Ultralow Compressibility Silicate without Highly Coordinated Silicon

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The bulk modulus of scheelite-structured $ZrSiO_4$ is 301.4 ± 12.5 GPa, as derived from static compression experiments to 52.5 GPa. It is as stiff as the most incompressible known silicate, SiO_2 stishovite. This high incompressibility indicates that octahedrally coordinated silicon is not required to generate ultrastiff silicates: $ZrSiO_4$ scheelite is the most incompressible material containing SiO_4 tetrahedra. Its incompressibility is in accord with a semitheoretical relation we derive for the bulk modulus of scheelite-structured materials. Based upon correlations between incompressibility and hardness, scheelite-structured oxides may thus represent a new family of ultrahard materials.

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The synthesis and characterization of ultrahard ceramics is an area of intense interest [1–7]. The isothermal bulk modulus [$K_{0T} \equiv V(dP/dV)_T$] is frequently used as a proxy for hardness; materials with high bulk moduli are typically very hard [8]. In contrast to hardness, K_{0T} is an intensive thermodynamic property and can be measured with a high degree of precision. The hardest and least compressible (large K_{0T}) materials are empirically observed to be based on tetrahedral, covalent networks. Specifically, diamond is the hardest and least compressible material known ($K_{0T} = 444$ GPa [9]), and isostructural cubic boron nitride is the second hardest ($K_{0T} = 369$ GPa [10]). Other cubic nitrides have also been shown to be highly incompressible, such as spinel-structured Si_3N_4 (with highly coordinated silicon and substantial covalent bonding), with a K_{0T} of 308 GPa [11]. A hexagonal silicon nitride polymorph, β-Si_3N_4, has a substantially lower bulk modulus of 259 GPa [12]. Highly coordinated dioxides, particularly the high-pressure polymorphs of SiO_2, TiO_2, RuO_2, and HfO_2 are also potential superhard materials, with bulk moduli exceeding 300 GPa [7,13,14]. In this Letter, we present the identification of a new family of highly incompressible (and therefore likely to be extremely hard) materials: IV-IV scheelite-structured oxides, and specifically $ZrSiO_4$ scheelite.

At pressures above ~12 GPa, $ZrSiO_4$ zircon undergoes a phase transition to a structure identical to that of $CaWO_4$ scheelite (space group = $I4_1/a$), a transformation undergone by many zircon-structured ABO_4 oxides under compression [15]. The zircon and scheelite structures are very similar in that both are tetragonal, with silicon in fourfold coordination with respect to oxygen, and zirconium in eightfold coordination. The zircon to scheelite transition is also accompanied by an increase in density of ~10%, and the high-pressure phase is metastably quenchable to ambient conditions. This transition has been observed under both static and shock high pressure/high temperature conditions, with the onset of this transition occurring near 12 GPa in static high temperature experiments [16] and at over 40 GPa in microsecond-scale shock wave studies

[17]. This transition also occurs at room temperature following static compression of zircon to 23 GPa [18]. A key observation is that $ZrSiO_4$ in the zircon structure is the least compressible compound previously known containing Si in tetrahedral coordination, with an isothermal bulk modulus of 227 GPa [19,20]. Typically, pressure-induced crystal to crystal phase transitions in oxides are accompanied by an increase in bulk modulus, and it is for this reason that we examined the bulk modulus of $ZrSiO_4$ scheelite.

Samples of scheelite-structured $ZrSiO_4$ were synthesized from a natural, nonmetamict zircon sand. This sand has previously been characterized in both high-pressure Raman [18] and infrared [21] studies. Several single crystals of this sand were crushed and ground with approximately 3 wt % Pt black, which was used both as an absorber of infrared laser radiation during the heating process, and as an internal calibrant for sample to image plate distance determination in synchrotron x-ray measurements. This material, with the addition of several small (~5 μm in diameter) ruby grains for pressure calibration [22], was then loaded into a spring steel gasketed Mao-Bell–type diamond anvil cell (DAC) with a sample chamber 300 μm in diameter and compressed without a pressure medium to 20 ± 3 GPa. At this pressure, the sample was laser heated by a Nd:YAG infrared laser (operating in the TEM_{00} mode with a wavelength of 1064 nm) at a visually estimated temperature of >1500 K. After heating, the sample pressure dropped by ~5 GPa. We then increased the pressure to 20 GPa and again laser heated the sample. After three cycles of this process, the pressure drop was only ~2 GPa, indicating that nearly complete conversion to the scheelite structure had occurred; we infer that the pressure drop is largely produced by the volume change of this transition. We then pressure quenched the sample and verified it to be dominantly in the scheelite-structured phase by x-ray diffraction in a 114.6 mm diameter Debye-Scherrer camera using a conventional x-ray source. After synthesizing $ZrSiO_4$ scheelite, we reloaded this material into a DAC with a 125 μm diameter sample chamber and added a mixture of methanol-ethanol-water

in a ratio of 16:3:1 by volume as a pressure transmitting medium (this medium is liquid and is therefore truly hydrostatic to pressures of ~15 GPa).

We collected *in situ* synchrotron x-ray diffraction data as a function of pressure to 52.5 GPa; representative x-ray diffraction patterns are shown in Fig. 1. Synchrotron x-ray measurements were conducted at beam line 10-2 of the Stanford Synchrotron Radiation Laboratory. For the collection of diffraction patterns we used monochromatic ($E = 17.038$ keV) x rays collimated to 60 μm and utilized an image plate to record rings of Bragg diffracted x rays. We analyzed the patterns using standard computational techniques [23].

Notably, our compression results in the hydrostatic regime are completely indistinguishable from our higher pressure results, demonstrating that nonhydrostatic effects do not significantly affect our results. We do not observe any evidence for the breakdown of $ZrSiO_4$ into

its constituent oxides (rutile-structured SiO_2 and cotunnite-structured ZrO_2) at ambient temperature. Such a breakdown was reported in a previous static compression experiment at 22 GPa upon heating to ~1300 K [16]. However, shock-wave studies [17,24] suggest that much higher temperatures (of order several thousand degrees) are required for this reaction to occur.

We inverted our x-ray data to determine the lattice parameters, **a** and **c**, and volume for $ZrSiO_4$ scheelite (Figs. 2 and 3). The response of this structure to pressure is observed to be highly anisotropic (Fig. 2); we calculate linear compressibilities for each lattice parameter:

$$\frac{1}{a_0}\frac{da}{dP} = 7.42 \times 10^{-4}/\text{GPa}, \qquad (1)$$

$$\frac{1}{c_0}\frac{dc}{dP} = 1.08 \times 10^{-3}/\text{GPa}. \qquad (2)$$

These results indicate that this phase is ~1.5 times more compressible in the [**001**] than in the [**100**] crystallographic direction.

We then determined the isothermal bulk modulus by fitting our data to the Birch-Murnaghan finite strain equation of state [25] (Fig. 3). Our results yield a value for K_{0T} of 301.4 ± 12.5 GPa with the pressure derivative of the bulk modulus (dK/dP) constrained to be equal to 4 (this result is essentially the same as a third order fit, which produced a value for dK/dP of 4.1). This extremely high bulk modulus is identical (within error) to that of SiO_2 stishovite, making $ZrSiO_4$ scheelite and stishovite the least compressible silicates known. Indeed, after diamond and cubic boron nitride, the only other materials with
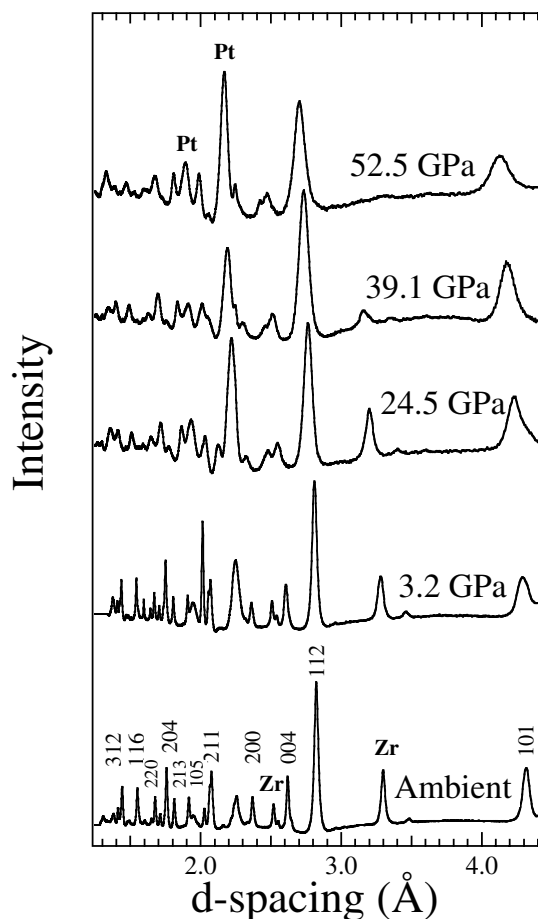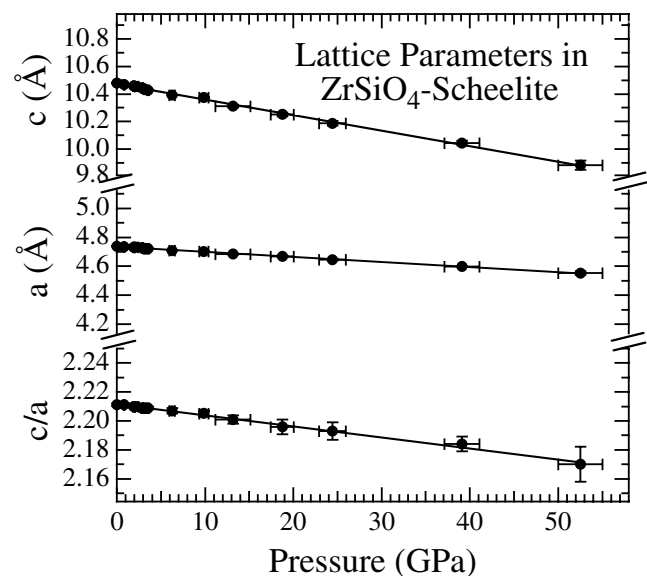

FIG. 1. Representative x-ray diffraction patterns of $ZrSiO_4$ scheelite under compression. Low-pressure patterns contain a small amount of residual zircon-structured material as indicated by the presence of the (200) and (112) x-ray reflections (these are the two most intense x-ray lines for $ZrSiO_4$ zircon): these are indicated by **Zr**. As expected from previous results [18], all of the zircon-structured material converts to scheelite on compression at 300 K. The (111) and (200) lines of Pt are also present in the diffraction patterns, which are indicated by **Pt**.

FIG. 2. Lattice parameters **a** and **c** with pressure for $ZrSiO_4$ scheelite. This phase is much more compressible along the **c** than along the **a** lattice parameter; this is quantified in Eqs. (1) and (2). The ratio of crystallographic axes varies considerably with pressure and is also shown in this figure (note breaks in vertical scale).
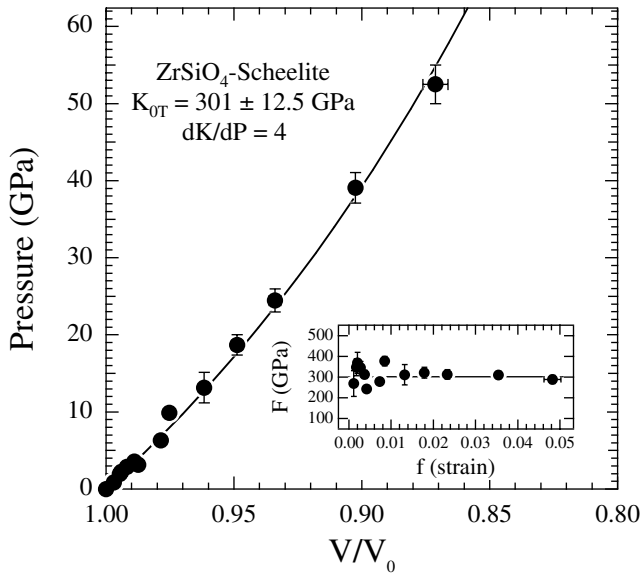
FIG. 3.   Volume as a function of pressure for $ZrSiO_4$ scheelite. The solid line is our second order fit to the Birch-Murnaghan equation of state. The inset shows our data plotted as a normalized pressure (F) vs Eulerian finite strain (f) [25], from which the value of K_{0T} is obtained.

bulk moduli exceeding 300 GPa are spinel structured Si_3N_4 [11], highly coordinated dioxides [7,13,14], and $ZrSiO_4$ scheelite. For reference, simple velocity-density systematics predict a bulk modulus near 330 GPa for scheelite-structured $ZrSiO_4$, based on the bulk modulus of the zircon-structured polymorph and the density change of this transition [26]:

$$K_2 \sim K_1 \cdot \left(\frac{\rho_2}{\rho_1}\right)^4. \tag{3}$$

The microstructural origin of the low compressibility of this material is dictated by the presence of SiO_4 tetrahedra (which are known to be exceptionally stiff, with a polyhedral compressibility of >700 GPa [27]), coupled to one another by high electron density Zr-O bonds. Such tetravalent metal-oxygen bonds have been shown to be the basis for a number of other ultrahard materials [14,28]. Because of the anisotropic nature of compression in $ZrSiO_4$ scheelite, crystals oriented along the [**100**] direction will likely be harder than a bulk aggregate of this material. This difference is attributable to the oxygen configuration within the (**001**) plane: the shortest oxygen-oxygen distances in the ZrO_6 polyhedra lie close to this plane [29], and oxygen-oxygen repulsion thus likely plays a crucial role in the unusual stiffness of this phase.

Previous work on scheelite-structured ABO_4 compounds (Tl, Ca, Cd, Pb, Sr, Bi, or La in the A site and Re, W, Mo, V, or Nb in the B site) has revealed that bulk modulus and zero-pressure volume are correlated (Fig. 4a) [30]. Indeed, trends exist for differing valences of the A and B cations (e.g., I-VII, II-VI, and III-V for A and B, respectively): Fig. 4a. Our measurements on $ZrSiO_4$ scheelite agree with these results and establish a new field for IV-IV
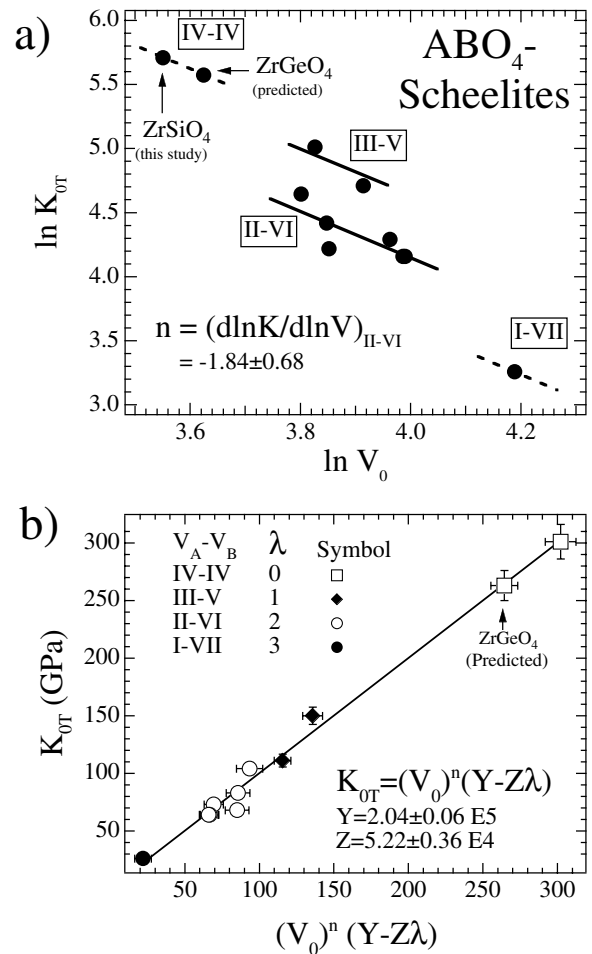
FIG. 4.   (a) Bulk modulus as a function of zero pressure volume for ABO_4 scheelites with differing valences of A and B cations (data from the compilation of Ming *et al.* [30] and this study). Our result for the bulk modulus of $ZrSiO_4$ scheelite agrees well with these systematics and expands the correlation of increasing bulk modulus with decreasing molar volume to IV-IV scheelites. Also shown is our predicted bulk modulus for $ZrGeO_4$ scheelite. (b) A structure-specific, semitheoretical correlation between bulk modulus and zero-pressure volume for all scheelites using a similar formalism as Cohen [31]. We estimate error bars by propagating 1 standard deviation uncertainties on our values for Y and Z and assuming 1% and 5% error on previously measured data for volumes and bulk moduli, respectively.

cations with the following linear relationship (the slope, **n**, is derived from the II-VI field):

$$\ln(K_{0T}) = 12.22 - 1.84 \ln(V_0) \tag{4}$$

(K_{0T} in GPa and V_0 in cm^3/mole). Clearly, the observation of a linear relationship for Eq. (4) implies that $K_{0T} \alpha (V_0)^n$; we use this result to derive a scheelite-specific, semitheoretical expression for bulk modulus as a function of volume based on the formulation for the diamondlike semiconductors of Cohen [31]. We choose a slightly modified form which we express as

$$K_{0T}(\text{GPa}) = (Y - Z\lambda)(V_0)^n. \tag{5}$$

Here, λ is Cohen's polarization factor which takes integer values between 0 and 3 as determined by one-half of

the difference in valence between the A and B cations, and $\mathbf{Y}$ and $\mathbf{Z}$ are fitting parameters with values of $2.04 \pm 0.06 * 10^5$ and $5.2 \pm 0.4 * 10^4$, respectively. We find that such an equation, demonstrated to be an accurate predictor of the bulk moduli of diamond-structured phases [31], accurately reproduces the bulk modulus for the ABO_4-scheelite family; the correlation for all known ABO_4 scheelites is shown in Fig. 4b.

These relations allow us to predict that other IV-IV scheelite-structured materials (such as germanate-silicate solid solutions) should also be highly incompressible and therefore good candidates to be extremely hard. Such germanate-silicate solid solutions have long been known to be synthesizable at lower pressures than the silicate end member [32]. Indeed, our trend for IV-IV scheelites predicts a bulk modulus of 263 GPa for $ZrGeO_4$ scheelite, implying that solid solutions of $ZrGeO_4$-$ZrSiO_4$ likely have bulk moduli lying between these two end members. Accordingly, IV-IV oxide scheelites are expected to be uniformly stiff: this stiffness is plausibly generated by the low compressibility of tetravalent cation-oxygen bonds, coupled with the efficient packing of oxygen anions.

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