

energy x-ray diffraction and diamond anvil cell techniques were used to study the structural evolution of powder and amorphous materials under pressure, as well as the time dependence of the crystallization procedure. These will provide new insight on the nature of phase transition, provide new invitation for the electronic theoretical studies for the phase stability, and improve our understanding of the kinetic process of the common pressure induced crystallization.

Keywords: high pressure, phase transition, high energy XRD

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Pressure-induced change of the chemical short-range order in liquid compounds

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To reveal the effect of chemical bonding character on the pressure-induced structural changes, we have investigated the structures of various tetrahedrally bonded materials, such as liquid group 14 elements, III-V, II-VI and I-VII compounds, under high pressure. The results have shown that these liquids show various high-pressure behaviors (local structures and the sharpness of structural changes), depending on the covalent/ionic character [1]. However, these results are based on the average structure, which does not differentiate the chemical component around each atom. To observe partial structures is inevitable to understand the nature of the various structural changes in liquid compounds. For this purpose, we have developed the method to determine the partial structure in liquid compounds at high pressures using an anomalous x-ray scattering method (AXS) and applied it to liquid AgI. The experiment was performed at a JAEA undulator beamline BL22XU in SPring-8. The high pressure and high temperature condition was generated with a multi-anvil high-pressure apparatus, SMAP180. The data was collected by an angular dispersive x-ray diffraction method using a solid state detector. The incident x-ray energy was tuned into the energies below 300 and 20 eV from the absorption edge of two constituents. The obtained partial structural functions are in good agreement with the results of ab-initio MD calculation [2], which supports the validity of the AXS method to investigate the chemical short-range order in the liquid compounds. [1] T. Hattori et al., PRB 68, 224106 (2003), T. Hattori et al., PRB 72, 064205 (2005), T. Hattori et al., PRB 73, 054203 (2006), T. Narushima et al., PRB 76, 104204 (2007), T. Hattori et al., PRB 76, 144206 (2007), [2] F. Shimojo, (private comm.)

Keywords: high pressure, liquid, anomalous x-ray scattering

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A method for analysis of energy-dispersive X-ray diffraction from disordered systems under pressure

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Energy-dispersive x-ray diffraction method is commonly used for x-ray diffraction measurements using a cubic-type multi-anvil-press

because good background elimination and short data acquisition time can be achieved simultaneously. However, diffraction intensity is affected by several energy-dependent factors, such as intensity spectrum of a synchrotron radiation source, sensitivity spectrum of a detector, absorption spectra of the sample and those of the surrounding materials. Because it is difficult to estimate these factors separately, Tsuji et al., proposed a new empirical method for determination of structure factor of liquids and glasses [1]. Furthermore, Funakoshi et al., developed a Monte Carlo simulation code to carry out the procedure [2]. But these analyses sometimes give unreasonable results. We improved the method by implementing a common normalization method in a new code. The obtained structure factors of silica glass and liquid water at ambient conditions agree well with those reported previously.

[1]K. Tsuji, et al., Rev. Sci. Instrum. 60 (1989) 2425.

[2]K. Funakoshi, Ph.D thesis, (1997, Tokyo Institute of Technology).

Keywords: liquid-state diffraction, high-pressure structure determination, energy-dispersive X-ray diffraction

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Pressure- and temperature-induced structural phase transition mechanisms of nitrogen

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A theoretical description is proposed for the pressure and temperature induced structural transitions of nitrogen. Three regions of the phase diagram are distinguished corresponding to different types of transition mechanisms and parent structures. Combined ordering and displacive reconstructive transitions are found in the lowest pressure region, from the parent disordered β structure to the ordered α and γ structures. In a second region, which extends from about 2 to 140 GPa at room temperature, group-subgroup related structures occur, which realize ferroelastic or ferroelectric distortions of the parent δ structure. Space-group symmetries, consistent with the assumed structural mechanisms, are proposed for the δ_{loc} , ζ , κ , ι and θ molecular phases. Above 140 GPa, in the molecular dissociation region, the local structure of the η phase is assumed to realize a link between the molecular ζ and κ phases and the high-temperature cg-N phase.

Keywords: nitrogen, phase transitions in solids, Landau theory

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Thermodynamic exploration of conformational space of 1,2-ethylene glycol

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Ethylene glycol (1,2-Ethanediol, EG) is wide by applied mainly as an anti-freezing additive, but also as a substrate and solvate in many industrial. Owing to the vicinal location of two hydroxyl groups (-OH) in this very simple molecule, EG serves as a model

for biological compounds, such as sugars and polysaccharides. The molecule of EG is a triple rotor about the O-C, C-C and C-O bonds. Following the common assumption that each of the rotors can assume 3 positions, the molecule can exist as $3^3=27$ conformers of which 10 are unique [1]. We have looked at the crystal structures of EG frozen at varied thermodynamical conditions. This study also pertains to a basic problem of the relation between the conformational preferences of isolated molecules and their conformation adopted in the crystalline state [2]. Till now one EG structure crystallized by temperature freezing was determined at 130 K: crystal was orthorhombic, in $P2_12_12_1$ (phase I) with $Z'=1$ [3]. Two new crystal phases of EG have been obtained by *in-situ* pressure-freezing in a Merrill-Bassett DAC [4]. These new crystal structures were solved straightforwardly by direct methods in space group $P2_1$ at 1.2 and 2.0 GPa (phase II), and in space group $Pbcn$ at 2.2 GPa (phase III).

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[3] Thalladi, V. R.; Boese, R.; Weiss, H. C.: *Angew. Chem. Int. Ed.* **2000**, *39*, 918 – 922.

[4] Budzianowski, A., Katrusiak A. *In High-Pressure Crystallography*; A. Katrusiak, P. F. McMillan Eds.; Dordrecht: Kluwer Academic Publisher, **2004**, 157-168.

Keywords: high-pressure phases, hydrogen bonds in organic crystals, molecular interactions

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The structure and nature of ice VII to 20 GPa

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Ice VII has a simple average structure in which the oxygens form a body-centred cubic (bcc) arrangement and the protons are disordered over two off-centre sites in H-bonds that connect the oxygens into two interpenetrating tetrahedral networks. However, there is a complication in that the oxygens are disordered over a number of sites that are displaced $\sim 0.1\text{Å}$ from the mean bcc positions [1]. The protons must also be disordered over several sites around their mean position. The direction of these displacements affects both the number of sites – and hence the number of structural configurations – and the geometry of the H-bonds. Some possible displacement directions would require there to be a range of quite different bondlengths, which could have implications for understanding the bond centring to ice X at much higher pressures. Because of the small magnitude of the displacements, it is difficult to obtain a decisive determination of their direction. But overcoming this problem is crucial to a full understanding of the ice VII phase. There are also other questions about this phase, including the nature of its short-range structure, the possibility of incommensuration [2] and some form of discontinuity around 14 GPa (~ 18 GPa in the deuterated form) [3]. We will report a range of studies, using both neutron and x-ray diffraction techniques, that provide new information on the structural disorder and also on the evidence for or against any change in structure in the range up to 20 GPa.

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[3] P.Pruzan et al, *J. Raman Spec.*, **34** (2003) 591-610.

Keywords: neutron and X-ray diffraction, ice structures, high-pressure structures

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High pressure X-ray cell for soft matter

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There is currently high demand for development of techniques that will allow probing of the time-dependent structural behaviour of out-of-equilibrium soft condensed matter systems. An ideal technique for monitoring and triggering the structural evolution of such systems within the millisecond regime is time resolved X-ray diffraction, employing pressure as the triggering variable. Using pressure jumps to trigger structural change has several major advantages over other methods, e.g. temperature jumps: The pressure step propagates at the speed of sound and thermodynamic equilibrium is achieved far more rapidly than the rate of acquisition, bi-directional pressure jumps propagate at the same speed, if structural changes are fully reversible, pressure jumps can be repeated with identical experimental parameters to allow for data averaging, pressure does not normally disrupt intramolecular bonds below 2GPa (20 kbar) While changing pressure is an ideal technique for studying phase changes, it is technically challenging which has limited its use as a common laboratory technique. We have recently used synchrotron light and the pressure jump technique to elucidate and investigate a novel liquid crystalline mesostructure in a hydrated lipid system and are now developing a high performance, robust and user friendly facility for investigation of soft condensed matter systems at high pressure. This facility will be freely available to users at Diamond Light Source and it is hoped that this will allow this highly advantageous technique to become accessible to a much wider section of the community than is currently possible.

Keywords: soft condensed matter, high pressure X-ray diffraction, lipid mesophases

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High-pressure structural studies of pharmaceutical materials

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The phenomenon of polymorphism is of crucial importance to many industries including the pharmaceutical, pigments and energetics industries. Polymorphism is an extremely interesting research topic for the structural scientist, however, the appearance of an unidentified polymorph during the production of an active pharmaceutical ingredient (API) can cause serious problems for both the production and processing of the pharmaceutical. The physical properties of an API e.g. solubility and hence bioavailability can vary dramatically depending on the polymorph that is isolated and so the emergence of a new polymorph requires a cessation of production together with a full investigation of the polymorphism exhibited by the API. For this reason the pharmaceutical industry places great