

***In situ* high pressure-temperature Raman spectroscopy technique with laser-heated diamond anvil cells**

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We describe an *in situ* high pressure-temperature Raman technique for studying materials in laser-heated diamond anvil cells using a Nd:YLF laser (1053 nm) as the heating source and an ion laser as the Raman exciting source. Here we introduce the method of laser heating transparent samples using a metallic foil (Pt, Re, or W) as the laser absorber (internal heating furnace) in a diamond cell. The YLF laser is used to effectively laser-heat one side of a metal foil 5–15 μm thick with a small hole of 10–20 μm in diameter at the center. The foil, in turn, heats a transparent sample while the Raman signals excited by an Ar⁺ or Kr⁺ laser are measured. Temperature of the laser-heated foil is measured by means of spectroradiometry whereas the average temperature of the heated sample is independently determined from the intensity ratios of the anti-Stokes/Stokes excitation pairs. The intrinsic temperature-dependent asymmetry of the Raman spectra arises from the principle of the detailed balance and is independent of sample properties other than the temperatures. The average determined by the signal-to-noise ratio of anti-Stokes/Stokes excitation pairs gives the sample temperature with the statistical accuracy of the Raman spectra. Transparent samples such as CO₂ have been heated up to 1600 K and 65 GPa and Raman spectra have been measured with temperature uncertainty of 50–100 K. *In situ* Raman spectroscopy by laser heating represents a powerful technique to characterize high pressure-temperature properties of materials including molecular systems present in planetary interiors. © 2004 American Institute of Physics. [DOI: 10.1063/1.1791811]

I. INTRODUCTION

Laser-heated diamond anvil cell (LHDAC) technique has been a unique method to reach ultrahigh static pressure and temperature conditions ($P > 100$ GPa and $T > 3000$ K) deep in the planetary interiors.^{1–4} Since the birth of the LHDAC in late 1960s,¹ the LHDAC technique has been widely used with *in situ* x-ray diffraction, melting point studies by observing melting features, and chemical analyses of the quenched sample.^{3,4} A variety of materials such as silicates, oxides, metals, and metal alloys have been subjected to extreme pressures and temperatures, and their equations of state and crystal structures have been examined by *in situ* x-ray diffraction. The technique has also been widely used to synthesize new materials under high pressures and temperatures. Recently, this technique has also been coupled with nuclear resonant inelastic x-ray scattering (NRIXS) and synchrotron Mössbauer spectroscopy (SMS) to study the sound velocities and magnetic hyperfine parameters of ⁵⁷Fe-enriched materials under high pressures and temperatures.⁵ These studies provide rich information in understanding geophysical and geochemical models of the Earth's mantle and core.

The LHDAC technique has also been applied to study planetary molecular materials such as CH₄ and CO₂, but these studies are often limited to temperature-quenched experiments in which samples were laser-heated under high pressures and then examined after the temperature was quenched,^{6,7} making the interpretation of the data difficult. Simple molecular systems such as H₂, CH₄, H₂O, NH₃, and CO₂ are important components of planetary interiors such as those of Jupiter, Saturn, and icy satellites. These species are also model systems for high-pressure physics and chemistry. Therefore, it is important to study the physical and chemical properties of these molecular systems under high pressure and temperature conditions simultaneously. However, these molecular systems consist of light elements (H, C, O, N), making *in situ* x-ray diffraction study of the solid or even liquid phases in a LHDAC technically challenging as these light elements are very weak x-ray scatterers. On the other hand, relatively high Raman cross sections of many of these systems suggest that *in situ* Raman spectroscopy could be a useful tool to investigate them if combined with the LHDAC technique.⁸

Dynamic shock-wave experiments have served as the main tool to characterize the properties of the solid and liquid states of the molecular systems at ultrahigh pressures and temperatures,^{9,10} but the technique is often limited to a very short time scale. The results have been used to derive equations of state and to characterize physical and chemical properties of the fluid and solid states of the materials. For ex-

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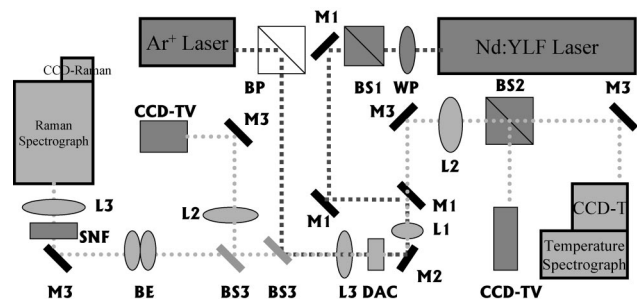


FIG. 1. Schematic of the DAC laser-heating system combined with Raman spectroscopy. A continuous wave Nd:YLF laser beam in TEM₀₁ mode (donut mode) with a maximum output power of 80 Watts is focused down to $\sim 40 \mu\text{m}$ on the metal foil in a diamond anvil cell. Thermal radiation signals emitted from the metallic foil surface are collected by a CCD and then fitted to the Planck radiation law (Refs. 2 and 3). The laser-heating system is similar to that at GSECARS, Argonne National Laboratory (Ref. 3). The 488 nm line of an Ar⁺ laser is used as Raman excitation source and the Raman signals are dispersed by a spectrometer (HR-460) and detected by a CCD simultaneously. Red dashed line: YLF laser beam path; blue dashed line: Argon laser beam path; grey line: white light or Raman signal path; YLF: Photonics Nd:YLF laser of 1053 nm in TEM₀₁ mode; Ar⁺ Laser: Coherent Argon laser with a 488 nm laser line; WP and BS1: wave plate and polarized beamsplitter to regulate the Nd:YLF laser; M1: dichroic laser mirror reflects at least 99.5% of the YLF laser and transmits more than 90% of the visible light; M2: gold coated mirror; M3: aluminum coated mirror; L1: laser focusing lens; L2: achromatic lens (100 cm focus length); L3: lens (5 cm focus length); BS2: 50/50 nonpolarized beamsplitter; BS3: 30/70 nonpolarized beamsplitter; CCD-Raman: liquid nitrogen cooled CCD for Raman measurement (Spec-10:100B(LN), Roper Scientific); CCD-T: back-illuminated CCD for thermal radiation measurement (SpectruMM120B, Roper Scientific); CCD-TV: camera for viewing; DAC: diamond anvil cell; SNF: super plus notch filter (488 nm).

ample, Raman spectra of fluid water have been measured up to 26 GPa and 1700 K in shock-wave experiments.¹⁰ On the other hand, externally heated DAC has been commonly used as the main static tool to study molecular systems *in situ*,^{11–14} but the temperature is often limited to ~ 1200 K due to the lack of strength of diamonds and DAC at high temperatures. Recently, an internal resistive heater in a DAC has been used to conduct experiments up to 10 GPa and 3000 K and *in situ* Raman spectra of BN and SiO₂ have been collected up to 1700 K and 9 GPa, providing a new method for high pressure-temperature Raman spectroscopy.¹³ Moreover, *in situ* Raman spectroscopy in a LHDAC using type IIa diamonds and CO₂ lasers has also been built and used to study carbonates and calcium perovskite (CaTiO₃).^{15–17} The use of the CO₂ laser (10.64 μm) generally requires rarer type IIa diamonds (transparent to the CO₂ laser) and special optics, posing a practical limitation to this approach.

Here we have built an *in situ* Raman system to study molecular materials in a LHDAC using a Nd:YLF laser (1053 nm) as the heating source and an ion laser for excitation of the Raman signals. In fact, this system has a wide range of applications in studying materials, but in this paper we emphasize the use of a small piece of metal foil (Re, Pt, or W of 5–20 μm thick) inserted in the sample chamber to effectively absorb the laser energy and then to efficiently transfer it to heat up the transparent sample.¹⁸ Temperatures of the laser-heated foil are determined from the thermal radiation spectra fitted to the Planck's radiation law^{2,3} whereas the average temperature of the heated sample is determined

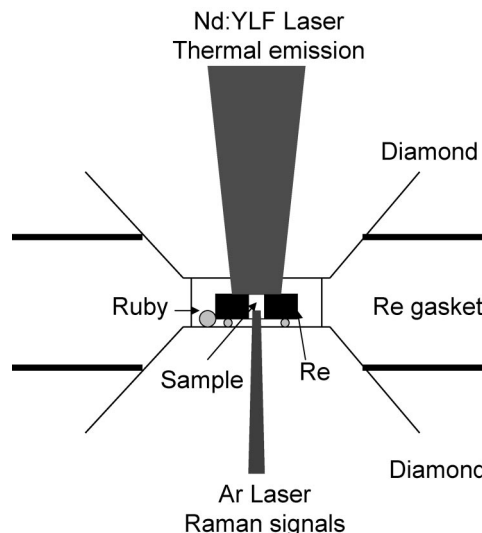


FIG. 2. Schematics of the LHDAC with *in situ* Raman spectroscopy. The YLF laser beam is focused down to 40 μm onto the metal surface. The metal foil (Re) with a small hole of 20 μm at the center is used to absorb YLF laser energy and then to heat up the sample (Ref. 17). Thermal emission from the foil is collected for temperature determination. Ar⁺ laser is introduced from the other side of the diamond cell to probe simultaneously the Raman signals (see Figs. 1 and 3). Small ruby chips are placed in the sample chamber as a pressure calibrant and a spacer to avoid direct contact of the foil with the diamond.

from the temperature-dependent intensity asymmetry of the anti-Stokes/Stokes Raman spectra based on the detailed balance principle and Boltzmann factor.^{5,8,19} We show that the application of the LHDAC technique in Raman spectroscopy provides a new arsenal to unveil the vibrational properties, structures, chemical reactivity, and phase transformations of molecular systems *in situ*.

II. SYSTEM SETUP AND SAMPLE CONFIGURATION

We have developed an *in situ* Raman spectroscopic system for high-pressure laser-heating in a DAC. Figure 1 is a schematic diagram of the system setup consisting of the Nd:YLF laser-heating optics, optics for temperature measurement and imaging, and optics for Raman spectroscopy. A Nd:YLF laser, operating in continuous donut mode (TEM₀₁), is used to heat a metal foil from one side of the DAC (Figs. 2 and 3).³ The diameter of the focused laser beam on the metal foil is approximately 40 μm . Since the YLF laser provides a better beam quality while operated at high power (35 Amps, 80 Watts), the horizontally polarized laser is regulated by changing the polarization direction using a wave plate (WP) and polarized beamsplitter (BS1) to control the total output power to the sample.³ The dichroic laser mirror (M1) reflects the laser beam and transmits the white light, making the thermal radiation signals from the laser-heated spot go through the dichroic laser mirror and get measured by a charge-coupled device (CCD). After the system spectral response was calibrated using a standard tungsten ribbon lamp with known radiance, greybody temperatures of the heated metal foil were determined by fitting the thermal radiation spectrum between 670 and 830 nm to the Planck radiation function.^{2,3} Although the system can be easily modified to a double-sided laser heating system, only single-

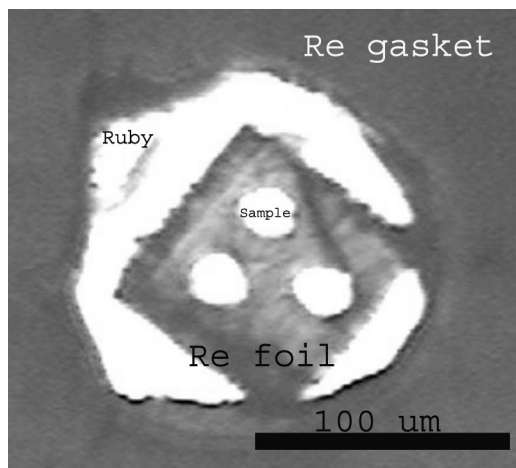


FIG. 3. Photo of a transparent sample in the sample chamber together with a Re metal foil as a laser absorber (Ref. 17). Three small holes of $\sim 20 \mu\text{m}$ in diameter in the metal foil were made using a pulsed YAG laser (see Fig. 2). A small piece of ruby was used as an internal pressure calibrant.

sided laser heating was employed for the Raman spectroscopy.

Raman spectra were measured from the other side of the DAC in back-scattering geometry. The Ar^+ laser with a maximum output power of a few hundred mW (457, 488, or 514 nm line) was used as the Raman excitation source and the Raman signals were dispersed by a HR-460 spectrometer and collected by a CCD simultaneously.⁸ The diameter of the focused Argon laser beam was less than $10 \mu\text{m}$ [full width at half maximum (FWHM)]; the small beam size insured that the signal from the sample was only measured within the small hole of the metal foil (Figs. 2 and 3) and unwanted thermal radiation background was significantly reduced with a spatial filter. Ultraviolet (UV) Ar^+ or Kr^+ laser lines such as 488.0, 457.9, 454.3, 413.1, 363.8, 337.5 nm are preferred in this type of experiments because one avoids unnecessary interference of the thermal radiation background.^{20–23} Alternatively, the anti-Stokes spectra provide lower thermal emission background in comparison with the Stokes spectra.²⁰ While the 514 nm green laser was used, strong thermal radiation signals overwhelmed the Raman signals above $\sim 1600 \text{ K}$ as the thermal emission intensity increases proportionally with T^4 . In principle, an UV Raman system is favored for ultrahigh temperature experiments so that one can separate the Raman signals from the thermal radiation background.^{20,21}

A rhenium gasket with a thickness of $250 \mu\text{m}$ was preindented to a thickness of $30 \mu\text{m}$ between two diamonds with a culet of $200\text{--}400 \mu\text{m}$. A hole of approximately $100\text{--}150 \mu\text{m}$ in diameter was drilled in the indented area. A metal foil (Pt, Re, Mo, or W) of $50\text{--}100 \mu\text{m}$ in diameter and $5\text{--}15 \mu\text{m}$ in thickness with a small hole(s) of $10\text{--}20 \mu\text{m}$ at the center was inserted into the sample chamber and used to effectively absorb the laser energy and then to heat the sample.¹⁸ A small ruby was also inserted into the sample chamber as a pressure calibrant. We observed no significant pressure change before and after laser heating from the adjacent ruby chips. The metal foil was prepared using a pulsed Nd:YAG laser to make the small square foil and a hole of

$20 \mu\text{m}$ at the center (Figs. 2 and 3). We used the metallic foil as an internal heating furnace because most of the molecular samples are transparent to the YLF laser wavelength of 1053 nm . The thickness of the metal foil should be about one-third of the thickness of the sample chamber as this ratio provides better heating and less chance of surface contact with diamond culets. Visual and optical observation of the incandescent light from the laser-heated area showed that the metal foil can be heated homogeneous for more than 10 min. Metal powders such as Pt, Re, and Ir have also been used as laser absorbers, but we found that powders tend to move around after the sample is heated, making homogeneous and continuous laser heating difficult. Different thermal insulating layers have also been used in between diamond anvils and the sample, but these insulating materials may react with the sample.

III. TEMPERATURE MEASUREMENTS BASED ON DETAILED BALANCE

We have measured temperatures by two different methods, spectroradiometry^{2,3} and temperature-dependent intensity asymmetry of the Raman spectra.^{5,8} The thermal radiation spectra fitted to the Planck radiation function provided the surface temperatures of the metal foil, but this is not necessarily a measurement of the actual sample temperature because the thermal emission can be dominated by the metallic laser absorber (Fig. 2). Consequently, the average sample temperature can be lower than that obtained by spectroradiometry.

Therefore, the temperature-dependent intensity asymmetry of the Raman spectra is used to independently determine the average temperature of the heated sample.^{19,24,25} This method is a result of the principle of detailed balance and has been applied to determine temperatures of laser heated iron under pressure from the nuclear resonant inelastic x-ray scattering spectra.⁵ The intensity asymmetry is independent of sample properties other than temperature and is essentially controlled by the Boltzmann factor, $e^{[-h\Delta\nu/k_B T]}$ with the Boltzmann constant k_B , temperature T , and transition energy $\Delta\nu$. Each anti-Stokes/Stokes excitation pair with measured intensities $I(\pm\Delta\nu)$, where $\nu_0=0$ corresponds to the incident laser energy, gives the temperature,^{19,21,24,25} specifically given by

$$\frac{I_{\text{anti-Stokes}}}{I_{\text{Stokes}}} = \left[\frac{\nu_0 + \Delta\nu_i(T)}{\nu_0 - \Delta\nu_i(T)} \right]^4 f(\nu) \exp \left[\frac{hc\Delta\nu_i(T)}{k_B T} \right] \\ = \left[\frac{\nu_0 + \Delta\nu_i(T)}{\nu_0 - \Delta\nu_i(T)} \right]^4 f(\nu) \exp \left[-1.4387 \frac{\Delta\nu_i(T)}{T} \right],$$

where c is the speed of light, ν_0 is the wavenumber of the exciting laser light, and $\Delta\nu_i(T)$ is the wavenumber of i th Raman mode (cm^{-1}), and $f(\nu)$ is the spectral response of the system.¹⁹ We used the maximum peak intensity or the integrated area of the peaks to determine the average sample temperature. After correcting the spectral response of the system (including quantum efficiency of the CCD, optics, and monochromator), the average overall data pairs give the sample temperature within the statistical accuracy of the spectra which is approximately $\pm 50\text{--}100 \text{ K}$ (Fig. 4).

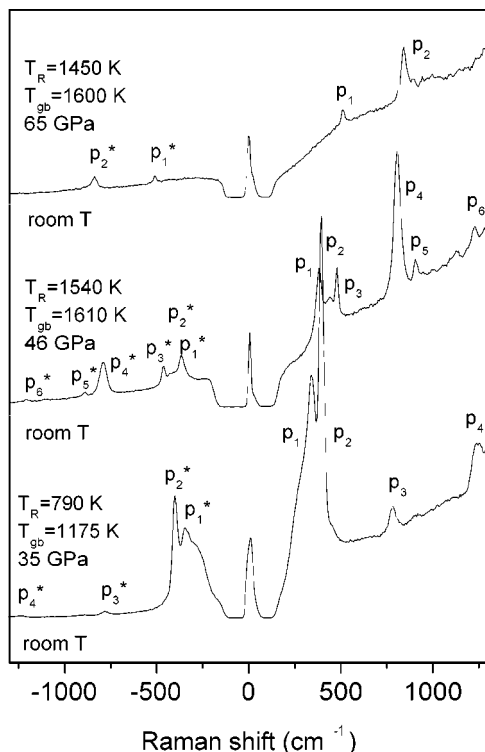


FIG. 4. Representative Raman spectra of a CO_2 sample measured in a laser-heated diamond anvil cell at 35, 46, and 65 GPa. The strong intensities of the anti-Stokes peaks at ~ 1600 K prove that the sample has been subjected to high temperatures. The intensity asymmetry of these spectra was used to determine the average temperature of the laser-heated sample. Thermal radiation background increases at higher temperatures and is more notable in the Stokes spectral region. Black line: Raman spectra at high temperatures; grey line: corresponding Raman spectra at 300 K; T_{gb} : Greybody temperatures; T_R : temperatures determined from the principle of detailed balance. $P_{\#}$ and $P_{\#}^*$: Stokes and anti-Stokes Raman peaks, respectively (the labels of the peaks are for the purpose of excitation pairs only).

In Fig. 4 we show representative high-temperature Raman spectra of carbon dioxide at three different pressures; the corresponding Raman spectra at 300 K are also reported for comparison. The anti-Stokes/Stokes ratios are low at 300 K; the anti-Stokes peaks can be barely seen above 500 cm^{-1} . This intensity imbalance is reduced with increasing temperature due to the rising thermal population of the upper energy level of the Raman transition. We measured an average temperature of $1610 \text{ K} (\pm 100 \text{ K})$ for the laser-heated foil and $1540 (\pm 50) \text{ K}$ for the heated sample at 46 GPa, indicating that the internal heating by using a laser-heated metal foil is an efficient way to laser-heat transparent samples in the DAC. On the other hand, we observed that the temperature difference between the two methods was as high as several hundred degrees at relatively lower pressures ($< 40 \text{ GPa}$) but the difference was decreased as the pressure was stepped up, due to the increased thermal conductivity of both the sample and the metal foil. To the best of our knowledge, this is the first *in situ* Raman study in a LHDAC using detailed balance as an independent determination of the sample temperature, providing a novel technique to quantitatively investigate vibrational properties, structures, chemical reactivity, and phase transformations of molecular systems *in situ*. We have independently tested the validity of the temperature determination based on detailed balance prin-

ciple by collecting Raman spectra in an externally heated DAC using two thermocouples attached to the diamond surface as the temperature sensors up to $\sim 1000 \text{ K}$.^{11,12} The temperature difference between thermocouples and detailed balance method is about 50–100 K within statistical errors. Since the sensitivity of the intensity imbalance for low-frequency phonon peaks of the molecular systems ($< 1000 \text{ cm}^{-1}$) is expected to be highly reduced at higher temperatures ($\sim 2000 \text{ K}$), vibron peaks in higher frequencies in the molecular systems can then be used as the absolute temperature determination at ultrahigh temperatures; however, the high-frequency Stokes peaks are more susceptible to the interference of the thermal emission at high temperatures. The use of the UV laser excitation in the LHDAC would then reduce the thermal emission background in the measured spectra region at these temperatures.^{20,21} Alternatively, a gated-CCD coupled with a pulsed laser could be employed to effectively suppress blackbody radiation background in the spectra.^{22,23}

IV. DISCUSSION

An *in situ* Raman system with YLF laser heating has been developed to study physical and chemical properties of planetary materials under high pressures and temperatures simultaneously. The system has been tested in studies of molecular systems such as CO_2 up to 65 GPa and 1610 K. Here we introduce the use of a metal foil as an internal heating furnace to effectively heat up transparent samples to thousands of degrees. The temperature-dependent asymmetry of the Raman spectra is used to determine the absolute average temperature of the heated sample. This *in situ* Raman spectroscopic technique with laser-heated diamond anvil cells represents an important new method to characterize the structures, chemical reactions, and phase diagrams of materials under high pressures and temperatures. The use of other wavelengths of the heating laser such as CO_2 laser and the exciting laser such as UV Ar^+ or Kr^+ would increase the pressure and temperature range of the *in situ* high pressure-temperature Raman technique.^{20,21} Moreover, a gated-CCD coupled with a pulsed laser could be employed to effectively suppress blackbody radiation background,^{22,23} however, the present technique shows that high pressure-temperature Raman measurements can also be performed with continuous wave lasers.

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