

Deformation Behavior across the Zircon-Scheelite Phase Transition

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The pressure effects on plastic deformation and phase transformation mechanisms of materials are of great importance to both Earth science and technological applications. Zircon-type materials are abundant in both nature and the industrial field; however, there is still no *in situ* study of their deformation behavior. Here, by employing radial x-ray diffraction in a diamond anvil cell, we investigate the dislocation-induced texture evolution of zircon-type gadolinium vanadate (GdVO_4) *in situ* under pressure and across its phase transitions to its high-pressure polymorphs. Zircon-type GdVO_4 develops a (001) compression texture associated with dominant slip along $\langle 100 \rangle \{001\}$ starting from 5 GPa. This (001) texture transforms into a (110) texture during the zircon-scheelite phase transition. Our observation demonstrates a martensitic mechanism for the zircon-scheelite transformation. This work will help us understand the local deformation history in the upper mantle and transition zone and provides fundamental guidance on material design and processing for zircon-type materials.

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Zircon (ZrSiO_4) is a ubiquitous accessory mineral in nature which can be found in a wide variety of sedimentary, igneous, and metamorphic rocks [1]. Its high-pressure polymorph, reidite with the scheelite-type structure has also been discovered in terrestrial impact craters [2]. The ability to retain substantial chemical and isotopic information about zircon has made it useful in a wide range of geochemical investigations, from studies of the chemical evolution of Earth's crust and mantle to age dating [3,4]. During its history, zircon can be subject to plastic deformation, either through geodynamical processes [5] or shock metamorphism [6]. As such, the remains of plastic deformation in zircon grains are used as a marker for deformation or records of impact in Earth's history. Hence, the plastic deformation of zircon and its high-pressure polymorphs is of general interest to the Earth science community.

In fact, there are many minerals or materials with the zircon-type structure. The orthovanadates (AVO_4) are such examples. They are a group of materials with promising optical, chemical, and mechanical properties, which make them interesting for application in devices such as lasers, scintillators, and also catalysts and phosphors [7–10]. Because of the technological importance of zircon-type orthovanadates, besides their electronic and optical properties, their mechanical properties are also of interest in several areas of materials research [11]. Previous studies of orthovanadates including x-ray diffraction [12–16], Raman scattering [17], theoretical calculations [18,19],

and combined methods [20,21] show that many AVO_4 compounds with the zircon-type phase transform to a scheelite-type structure (space group: $I4_1/a$) under high pressure irreversibly. However, while multiple studies focused on pressure-induced structure changes in orthovanadates, there are few reports on their plastic behavior and orientation relationships between the low- and high-pressure phases. Such information is critical for the design of advanced materials, such as shape-memory alloys that rely on martensitic transformations to recover their original shape after the application of external loading conditions [22,23].

Considering the importance of zircon-type materials for geology and material science, it is necessary to study their deformation behavior under high pressure. There are already some reports about the slip system of zircon-type materials during plastic deformation [5,24–27]. However, the deformation mechanism of the zircon phase under pressure is still controversial. A transmission electron microscopy (TEM) study of shock deformed zircon suggested a dominant system of $\langle 001 \rangle \{010\}$ [25], while an electron backscatter diffraction investigation of natural zircon led to dominant slips along $\langle 010 \rangle \{001\}$, $\langle 010 \rangle \{100\}$, and $\langle 001 \rangle \{010\}$ [5]. Dislocation structures in single crystal of yttrium orthovanadate has also been identified by TEM with vector $1/2[111]$ and (11-2) as a possible slip plane [24]. Hence, further investigation of the deformation mechanism of zircon is still needed to address this controversy.

Here, by taking the advantage of the radial x-ray diffraction technique in the diamond anvil cell (DAC) [28–32], we investigate *in situ* the deformation behavior of zircon-type material GdVO_4 across the zircon-scheelite phase transition under high pressure up to 38 GPa. Unlike in conventional axial geometry, the x ray is sent through the x-ray transparent boron-kapton gasket and sample polycrystals perpendicular with the compression direction in radial diffraction [33]. A small fragment of $\sim 10 \mu\text{m}$ thick platinum foil was added on top of the sample and was used as a pressure calibrate in each experiment, using the equation of state (EOS) for Pt [34]. In order to maximize the deviatoric stress on the samples, no pressure medium was used. Under the nonhydrostatic condition, the pressure uncertainty increases with pressure, and the pressure error is ± 2 GPa at 25.6 GPa. The samples were compressed between diamond culets of $300 \mu\text{m}$ diameter. The *in situ* radial x-ray diffraction and DAC deformation experiment was performed at beam line 12.2.2 of the Advanced Light Source at Lawrence Berkeley National Laboratory. A panoramic-type diamond anvil cell with large openings was used to allow radial x-ray diffraction. A monochromatic x ray of wavelength 0.4959 \AA was collimated to a beam size of $20 \times 20 \mu\text{m}^2$ and focused onto the sample. A Mar345 image plate was used to record the diffraction rings of the samples. Instrument parameters such as sample-to-detector distance, beam center, and detector tilt were calibrated using a LaB_6 standard prior to the experiment. The diffraction data were analyzed by the Rietveld refinement method [35] as implemented in the software package MAUD [36]. The lattice parameters, lattice strain, and preferred orientations of both zircon and scheelite structures were extracted from the refinement results.

At ambient condition, GdVO_4 is in the form of a zircon-type tetragonal structure with space group $I4_1/amd$, as seen in Fig. 1(a). Under high pressure, the zircon-type structure transforms to a scheelite-type tetragonal phase with space group $I4_1/a$ at 5.0 GPa. The zircon-type phase and scheelite-type phase coexist in a wide pressure range up to 23.0 GPa. With further pressure increase, a monoclinic *M*-fergusonite (*Mf*) (space group: $I2/a$) phase appears above 31.2 GPa. However, a full conversion to the *Mf* phase was not achieved in the current experiment. Therefore, the deformation behavior of the third phase will not be discussed in this Letter. The atomic structures of these two high-pressure polymorphs are given in Figs. 1(b) and 1(c). After decompression, the quenched sample shows a pure scheelite structure indicating that the transformation to the *Mf* phase is reversible, unlike that of zircon to scheelite structures which is nonreversible. This observation is in good agreement with the irreversible changes detected in Raman and luminescence measurements [17]. This phenomenon has also been reported in high-pressure studies of natural zircon [37] and other AVO_4 materials like TbVO_4 , EuVO_4 , LuVO_4 , and ScVO_4 [12,15]. There is also a rare case in which the phase transition does not follow this

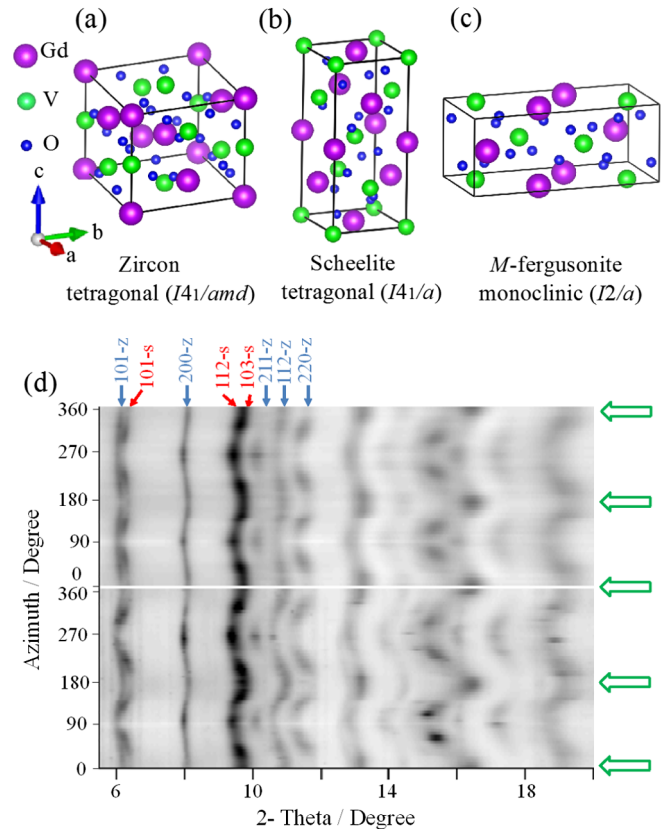


FIG. 1. Crystal structures and fitting example of GdVO_4 . (a) Zircon, (b) scheelite, and (c) *M*-fergusonite phases. The zircon phase begins to transform to a scheelite phase below 5 GPa. The transition is complete at 23 GPa. A subsequent transformation to an *M*-fergusonite phase occurs at 31 GPa. (d) Fitting example at 11 GPa. The bottom half of the pattern is the experimental data, and the top is the calculated pattern from the Rietveld refinement. The chi square (χ^2) is 1.071. Some of the diffraction lines from the zircon and scheelite phases are labeled (“z” for zircon and “s” for scheelite). Others are not labeled due to multiple peak overlaps between the two phases. The green arrows indicate the compression direction.

trend. Zircon-type $\text{Tb}_{0.5}\text{Gd}_{0.5}\text{PO}_4$ transformed to monazite through an intermediate anhydrite-type structure showing a different phase transition sequence for zircon-type materials under high pressure [38].

One fitting example is shown in Fig. 1(d) at 11.0 GPa where both the zircon-type phase and scheelite-type phase are present. More information concerning the refinement of patterns for different phases can be found in the Supplemental Material [39] Figs. S1 and S2. The volume fractions and hydrostatic lattice parameters of zircon, scheelite, and *Mf* phases of GdVO_4 were obtained from the refinement [39] and plotted in Fig. 2. The onset pressure of the zircon-scheelite phase transformation for GdVO_4 in our work is 5 GPa, which is lower than the 7 GPa reported using Raman measurements [17]. Do note, however, that a 4:1 methanol-ethanol mixture was used as the pressure transmitting medium in the previous study, while we did not use any in our study. Such effect of nonhydrostatic

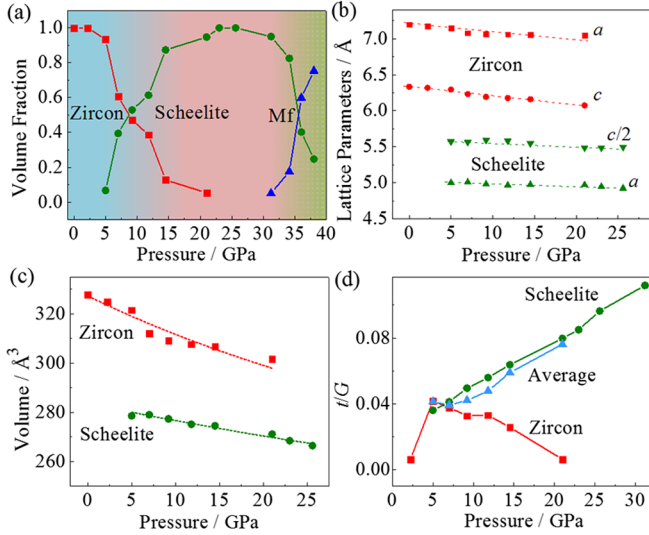


FIG. 2. Refinement results for GdVO₄ under pressure. (a) Volume fraction, (b) unit-cell parameters, (c) unit-cell volume (dashed lines are EOS fitting results), and (d) t/G ratio of the zircon and scheelite phases as a function of pressure. The average values of t/G shown in (d) are weighted means of those measured in both phases, t is the differential stress, and G is the shear modulus. For the *M*-fergusonite phase, only the volume fraction is shown.

conditions on transition pressure is well known in high-pressure experiments [47,48]. The unit-cell parameters and volumes for the zircon and scheelite phases of GdVO₄ under pressure are summarized in Figs. 2(b) and 2(c). The volumes as a function of pressure have been fitted using third-order Birch-Murnaghan EOS for both phases [39]. The c/a ratio was plotted as a function of pressure in Ref. [39] Fig. S3. We observe a decrease of about 10.6% in volume for the zircon to scheelite phase transformation.

Figure 2(d) displays t/G as a function of pressure for the zircon and scheelite phases. The stress state in a polycrystalline sample under uniaxial compression in the diamond anvil cell can be described by a maximum stress along the cell loading axis σ_3 and a minimum stress in the radial direction σ_1 . The difference between σ_3 and σ_1 is termed the differential stress t . According to the lattice strains theory developed by Singh *et al.* [49], we have t/G equal to 6 times $\langle Q(hkl) \rangle$, where $\langle Q(hkl) \rangle$ represents the average lattice strain value over all observed reflections, and G is the aggregate shear modulus of the polycrystalline sample. The t/G ratio can be readily extracted from the diffraction data and is most appropriate for comparing different materials. Such model does not account for intragranular plastic relaxation [50]. It has been shown, however, that it could be used for a first evaluation of the stress level in plastically deforming aggregates [51]. In order to extract t/G with MAUD, we used the triaxial stress isotropic E strain model to refine a first value of differential stress t using the Young's modulus E and Poisson ratios ν of GdVO₄ at ambient condition, from which we calculated $t/G = 2t(1 + \nu)/E$, which is independent of the choice of E and ν .

For the zircon phase, t/G first increases from 0 at 1 atm to 0.0412 at 5 GPa. With the appearance of the scheelite phase, this value begins to decrease gradually and reaches 0.006 at 21 GPa. For the scheelite phase, the initial value is 0.036 at 5 GPa; it increases to 0.096 at 25.6 GPa. The lattice strains of the zircon phase first increase with increasing pressure. They then decrease with the appearance of the second phase. This may imply that the grains with higher deviatoric strains transform to the scheelite phase earlier, in agreement with the lower phase transformation pressure observed in our nonhydrostatic experiment. A displacive mechanism has been reported for the zircon-scheelite transformation, which is claimed to be the result of simple shearing of the zircon structure followed by small atomic adjustments [52]. As a consequence, the high-pressure scheelite phase should inherit the lattice strain of the zircon phase during phase transformation, hence, the high initial t/G value for the scheelite phase that is measured at the beginning of the phase transformation.

The high differential stress under nonhydrostatic pressure can produce plastic deformation, and this behavior is investigated by the texture analysis. Upon compression, the zircon-type GdVO₄ develops a texture characterized by a maximum along the 001 direction and minima along the 010 and 110 directions in the inverse pole figures, as seen in Fig. 3. The intensity of the 001 texture increases with the initial compression. It then decreases during the phase transformation to the scheelite phase. The appearance and increase of the texture strength in the initial compression stage is induced by the plastic deformation of zircon GdVO₄ under pressure. After the zircon-scheelite phase transition, the scheelite phase readily shows a texture with a maximum at 110 and minima at 001 and 010. The texture becomes stronger with pressure while the volume ratio increases. At 23 GPa, the zircon phase completely disappears, while the scheelite phase shows a remarkable texture with a maximum pole density of 7.11 at 110.

The development of textures depends on the deformation geometry and the relative activities of slip systems. In order to infer the active slip systems in the zircon phase under high pressure, we compare the experimental textures with

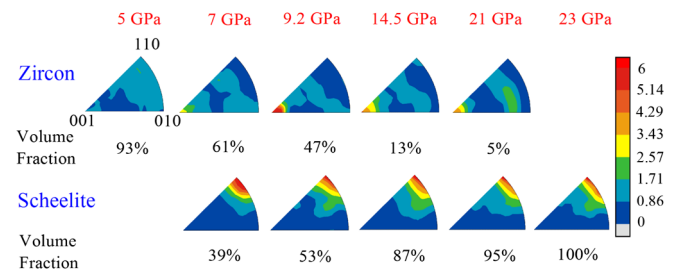


FIG. 3. Texture evolution of GdVO₄ through the phase transition. Inverse pole figures of the compression direction are shown up to 23 GPa for both the zircon and scheelite phases. For each case, the experimental pressure and phase proportions are shown in the figure. Pole densities are measured in multiples of a random distribution (mrd). Equal area projections.

TABLE I. VPSC calculation parameters. Each line is a simulation with a different dominant slip system. For each, we report the CRSS (critical resolved shear stresses) of each slip system and their relative plastic activity (Act, in percent). The corresponding compression textures are shown in Fig. 4(b).

	$\langle 100 \rangle \{001\}$		$\langle 110 \rangle \{001\}$		$\langle 100 \rangle (010)$		$[001](010)$		$\langle 1-10 \rangle \{111\}$		$\langle 11-1 \rangle \{112\}$	
	CRSS	Act	CRSS	Act	CRSS	Act	CRSS	Act	CRSS	Act	CRSS	Act
Model 1	0.5	57%	...	0%	1	16%	1	0%	10	27%	...	0%
Model 2	0.5	54%	...	0%	1	16%	1	0%	100	0%	10	30%
Model 3	1	25%	...	0%	0.5	27%	1	25%	10	23%	...	0%
Model 4	1	27%	...	0%	0.5	29%	1	27%	100	0%	10	17%
Model 5	1	0%	...	0%	1	35%	0.5	41%	10	24%	...	0%
Model 6	1	0%	...	0%	1	41%	0.5	45%	100	0%	10	13%
Model 7	...	0%	0.1	0%	1	5%	1	10%	100	85%	10	0%

those generated from polycrystal plasticity. For these simulations, we used the Los Alamos viscoplastic self-consistent code (VPSC), which treats each grain as an inclusion in a homogeneous but anisotropic matrix that has the average properties of the polycrystal. As deformation proceeds, crystals deform and rotate to generate preferred orientation. By applying different critical resolved shear stresses (CRSSs) to slip systems, the model will favor one deformation mode over another. This results in different textures for different combinations of deformation models. By determining which simulated texture most closely resembles the experimental texture, we can infer which slip systems are active under the experimental conditions. By applying different CRSSs to various slip systems, seven different models were generated to find a best match to the experiment result. The parameters used for each model are shown in Table I. Some example slip systems are shown in Fig. 4(a). For each model, we start with a randomly oriented sample of 3000 grains. We deform the sample incrementally in 100 steps to a total of 50% strain to match the intensity of the textures observed experimentally. The results of the modeling are displayed in Fig. 4. It can be clearly seen that model 2 provides textures that best agree with the experimental results. In this case, deformation is strongly dominated by the $\langle 100 \rangle \{001\}$ slip system (54% of the total plastic activity), while the slip system $\langle 100 \rangle (010)$ shows a plastic activity of 16%. The rest of the deformation is accommodated by the $\langle 11-1 \rangle \{112\}$ slip (30%). The agreement between the experimental textures and simulated textures could not be improved with other slip system combinations.

The zircon to scheelite phase transformation has been investigated by Leroux *et al.* [25] using TEM on quenched shock deformed samples. They found that the scheelite phase was in a close epitaxial relationship with zircon, with $\{100\}_z // \{112\}_s$ and $[001]_z // \langle 110 \rangle_s$. This conclusion is consistent with the result reported by Kusaba *et al.* [52] on the shock-induced zircon to scheelite transformation, in which the $[110]$ direction in zircon was observed to become the $[001]$ direction in the scheelite. It is also consistent with observations in natural samples [6]. In our work, the zircon-type GdVO_4 shows a (001) texture, while the scheelite

phase shows a (110) texture, which agrees well with the above relationship. The (110) texture of scheelite is, hence, inherited from the (001) texture of the zircon phase. The observed textures in the scheelite phase do not evolve upon further compression. Therefore, it can be concluded that the measured textures in the scheelite phase are mainly inherited from that of the zircon phase during the phase transformation, with little contribution from the further plastic deformation in the experiment.

In our work, the texture evolution of zircon-type GdVO_4 under plastic deformation and through phase transition was

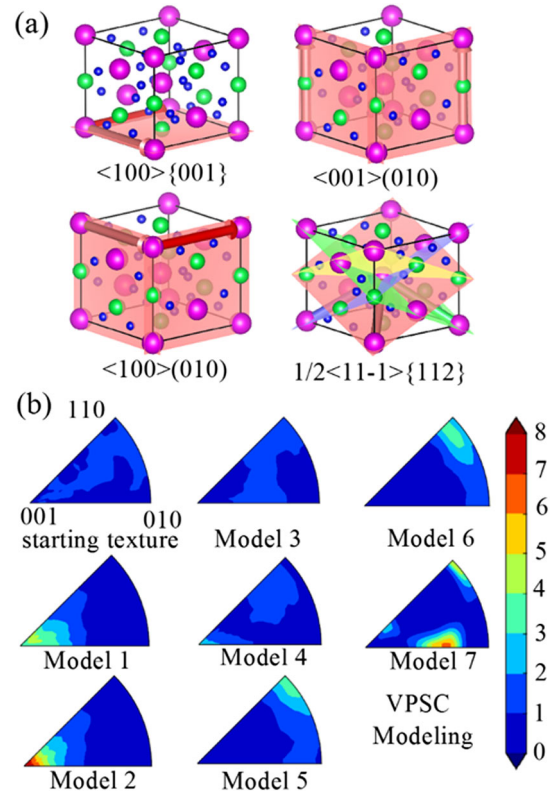


FIG. 4. Dominate slip systems for the zircon phase under plastic deformation. (a) Slip systems reported in the literature. (b) Inverse pole figures calculated from seven VPSC models. The corresponding slip system activities for each model are shown in Table I. Pole densities are in mrd. Equal area projections.

systematically investigated via radial x-ray diffraction in a diamond anvil cell. In the low-pressure zircon phase, we observed preferential alignment of the (001) poles with the compression direction. This is attributed to dominant slip on $\langle 100 \rangle \{001\}$ combined with two other slip systems $\langle 100 \rangle \{010\}$ and $\langle 11-1 \rangle \{112\}$. Because of the topotactic relationship $[001]_z // \langle 110 \rangle_s$ during the phase transformation, the high-pressure scheelite phase inherits the texture from the previous zircon phase and develops a texture with a maximum at 110. The present work contributed to achieving a deeper understanding of the plastic deformation of zircon-type oxides which are of technological and geophysical importance. It is also an important contribution to the understanding of pressure-induced martensitic transformations, which could be useful for the development of new shape-memory materials.

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