In situ determination of the compressibility of synthetic pure zircon (ZrSiO₄) and the onset of the zircon-reidite phase transition

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ABSTRACT

We have determined the room temperature compressibility of pure, synthetic zircon (ZrSiO₄). Unit cell volumes of a powdered sample were determined *in situ* as a function of pressure up to 27 GPa in a diamond anvil cell, by using angle-dispersive synchrotron X-ray diffraction techniques. Unit cell volumes were fitted to a Birch-Murnaghan equation of state, resulting in a room temperature bulk modulus for the zircon structure, $K_{T0} = 199 \pm 1$ GPa , and ambient pressure unit cell volume $V_0 = 260.89 \pm 0.03$ Å³, when $(\partial K_{T0} / \partial P)_T = K_{T0}$ is fixed at 4. This bulk modulus is over 12 % lower than suggested by earlier measurements using impure, natural zircon sample. In addition, we observe the start of the transformation of zircon to reidite (scheelite-structured ZrSiO₄) at a pressure of 19.7 GPa, over 3 GPa lower than previously determined for natural (impure) zircon. Together with compressibility measurements of a trace element doped zircon, these observations suggest that impurities affect the phase transition kinetics and compressibility of zircon, and by analogy perhaps of other silicate minerals.

INTRODUCTION

Zircon (ZrSiO₄) is a ubiquitous accessory mineral. Its presence in a wide variety of sedimentary, metamorphic, and igneous settings, combined with its ability to retain trace element and isotopic information, makes it an important phase for geochemical and geochronological studies (e.g. Heaman and Parrish 1991, Dickin 1995, Hanchar et al. 2003). The refractory nature of zircon has also prompted suggestions for its use as a storage material for radioactive waste (e.g. Ewing 1999).

At ambient conditions, zircon is tetragonal (space group = $I4_1/amd$), and is among the few silicates containing only nominally tetravalent cations (Zr^{4+} and Si^{4+}) that ensure a strong linkage between the structure's polyhedra. At high pressure, zircon transforms to reidite (scheelite structure, space group = $I4_1/a$, see Glass et al. 2002). Reidite is approximately 10 % more dense than zircon and can be quenched to ambient pressure. Knittle and Williams (1993) observed this transition at room temperature in natural zircon at a pressure of 23 ± 1 GPa using Raman spectroscopy. Scott et al. (2000) subsequently presented infrared (IR) spectroscopic measurements that were consistent with this transition pressure. High-pressure crystal to crystal phase transitions at room temperature are usually hampered by sluggish kinetics, so that the observation of this transition in zircon suggests "an anomalous and possibly unique silicate transformation mechanism" (Knittle and Williams 1993).

Because of these unique properties of zircon, detailed studies of the $ZrSiO_4$ structure at elevated pressures (*P*) and temperatures (*T*) should improve our understanding of fundamental aspects of material bonding and phase transitions. To date, only limited information about the effects of elevated *P* on the zircon structure are available. The elastic constants of radiation-damaged (metamict) and nonmetamict zircon were determined in the 1970s by Özkan and co-workers by using ultrasonic

measurements (Özkan et al. 1974, Özkan 1975, 1976, Özkan and Jamieson 1978). Özkan (1976) and Ríos and Boffa-Ballaran (2003) showed that the elastic moduli of zircon decrease substantially in response to increasing radiation damage. Room temperature compressibility measurements on both nonmetamict and metamict zircons have only been reported at pressures up to 8 GPa (e.g., Hazen and Finger 1979, Ríos and Boffa-Ballaran 2003), which is approximately one third of the pressure stability range reported by Knittle and Williams (1993).

The isothermal bulk modulus K_{T0} of nonmetamict zircon derived from these previous high-pressure studies, 225-230 GPa, is the highest reported value among silicates with tetrahedrally coordinated silicon. These values are consistent with the ultrasonic measurements by Özkan and co-workers. However, as noted by Smyth et al. (2000) the small pressure range covered in the compressibility studies, combined with potential problems related to the merging of data from different experimental techniques, casts some doubts on these earlier results. All previous work on nonmetamict zircon used natural (hence impure) samples that typically contained over 1 wt% impurities (mainly Hf substituting for Zr, but also varying amounts of U, Th, Y and the heavy rare earth elements [HREEs], Sc and other elements). In several cases, the composition of the starting material was never measured or reported, which hampers proper interpretation of the data. Thus, evaluating the effect of zircon composition on its volumetric and thermodynamic properties from literature data is difficult.

We have determined for the first time the room temperature compressibility of pure, synthetic zircon over its complete pressure stability range. Lattice parameters and unit cell volumes of powdered samples in a diamond anvil cell were determined *in situ* at pressures up to 27 GPa. In addition we have studied the kinetics of the phase

transition from the zircon to the scheelite structure in pure $ZrSiO_4$. Our objectives were first, to derive an accurate value for the compressibility of pure zircon, and second, to study the possible effect of impurities on phase transition kinetics and compressibility in silicate minerals.

EXPERIMENTAL AND ANALYTICAL TECHNIQUES

Starting material

Pure, undoped zircon crystals were grown from a Li-Mo flux in a MoSi₂ vertical tube furnace at The George Washington University, with the techniques described in Hanchar et al. (2001). Scanning electron microscope (SEM) images of representative crystals (Figure 1) were recorded with an R.J. Lee SEM (Argonne National Laboratory) operating with an accelerating voltage of 30 kV and a beam current of 50 nA. The chemical composition of zircon crystals was determined by using a JEOL 8900 electron microprobe at the University of Maryland, following the methods of Hanchar et al. (2001). The mean ZrO₂ concentration of the zircon crystals (n = 130 analyses) is 67.09 wt% (16.65 mol% Zr), and the mean SiO₂ content is 32.79 wt% (16.68 mol% Si). The expected stoichiometric values are 67.22 wt% ZrO₂ (16.67 mol% Zr) and 32.78 wt% SiO₂ (16.67 mol% Si). The small differences from the expected values are within the analytical uncertainty of the analyses. Secondary ion mass spectrometry analyses (n = 3) of a single crystal selected at random from the same batch as that from which we obtained crystals for this study detected very minor amounts of P (122 ppm), Li (0.12 ppm), and Mo (2.0 ppm) (Hanchar et al. 2001).

Powder X-ray diffraction data, acquired at The George Washington University with a Scintag 2000 diffractometer (45 kV, 40 mA, 0.02 degree step, 10 sec./step),

confirmed that the starting material had the zircon structure (space group $I4_1/amd$). Approximately 10 mg of sample was crushed to a powder in an agate mortar under ethanol, to a grain size of roughly 5 µm. This fine powder was used as a starting material for our high pressure experiments, described below.

High-pressure experiments

A Mao-Bell type diamond anvil cell (Mao et al. 1979) was used to generate high pressures, with neon serving as a quasi-hydrostatic pressure medium. Diamonds with 300 μ m culet diameters were aligned on the piston and cylinder parts of the diamond anvil cell. Rhenium gaskets, 3.8 mm in diameter and 0.38 mm thick, were pre-indented between the diamonds to a pressure of 20 GPa, corresponding to an indentation thickness of 35 μ m. An erosion drill was used to make a 200 μ m diameter hole in the center of the pre-indented gasket. The resulting sample cavity was partially filled with powdered zircon, as well as several ruby grains, distributed throughout the sample chamber, for pressure determinations before and after the measurements. The sample chamber was sealed to a pressure of approximately 3 GPa under a 180 MPa pure neon gas atmosphere, created in a high-pressure gas loading device at the Geophysical Laboratory (see Jephcoat et al. 1987 for details).

Angle-dispersive powder X-ray diffraction patterns of the sample were obtained with monochromatic synchrotron radiation at beam line B2 at Cornell High Energy Synchrotron Source (CHESS), Wilson Lab, Cornell University. The incoming beam, monochromated to an energy of 25 keV by using two tilted, parallel Ge (111) crystals, was collimated to a spot size of 35 μ m diameter, and centered onto the sample cavity. Five minutes was found to be the optimal image plate exposure time. At regular pressure intervals, a thin layer of NaCl was applied to the back surface of

one of the diamonds to calibrate the sample-image plate distance and the tilt and rotation angles of the image plate with respect to the beam. Sample pressures were measured repeatedly on several ruby grains distributed throughout the sample chamber before and after each exposure by using the pressure dependent shift of the R1 ruby fluorescence line (Mao et al. 1986):

$$P(\text{GPa}) = \frac{2.74 \cdot \lambda_{R1}(0, \text{nm})}{7.665} \left(\left(\frac{\lambda_{R1}(P, \text{nm})}{\lambda_{R1}(0, \text{nm})} \right)^{7.665} - 1 \right)$$
(1)

In Eqn. 1, $\lambda_{R1}(0, \text{nm})$ is the wavelength of the ruby R1 fluorescence line at ambient pressure (694.29 nm), and $\lambda_{R1}(P, \text{nm})$ the wavelength, in nm, of this line at elevated pressure *P*.

In addition to the high-pressure diamond anvil cell measurements, the roompressure unit-cell dimensions of the starting material were determined at CHESS, again with NaCl as an internal calibrant. Data from developed image plates of calibrants and samples were reduced with FIT2D software (Hammersley 1997). Zircon unit-cell parameters were obtained through Rietveld refinement (Le Bail fitting) of the resulting intensity-versus-20 patterns, by using Rietica software (Hunter and Howard 2000).

Both starting material and the sample retrieved after compression were analysed by using a Raman microprobe. Unpolarised spectra for both zirconstructured and scheelite-structured ZrSiO₄ were obtained with a confocal Dilor XY microRaman spectrometer with a cryogenic Thompson Model 4000 CCD (e.g., Mysen 1995). Samples were excited by using the 488 nm line of an Ar laser (Spectra Physics 2025) operating at 800 mW, and spectra were recorded under 180° backscattering geometry.

RESULTS

Figure 2 shows a typical high-pressure XRD spectrum obtained from our ZrSiO₄ sample, as well as a LeBail fit to the spectrum. All peaks could be assigned to zircon, its high-pressure form reidite, or in some cases the solid neon pressure medium (at room temperature Ne solidifies at 4.7 GPa, e.g., Hemley et al. 1989) – the spectrum shown in Figure 2 contains zircon peaks only. No rhenium (gasket material) or ruby was detected in any of our spectra.

Figure 3 illustrates the position shift of some of the most intense zircon peaks as a function of pressure. Up to our measurement at a pressure of 19.66 ± 0.03 GPa, all ZrSiO₄ peaks can be assigned to the zircon structure. At this pressure, an additional broad peak emerges at a 20 angle of approximately 10.6°. The position of this peak is consistent with that expected position for the 112 reflection of reidite (Scott et al. 2002). The intensity of this reidite reflection increases substantially with time and with increasing pressure (arrows in Figure 3). At 22.2 ± 0.3 GPa, a second reidite peak (20 angle of approximately 6.9°) appears as a shoulder on the 101 zircon reflection. With increasing pressure, the zircon peaks decrease in intensity and sharpness, until at 27 GPa no more clear zircon peaks can be distinguished (Figure 3, top spectrum).

The transition from zircon to reidite was confirmed by using Raman spectroscopy. After completion of our measurements, the sample was kept in the diamond anvil cell at the highest pressure reached (27 GPa) for 106 hours, then quenched to room pressure and analysed by Raman microprobe. The resulting spectrum (Figure 4), which is similar to the reidite spectrum presented by Knittle and Williams (1993), is clearly distinct from the spectrum obtained from the original

zircon, although the three most intense zircon modes at ~350, 440, and 1010 cm^{-1} are still evident. The ~400, 550, 600, 840 and 880 cm⁻¹ modes, absent in zircon, can all be attributed to reidite (Knittle and Williams 1993). We identified a hitherto unknown lattice mode of reidite at ~300 cm⁻¹. Comparing our zircon and reidite spectra leads us to suspect that, due to incomplete transformation, the three most intense zircon Raman modes are also present in the reidite spectrum published by Knittle and Williams (1993). This could partly explain why these authors assigned 14 Raman modes to reidite, whereas only 13 are expected from factor-group analysis.

For all XRD spectra in which zircon diffraction peaks could be identified, peak positions and intensities in the 2θ range 5 - 25° were refined by the Rietveld method, with the Rietica software package (Hunter and Howard 2000). Typically at least 26 zircon peaks could be identified across the pressure range studied (e.g., Figure 2). The number of identifiable zircon peaks decreased once reidite peaks became apparent in the spectra. No attempts were made to fit data to the reidite structure because of the broadness of the peaks. For a study of the compressibility of reidite we refer to the recent study of Scott et al. (2002).

Zircon lattice parameters, unit-cell volumes, and associated errors, are shown in Table 1, together with ruby fluorescence pressure determinations (obtained with Eqn. 1). As indicated by the small values of agreement factors R_p and wR_p in Table 1, and the small residuals between observed and fitted spectra of Figure 2, agreement between measured and calculated spectra is very satisfactory. The shift of the R1 fluorescence line of at least three ruby grains, distributed throughout the sample volume, was measured both before and after increasing pressure. Up to the highest pressure reached in this study, different ruby grains give consistent fluorescence results at each pressure. This is borne out by the small error bars on pressure

measurements given in Table 1. Another indication of quasi-hydrostatic conditions through the use of neon as a pressure medium is that the R1 and R2 fluorescence lines remained split over the entire pressure range. There is no evidence that deviatoric stresses are a problem in these experiments.

Figure 5 shows the variation in zircon unit cell volume as a function of pressure. Variations in the unit cell volume *V* at pressures *P* up to 19.66 ± 0.03 GPa can be described accurately with a Birch-Murnaghan equation of state (Birch 1947),

$$P(V) = 3K_{T0}f(1+2f)^{\frac{5}{2}}\left(1+\frac{3}{2}(K_{T0}-4.0)f\right),$$
(2)

where K_{T0} is the isothermal bulk modulus, and K_{T0} its pressure dependence. The Eulerian strain *f* in Eqn. 2 is defined as

$$f = \frac{1}{2} \left(\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right)$$
(3)

with V_0 the zircon room pressure volume. A non-linear least-squares unconstrained fit of the data to Eqn. 2 yields $K_{T0} = 201 \pm 2$ GPa, $K_{T0} = 3.9 \pm 0.2$, and

 $V_0 = 260.78 \pm 0.04$ Å³. It is difficult to justify an unconstrained fit, however, because of the overall small (approximately 7.5%) zircon compression over the pressure range in this study. As is customary in these situations, a range of plausible fixed values for $K_{T0}^{'}$ was chosen, and data were re-fitted to Eqn. 2 by using these fixed values. If $K_{T0}^{'}$ is set to 4, the most commonly observed value in orthosilicates (e.g. Smyth et al. 2000), $K_{T0} = 199 \pm 1$ GPa and $V_0 = 260.89 \pm 0.03$ Å³. If K_{T0} is set to 6.5, the value from Özkan and Jamieson (1978) subsequently used by Hazen and Finger (1979), we obtain $K_{T0} = 180 \pm 1$ GPa and $V_0 = 261.23 \pm 0.03$ Å³.

The so-called *F-f* plot (e.g., Angel 2000) is illustrated in the inset of Figure 5 for the case of $K_{T0}^{'} = 4$. In a *F-f* plot, the Eulerian strain *f* (Eqn. 3) is plotted against the Birch-normalised pressure *F*, where

$$F = \frac{P}{\left(3f\left(1+2f\right)^{\frac{5}{2}}\right)} = K_{T0}\left(1+\frac{3}{2}\left(K_{T0}^{'}-4.0\right)f\right).$$
(4)

It is obvious from the inset of Figure 5 that within error the slope of our data in *F*-*f* space is zero, consistent with $K_{T0} = 4$ as chosen for this particular fit.

In the remainder of this paper, we will assume $K_{T0} = 4$. As mentioned above, this value is most commonly observed in orthosilicates, and is consistent with results from our unconstrained fit. Furthermore, the best-fit value for the room-pressure unitcell volume is within 1 σ of our experimental measurement (260.82±0.05 Å³) if $K_{T0} = 4$, which is not the case if $K_{T0} = 6.5$.

For all data in which reidite peaks appear in the X-ray diffraction patterns, the unit-cell volumes derived from what appear to be zircon reflections are significantly smaller than expected from any reasonable extrapolation of lower pressure data. One possible explanation for this is that the onset of the zircon-to-scheelite phase transition "softens" the zircon structure, making it more compressible. There are several examples of softening of elastic moduli in the vicinity of a phase transition (e.g., Carpenter and Salje 1998). An alternative explanation is that some of the zircon peaks are partly overlapped by reidite peaks, which could lead to inaccurate or incorrect peak assignments, and hence to an apparent change in the rate at which lattice parameters decrease with pressure. More detailed measurements, possibly on single crystals, would be needed to resolve this issue, and is beyond the scope of this study. In any case, unit-cell volumes of zircon coexisting with reidite were not used for determining the zircon bulk modulus.

DISCUSSION

Table 2 summarises available determinations of zircon compressibility. Our values for both the bulk modulus of zircon (199 \pm 1 GPa), and the pressure at which zircon starts to transform to reidite (19.7 GPa) differ significantly from previously published values. Our value for the zircon bulk modulus is 28 \pm 4 GPa (more than 12 %) lower than the hitherto accepted value of 227 \pm 2 GPa (Özkan et al. 1974, Özkan and Jamieson 1978, Hazen and Finger 1979, Ríos and Boffa-Ballaran 2003). In the case of radiation damage, the presence of lattice defects and small amorphous domains in the zircon structure would significantly lower the zircon bulk modulus (Özkan 1976, Ríos and Boffa-Ballaran 2003). Any damage, however minor, in the natural zircons used in previous studies would therefore have lowered the bulk modulus from its true, nonmetamict value, further increasing the discrepancy with our new results.

Systematic differences on the order of 5% in bulk modulus measurements between different research groups are not uncommon, resulting from errors that reflect slight differences in experimental and analytical procedures. For example, Andrault et al. (1998) showed differences on the order of 5-8% for the bulk modulus

of compositionally simple stishovite (SiO_2) between recent Brillouin and X-ray diffraction measurements done by different groups. Although part of the difference between our results and data in the literature may be a result of the different techniques used, the total observed difference of at least 12% is too large to be explained in this way.

There are several alternative explanations for the difference. As noted by Smyth et al. (2000), the pressure range covered by the study of Hazen and Finger (1979), 1 atm to 4.8 GPa, is comparatively small. This leads to a less precise bulk modulus determination. The value determined by Hazen and Finger (1979) is however consistent with the results of Özkan and co-workers, who used ultrasonic measurements to determine zircon elastic properties (Özkan et al. 1974, Özkan and Jamieson 1978), and with more recent X-ray diffraction data of Rios and Boffa-Ballaran (2003), with data up to 6.9 GPa.

We attempted to reconcile our measurements with literature data by fixing the bulk modulus K_{T0} to 228 GPa, equal to the ultrasonic measurements of Özkan and Jamieson (1978), before refitting the data to Eqn. 2. We obtained best fit values of $V_0 = 260.32 \pm 0.03$ Å³ and $K_{T0} = 1.3 \pm 0.2$ (Table 2). The resulting value of V_0 is unrealistically low, and the exceedingly low K_{T0} value is physically implausible. This reinforces our conclusion that the compressibility of pure undoped synthetic zircon differs significantly from previous work.

Previous measurements were done on impure natural samples, containing over 1 wt % of trace elements (mainly hafnium, but also uranium, rare earth elements, yttrium, phosphorus, etc.). It is possible that these impurities affect the compressibility of the zircon structure. The most abundant impurity in natural zircon is hafnium

(natural zircons commonly contain > 1, and up to 8 wt% of Hf). Hafnon (HfSiO₄) has a smaller unit cell volume than zircon (Speer and Cooper 1982). Natural Hf-rich zircons will therefore have a slightly smaller unit-cell volume than pure zircon. If zircon, like most other silicates, follows Birch's law, i.e., if an inverse relationship exists between room-pressure unit-cell volume and bulk modulus (e.g., Anderson 1972), we would expect a higher K_{T0} for natural, Hf-rich zircon. Conversely, zircons containing large amounts of rare earth elements and small amounts of Hf, which have a unit-cell volume that is greater than that of pure zircon (e.g., Finch et al. 2001), would then be expected to have a lower bulk modulus than pure zircon.

To test this hypothesis, with the same technique described in this paper, we also determined the compressibility of a synthetic zircon crystal purposely doped with a range of trace elements (rare earth elements charge balanced by phosphorus) excluding Hf (Van Westrenen et al. 2003). This synthetic zircon, which has a unit-cell volume approximately 1.0 % larger than the pure undoped sample ($V_0 = 263.94 \pm 0.04$ Å³), has a significantly lower K_{T0} , 189 ± 1 GPa at K_{T0} = 4, than the pure sample (Table 2). This shows that zircon composition does affect the compressibility of zircon. The inverse relationship between room-pressure unit-cell volume and bulk modulus is consistent with Birch's law.

This inverse relationship between volume and bulk modulus suggests that, for Hf-rich natural zircon crystals with relatively small unit-cell volumes, a bulk modulus exceeding our measured value of 199 ± 1 GPa is expected. The zircon unit-cell volumes measured by Hazen and Finger (1979), 260.80 ± 0.03 Å³ for a zircon containing 1.2 wt % Hf, with no other trace elements measured) and Rios and Boffa-Ballaran (2003), 260.82 ± 0.07 Å³ for zircon containing 1.3 wt % Hf and < 20 ppm

other trace elements, are indeed slightly lower than our best fit value of 260.89 ± 0.03 Å³ (Table 2). On the other hand, the room-pressure volumes given by Özkan et al. (1974) and Özkan and Jamieson (1978) for a different set of natural zircon samples (containing significant amounts of Sc and Ba with no reported Hf) are slightly higher (260.96 ± 0.08 Å³) with a reported bulk modulus of approximately 228 GPa.

Although our measurements clearly suggest an effect of impurities on bulk modulus, we note that the differences among different studies for unit-cell volumes for natural samples appears small compared with the difference in volume between our pure undoped and doped synthetic zircon samples. We conclude that a combination of effects, including small pressure ranges in previous diffraction studies, the use of different analytical techniques to determine the unit-cell parameters, and real variations due to zircon compositional variation, are responsible for the differences between our results and those published previously.

Our bulk modulus, K_{T0} , of pure zircon, although smaller than previously measured for impure natural samples, is still a minimum of 10 per cent higher than the bulk moduli of other orthosilicates such as olivines, spinels and garnets (see the compilation in Smyth et al. 2000). This is most likely a result of the strong bonding between silica tetrahedra provided by the highly charged Zr^{4+} cations.

The pressure marking the observed onset of the zircon-to-reidite phase transition also deviates significantly from previous studies. Our data show that pure zircon starts transforming to scheelite-structured reidite at pressures around 19.7 GPa, which is 3 GPa lower than previously observed for natural zircon studied by Raman $(23 \pm 1 \text{ GPa}, \text{Knittle and Williams 1993}).$

The zircon-reidite transition has been observed at high temperatures in both shock wave (e.g. Kusaba et al. 1985) and static experiments (e.g. Reid and Ringwood

1969, Liu 1979). Liu (1979) determined the equilibrium transition pressure at a temperature of around 1300 K to be 12 GPa. At room temperature, assuming a positive Clapeyron slope for the transition, the equilibrium transition pressure is likely to be lower (Knittle and Williams 1993). One model for the transformation, proposed by Kusaba et al. (1986), requires small atom displacements which eventually lead to conversion of zircon <110> directions into reidite <001> directions. Knittle and Williams (1993) postulated that at room temperature, the small displacements needed to trigger this conversion can only take place if the equilibrium transition pressure is sufficiently overstepped.

Our data strongly suggest that the *composition* of zircon is an additional important factor in determining the kinetics of the zircon-reidite phase transition. Pure zircon starts transforming to the scheelite structure more easily than impure, natural zircon. It is conceivable that the impurities impede the displacements needed in the Kusaba et al. model to complete the transformation. This hypothesis is supported by our observation of the zircon-reidite transition in the trace element doped zircon discussed earlier (Van Westrenen et al. 2003). X-ray diffraction of that REE-doped sample did not show evidence for below 22.5 GPa. This pressure is significantly higher than the transition pressure for pure zircon, and indistinguishable from the transition pressure of 23 ± 1 GPa in natural zircon determined by Knittle and Williams (1993). Additional high-pressure X-ray diffraction measurements on zircon samples with well-known compositions are clearly needed to further explore whether there is a systematic effect of trace and minor element impurities on the phasetransition kinetics and compressibility of zircon. Identification of such systematics could lead to a much improved understanding of the microscopic processes responsible for phase transitions in silicate minerals.

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Spectrum	<i>P</i> (GPa) †	<i>a</i> (Å)	<i>c</i> (Å)	$V(\text{\AA}^3)$	R_p (%)‡	wR_p (%) ‡
ZR2026	0.00010(1)	6.6058 (8)	5.9772 (8)	260.82 (5)	2.12	3.50
ZR2004	2.65 (5)	6.5729 (6)	5.9665 (6)	257.77 (4)	1.41	2.22
ZR2005	4.37 (3)	6.5451 (6)	5.9478 (5)	254.80 (4)	1.34	2.12
ZR2001	5.92 (3)	6.5343 (19)	5.9401 (8)	253.62 (6)	1.45	2.17
ZR2007	6.20 (10)	6.5319 (5)	5.9373 (6)	253.32 (4)	1.27	1.99
ZR2008	7.20 (20)	6.5161 (5)	5.9286 (5)	251.72 (3)	1.36	2.09
ZR2009	9.30 (20)	6.5015 (9)	5.9192 (8)	250.20 (6)	1.87	3.48
ZR2010	10.89 (3)	6.4851 (6)	5.9069 (7)	248.43 (4)	1.59	3.14
ZR2011	12.02 (10)	6.4727 (9)	5.9001 (10)	247.19 (6)	1.56	2.47
ZR2012	13.50 (10)	6.4540 (10)	5.8978 (10)	245.67 (7)	1.50	2.34
ZR2013	14.84 (3)	6.4454 (11)	5.8804 (8)	244.29 (6)	1.54	2.38
ZR2014	16.10 (10)	6.4361 (7)	5.8813 (8)	243.62 (5)	1.45	2.38
ZR2015	17.70 (10)	6.4134 (10)	5.8673 (10)	241.33 (7)	1.35	2.61
ZR2016	19.66 (3)	6.3884 (11)	5.8456 (10)	238.56 (7)	1.33	2.71
ZR2017	20.36 (5)	6.3873 (14)	5.8489 (16)	238.62 (10)	1.82	3.94
ZR2018	20.95 (7)	6.3694 (14)	5.8337 (13)	236.67 (9)	1.50	2.44
ZR2019	21.42 (3)	6.3638 (13)	5.8304 (15)	236.12 (9)	1.85	3.28
ZR2020	22.16 (30)	6.3610 (12)	5.8265 (12)	235.76 (8)	1.90	3.80

TABLE 1. Structure refinement details for pure, undoped zircon (ZrSiO₄) as a function of pressure^{*}

* Values in parentheses are 1σ standard deviation in the last decimal place.

[†] Calculated from ruby R1 fluorescence peak (Eqn. 1). 1σ errors in this column are derived from fluorescence measurements on multiple (n > 3) ruby grains distributed around the sample chamber, made both before and after each pressure increase. No account was taken of possible systematic errors in the calibration of the ruby fluorescence method.

$$\ddagger \text{ Agreement factors: } R_p = \frac{\sum \left\| F_o \right| - \left| F_c \right\|}{\sum \left| F_o \right|}, wR_p = \sqrt{\frac{\sum \left(w [F_o - F_c]^2 \right)}{\sum w F_o^2}}.$$

 F_o and F_c are observed and calculated structure factors respectively

			$P_{\rm max}$	$V_{\rm c}$ (CD _a)	V'	\mathbf{V} $(\overset{\circ}{\lambda}^3)$
Reference*	Sample	Method	(GPa)	\mathbf{A}_{T0} (GPa)	$\mathbf{\Lambda}_{T0}$	V_0 (A)
	Synthetic,					
This study	pure	XRD	17.7	201 (2)	3.9 (2)	260.78 (4)
	Synthetic,					
This study	pure	XRD	17.7	199 (1)	4 †	260.89 (4)
	Synthetic,					
This study	pure	XRD	17.7	180 (1)	6.5 †	261.23 (3)
	Synthetic,					
This study	pure	XRD	17.7	228 †	1.3 (2)	260.32 (3)
[1]	Natural	Ultrasonic	-	225 (2)	-	260.96 (8)
[2]	Natural	Ultrasonic	1.2	227.9	6.5	260.96 (8)
[3]	Natural	XRD	4.8	227 (2)	6.5 †	260.80 (3)
[3]	Natural	XRD	4.8	230 (2)	4 †	260.81 (3)
[4]	Natural	XRD	6.9	226 (3)	4 †	260.82 (7)
	Synthetic,					
[5]	doped	XRD	21.5	189 (1)	4 †	263.93 (4)

TABLE 2. Compilation of zircon compressibility data

 [5] aopea
 AKD
 21.5 189(1) 4 + 205.93(4)

 * [1] Özkan et al. (1974) [2] Özkan and Jamieson (1978), [3] Hazen and Finger (1979), [4]

 Ríos and Boffa-Ballaran (2003), [5] Van Westrenen et al. (2003)

† Fixed values

FIGURE CAPTIONS

Figure 1. Scanning electron microscope images of representative synthetic pure zircon crystals used as starting material in this study. Scale bars are 200 µm.

Figure 2. XRD spectrum of the zircon sample (solid line) obtained at a pressure of 13.5 ± 0.1 GPa (ZR2012, Table 1). Results of Rietveld refinement using Rietica software (Hunter and Howard 2000) indicated by dotted best-fit line, slightly offset for clarity. Positions of allowed Bragg reflections for zircon are shown by vertical tick marks. Residuals (in per cent of observed intensity) are shown at the bottom of the graph.

Figure 3. Details of six typical ZrSiO₄ X-ray diffraction spectra as a function of pressure. Three main zircon peaks assignments are given in the lowest-pressure spectrum. Zircon peak positions shift to higher 2 θ values (i.e., smaller unit-cell volumes) as pressure increases. Arrows point to clear indications for the presence of reidite (scheelite-structured ZrSiO₄) from a pressure of 19.66 ± 0.03 GPa onward (see text for details).

Figure 4. Unpolarised, ambient-pressure Raman spectra of starting material (zirconstructured $ZrSiO_4$) and recovered sample (scheelite-structured $ZrSiO_4$, reidite, with most intense zircon bands also still present). The reidite spectrum was recorded after decompression of the sample, which had been left in the diamond anvil cell at a pressure of 27 GPa for a total of 106 hours after diffraction analyses. The dotted line shows the reidite spectrum reported by Knittle and Williams (1993), which also appears to contain several of the most intense zircon Raman modes.

Figure 5. Main panel: Zircon (ZrSiO₄) room temperature unit cell volume as a function of pressure (data from Table 1). Solid symbols: zircon peaks only present in XRD spectrum. Open symbols: both zircon and reidite peaks present in XRD spectrum. Line is best-fit of data to a Birch-Murnaghan equation of state (Eqn. 2), with $K_{T0}^{'}$ set to 4. 1 σ error bars are shown if bigger than symbol size. Inset: Birchnormalised pressure *F* (Eqn. 4) plotted against Eulerian strain *f* (Eqn. 3). Broken line shows that data are consistent with $(\partial K_{T0} / \partial P)_T = 4$ and $K_{T0} = 199 \pm 1$ GPa, as suggested by the fit shown in the main figure. Error bars in inset figure are 2σ .





Fig 2



 $ZrSiO_4$ diffraction patterns as a function of pressure

Fig 3



Fig 4



Fig 5