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Melting curve of H₂O to 90 GPa measured in a laser-heated diamond cell

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Abstract

We report new data on the melting curve of H₂O in the range 20–90 GPa and 1000–2400 K obtained in a laser-heated diamond anvil cell. We found a marked discrepancy between our present results and previous work which covered the pressure range up to 38 GPa. The melting curve shows a discontinuous change in slope at about 43 GPa, indicating a first-order phase transition most likely to the ice X phase. We could find no evidence for a strong dissociation of H₂O up to 200 K above the melting temperatures.

The high-temperature phase diagram of H₂O has only been previously measured to about 38 GPa. At room temperature the cubic phase ice VII is observed at pressures above 2.3 GPa, and above 40–60 GPa the existence of a non-molecular symmetric phase ice X has been postulated, e.g. [1–5]. In the higher pressure and temperature range a superionic state of H₂O was postulated from *ab initio* molecular dynamic simulations [6].

Previous work on melting of H₂O covers the range up to 38 GPa. The study by Pistorius *et al* [7] used a simple squeezer high-pressure and high-temperature device; melting was determined by a drop in electrical resistance of an aqueous copper sulfate solution. In another study a multianvil pressure device was used and melting was determined by the change in resistance of a strain-sensitive manganin wire placed inside the sample [8]. During measurements in a resistively heated diamond anvil cell melting was determined by the disappearance of the 110 peak in the x-ray diffraction pattern [9]. Another study also used a resistively heated diamond anvil cell and gave the highest values for the melting temperatures [10]; temperatures were determined from the wavelength shift of the fluorescence of the ruby R₁ line and melting was detected by visual observation of the sample. In the most recent study using an externally heated diamond anvil cell melting was determined from changes in the x-ray diffraction pattern [11, 12]. The results of these previous studies show a large discrepancy in the melt slope at 20 GPa.

In the present work we present new melting data for H₂O in the pressure range between 20 and 90 GPa and the temperature range 1000–2400 K. The samples consisted of pure deionized

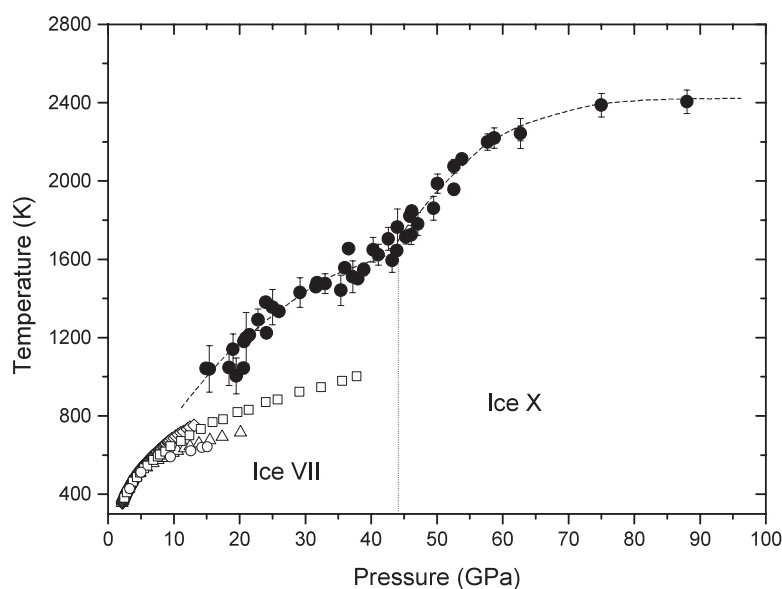


Figure 1. Melting phase diagram of H_2O (solid circles present work; squares [11, 12]; diamonds [10]; triangles [7]; open circles [8]). The phase line between ice VII and ice X is obtained from the observed discontinuity in the melting curve.

H_2O (total dissolved solids <20 ppb) and a metal to absorb the laser radiation. Various metals were tested for chemical reaction with H_2O at high pressure and temperature. Reaction with rhenium and platinum was observed at temperatures of about 1500 K. We found that iridium reacts with H_2O only if heated to several hundred degrees above the respective melting point of H_2O . Iridium was used mainly in form of fine-grained powder ('iridium black') with a purity of 98.8%. It was either loosely packed into the cell or pressed into foils in order to observe surface reactions. The samples were heated with YLF and YAG lasers ($1.05\text{--}1.06\ \mu\text{m}$ wavelength) and temperatures were determined by fitting temperature and emissivity using the Planck equation. Melting of H_2O was detected by direct visual observation of the laser-speckle pattern of a 488 nm argon laser beam. The pressure was determined from ruby chips on the basis of the ruby pressure scale with an uncertainty of about ± 1 GPa in thermal pressure. Melting temperatures were measured by temperature cycling through melting and freezing with a precision of about 100 K.

The melting temperature data are shown in figure 1 together with previous work. There is a marked discrepancy between the present results and previous work with respect to the melt slope near 20 GPa. In order to exclude the possibility of a new phase and a triple point in this pressure region we performed angle-dispersive x-ray diffraction measurements on H_2O at about 30 GPa and to about 2000 K at the ID30 beamline at ESRF in Grenoble. Only the ice VII 110 and 200 peaks were found. Raman studies of temperature-quenched samples at pressures to 60 GPa showed the broad band around $500\ \text{cm}^{-1}$ described in the literature for ice VII, e.g. [1, 13].

The melting curve given in figure 1 shows a change in slope at about 43 GPa indicative of a first-order phase transition. Evidence for such a phase transition was also obtained from room-temperature Brillouin measurements [4], showing a discontinuous frequency shift with pressure at ~ 44 GPa. We consider this transition at ~ 43 GPa to correspond to the ice VII–ice X–liquid triple point. We could find no evidence for a reaction of H_2O with iridium up to

the melting point; at temperatures 200–400 K above the melting point surface changes in the iridium foils showed that reaction occurred, indicating an increase in dissociation of H₂O with increasing temperature.

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