

Probing dynamic crystal growth of compressed hydrogen using dynamic-DAC, time-resolved spectroscopy and high-speed micro-photography

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Abstract. Solidification and crystal growth processes of hydrogen (H₂) have been studied under dynamic compression using dynamic-DAC (dDAC) in conjunction with time resolved Raman spectroscopy and high-speed microphotography. Liquid H₂ was compressed at a compression rate of 43 GPa/s across the liquid/solid phase boundary, causing a discontinuous vibron shift at the onset of solidification. The real time sample images, on the other hand, showed that H₂ solidifies into a characteristic, grain boundary free crystal, formed initially from the outside (or the edge of liquid) then grew into the central area within 11 ms. Interestingly, the time scale associated with the glassy solid formation is in good agreement with that of the discontinuous Raman frequency shift. The rate of crystal growth was measured to be 0.3 cm/s.

1. Introduction

Crystallization is a first order phase transition whereby nucleation is controlled by two factors; the difference in bulk free energy of the liquid and solid, and the interfacial free energy of the crystallite [1]. The interplay between the thermodynamics and kinetics of a system directs growth rates and polymorphism generating complexity in understanding crystallization process, which remains challenging even for simple systems [1, 2]. In efforts to better understand the process of solidification in simple molecular systems a wealth of research has come from computational work of crystallization in super-cooled liquids [3-8]. Despite the significance, the experimental work studying the crystallization process of low-Z elemental molecules is lacking, as they are gaseous at ambient pressures [9]. Hydrogen, in particular, is of intense interest with predictions of conductivity in the condensed state [10] and superfluidity in the deeply cooled liquid [11]. Still, there is an incomplete understanding of the solidification and crystal growth process in hydrogen, especially at room temperature under high compression. This is, in part, due to a lacking diagnostic technique capable of probing the rapid process of solidification at time scales less than 1 s.

In this paper we provide insight into the crystallization process of by novel spectroscopic and visual means in a highly compressed environment. To study the dynamic phenomena of rapid events such as solidification and melting in-situ the use of the dynamic diamond anvil cell (dDAC) [12] was employed in conjunction with time-resolved Raman spectroscopy (TRS). The dDAC has been used extensively to study pressure-induced crystal growth kinetics and morphology changes in water [13, 14]. More interestingly, dDAC allows for the study of formation of metastable structures in super-compressed materials [15]. It has been well demonstrated that subjecting materials to sufficiently fast shock pressurization or thermal quenching may force a material of a particular phase out of its region



of p-T stability and transform it into a new metastable or possibly stable phase resulting in unique structures [16, 17]. These fascinating transformations invariably lead one to ask some interesting questions about hydrogen crystal growth, morphology, potential novel metastable phases, and compression rate dependence during solidification under high compression at room temperature.

2. Methods and Materials

To answer these questions a dDAC that has diamond anvils with 16 sided 300 μm culets was used for the experiments. The sample was loaded by first pre-indenting a spring-steel gasket to 65 μm and drilling a 125 μm hole with electric discharge machining. A small ruby sphere approximately 10 μm in diameter was placed on the edge of the gasket sample chamber to measure initial and final pressures through ruby luminescence [18]. Hydrogen gas of 99% purity was then loaded in the prepared cell with an in house high pressure loading device. The dDAC apparatus adapts the traditional DAC by integrating three electro-mechanical piezo-actuators which can compress and decompress the sample. The pressure of the sample is controlled by the load applied by the actuators which is operated by the input voltage. The voltage input can be tailored to a particular wave form such as saw, sinusoidal, and pulse.

Utilizing the dDAC allows compression rates ranging from as slow as 0.1 to greater than 500 GPa/s [13]. The pulse profile used to drive compression is seen in figure 1(a) in which a steady voltage output drives the piezos over an arbitrary time period. Increasing the voltage drives the final pressure higher while increasing or decreasing the pulse length decreases or increases the compression rate. The piezo actuators were ramped to a 100 V output with control of the compression rate achieved by varying the actuator output time to 50, 150, 300, and 500 ms. TRS measurements were made by synchronizing a high powered Q-switched 532 nm Nd:YAG laser (Photonics Industries) with a gated and intensified CCD detector (Andor iXon) which permits the acquisition of Raman spectra snapshots of the sample while undergoing a dynamic transition.

Further experiments were performed utilizing fast-camera video acquisition. High speed micro-photographic video (Photron FASTCAM APX RS) was taken during the compression cycle with the same sample preparation and compression rate as the Raman analyzed samples. The frame rate was recording at 60,000 frames per second, with the sample being imaged with transmitted light.

3. Results and Discussion

For the experiment reported 50 Raman spectra were collected during the compression cycle with a detector exposure of 1 ms and each spectra spaced 0.125 ms. Raman measurements were made near the middle of the compression cycle to capture changes made during the solidification process. Initial sample pressure was 4.0 GPa and with a 100 V piezo output a final pressure of ≈ 8 GPa was achieved. The acquired Raman spectra were fit to a Gaussian distribution to aid in data analysis (figure 1b inset). The characteristic Raman spectra show a discontinuous shift during the compression cycle. The pressure was determined from the hydrogen vibrational frequency during the solidification cycle, and the compression rate was then determined from $\partial P/\partial t$ at 43 GPa/s (figure 1c). The hydrogen vibrational frequency initially increases as the molecules are compressed. The start of solidification is marked as the downturn in the vibrational frequency at $\approx 4207\text{ cm}^{-1}$, caused from the sudden change in the volume of the sample chamber. This yields the onset of solidification at 5.2 GPa, which agrees well with the known room temperature solidification pressure [19]. Thus, with a compression rate as high as 43 GPa/s we were unable to compress liquid hydrogen beyond its thermodynamic stability limit. Once the sample has completely solidified the vibrational frequency again shifts, at $\approx 4206\text{ cm}^{-1}$, increasing at approximately the same rate as before the transition occurred. The start of solidification is also accompanied by a sharp increase in the Raman intensity from the increase in the local density, and a decrease in the spectral line width as the effects of collision induced broadening in the solid are reduced (figure 1b).

The observed vibron frequency downturn (or red shift) upon solidification is probably due to an increase of intermolecular hydrogen interaction in solid – not by a heating of hydrogen from latent

heat of fusion energy release upon solidification. The approximate value of temperature increase, for example, can be calculated from the latent heat of fusion (ΔH_{fus}) and the heat capacity of solid hydrogen (C_p) at the melting point. The heat of fusion can be calculated from the Clapeyron equation ($\frac{\partial p}{\partial T} = \frac{\Delta H}{T\Delta V}$) using the well established melt curve, $P_m = -0.5149 + 1.702 \times 10^{-3}(T_m + 9.689)^{1.8077}$ [20], and theoretically calculated change in volume $\Delta V = 0.27 \text{ cm}^3/\text{mol}$ [21].

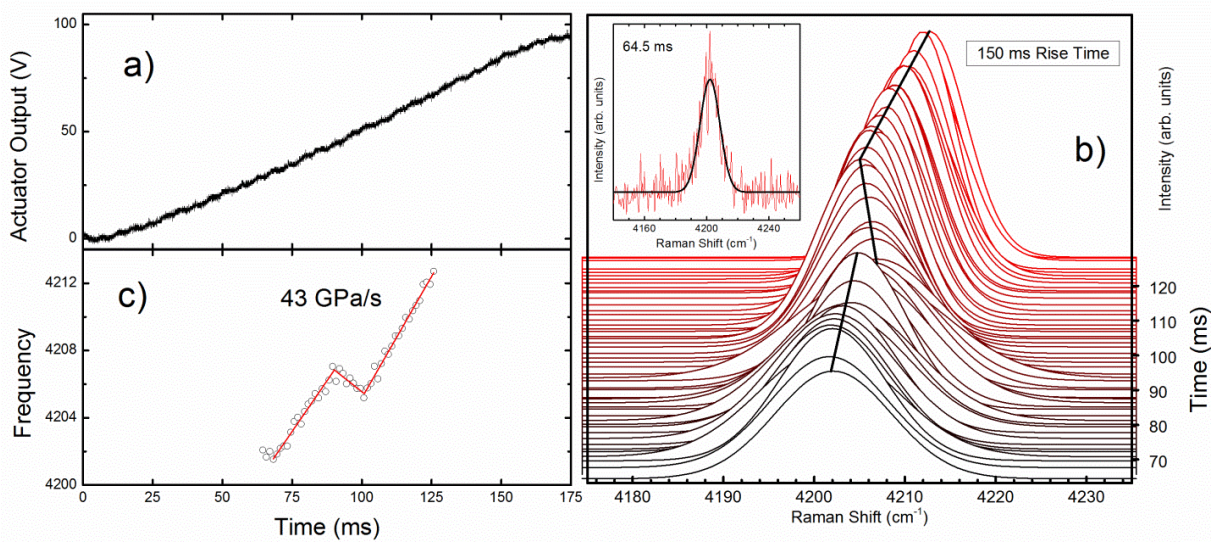


Figure 1. a) Piezo input voltage for a 150 ms pulse. b) Characteristic Raman spectra of hydrogen as it is compressed from 4 to 8 GPa. Spectra are fit assuming a Gaussian distribution. c) Raman frequency dependence during the compressive cycle of the dynamic-diamond anvil cell

The constant pressure heat capacity was taken from [22] to be $C_p = 14.49 \text{ J/mol K}$ extrapolated for the melting temperature at $T_m = 298 \text{ K}$. The calculated change in temperature was found to be $\Delta T \approx 174 \text{ K}$ in an adiabatic system. Given that the hydrogen sample is in direct contact with the diamond face, heat release from the sample would be almost instantaneously absorbed by diamond preventing an appreciable heating of the bulk hydrogen sample. This precludes the possibility that the Raman vibrational frequency increase is caused from a bulk heating of the sample from heat release upon solidification.

Figure 2 shows a micro photographic image series of the solidification of hydrogen compressed at a rate of $\approx 43 \text{ GPa/s}$. The small black sphere in the bottom right corner is a ruby piece. The image at 89.5 ms shows the onset of the solidification process. As the liquid hydrogen begins to solidify a ring forms on the outer diameter of the sample chamber (90.5 ms) while the inside area of the ring begins to take on a different depiction best described as “granular” where it was optically clear before the transition onset. As the solidification process progresses in time the ring closes in on the granular inner crystallites until the entire sample chamber has transformed back into an optically clear state once again. This shows visually what the Raman shows with a change in frequency that the solidification process is not an instantaneous event. Instead, it appears the hydrogen molecules undergo a transition to a metastable polymorph of small crystallites formed stochastically, before completely freezing into a single crystal of the *fcc* lattice [23]. This crystallization process observed by fast camera acquisition shows a very comparable process across the varying compression rates studied. Previous studies of super-cooled hydrogen [9] quenched to $\approx 0.65 T_m$ show a similar process of a structural transition before freezing into a random hexagonal closed-packed phase. Seen here may be a solidification process in which multiple structures are forming simultaneously. This crystal phase selection is consistent with *Ostwald’s Principle* [24] known as the *Rule of Stages* [25] indicating that the

crystallization process may be complex in that the system nucleates from the least stable phase finishing in the most stable phase.

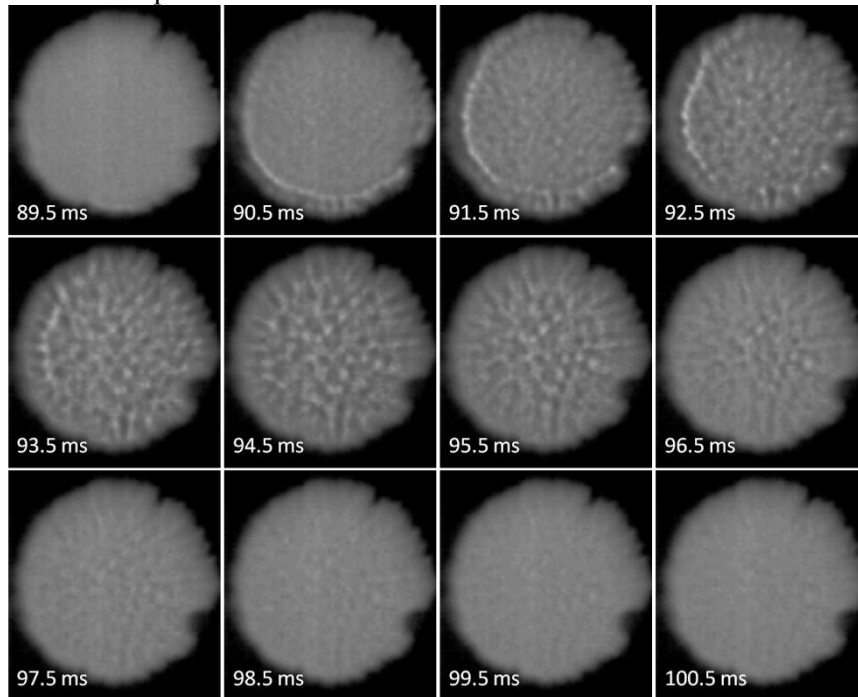


Figure 2. Micro-photographic image series of hydrogen being compressed at 43 GPa/s. Frame rate of camera is 60,000 frames per second. Only select images are shown to illustrate the solidification process

Further investigation of the crystallization process was made by analyzing the transition time of solidification (figure 2) which is in close agreement with the time scale of the changes seen in the Raman vibrational frequency (of the same compression rate) at 10.53 ms. By assuming two-dimensional (2D) crystallization process across the face of the DAC the crystal growth rate can be determined. The diameter of the DAC is well determined by calibration to a known pinhole source. By dividing the distance of crystal growth by the associated transition time ($\frac{l}{\Delta t}$) the crystal growth rate (v) can be computed to be 0.3cm/s. This value is a couple of orders of magnitude slower than the previously reported ≈ 33 cm/s in under-cooled hydrogen [9], but match well with the theoretical growth rate of hydrogen, ≈ 0.9 cm/s, determined by a super-cooled Lennard-Jones liquid [3].

4. Conclusion

In conclusion the use of fast acquisition time-resolved Raman spectroscopy in conjunction with the dynamic diamond anvil cell provides a novel method to probe rapid events such as crystallization. This method could be applied to many systems to better understand the pressure/volume and morphological changes that occur under a dynamic compressive load at high pressures and temperatures. Furthermore, the use of high-speed micro photographic video provides unique insight into the crystal growth process and the ability to calculate crystal growth rates.

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