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New transformation of ice in aqueous RbCl solution to a high-pressure phase at low temperature

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Summary

The changes in *in situ* Raman spectra of ice in aqueous RbCl solution ($RbCl \cdot 12H_2O$) have been measured as a function of pressure at liquid nitrogen temperature (77 K). It is found that the ice in aqueous RbCl solution transforms to a crystalline phase of ice VII' (the frozen-in disorder of ice VII) at ～800 MPa. Compiling the previous results of ices in aqueous LiCl and KCl solutions, we suggest that there are tendencies that the aqueous salt forming a crystalline state on cooling at a normal pressure transforms to a high-pressure crystalline ice phase, such as ice VII', whereas that the aqueous salt solution to form a glassy state upon cooling becomes an amorphous phase on compression.

Key words: In-situ Raman spectra, Pressure-induced phase transition, Aqueous RbCl solution, ice VII'

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1. Introduction

It is well known that H_2O ice shows structural versatility depending on pressure and temperature [*Bridgman*, 1937; *Hobbs*, 1974; *Whalley*, 1976] Phase diagram of ice is very complex especially in the lower pressure region, but it becomes simpler under extremely high-pressures (above 2 GPa). We have to keep investigating it at various p-T regions to fully understand the phase transition behaviour.

Apart from the pure ice phases, we have found that the ice phase in aqueous LiCl solution ($LiCl \cdot 12H_2O$) transforms to an amorphous phase at 500 MPa [*Yoshimura*, 2002, 2005], as in the case of pressure-induced amorphization of ice I_h to a high-density amorphous ice (HDA) [*Mishima*, 1984], whereas that the ice phase in aqueous KCl solution transforms to a crystalline ice VII' phase (the frozen-in disorder of ice VII) at 800 MPa [*Yoshimura*, 2004]. The remarkable point is that the onset transition pressures decrease very much as compared to those of pure ice phases, *e.g.*, 4 GPa to $\sim$1 GPa in the case of ice VII'. Since salts are normally considered to not dissolve interstitially in the ice lattices, it is very intriguing that the results show differences depending on the salts. Thus, it is very interesting to study the phase transition behaviour of other ices in alkali salt solutions as a function of pressure at low-temperatures.

At ambient pressure, it is known that doping with the alkali hydroxides in ice has the remarkable effect of maintaining sufficient proton mobility at low temperature resulting the formation of ice XI [*Tajima*, 1982]. However, there have been few studies of salt impurities such as inorganic substances in ice at high pressures.

Here we show that the ice in aqueous RbCl transforms to ice VII' phase at 800 MPa(0.8 GPa), as like ice in aqueous KCl. The aqueous LiCl solution is well known to be a good glass former, but aqueous solutions of alkali halide, such as KCl, RbCl, etc., except for Li-salts, do not become amorphous state with a standard cooling rate of $\sim 10^3$ K/min [*Angell*, 1970]. Therefore, there might be tendencies that the aqueous salt solution to form a glassy state upon cooling becomes an amorphous phase on compression, while that the aqueous salt forming a crystalline state on cooling at a normal pressure transforms to a high-pressure crystalline ice phase, such as ice VII'.

2. Experimental

Sample solution was prepared by dissolving the required amount of anhydrous rubidium chloride (dried under vacuum at about 80 ℃) in distilled water. The concentration of the solution was set to be $RbCl \cdot 12H_2O$. 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 (～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 of 0.15 mm thick with an opening of 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 [*Mao*, 1978].

In this study, we compressed $RbCl \cdot 12H_2O$ solutions in a diamond anvil cell (DAC: Kyowa co ltd.) up to ～1 GPa at 77 K. The sample solution was cooled by immersing the DAC directly into liquid nitrogen. The overall cooling rate was estimated to be over ～150 K/min. At ambient pressure, the $RbCl \cdot 12H_2O$ solution in the DAC crystallized at this cooling rate. The samples appeared milky, probably because of the inclusions of salts or of concentrated RbCl solution. At a normal pressure, the spectrum of ice in $RbCl \cdot 12H_2O$ absolutely corresponds to that of pure ice I_h.

3. Results and Discussion

The spectral changes of ice I_h in the $RbCl \cdot 12H_2O$ solution in the OH stretching range at 77K are shown in Fig. 1. The pressure values in the figure show applied pressure in the system. We immediately notice that the lowest frequency peak that is characteristic of the ice I_h phase completely vanishes at ～800 MPa and a transition to a phase having a new sharp peak at ～3090 cm^{-1} occurs. In viewing the spectral profiles and considering with the previous results [*Yoshimura*, 2004], this phase is not an amorphous state, but probably a crystalline state of ice VII'.

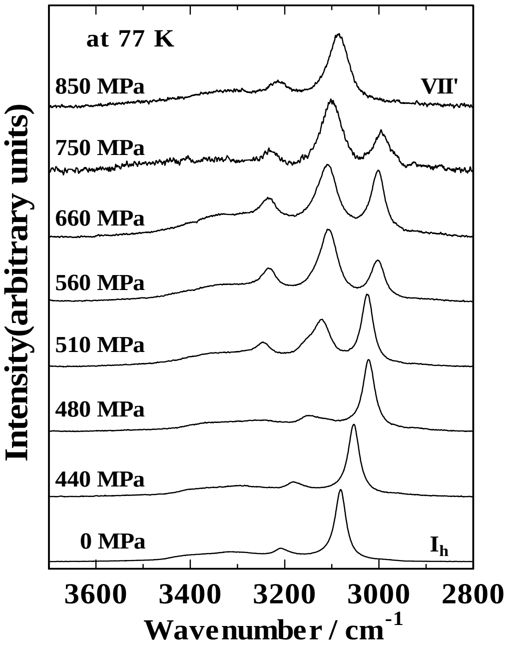

Figure. 1. In situ Raman OH stretching spectral changes of the ice in $RbCl \cdot 12H_2O$ solution as a function of pressure at 77 K.

Therefore, we compared the spectrum of ice VII’ to that of phase transformed ice in aqueous RbCl solution at 800 MPa, as shown in Fig. 2. Ice VII’ was firstly found by Hemley et al. [1989]. They showed that HDA (high-density amorphous ice), which is originally transformed from ice I_h [*Mishima*, 1984], changed at ～4 GPa and 77 K to a crystalline phase close in structure to disordered ice VII. One can easily see that the comparison of the spectrum between the transformed phase from ice in aqueous RbCl solution and in ice VII’ show that the spectral profiles are very similar. Thus, the “new” high-pressure phase of ice in aqueous RbCl could be ice VII’. It is also substantiated in this study that the ice formed from aqueous RbCl can directly transform to ice VII’ at much lower pressures (need less than 1/4 applied pressure), not via HDA. As for the other ice VII’ formation conditions, there are a few reports so far. By cooling ice VI below 95 K at 1.5 GPa and compressing it isothermally, metastable ice VII can be obtained at 3.8 GPa through a non-equilibrium transition from ice VI, not via HDA [*Klotz*, 1999]. Song et al. [2003] obtained ice VII’ by isothermally compressing ice II or VI up to 4-10 GPa below 100 K and investigated phase stability of low-temperature ice VII’.

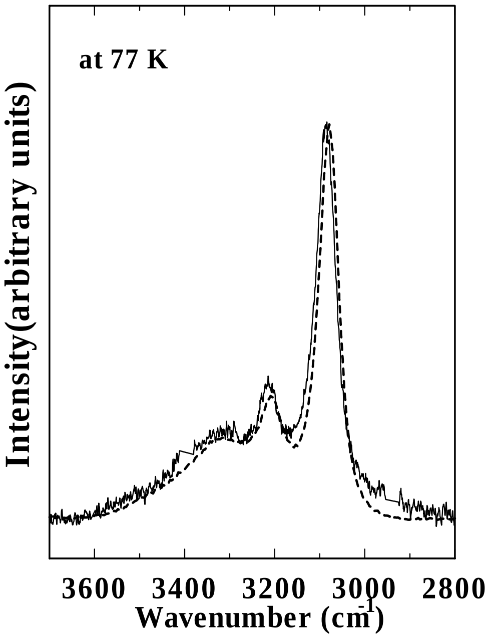

Figure. 2. Comparison of the Raman spectra in the OH stretching region of RbCl・12H_2O solution and ice VII ’ at 77 K .

—: RbCl・12H_2O solution at 0.8 GPa

⋯: ice VII’ at 7.5 GPa

Using the same scenario previously made in the results of ice in aqueous KCl solution [*Yoshimura*, 2004], we can explain the phenomenon that the ice phase in aqueous RbCl solution also transforms to ice VII'. That is, there are three main factors that the transition occurs at other than original stability field of ice: (1) The solutes work as nucleation sites for high pressure ice phases (VII') and this nucleation is enhanced by application of pressure. (2) The rate of cooling and the nature and concentrations of dissolved solutes should influence morphology and crystal dimensions. In this connection, if we cool the RbCl・$12H_2O$ solution at slower rates (e.g., 5 k/min.), the samples show "normal " transition behaviour (i.e., I_h-hda-VII '). (3) Most of the salt probably segregates at grain boundaries. Such segregation would lead to very small particles of ice in the sample and reduce the size of the ice crystals, causing the unexpected transition at very low pressure. When an ice in aqueous salt solution forms upon rapid cooling at a normal pressure, tiny clusters with structures very similar to the transformed phase of ice VII' may already exist in a system and can therefore act as nucleation sites, though the fraction of these "quasi structures" in a sample should be very small, and there may be a structural heterogeneity in the frozen ice sample.

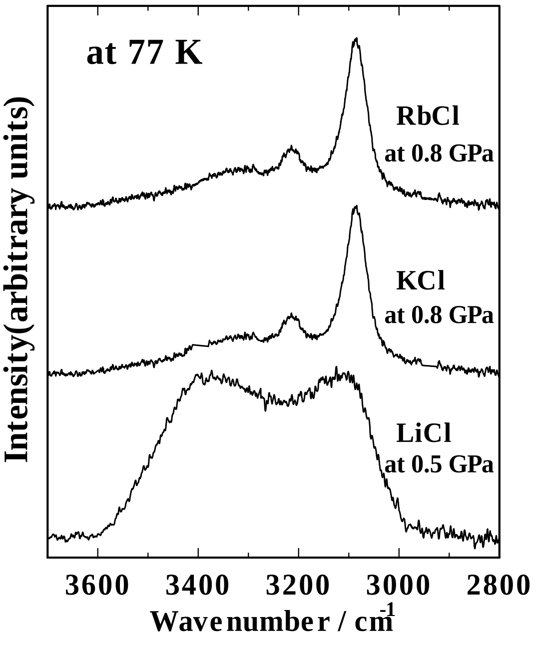

Figure. 3. Comparison of the Raman spectra in the OH stretching region of RbCl・$12H_2O$, KCl・$12H_2O$, and LiCl・$12H_2O$ solutions at 77 K .

Figure 3 compiles the results of pressure-induce phase transition of LiCl, KCl, and RbCl solutions at 77 K. This figure clearly shows that ice in other alkali chloride solutions such as KCl, RbCl do not produce an amorphous state upon compression, but ice in aqueous LiCl solution make an amorphous state. In a separate study, we have found that ice in other alkali chloride solutions of NaCl and CsCl also do not make an amorphous state upon compression, whereas ice in aqueous $MgCl_2$ solution becomes amorphous state [*Yoshimura*, to be submitted]. Thus, it can be concluded that there may be a tendency for that the salt to form a glassy state upon cooling, when dissolving in water becomes an amorphous phase on compression, and that the salt solution to form a crystalline state on cooling becomes crystalline ice phase, such as ice VII'.

4. Conclusion

The present study shows that ice I_h in aqueous RbCl transforms to ice VII ' phase. We must mention that the obtained results show differences depending on the salts that are dissolved in water. Recently, Koza et al. [2000a, b] reported that ice XII can form at *p-T* regions (～1 GPa and 77 K) of the phase diagram of pure H_2O, despite that ice XII was originally found within the stability region of ice V by Lobban et al. [1998]. Subsequently, Kohl et al. [2001] and Salzmann et al. [2003] concluded that shock waves cause transient local heating to the temperature range of the stability field of ice V, and this causes nucleation and crystal growth of ice XII. Thus, it seems that these *p-T* ranges around 77 K of ice is intriguing subject and still remains to be clear.

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