Image analysis as an improved melting criterion in laser-heated diamond anvil cell

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The precision of melting curve measurements using laser-heated diamond anvil cell (LHDAC) is largely limited by the correct and reliable determination of the onset of melting. We present a novel image analysis of speckle interference patterns in the LHDAC as a way to define quantitative measures which enable an objective determination of the melting transition. Combined with our low-temperature customized IR pyrometer, designed for measurements down to 500K, our setup allows studying the melting curve of materials with low melting temperatures, with relatively high precision. As an application, the melting curve of Te was measured up to 35 GPa. The results are found to be in good agreement with previous data obtained at pressures up to 10 GPa.

I. INTRODUCTION

The laser-heated diamond anvil cell (LHDAC) has been widely used to synthesize new materials and to study matter under extreme conditions of pressure and temperature.[1,2] One of the main applications of the LHDAC is the study of high pressure melting curves of elements and compounds.[3,4] Major advances in this technique in the last three decades have provided a valuable information on the melting curve of a wide variety of materials at pressures up to a few megabars and temperatures up to several thousands of degrees Kelvin. Special attention has been paid to the improvement of heating capability,[5] temperature measurement,[6] temperature control,[7] minimization of temperature gradients within the sampled region,[8,9] and the correct identification of the onset of melting.[10]

Despite the advances described above, many investigations of apparently simple materials have generated controversy due to disagreements among experiments,[11,12] and between experiments and theory.[13,14] Some studies have identified possible errors in temperature measurement.[15] Others have found that chemical reactions or diffusion can alter the composition of the sample.[16] In particular, the correct determination of the melting transition has been a highly controversial subject.[17,18] A variety of melting criteria have been used, including visual observation of fluid motion in a speckle interference pattern,[19,20] appearance of diffuse scattering via in situ X-ray diffraction,[21,22] appearance of plateaus in curves of temperature as a function of laser power,[23] formation of glass or a change of texture upon quenching,[24,25] and changes in sample properties such as reflectivity, absorption[26,27] and resistivity.[28] Among these, the first two are the most commonly used criteria. However, the use of X-ray diffraction in LHDAC experiments is limited to large-scale synchrotron radiation facilities. Most small-scale laboratories therefore employ the direct fluid motion observation as the main melting criterion. It has been argued, however, that this criterion has two shortcomings. First, the precise identification of the onset of fluid motion can be difficult, resulting in an overestimated melting temperature.[19] This becomes more pronounced as the pressure increases and fluid motion becomes more sluggish.[23] It is thus important to define this criterion more objectively, based on quantitative measures. Second, this criterion becomes increasingly subjective at temperatures above 2500 − 3000 K, as intense thermal radiation makes it impractical to obtain a reliable image with adequate contrast across the hotspot within the sample.[19] This limits the validity of this criterion to relatively low temperatures (T < 2500 − 3000 K).

In this paper we describe an image analysis procedure used to extract quantitative information on the speckle interference pattern. This allows us to define several quantitative measures, the abrupt change of which indicates the onset of melting. To further corroborate the correct melting point determination, we have also monitored the temperature as a function of laser power and interpreted plateaus or change of slope as the onset of melting. This method is applied to the measurement of the melting curve of Tellurium (Te) up to 35 GPa. At low pressures, up to 10 GPa, our measurements are in excellent agreement with a previous measurement of the melting curve of Te using large-volume press.[29] Furthermore, at higher pressures our measurements are in line with the solid-solid coexistence curve reported in Ref. [30].

The paper is organized as follows: In Sec. II we describe the experimental setup including the sample preparation procedure (Sec. II A), the optical setup and temperature measurement (Sec. II B), and the image analysis of the speckle interference pattern (Sec. II C).

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The measurement of the melting curve of Te using this improved melting criterion is presented in Sec. III. Finally, we summarize and discuss our results and their implications in Sec. IV.

II. EXPERIMENTAL

A. Sample preparation

Samples of high purity Te (99.999%) were used without further treatment. The samples were cut and pressed between diamond culets to form pieces of 30 µm thickness and a diameter of about 80 µm. The samples were mounted in a DAC with 300 µm diameter culets. Rhenium gaskets, pre-indented to 50 µm thickness were used. Thermal isolation was achieved by loading a thermally isolated epoxy in the laser drilled 200 µm diameter sample chamber and drilling in situ with a 100 µm diameter drill bit. The bottom culet was covered with a 5 – 10 µm layer of ruby by crushing a large ruby grain between the bare culets. In some loads 3 – 5 µm thick KCL plates were used as an additional thermal isolation layer. The sample was topped with a few 10 µm ruby chips and the top diamond was mounted on it. Finally, the cell was cryogenically loaded with 99.999% argon as a pressurization medium.

B. The optical system and temperature measurement

The optical setup is shown schematically in Fig. 1; see Ref. [30] for more details. CW Nd:YAG laser is focused on the sample. Thermal radiation emitted by the hotspot is focused on the IR detector via a Schwarzschild objective. An auxiliary HeNe laser is used to generate a speckle interference pattern on a CMOS camera. An example for a speckle image obtained by the CMOS camera is shown in the upper right side of the image.

![Figure 1](image.png)

**FIG. 1.** (Color online) Schematic of the optical setup. CW Nd:YAG laser is focused on the sample. Thermal radiation emitted by the hotspot is focused on the IR detector via a Schwarzschild objective. An auxiliary HeNe laser is used to generate a speckle interference pattern on a CMOS camera. An example for a speckle image obtained by the CMOS camera is shown in the upper right side of the image.

The optical system and temperature measurement

The optical system is shown in situ. A homemade IR pyrometer, designed for spectrum to Planck’s spectral radiance law

\[ I(\lambda, T) = \varepsilon(\lambda, T) \frac{2\pi c^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1}, \]

(1)

where \( \lambda \) is the wavelength, \( T \) is the temperature, \( \varepsilon(\lambda, T) \) is the sample emissivity and \( h \), \( k_B \) and \( c \) are Planck’s constant, Boltzman’s constant and the speed of light, respectively. Invoking the grey body approximation which assumes \( \varepsilon(\lambda, T) = \varepsilon \) to be a constant independent of wavelength and temperature, we fit the measured spectrum to Eq. (1) using two free parameters, the constant emissivity and the temperature. At fixed pressure and hotspot within the sample, temperatures are measured with increasing heating beam power.

It should be noted that the emissivity extracted in this fitting procedure is an effective emissivity, which is strongly affected by the surface texture and local optical properties of the hotspot. At the melting transition the surface texture changes and the effective emissivity can vary and generate errors in the temperature measurement. For better accuracy of the temperature measurement we perform a second temperature calculation after completing a series of temperature measurements at the same hotspot; each temperature in the series is recalculated assuming a common emissivity, which serves as a single free parameter for a series of measurements at the given hotspot. Having determined the melting point (see details in the next section) for each series of measurements, we extract the value of the emissivity by fitting the measured spectra to Eq. (1) for temperatures below the melting point. The extracted solid phase emissivity is then used to calculate the temperatures of all the measurements in the series. Temperatures measured above the melting point might have larger error due to this procedure. However, the melting temperature is determined by measurements carried out just before melting and in the vicinity of the melting transition. Therefore, errors in temperature measurements above the melting point do not significantly affect the correct determination of the melting temperature.

Figure 2 shows a series of temperature measurements, performed at a pressure of 10.5 GPa, as a function of heating beam power. As can be observed, tempera-
tures calculated using two free parameters for each measurement separately (blue stars) have strong fluctuations around the melting temperature, \( T_m \approx 1000\, \text{K} \). Once the melting point was determined and the temperatures were recalculated using a common emissivity (red points in Fig. 2), one can observe a plateau around the melting temperature of Te. As evident from Fig. 2, temperatures below the melting point are not very sensitive to the fitting procedure (the corrections are smaller than 50 K), whereas variations between the two fitting procedures are significant for temperatures well above the melting point.

A second, longer plateau can be seen in Fig. 2 at \( T \approx 1100\, \text{K} \). We attribute this plateau to the melting of Ar, the pressure medium. We observed this second plateau in all measurements in which the sample was heated to the Ar melting temperature and it occurred at temperatures consistent with the melting curve of Ar. \(^{112}\)

In both methods, the determination of the exact melting temperature is somewhat subject to personal interpretation. In order to avoid this subjectivity, we have developed an image analysis method to quantify changes in the speckle interference pattern.

For direct visual observation of melting the hotspot was illuminated with a HeNe laser beam, which generates a speckle interference pattern on a CMOS camera (Fig. 1). At each heating beam power, a series of 8 speckle pattern images was recorded by the CMOS camera. Laser line filter (633 nm) was used to prevent the heating laser beam and the thermal radiation from reaching the camera.

For a quantitative analysis of temporal changes in the speckle interference pattern, the software calculates the standard deviation (STD), \( \sigma_{ij} \), of each pixel \((i,j)\) in the series of images,

\[
\sigma_{ij} = \sqrt{\frac{1}{N} \sum_{k=1}^{N} (x_{ijk} - \langle x_{ij} \rangle)^2},
\]

where \( N = 8 \) is the number of images, \( x_{ijk} \) is the intensity of pixel \((i,j)\) in the \( k \)th image and \( \langle x_{ij} \rangle = \sum_{k=1}^{N} x_{ijk}/N \) is the averaged intensity of that pixel. The STD per pixel is summed over a region of interest, giving a parameter that quantifies the amount of temporal changes generated during the heating process. The outcome was then compared to the corresponding quantity obtained for a second series of images recorded at room temperature in the absence of heating laser beam. Typical plot of the temporal changes (averaged STD per pixel) at the hotspot as a function of the measured temperature is shown in the middle panel of Fig. 3.

At low temperatures there is no apparent change in the STD of the hotspot during heating and after cooling. Such differences become evident as the heating beam power increases. The increasing differences are attributed to melting of the sample, since liquid motion at the hotspot gives rise to rapid changes in the speckle interference pattern, which in turn lead to increase in the STD of the series of images recorded during heating.

For a more accurate determination of the onset of melting, the speckle interference patterns were analyzed in a second way. Typically, melting and resolidification of the sample result in changes of texture of the melted surface. This is reflected by a change in the speckle interference pattern after melting and resolidification. We have quantified such changes by measuring the correlation of the speckle interference pattern recorded at room temperature after each heating cycle, with respect to a reference speckle image recorded at the beginning of the experiment, prior to any heating process. The correlation coefficient, \( \rho \), is defined as

\[
\rho = \frac{\sum_{i,j} (y_{ij} - \overline{y})(z_{ij} - \overline{z})}{\sqrt{[\sum_{i,j} (y_{ij} - \overline{y})^2][\sum_{i,j} (z_{ij} - \overline{z})^2]}},
\]

where \( y_{ij} \) and \( z_{ij} \) are the intensities of the reference and test images, respectively, at the pixel location \((i,j)\), and \( \overline{y} \) and \( \overline{z} \) are the averaged intensities of these images.
where $y_{ij}$ and $\overline{y}$ are the intensity of pixel $(i,j)$ and the mean pixel value of the image recorded after a heating cycle, whereas $z_{ij}$ and $\overline{z}$ are the corresponding quantities of the reference image. A typical plot of this correlation as a function of the measured temperature is shown in the lower panel of Fig. 3. One can clearly observe a drop in the correlation of the speckle interference patterns once the sample is melted.

To further corroborate the applicability of these two melting criteria, we also employed a third criterion by monitoring the changes in the slope of the temperature as a function of heating beam power (upper panel of Fig. 3). This provides us with three independent criteria for the detection of melting, as shown in Fig. 3.

![Graph](image)

**FIG. 3.** (Color online) Melting point determination. Measurements were performed on Te sample at a pressure of 19.5 GPa. The melting temperature is determined by using three distinct criteria: a. (upper panel) Observation of changes in the slope of the temperature as a function of heating beam power. The dotted line corresponds to the melting temperature. b. (middle panel) An increase in the temporal vibrations of a series of speckle images taken at each temperature (red line and dots) with respect to temporal vibrations measured at room temperature after each heating cycle (blue line and dots). c. (lower panel) A sharp decrease in the correlation of speckle images taken after heating the sample, with respect to a reference image taken before heating the sample. Using these criteria the melting temperature in this measurement was determined to be 1150 K.

### III. MELTING CURVE OF TELLURIUM

The melting curve of Te was previously studied in a large volume press up to 10 GPa, by means of differential thermal analysis, thermobaric analysis and electrical resistance measurements. However, to the best of our knowledge, no measurements of the melting curve of Te using LHDAC have been reported to date. Typically, LHDAC setups are designed for measurements of melting temperatures above 1000 K, utilizing appropriate optical components for thermal radiation in the visible range. Measurements of melting temperatures below 1000 K require different optical components sensitive to thermal radiation in the IR range. Our IR pyrometer, described in detail in Ref. 36, was designed to extend the applicability of LHDAC experiments to temperatures down to 500 K and is thus suitable for studying the melting curve of Te at high pressures.

Using the experimental setup described above, the melting curve of Te was measured up to a pressure of 35 GPa. At each pressure we repeated the measurement in at least 4 different positions on the sample surface. At each position, the melting temperature was determined using at least two of the criteria described in the previous section. The measured melting curve is shown in Fig. 4. With our improved melting criteria, we could determine the melting temperature with an estimated error of 50 K.

Up to 10 GPa our measurements agree with previous data. Above this point until $P \approx 25$ GPa the melting temperature increases with increasing pressure but its slope slightly decreases (i.e., $d^2T_m/dP^2 < 0$). At $P \approx 25$ GPa a small change of slope can be observed. This change of slope is possibly related, via the Clausius-Clapeyron relation, to a solid-solid phase transition (The IV/V transition, see Fig. 4) reported in Ref. 35 at temperatures up to 700 K. Extrapolation of the IV/V phase boundary (dashed line in Fig. 4) intersects the melting curve at $P \approx 23$ GPa, in reasonable agreement with the pressure at which a change of slope occurs in the melting curve.

### IV. DISCUSSION AND CONCLUSIONS

We have demonstrated a simple image analysis procedure to quantify changes in speckle interference patterns, which are widely used as a probe for the detection of melting transitions in LHDAC experiments. Two distinct quantities can be defined: 1) STD of a series of images recorded during heating and 2) a correlation between an image recorded at room temperature after each heating cycle and a reference image recorded prior to heating. Abrupt changes in these two quantities indicate the onset of liquid motion at the hotspot and changes of texture due to melting and resolidification, respectively. This method improves the reliability of melting criteria which are based on changes in an image of the hotspot surface.

The image analysis procedure was employed to measure the melting curve of Te up to 35 GPa. Our measurements are in excellent agreement with previous measurement of the melting curve of Te using large-volume press up to 10 GPa. At higher pressures our measurements are in line with the solid-solid coexistence curve, reported in Ref. 35. However, an additional study of the
melting curve in this region is necessary in order to draw further conclusions. While the use of an image analysis to improve the accuracy of melting detection was demonstrated at relatively low temperatures (below 1400K), the method should also be applicable to temperatures beyond the measured range.

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