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In Situ Raman spectroscopy of reversible low-temperature transition between low-density and high-density amorphous ices

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Abstract

We have measured a series of changes in *in situ* Raman spectra of the reversible transition between LDA (low-density amorphous ice) and HDA (high-density amorphous ice) as a function of pressure at 135 K. Here we show spectral evidence for a first-order transition between LDA and HDA. The present results favor the existence of a liquid–liquid phase transition under high pressure at low temperatures.

1. Introduction

The behavior of liquid water has intrigued scientists for centuries. Mishima *et al* [1, 2] showed that at least two different forms of amorphous H₂O ice (HDA: high-density amorphous ice; LDA: low-density amorphous ice) can exist at low temperatures. They also found that LDA, which is ordinarily made by heating quenched HDA at normal pressure, transforms to HDA at ~ 0.6 GPa and 77 K with an apparently first-order-like transition [2]. It is remarkable that the transition shows reversibility in the temperature range of about 130–150 K, i.e., HDA reverts to the LDA phase at ~ 0.2 GPa on decompression. This transition was subsequently observed *in situ* in diamond anvil cells [3]. Although the results are usually referred to as arising from a first-order transition between HDA and LDA, there are still questions about the *P–T* conditions of the transition [4–6]. To address the problem and to fully understand the mechanism, it is necessary to have more detailed knowledge of the HDA–LDA transformation over true (meta)stable regions under high pressures and low temperatures.

In this study, we have measured *in situ* Raman spectra at the reversible transition between LDA and HDA as a function of pressure at 135 K. The present measurements provide information on the possible existence of a first-order liquid–liquid phase transition with the

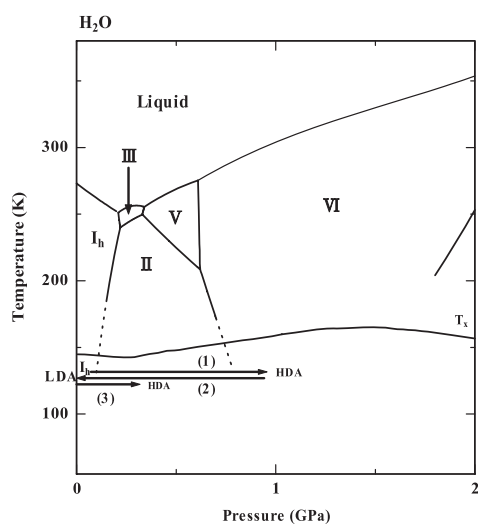


Figure 1. The experimental paths ((1)–(3)) observed in the present study on the equilibrium phase diagram of H₂O. The indications (2) and (3) correspond to the results of Raman spectral changes as shown in figures 2 and 3, respectively.

boundary line terminating at the second critical point in the supercooled region [7]. We show spectral evidence for a first-order transition between LDA and HDA.

2. Experimental details

Raman spectral changes were measured *in situ* at ~ 135 K by microspectroscopy using a diamond anvil cell (Bell–Mao-type DAC) and a cryostat system at high pressures and low temperatures. Doubly distilled and deionized water was used as a sample. The experimental procedure is described in detail elsewhere [8]. Although for regions of relatively low pressure around 0.1–0.2 GPa it was difficult to obtain the precise transition pressure value due to the insensitivity of the ruby fluorescence, we can obtain the applied pressure as a rough estimate from a mechanical change in the load on the DAC lever arms. Raman spectra were collected using a single-grating ISA HR-460 spectrometer equipped with holographic notch filters and a charge-coupled device (CCD) detector. The 514.5 nm line of argon ion laser excitation (~ 300 mW) was selected for use.

3. Results and discussion

The experimental paths followed in this study are shown as (1)–(3) schematically on the pressure–temperature equilibrium phase diagram of H₂O in figure 1. Firstly, we made HDA by compressing ice I_h at 135 K up to ~ 1.2 GPa (path (1)). Subsequently, the HDA sample was decompressed down to near 1 bar to make LDA (path (2)), and recompressed again up to 1 GPa (path (3)), maintaining the temperature of ~ 135 K. We measured *in situ* Raman spectra of OH stretching vibrational modes of these compressing–decompressing sequences as depicted in figures 2 and 3.

Figure 2 shows the Raman spectral changes of HDA down to 0 GPa at 135 K (path 2). With decreasing pressure, a band at ~ 3100 cm⁻¹ appears and begins to grow at the expense of the bands of HDA. It is remarkable that we succeeded in capturing a mixture of LDA and HDA

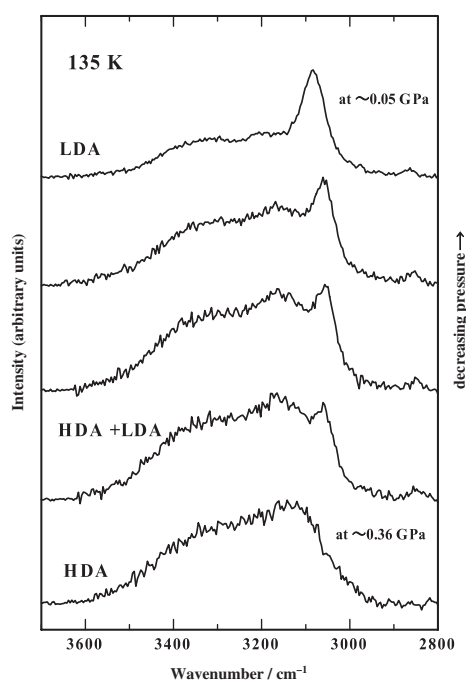


Figure 2. The spectral change of HDA to LDA probed *in situ* via the Raman OH stretching mode at 135 K.

spectra at ~ 0.1 GPa upon decompression. For regions of relatively low pressure below 0.1 GPa, it was difficult to obtain the precise transition pressure value due to the insensitivity of the ruby fluorescence [9]. The formation of the LDA phase is readily identified from the spectral profiles by comparing against previous results from the literature [10, 11]. The important finding here is that the HDA changed to LDA through a state of coexistence of HDA and LDA, not forming other intermediate structures, as we decreased the pressure little by little. The present results show an unambiguous discontinuity in the reverse conversion of HDA to LDA in contrast to the recent Raman scattering and visual observation of Mishima *et al* [12] of a thermally activated ambient pressure transition. It is only fair to mention that very recently Klotz *et al* [13] carried out an *in situ* neutron diffraction study of the transition from LDA to HDA under high pressure at ~ 0.3 GPa and 130 K. Since the reverse transition from HDA to LDA occurs at a low pressure of ~ 0.06 GPa where it is difficult to control the pressure cell used for their neutron diffraction studies, they also reported the complementary Raman measurements (and visual observation) of the reverse transition, i.e., HDA to LDA at ~ 0.1 GPa, obtained by taking spectra at different locations in the sample (crossing a dark area of LDA). According to their results, a first-order transition between LDA and HDA was strongly suggested. However, we have to point out that in view of the Raman spectra of the reverse transition, the first-order transition is still not very clear. This is probably because the transition from HDA to LDA is very quick and completes in a very narrow pressure region.

On the other hand, figure 3 shows the repressurizing sequence of the LDA (path 3). The LDA sample began to transform to HDA at around 0.15 GPa. It should be stressed again that LDA changed to HDA showing a state of coexistence of LDA and HDA if we increased the pressure very gradually. This transformation of LDA to HDA phase appears to behave similarly

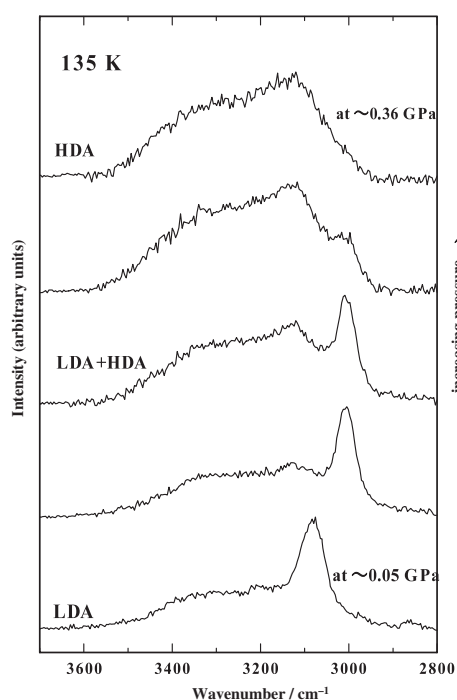


Figure 3. *In situ* Raman OH stretching spectral changes, from LDA to HDA, with decrease in the pressure at 135 K.

to that of I_h to HDA [18]. The facts obtained in this study imply that the phase transition between LDA and HDA is a first-order one, though the transition pressures ($p_{\text{cLDA} \rightarrow \text{HDA}}$ and $p_{\text{cHDA} \rightarrow \text{LDA}}$) are not exactly the same, as previously reported [4]. If we further compress the sample, the HDA transforms to ice VII' at 2.9 GPa, which is a crystalline phase close in structure to orientationally disordered ice VII [3].

It is interesting to note that Loerting *et al* [14] very recently reported a stepwise formation process, LDA \rightarrow HDA \rightarrow VHDA (amorphous–amorphous–amorphous transformation), for a similar temperature region of ~ 125 K. On compressing HDA isothermally, the HDA sample transformed to VHDA (very high-density amorphous ice) at ~ 1.2 GPa, which may be a structural versatility of HDA [15]. At a lower temperature of 100 K, this transformation does not take place, and at a higher temperature of 150 K, LDA crystallizes. The authors also reported that on decompressing VHDA isothermally at 135 K, LDA can be recovered at ambient pressure [14]. They claimed that in principle both the HDA and VHDA, and LDA and HDA transformations are reversible, though they are difficult to observe directly, probably due to the different activation energies. However, in our previous work we found that ice VII' can also transform to LDA on release of pressure to ambient pressure [8].

Figure 4 shows the peak frequency change for both the LDA to HDA and HDA to LDA transitions as a function of pressure. The characteristic points are that the frequency decreases or increases rather sharply initially but at around the transition pressure it has nearly constant value (a plateau region). At the transition point, discontinuity in the frequency between LDA and HDA is clearly seen.

The structural transformation from LDA to a denser HDA phase is accompanied by an increase of elastic moduli [16]. The first stage corresponds predominantly to the elastic

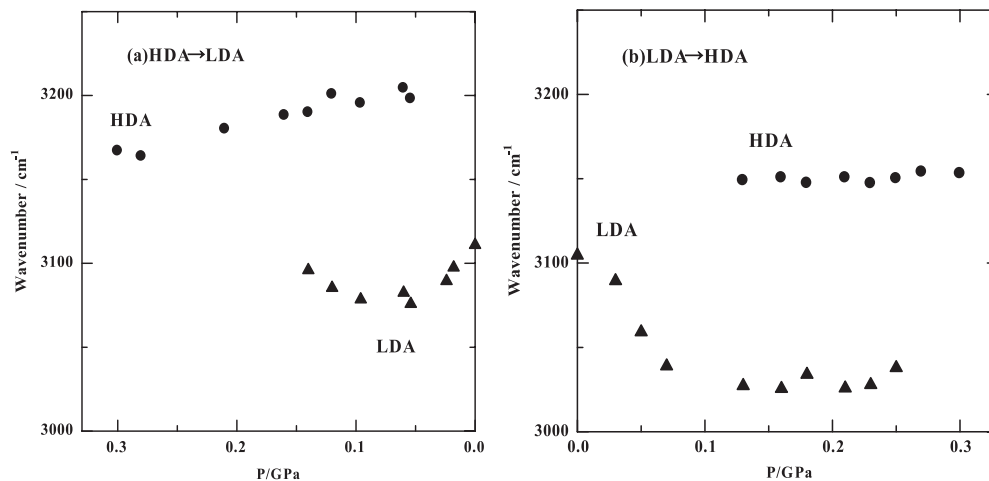


Figure 4. Peak frequency changes in the *in situ* Raman OH stretching spectra of both (a) HDA to LDA and (b) LDA to HDA processes as a function of pressure at 135 K.

softening as an inherent property of the LDA network, and the second one is the structural transformation starting rather abruptly. That is why the transformation did not finish at the reported pressure of 0.3–0.4 GPa [4] and continued at a higher pressure. We suppose that the plateau region in the figure is showing the latter stage effect. In addition, LDA to HDA transformations are supposed to be shear or collapse driven [16]. Therefore, there is a large hysteresis and it needed more applied pressure to complete the reversible transformation as compared to the HDA to LDA transition.

The mechanism of a reverse HDA to LDA transformation upon decompression is also connected with shear elastic softening [17]. Before the volume jump, the transformation starts from the elastic softening both as an inherent property of an amorphous network and as a result of the relaxation induced by irreversible local atomic rearrangements. Koza *et al* [5] stated that the HDA \rightarrow LDA transition comprises at least two conversion steps, i.e., an annealing of HDA and a subsequent transition of apparently first order to LDA. They also stressed the importance of the relaxation processes both before and after the apparent first-order transformation. Therefore, the HDA to LDA transformation incorporates three stages, which may be understood as an annealing of a high-density state, followed by an accelerated transition from the high-density to the low-density modification, and ending with an annealing of the low-density form.

Johari [18] claimed that lack of evidence for reversibility at a unique pressure and temperature seem to put into question the basis for the conjecture of a critical point of supercooled water. However, as Gromnitskaya *et al* [17] suggested, the concept of a thermodynamic first-order transition cannot be completely applied to the transformations between amorphous ices. That is, as mentioned above, the wide tail of pressure-induced LDA to HDA transformation cannot be interpreted in the framework of an ordinary first-order transition. The important point is that many varieties of amorphous ice prepared by different methods can be distinctly divided into two groups: low-density amorphous ices (LDA) and high-density amorphous ices (HDA).

Finally we should mention the temperature-induced HDA to LDA transition which shows the complicated picture with the relaxation precursor. The exothermic nature of the transformation makes investigations of the kinetics challenging, as the sample will generally

not be in equilibrium with its environment. As a result of the evolved heat, the transformation has a tendency to run to completion once initiated; thus the kinetics depends largely on details of the individual experimental conditions [16]. On the other hand, the pressure-induced transformation is not effected by evolved heat and has merit for investigating the nature of the reversible transition between LDA and HDA. The present experiment can discriminate between a discontinuous transition from HDA towards LDA and a kinetically slowed down first-order transition in a two-state coexistence region.

Acknowledgments

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