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# Pressure-induced amorphization of ice in aqueous LiCl solution

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## Abstract

Raman spectra of ice in aqueous LiCl solution ( $\text{LiCl}\cdot 12\text{H}_2\text{O}$ ) have been measured as a function of pressure (0.1–700 MPa) at liquid nitrogen temperature ( $-196^\circ\text{C}$ ). It is found that the ice phase in  $\text{LiCl}\cdot 12\text{H}_2\text{O}$  transforms to an amorphous phase at  $\sim 520$  MPa, as in the case of pressure-induced amorphization of ice  $\text{I}_h$  to a high-density amorphous ice. We have also observed the spectral changes of the amorphous phase as a function of temperature ( $-196^\circ\text{C}$  up to room temperature) under high pressure. We show spectral evidence for the existence of a transition from the relaxed amorphous phase to the supercooled liquid at high pressures and low temperatures.

## 1. Introduction

It has been reported that a number of materials, such as various elements, compounds, and alloys, can be made amorphous phases by means of high-pressure techniques [1]. The transformation of ice  $\text{I}_h$  to a high-density amorphous (HDA) ice [2] is certainly one of the most interesting phenomena. As in the case of ice  $\text{I}_h$ , some hydrates can also be transformed to an amorphous phase when subjected to high pressures. In fact, Ross and Anderson [3] reported that structure II tetrahydrofuran (THF) hydrate undergoes a transition to a HDA phase at 1.1 GPa and 130 K<sup>2</sup>. Handa *et al* [4] studied the pressure-induced phase transitions in structure I Xe and structure II THF and SF<sub>6</sub> clathrate hydrates, though the high-density phases of the hydrates could not be preserved at atmospheric pressure as they could in the case of HDA.

The glass formation of the aqueous LiCl solution has been extensively studied because it is a good glass former. According to the study of Angell and Sare [5], aqueous LiCl solutions of  $R \gtrsim 12$  ( $R = \text{moles of water/moles of salt}$ ) are not glass forming with a normal cooling rate. Here we have investigated whether the ice phase in aqueous LiCl solution can be changed to an amorphous phase with applied pressure. *In situ* Raman spectra of ice in aqueous LiCl solution ( $\text{LiCl}\cdot 12\text{H}_2\text{O}$ ) as a function of pressure have been reported.

## 2. Experimental details

The sample solution was prepared by dissolving the required amount of anhydrous lithium chloride (dried under vacuum at about 80 °C) in distilled water. The concentration of the solution was set to  $R = 12$ . Raman spectra were measured with a JASCO NR-1800 microscopic Raman spectrophotometer equipped with a CCD. We used 514.5 nm line of a LEXEL argon-ion laser ( $\sim 250$  mW) as an excitation source. For the measurement of Raman spectra under high pressure, the sample solution and fine ruby chips were held in a diamond anvil cell (SR-DAC-KYO-3-1; Kyowa Co. Ltd) using a phosphor bronze gasket 0.15 mm thick with an opening 0.4 mm in diameter. The pressure generated in the DAC was determined by the spectral shift of the  $R_1$  fluorescence line of the ruby [6, 7].

In this study, we performed two kinds of experiment:

- (1) The ice in the aqueous LiCl solution was compressed up to  $\sim 700$  MPa at  $\sim -196$  °C. Cooling of the sample solution was achieved by immersing the DAC in liquid nitrogen. At 0.1 MPa, the aqueous lithium chloride solution of  $R = 12$  in the DAC is not glass forming, with a cooling rate of  $\sim 100$  K  $\text{min}^{-1}$ . The sample was maintained at liquid nitrogen temperature during the Raman measurements.
- (2) *In situ* Raman spectral changes were monitored when the amorphous phase was warmed slowly (at  $\sim 2$  °C  $\text{min}^{-1}$  on average) up to room temperature. The temperature of the sample during the Raman measurements was monitored by differential thermocouples (alumel–chromel thermocouples) with one junction mounted on the gasket and the other in ice. The spectral shift of the  $R_1$  ruby fluorescence line was corrected for the temperature [7] monitored by the thermocouples.

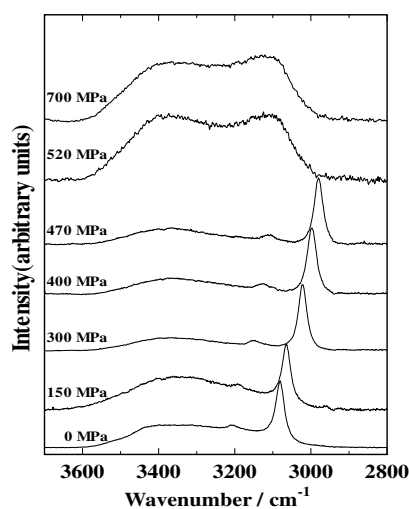
## 3. Results and discussion

Figure 1 shows the spectral changes of the ice in the  $\text{LiCl}\cdot 12\text{H}_2\text{O}$  solution probed by means of *in situ* Raman OH stretching spectra at  $\sim 77$  K. The frequency of the highest peak of  $\sim 3082$   $\text{cm}^{-1}$  at ambient pressure decreases with increasing pressure. According to Whalley *et al* [8], the frequency shift to the lower-frequency side indicates that stronger hydrogen bonds are formed. At  $\sim 520$  MPa, the lowest-frequency peak which is characteristic of the ice phase completely vanishes and the occurrence of a phase transition is readily identified.

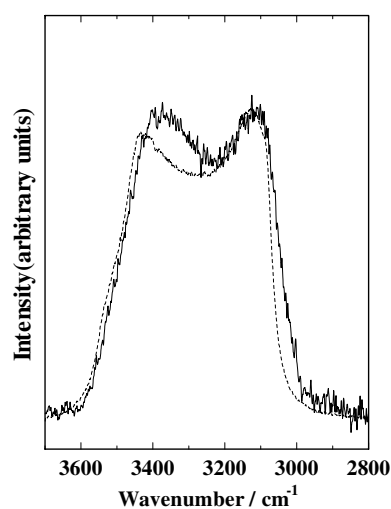
It is known that the concentrated aqueous LiCl solution easily becomes an amorphous (glassy) state when it is supercooled below its glass transition temperature. Figure 2 shows the comparison of the spectra for the pressure-induced and supercooled amorphous states. Interestingly, the spectrum at 520 MPa is almost identical in spectral shape and peak frequency to the glassy spectrum obtained with a normal quenching from the liquid state at 0.1 MPa. Judging from the similarity in spectral shape, we think that the ice phase in the  $\text{LiCl}\cdot 12\text{H}_2\text{O}$  solution changes into an amorphous phase at  $\sim 520$  MPa.

The present results clearly indicate that the distances between oxygen atoms of hydrogen bonds in the ice phase are shortened and the hydrogen bonds are strengthened with increasing pressure. Then the ice lattice collapses when it cannot bear further applied pressure, and the ice phase changes into an amorphous phase.

Many phase transitions of ice have already been investigated under high pressure [9, 10]. Mishima *et al* [2] found that the transformation of ice  $I_h$  to a HDA phase occurs when ice  $I_h$  is pressurized to  $\sim 1$  GPa at liquid nitrogen temperature. Our present findings show that the onset amorphization pressure decreases almost by half. In connection with this, Johari [11] has recently reported that amorphization pressure decreases on decreasing the crystal grain size



**Figure 1.** *In situ* Raman OH stretching spectral changes of the ice in the LiCl·12H<sub>2</sub>O solution as a function of pressure at  $-196^{\circ}\text{C}$ .



**Figure 2.** Comparison of the Raman spectra in the OH stretching region of aqueous LiCl solutions ( $R = 12$ ) at  $-196^{\circ}\text{C}$ . —: pressure-induced amorphous state at 520 MPa; ·····: amorphous (glassy) state obtained by normal quenching from the liquid state at 0.1 MPa.

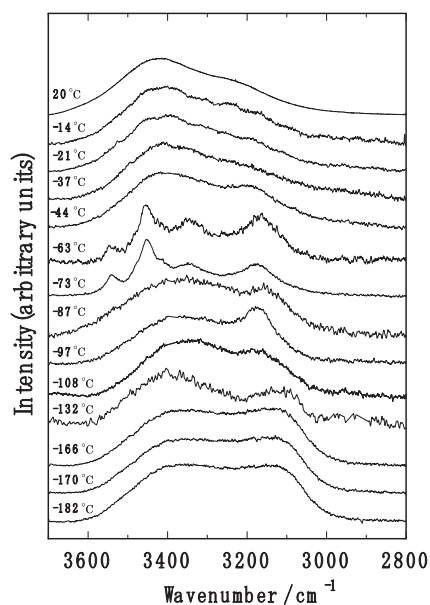
of ice. He stated that because a microcrystalline sample has a larger surface area, production of an elastic instability at the grain boundaries and grain junctions of polycrystalline ice is important in the amorphization of ice I<sub>h</sub>.

To interpret the phenomenon of the spectrum taken after compression of the crystalline state being very similar to the spectrum of quenched glass at atmospheric pressure, the following points are considered. As already mentioned, it is most likely that the amorphous state of aqueous LiCl solution produced by pressure-induced amorphization arises from the collapse of ice I and is not a glassy state. In addition, we think that the Raman spectral shape of the pressure-induced amorphous state consists of a combination of the Raman spectra of HDA and the aqueous LiCl solution with  $R = 12$ . Therefore the amorphous phase produced at high pressures is different from the quenched glass at normal pressure. That is, the amorphous phases of aqueous LiCl·12H<sub>2</sub>O solution produced by different pathways are not necessarily similar in structure.

Figure 3 shows Raman OH stretching spectral changes for the amorphous phase of LiCl·12H<sub>2</sub>O solution as a function of temperature at  $\sim 700$  MPa. It can be noted that at  $\sim -132^{\circ}\text{C}$  the relative intensity of the band centred at  $\sim 3400\text{ cm}^{-1}$  increases significantly and the half-bandwidth clearly broadens out. At  $\sim -97^{\circ}\text{C}$ , an increase of the band intensity at  $\sim 3150\text{ cm}^{-1}$  is observed. Then, with further temperature rise, the spectrum at  $-87^{\circ}\text{C}$  comes to resemble that obtained at  $-108^{\circ}\text{C}$ . One can readily see that another phase grows up at  $\sim -73^{\circ}\text{C}$ .

In view of the spectral profile, the phase probably corresponds to a crystalline state of the aqueous LiCl solution. At  $-44^{\circ}\text{C}$ , it is clearly observed that this phase has completely transformed to a liquid state. It is very interesting that the spectra at  $-108$  and  $-87^{\circ}\text{C}$  resemble in spectral features that for supercooled liquid at  $-44^{\circ}\text{C}$  apart from the differences in half-bandwidths and peak frequencies.

From the spectral changes with temperature, we can interpret the results as follows. Upon warming, relaxation of the pressure-induced amorphous phase occurs due to annealing. Then, it



**Figure 3.** *In situ* Raman OH stretching spectral changes of the amorphous phase for LiCl·12H<sub>2</sub>O solution as a function of temperature at ~700 MPa.

becomes a glass at around  $-132^{\circ}\text{C}$ . With further temperature rise, the glass possibly transforms to a ‘high-density’ supercooled liquid at  $\sim -108^{\circ}\text{C}$ . It seems that a crystallization of this high-density supercooled liquid occurs at around  $\sim -97^{\circ}\text{C}$ . At  $\sim -87^{\circ}\text{C}$  this crystalline state appears to transform to a supercooled liquid again. In this connection, Kanno [12] reported that a double glass transition phenomenon (two  $T_g$ -values) is observed for an aqueous LiCl solution vitrified above 100 MPa. That is, there are two different vitreous phases in the glassy lithium chloride solution quenched at high pressures. This shows that a liquid–liquid immiscibility occurs at high pressures and low temperatures. The phase separation was induced by high pressure. Kanno assigned  $T_{g1}$  (the first glass transition) as corresponding to the salt-rich phase to which the supercooled liquid transforms and  $T_{g2}$  (the second glass transition) is due to the water-rich phase of the phase-separated quenched glasses. Considering his results, the spectra at  $-108$  and  $-87^{\circ}\text{C}$  in our results of figure 3 may correspond to the two supercooled liquid states to which the two respective glassy phases (salt-rich and water-rich phases) transform.

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