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Melting-Point Measurements at High Static Pressures from Laser Heating Methods: Application to Uranium[1]

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Two experimental approaches dealing with the determination of melting at high static pressures are described and analyzed. With the sample squeezed inside a diamond anvil cell, high temperatures up to the solid–liquid transition are obtained using Nd:YAG laser heating. Two methods have been investigated. In the first technique, the heating is accomplished with a pulsed laser and the brief radiation variations ($t < 10$ ms) emitted from the sample are recorded with two high-speed infrared detectors. The melting location is defined by a plateau or changes of slope of the signals, and the temperatures are calculated by assuming a constant value of emissivity factor at the end of the transition over the studied pressure range. The second system employs a continuous laser and a two-dimensional CCD detector to measure temperatures using multispectral pyrometry. Melting is detected from criteria related either to textural change in the sample involving interference contrast under a laser illumination or to the specific variations of temperature and emissivity as a function of laser power. Thermal radiation is fitted to Planck's law with temperature and emissivity as the free parameters. Advantages and drawbacks are presented from results obtained on pure uranium.

KEY WORDS: diamond anvil cell; emissivity; high pressure; laser heating; melting; uranium.

1. INTRODUCTION

Referring to literature data, for a great number of pure elements, their melting curves are still limited to the experiments performed with a piston-cylinder apparatus up to 3 GPa or with a multianvil press up to 16 GPa

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[1]. Consequently, despite the broad interest for this equilibrium transition between crystalline and liquid states, there is as yet only a poor understanding of the detailed physical mechanism by which a crystal melts.

Over the last 20 years, several devices have been developed in order to investigate melting at simultaneous high pressures and high temperatures in the diamond anvil cell (DAC) [2]. From the different approaches, the use of a laser beam has appeared as the most suitable way to achieve very high temperatures up to 5000 K. Indeed with such a method, the heating area stays very localized on the sample, and consequently, the mechanical stability of the DAC is not affected and the oxidation of diamond anvils is also avoided. Furthermore, laser heating in DACs allows pressure and temperature to be controlled independently and has an advantage over the shock-wave technique in this respect.

Since 1990, the combination of laser heating and DAC pressure generation has been undertaken in our laboratory, with a specific interest in the melting behavior of lanthanide and actinide elements, for which calculation is difficult due to the complexity of their electronic structures. In this paper we briefly describe two laser heating devices which have been successively developed using pulsed and continuous Nd:YAG lasers. Main differences are analyzed from new experimental results on pure uranium.

2. HIGH-PRESSURE GENERATION

High static pressures have been generated with a new pressure cell developed from the general DAC principle (Fig. 1). Its main characteristics are a large numerical aperture of 0.38 (from visible to infrared domains) and a small external geometry cell (50 mm in diameter and 60 mm in

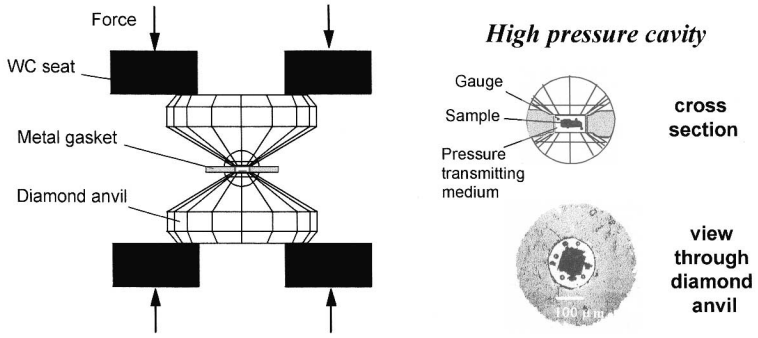

Fig. 1. Basic principle of the diamond anvil cell (left drawing) and details of the high pressure cavity from an enlarged cross section and an optical photograph taken through the diamond anvil.

length) compatible with a gas loading facility. Details of this DAC and of the 0.3-GPa gas pressure vessel designs are given in the Dahan et al. patent [3].

Pure uranium (99.9%) has been supplied by Goodfellow Metal Ltd. from thin foils cold-rolled to a thickness of 25 μm, which are reduced to 15 μm by an electropolishing chemical treatment before cutting. The samples, roughly square-shaped with an approximate width of 100 μm, are carefully centered inside the experimental cavity, which is formed from a 200-μm hole electro-erosion drilled in a preindented rhenium gasket mounted on a DAC.

Due to the high thermal conductivity of diamond, good sample insulation is needed for heating metals to their melting point from available laser power. The problem of thermal insulation has been overcome (i) by inserting three or four small ruby balls between the back side of the sample and the lower diamond culet and (ii) by using argon as the pressure transmitting medium. Argon is suitable based on its low thermal conductivity compared to that of diamond but also based on its low strength (quasi-hydrostatic condition) and its chemical inertness, which is extremely important at high temperatures.

During all experiments pressure was estimated from measurements using the calibrated pressure shift of the ruby R1 fluorescence line in the case of hydrostatic conditions [4] at room temperature before and after thermal treatment.

3. HIGH-TEMPERATURE GENERATION

3.1. Pulsed Laser Heating

Heating of samples under pressure is accomplished with a multimode Nd:YAG pulsed laser (CHEVAL model) providing a maximum power output of 5 kW at 1.064 μm. A schematic diagram of this apparatus is given in Fig. 2. The laser operates in the free-running mode, and the pulse durations are therefore of the order of 0.1 to 10 ms. The beam enters through the rear of the DAC and is focused by a planarchromatic microscope objective lens onto the sample. The beam profile is rectangular, leading to a homogeneously heated area of approximately 80 μm in diameter with small temperature gradients inside the central part.

The thermal radiation emitted from the sample surface opposite to the heating source is focused without chromatic aberrations by two off-axis parabolic reflectors onto a metallic diaphragm providing a continuously variable square aperture to define the true area viewed by the detectors.

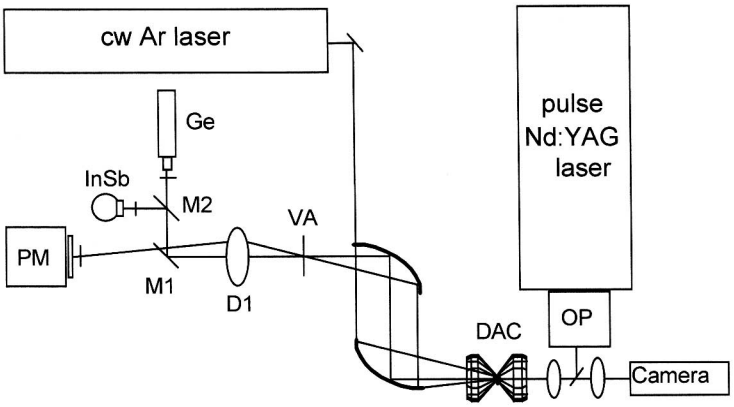

Fig. 2. Schematic of the pulsed laser heating system. OP, optical attenuator; VA, variable aperture; D1, infrared doublet; M1, dichroic mirror; M2, beam splitter.

After wavelength selection through a dichroic mirror and filters, the selected radiations are focused onto two infrared detectors: a Ge photodiode (ADC, Type 403 H) and an InSb detector (CE, Model 0410) with effective wavelengths of 1.50 and 2.00 μm, respectively. A high-speed oscilloscope (Nicolet, Model 440) is used to record simultaneously the transient signals from the outputs of the detectors and from a photodiode mounted on the laser head.

The melting location is defined *in situ* either directly from observations of the plateau or changes in slope of the signals of the infrared detectors or by correlation with sudden variations in intensity received by a photomutiplier tube of reflected 0.514-μm Ar laser light from the hot spot. An analyzed area of 10×10 μm on the sample is generally considered at temperatures above 1500 K. Melting temperatures are calculated by assuming a constant value of emissivity factor for the investigated material at the end of the solid-to-liquid transition over the studied pressure range. A sample shot under atmospheric pressure inside the DAC is included in each run as the melting reference. Details of the melting temperature determination have been given elsewhere [5].

3.2. Continuous Laser Heating

Figure 3 shows the continuous laser heating setup. A cw Nd–YAG laser (Spectron, SL903/904 series) provides maximal powers of 20 or 30 W, depending on the selected configuration, in single mode operation TEM00 of vertically polarized light, at wavelength 1.064 μm, with an amplitude

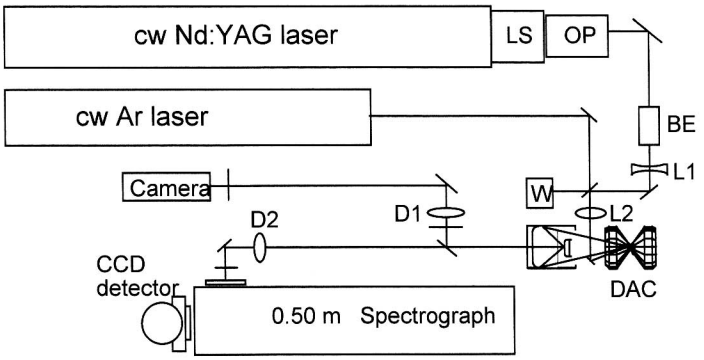

Fig. 3. Diagram of the continuous laser heating system. LS, light stabilizer; OP, optical attenuator; BE, beam expander; W, power meter; L1, concave lens; L2, convex lens; D1, doublet; D2, achromatic doublet.

stability of 0.1% rms. The YAG laser light travels through an optical attenuator and a 3× beam expander before being focused with a set of two lenses and reflected on a small mirror at an angle of 20° from the normal direction. The diameter of the spot on the sample is approximately 40 μm.

Thermal radiation emitted by the sample is collected by a reflecting objective and focused onto the slit of an imaging spectrograph (0.5 m; Chromex) by a specific doublet which eliminates the chromatic aberrations resulting from use of the diamond anvil. The signal collected from an area of 4 μm in diameter of the sample is then dispersed by a 150 gr $\cdot$ mm^{-1} grating before being recorded in a two dimensional CCD detector (Princeton Instrument) with 1100×330 pixels. After spectral response corrections of the optical system, the spectrum is fitted from 500 to 850 nm to Planck's radiation function, with temperature and emissivity as the free parameters. The wavelength dependence of emissivity is not taken into account for the temperature determination (gray-body approximation).

An Ar laser beam (458 nm) is used for constant illumination of the sample during heating, providing a visual method for melting detection. The coherent light reflected from the sample surface gives a speckle figure on the observation camera. During a step-by-step power increase in the YAG laser, the onset of melting is detected from continuous variations of the speckle intensity which correspond to the reduction of the surface roughness.

4. RESULTS AND DISCUSSION

Typical time–radiance and time–reflectivity profiles recorded on uranium during a pulse duration of 0.6 ms are shown in Fig. 4. These

signals are characteristic of the solid–liquid transition during heating for a pure element. Melting was indeed confirmed by microscopic examinations of the sample after the thermal treatment. Based on the data recorded at 21 GPa, the first major change of slope of the radiance signal (Fig. 4b) associated with the small reflectivity value (Fig. 4c) at around 0.15 ms has been attributed to the onset of melting relating to the detection threshold of the system. The initial drop in reflectivity up to 0.1 ms is associated with the decrease in the emissivity of the solid state with increasing temperature. This assumption was confirmed by the data deduced from experiments with continuous laser heating. Consequently, the constant value obtained on the radiance curve from 0.15 to 0.3 ms during the heating process corresponds to the melting plateau of the analyzed area. Afterwards, the radiance

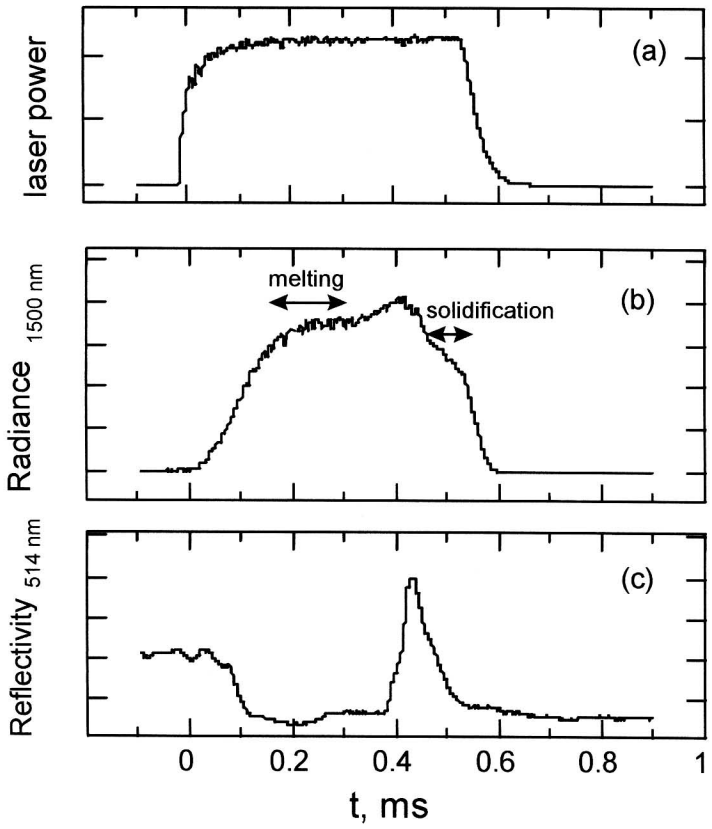

Fig. 4. Experimental measurements (b, c) on pure uranium at 21 GPa during pulsed laser heating (a). Melting is detected from the plateau, and in this example, solidification is also clearly observed before the end of the laser pulse.

temperature at 1.5 μm of the viewed surface slightly increases to a maximum value and then gradually decreases before rapidly dropping off after the end of the laser pulse. The peak of the reflectivity measurement, which is easily observed over the time period, might result from changes in the surface texture or convective motion of the liquid sample area rather than from variations in the emissivity factor.

The basic approach used for melting determination from *in situ* characterizations during the dynamical heating is directly related to complex processes involved during the laser–sample interaction. The key parameters are the heating rate, the sample geometry, the thermal properties of the material, and those of the surrounding medium, which are the latent heat of melting and the relative importance of the emissivity and temperature contributions in the radiance variations. In our case, the geometrical factors are largely constrained to the volume of the high-pressure cavity of the DAC, and thus, the sample sizes are nearly equal for all the studied materials. Thus, in practice only the melt-front velocity can be adjusted from the intensity and the duration of the laser pulse. Therefore, the capability of performing reliable experiments with the pulsed laser heating method is determined and governed by the physical properties of each element, which are generally unknown at high pressures.

Figure 5 shows a spatially resolved thermal emission spectrum obtained from one of the first experiments on uranium under a pressure of

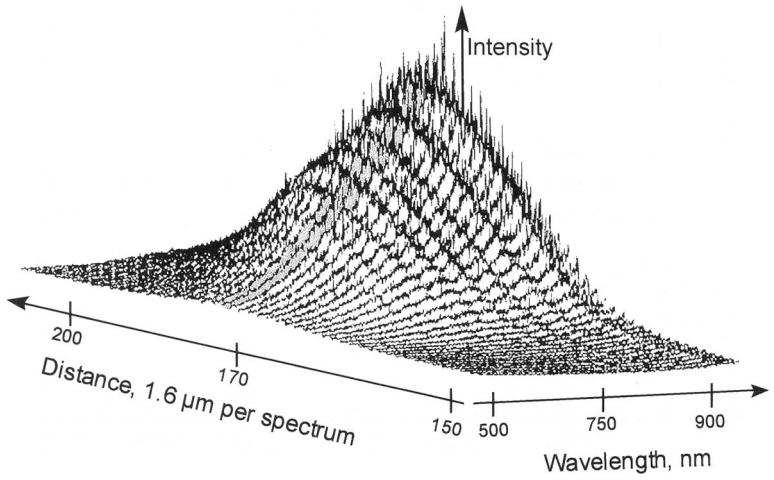

Fig. 5. The spatially resolved thermal emission spectra in the three-dimensional graph obtained from the cw laser-heated sample of uranium at 13 GPa at a given laser power. Only the central part (the shadow curves) of this Gaussian distribution is considered for temperature and emissivity calculations.

13 GPa. From this figure it is evident that there is a significant temperature gradient along the vertical direction. Consequently only three spectra of the central area were considered for temperature determination. In this work the calibration was performed from melting experiments at ambient pressure and theoretical thermal radiation calculations for specific elements. In

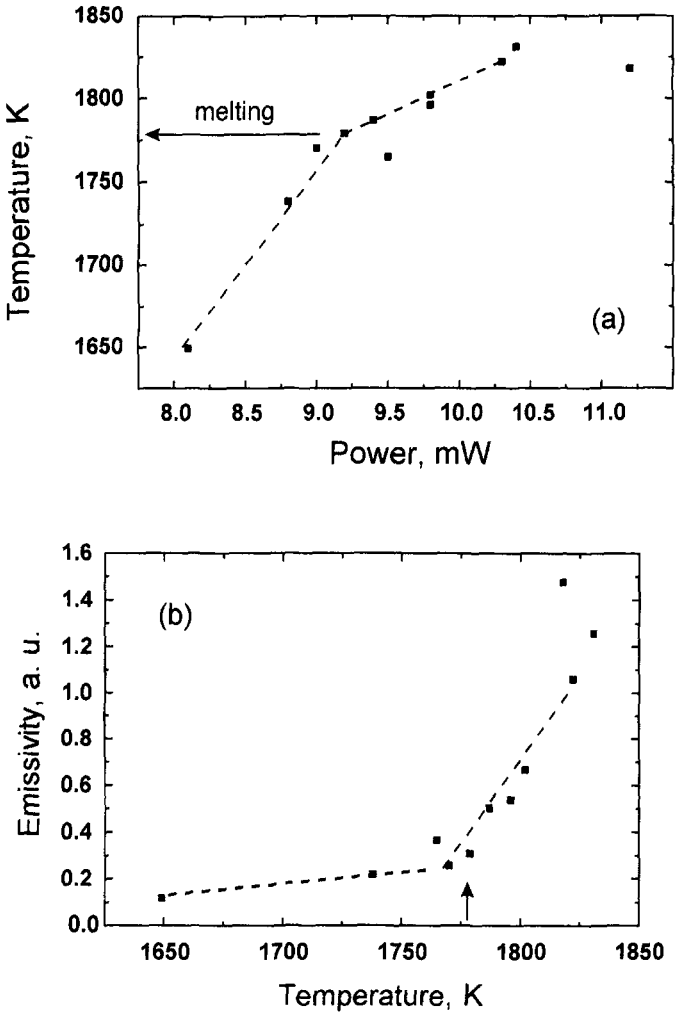

Fig. 6. Melting of uranium at 13 GPa as determined from plots of (a) temperature versus laser power and (b) emissivity factor versus temperature.

the latter case, the accuracy of the calibration is then correlated with the uncertainty in the detection of the solid–liquid phase transition. During this experiment, melting is well defined from a change in the slope of the sample temperature as a function of increasing laser power, as shown in Fig. 6a. This correlation is supported by a large increase in the emissivity factor above the defined temperature (Fig. 6b), and this event is consistent with the melting criterion based on the direct observation of fluid flow.

5. CONCLUSION

Although the number of our experiments with both laser heating devices is still limited, several observations lead to the following concluding remarks showing their complementary aspects.

(i) The P–T range for a pure element could be investigated. The thermal detectivity (e.g., measurements of low melting temperature) seems to be slightly higher in the pulsed laser system. This difference is explained by the use of infrared detectors combined with the large viewing area on the surface sample. High pressures, above 50 GPa, could be more easily achieved with the continuous device with respect to its optical arrangement (same small heated and emitting sample area).

(ii) The heating being very localized (a small thermally affected area for each run) with the continuous laser system, several experiments under pressure at different surface locations can be performed with the same sample.

(iii) Since the pulsed heating method is sensitive to the thermophysical properties of material, experiments will probably be limited to the studies of some pure elements. The solid–liquid plateau is indeed related mainly to the latent heat of fusion. On the other hand, the different melting criteria used with the cw laser heating system should be applicable to most of the materials.

From these first experiments performed on uranium under pressure, relatively good agreement has been achieved between the two laser heating methods. For example, at around 13 GPa, melting temperatures of 1700 ± 70 and 1760 ± 30 K have been determined from measurements performed during pulsed and continuous laser heating, respectively. Despite these contributions, there remain important questions regarding the quantitative reliability of high-temperature studies using the laser-heated diamond anvil cell. Indeed, our melting temperatures are significantly lower than those in a previously published study [6], in which a value of

1982 ± 60 K was given at 13.9 GPa. In order to explain this discrepancy of about 200 K, further investigations have to be performed, in which the main sources of errors such as the temperature distributions, melting criteria, and temperature calculations should be quantified.

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