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Comment on Y. Yoshimura: "Pressure-induced phase transition of ice in aqueous KOH solution"

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Solid water exists in a variety of forms, both crystalline and amorphous. The relations between those poly(a)morphs continue to puzzle researchers. In addition, the fact that it is suspected that the amorphous forms, in contrast to the crystalline forms, are closely related to liquid water lifts this topic to an even higher level of interest [1,2]. Experiments at high pressure and low temperature are necessary for improving our understanding of the phase relations and metastability. Also, experiments in the presence of salts such as KOH or LiCl are done, because these salts are known to modify the hydrogen-bonding network.

We here report compression/decompression experiments of a $KOH{\cdot}15H_2O$ solution. Throughout our experiments, we followed the thermodynamic path followed by Yoshimura [3]. As high pressure equipment, we used a piston cylinder setup along with a material testing machine (ZWICK, model BZ100/TL35) instead of the diamond anvil cell (DAC) in Yoshimura's case. We prepared a solution of $KOH{\cdot}15H_2O$ (3.7 M KOH), froze 500 µl at 77 K and compressed and decompressed it isothermally. Afterwards, the samples were characterized with powder X-ray diffraction (XRD) (Cu Kα_1, θ–θ arrangement, SIEMENS, model D5000) at ambient pressure and ≈80 K.

The first sample was compressed up to 1.1 GPa – the corresponding piston displacement curve and XRD are depicted in Figure 1(a) and (b), respectively. One can clearly see that the volume decreases nonlinearly at low pressures. This decrease is due to the elimination of air between the ice grains. The XRD just shows the hexagonal ice and a weak indication of an amorphous halo peak. Ice IX, which was reported by Yoshimura at ≈1 GPa, is clearly absent in our experiment [3].

The second sample was compressed to 1.8 GPa. The piston displacement curve is qualitatively identical to the one discussed above and, in addition, shows a transition between ≈1.2 and ≈1.5 GPa (Figure 1(c)). The XRD of the quench-recovered state shows an entirely amorphous sample with a first halo maximum at $2\theta = 31.7°$ (Figure 1(d)). That is, the decrease in the sample volume observed at >1.26 GPa is a result of pressure-induced amorphization (PIA). This fact also stands in contrast to Yoshimura's findings who stated that this "KOH solution can directly transform to ice IX at 77 K, not via HDA" [3].

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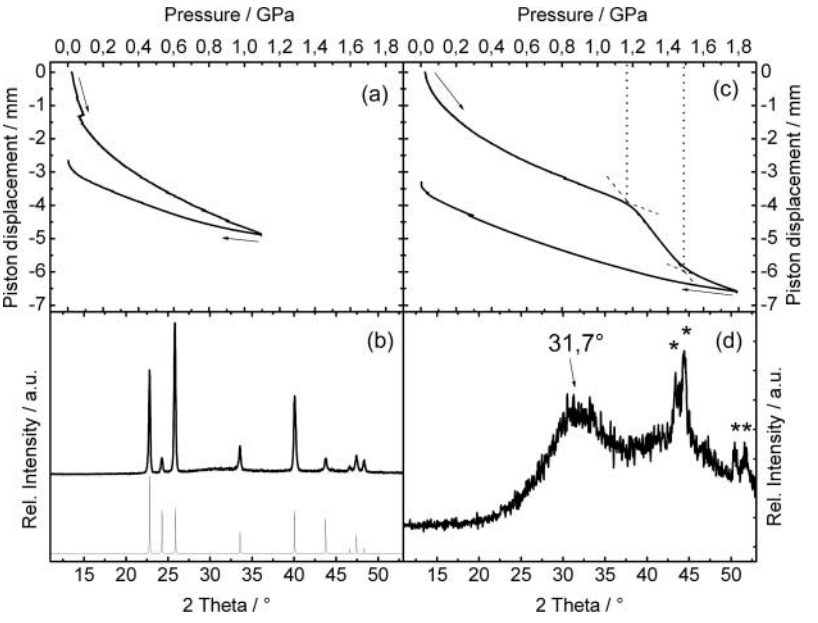

Figure 1. (a) Piston displacement and (b) black line (top): XRD (Cu Kα_1) of sample 1 (quench-recovered from 1.1 GPa); blue line (bottom): calculated XRD of hexagonal ice; data from [4]. (c) Piston displacement (with p_{onset} and p_{end} of PIA marked by dotted lines) and (d) subsequent XRD of sample 2 (quench-recovered from 1.8 GPa). The asterisks mark the reflexes of the XRD sample holder.

To sum up our findings, the frozen aqueous KOH solution can be compressed up to ≈1.2 GPa without any transition and it undergoes a subsequent PIA in the range between ≈1.2 and ≈1.5 GPa. The onset of the PIA is slightly shifted to higher pressures in comparison with pure water ($p_{\text{onset}} \approx$ 1.1 GPa [5]) and is also a bit broader (pure water 0.2 GPa transition width, KOH 0.3 GPa transition width [5]). Also the amorphous halo peak is shifted to a higher angle and is closer to the one observed in VHDA than to the one observed in (unrelaxed) HDA [6]. The position of the maximum corresponds to $Q = 2.2$ Å^{-1}, and therefore the state produced by PIA at 77 K is similar to the salty-VHDA reported recently by Bove et al. [7]. We showed in 2009 that it is possible to maintain the ice IX state after a quench-recovery procedure [8], and since there is no sign of a transition in the reported piston displacement curve upon decompression, we do not find ice IX, not even as an intermediate species.

We do not know why different phases are observed in Yoshimura's and our experiment. Our speculation is that unwanted shock-wave heating may have resulted in the crystallization of the sample in the DAC. We think two scenarios are possible. First, it was shown by Kohl et al. [9] that shock-wave heating during the hexagonal ice→HDA transition results in ice XII formation. The appearance of the amorphous phase was also not detected by Koza et al. [10] who studied ice XII and a similar situation may be the case in the study by Yoshimura [3]. Second, we have also shown that hexagonal ice may convert directly to ice III (the proton-disordered variant of ice IX) at ≈170 K and subsequently to ice IX when cooled to 77 K [8]. However, this is only possible at high compression rates of the order of 100 MPa/min. Taking all these facts into account, we think that Yoshimura's findings [3] are reasonable, because shock-wave heating of hexagonal ice to ≈170 K could have resulted in the polymorphic transition to ice III/IX or, alternatively, shock-wave heating of HDA may have resulted in the crystallization of ice XII. We believe both ice IX and ice XII are compatible with the Raman spectra reported by Yoshimura at 1.0 GPa and 77 K [3], because the band shapes and positions of the OH-stretching band are quite similar for ice XII and ice IX [11–13].

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