Calibration of zircon as a Raman spectroscopic pressure sensor to high temperatures and application to water-silicate melt systems

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ABSTRACT

The shifts in wavenumber of the ν3(SiO3) (~1008 cm⁻¹) Raman band of fully crystalline synthetic zircon with changing pressure (P) and temperature (T) were calibrated for application as a Raman spectroscopic pressure sensor in optical cells to about 1000 °C and 10 GPa. The relationship between wavenumber (ν) of this band and T from 22 to 950 °C is described by the equation ν (cm⁻¹) = 7.54×10⁻⁹·T³ – 1.61×10⁻⁵·T² – 2.89×10⁻³·T + 1008.9, where T is given in °C.

The pressure dependence is nearly linear over the studied range in P. At ~25 °C, the ∂ν/∂P slope to 6.6 GPa is 5.69 cm⁻¹/GPa, and that to 2 GPa is 5.77 cm⁻¹/GPa. The ∂ν/∂P slope does not significantly change with temperature, as determined from experiments conducted along isotherms up to 700 °C. Therefore, this pressure sensor has the advantage that a constant error. The pressure sensor was tested to determine isochores in experiments with H2O+Na2SiO3 and H2O+NaAlSiO3 fluids to 803 °C and 1.65 GPa. These pressures were compared to pressures calculated from the equation of state (EoS) of H2O based on the measured vapor dissolution or ice melting temperature for the same experiment. Pressures determined from the zircon sensor in runs in which NaAlSiO3 melt dissolved in aqueous fluid were close to or lower than the pressure calculated from the EoS of H2O using the vapor dissolution or ice melting temperature. In experiments with H2O+Na2O+SiO2 fluids, however, the pressure obtained from the Raman spectrum of zircon was often significantly higher than that estimated from the EoS of H2O. This suggests that the pressures along some critical curves of water–silicate melt pseudobinary systems should be revised.

Keywords: Zircon, Raman spectroscopy, temperature, pressure sensor, diamond-anvil cell

INTRODUCTION

Experiments using diamond-anvil cells have been pivotal in many studies of minerals and fluids at high pressure (P) and temperature (T) because these cells permit not only optical observation of the sample but also in situ measurement of physical and chemical properties by “photon-in – photon-out” techniques. The pressure in the sample chamber of such cells must be determined indirectly, which is commonly done by measurement of the liquid-vapor homogenization temperature of the fluid pressure medium with application of an appropriate equation of state or using the shift in the wavenumber of a Raman or fluorescence line of a calibrant inside the sample chamber. However, fluorescence intensities decrease rapidly with increasing temperature, such that Raman lines are the often better option for pressure determination at elevated temperatures, particularly above 400 °C. The 2D0→F0 fluorescence line of SrB2O3:Sm⁺ is still detectable at 627 °C, but this pressure sensor is quite soluble in aqueous fluids (Datchi et al. 2007). The 464 cm⁻¹ Raman line of quartz is often applied to determine pressure because of its large shift with

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P \frac{\partial ν}{\partial P} \approx 9 \text{ cm}^{-1}/\text{GPa} \]

and relatively small shift with \(T \frac{\partial ν}{\partial T} \approx –0.014 \text{ cm}^{-1}/\text{K}\) (Schmidt and Ziemann 2000). However, its use is limited by phase transitions and high solubility of quartz in many fluids and melts. The wavenumber difference between two Raman lines of berlinite, AlPO4, is more sensitive to pressure than that of the 464 cm⁻¹ Raman line of quartz, and its determination does not require a high-resolution Raman spectrometer, but berlinite reacts readily with aqueous fluids (Watenphul and Schmidt 2012). In situations in which quartz or berlinite are not suitable for use as spectroscopic pressure sensors, zircon is one alternative because it is stable over a large range in P, T, and fluid composition (e.g., Watson and Harrison 1983). Other inert Raman spectroscopic calibrants such as 13C diamond or cubic boron nitride (c-BN) display only small wavenumber shifts with pressures of ~2.83 cm⁻¹/GPa (first-order Raman line, Schiffler et al. 1997; Datchi et al. 2007), or ~3.27 cm⁻¹/GPa (TO mode, Datchi and Canny 2004), and also fairly large and nonlinear shifts in the wavenumber with temperature. This makes the application of 13C diamond or c-BN more difficult at relatively low pressures because of limitations in the attainable accuracy and precision in determining wavenumbers and actual sample temperatures. As described in the following sections, zircon offers the advantage

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