

identifying known polymorphs of organic molecules, but also completely new polymorphs, and solvates, as illustrated by the nootropic drug piracetam, for which new polymorphs and hydrates were prepared and characterised at pressures below 1.0 GPa [3].

We believe that this methodology has the potential to make a significant impact for the discovery of new polymorphs and solvates.

[1] Allan D.R., Clark S.J., Ibberson R.M., Parsons S., Pulham C.R., Sawyer L., *Chem. Commun.*, 1999, 751. [2] Fabbiani F.P.A., Allan D.R., Dawson A., David W.I. F., McGregor P.A., Oswald I.D.H., Parsons S., Pulham C.R., *Chem. Commun.*, 2003, 3004. [3] Fabbiani F.P.A., Allan D.R., Parsons S., Pulham C.R., *CrystEngComm.*, in press.

**Keywords:** polymorphism, high pressure, pharmaceuticals

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##### Complex Structures in Barium at High Pressure

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Barium has a bcc structure at ambient pressure, transforms to an hcp phase II at 5.5 GPa, and then to phase IV at 12 GPa which transforms to another hcp phase at 45 GPa. Phase IV is characterised by complex structures and a number of different forms. IVa, which exists from 12 to 12.5 GPa, was the first example discovered of a composite incommensurate host-guest structure in an element [1]. The structure comprises a 'host' framework, with 8 atoms in a tetragonal unit cell, and chains of 'guest' atoms that lie in channels formed by the host framework. These chains form tetragonal and monoclinic guest structures that are incommensurate with the host along the *c*-axis of the host. Similar composite structures have now been found in Sr, K, Rb, As, Sb and Bi. In barium above 12.5 GPa, there is a IVb form with the same host structure as IVa but with the guest chains forming an orthorhombic structure. There is evidence of further structural changes to a IVc form at ~16 GPa and a IVd form at ~18 GPa [1]. New structural studies have revealed these to have remarkably complex structures.

[1] Nelmes R.J., Allan D.R., McMahon M.I., Belmonte S.A., *Phys. Rev. Letters*, 1999, **83**, 4081.

**Keywords:** high-pressure crystallography, barium, phase transitions

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##### Structures and Phase Transitions of CuInSe<sub>2</sub> under High Pressure

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The ternary compound semiconductor CuInSe<sub>2</sub> has a rich variety of potential applications and has stimulated a substantial number of experimental and theoretical studies. In previous high-pressure energy-dispersive powder diffraction studies of this material, the structural phase transition from the tetragonal chalcopyrite phase to the face-centred cubic at 7.6 GPa have been reported [1]. This NaCl-like structure exists up to 29 GPa, the highest pressure obtained in their experiment. We have embarked on a re-examination of the high-pressure structures and transitions in CuInSe<sub>2</sub> using angle-dispersive powder diffraction techniques with the image-plate detector on station 9.1 at the SRS Daresbury Laboratory, U.K. We find the same structural phase transition as has been previously reported up to 29 GPa. On further compression, we have obtained extensive data through a next phase transition at 39.2 GPa. This newly discovered phase has now been identified as an orthorhombic distortion of the NaCl structure. This high pressure phase is stable up to 53.2 GPa, the maximum pressure reached for this experiment.

[1] Tinoco T., Polian A., Gomez D., Itie J.P., *phys. stat. sol. (b)*, 1996, **198**,

433.

**Keywords:** ternary chalcopyrite, high-pressure X-ray diffraction, diamond anvil cells

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##### Resolution of the Intermediate High Pressure Phase of PbTe

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The lead chalcogenides PbX (X=Te, Se, S) are narrow-gap semiconductors (group IV-VI), which crystallise at ambient conditions in the cubic NaCl (B1) structure. It has been known for 20 years that they transform at ~3-6 GPa to an intermediate phase, and at higher pressures to the 8-fold coordinated CsCl (B2) structure. There has been much controversy on the crystal structure of the intermediate high pressure phase [1,2,3].

We report recent X-ray powder diffraction obtained at synchrotron sources under pressure, that allowed us to solve the structure of the intermediate phase of PbTe, from simulated annealing techniques and Rietveld refinement : the phase transition at 6 GPa is not to the GeS (B16) or TlI (B33) type structures as previously reported, but to an orthorhombic Pnma structure, with cell parameters *a*=8.157(1), *b*=4.492(1), *c*=6.294(1) Å at 6.7 GPa. This structure corresponds to a distortion of the low pressure NaCl structure with a coordination intermediate between the six-fold B1 and the eightfold B2 structure. These new results may modify the admitted paths of phase transitions between the B1 (NaCl) and B2 (CsCl) structures.

[1] Fujii Y., Kitamura K., Onodera A., Yamada Y., *Solid State Comm.*, 1984, **49**, 135. [2] Chattopadhyay T., Pannetier J., von Schnering H. G., *J. Phys. Chem. Solids*, 1986, **47**, 879. [3] Ahuja R., *Phys. Stat. Sol. B*, 2003, **2**, 341.

**Keywords:** high-pressure structure determination, semiconductor structures, synchrotron powder diffraction

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##### Structural Study of Solid Mercury at High Pressures

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Liquid mercury solidifies at about 1.2 GPa at room temperature. After solidification, it undergoes several structural phase transitions under high pressure. The highest-pressure  $\bar{a}$ -phase with the hcp structure appears above about 37 GPa [1], which is reported to be stable to at least 67 GPa [2]. We have investigated the structural stability of the  $\bar{a}$ -phase at ultrahigh pressures.

Angle-dispersive powder x-ray diffraction experiments have been done with the diamond-anvil cell at high pressures at room temperature on the beam line 10 XU at Spring-8. The  $\bar{a}$ -phase was found to be stable up to 193 GPa, the highest pressure investigated. The *c/a* axial ratio continuously decreased with pressure from 1.73 at 50 GPa to 1.64 at 193 GPa. The equation of state for the  $\bar{a}$ -phase was obtained over the pressure range 50-193 GPa. The bulk modulus and its pressure derivative for the  $\bar{a}$ -phase at 50 GPa were determined as 292 GPa and 5.5, respectively.

[1] Schulte O., Holzapfel W.B., *Phys. Rev. B*, 1993, **48**, 14009. [2] Schulte O., Holzapfel W.B., *Phys. Rev. B*, 1996, **53**, 569.

**Keywords:** mercury, high pressure, diamond anvil cells

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##### High Pressure Effect on Bonding Nature in KMnF<sub>3</sub>

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Bonding nature between atoms in ABX<sub>3</sub> perovskites is considered to be closely related to their phase instability [1]. The bond length would have primary importance to bonding nature. The bond length can be easily controlled by applying pressure onto the materials. In this study, bonding nature of KMnF<sub>3</sub> is investigated by visualizing the charge density distributions under high-pressure.

The synchrotron-radiation powder diffraction experiment was carried out at Spring-8 BL10XU up to 5 GPa under ambient temperature. The pressure-induced phase-transition from cubic to tetragonal phase was confirmed by observing superlattice-reflections at R points, such as (3/2 1/2 1/2), at the vicinity of 3.2 GPa.

The charge-density distributions of the both phases were obtained by the MEM/Rietveld analysis. From the MEM charge densities of the cubic phase, it was revealed that the covalency of Mn-F bond is weakened as the pressure increases. This shows high contrast to the fact that the bond length is shortened as the pressure increases, which is very normal behavior under high pressure. Accompanying these changes under high pressure, the atomic vibration of F atoms perpendicular to the Mn-F bond became greater, which should be related to the softening of rotational mode of the Mn-F<sub>6</sub> octahedron.

[1] Aoyagi S., et al., *J. Phys. Soc. Jpn.*, 2002, **71**, 2353.

**Keywords:** perovskites, powder diffraction under non-ambient condition, charge density studies

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#### High Pressure X-ray Diffraction Studies Of Purely Siliceous Zeolites

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High pressure synchrotron X-ray powder diffraction measurements of purely siliceous zeolites were performed using a diamond anvil cell. The behaviour under pressure is partly driven by the ability of the pressure transmitting fluid to enter the neutral SiO<sub>2</sub> framework.

Measurements of purely siliceous zeolite Y (Sil-FAU) using silicone oil as the pressure transmitting medium show compression of the zeolite followed by a loss of long range ordering at 2.2 GPa. When using a methanol:ethanol:water mixture (16:3:1) as the pressure transmitting medium, two distinct compressibility regions are observed with a dramatic change in the compression mechanism at 4 GPa. Rietveld refinement analysis of the powder patterns explains the different regions as sequential pore filling being the main response to pressure up to 4 GPa and distortion of the framework involving the sodalite and double 6 ring (D6R) units at higher pressures.

Purely siliceous chabazite (Sil-CHA) was measured to 5.5 GPa using an alcohols/water mixture, previously described, as the pressure transmitting fluid. As with Sil-FAU, two distinct regions of compressibility were observed. Rietveld refinements indicated initial pore filling occurs upon application of pressure to ~3 GPa in the case of Sil-CHA. This is followed by framework distortion as a response to increased pressure. Further experiments on these and related systems will be performed in April, and results presented.

**Keywords:** synchrotron X-ray diffraction, zeolite, diamond anvil cell

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#### High Pressure High Temperature Carbon Dioxide

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Carbon dioxide is widely studied molecular compound because of

its importance in life and geological sciences. Despite the simplicity of the molecule, the solid shows several high-pressure polymorphs quenchable at room temperature and its phase diagram isn't still fully characterized [1,2,3]. In particular the structure of the high temperature phases II and IV have not been well established and the claimed molecule pairing in phase II [4] and bent molecular geometry in phase IV [5] have been recently questioned [6].

I present here a FTIR and Raman study of high pressure high temperature CO<sub>2</sub> phases up to 30 GPa performed between 80 and 650 K by using a resistively heated diamond anvils cell and an N<sub>2</sub> flux cryostat. The complete vibrational information gives some constraints on the crystal symmetry, allowing to choose the crystal structures of phases II and IV among those proposed in the literature.

Moreover we have determined the melting curve and the transition lines for high temperature phases, between 300 and 800 K, and found them quite different from published results.

[1] Iota V., Yoo C.S., *Phys. Rev. Lett.*, 2001, **86**, 5922. [2] Santoro M., et al., *J. Chem. Phys.*, 2004, **121**, 2780. [3] Gorelli F.A., Giordano V.M., et al., *Phys. Rev. Lett.*, 2004, **93**, 205503. [4] Yoo C.S., et al., *T. Phys. Rev.*, 2002, **B65**, 104103. [5] Park J.H., et al., *Phys. Rev. B*, 2003, **68**, 014107. [6] Bonev S.A., et al., *G. Phys. Rev. Lett.*, 2001, **91**, 065501-1.

**Keywords:** high-pressure phase transformations, spectroscopy and molecular structure, crystal symmetry

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#### High P-T phase Diagram of Solid Benzene, and Transformation to an Extended Amorphous State

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The high pressure structural properties of solid benzene have been investigated in the P-T range where the chemical reaction does occur, e.g. above 15-40 GPa depending on temperature, by x-ray diffraction and infrared absorption techniques. Sample annealing above 500 K produces pure phase II crystals (monoclinic P2<sub>1</sub>/c). X-ray diffraction patterns collected at 540 K on these crystals allowed the equation of state of benzene to be obtained. These results indicate the stability of phase II up the pressure where benzene reacts and no evidences of the III and III' crystal structures is gained. On these bases the existing thermodynamic phase diagram of benzene was reinterpreted and a simplified new one is proposed [1]. Unique features of the high pressure transformation to the extended amorphous state of this important model system were unveiled by observing, *in situ*, the pressure evolution of the Bragg peaks. Indeed the crystalline pattern merges, at high pressure, into a broad amorphous-like diffraction profile related to the static structure factor S(Q) of the final product.

[1] Ciabini L., Gorelli F.A., Santoro M., Bini R., Schettino V., Mezouar M., *High temperature equation of state and phase diagram of solid benzene, submitted to PRB.*

**Keywords:** high pressure, benzene, amorphization

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#### Molecular Dynamics Simulations of Cubic CaSiO<sub>3</sub> at Lower Mantle Conditions

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First-principles projector-augmented wave (PAW) molecular dynamics was used to investigate structure and properties of what is thought to be the third most abundant phase in the Earth's lower mantle,