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Phase behavior of metals at very high *P–T* conditions: A review of recent experimental studies

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Abstract

Studies at extreme pressures and temperatures are helpful for understanding the physical properties of the solid state, including such classes of materials as, metals, semiconductors, superconductors, or minerals. In particular, the phase behavior of metals at extreme pressures and temperatures is a challenging problem with many implications for other fields including Earth and planetary sciences. However, despite the efforts performed, the phase behavior of metals at very high pressures (HPs) and temperatures has been proven hard to predict accurately and only a limited number of experimental methods for making measurements in the regime of megabar pressures and thousand degree temperatures exist. In this contribution, we will review recent laser-heated diamond-anvil cell (DAC) studies on the phase behavior of different metals. In particular, we will focus on discussing the results obtained for the alkaline-earth metals, the transition metals, and the rare-earth metals, which we had extensively studied up to 1 Mbar and 4000 K. Differences and similarities of the phase behavior of these elements will be discussed aiming to improve the actual understanding of melting behavior at HP. We will also describe different experimental techniques for obtaining reliable data at simultaneously HP and high temperature employing the laser heated DAC. Drawbacks and advantages of the different techniques are discussed along with recent developments involving X-ray diffraction.

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1. Introduction

Extreme pressures and temperatures provide a valuable tool for studying the physical properties of the solid state, and in particular of the minerals forming the Earth's core and mantle. Nowadays the changes generated in the material properties by the simultaneous application of pressure (*P*) and temperature (*T*) can be explored in situ using several experimental techniques, which include shock-wave compression [1], large-volume apparatuses (LVA) [2], and diamond-anvil cells (DACs) [3,4]. In particular, DACs allow to reach pressures above 5 Mbar (1 Mbar = 100 GPa) [5] and its use combined with the laser-heating (LH) technique allows to realistically simulate the conditions in the Earth's interior [6]. The maximum pressure experimentally obtained using laser heated DACs is 200 GPa at temperatures of 4000 K [7]. Temperatures between 1200 and 6000 K can be achieved and measured accurately below 1 Mbar. On the other hand, the combination of DACs with synchrotron radiation enables the examination of solid–solid and solid–liquid phase transitions [8,9], and therefore the determination of the *P–T* phase behavior of many different materials. The aim of this work is to review different challenging techniques used to accurately characterize the phase behavior of materials under extreme *P–T* conditions. In particular, we will focus our attention in those techniques we employed to study the phase behavior of metals under high pressure and high temperature (HP–HT). Experimental details concerning the LH of DACs will be discussed in detail as well as the combination of this technique with synchrotron X-ray diffraction. Results obtained for different metals, such as alkaline-earth metals [10,11], transition metals [12–14], and

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the rare-earth metals [15] will be presented and discussed. Melting data obtained for these metals will be reviewed and the influence that electronic and crystal structures impose on the melting of metals at HP will be examined. Finally, comments on the existent discrepancies among results obtained using different experimental techniques as well as discrepancies between experiments and theoretical calculations will be presented.

2. Experimental techniques

The LH of DACs technique covers a wide *P*–*T* range: $P > 200$ GPa and $T = 1200$–6000 K. In particular, by means of this technique combined with the use of resistive heated DACs [16] or LVA [2], the *P*–*T* phase diagram of most metals can be extensively studied. A typical arrangement of a laser heated DAC is shown in Fig. 1. Since diamond is a superb thermal conductor, a pressure medium with low thermal conductivity or the use of insulation layers between diamond culets and the sample are highly desired to achieve a good quality heating. Noble gases, alkali halides, magnesium oxide , and aluminum oxide (Al_2O_3) are well suited for these purposes. However, special care has to be taken to avoid chemical reactions with the sample. One important caution to be taken during sample preparation is the elimination of any remaining water from the pressure medium and the sample. In addition, special attention has to be paid when alkaline-earth oxides are used as pressure-transmitting medium since usually they react with transition metals; e.g. CaO and W react at HP–HT forming $CaWO_4$ (in any of its known polymorphs [17–19]). Another important issue regarding sample preparation is the use of high-purity samples. In our experiments, we always used samples with stated purity higher than 99.9% and fresh surfaces. In addition, in the event of using reactive samples, like the rare-earth metals or the alkaline-earth metals, the sample loading was done in a glove box under high-purity argon (99.999%) in order to avoid oxidation. It is important here to note that in our experiments most data were obtained using different pressure media, the obtained results being consistent. This fact shows that the observed pressure behaviors are independent of the pressure medium employed.

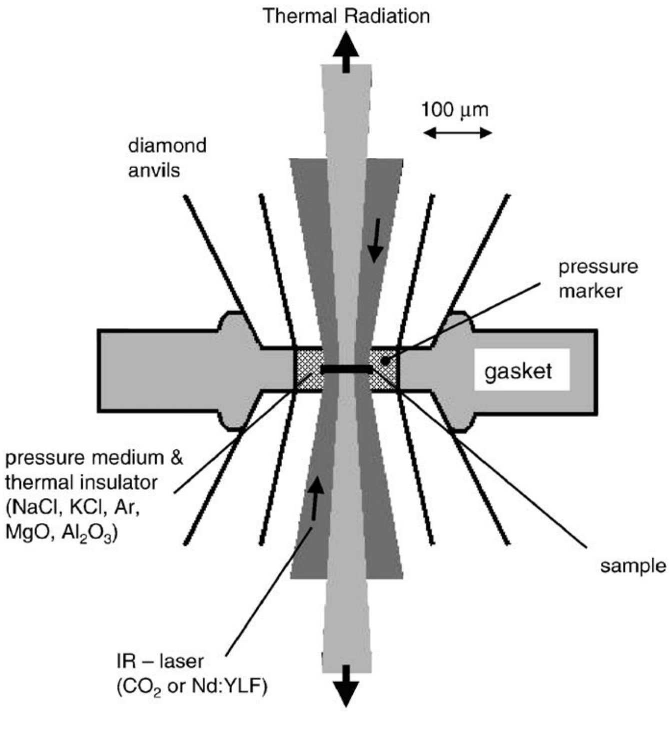

Fig. 1. Schematic view of a laser-heated diamond-anvil cell.

In our studies, we performed both single-sided and double-sided LH and, since metals are extremely good absorbers at wavelengths close to 1000 nm, Nd:YLF lasers ($\lambda = 1053$ nm) were used to heat our opaque metallic samples. Nd:YAG lasers ($\lambda = 1064$ nm) can be used also for LH opaque samples, but they have a poorer power and beam pointing stability than the Nd:YLF lasers [20]. On the other hand, the use of a CO_2 laser ($\lambda = 10600$ nm) is very convenient for heating transparent mineral and oxides, due to their high lattice absorption (10^{-3}–10^{-4} cm^{-1}) at the wavelength (λ) of 10600 nm [21,22]. Using the LH technique of DACs, we investigated the melting curves and structural stability of different metals. In all the cases, the defocused laser beams created a hot spot on the sample of about 30–50 µm diameter. Melting studies were mostly performed using a single-sided LH configuration at the Max-Planck-Institut für Chemie at Mainz (continuous wave, 50 W Quantronix laser, TEM_{00} mode) and the rest of the studies were conducted at the Advanced Photon Source (APS) employing a double-sided LH system (two continuous wave, 85 W Photonics lasers, TEM_{01} mode) see Fig. 2 or an LVA. In most of the experiments, melting was determined as the onset of convective motion during increasing laser power (speckle method), changes in reflectivity or discontinuities in laser power–temperature function. However, melting can also be determined by observing in recovered samples the changes introduced in their surface texture (see for example Fig. 1 in Ref. [12]), and in X-ray diffraction experiments by the disappearance of all Bragg peaks altogether with the appearance of a broad diffuse scattering and the increase of the background [23]. Fig. 3 shows the results of an X-ray diffraction experiment where melting of Ta is observed at 8.8 GPa and 3450 K. We have used all the above-described techniques to study the melting of different metals obtaining similar results. We would like to highlight this fact since the speckle method has been recently disputed [24,25]. However, the agreement observed between the different techniques used for melting determination, strongly suggests that the LH DAC measurements, in spite of their own sources of uncertainties, provide nowadays the best estimates for the melting curves of metals.

The combination of the LH of DACs with in situ X-ray diffraction [9] is a powerful tool to study the HP–HT phase diagram of metals. The high brilliance of synchrotron radiation allows the focalization of the X-ray beam to a size smaller than the heated portion of the sample, this fact