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Experimental evidence for a second hydrogen ordered phase of ice VI

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In the last decade five new ice phases were experimentally prepared. Two of them(1, 2) are empty clathrate hydrates and three of them(3, 4) represent hydrogen ordered counterparts of previously known disordered ice phases. In our experiments, we investigated hydrogen ordering in ice VI samples upon cooling at pressures up to 1.8 GPa. Using calorimetry, dielectric relaxation spectroscopy, Raman spectroscopy, and powder X-ray diffraction we provide evidence for the existence of a second hydrogen ordered phase related to ice VI, that we call ice β-XV. This phase is more ordered than ice XV by 14% and directly transforms to ice XV above 103K and to ice VI above 129K. That is, upon heating an order->order->disorder transition is experienced. The new phase is thus thermodynamically more stable than ice XV requiring a new stability region in the phase diagram of water. Raman spectroscopy indicates ice XV and ice β-XV to be different in terms of symmetry and space group. The activation energies, measured by dielectric spectroscopy, are 45 kJ mol-1 in ice β-XV compared to 18 kJ mol-1 in ice XV. Powder X-ray data show the oxygen network to be the one of ice VI. The ordering of hydrogen atoms induces a significant peak shift to lower d-spacings at d=0.265 nm in ice β-XV, whereas for ice XV shifts to higher d-spacings are found. The reproduction of these effects with fully deuterated samples would be desirable to refine the crystal structure of ice β-XV. Unfortunately, a pronounced isotope effect precludes such experiments and leads us to the temporary name ice β-XV. We suggest to change this name to ice XVIII as soon as the crystal structure is known. Our experiments represent a unique realization of a second electric ordering in an ice phase, including the identification of two triple points between three hydrogen ordered phases.

1. del Rosso L, et al. (2016) Refined Structure of Metastable Ice XVII from Neutron Diffraction Measurements. J. Phys. Chem. C 120(47):26955-26959.
2. Falenty A, Hansen TC, & Kuhs WF (2014) Formation and properties of ice XVI obtained by emptying a type sII clathrate hydrate. Nature 516(7530):231-+.
3. Salzmann CG, Radaelli PG, Hallbrucker A, Mayer E, & Finney JL (2006) The preparation and structures of hydrogen ordered phases of ice. Science 311(5768):1758-1761.
4. Salzmann CG, Radaelli PG, Mayer E, & Finney JL (2009) Ice XV: A New Thermodynamically Stable Phase of Ice. Phys. Rev. Lett. 103(10):105701.

Significance statement

We found experimental evidence for an unknown hydrogen ordered proxy of ice VI, which has been scrutinized by differential scanning calorimetry, dielectric relaxation spectroscopy, Raman spectroscopy and X-ray diffraction. Therefore, ice VI is the first polymorph of ice with two experimentally realized types of hydrogen ordering.

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