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

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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^{-1} vs. diamond at ~1331 cm^{-1} 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_{TO}) 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^{2+}:SrB_4O_7 (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 [$\partial\nu_{TO}/\partial_T = -0.02206(71)$] but positively correlated with pressure [$\partial\nu_{TO}/\partial_P = -3.35(2)$]. 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:

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

where $\mathrm{A}(T) = 3.47(6) + 0.00105(7)T$, $\mathrm{B}(T, \Delta\nu_{TO}) = 2.81(51) - 0.0053(16)T - 1.78(11) \times 10^{-5}\,T^2 - \Delta\nu_{TO}$. The *c*-BN Raman shift *P-T* sensor in this study fills the *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^{2+}:SrB_4O_7, 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