Raman shifts of c-BN as an ideal P-T sensor for studying water-rock interactions in a diamond-anvil cell

LU’AN REN1,2, CHAO WANG1,3, XIAOWEI LI2†, AND RENBIAO TAO1,*

1Center for High Pressure Science and Technology Advanced Research (HPSTAR), Beijing 100094, China
2School of Earth Science and Resources, China University of Geosciences, Beijing 100083, China
3School of Earth and Space Sciences, Peking University, Beijing 100871, China

Abstract
Cubic boron nitride (c-BN) has the same structure as diamond, and it shows very inert reaction activity in different chemical environments, even under high-pressure (P) and high-temperature (T) conditions. Furthermore, the P- and T-dependent Raman shift of c-BN (e.g., TO mode) can be distinguished from that of the diamond anvil (c-BN at ~1054 cm<sup>-1</sup> vs. diamond at ~1331 cm<sup>-1</sup> at ambient conditions), making c-BN a potential P-T sensor for diamond-anvil cell (DAC) experiments. However, the Raman shift of c-BN has not been well studied at high P-T conditions, especially at temperatures above 700 K. In this study, we systematically calibrated the Raman shift of the TO mode (ν<sub>TO</sub>) for synthetic c-BN grains at high-P and high-T conditions up to 15 GPa and 1300 K. Both ruby (Mao et al. 1986) and Sm<sup>2+</sup>:SrB<sub>4</sub>O<sub>7</sub> (Datchi et al. 2007) were used as internally consistent standards for calibration of c-BN P-T sensor. Our results show that the Raman shift of c-BN is negatively correlated with temperature \[\Delta \nu_{TO}/\Delta T = -0.02206(71)\] but positively correlated with pressure \[\Delta \nu_{TO}/\Delta P = -3.35(2)\]. More importantly, we found that the P-T cross derivative for the Raman shift of c-BN \[\partial^2 \nu_{TO}/\partial P \partial T = 0.00105(7)\] cannot be ignored, as it was assumed in previous studies. Finally, we calibrated a Raman shift P-T sensor of c-BN up to 15 GPa and 1300 K as follows:

\[P = \frac{\Delta A(T) - \sqrt{A(T)^2 + 0.2194B(T, \Delta \nu)}}{0.1097}\]

where \(A(T) = 3.47(6) + 0.00105(7)T\), \(B(T, \Delta \nu_{TO}) = 2.81(51) + 0.0053(16)T - 1.78(11) \times 10^{-5} T^2 - \Delta \nu_{TO}\). The c-BN Raman sensor P-T gap ranging from previously performed externally resistance-heated to laser-heated DAC experiments. The effect of c-BN grain size and Raman system laser power on the calibration were also tested for the P-T sensor. In addition, we conducted three sets of high-P-T experiments to test the practicability of c-BN P-T sensor for water-rock interaction experiments in DAC. Testing experiments showed c-BN has very stable chemical activity in water and clear Raman signal at high-P-T conditions in comparison with other P-T sensors (e.g., ruby, Sm<sup>2+</sup>:SrB<sub>4</sub>O<sub>7</sub>, and quartz). Hence, the Raman shifts of c-BN may serve as an ideal P-T sensor for studying water-rock interactions in a DAC, especially at high-P and high-T conditions relevant to subduction zones.

Keywords: Cubic boron nitride (c-BN), Raman shift, high-P-T sensor, diamond anvil cell, water-rock interactions

Introduction
Monitoring, recording, and reproducing the extensive thermo-dynamic variables such as pressure and temperature are crucial for all kinds of high-P and high-T experiments, particularly for in situ diamond-anvil cell (DAC) experiments (Mao et al. 1986; Datchi et al. 2007). Dynamic shock compression measurements of materials could provide a primary pressure scale, i.e., an equation of state (EoS) where the density is a function of absolute pressure determined independently from a secondary standard. For instance, the accuracy determinations of the molar volumes of metals (e.g., Au, Ag, or Cu) by X-ray diffraction (XRD) can give precision to the corresponding pressure measurements (Mao et al. 1986; Datchi et al. 1997; Fei et al. 2007; Trots et al. 2013). However, to use these EoS pressure scales, the shock Hugoniot data must be reduced to an isothermal EoS, which can reduce the accuracy of the pressure scale (Goncharov et al. 2007). On the other hand, in situ XRD patterns for EoS have to be collected from a synchrotron radiation station, which dramatically limits the use of the EoS P-T sensor for DAC experiments in a routine laboratory.