Raman spectroscopy of cubic boron nitride under high temperature and pressure conditions: A new optical pressure marker

Tatsuhiko Kawamoto
Institute for Geothermal Sciences, Graduate School of Science, Kyoto University, Beppu 874-0903, Japan

Kyoko N. Matsukage
Department of Environmental Sciences, Ibaraki University, Mito 310-8512, Japan

Takaya Nagai
Division of Earth and Planetary Sciences, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

Koshi Nishimura
Institute for Geothermal Sciences, Graduate School of Science, Kyoto University, Beppu 874-0903, Japan

Takeshi Mataki and Shukichi Ochiai
ST Japan Incorporated, 1-14-10 Kakigara-cho Nihonbashi, Tokyo 103-0014, Japan

Takashi Taniguchi
Advanced Materials Laboratory, National Institute for Materials Science, Namiki, Tsukuba 305-0044, Japan

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The pressure dependence of Raman peaks of cubic boron nitride (cBN) is determined at 100, 200 and 300 °C using pressure scales of ruby and gold. At pressures lower than 6 GPa, the pressure dependences of cBN Raman determined with the ruby pressure scale for transverse-optical (TO) and longitudinal-optical (LO) modes are 3.45±0.02 and 3.36±0.02 cm⁻¹/GPa at 100 °C and 3.43±0.02 and 3.44±0.07 cm⁻¹/GPa at 300 °C, respectively. These values are consistent with those in a previous study conducted at room temperature using the ruby pressure scale. Synchrotron x-ray diffraction experiments using a gold pressure marker also yield 3.45±0.03 cm⁻¹/GPa for TO mode at 200 °C in a range of pressure up to 32 GPa. Under the present pressure and temperature conditions, the pressure dependence of Raman peaks of cBN seems to be independent of the temperature conditions. cBN can be used as an optical pressure marker under high temperature conditions.

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I. INTRODUCTION

Cubic boron nitride (cBN) is a high-pressure form of hexagonal boron nitride that is characterized by its hardness and high thermal conductivity similar to those of diamond. Therefore, its physical properties have been extensively investigated under high temperature or high pressure conditions. Yet, physical properties of cubic boron nitride under simultaneously high pressure and high temperature have not been investigated up to the present.

Since cBN is chemically inert to many substances, it can be a good candidate as a pressure marker at high temperature. Determination of pressure at temperatures higher than 400 °C using a ruby pressure scale is difficult because the intensity of fluorescence light from ruby becomes weak. Alternative substances such as Sm:YAG and SrB₄O₇:Sm²⁺ were proposed for pressure determination for a moderate temperature range up to 500–600 °C. However, those materials are not inert to samples and easily dissolve into supercritical H₂O fluid. Using gold foil, Datchi et al. needed to separate a sample chamber into two parts: H₂O as a sample and large SrB₄O₇:Sm²⁺ crystals with H₂O as the pressure medium to determine the melting temperature of ice VII. Pressure is also determined by the P–V–T equations of some metals with synchrotron x rays. Nowadays, many investigators go to a synchrotron facility in order to determine pressures under high temperature conditions. Since beamtime at synchrotron facilities is limited for general users, it has been desirable to have a chemically inert pressure marker to allow use at high temperature with a standard optical spectrometer. Schiferl et al. demonstrated the use of ¹³C doped diamond for this. ¹³C diamond has a Raman peak at lower frequency than a usual ¹²C diamond. However, such diamond chips are not commercially available and the range of pressure is limited; it can be used in pressures lower than 13 GPa but overlaps with a Raman peak from an anvil composed of ¹²C diamond at higher pressures.

cBN has a Raman spectrum with two strong lines representing transverse-optical (TO) and longitudinal-optical (LO) modes at 1054.7±0.6 and 1305±1 cm⁻¹, respectively, under ambient conditions. Because the Raman peak of LO mode overlaps the strong Raman peak of diamond in pressures greater than 3–6 GPa, it is difficult to determine this peak using a diamond anvil cell (DAC). Therefore, TO mode
of cubic boron nitride can be a pressure marker in diamond anvil cells under high pressure and temperature conditions. Recently Zha and Bassett showed Raman spectra of cBN as a possible pressure scale at high temperature with the assumption that the pressure and temperature dependences are independent. We want to address this assumption by carrying out high pressure and temperature experiments using ruby and gold pressure markers.

II. EXPERIMENT

Powder of cBN synthesized at the Advanced Materials Laboratory of the National Institute for Material Science (M33), Tsukuba, was used for the present Raman measurement. The grain size was 0.01 mm. We also wanted to obtain powder diffraction data of cBN with synchrotron x-rays. For this we used another batch of cBN powder commercially available from Show Denko SBN.T. Their grain size was between 0.002 and 0.004 mm. The quality of the diffraction data was found to be rather poor, so that we could not use those data.

We carried out three series of experiments: (1) at atmospheric pressure, to determine temperature dependence of Raman frequency of cBN up to 1400 °C, (2) under high pressure conditions at 100 and 300 °C with a ruby pressure scale, to determine the pressure dependence, and (3) at 200 °C with pressure determination by synchrotron x-ray diffraction of gold, to determine the pressure dependence.

At atmospheric pressure, we used a Linkam TS 1500 heating stage up to 1400 °C. For high pressure and high temperature experiments, cBN powder was loaded into a diamond anvil cell together with a few pieces of ruby or a piece of gold foil and pure (Milli-Q) water. To estimate pressure at high temperature by use of ruby fluorescence, the temperature and pressure dependence are assumed to be independent of each other. For x-ray diffraction experiments, pressure was determined from the measured unit-cell volume of gold foil using the P = F − T equation of state for gold given by Anderson et al. from four diffraction lines (111, 200, 220, and 311) at elevated temperature. A Bassett-type externally heated diamond anvil cell was placed in a gearbox-governed container and subsequently pressurized up to 6 GPa. At pressures greater than 8 GPa, a Mao-bell type cell was used with an oil pressure controller. The temperature of the anvil under ambient pressure was measured and controlled with K-type thermocouples.

Unpolarized Raman spectra were collected with a Raman microscope consisting of a 532 nm YAG laser (17 mW at the sample surface), holographic transmission gratings, and a charge coupled device (CCD) detector of 2048 pixels for 291–4573 cm−1 spectral range (Kaiser HoloLab 5000 system) at the Institute for Geothermal Sciences of Kyoto University at Beppu and also at SPring-8. Raman frequency was calibrated with a neon lamp.

We obtained a spectrum of cBN for 15–60 s and then we took fluorescence spectra from ruby chips under high pressure conditions at our laboratory, or at SPring-8 we took an x-ray diffraction pattern for 5–10 min. At temperature higher than 800 °C under atmospheric pressure, the intensity of incandescent light from the sample becomes larger; we cut a laser and took a radiation spectrum, which was subtracted from a sample spectrum as background. Otherwise we did not subtract the background to determine the Raman peak of cBN. Raman frequency of cubic boron nitride varies among individual crystal grains depending on the crystal size, residual stress and possible other unknown factors. In the present study we do not correct the Raman frequency data using any standard values. Therefore, only the temperature and pressure dependences should be important; the absolute values do not have any significance.

Angle-dispersive x-ray diffraction experiments were performed using the diamond anvil cells at synchrotron beamline BL04B2 at SPring-8 synchrotron facility operating at 8 GeV and 100 mA in Nishi-Harima, Japan. The incident x-ray beam was monochromatized to a wavelength of 0.328 Å and its cross section was collimated to 0.04 × 0.04 mm2 or a 0.1 mm diam circle. Angle-dispersive x-ray diffraction patterns were obtained with an imaging plate placed about 450 mm from the sample. CeO2 was used as a standard to know a wavelength. The intensities recorded on the imaging plates were integrated as a function of 2θ to produce conventional one-dimensional diffraction profiles. The Raman microscope was set on an arm of a goniometer stage and used to take spectra of identical samples that were exposed to the synchrotron x rays (Fig. 1).

III. RESULTS

At atmospheric pressure, the temperature dependences for LO and TO from our data are −0.0276 ± 0.0005 and −0.0319 ± 0.0005 cm−1/K in the temperature range of 27–1350 (LO) or 1400 °C (TO), respectively. These are slightly smaller than the previously reported values obtained from 20 to 800 °C (LO, −0.030 ± 0.006 cm−1/K) or 1327 °C (TO, 1327 °C).
−0.038±0.002 cm⁻¹/K.² Herchen and Cappelli³ reported a nonlinear fitting equation for the data obtained in temperatures (300–1830 K) higher than in the present experiments (300–1673 K): frequency (cm⁻¹) = a₀ + a₁ T(K) + a₂ T² with coefficients 1060.6 cm⁻¹, −0.010 cm⁻¹K⁻¹, and −1.42×10⁻⁵ cm⁻¹ K⁻², respectively, for TO mode and 1307.6 cm⁻¹, −0.003 cm⁻¹K⁻¹, and −1.46×10⁻⁵ cm⁻¹ K⁻², respectively, for LO mode. We also found a better fit for the present data by a nonlinear function: frequency = a₀ + a₁ T + a₂ T² with coefficients 1063.5 cm⁻¹, −0.0220 cm⁻¹K⁻¹, and −4.95×10⁻⁶ cm⁻¹ K⁻², respectively, for TO mode and 1311.9 cm⁻¹, −0.0167 cm⁻¹K⁻¹, and −4.64×10⁻⁶ cm⁻¹ K⁻², respectively, for LO mode (Fig. 2).

In pressures lower than 6 GPa, series of experiments were carried out at 100 and 300 °C using the ruby pressure scale. The pressure dependences of cBN Raman determined with the ruby pressure scale for TO and LO are 3.45±0.02 and 3.36±0.02 cm⁻¹/GPa at 100 °C and 3.43±0.02 and 3.44±0.07 cm⁻¹/GPa at 300 °C, respectively (Fig. 3). The pressure dependence of Raman scattering modes of cBN was investigated by Sanjurjo et al.⁴ and they found a linear dependence, suggesting 3.39±0.08 cm⁻¹/GPa for TO mode with pressure up to 8 GPa and 3.45±0.07 cm⁻¹/GPa for LO mode with pressure up to 6 GPa, respectively. Our values are consistent with their previous study conducted at room temperature using the ruby scale.⁴ Synchrotron experiments using the gold pressure marker also yields 3.45±0.03 cm⁻¹/GPa for TO mode at 200 °C in a pressure range up to 32 GPa (Fig. 4). Under the present pressure and temperature conditions, it is likely that the temperature and pressure dependences are independent. Obviously further study should be carried out at higher temperatures to establish this hypothesis.

This study was the first experimental investigation to determine the pressure dependence of Raman frequency of cBN at high temperature. The present study has shown the possibility of cBN as a new pressure marker under high temperature conditions and also the feasibility of Raman scattering study combined with synchrotron x-ray diffraction study.
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