TOPICAL REVIEW — High pressure physics

How to detect melting in laser heating diamond anvil cell

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Research on the melting phenomenon is the most challenging work in the high pressure/temperature field. Until now, large discrepancies still exist in the melting curve of iron, the most interesting and extensively studied element in geoscience research. Here we present a summary about techniques detecting melting in the laser heating diamond anvil cell.

Keywords: high pressure, laser, melting, diamond anvil cell

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1. Introduction

High pressure conditions usually exist in the interior of planets accompanying high temperatures in the universe. It is well known that creatures only can live and survive in a very small pressure and temperature range (∼1 atm, 300 K), so our familiar world is a very special one. In the last century, the invention of large volume compress (LVP)[1] and diamond anvil cell (DAC)[2] made a great improvement of ability in high-pressure research. Especially, DAC provides opportunities to rebuild pressure conditions of Earth's core in microns scale for a long time.[3] Now in the high-pressure research field, DAC has become a popular tool due to its low cost and easy connection with laser and synchrotron light source. In the geophysical field, the final goal is to reveal states of matters under high pressure/temperature conditions. Following the development of the high-pressure technology, lots of efforts were paid to achieve high temperatures in highly compressed samples, such as internal/external resistance heating[4–7] and laser heating.[8–10] In 1967, the first laser heating experiment in DAC was performed by Taro Takahashi and William A. Bassett.[11] Now, the yttrium–aluminum–garnet (YAG) laser has been applied widely in laser heating diamond anvil cell (LHDAC), because a diamond anvil is transparent from visible to infrared light and it is easy to combine with a normal microscope light path to focus in microns area. In DAC, the laser heating method processes unique advantages: highly focused heating zone (micron), very high temperature available (thousands K), and precise controlled heating time (nanoseconds). For detecting melting signals, the most challenging part is how to obtain a stable and uniform high temperature in the micron scale at the same time to avoid possible chemical reactions with the surrounding pressure medium, gasket, even diamond anvil. Next we present a review of laser heating techniques and ways to detect melting in LHDAC.

2. Optical setup of laser heating system

Figure 1(a) shows a general optical setup of the laser heating system in LHDAC. For YAG laser, there are the usual two light paths to focus on the sample. Firstly, one objective is used for focusing YAG laser and collecting radiation light together, which will enhance the system to maintain ability and reduce the laser performance. Secondly, objectives for YAG laser focusing and image collecting are separated, which will improve the laser focus ability following an increase of the system complexity. More details about the optical setup of the laser heating system can be found in many previous articles.[12–14]

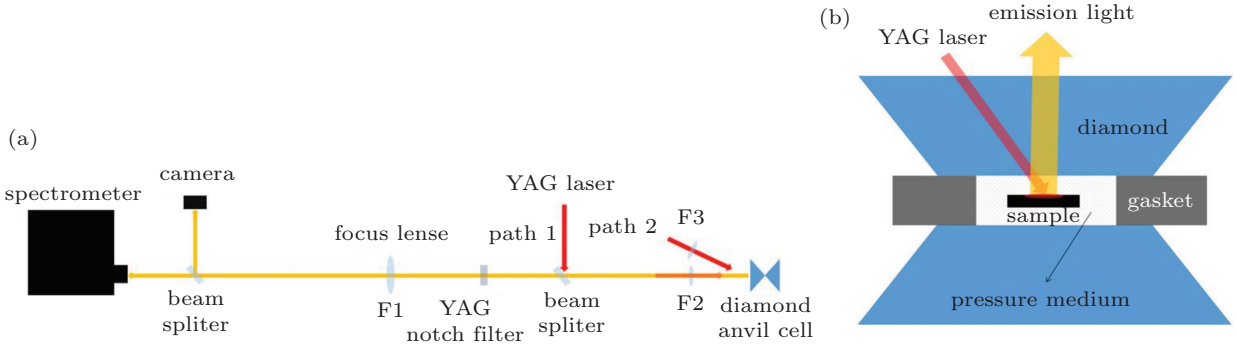


Fig. 1. (color online) (a) Optical setup of laser heating system. (b) Sample alignment in LHDAC.

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Diamond's thermal conductivity is five times higher than cooper and the distance between the diamond anvil and the thousands kelvin sample is only several microns, so how to align the sample and the thermal insulate layer is critical for a steady temperature in LHDAC. Schematics of general sample alignment for laser heating in LHDAC are shown in Fig. 1(b). The sample is embedded in a pressure medium and isolated from the diamond anvil. The pressure medium can work as the thermal insulator layer at the same time. The materials with low thermal conductivity, high temperature stability, excellent chemical inertness, and low laser absorption, such as oxides (MgO, Al_2O_3, SiO_2) and alkali halides (NaCl, KCl, KBr, CsI, LiF), are usually selected as the thermal insulating layer. Noble gases are also good candidates, but high compress abilities make their thermal insulating performance worse at higher pressure. Sample alignments in LHDAC have been summarized in Boehler's article.[15]

3. Temperature measurement

Measuring the accurate temperature in LHDAC is a critical and challenging work. Now a generally accepted method is to fit the intensity (I) versus wavelength (λ) dependence curve of emission from the sample by the Plank radiation function

$$I(\lambda) = \varepsilon c_1 \lambda^{-5}/(\mathrm{e}^{c_2/\lambda T} - 1),$$

where c_1 and c_2 are constants. Emissivity ε as a material dependent parameter varies from 0 to 1. In temperature fitting, ε is usually taken as 1 (an ideal black body irradiation) and earlier researches have proved the reliability of such temperature measurement in LHDAC.[16] The melting temperatures of some refractory metals (Ta, W, Mo, Re) measured by this method are also well consistent with the data in hand books.[17]

Melting is a process from solid to liquid associated with breaking down of the long range ordering structure. It can be imagined that the most direct observation of melting is the disappearance of solid signs and the appearance of liquid unique properties together. But more often, we can only detect melting by some indirect evidences, such as changes of reflectivity, electrical transport, and sample surface. We will describe ways to monitor melting in LHDAC in the next section.

4. Ways to detect melting

4.1. X-ray diffraction to determine melting

Synchrotron x-ray source is a powerful tool to detect crystal structures, so it is an ideal method to show structure information during a melting process. In high temperature x-ray diffraction experiment, disappearance of diffraction peaks cannot assure that it is melting, it may just be a re-crystallization process. So the most direct evidence about melting is the appearance of a liquid unique diffuse diffraction pattern. At the beginning, the weak diffraction ability of micron size highly compressed liquids made the detection of high temperature/pressure liquid in LHDAC impossible. Following the development of the synchrotron x-ray technology, more and more articles announced the successful probe of melting by the x-ray diffraction method.[18–21] It is well known that the x-ray diffraction intensity is proportional to the quality of the sample and the melting portion will directly determine the diffraction pattern intensity. So for detection of melting by x-ray diffraction, a homogeneous temperature distribution inside the sample will be crucial and the two-side laser heating technology has been developed to reduce the temperature gradient in the sample. In general, the x-ray diffraction method is an emerging promising way to detect bulk melting.

4.2. Laser speckle method

In the melting zone of the sample chamber, the sample is usually micron size with a large temperature gradient on its surface, so a strong convection exists at the interface between solid and liquid. Boehler developed a laser speckle method to detect the melting phenomenon by direct visual observation on motion of speckle patterns on the melting sample surface. It has been successfully applied to measure the melting curves of materials.[22–29] The motion sensitive character of this method makes it easy to monitor starting melting on the surface.

4.3. Surface change on molten sample

A sample under high pressure and high temperature is difficult to *in-situ* detect its melting phenomenon. However, the surface change on a quenched sample can be observed due to the difference between fast crystallization of molten and un-molten parts. The phase diagram of the refractory metal tantalum and glass sample has been obtained by this way.[30,31] We have also tried to measure the pressure dependence of melting points of rhenium by surface change. We found that the rhenium surface is not stable at around the melting temperature and is usually destroyed after continuous laser heating for several seconds. So we developed a 20-ms flash laser heating method to avoid it, which can be found in our previous paper.[32] At first, some selected metals (Ta, W, Mo, Re, Ir, Pt) have been treated by flash laser heating at ambient pressure in argon gas to prevent chemical reaction with air. Figures 2(a) and 2(b) show the SEM images of tantalum at ambient pressure before and after melting, respectively. A clear surface change appears as a smooth drop at the center of the laser spot, which can be considered as a product of fast crystallization of liquid Ta. The determined melting point 3303 ± 80 K is very close to the standard value of 3290 K in hand books.[17] Specific surface shapes on molten parts are determined by the sample's intrinsic thermal

properties and some highly compressed liquid metal properties are also possible to be obtained through analyzing the shape of the molten part. Similar phenomena have been found in other metals, such as tungsten, iridium, rhenium, and molybdenum, and their ambient melting points all keep consistent with the previous data. Figure 3(a) shows the SEM image of the recovered iron sample from 31 GPa. The surface change is similar with that of the above ambient tantalum and a smooth center is molten before quench. The wavy part outside of melting can also be observed in the recovered rhenium sample and it possibly indicates that iron will become soft and lose its strength at around the melting temperature. Figure 3(b) shows the phase diagram of iron including this study and the previous results. The blue and red solid dots represent the heating parts before/after melting and the mixed color dot means the boundary between solid and liquid, which does agree well with the previous plot.

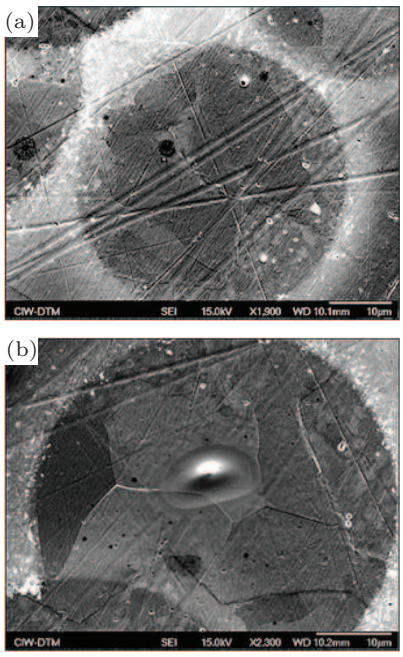


Fig. 2. (color online) SEM images of 1 atm Ta samples quenched at (a) 3227 K and (b) 3380 K.

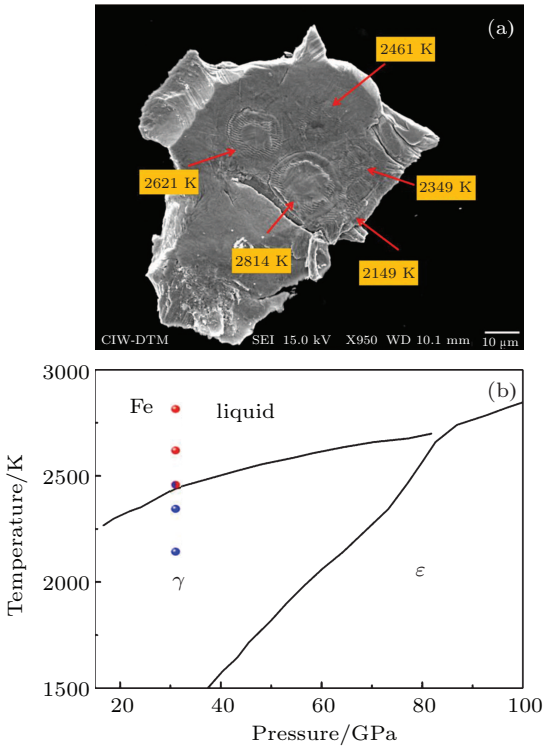


Fig. 3. (color online) (a) SEM image of recovered iron sample from 31 GPa, blue and red colors represent positions heated below and above melting. (b) Phase diagram of iron, the blue and red dots are our data points.

This method is a good and reliable way to detect melting phenomena, however it is time consuming and can only work on some specific samples at pressure below 50 GPa.

4.4. Power dependence of temperature

In order to detect the melting phenomenon under high pressure, researchers tried to obtain the laser power dependent curve of temperature due to the large latent heat of the solid–liquid transition. Some earlier studies also announced observations of melting by means of this method,[33,34] but recently one article pointed out that it is not possible for the plateau to be caused by the latent heat in melting.[35] Usually, in laser heating experiments, under a constant power, the temperature is determined by the laser absorption, sample thermal parameters, and thermal leak together. We can assume that the last two parameters are constant at different temperatures and only the laser absorption is taken into account, but even the laser absorption is effected by many factors, such as the re-crystallization induced surface change, thermal parameters change of solid to liquid, and some possible chemical reactions on the surface. In order to analyse this method, we performed experiments about power dependence of temperature on iron and tungsten in LHDAC, in which the laser power was modulated in a 20-ms square pulse in a 0.2 W step scale in order to reduce possible chemical reactions. Figure 4(a) shows two runs of power dependence of iron at 25 GPa and they all exhibit two kinks at around 1150 K and 2480 K, respectively. The 1120 K should be the boundary from γ to ε phase transition and another one at 2480 K is close to the previous measured melting temperature. However, the temperature shows a continually slow change, so it is hard to accurately define the melting temperature. At around 2500 K, the temperature reaches a maximum and then it starts to go down with power. In microscope observations, a dark zone appears at the center of the hot spot on the sample, which means that liquid iron is possibly unstable or some chemical reactions happen. Figure 4(b) shows the result on refractory metal tungsten by the same method. It can be divided into three parts: below 2500 K, a small power dependence is observed; between 2500 K and

3800 K, the temperature increase rate is much larger than that of the low power part; and a platform appears at a higher temperature. The first kink should come from the laser absorption change and it can be induced by melting of thermal insulator Al_2O_3. At the final part, it keeps a very small power coefficient in a large power range and the platform looks like induced by the latent heat in melting of tungsten, but the enhancement of the thermal leak can be another possibility.

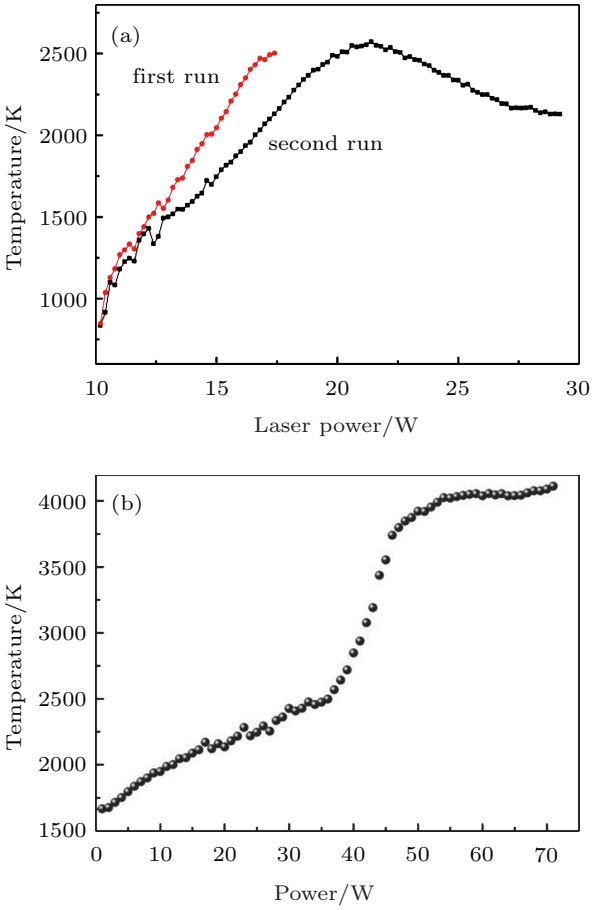


Fig. 4. (color online) (a) Two runs of power dependence of temperature of iron at 25 GPa in Al_2O_3 pressure medium. (b) Power dependence of temperature of tungsten sample at 25 GPa.

In order to further avoid the thermal instability and possible chemical reactions, we tried to heat the sample by a lineally increased power laser in 60 ms. Figure 5 shows the emission intensity evolution with power on a platinum sample at 25 GPa. Time dependent emission light of the sample was collected by photomultiplier tubes (PMT) with nano-second resolution. The radiation light intensity of a black body is directly proportional to the fourth power of its absolute temperature and then a relation between the emission intensity and the temperature can be considered. Three parts can be clearly observed in the figure and it is similar with the above result on the iron sample. The first kink between the blue and purple solid lines should come from re-crystallization and the second one looks more like melting. There is no temperature platform during the solid to liquid transition.

Generally, detecting melting by the power dependence of temperature is not so clear and it is also easily disturbed by other factors.

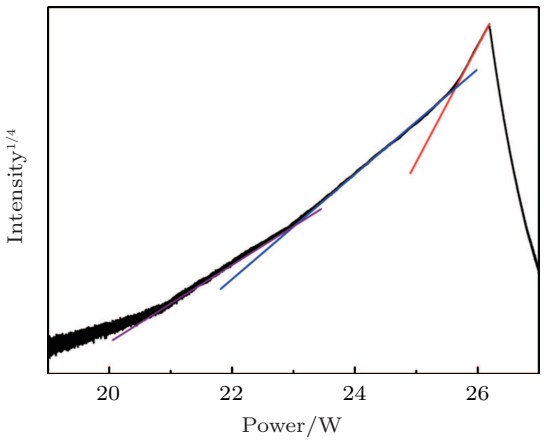


Fig. 5. (color online) Power dependence of black body radiation of platinum at 25 GPa.

4.5. Reflectivity on melting metal

Reflectivity change can be used to detect melting metallic liquids, especially the starting matter is an insulator or semiconductor with low light reflectivity. The most successful example is an increase in reflectivity of liquid silicon by a factor of 2.[36] Recently, melting of diamond was also observed by this way in dynamic compress conditions.[37] There is no experiment to study the reflectivity of metals in LHDAC due to their intrinsic high reflectance (90%) in the visible light range. The real reflected light intensity on metal also depends on the surface flatness. Liquid metal has a more flat and smooth surface than solid, especially under high pressure. Platinum was selected to monitor the reflectivity change before and after melting in LHDAC. Figure 6(a) shows the spectra of Pt emission at different temperatures with the same exposure time (40 ms) at 16 GPa in argon pressure medium. During heating, the power of the blue laser keeps constant. The waved part is black body radiation from the sample and is used to measure the sample temperature. An intensity increase of probing 473 nm blue laser can be found and the real value evolution is shown in Fig. 6(b). Below 2150 K, the reflectivity keeps constant then a 50% increase can be found at higher temperature. The temperature 2150 K is close to the melting point in the previous study.[38] This phenomenon does not mean that the intrinsic reflectivity of liquid Pt changes so much and it should be dominated by smoother surface of fluid Pt. In this way, the surface change between solid and liquid can be monitored, but it is not good enough for melting temperature determination in LHDAC.

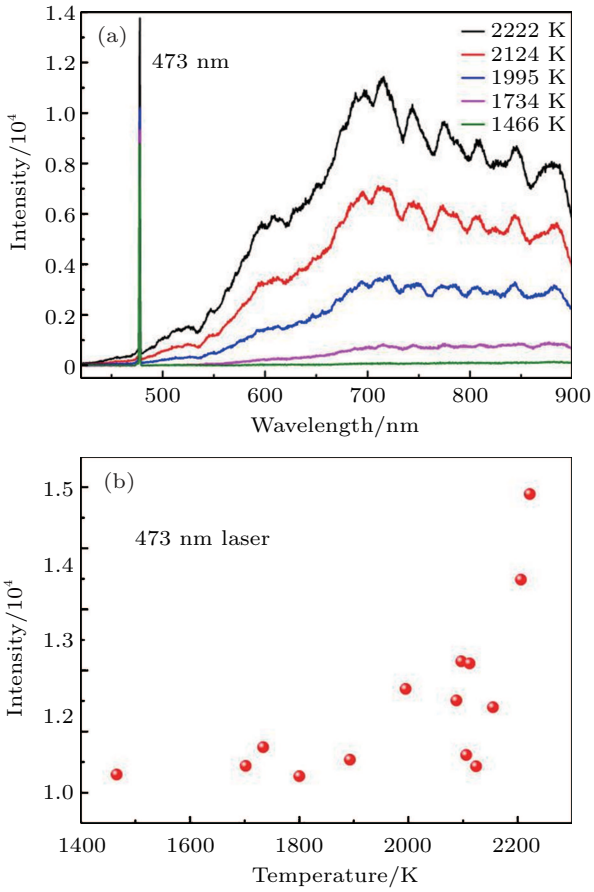


Fig. 6. (color online) (a) Black body radiation spectra of platinum at different temperatures under 16 GPa in Ar pressure medium. (b) Temperature dependence of reflectivity intensity of 473 nm blue laser on the platinum sample.

5. Summary

The most general ways to detect the melting phenomenon in LHDAC have been described above. They all have their own advantages and disadvantages. The melting temperatures obtained by different methods usually agree well, but some disagreements even serious discrepancies still exist. In general, a fast heating and detecting method will avoid some difficulties under extremely high temperature conditions. Melting can also be detected by other physical properties, such as resistance[39,40] and spectroscopy.[41,42] Melting of highly compressed matter is very challenging and interesting work and there is almost no fluid properties of liquid under extremely high pressure. In order to push forward research on melting, we should spend more effort to find better solutions.

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