Deformation of single-crystals of water ice VI

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Water ices form significant portion of the satellites which orbit the giant planets of our solar system. The formation, early evolution and internal structure of these icy satellites is of particular importance to planetary sciences as they include the only objects in the solar system, other than Earth, to show evidence of recent tectonic activity and volcanism. The aim of our study is to constrain the deformation mechanism of ice VI, an high-pressure polymorph of ice likely present in the deep interior of the large icy satellites, using high-pressure single-crystal X-ray diffraction. Two crystals of ice VI have been grown in situ inside a four-screw diamond anvil cell at room temperature from liquid water. The single-crystal X-ray diffraction experiments were performed at 1.2-1.4 GPa and room temperature. Because the two crystals refill the entire sample chamber, they are experiencing a uniaxial stress. As a consequence, broadening of different sets of reflections is observed with time and the evolution of such broadening has been monitored by measuring the profile of selected reflections using an Huber 4-circle diffractometer. After c.a. 20 hours, the appearance of an additional peak in the omega profiles of several reflections of one of the crystals was observed. The difference in the positions of the two peaks in the omega profiles, Δω, increases with time. The larger Δω was observed for planes oriented perpendicular to the (0 2 1) plane which instead remains sharp. Planes with smaller interplanar angles to the (0 2 1) have smaller Δω value. A further increase in pressure to 1.3 GPa also led to significant broadening of the reflections of the second crystal. These results suggest that the uniaxial compression leads to bending of the two crystals and consequent formation of randomly distributed dislocations resulting in broadening of the initial ω-profiles. The energy associated with the elastic bending of the crystal lattice is reduced by rearranging the dislocations into a vertical wall to form low angle boundaries. The slip system, deformation mechanism and microstructural evolution of ice VI single crystal will be discussed.

Keywords: icy satellite, ice VI, high-pressure single-crystal diffraction

New cryohydrates of potential relevance to extra-terrestrial mineralogy

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Divalent metal sulfate hydrates of the general form M2+SO4·nH2O are known with n = 1 to 11 and M commonly being Mg or a range of first-row transition metals. Their occurrence as naturally occurring minerals is fairly limited on Earth by virtue of the abundance of NaCl-rich brines (i.e., Earth’s oceans) from weathering of continental rocks. However, such rocks are practically unique to the Earth; elsewhere in the solar system, on Mars and ice-rich bodies orbiting the Gas Giant planets, brine composition is thought to be dominated by aqueous interaction with basaltic/chondritic rocks and therefore largely aqueous Mg/Na-sulfate. This is borne out by the abundance of Mg-sulfates present in the martian regolith and the detection of Mg-sulfate hydrates on the surfaces of some icy satellites of Jupiter.

However, among the more water-rich hydrates, only one example with n = 11 is known (meridianite, MgSO4·11H2O) and there has been, for over 170 yr, a gap between n = 7 and n =11 with no known examples.

We have been able to synthesise and characterise two new M2+SO4 hydrates with n = 8 and 9 by rapid quenching of aqueous solutions in liquid nitrogen. The complete atomic arrangements of both structures have now been determined by neutron powder diffraction. The 9-hydrate is monoclinic (P21/c) and can be formed with M = Mg, Ni, Zn and Fe; the 8-hydrate is triclinic (P-1) and has only been prepared thus far with M = Ni. Both structures are characterised by similar motifs, notably H-bonded chains of M2+O4(H2O)8 octahedra and a lack of polymerised water clusters. The thermal expansivity (4 – 250 K) and incompressibility (0 – 900 MPa) of MgSO4·9H2O has been determined, as well as the variation in unit-cell parameters and site ordering across the solid-solution series from Mg- to NiSO4·9H2O.

Both the 8- and 9-hydrates are metastable at ambient pressure and will transform over a period of hours at T > 250 K into the stable low-temperature phase (11-hydrate for Mg and 7-hydrate for Ni, Zn and Fe). However, MgSO4·9H2O is now confirmed to be the product of meridianite’s pressure-induced decomposition at 1 GPa, 240 K and it therefore becomes a candidate rock-forming mineral in the deep interiors of icy planetary bodies. Equally, cryovolcanic spraying of MgSO4-rich brine into the cold airless environment of an icy satellite’s surface should produce glassy beads that devitrify to MgSO4·9H2O + ice and persist over geological time at ambient temperatures of < 100 K.
Keywords: neutron diffraction, cryohydrate, MgSO$_4$·9H$_2$O, meridianite, Mars, icy satellites

Advanced transmission electron microscopy for Li-ion battery cathodes

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Advanced transmission electron microscopy (TEM) is by far the most suitable and direct tool to view materials down to atomic scale. Recent progress in the electron diffraction methods, related to implication of electron diffraction tomography, and in the aberration-corrected scanning TEM imaging will be illustrated here with the examples of atomic structure investigation on cathode materials for Li-ion batteries. Precession electron diffraction and electron diffraction tomography provide quantitative diffraction data with substantially suppressed dynamical effects, enabling reliable structure solution and refinement. The electron diffraction experiments require very small quantity of material, typically less than 1 μm$^3$, making this method applicable to virtually all samples extracted from electrochemical cells. Electron diffraction patterns can be taken at a very low electron dose, enabling investigation of the materials sensitive to the electron beam damage, such as polyaniion Li-ion battery cathodes, particularly in their charged state. The capabilities of quantitative electron diffraction will be demonstrated using the Li$_2$CoPO$_4$F, Li$_2$FePO$_4$F and LiMn$_{0.5}$Fe$_{0.5}$PO$_4$ cathode materials. Aberration-corrected scanning TEM (STEM) techniques deliver the information on the local structural state with sub-angstrom resolution. High angle annular dark field STEM (HAADF-STEM) imaging provides clear visualization of the cation positions, whereas annular bright field STEM (ABF-STEM) shows the location of the “light” elements, such as O and Li. HAADF-STEM method has been applied to investigate the capacity and voltage fading in the layered rock-salt type oxides, which are determined to large degree by the cumulative local structure changes upon continuous electrochemical cycling. A comparative HAADF-STEM study of the layered oxides in the Li-Ru-Ti-O and Li-Ru-Sn-O systems at different stages (pristine, fully charged, discharged and cycled over different number of times) allowed establishing the cation migration pathways and identifying the cation traps responsible for the degradation of the electrochemical performance. ABF-STEM visualizes changes in the oxygen sublattice upon Li extraction and provides direct observation of O-O peroxo dimers in Li$_{0.5}$IrO$_3$ and O vacancy formation in Li$_x$Fe$_{0.56}$TeO$_6$ helping us to establish the fundamental