Raman spectroscopic investigation of α-β quartz phase transition in hydrothermal diamond-anvil cell and acquisition of equation of states of aqueous solutions

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The α-β quartz phase transition temperatures ($T_{tr, qtz}$'s; up to ~781 ºC) were determined at various pressures (P's; up to ~802 MPa) in a hydrothermal diamond-anvil cell (HDAC; Li et al., 2016; Rev. Sci. Instrum., **87**, p. 053108-1) by monitoring the Raman shift of the α-quartz band near 128 cm^{-1} (at 24.2 ºC). When compared with the commonly used α-quartz band near 465 cm^{-1} (e.g., Schmidt and Ziemann, 2000; Am. Mineral. **85**, p. 1725), the rate of reduction in wavenumber during H_2O isochoric heating is about five times higher. In addition, the sudden change of the rate of reduction in wavenumber at $T_{tr, qtz}$ is much more sharp and clear, making the α-quartz band near 128 cm^{-1} a much better choice for detecting the phase transition.

Our experimental procedures were similar to those of Shen et al. (1993; Am. Mineral. **78**, p. 694), except Raman spectroscopic method instead of laser interferometry was used to determine $T_{tr, qtz}$. A quartz wafer (prepared from a natural crystal from Asikaerte Be pegmatite in Xinjiang, China) together with or without H_2O were loaded in the sample chamber, which was a hole in a Re gasket between two diamond anvils; H_2O pressure medium was not needed for experiments at 0.1 MPa total pressure.

Raman spectra were acquired during a heating cycle of the experiments after the sample was kept at a constant T for more than 3 minutes. We used a JY/Horiba LabRam HR Evolution Raman system, with 532.06 nm (frequency doubled Nd:YAG) laser excitation, a SLWD 50x Olympus objective having 0.35 numerical aperture, a 1800-groove/mm grating with a spectral resolution of about 0.2 cm^{-1}, and ~14 mW laser light was focused on the sample during the measurement. Spectra were collected in one spectrographic window (from 77 to 593 cm^{-1}) for either 30 s (below 700 ºC) or 60 s (above 700 ºC) with two accumulations per spectrum.

The bulk density of H_2O in the sample chamber for the observed $T_{tr, qtz}$ was determined by measuring the homogenization T (T_h) after the liquid-vapor phase separation during isochoric cooling. The two K-type thermocouples in HDAC were calibrated with the melting points of $NaNO_3$ (306.8 ºC) and NaCl (800.5 ºC), and the uncertainties in T measurements are ±1.5 ºC. The associated pressures at T_h (P_h) and $T_{tr, qtz}$ ($P_{tr, qtz}$) were calculated based on the equation of state (EOS) of H_2O (Wagner and Pruβ, 2002; J. Phys. Chem. Ref. Data **31**, p. 387). The straight line connecting (T_h, P_h) and ($T_{tr, qtz}$, $P_{tr, qtz}$) in a P-T space is near the isochore of that bulk density of H_2O. Similar approach was successfully applied to obtain isochores of 2 m $ZnCl_2$ solution (Bassett et al., 2000; Zeitsch. Kristallogr. **215**, p. 711), and will be extended to other geologically important aqueous solutions at T's up to 1000 ºC using HDAC and Raman spectroscopy.

The α-β quartz phase boundary obtained in this study can be represented by: ($P_{tr, qtz}$) (±8.8 MPa) = 0.0015 ($T_{tr, qtz}$)^2 + 1.8268 ($T_{tr, qtz}$) −1544.5, where ($T_{tr, qtz}$) is between 574 and 781 ºC; with R^2 = 0.9998. Our results agree, within experimental uncertainties, with those reported by Mirwald and Massonne (1980; J. Geophys. Res. **85**, p. 6983), but with some deviations from other previous data.

Keywords: α-β quartz phase transition, Raman spectroscopy, Equation of states of aqueous solutions, Hydrothermal diamond-anvil cell, Isochore

