In situ Raman thermometry for temperature determination in externally heated diamond anvil cells?

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Abstract

Externally heated diamond anvil cells (DAC) are widely employed in high-pressure and high-temperature experiments. They allow a precise and stable control of the temperature inside the sample chamber, unlike the laser heating DACs, but can only reach lower temperatures, usually limited to ~1000 K. In HP-HT experiments, temperature measurement is mainly performed using a thermocouple fixed to the diamond table, or through radiothermometry, though the latter method requires a higher temperature range and is affected by the emissivity problem. While the thermocouple method is precise, the geometry of the cell can significantly alter the result, either through direct heater-thermocouple interaction or suboptimal thermocouple positioning, leading to high discrepancies between the measured and the sample temperatures.

This study employs a Helios DAC from Almax easyLab with a resistive heating and a gas-membrane drive for pressure control, all enclosed in a vacuum chamber made by BETSA to prevent oxidation and minimize heat loss. Temperature is monitored by in situ Raman thermometry[1] through analysis of the Stokes and anti-Stokes Raman signals collected from both the DAC diamond cullet and a cubic boron nitride (c-BN) crystal enclosed in the sample chamber. c-BN exhibits no known reactivity with water below 1300 K, making it ideal for hydrothermal studies[2]. Pressure is simultaneously measured via ruby fluorescence shift[3], diamond Raman shift[4] and c-BN Raman shift[5].

The reliability of the Raman thermometry method is first validated in an Linkam setup at atmospheric pressure, using the spectra of c-BN, quartz and GeO_2. The α-β quartz phase transformation and the GeO_2 melting point, both observable through Raman spectroscopy, serve as fixed reference points. A maximum temperature of 1600 K is reached under nitrogen atmosphere, limited by the c-BN → phase transition to h-BN. C-BN is then used inside the DAC at temperatures up to 850 K and pressures up to 15 GPa, with argon and nitrogen as pressure-transmitting media. The melting curves of argon and nitrogen serve as fixed reference points[6], with the transition observed optically and via Raman spectroscopy for nitrogen at pressure higher than 7 GPa[7].

Linkam experiments demonstrate a temperature precision of ±50 K up to 1300 K for Raman thermometry. Initial DAC results evidenced a temperature gradient between the thermocouple and the sample of up to 400 K. This difference in temperature arises from the cell geometry, which heats the thermocouple primarily through conduction while the sample is heated through radiation. The deposition of graphite ink between the heater and the diamond reduces the gradient to a maximum of 200 K, enabling temperatures up to 850 K to be reached. The results also reveal a homogeneous temperature within the sample chamber and the diamonds, with diamonds, c-BN and ruby all remaining within a 50 K range, indicating that the diamond temperature effectively matches the sample temperature, and that temperature can be accurately measured via Raman thermometry on the diamonds alone.

This method offers a simple and precise temperature detection approach that overcomes the limitations of traditional measurements in externally heated DACs. Using the diamonds themselves eliminates the need for additional sensors inside the sample chamber, it allows reducing experimental complexity while maintaining accuracy (±50 K).

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