

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.

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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 CuInSe₂ under High Pressure

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The ternary compound semiconductor CuInSe₂ 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 CuInSe₂ 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.

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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.

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Keywords: mercury, high pressure, diamond anvil cells

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High Pressure Effect on Bonding Nature in KMnF₃

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