CO$_2$ laser-heated diamond-anvil cell methodology revisited

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Abstract
A description is given of CO_2 laser heating system for attaining high
temperatures at pressure in a diamond-anvil cell (DAC). The main purpose
of this paper is to demonstrate that a relatively inexpensive set-up, perhaps
affordable to many high-pressure laboratories, may be commissioned for laser-
heated DAC experiments to achieve comparable extreme P–T conditions to
those attained with more sophisticated stations documented in the literature.
A novel idea of using the analogue output of a CCD camera to estimate the
peak temperature and map the temperature distribution across the hot-spot has
been tested. In an additional initial experiment on cubic zirconia (c-ZrO_2) we
present evidence from a Raman characterization of the sample that temperatures
exceeding 4000 K have been obtained at pressure in the DAC.

1. Introduction

The CO_2 laser is the heating source of choice for attaining extreme P–T conditions for
compounds (especially oxides and nitrides) pressurized in a diamond-anvil cell (DAC). This is
because of the high absorption of these compounds at the laser emission wavelength, namely,
10.6 μm. To date, relatively expensive experimental stations have been used to achieve peak
temperatures ($T > 3000$ K) in hot-spot diameters of 30–50 μm on samples pressurized in a
DAC. A high-power (>100 W) cw CO_2 laser is used in conjunction with the rarer and more
expensive type-IIa diamond anvils that are highly transparent at 10.6 μm.

We demonstrate that, contrary to suggestions in the literature, a comparatively low-power
$\sim$30 W cw CO_2 laser can be used to obtain peak temperatures in excess of 4000 K at pressure,
using more commonly available type-Ia diamond anvils. This is in spite of attenuation at
10.6 μm that may be as high as $\sim$70% due to bulk absorption and interface reflections by the
type-Ia diamond window. Peak temperatures are obtained in areas of $\sim$10 μm diameter of the
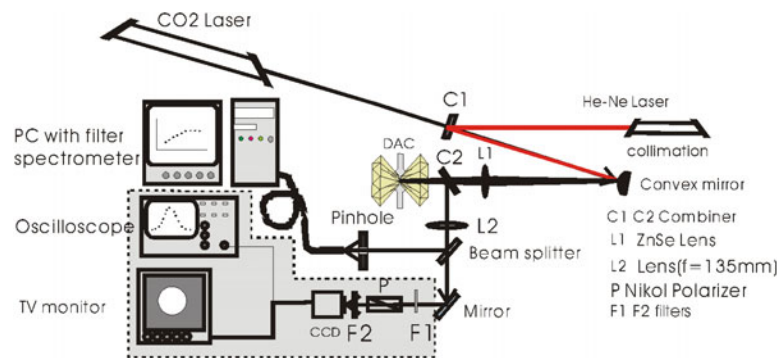focused laser spot of $\sim$50 μm diameter.

Figure 1. A schematic diagram of the laser heating system.
(This figure is in colour only in the electronic version)

2. Laser heating methodology

As shown in figure 1, a convex mirror is used to expand the beam of a CO_2 laser (SYNRAD Inc., maximum power $\sim$30 W cw) to a diameter of approximately 1 cm at the optical plane of the ZnSe focusing lens L1 ($f = 55$ mm) which then focuses the beam to a $\sim$20 μm spot size. A He–Ne laser pointer is combined with the CO_2 laser beam by means of the combiner C1 and used as a collimated beam. The emission spectrum from the laser-heated hot-spot is reflected off the ZnSe window C2 (thickness 5 mm and transparent to the incident 10.6 μm laser beam) onto objective L2 with a focal length of 135 mm and aperture 2.8. Part of this emission spectrum is directed into a CCD camera (depicted by the grey region in figure 1) and part to the entrance point of an optical fibre linked to a spectrometer (Ocean Optics Inc., PC2000 PC plug-in module). Both the analogue output of the CCD and optical fibre spectrometer are used separately to measure the temperature of the hot-spot. The ZnSe window C2 also serves as an effective reflector in the visible range, so the sample may be viewed on a TV monitor using the output derived from the CCD.

In the laser-heated DAC a spectro-radiometric method is often used to measure the grey-body emission from the sample at high temperature ($T > 1500$ K). Once an emission spectrum is obtained, the temperature is extracted from the Planck black-body radiation formula fitted to the data. Alternatively the Wien approximation to the Planck formula may be used to linearize the data as follows and the temperature more easily extracted from the linear fit [1]:

$$J(\lambda) = \ln(\varepsilon(\lambda)) - w(\lambda)T^{-1}, \tag{1}$$

where $J(\lambda) = \ln(I_\lambda \lambda^5 / c_1)$, I_λ is the spectral intensity and $w(\lambda) = c_2/\lambda$. The constants $c_1 = 2\pi hc^2 = 3.7418 \times 10^{-16}$ W m^2 and $c_2 = hc/k_B = 1.4388 \times 10^{-2}$ mK.

The wide-band grey-body emission spectrum (usually 500–800 nm) from which the temperature is extracted is often distorted due to several factors: wavelength-dependent efficiency of the detector, a filter and the effect of optical elements (e.g., chromatic aberration effects of lenses). By using a standard lamp (LS-1-CAL, Radiometrically Calibrated Miniature Tungsten Halogen Source, Ocean Optics, Inc.), a corrected emission spectrum may be obtained.

A method has been developed to measure in real time the peak temperature, the profile of the temperature distribution across the hot spot, and the temperature stability. All of this information may be obtained concurrently by monitoring the analogue output of a conventional black-and-white CCD camera used to image the intensity or 'brightness' of the laser-heated contents of the sample cavity. This may also be conveniently used to predetermine the laser

power required to achieve an intended final temperature. The optical system has as an essential component relatively inexpensive crossed polarizers and a filter. This arrangement may be used to measure accurately the relative peak intensities at the filtered wavelength emitted from the Gaussian profile of the hot-spot (e.g., at different laser powers), so the ratio of the radiance temperatures may be obtained. One of the measured temperatures may be a reference temperature obtained from the melting or boiling temperature of some standard material.

The optical system in figure 1 (grey region), used to measure the relative intensity of the hot-spot at different temperatures or the intensity profile of the hot-spot, consists of a green filter (F1), an IR cut-off filter (F2), Nicol prism polarizers, a black-and-white CCD camera, an oscilloscope to monitor the analogue output of the CCD and TV monitor for viewing the sample area. The centre wavelength λ_0 of this filter is at $\sim$500 nm with a bandwidth of $\sim$100 nm. The prism polarizers are used to accurately measure relative intensities associated with radiation emission from the hot-spot at the filtered wavelength.

The Wien formula is then used to obtain relative temperatures from the following relation:

$$\frac{\varepsilon_R}{\varepsilon_U} \exp\left[\frac{c_2}{\lambda_0}\left(\frac{1}{T_R} - \frac{1}{T_U}\right)\right] = \frac{\cos^2(90° - \varphi_U)}{\cos^2(90° - \varphi_R)} \tag{2}$$

where subscripts R and U refer to sample and measurement conditions at the reference and unknown temperature, respectively. The emissivity is denoted by ε, λ_0 is the wavelength at which the grey-body emission is sampled by the CCD, and φ is the polarization angle set to ensure that the intensity incident on the CCD sensing element results in saturation of the CCD analogue output, i.e., some convenient reference value. The left-hand side of equation (2) involving the temperatures is the ratio of intensities from the Wien approximation to the Planck formula. The right-hand side is the ratio of intensities as obtained from the settings of the crossed Nicol polarizers. The unknown temperature may then be estimated from equation (2) using the measured polarization angles and T_R. The main source of error may be due to the emissivities. An accuracy of better than 5% for the estimate of the temperature T_U may be achieved for samples having comparable emissivities to the reference compound.

Using this CO$_2$ laser-heated DAC methodology, temperature measurements of numerous metal oxide compounds, e.g., α-Al$_2$O$_3$ and Yb$_2$O$_3$, have been checked, including initial experiments of ZrO$_2$ pressurized in a DAC.

3. Results

In two separate tests of the method used to obtain relative temperatures from equation (2), the heated sample was a pellet of α-Al$_2$O$_3$ or Yb$_2$O$_3$ in place of the DAC in figure 1. The laser-heated spot had diameter $\sim$250 μm. The emission spectrum was collected from an area 40×40 μm in the centre of the hot-spot. Temperatures of the central region of the hot-spot at different laser power settings were obtained from the linearized data of the emission spectrum using equation (1). At each laser power setting, and thus temperature, the polarization angle was changed to ensure that a convenient analogue reference value was attained on the oscilloscope, i.e., the onset of saturation of the CCD. Thus the polarizers were used to obtain the relative change in intensity as the laser power was varied.

The symbols in figure 2 display the spectro-radiometric temperature deduced from equation (1), versus the corresponding polarizer angle φ required to attain a fixed value (reference level) of the analogue output of the CCD. The solid curve with error bars is calculated using equation (2) for $\lambda_0 = 500$ nm. Different values of the angle of the polarizer relative to a reference value are used to find the change in temperature relative to the reference temperature $T_R = 3077$ K near to the melting point of the compound, and corresponding to
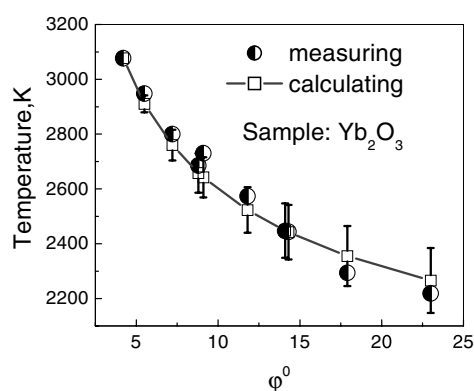
Figure 2. Symbols show 'true' temperatures measured independently by the optical fibre spectrometer versus the corresponding polarizer angle φ. The solid curve shows the temperatures deduced from equation (2) with $\lambda_0 = 500$ nm, as a function of polarizer angle.
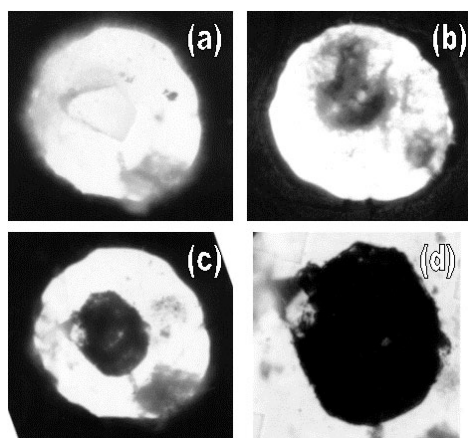

Figure 3. Images taken of a cubic zirconia single crystal pressurized in a Merrill–Bassett-type DAC. (a) The transparent sample before laser heating, (b)–(d) the transition to opaque appearance in progressive heating steps.

the highest laser power setting. The error bars are error estimates of T_U obtained by assuming that $\Delta\lambda_0 = 100$ nm in equation (2). Good agreement between the independently measured temperature (symbols) and the deduced temperature (solid curve) suggests that the method based on equation (2) is able to accurately track the true temperature.

A Merrill–Bassett-type DAC made of Cu–Be was employed in the laser heating test. A piece of transparent single-crystal cubic zirconia was loaded into the aperture (diameter $200 \ \mu$m) of a T301 stainless-steel gasket. Liquid argon was used as a pressure-transmitting medium as shown in figure 3(a). The DAC was encased in a water-cooled jacket to dissipate the heat from the laser power absorption by the diamond-anvil window. Bulk absorption at $10.6 \ \mu$m for the type-Ia diamond-anvil window typically 2.0 ± 0.1 mm thick was measured to be 60–70%.

The main purpose of this experiment was to check the highest temperature that could be achieved in the pressurized sample cavity of the DAC at conditions close to the maximum laser power.
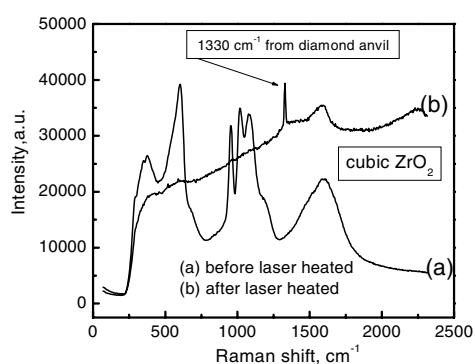
Figure 4. Raman spectra of cubic zirconia (a) before laser heating and (b) after unloading to ambient conditions subsequent to laser heating.

Figures 3(b)–(d) show the images taken from the laser-heated sample in the DAC. As the laser power was increased there was clear evidence on the TV monitor of a drastic disruption of the original shape of the single crystal and fluidity, signalling melting. The melting temperature of cubic zirconia is ∼3000 K. As the laser power was increased further, the pressurized sample changed from transparent to opaque. These experiments were repeated more than once for new samples reloaded into the DAC, always yielding the same pattern of behaviour upon increasing the temperature.

In one of the runs, Raman spectra were taken of the opaque regions of the recovered specimen and compared with that obtained for cubic zirconia before laser heating; see figure 4. There is no evidence from the Raman result in figure 4 that the cubic phase of ZrO$_2$ has transformed to either the tetragonal or the orthorhombic phase [2]. The stability range of these phases is up to ∼2500 K at low pressure according to the P–T phase diagram for ZrO$_2$ [3, 4]. This suggests that the laser-heated cubic zirconia may have dissociated into opaque metallic Zr and O$_2$. If this is the case it may be inferred that the peak temperature was well in excess of 4000 K, given that for cubic zirconia the vaporization point is 4573 K and the dissociation temperature is likely to be even higher than this.

A series of experiments are currently under way to use the optical fibre spectrometer or the pyrometric method involving equation (2) for a more direct measurement of the temperature of a pressurized cubic zirconia sample heated to conditions similar to those of this initial experiment.

Acknowledgments

References

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