Melting of Sn to 1 Mbar

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Abstract. The melting point of Sn was determined between 20-105 GPa using laser-heated diamond anvil cell experiments, coupled with in situ synchrotron X-ray diffraction studies. In agreement with previous LH-DAC speckle experiments, we observe a flattening of the melting slope between P = 40–60 GPa. However, we also observe that this plateau is followed by a further increase in the melting slope above P ~ 70 GPa, leading to a remarkably high melting point of Tm = 5500 K by P = 105 GPa.

1. Introduction

The determination of melting points of elements and compounds to pressures in the megabar range is of interest for planetary sciences, as well as fundamental and applied materials physics studies. Typically such studies have been carried out using shock methods accompanied by empirical or ab initio simulations [1-3]. Recent advances in laser-heated diamond anvil cell (LH-DAC) techniques have extended static determinations into the megabar pressure range, with melting temperatures recorded up to between 6000-7000 K [4]. Several techniques have been explored to provide diagnostics of the melting event during LH-DAC experiments. Two main methods have emerged as providing the most understandable results. The first is a laboratory-based technique that relies on observation of the onset of changes in the laser ‘speckle’ derived from reflections and interference of coherent light reflected from the sample surface [5]. The observation of rapid fluctuations in the speckle pattern during laser heating is presumed to signal the melting event, although it is also possible that surface reconstruction phenomena or chemical reaction events may also contribute. A second technique has emerged recently based on synchrotron X-ray scattering (SXS) that relies on the observation of a liquid S(Q) pattern produced within the bulk sample [6].

In a first set of LH-DAC + SXS experiments performed on elemental Pb, Dewaele et al. studied the melting relation to below megabar pressures and determined dTm/dP values in close correspondence with both ab initio theory and shock wave studies [6]. Unexpected divergences had been noted previously between melting curves for elements determined by the speckle technique and the results of ab initio calculations, SXS melt results and shock wave experiments [4,7]. The advent of the SXS method has now begun to resolve some of these discrepancies by identification of chemical

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reactions occurring during the LH-DAC experiments, with C derived from the diamond surfaces reacting to form metal carbidies [4].

Sn is a well-known element that occupies an intermediate position in the periodic table below the semiconductors Si and Ge and above metallic Pb. Its melting relations have been studied using explosive gas gun techniques and it is established that the Hugoniot crosses the melting curve near 50 GPa [8]. The LH-DAC speckle method was used to study Sn melting to P ~ 68 GPa and T ~ 2300 K. Those results found that flattening of the melt curve occurred above 38 GPa to achieve a constant value near T_m ~ 2300 K [9]. Here we obtained new data on the melting of Sn to P > 1 Mbar using the LH-DAC heating and the SXS technique. The data below 60 GPa are in agreement with the speckle results. However we find an sharp rise occurring in the melting temperature above P ~70 GPa, leading to the remarkably high melting value T_m = 5500 ± 500 K at P ~ 105 GPa.

2. Experimental Methods

Experiments were conducted at beamline ID27 of the European Synchrotron Radiation Facility (\( \lambda = 0.3738 \) Å). Samples of pure Sn powder (99.99% Aldrich, packed under Ar) were pre-compressed into discs (~ 5 μm thick) and loaded into membrane driven diamond anvil cells under an inert atmosphere. 200 μm or 150/300 μm bevelled diamond anvils were used. NaCl or KBr were used as pressure transmitting media and to thermally insulate the diamonds. Re was used as a gasket material and was pre-indentet to ~30 μm thickness. Ruby grains were added to the sample chamber as an internal pressure gauge: pressures were also established during the X-ray diffraction experiments using the NaCl equation of state [10]. The samples were compressed to the target pressure and then heated simultaneously from both sides using Nd:YAG IR lasers (\( \lambda = 1064 \) nm). To reduce thermal gradients, the lasers were slightly defocused on each side. The X-ray beam was focused to a 2 x 2 μm² area at the center of the hot spot. Thermal emission spectra were recorded from the same 2 x 2 μm² area and fitted to Planck and Wien functions to determine T. X-ray diffraction patterns were recorded at 1–2 s time resolution to monitor the state of the sample continuously. Raw XRD patterns were integrated as a function of 2θ using FIT2D [11]. XRD refinements were carried out using POWDERCELL [12] and GSAS [13-14]. No oxides or carbides were observed to form during any of the laser heating experiments, with no differences in results from loadings conducted under inert atmosphere or ambient. The appearance of a liquid S(Q) signature in the XRD patterns was taken to indicate the onset of melting (Fig. 1) [15-16].

Figure 1: Temperature profiles of LH-DAC samples determined by fitting Planck and Wien functions to the thermal emission spectra. This diagram illustrates typical results from a heating series at P~49 GPa. The inset shows integrated XRD patterns (\( \lambda=0.3738 \) Å) for 3 different T values. The liquid S(Q) scattering is clearly observed to appear in pattern 3, corresponding to the arrowed position in the heating ramp.
3. Results and Discussion

Our LH-DAC melting data determined between 20-105 GPa are shown in Figure 2. The results obtained below $P < 40$-60 GPa agree well with previous shock data and LH-DAC melting points determined using the laser speckle method [8-9]. The melt slope increases smoothly above the β-Sn / bct-Sn / liquid triple point until $P \sim 40$ GPa, above which the melting relation flattens to attain a nearly constant $T_m$ value. A similar result has been found for a wide range of elements studied using the LH-DAC speckle technique and has been used to support new models for the melting event and melt structures [5], though they are not always supported by ab initio calculations or shock studies [7]. In the case of Sn, the shock Hugoniot crosses the melting curve at $P \sim 50$ GPa and $T \sim 2300$ K [8]. Isentropic shock compression experiments have been carried out using Sn samples preheated to $T \sim 600$ K [17], but these provide no further information on the higher P melting behavior.

Recently Hu et al. studied shock properties of Sn using sound velocity measurements as a diagnostic technique to indicate onset of melting or other phase transformation phenomena [18]: however, the incipient melting temperature suggested by these authors was significantly lower than that suggested by previous shock studies [8] or the static melting results.

In our present study using LH-DAC + SXS techniques, we observe a sharp rise occurring in the melting slope at above $P > 70$ GPa, leading to a remarkably high melting value of $T_m \sim 5500 \pm 500$ K at $P \sim 105$ GPa that could not have been predicted from the previous experiments. The usual explanation for such a change in melting slope would be occurrence of an underlying solid-solid transition, with an associated triple point. Sn is reported to undergo a bct to bcc phase transition in this region. However, the two polymorphs coexist over a wide pressure range with an upper limit of coexistence reported at $P \sim 56$ GPa, that does not correspond to the pressure where a triple point would be expected from our melt data ($P \sim 70$ GPa) [19,20]. Even ignoring the absolute transition pressure values that might be affected by the use of different pressure-transmitting media and the presence of non-hydrostatic environments, the volume change associated with the bct-bcc transition is minimal ($\sim 0.5 \%$) and could not account for the dramatic rise in the melting temperature. Likewise, if entropy effects were responsible, this would require the entropy of bcc-Sn to be significantly higher than that of bct-Sn. This is unlikely. We are now examining alternative models to explain the unusual melting properties of this apparently simple element with unexpectedly complex behavior.

![Figure 2: Melting curve of Sn to P > 1 Mbar. Our data are shown as filled squares. Open circles represent LH-DAC speckle data [9] and open stars are shock data [8]. Triangles represent experimental runs where only solid-Sn was observed in the LH-DAC X-ray diffraction patterns.](image-url)
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