

The recent discovery of "very high density amorphous ice" (VHDA) [T. Loerting et al., Phys. Chem. Chem. Phys., 3 (2001) 5355-5357] and the characterization of its structure at 77 K and 1 bar [J. L. Finney et al., Phys. Rev. Lett., 89 (2002) 205503] have raised many questions in the field of water's polyamorphism and the postulated second critical point. In particular, the relation of VHDA to the second polyamorph showing a density >1.0 g/cm³ at 77 K and 1 bar, namely "high density amorphous ice" (HDA), is unclear at present. Whereas some researchers presume VHDA and HDA to be within the same "megabasin" on the potential energy hypersurface, it is also possible that VHDA and HDA are low-lying states in distinct "megabasins", raising the possibility of a postulate of a third critical point. Such a third critical point has already been located in computer simulations. To address the question of the relative stabilities of VHDA and HDA we plan to systematically investigate the relevant regions of water's p-V-T-space both under isochoric and isobaric conditions and characterize the recovered samples by means of powder X-ray diffraction, differential scanning calorimetry (DSC) and Raman spectroscopy. In situ structural information at elevated pressures will be gained by conducting Raman studies in a hydrothermal diamond anvil cell. In order to obtain information on the relative kinetic barrier heights to the transformations between the polyamorphs VHDA, HDA and "low density amorphous ice" (LDA) we will dope hexagonal ice at interstitial lattice positions with HF or KOH. This presumably accelerates transformations, which are possibly too slow on the experimental time-scale otherwise.

Another question we plan to address is whether HDA as well as VHDA and LDA, which are prepared starting from HDA, are truly amorphous materials or collapsed crystals. For this reason we will prepare HDA, VHDA and LDA both by pressurizing crystalline material, i.e., hexagonal ice, as well as by pressurizing material regarded to be truly amorphous, i.e., amorphous solid water (ASW) and hyperquenched glassy water (HGW). A detailed comparison of DSC-curves and (in situ) Raman spectra will serve the purpose of addressing this question.