



Article In Situ Raman Spectroscopy and DFT Studies of the Phase Transition from Zircon to Reidite at High P–T Conditions

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Abstract: Zircon (ZrSiO₄) provides a good pressure-holding environment for ultra-high-pressure metamorphic minerals during crust exhumation due to its high incompressibility and chemical stability. At high pressure, the zircon can transform to reidite. Previous studies show much higher phase-transition pressures at room temperature than those at high temperature (>1000 K) due to kinetic hindrance. To further investigate the kinetics of the zircon–reidite phase transition at relatively low temperatures, the phase boundary at 298–800 K was determined using a diamond anvil cell combined with in situ Raman spectra. The results show that reidite becomes thermodynamically more stable compared with zircon at 8 GPa at room temperature, and the slope of the phase boundary at 298–800 K abruptly differs from that of previous studies at 1100–1900 K. Compared with the equilibrium phase boundary calculated by the density functional theory, it indicates that the kinetic effect of the zircon–reidite phase transition is obvious, and there exists a sufficiently large energy driving force provided by an overpressure to overcome the activation energy barrier below a critical temperature of approximately 880 K. The temperature dependence of overpressure is about 0.023 GPa/K.

Keywords: zircon; reidite; phase transition; high P–T experiment; diamond anvil cell; in situ Raman spectroscopy; density functional theory

1. Introduction

Zircon is a ubiquitous mineral in many igneous, sedimentary, and metamorphic rocks [1]. It can accommodate radioactive trace elements and is therefore widely used in geochemical and geochronological studies [2–4]. Owing to its high incompressibility and chemical stability, zircon can form a good container for ultra-high-pressure metamorphic (UHPM) minerals during pressure release caused by the rapid exhumation of plates, leading to its application in exploring the geological pressure-temperature (P-T) record of the evolution of UHPM minerals [5–7]. Under ambient conditions, zircon exhibits tetragonal symmetry (space group $I4_1/amd$), whereas, under high pressure, zircon undergoes a first-order phase transition to reidite (scheelite structure, space group $I4_1/a$). Moreover, reidite has been found to be critical for understanding impact events [8–10]. For example, some reidite-bearing zircon samples were found in an upper Eocene impact ejecta layer in marine sediments on the upper continental slope off New Jersey and in Barbados [11–13]. Furthermore, zircon can be used as high-quality ceramics [14], refractories [15], and potential storage material for radioactive waste [16]. Therefore, understanding the phase transition of zircon to its high-pressure phase reidite and their physical properties under extreme conditions are of great significance in both geoscience and industries.



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The zircon–reidite phase transition has been studied both experimentally [17–21] and theoretically [22–25]. Previous studies show that the phase transition pressure at room temperature is much higher than that at high temperature (>1000 K). For example, static compression experiments at room temperature indicated a transition pressure of 23 GPa via Raman spectroscopy [17] and 19.7 GPa via synchrotron radiation X-ray diffraction [20]. On the other hand, Ono et al. [18,19] reported that the zircon–reidite phase transition occurred at 8–10 GPa and 1100–1900 K by the multi-anvil apparatus and synchrotron radiation X-ray diffraction. In addition, Akaogi et al. [21] reported an equilibrium transition pressure of 8 GPa at 298 K by thermodynamic calculations. Based on the first principle calculations, the zircon–reidite equilibrium boundary is located around 5.2–7.3 GPa at 0 K [23–25]. The much higher transition pressure compared to the equilibrium transition pressure under room temperature suggests that a substantial activation barrier exists for the zircon-reidite transition. Interestingly, the zircon–reidite phase transition at room temperature exhibits "an anomalous and possibly unique silicate transformation mechanism" [17], since first-order phase transitions at room temperature are unusual among silicates. Regarding phase transition mechanics, Kusaba et al. [26,27] proposed a two-step mechanism, and Marques et al. [23] proposed a quasi-monoclinic transition path. The phase transition activation energy decreases with increasing pressure; thus, the transition can occur at room temperature.

However, the kinetics of the zircon–reidite phase transition is not well constrained experimentally at relatively low temperatures (298–1000 K). To refine the high P–T phase diagram of zircon–reidite, we determined the kinetic phase boundary between zircon and reidite in the range of 300–800 K using a diamond anvil cell (DAC) in conjunction with in situ Raman spectroscopy. Furthermore, combined with the thermodynamic equilibrium phase boundary calculated by the density functional theory (DFT), the influence of kinetic hindrance on the zircon–reidite phase transition was investigated quantitatively.

2. Materials and Methods

We selected natural zircons from a meta-gabbro sample from the Langmuri platinum group elements deposit in the Eastern Kunlun Orogenic Belt. Zircon grains were separated from bulk samples using conventional heavy liquid and magnetic techniques and then purified by handpicking under a binocular microscope.

High-pressure experiments were performed using a BX90 DAC [28] with a culet size of 500 μ m in diameter. Zircon samples were manually ground and polished to a size of ~60 × 60 × 20 μ m³. Then, they were loaded into a chamber (200 μ m in diameter) that was drilled by laser into a pre-indented rhenium gasket to about 40–50 μ m thickness. A 16:3:1 mixture of methanol/ethanol/water was used as the pressure transmitting medium to ensure a quasi-hydrostatic pressure environment. The fluorescence of 5 at.% doped Sm:YAG was used to monitor the pressure of the sample chamber by using the pressure-dependent shift of its Y1 fluorescence line [29]:

$$P(\text{GPa}) = (A/B) \times \{[1 + (\Delta\lambda/\lambda_0)]^B - 1\}$$
(1)

where A = 2089.91(23.04), B = -4.43(1.07), $\Delta\lambda = \lambda - \lambda_0$, and λ and λ_0 are the wavelengths of the Y1 line at ambient pressure and elevated pressure in nanometers, respectively. The sample chamber was heated with an external resistive (Ni-Cr) heater, and the temperature was measured using a K-type thermocouple (CHAL-010, Omega Engineering Inc., Stamford, CT, USA) attached to the diamond anvils.

For the convenience of pressure loading under high temperatures, the DAC was integrated into a piezoelectric ceramic pressure loading system. In the system, when an input electric signal is applied to the piezoelectric ceramic using a function generator and a power amplifier, the piezoelectric ceramic expands and compresses the DAC in a controlled and continuous manner. In this study, a stepped voltage-time signal was used to drive the piezoelectric ceramic with 3 stages, rising, constant, and falling, corresponding to compression, pressure-holding, and decompression, respectively. In the experiments, the sample was first slowly heated (25 K/min) to the target temperature; then, the input signal was applied to the piezoelectric ceramic, and the pressure loading procedure commenced. Since the low signal-to-noise ratio of Raman signal at high P–T, the experiments were carried out in situ below 500 K and ex situ above 500 K, respectively. In the in situ Raman spectra of the sample and the fluorescence spectra of Sm:YAG were simultaneously obtained 12 min after each pressure-holding stage began, and in the ex situ Raman experiments, the samples were held at the chosen pressure for 20 min. After decompression, the temperature was reduced to room temperature at a rate of 25 K/min, and the Raman spectra of the samples for the ex situ experiments were observed at room temperature and atmospheric pressure.

The confocal micro-Raman spectroscopy equipment comprises two spectrometers (Andor Shamrock 500i) equipped with a CCD detector (Andor iVac 316) and a 532 nm laser with 251 mW laser power (MLL-FN-532/1–800 mW, Changchun New Industries Optoelectronics Technology Co. Ltd., Changchun, China) [30]. A spectrometer was used to record the Raman signal of zircon with a 10 s exposure time, a 100 μ m aperture slit, and an 1800 g/mm grating affording a resolution of 3.02 cm⁻¹. The other spectrometer was used to record the fluorescence signal of Sm:YAG with 0.1 s exposure time, 10 μ m aperture slit, and 1200 g/mm grating affording a resolution of 0.06 nm. Before each experiment, two spectrometers were thoroughly calibrated using a standard mercury lamp.

The thermodynamic equilibrium phase boundary of zircon-reidite was calculated by DFT. To account for the temperature and pressure dependence of the Gibbs free energy, the quasi-harmonic approximation method [31,32] was employed to calculate the total Helmholtz free energy F(T;V), including the internal energy U(V) and the phonon Helmholtz free energy $F_{phonon}(T;V)$ of zircon and reidite at 11 cell volume points (V) with temperatures (T) ranging from 0 to 1900 K in steps of 2 K. DFT calculations were performed using the Vienna ab initio simulation package (VASP) [33,34]. The exchange–correlation interactions were treated with the local density approximation (LDA) functional [35]. The valence-core interactions were described using the projector-augmented wave method [36] with a cutoff energy of 600 eV for the plane-wave basis set, where the valence electron configurations of Zr (4s4p5s4d), Si (s2p2), and O (s2p4) were selected. The convergence criteria were 10^{-6} eV and -10^{-4} eV/Å for electronic and ionic relaxations, respectively. The PHONOPY code [32] was applied to obtain the phonon properties using the density functional perturbation theory methods [37] with a $9 \times 9 \times 9$ k-point mesh for the primitive unit cell. The Vinet equation of state [38] was used to fit the F–V points to the curves, the minimums of which correspond to the equilibrium volumes and the Helmholtz free energy. Additionally, the Gibbs free energy G(T,p) at a given temperature T and the pressure p was obtained from the Helmholtz free energy F(T;V) through the following transformation:

$$G(T, p) = \min_{V} [F(T; V) + pV]$$
⁽²⁾

3. Results and Discussion

We conducted a series of high pressure experiments at different temperatures (300–800 K) to build the zircon–reidite phase boundary. All experimental conditions and results are summarized in Table 1. As shown in Figure 1, the Raman spectrum of the initial zircon sample in the experiment DD0159 contains seven peaks at 202, 215, 225, 356, 440, 975, and 1006 cm⁻¹, which represent the $E_g(1)$, $B_{1g}(1)$, $E_g(2)$, $E_g(3)$, $A_{1g}(1)$, $A_{1g}(2)$, and $B_{1g}(4)$ vibrational modes of zircon, respectively. This feature is in good agreement with previous experimental and computational results [39–42]. The other spectra in Figure 1 (DD0115, DD0162, and DD0159) represent the recovered samples after experiments under different P–T conditions. The typical Raman vibrational modes of reidite observed in our experiments and related assignments are listed in Table 2, which well correspond to the results of former researchers [40,41,43]. Furthermore, the Raman peaks of the recovered sample in DD0115 and DD0162 shift by about 3–10 cm⁻¹ toward high wave numbers, in contrast to those in DD0159, and the reasons have not yet been identified.

Run	Temperature (K)	Pressure (GPa)	Zircon–Reidite Transition Pressure (GPa)					
(In situ Raman observation at high temperature and high pressure)								
DD0079	298	1.2–7.6	1					
DD0080 ²	298	6.6-15.1	_					
DD0091	298	9.2-19.5	19.1					
DD0114	298	4.4-18.4	_					
DD0115	298	11.4-26.0	19.5					
DD0123	298	13.6-25.0	21.0					
DD0214	298	0.6-21.8	20.0					
DD0162(1)	373	6.5-14.3	_					
DD0162(2) ³	373	10.4-25.0	18.7					
DD0159	473	13.7-25.0	16.0					
Run	Temperature (K)	Pressure (GPa)	Recovered Samples					
(Ex situ Raman observation at room temperature and atmospheric pressure)								
CD0155	298	24.0	zircon + reidite					
CD0031	373	8.7	zircon					
CD0039	373	13.2	zircon					
CD0032	473	9.4	zircon					
CD0154	500	16.1	zircon + reidite					
CD0033	573	8.7	zircon					
CD0172(1) ⁴	600	12.5	zircon					
CD0172(2)	700	10.0	zircon					
CD0172(3)	800	15.2	zircon + reidite					

Table 1. Experimental conditions and results.

¹ No phase transition was observed; ² DD0079 and DD0080 are two cycles of one pressure-loading procedure using the same sample; ³ DD0162 (1) and (2) are two cycles of one pressure-loading procedure using the same sample; ⁴ CD0172 (1), (2), and (3) represent three experiments performed sequentially using the same sample.



Figure 1. Raman spectra of the initial and recovered samples in the experiments. Due to the overlap of the peak, we cannot distinguish the peak at 202 cm⁻¹ as belonging to reidite or zircon in the spectrum of recovered sample DD0159.

Vibrational Modes	${\displaystyle {{ u_0}}^{1}}$ (cm $^{-1}$)	${\nu_0}^2$ (cm ⁻¹)	${\nu_0}^3$ (cm ⁻¹)	${ u_0}^4$ (cm ⁻¹)	ν_0^{5} (cm ⁻¹)
Eg (1)	202	196 (+6) ⁶	204 (-2)	_	209 (-7)
$B_{g}(1)$	_	_	238	237.9	242
$E_{g}^{\prime}(2)$	297	—	297 (0)	297.0 (0)	300 (-3)
$A_{g}^{\prime}(1)$	327	320 (+7)	327 (0)	326.4 (-0.6)	326 (+1)
$B_{g}^{\circ}(2)$	355	343 (+12)	353 (+2)	349 (+6)	350 (+5)
$A_{g}^{\prime}(2)$	403	—	406 (-3)	406.1 (-3.1)	409 (-6)
$E_{g}^{\prime}(3)$	453	—		—	458 (-5)
$B_{g}^{o}(3)$	463	456 (+7)	464 (-1)	465.8 (-2.8)	465 (-2)
$E_{g}^{\prime}(4)$	558	552 (+6)	558 (0)	558.4 (-0.4)	558 (0)
$B_{g}^{\prime}(4)$	610	604	610 (0)	610.9 (-0.9)	608 (+2)
$B_{g}^{o}(5)$	844	842 (+2)	847 (-3)	847 (-3)	852 (-8)
Ag (3)				—	861
E _g (5)	884	880 (+4)	887 (-3)	886.4 (-2.4)	891 (-7)

Table 2. Raman shifts of reidite.

¹ Data were from DD0159. ² Data were from Knittle and Williams [17]. ³ Data were derived from Gucsik [43]. ⁴ Data were reported by Mihailova et al. [40]. ⁵ Data source was Stangarone et al. [41]. ⁶ The numbers in brackets represent the difference in the vibration frequency from the values in DD0159.

The characteristics of the zircon Raman spectra at different pressures are listed in Figure 2. In DD0115, new peaks were observed at 508 and 611 cm^{-1} at 19.5 GPa; they are labeled by blue and red arrows in Figure 2a and are attributed to the B_g(3) and E_g(4) vibrational modes of reidite, respectively, while these two vibrational modes are located at 463 and 558 cm⁻¹ under ambient conditions. Likewise, in DD0162(2), the B_g(3) and E_g(4) modes of the reidite were observed at 18.7 GPa, as denoted with blue and red arrows in Figure 2b, respectively. In DD0159, the E_g(4) modes of reidite was observed at 16.0 GPa, as denoted with a red arrow in Figure 2c, and the B_g(3) mode was not observed, possibly due to the low signal-to-noise ratio at high P–T. Our results indicate that zircon–reidite phase transitions occur at 19.5, 18.7, and 16.0 GPa when the temperature is 298, 373, and 473 K, respectively.



Figure 2. The characteristics of zircon Raman spectra at different pressures for (**a**) DD0115, (**b**) DD0162(2), and (**c**) DD0159. The peaks of zircon and reidite are marked by Z and R, respectively. The blue and red arrows denote the novel peaks that are attributed to the vibrational modes of reidite $B_g(3)$ and $E_g(4)$, respectively.

Before the zircon–reidite phase transition occurs, the Raman spectra of zircon show some anomalous features with increasing pressure. Figure 3a,b display the Raman spectra of the sample in DD0079 and DD0080, corresponding to the pressure ranges of 1.2–7.6 and 6.6-15.1 GPa, respectively, at room temperature. Figure 3c summarizes the pressure dependence of the wavenumber of the $B_{1g}(1)$ (215 cm⁻¹ under ambient conditions), $E_g(1)$ (202 cm⁻¹ under ambient conditions), and $E_g(2)$ (224 cm⁻¹ under ambient conditions) modes. As shown by the red arrows in Figure 3a,b, the $B_{1g}(1)$ and $E_g(2)$ modes merge into a peak at 6.1 GPa. As the pressure further increases, it splits into two peaks at 8.8 GPa. These phenomena can be attributed to the crossing of the $B_{1g}(1)$ and $E_g(2)$ modes due to the larger pressure dependence of the wavenumber $d\omega/dP$ of the B_{1g}(1) mode than that of the $E_g(2)$ mode. In addition, in Figure 3a, the intensity of the $E_g(2)$ mode relative to the $B_{1g}(1)$ mode decreases with increasing pressure, resulting in the intensity of the $B_{1g}(1)$ mode being greater than that of the $E_g(2)$ mode in Figure 3b. At about 8 GPa, the value of $d\omega/dP$ of the $E_g(2)$ mode changes from slightly positive to negative, while the value of $d\omega/dP$ of the $B_{1g}(1)$ mode remains relatively unchanged, as shown in Figure 3c. Furthermore, the split of the $E_g(1)$ mode into two peaks is indicated with a blue arrow in Figure 3b at 10.6 GPa, which is caused by the sudden decrease of $d\omega/dP$ of the E_g(1) mode of some zircons at around 8 GPa, as shown in Figure 3c, while the other zircons maintain its original $d\omega/dP$ value. The abrupt changes of $d\omega/dP$ of the $E_g(1)$ and $E_g(2)$ modes are related to the change of the interatomic force constants [40], resulting in the thermodynamic metastability of zircon above 8 GPa below room temperature, which is generally consistent with the previously experimental results (10 GPa) by in situ Raman [40].



Figure 3. The characteristics of zircon Raman spectra at different pressures for (**a**) DD0079 and (**b**) DD0080. The red arrow in (**a**) represents the merger of the $B_{1g}(1)$ and $E_g(2)$ modes into one peak, which splits into two peaks, as shown by the red arrow in (**b**). The blue arrow in (**b**) represents the split of the $E_g(1)$ mode into two peaks. (**c**) The Raman shift of the $E_g(1)$, $B_{1g}(1)$, and $E_g(2)$ zircon modes as a function of pressure for DD0079 and DD0080. The vertical dashed lines correspond to the abrupt changes of $d\omega/dP$ of the $E_g(1)$ and $E_g(2)$ modes.

Additionally, a similar variation of the $B_{1g}(1)$ and the $E_g(2)$ modes in the zircon–reidite phase transition at high temperatures was observed (Figure 4). The results indicate that zircon becomes thermodynamically metastable at about 8 GPa/373 K and 11.1 GPa/473 K.

Moreover, we calculated the thermodynamic equilibrium phase boundary of zirconreidite in the 0–1900 K temperature range using DFT. By comparing the Gibbs free energy at a fixed temperature and different pressures, the thermodynamic stability differences between the two phases were obtained. When $\Delta G = 0$, the pressure at this point corresponds to the equilibrium phase transition pressure under the current temperature. For example, the phase transition pressures were 5.69, 6.53, 7.65, and 8.70 GPa at temperatures of 0, 500, 1000, and 1500 K, respectively (Figure 5).



Figure 4. The characteristics of zircon Raman spectra at different pressures in (**a**) DD0162(1) and (**c**) DD0159. The red arrows represent the split of the peak containing the $B_{1g}(1)$ and $E_g(2)$ modes. Raman shift of the zircon $B_{1g}(1)$ and $E_g(2)$ modes at different pressures in (**b**) DD0162(1) and (**d**) DD0159. The dashed lines represent the second-order polynomial fit to the data. The vertical dot-dashed lines correspond to the abrupt change of $d\omega/dP$ of the $E_g(2)$ modes.



Figure 5. The Gibbs free energy of zircon and reidite unit cells as a function of pressure at 0 K (**a**), 500 K (**b**), 1000 K (**c**) and 1500 K (**d**). The vertical dashed lines correspond to the phase transition pressures.

Figure 6 compares the high P–T phase boundary of zircon–reidite determined through experiments and calculations in this study with those of previous studies. Our experimental results show the phase transition pressure of zircon–reidite at room temperature is 19.5 GPa,

which is consistent with that (19.7 GPa) reported by van Westrenen et al. [20] via DAC and synchrotron radiation X-ray diffraction but 3 GPa lower than that (23 GPa) reported by Knittle and Williams [17] via DAC and Raman. The reason for their higher transition pressure might be the fact that their experimental samples are the metamorphic zircon, which contains more impurities than the magmatic zircon we used. Our calculated equilibrium phase boundary by DFT using the LDA functional agrees well with the equilibrium phase boundary by the multi-anvil apparatus and synchrotron radiation X-ray diffraction between 1100 and 1900 K from Ono et al. [18] and has essentially the same slope as the results by thermodynamic calculations between 298 and 1900 K from Akaogi et al. [21]. Our in situ Raman experimental results suggest reidite becomes thermodynamically more stable compared with zircon at 8 GPa, which is close to the calculational equilibrium transition pressure (about 6 GPa) by us and the experimental results (about 10 GPa) by Mihailova et al. [40] at room temperature. Other DFT calculations show similar equilibrium transition pressures around 5.2, 5.3 and 7.3 GPa at 0 K reported by Dutta and Mandal [25], Marques et al. [23], and Du et al. [24], respectively.



Figure 6. Experimental and computational high P–T results for the zircon–reidite phase transition. The blue circles and orange squares represent the stable domains of zircon and reidite, respectively. Abbreviations are as follows: (a) the kinetic phase boundary determined by linear fit of our experiments results; (b) the equilibrium phase boundary calculated at 298 to 1900 K by DFT in this study; (c) the equilibrium phase boundary at 1100 to 1900 K experimentally determined by Ono et al. [18]; (d) the equilibrium phase boundary at 298 to 2000 K from Akaogi et al. [21]; (e,f) the phase transition pressure at room temperature experimentally determined by van Westrenen et al. [20] and Knittle and Williams [17], respectively; (g) the pressure above which zircon becomes thermodynamically metastable with respect to the reidite reported by Mihailova et al. [40]; and (h–j) the calculated equilibrium transition pressures from Dutta and Mandal [25], Marques et al. [23], and Du et al. [24], respectively.

According to the numerical fitting of experimental points, the zircon–reidite phase boundary is approximately linear, with a negative Clapeyron slope in the temperature range of 298–800 K, as indicated by the red dashed line in Figure 6. The experimentally obtained phase boundary will intersect with the calculated equilibrium phase boundary (shown as the purple solid line in Figure 6) at a critical temperature of approximately 850 K, which divides the phase transition into two stages: (1) above 880 K, the phase transition occurs under thermodynamic equilibrium conditions where the phase boundary has a positive dP/dT slope, and (2) below 880 K, the slope of dP/dT changes from positive to negative. Compared with the calculated equilibrium phase boundary, it indicates that there exists an overpressure (ΔP) at low temperatures to provide a sufficiently large energy driving force (ΔG_f) and to overcome the kinetic energy barrier that is caused by small displacements of atoms within a two-step model for the zircon–reidite phase transition proposed by Kusaba et al. [27]. Thus, the zircon–reidite phase boundary obtained experimentally at 298–800 K represents a kinetic boundary. Moreover, the driving force for the zircon–reidite phase transition was calculated using the following formula [44]:

$$\Delta G_f = \Delta V \Delta P \tag{3}$$

where ΔV is the cell volume change upon the phase transition obtained by DFT calculations. Considering the various values of ΔV at different pressures, Formula (3) should be modified as follows:

$$\Delta G_f = \int_{P_e}^{P_k} \Delta V \mathrm{d}P \tag{4}$$

where P_e and P_k are equilibrium transition pressures and kinetic transition pressures, respectively. In addition, the activation energy (ΔG) affected by the overpressure can be overcome by an available vibrational energy, which can be calculated by subtracting the zero point energy from the Gibbs free energy at finite temperatures from DFT calculational results.

As listed in Table 3, the values of ΔG_f and ΔG were calculated at each temperature. It is obvious that ΔG_f increases with the decreasing temperature, resulting in a decrease of ΔG . The temperature dependence of overpressure is about 0.023 GPa/K, which is consistent with the value of ~0.02 GPa/K estimated from Figure 1 of [23]. When the temperature is higher than about 880 K, ΔG_f is close to 0, and the vibrational energy is sufficiently large to overcome the activation energy barrier. Since the barrier height of the zircon–reidite phase transition is mainly affected by pressure, with negligible influence of temperature [23], the sum of ΔG_f and ΔG will be equal to a constant. However, in Table 3, we can note that the values of $\Delta G_f + \Delta G$ are in the range of 58.4–68.9 kJ/mol below 573 K, while those above 673 K are relatively larger. Therefore, the actual kinetic phase boundary may be located under the red dashed line in Figure 6 above 673 K, and the critical temperature may be relatively lower than 880 K.

Temperature T (K)	Kinetic Transition Pressure P _k (GPa)	Equilibrium Transition Pressure P_e (GPa)	Driving Force ΔG_f (kJ/mol)	Activation Energy ΔG (kJ/mol)
298	19.5 ¹	6.1	49.0	9.4
373	18.7	6.3	45.3	16.2
473	16.0	6.5	34.9	27.9
573	14.0 ²	6.7	26.8	42.1
673	11.8	6.9	18.0	58.7
773	9.7	7.1	9.6	77.4
873	7.5	7.3	0.7	98.0

Table 3. The values of ΔG_f and ΔG .

 $\frac{1}{1}$ The values of P_k at 298, 373, and 473 K were obtained from our experiments. ² The values of P_k at the temperature above 473 K were obtained by the linear fit of those at 298, 373, and 473 K.

4. Conclusions

In summary, our research reveals that the zircon–reidite phase transition is significantly hindered by kinetic factors. The slope of the experimentally determined kinetic phase boundary differs significantly from that of the calculated equilibrium phase boundary at 298–800 K. There exists an overpressure to provide the sufficiently large energy driving force and to overcome the kinetic energy barrier below a critical temperature of approximately 880 K, and temperature dependence of overpressure is about 0.023 GPa/K.

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