

**MS67.28.4***Acta Cryst.* (2005). A61, C87**Anomalous Thermal Expansion in Cyanide-bridged Molecular Framework Materials**Karena W. Chapman, Cameron J. Kepert, *School of Chemistry, University of Sydney*. E-mail: chapmank@chem.usyd.edu.au

We have recently uncovered unprecedented negative thermal expansion (NTE) behaviour in a broad family of molecular framework materials,[1] remarkable in exhibiting coefficients of thermal expansion ( $\alpha = d\ell/dT$ ) up to three times those of known existing materials. The mechanism underlying this unusual phenomenon involved the thermal population of librational modes, which results in a net contraction of non-nearest neighbour bond lengths.

The structural flexibility and control inherent in such molecular frameworks present a unique opportunity to systematically investigate this NTE behaviour and the influences of framework topology, composition and host-guest interactions.

These studies have combined conventional Bragg crystallographic techniques with consideration of diffuse scattering which allow the dynamic aspects of the structure to be probed. These techniques include single crystal x-ray diffraction at laboratory and synchrotron sources, neutron and synchrotron powder diffraction, and total neutron scattering and high energy x-ray scattering for pair distribution function analysis and reverse Monte Carlo modelling.

[1] Goodwin A.L., Kepert C. J., *Phys. Rev. Lett.*, 2005, *submitted*.

**Keywords:** thermal expansion, lattice vibrations, pair distribution function

**MS67.28.5***Acta Cryst.* (2005). A61, C87**In-situ Synchrotron XRD Studies of Combustion Processes**Gilberto Artioli, *Dipartimento di Scienze della Terra, Università di Milano*. E-mail: artioli@iummix.terra.unimi.it

Synchrotron based diffraction techniques are powerful tools for the characterization of the crystal phases involved in fast chemical reactions. The flexibility of the instrumental setup and the brilliance of the source allow for optimal selection of the experimental parameters, so that reliable structural information can be obtained even on metastable or transient species.

Two in situ experiments were selected, related to the high temperature combustion processes on catalytic materials. In both cases the full-profile analysis of the diffraction data, including cell parameters, phase abundance, peak width, and Rietveld-type structure refinement yield a wealth of information on the reaction mechanisms and kinetics.

In the first case, the burning of the organic template within the cavities of a high-silica MFI zeolites has been followed in situ using the ESRF BM-8 translating image plate [1]. The structural refinements allow quantification of the template occupancy in the channels, and the dimensionality of the diffusion kinetics of the reaction products [2]. In the second case, the combustion of methane over iron oxide catalysts has been followed by coupled XRD and gas MS, gaining insight on the changes taking place in the solid state catalysts during the production of hydrogen [3].

[1] Meneghini C., et al., *Journ. Synch. Rad.*, 2001, **8**, 1162. [2] Milanesio M., et al., *J. Am. Chem. Soc.*, 2003, **125**, 14549. [3] a) Gemmi M., et al., *Journ. Appl. Cryst.*, 2005, *in press*; b) Ghisletti et al., *this conference*.

**Keywords:** in-situ dynamic XRD, catalysts, reaction kinetics

**MS68 LIQUIDS AND AMORPHOUS SYSTEMS AT HIGH PRESSURE****Chairpersons:** Christopher Tulk, Dennis Klug**MS68.28.1***Acta Cryst.* (2005). A61, C87**Intermediate Range Chemical Ordering in H<sub>2</sub>O, Si and Ge under Pressure**Chris J. Benmore<sup>a</sup>, R.T. Hart<sup>a</sup>, Q. Mei<sup>a,b</sup>, D.L. Price<sup>c</sup>, J. Yarger<sup>b</sup>, C.A. Tulk<sup>c</sup>, D.D. Klug<sup>d</sup>, <sup>a</sup>*Argonne National Laboratory, Argonne, IL, 60439 USA*. <sup>b</sup>*University of Wyoming, Department of Chemistry,**Laramie, Wyoming 82071-3838, USA*. <sup>c</sup>*HIFR and SNS project, Oak Ridge National Laboratory, Oak Ridge TN 37831, USA*. <sup>d</sup>*National Research Council of Canada, Ottawa, Ontario K0A 0R6, Canada*. E-mail: benmore@anl.gov.

Neutron and x-ray diffraction data for low, high and very high density amorphous and liquid water, silicon and germanium have been compared in terms of the first sharp diffraction peak in the structure factor and at the radial distribution function level. The low density amorphous and high density liquid forms of water, Si and Ge are shown to have very similar structures if the contributions from the hydrogen correlations in water are neglected. The very high density liquid forms of Si and Ge are also analogous, but differ slightly from amorphous and liquid water by the way in which the interstitial atoms or molecules are pushed into the nearest neighbour shell. Both the low and very high density forms show a higher degree of chemical ordering compared to the high density form.

**Keywords:** amorphous diffraction, liquid structure, intermediate range order of glasses

**MS68.28.2***Acta Cryst.* (2005). A61, C87**Evolution of the Structure of Amorphous Ice - from LDA through HDA to VHDA**Roman Martonak, D. Donadio, M. Parrinello, *Computational Science, Department of Chemistry and Applied Biosciences, ETH Zurich, c/o USI Campus, Via Giuseppe Buffi 13, CH-6900 Lugano, Switzerland*. E-mail: martonak@phys.chem.ethz.ch

We report results of molecular dynamics simulations of amorphous ice for pressures up to 22.5 kbar [1,2]. The high-density amorphous ice (HDA) as prepared by pressure-induced amorphization of Ih ice at T=80 K is annealed to T=170 K at various pressures to allow for relaxation. Upon increase of pressure, relaxed amorphous ice undergoes a pronounced change of structure, ranging from the low-density amorphous ice (LDA) at p=0, through a continuum of HDA states to the limiting very high-density amorphous ice (VHDA) regime above 10 kbar. The main part of the overall structural change takes place within the HDA megabasin, which includes a variety of structures with quite different local and medium-range order as well as network topology and spans a broad range of densities. The VHDA represents the limit to densification by adapting the hydrogen-bonded network topology, without creating interpenetrating networks. The connection between structure and metastability of various forms upon decompression and heating is studied and discussed. Comparison with experimental results is presented and some conclusions concerning the relation between amorphous ice and supercooled water are drawn.

[1] Martonak R., Donadio D., Parrinello M., *Phys. Rev. Lett.*, 2004, **92**, 225702. [2] Martonak R., Donadio D., Parrinello M., *J. Chem. Phys.*, *in press*.

**Keywords:** amorphous solids, water, ice

**MS68.28.3***Acta Cryst.* (2005). A61, C87-C88**Structure of High-pressure Liquids: X-ray Diffraction and RMC Modelling**Shinji Kohara<sup>a</sup>, Yuichi Akahama<sup>b</sup>, Yasuo Ohishi<sup>a</sup>, László Temleitner<sup>c</sup>, László Pusztai<sup>c</sup>, Masaki Takata<sup>a</sup>, Haruki Kawamura<sup>b</sup>, <sup>a</sup>*Japan Synchrotron Radiation Research Institute, Hyogo, Japan*. <sup>b</sup>*University of Hyogo, Hyogo, Japan*. <sup>c</sup>*Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, Budapest, Hungary*. E-mail: kohara@spring8.or.jp

With the arrival of the latest generation of synchrotron sources and the introduction of advanced insertion devices (wiggler and undulators), the high-energy ( $E > 30$  keV) X-ray diffraction technique has become feasible, leading to new approaches in the quantitative study of the structure of simple liquids at high pressure.

We report reliable diffraction data of high-pressure liquids in a diamond anvil cell (DAC), measured at the Spring-8 high-energy X-ray diffraction beamline BL04B2 using 37.6 keV X-rays. Moreover, we performed reverse Monte Carlo modelling [1] to investigate structural modification of the liquids under high pressure. The