities, sample to detector distance and tilt were calibrated using LaB$_6$. High-temperature samples were compressed to a target pressure and laser heated while XRD measurements were simultaneously collected. The heating laser was co-aligned with the X-ray beam using the X-ray-induced fluorescence of the KCl or KBr insulator. Laser-heating was done from both sides of the sample, adjusting upstream and downstream laser power to balance the temperature. Surface temperatures were measured spectro-radiometrically using the Planck radiation function (Prakapenka et al. 2008), and corrected by ~3% to account for the axial temperature gradient across the sample (Campbell et al. 2007). The temperature of the alkali halide thermal insulator was estimated as the midpoint between the surface of the sample and the surface of the diamond anvil as described by Campbell et al. (2009).

Powder XRD patterns were collected on a CCD and azimuthally integrated to in-situ pressure versus 2θ (degrees) plots using DIOPTAS (Prescher and Prakapenka 2015). Lattice parameters as a function of pressure and temperature were determined by fitting reflection positions using PeakFit (Systat Software). At least one XRD pattern per heating cycle was fully indexed to confirm the space group and lattice parameters at each pressure step using GSAS-II (Toby and Von Dreele 2013) or DICVOL04 (Boultif and Louër 2004), which is part of the FULLProf Suite (Rodriquez-Carvajal 1993).

In addition to XRD measurements, the room-temperature phase behavior of ThO$_2$ was investigated using Raman spectroscopy in the Laboratory for Mineral Physics at the University of Chicago. Samples were prepared either as ThO$_2$ powder pressed between two MgO flakes, which acted as a Raman-inactive pressure-transmitting medium, or without a pressure medium. All samples were loaded in a steel gasket with an 80 μm sample chamber and 300 μm culet DAC. Measurements were taken using a 0.75 m Acton SpectraPro monochromator with a 473 mm 150 mW blue laser. Pressure was determined using the Raman shift of the diamond, which was calibrated to ruby under quasi-hydrostatic conditions after Akahama and Kawamura (2007). Raman acquisitions were centered at 712 cm$^{-1}$ to minimize nearby diamond Raman interference and were the average of 600 one-second exposures at full laser power.

Compression measurements began at 3–5 GPa and samples were incrementally brought to ~60 GPa before decompressing to ambient pressure. Raman mode frequencies were determined by peak fitting using PeakFit (Systat Software). The reported frequencies are an average of three individual fits and the reported uncertainty is the corresponding standard deviation.

**Results and Discussion**

Phase diagram ThO$_2$

The measured lattice parameters and pressure-volume-temperature ($P-V-T$) data points from the in situ XRD experiments are listed in Supplemental Table 1 (thorianite) and Supplemental Table 2 (cotunnite-type ThO$_2$). Ambient-pressure XRD measurement of the ThO$_2$ starting material confirmed an initial fluorite-type structure (Fig. 1a) with a lattice parameter of $a = 5.5958 \pm 0.0005 \text{ Å}$. The ambient-pressure XRD measurements at high pressure and room temperature demonstrate that thorianite exists in this fluorite-type structure until ~34 GPa, at which point new diffraction peaks appear between the (111) and (200) fluorite peaks, indicating the emergence of the cotunnite-type phase, illustrated in Figure 1b (Dancausse et al. 1990; Idiri et al. 2004; Jayaraman et al. 1988; Olsen et al. 2004). Figure 2 shows high-temperature examples of raw diffraction images and their corresponding integrated spectra (intensity vs. 2θ) for this phase transition, as well as a higher $P-T$ pattern containing only the cotunnite-type phase.

The fluorite–cotunnite phase transition requires a crystallographic reconstruction, which is characterized by a large degree of kinetic inhibition. With previous XRD measurements at room temperature, the fluorite-type phase was present up to the highest pressures achieved at room temperature in this study, ~54 GPa (Dancausse et al. 1990; Idiri et al. 2004; Olsen et al. 2004). This kinetic barrier has been previously observed in room-temperature compression studies using different techniques. Using Raman spectroscopy, Jayaraman et al. (1988) observed the initiation of...
the phase transition between 30 and 37 GPa, but did not reach high enough pressures to observe the disappearance of the fluorite-type phase. The slight differences in the observed transition pressure range in these studies (i.e., 54–57 GPa) are likely due to the use of different pressure-transmitting media. Klotz et al. (2009) have measured the hydrostatic limits, as well as the standard deviation from true pressure (calibrated to ruby) across the sample chamber over a wide range of pressures for all of the pressure media used in the studies described here. Our study used Ar as the room-temperature pressure medium, which is more hydrostatic (i.e., exhibits a lower standard deviation from true pressure) at these pressures and allows for a greater range of metastability than the pressure media in previous studies, silicone oil, N\textsubscript{2}, or 16:3:1 methanol:ethanol:water (Dancausse et al. 1990; Idiri et al. 2004; Klotz et al. 2009; Olsen et al. 2004). The less hydrostatic conditions in these studies created higher strains, resulting in more abrupt phase transitions compared to the more hydrostatic conditions reported here.

In the room-temperature volume vs. pressure \((V-P)\) XRD data from this study and those from the literature (Fig. 3), a discontinuity in compression behavior is observed around \(\sim 16\) GPa, similar to the discontinuities observed previously in other fluorite-type and pyrochlore materials at high pressures (Rittman et al. 2017; Zhang et al. 2010). Although the crystal structure remains in the fluorite-type phase above this pressure, the measured volume is greater than expected by normal compressibility. We interpret this as evidence of anion sub-lattice disorder in ThO\textsubscript{2} (Boulfelfel et al. 2006).

As described in the Introduction, during the fluorite–cotunnite transition the anions are subject to local disordering, described by Boulfelfel et al. (2006) as “melting” of the anionic sub-lattice. This effectively increases the local volume, and allows the cations to subsequently rearrange. Thus, the change in compressibility is interpreted as the onset of the fluorite–cotunnite phase transition. Our data show this discontinuity much more intensely than the earlier literature data for ThO\textsubscript{2} (Idiri et al. 2004; Olsen et al. 2004), which again is likely due to the differences in deviatoric stress conditions of the measurements (Klotz et al. 2009). It is unclear whether this process is also evident in the room-temperature compression curve for the cotunnite-type phase because the room-temperature XRD patterns that contained that phase were not well enough resolved to extract lattice parameters or volumes.

To further investigate this phase transition process, we performed Raman spectroscopy at room temperature under non-hydrostatic conditions. As described in the Methods section, measurements were made both on compression and decompression. Examples of the compression spectra are shown in Figure 4. Under these conditions, thorianite exhibits a single (triply degenerate) Raman absorption mode representing the symmetric breathing of the O anions around the Th cation \((F\text{2g})\) at \(\sim 474\ \text{cm}^{-1}\) at 5 GPa. This peak broadens and shifts to higher wavelengths with increasing pressure throughout the pressure range investigated. At \(\sim 22\) GPa new peaks appear as a shoulder or very near the \(F\text{2g}\) peak at

**Figure 3.** Room-temperature \(P-V\) data for thorianite from this study and the available literature. The ab initio curve from Olsen et al. (2004) was developed using the generalized gradient approximation. The difference between the pressures predicted from calculations and the measured pressure is shown in the bottom panel. The solid line corresponds to the offset in ambient pressure volumes (predicted–measured). A discontinuity is apparent in the data beginning around 15 GPa. (Color online.)

**Figure 4.** Raman spectra of ThO\textsubscript{2} collected at room temperature on increasing pressure. Lines indicate the trajectories of peaks with increasing pressure. Colors are coordinated with frequencies plotted in Figure 5. (Color online.)
540 (M1) and 622 (M2) cm$^{-1}$. Above 32 GPa a triplet of absorption modes (M3–M5) become apparent at low wavenumbers, 330–390 cm$^{-1}$ and a single peak becomes resolvable at 495 cm$^{-1}$ (M6). One final peak at ~330 cm$^{-1}$ (M8) is resolved above 50 GPa (Figs. 4 and 5). Group theory indicates that the cotunnite-type structure should result in 18 distinct Raman modes. We observe 8 at the highest pressures reached. Although our spectra are broad due to pressure effects, they are very similar to those observed at ambient pressures in samples of cotunnite-type ZrO$_2$ and HfO$_2$ recovered from high pressures (Haines et al. 1997). The pressure dependence of these high-pressure absorption frequencies is shown in Figure 5 and tabulated, along with calculated mode Grüneisen parameters in Table 2. Mode Grüneisen parameters describe the volume dependence of the frequency of each individual vibrational mode. The thermodynamic Grüneisen parameter is a weighted mean of all mode Grüneisen parameters for the material, including the acoustic modes and other Raman-inactive modes that were not probed in this study.

We interpret the additional peaks in the 20–30 GPa range as the rearrangement of the anion sub-lattice, which is consistent with previous interpretations of Raman measurements of ThO$_2$ (Kamali et al. 2017), although these limited data cannot be used to determine the extent of disorder. The peaks appearing at 32 GPa are the final stages of the fluorite–cotunnite phase transition. The vibrational modes exhibit a regular linear slope as a function of pressure above 37 GPa. Thus, the full crystallographic reconstruction of the cubic fluorite-type structure to the orthorhombic cotunnite-type structure appears to be complete for both the anions and cations between 32 and 37 GPa. This is approximately the pressure at which the cotunnite phase emerges in the room-temperature XRD data (Fig. 6) (Dancauss et al. 1990; Idiri et al. 2004; Olsen et al. 2004). Since XRD is more sensitive to the Th atoms in this material, it appears that the phase transition will not be evident using diffraction until a significant portion of the cation sub-lattice has undergone transformation (i.e., above 32 GPa). Given the change in slope of the Raman frequencies, none of the high-pressure modes appear to be directly related to the low-pressure phase. Upon decompression, the cotunnite-type absorption peaks remain until ~2 GPa while continually decreasing in Raman frequency. At ~1 GPa, there is only a single peak remaining, at 463 cm$^{-1}$, suggesting that it has fully reverted back to the fluorite-type structure.

The thorianite–cotunnite-type phase transition is also observed at high temperatures. In synchrotron XRD experiments at ~17 GPa, the phase transition occurred on increasing temperature between 1534 ± 114 and 1583 ± 119 K. Again, this transition is sluggish, even at high temperatures. The high-pressure phase was not

<table>
<thead>
<tr>
<th>Raman mode</th>
<th>$v_0$ (cm$^{-1}$)</th>
<th>$\frac{dv}{dP}$ (cm$^{-1}$/GPa)</th>
<th>$\gamma_i$</th>
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<tr>
<td>F$_{2g}$</td>
<td>468(2)</td>
<td>2.37(9)</td>
<td>0.96(4)</td>
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<tr>
<td>M1</td>
<td>497(3)</td>
<td>1.55(6)</td>
<td>0.51(2)</td>
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<td>M2</td>
<td>577(3)</td>
<td>2.04(8)</td>
<td>0.59(2)</td>
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<td>M3</td>
<td>294(3)</td>
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<td>325(4)</td>
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<td>0.54(4)</td>
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<tr>
<td>M5</td>
<td>365(3)</td>
<td>0.83(6)</td>
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<td>M6</td>
<td>465(3)</td>
<td>0.85(7)</td>
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</tr>
<tr>
<td>M7</td>
<td>497(3)</td>
<td>1.55(6)</td>
<td>0.41(4)</td>
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</table>

Notes: $v_0$ is the zero-pressure frequency, $\gamma_i$ are the mode Grüneisen parameters for each vibrational mode, defined as $K_0(d\ln v_i/dP)$.
observed at all in the pressure step at \(-18–19\) GPa, which suggests that in those cases heating was faster than the phase transition could proceed. Additionally, from 20–30 GPa at high temperatures both phases are observed, but only one of them (likely the cotunnite-type phase) can be thermodynamically stable. Above \(-30\) GPa at high temperatures, only the cotunnite-type phase is observed up to the highest pressures reached in this study, \(-62\) GPa. All of this information was compiled as our preferred \(P-T\) phase diagram for this material in Figure 6. Based on our observations, it is likely that the phase boundary is very close to vertical or slightly negative around \(18–20\) GPa in \(P-T\) space, although it is not observed in the XRD data until \(\pm 30\) GPa.

**Equations of state of ThO\(_2\) polymorphs**

Given the range of \(P-V-T\) data obtained for the polymorphs of ThO\(_2\) in this study, we were able to extract equation of state parameters for each phase. We fit both sets of data to the Mie-Grüneisen type equations of state (Eq. 1), where the reference pressure (300 K) equation took the Birch-Murnaghan form (Eq. 2).

\[
P = P_{300K} + P_{\text{thermal}}
\]

\[
P_{300K} = 3K_0f\left(\frac{1+2f}{2}\right)^{\frac{3}{2}}\left[\frac{3}{2}\left(K_0'-4\right)\right]
\]

Here, \(f\) is the finite Eulerian strain, \(V_0\) is the measure volume of the material at pressure, \(P\), \(V_0\) is the ambient-pressure volume, \(K_0\) is the ambient-pressure isothermal bulk modulus, and \(K_0'\) is its pressure derivative. For the thorianite equation of state, we only used the room-temperature data prior to the volume discontinuity (<15 GPa). For the cotunnite-type phase, there were no room-temperature patterns of high enough quality to extract lattice parameters. Thus, no room-temperature data were used in the fits for the high-pressure phase. Because of the limited room-temperature data, we chose to define the thermal pressure as in Equation 3.

\[
P_{\text{thermal}} = \alpha K_1\left(T - 300\right)
\]

\(\alpha\) is thermal expansion and \(K_1\) is the bulk modulus at temperature, \(T\). In this case, the coefficient on temperature is taken to be constant.

The equation of state parameters for each phase are given in Table 1, along with the available literature values. For thorianite, \(V_0\) was measured prior to the compression experiments to be 26.379(7) \(\text{cm}^3\text{/mol}\), so it was fixed in the fitting routine. Additionally, \(K_0'\) was fixed to a value of 4 to allow for more precise determination of the thermal term. Our choice of 4 of \(K_0'\) is slightly lower than has previously been measured (~5), so our measured bulk modulus is slightly higher at 204 GPa than other recent XRD studies (Idiri et al. 2004; Olsen et al. 2004). The thermal pressure coefficient, \(\alpha K_0\), for thorianite was determined to be 0.0035(3) GPa/K.

The properties of the high-pressure cotunnite-type phase of ThO\(_2\) are very similar to those of the low-pressure phase. Holding \(K_0'\) at a value of 4, the bulk modulus for this phase was determined to be 190(3) GPa. This is slightly more compressible, but very similar to the value for thorianite. Additionally, the thermal pressure coefficient was found to be 0.0037(4) GPa/K, suggesting that the high-pressure phase reacts very similarly to pressure and temperature as the low-pressure phase. The fitted zero-pressure volume for the cotunnite-type phase is 24.75(6) \(\text{cm}^3\text{/mol}\), which is 6.2% more dense than thorianite at ambient conditions. This is virtually the same volume contrast that was observed at \(-35\) GPa, by Idiri et al. (2004). The compiled \(P-V-T\) data from this study are plotted in Figure 7 along with calculated isotherms for comparison.

The values for the individual lattice parameters of the cotunnite-type phase are given in the top panel of Figure 8. Each one decreases with pressure, as expected, but the \(a\)-axis appears to be compressing at a faster rate than either \(b\) or \(c\), while the short \(b\)-axis changes very little. This relationship is best demonstrated in the lattice parameter ratios as a function of pressure in the lower panels of Figure 8. In general, the ratios of the lattice parameters change linearly with pressure, with only small dependencies on temperature. This would occur if the coordination polyhedra within the cotunnite-type structure are continuously distorting with pressure, and suggests that upon increasing compression the material will undergo another structural phase transition. A transition of this type has been predicted theoretically for ThO\(_2\) above \(-80\) GPa by Perry et al. (2017). In the calculation, the phase transition was signaled by a collapse in the \(a\)-axis and a corresponding expansion of the \(b\)- and \(c\)-axes, which is consistent with

![Figure 7](image-url)
the compression behavior observed here. Some likely options for this higher pressure phase are common post-cotunnite structures, including the hexagonal Fe₃P structure (P62m) observed in the ZrO₂ system (Nishio-Hamane et al. 2015) or the Ni₃In structure (P6₃/mmc) and orthorhombic distortions thereof (Song et al. 2012). For convenience, the ratios have been fitted to a linear dependence of pressure. The slopes and hypothetical zero-pressure values from these fits are given in Table 3.

**IMPLICATIONS**

This study explores the simultaneous high-pressure, high-temperature behavior of ThO₂. We find that the thorianite–cotunnite phase transition is kinetically inhibited, even at 2000 K. The onset of the transition at room temperature begins at ~15–20 GPa, as evidenced by an anomalously low compressibility of the cubic structure with pressure. We interpret this change as anion sub-lattice disorder, which has been theoretically predicted for the same phase transition in CaF₂ (Boulfelfel et al. 2006) and observed in several analogous phase transitions in the pyrochlore/disordered fluorite system under pressure (Rittman et al. 2017; Zhang et al. 2010). This transition pressure is corroborated by Raman spectroscopy measurements (Figs. 4 and 5) (Jayaraman et al. 1988; Kamali et al. 2017). At room temperature, the phase transition was not complete, even at the highest pressures reached in this study, ~55 GPa. At high temperatures, the onset of the phase transition was observed at ~18 GPa and was complete by ~30 GPa. If Th exists in oxide form in the Earth’s lower mantle, it is likely in a solid solution with other large cations of +4 valence whose oxides also take the cotunnite structure, e.g., (Zr,Th,U)O₂. Such a phase, with Zr as the dominant (i.e., most abundant) cation, could exist in the cotunnite-type structure to at least ~1430 km (~60 GPa), as ZrO₂ has been shown to be stable in the cotunnite-type structure well above this pressure (Nishio-Hamane et al. 2015).

The isothermal equation of state parameters measured here for thorianite are consistent with previous measurements (Idiri et al. 2004; Olsen et al. 2004). Additionally, this study provides a thermal dependence for the high-pressure behavior of thorianite, as well as thermal equation of state parameters for the high-pressure cotunnite-type phase. These parameters are necessary for predicting the behavior of this material at extreme conditions, such as within a nuclear reactor (a very high radiation environment at ~15 MPa and several hundred degrees Celsius for pressurized water reactors (U.S. Nuclear Regulatory Commission 2012) or in the Earth’s lower mantle (up to 137 GPa and ~4000 K at the core-mantle boundary). We find that, although the cotunnite-type phase of ThO₂ is ~6% denser than its lower-pressure polymorph, they have a very similar compressibilities and thermal pressure coefficients. We also find that the cotunnite structure is continuously deforming under pressure, which suggests that this material will undergo another phase transition on increasing pressure. Such a phase transition has been predicted above ~80 GPa theoretically (Perry et al. 2017). Thus, actinide-bearing oxides in the lowermost region of Earth’s lower mantle may not be stable in the cotunnite-type phase. This behavior has the potential to influence the distribution of large ion lithophile elements among accessory phases, particularly if the post-cotunnite structure exhibits a significantly different coordination environment than the cotunnite-type structure.

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**FIGURE 8.** Individual lattice parameters and their ratios for cotunnite-type ThO₂. Black lines are linear fits to the data. No temperature dependence was resolved for the lattice parameter ratios. (Color online.)

**TABLE 3.** Linear fits to the lattice parameter ratios as a function of pressure for cotunnite-type ThO₂

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Slope (GPa⁻¹)</th>
<th>Zero-pressure value</th>
</tr>
</thead>
<tbody>
<tr>
<td>c/a</td>
<td>0.00081(2)</td>
<td>1.1391(9)</td>
</tr>
<tr>
<td>b/a</td>
<td>0.00048(2)</td>
<td>0.5962(8)</td>
</tr>
<tr>
<td>c/b</td>
<td>-0.00015(3)</td>
<td>1.910(1)</td>
</tr>
</tbody>
</table>

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Endnote:

1Deposit item AM-18-56212, Supplemental Tables. Deposit items are free to all readers and found on the MSA web site, via the specific issue’s Table of Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/2018/May2018_data/May2018_data.html).