FOCUS ARTICLE

ChemComm
www.rsc.org/chemcomm

Chemistry of materials under extreme high pressure-high-temperature conditions

Paul F. McMillan

Department of Chemistry, University College London and Royal Institution of Great Britain, UK. E-mail: p.f.mcmillan@ucl.ac.uk

Most of our knowledge of chemistry is derived from experiments carried at the Earth's surface, at pressures near one atmosphere. However, most elements and compounds in the universe exist under conditions of extremely high pressures, often combined with high temperatures, deep within the planets and stars. Under these conditions, new high-density crystal forms occur, species usually known only as molecules become dense covalent or ionic solids, and insulators and semiconductors become metals and even superconductors. Valency states and coordination numbers are changed, and it is expected that chemical bonding and reactivity is modified. Paul McMillan describes how the field of condensed matter chemistry under extreme high pressure conditions now represents a vast new area to be explored.

Introduction

Pressure, temperature and chemical composition form the trilogy of thermodynamic variables that determine the stability and reactions of molecules and solids. We already know how to manipulate temperature and composition to yield a rich array of structures and compounds; however, the high pressure variable (HP) in solid-state chemistry has remained virtually unexplored. Experiments carried out at tens to hundreds of atmospheres reveal significant pressure effects on organic and inorganic reaction chemistry: hydrothermal syntheses and studies of supercritical fluids extend pressures to a few hundreds or thousands of atm (kbars). However, these pressures are still too low to cause any substantial changes in chemical bonding or crystal packing. New techniques now developed for studying the properties of minerals and condensed matter physics *in situ* under extreme high pressure-high temperature conditions are now being applied to explore the structural chemistry, bonding and reactions of solids:

Paul F. McMillan (seen here with a diamond-anvil cell) recently took up a newly-established Chair in Solid State Chemistry created jointly at the Royal Institution (RI) and at University College London (UCL), UK, partly financed by the Wolfson Foundation–Royal Society scheme developed to aid returning scientists establish research programmes in the UK. Prior to this, he was Professor of Chemistry and Biochemistry and Director of the Centre for Solid State Science in Arizona, USA, where he had established a programme in high-pressure solid-state and materials chemistry. His cross-disciplinary programme in London spans both institutions (RI and UCL) to explore the high pressure-high-temperature chemistry and synthesis of new solid-state materials, using diamond anvil cell and multi-anvil press techniques.

Photo courtesy of CCLRC/Daresbury Laborato

DOI: 10.1039/b300963g

the new results are leading to development of novel technological materials.[1,2]

Traditional high-pressure techniques

High pressures are traditionally achieved by machines that concentrate forces on the sample *via* systems of hydraulic pumps, pistons and anvils, such as those pioneered by Percy Bridgman (Nobel prize in Physics, 1946) (Fig. 1).[3] These devices permitted physicists to explore changes in electrical conductivity, molar volume, specific heat, *etc.*, occurring in the 80–100 kbar (8–10 GPa) range.[2] The experiments revealed a remarkable range of structural transitions that occur even for the simplest substances under compression. For example, solid H_2O shows eight different forms of ice up to 8 GPa (at least four more have now been reported), including ice-VII that melts at 100 °C at this pressure, the normal boiling point of water. The 'large volume' HP instruments were further developed by Earth scientists, who used them to establish the mineralogy of the deep Earth, and also by researchers engaged in the quest to synthesise industrial diamond.[4] 'Large volume' machines now permit routine materials syntheses and studies to P = 10–30 GPa and T = 2000–2300 °C (Fig. 1). The use of sintered diamond anvils in some devices has recently increased the maximum pressure to ~50 GPa.[1]

Using the large machines, dramatic changes in the electrical properties of substances were documented at high pressure, such as metallisation of the well-known semiconductor silicon. Calcium has a cubic closest-packed structure at ambient P; it transforms into a body-centred polymorph, with a *lower* atomic packing density, above P = 20 GPa. The result indicates 4s-3d mixing, so that Ca has formally become a transition metal at HP. Recent studies show that potassium exhibits an similar shift in chemical properties upon densification.[5] Despite such intriguing discoveries, HP studies have not yet entered the mainstream of solid state chemistry research. This is partly due to the fact that HP machines and experiments have a reputation as cumbersome, often dangerous, and difficult to operate. Also, samples can not usually be observed directly during the experiments, so that changes in structure and bonding must be deduced from indirect studies, or by examination of recovered materials. This situation is now changing with the advent of high-brilliance third-generation synchrotron sources, that provide highly-penetrating X-rays that can traverse sample assemblies during *in situ* experiments.[1] New HP devices with specially-designed geometries and neutron-transparent components also permit complementary neutron studies, into the 10–30 GPa pressure range.[6]

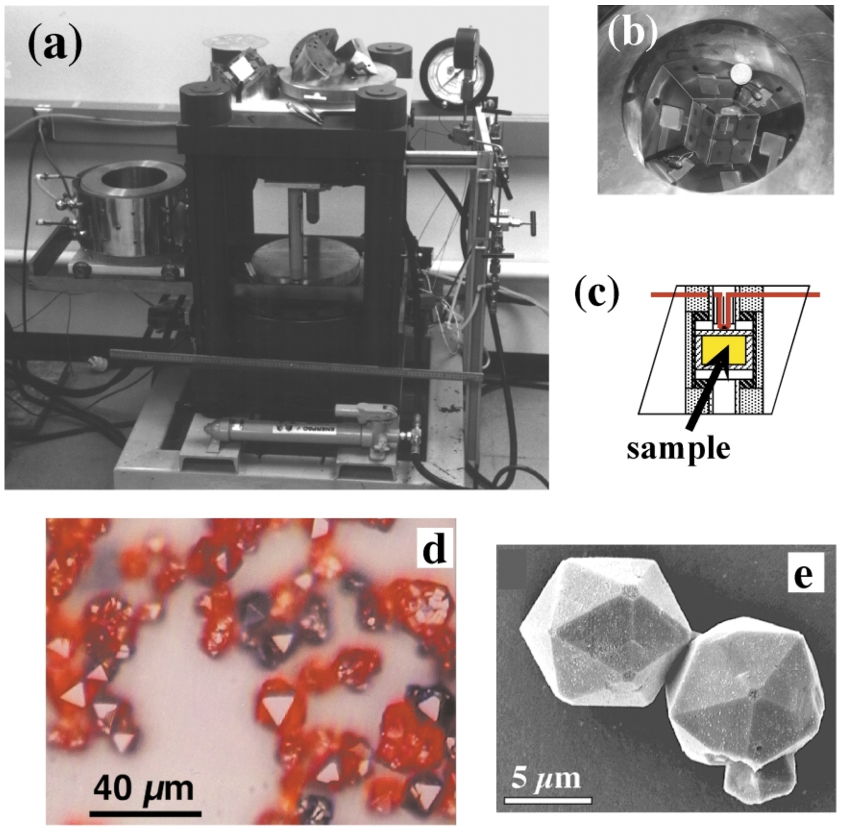

Fig. 1 (a) The Walker-type multianvil high pressure-high temperature synthesis device that was originally constructed in our laboratory in Arizona (A. Pawley *et al.*, *Science*, 1993, **261**, 1024), and is now installed in the Davy-Faraday Laboratory at the Royal Institution, London. The device consists of an oil-pumped ram that drives a set of steel wedges contained within the high-pressure containment module (at left), within a press frame that was designed to resist up to >1000 tons force (usually operated at up to ~500 tons). (b) Oblique top view of the high-pressure module, showing three steel wedges underneath an assembled cubic cluster of eight WC cubes that contain a sample assembly at the center, inside the steel containment ring. A US quarter piece (25 ¢) is shown for scale. (c) Schematic of the sample containment assembly used for a multi-anvil run. The sample (yellow) is held inside a metal or ceramic capsule (hatched), and is surrounded by a graphite or $LaCrO_3$ resistive heater. The temperature is measured by a thermocouple (red).This type of device is used routinely for synthesis experiments into the 10–30 GPa range, at temperatures of 2000–2300 °C. (d) and (e) show optical and SEM micrographs of icosahedral B_6O particles prepared using this device (see ref. 15). Photographs courtesy of H. Hubert.

Use of diamond anvil cells

The nature of HP research changed dramatically with the development of diamond anvil cells ('DACs').[1] Samples are held between opposed flat-polished 'culet' faces of gem-quality diamonds, and a force (F) is applied to the large diamond 'tables' (Fig. 2). The large area reduction (A_{table}/A_{culet} ~ 10 : 1) causes high pressures to be developed within the sample, because of the relationship $P = F/A$. Multi-megabar pressures ($P > 1,000,000$ atmospheres) are readily achieved. Diamonds are transparent to radiation extending from the IR into the visible, UV and X-ray regions, so that samples can be directly observed and studied spectroscopically *in situ* during extreme HP experiments (Fig. 2). Solid samples held in the DAC are usually surrounded by a pressure-transmitting medium that is often an inert condensed gas such as Ar, contained within the drilled metal gasket that provides the sample holder/reaction chamber.The pressure-transmitting medium can also be chosen to provide one of the reactants (N_2, O_2) for chemical synthesis experiments under HP–HT conditions. High temperatures are achieved either by resistively-heating the sample chamber to T~1000 °C, or by directing infrared (CO_2, Nd^{3+}:YAG) lasers through the diamond windows on to the sample. Temperatures reaching 2000–7000

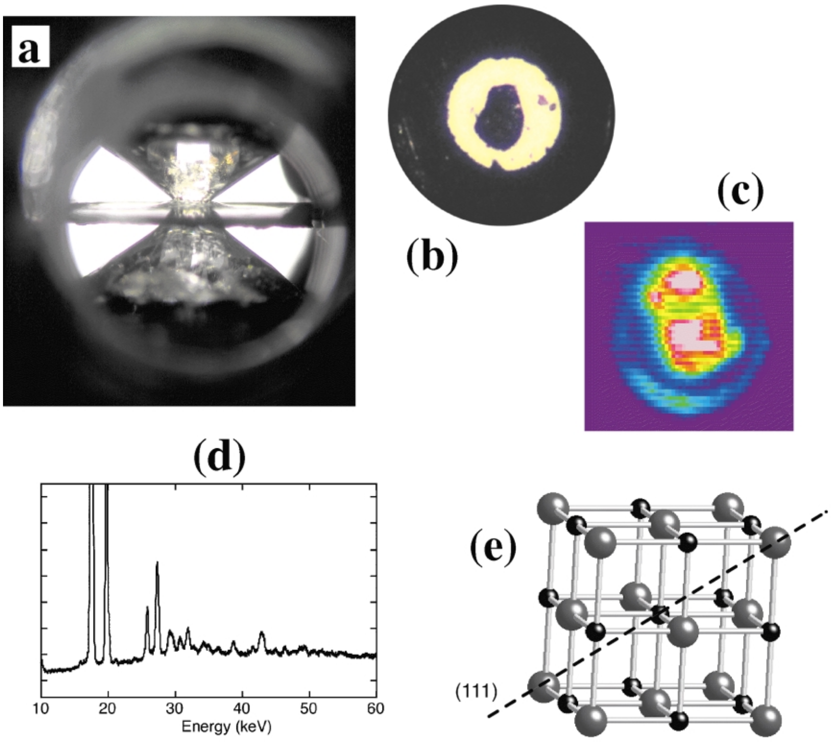

Fig. 2 (a) Side-view of one of the diamond anvil cells developed for HP–HT experiments at University College London. The gem-quality diamonds have had their culet points polished to provide 100–200 μm flat faces, and they are shown here with a Re gasket between them. (b) Top view down through a DAC loaded with a sample of molybdenum nitride crystal, inside a solid-N_2 pressure medium, pressurised to 40 GPa, ready for a HP–HT laser-heating experiment. (c) Thermal image of a ceramic sample heated by a CO_2 laser (40 mm focus spot) held within the DAC, indicating the temperature profile obtained during synthesis experiments: pale pink indicates temperatures >1250 °C, and blue is T <800 °C. (d) Energy-dispersive synchrotron X-ray spectroscopy and diffraction of the MoN sample following laser-heating to T >2500 ºC at 40 GPa: the strong peaks at low-energy correspond to the L emission peaks of the molybdenum atoms, and the peaks ate higher energy result from diffraction from a newly-synthesised HP phase, that is determined to have cubic symmetry (E. Soignard *et al.*, in preparation). (e) Structural model of the new HP MoN phase, that is based on the cubic B1 (NaCl) structure, with a 3-fold cell expansion along the (111) direction. Images taken by E. Soignard and T. Chaplin: the thermal imaging camera was loaned by Dr. D. Caruana (UCL).

°C are readily achieved by this technique (Fig. 2).

Condensed gases

The DAC has been used extensively to study condensed gases such H_2, H_2O, CH_4 and NH_3, that are important components of giant gas planets such as Neptune, Saturn and Jupiter and their moons.[7] Metallic conductivity was recorded in dense fluid hydrogen under extreme P-T conditions, during shock-wave studies. A new 'broken-symmetry' molecular-ionic solid phase (H_2^+ H_2^-) is also observed at high pressure. Electronic disproportionation reactions among molecular compounds also occur at HP among other systems: for example, nitrogen oxides (NO_2, N_2O) form ionic mineral-structured phases (NO^+ NO_3^-, related to the minerals calcite or aragonite ($CaCO_3$). Multiply-bonded CO_2 and N_2 molecules contain strong covalent bonds: it was long thought that these would remain intact even upon extreme compression. However, heating CO_2 at P = 10–20 GPa leads to formation of new sp^3-bonded framework structures based on singly-bonded CO_4 units, analogous to the SiO_2 minerals cristobalite or tridymite. The new solids are 'almost' recoverable to ambient pressure, and they possess useful properties, including non-linear optical behaviour. Compressed molecular N_2 gives rise to new semiconductors containing polymerised $(\text{-N-})_x$ oligomers. Condensed solid water (H_2O) transforms to fluorite-structured ice-X, that should be ionically-conducting above P = 10 GPa. H-bonded H_2O-'clathrates' containing trapped 'guest' species (Xe, CH_4, CO_2) are stabilised at lower pressures:[8] $CH_4@H_2O$ clathrates are formed on the deep ocean floor, and could have fuel storage applications; $CO_2@H_2O$ clathrates are being considered for CO_2 sequestration strategies. Unusual $(He,Ne,Ar,H_2)@H_2O$ clathrates and H_2–CH_4, H_2–Ar,Ne solids, as well as new $CH_4@H_2O$ clathrate polymorphs, are observed in HP experiments. Compressing Xe–H_2O clathrates and (Xe,Ar)–SiO_2 solid or liquid mixtures suggests that new rare-gas chemistries might occur at HP. The results reveal rich new solid-state chemistries that are likely to be present among condensed 'light element' or rare-gas containing solids. Developing these new chemistries represents a challenge and an opportunity for HP research.

Minerals

Results from high-pressure mineralogy provide a guide to developing solid state chemistry of main-group and transition elements under extreme HP–HT conditions. Silicate minerals are usually based on tetrahedrally-coordinated SiO_4. The situation changed dramatically with the discovery of a new rutile-structured polymorph of SiO_2, containing octahedrally-coordinated Si at P > 9 GPa (named 'stishovite', after discoverer Sergei Stishov).[9] Many other minerals are now known to give rise to dense HP structures containing octahedral silicon. $MgSiO_3$-pyroxene contains chains of corner-linked SiO_4 tetrahedra. Under HP–HT conditions, it successively transforms into: an ilmenite-structured phase isostructural with $Fe^{vi}Ti^{vi}O_3$; a silicate garnet (4 $MgSiO_3 = Mg_3(Si^{vi}Mg^{vi})Si_3{}^{iv}O_{12}$), and finally silicate perovskite ($Mg^{viii}Si^{vi}O_3$) above P = 24 GPa. The perovskite phase is stable throughout the entire P-T range of the lower mantle, and it likely constitutes the most abundant silicate mineral within our planet. These results revolutionised our understanding of seismic wave propagation, and the layered structure of the Earth.[1,9] Studies of silicate and germanate perovskites ($MgSiO_3$, $CaSiO_3$, $SrGeO_3$) are also relevant to materials research. Perovskites such as $BaTiO_3$ and $(Pb,Zr)(Zr,Ti)O_3$ ('PZT') are important ferroelectrics, and $LiNbO_3$ is a frequency-doubling material. Introducing small Si^{4+}, Ge^{4+} or V^{5+} cations into the metal sites at high pressure can enhance the dielectric and non-linear optic properties of the materials, both at HP and following decompression to ambient conditions.[10]

Olivine ($[Mg,Fe]_2SiO_4$) is a primary phase of the Earth's upper mantle. Below 400 km (15 GPa, 1300 °C), it first transforms into wadsleyite ('β-Mg_2SiO_4'), containing tetrahedral silicon and 5-coordinated Mg^{2+} ions, and then into silicate spinel. Spinel-structured compounds are well-known in oxide solid state chemistry: they provide important materials like magnetite (Fe_3O_4) for data recording applications. Recent HP–HT experiments have resulted in discovery of spinels that contain nitride ions (N^{3-}) in the place of oxygen.[11] New-discovered nitride spinels (Si_3N_4, Ge_3N_4, Sn_3N_4) contain the 4+ cations on both iv- and vifold coordination sites: these form an unusual new family of compounds containing the group 14 elements in octahedral coordination to nitrogen. The new materials have potentially useful properties: they possess high hardness, and $(Ge,Si)_3N_4$ spinels have wide, direct bandgaps (3–3.5 eV), that are comparable to the newly-developed blue/UV light-emitting diode/laser materials based on (Ga,Al,In) nitride[12]. The ‘elusive’ group 13 nitride P_3N_5 has a layered structure based on PN_4 tetrahedra at ambient P and T: HP treatment (P = 11 GPa) results in a new polymorph containing unusual PN_5 species, and studies at higher pressure indicate the appearance of new phases containing PN_6 octahedra.[13] These results show that there new solid-state chemistries await discovery under HP–HT conditions among dense nitrides, and other series of main-group solid-state compounds and materials.

The industrial synthesis of diamond provided an early grand challenge for HP–HT experimentation.[3] Industrial diamond and cubic-BN now give rise to multi-million £/year industries for the cutting/grinding abrasives markets, as well as providing specialty products for high-performance polycrystalline or single-crystal products, such as scalpels for microsurgery and high heat-load monochromators for synchrotron applications.[14] The technological benefits of HP–HT solid-state chemistry and materials research are now well demonstrated. Materials produced are usually obtained in powdered polycrystalline form, that can be developed as specialty single crystals; however, this limits their eventual applications. However, new materials identified from HP–HT chemistry experiments can also be obtained in thin film form, for example, by chemical vapour deposition (CVD). CVD diamond coatings and semiconductor substrates are now produced industrially. Research into CVD precursors and techniques for accessing high-density phases by metastable means should be pursued in parallel with HP–HT research. Research into new ‘superhard’ compounds occurring within the C–B–N–O system still constitutes an active area of investigation.[15] Cubic boron nitride (c-BN), containing B and N atoms ordered on the diamond lattice constitutes the second-hardest material known. Using similar crystal-chemical systematics used to predict, ‘B_2O’ was also thought to exist. However, boron *sub*oxide (B_6O_{1-x}) grows instead. This compound is based on packing of B_{12} icosahedra, with trigonal O atoms occupying sites between the B_{12} units. Under HP–HT conditions, the angle between trigonal crystallographic axes achieves a ‘magic’ value ~63.4 °, resulting in unusual multiply-twinned macroscopic icosahedra (Fig. 2).[15] HP–HT experiments have also resulted in synthesis of the analogous subnitride B_6N, that is metallic and perhaps a high-T_c superconductor.[2]

The stable form of carbon at ambient P is layered graphite. Low pressure BN also exists in a hexagonal layered form. Hetero-elements such as C and O can be substituted into h-BN layers.[16] Theoretical predictions of dense forms of C_3N_4 that could be harder than diamond led to HP–HT studies of C_xN_y materials. The ‘super-hard’ materials have not been achieved to date. However, new low-density planar polymorphs that are structurally related to graphite have been synthesised. The new C_xN_y ‘graphenes’ are expected to give rise to new ‘soft-chemistry’ reactions, including intercalation and ion-exchange reactions.[16] The appearance of new ‘elemental alloy’ chemistries among ‘simple’ metals and other elements at HP is signalled by recent studies of Cs, Rb, Ba, Ga, As, Sb and Bi.[17] These elements form unusual host-guest structures when compressed to P>10–20 GPa. Formation of the new compounds indicate that valency disproportionation occurs at high pressure, raising the possibility of unusual new ‘single-element’ chemistries to be explored at high densities.

Amorphous materials

Amorphous solids and liquids form a large class of condensed materials. HP treatment usually promotes crystallisation of amorphous substances: however, the ‘reverse’ phenomenon of ‘pressure-induced amorphisation’ (PIA) is now also well known.[18] Compressing solids at low temperatures to avoid transformation into dense crystalline phases results in ‘metastable melting’ to a solid amorphous material, as the metastable extension of crystal-liquid coexistence is crossed below T_g. PIA occurs for many different substances, and it provides a useful method for producing amorphous materials without passing through the liquid state. Dramatic changes in structure and bonding are observed within amorphous materials during densification that have many of the hallmarks of crystalline phase transitions. Such ‘polyamorphism’ and the phenomenon of PIA are linked to the underlying occurrence of density- and entropy-driven phase transitions within liquids, that are now observed in HP–HT experiments.[19] Phenomena associated with density- and entropy-driven changes in the structure and bonding of liquids and amorphous solids is a new branch of physical chemistry that is currently being developed under HP–HT conditions.

Future outlook

As a result of deep Earth and planetary science research, new techniques and instruments have emerged for carrying out experiments under extreme high pressure, combined with high temperature or ultra-low T conditions. The diamond anvil cell provides a versatile miniature chamber for exploring reactions, phase transitions, structures and electronic properties of solids and liquids, well into the multi-megabar regime. Complementary ‘large volume’ apparatus are also used at pressures up to ~50 GPa, for HP–HT syntheses of new materials and crystal growth experiments, and also for *in situ* studies. The stage is now set to exploit these techniques to explore and develop the emerging new areas of solid state and liquid phase chemistry under extreme high-pressure conditions.

References

1 Ed. R. J. Hemley, *Ultrahigh-Pressure Mineralogy: Physics and Chemistry of the Earth's Deep Interior*, Mineral. Soc. America, Washington D.C., 1998; ed. R. J. Hemley, G. L. Chiarotti, M. Bernasconi and L. Ulivi, *‘High Pressure Phenomena’, Proc. Int. School of Physics ‘ Enrico Fermi’, Course CXLVII*, IOS Press, Amsterdam, 2002; L.-G. Liu and W. A. Basset, *Elements, Oxides, Silicates: High-Pressure Phases with Implications for the Earth's Interior*, Oxford University Press, New York, 1986; H. K. Mao and R. J. Hemley, *Mineral. Mag.*, 2002, **66**, 791; T. Irifune, *Mineral. Mag.*, 2002, **66**, 769.

2 P. F. McMillan, *Nature Materials*, 2002, **1**, 19; *High Pressure Res.*, 2003, in press.

3 P. Bridgman, *The Physics of High Pressure*, G. Bell & Sons, London, 1958; W. B. Holzapfel and N. S. Isaacs, *High-Pressure Techniques in Chemistry and Physics*, Oxford University Press, Oxford, 1997.

4 R. M. Hazen, *The Diamond Makers*, Cambridge University Press, 1999.

5 L. J. Parker, T. Atou and J. V. Badding, *Science*, 1996, **273**, 95.

6 J. M. Besson, G. Hamel, T. Grima, R. J. Nelmes, J. S. Loveday, S. Hull and D. Haüsermann, *High Pressure Res.*, 1992, **8**, 625; S. Klotz, J. M. Besson, M. Braden, K. Karch, P. Pavone, D. Strauch and W. G. Marshall, *Phys. Rev. Lett.*, 1997, **79**, 1313.

7 H.-k. Mao and R. J. Hemley, *Rev. Mod. Phys.*, 1994, **66**, 671; R. J. Hemley, *Ann. Rev. Phys. Chem.*, 2000, **51**, 763; S. T. Weir, A. C. Mitchell and W. J. Nellis, *Phys. Rev. Lett.*, 1996, **76**, 1860; R. J. Hemley, Z. G. Soos, M. Hanfland and H.-k. Mao, *Nature*, 1994, **369**, 384; M. Somayazulu, A. Madduri, O. Tschauner, P. F. McMillan, H.-k. Mao and R. J. Hemley,

Phys. Rev. Lett., 2001, **87**, 135504; S. F. Agnew, B. I. Swanson, L. H. Jones and R. L. Mills, *J. Phys. Chem.*, 1985, **89**, 1678; V. Iota, C. S. Yoo and H. Cynn, *Science*, 1999, **283**, 1510; C. S. Yoo, H. Cynn, F. Gygi, G. Galli, V. Iota, M. Nicol, S. Carlson, D. Hausermann and C. Mailhiot, *Phys. Rev. Lett.*, 1999, **83**, 5527; J. Dong, O. F. Sankey, J. Tomfohr, M. Somayazulu, K. Leinenweber and P. F. McMillan, *Phys. Rev. B*, 2000, **62**, 14685; V. Iota and C. S. Yoo, *Phys. Rev. Lett.*, 2001, **86**, 5922; O. Tschauner, H. K. Mao and R. J. Hemley, *Phys. Rev. Lett.*, 2001, **87**, 75701; E. Gregoryanz, A. F. Goncharov, R. J. Hemley and H.-k. Mao, *Phys. Rev. B*, 2001, **64**, 52103; M. I. Eremets, R. J. Hemley, H.-k. Mao and E. A. Gregoryanz, *Nature*, 2001, **411**, 170.

8 D. Londono, W. F. Kuhs and J. L. Finney, *Nature*, 1988, **332**, 141; P. Loubeyre, M. Jean-Louis, R. LeToullec and L. Charon-Gerard, *Phys. Rev. Lett.*, 1993, **70**, 178; P. Loubeyere, R. LeToullec and J. P. Pinceaux, *Phys. Rev. Lett.*, 1994, **72**, 1360; M. S. Somayazulu, R. J. Hemley, A. F. Goncharov, H.-k. Mao and L. W. Finger, *Eur. J. Solid State Inorg. Chem.*, 1997, **34**, 705; I. M. Chou, A. Sharma, R. C. Burruss, J. Shu, H.-k. Mao, R. J. Hemley, A. F. Goncharov, L. A. Stern and S. H. Kirby, *Proc. Nat. Acad. Sci.*, 2000, **97**, 13484; J. S. Loveday, R. J. Nelmes, M. Guthrie, D. D. Klug and J. S. Tse, *Phys. Rev. Lett.*, 2001, **87**, 215501; J. S. Loveday, R. J. Nelmes, M. Guthrie, D. D. Klug, J. S. Tse and Y. P. Handa, *Nature*, 2001, **410**, 661; C. Sanloup, H.-k. Mao and R. J. Hemley, *Proc. Nat. Acad. Sci.*, 2002, **99**, 25.

9 S. M. Stishov, *High Pressure Res.*, 1995, **13**, 245; L.-G. Liu, *Geophys. Res. Lett.*, 1974, **1**, 277; E. Knittle and R. Jeanloz, *Science*, 1987, **235**, 668; E. Knittle and R. Jeanloz, *Science*, 1991, **251**, 1438.

10 A. V. G. Chizmeshya, G. H. Wolf and P. F. McMillan, *Geophys. Res. Lett.*, 1996, **23**, 2725; Grzechnik, H. Hubert, P. F. McMillan and W. T. Petuskey, *Integrated Ferroelectrics*, 1997, **15**, 191; Grzechnik, P. F. McMillan, R. Chamberlain, H. Hubert and A. V. G. Chizmeshya, *Eur. J. Solid State Inorg. Chem.*, 1997, **34**, 269; A. Grzechnik, A. V. G. Chizmeshya, G. H. Wolf and P. F. McMillan, *J. Phys. Condensed Matter*, 1998, **10**, 221.

11 A. Zerr, G. Miehe, G. Serghiou, M. Schwarz, E. Kroke, R. Riedel, H. Fueβ, P. Kroll and R. Boehler, *Nature*, 1999, **400**, 340; K. Leinenweber, M. O′Keeffe, M. Somayazulu, H. Hubert, P. F. McMillan and G. H. Wolf, *Chem. Eur. J.*, 1999, **5**, 3076; G. Serghiou, G. Miehe, O. Tschauner, A. Zerr and R. Boehler, *J. Chem. Phys.*, 1999, **111,**, 4659; T. Sekine, H. He, T. Kobayashi, M. Zhang and F. Xu, *Appl. Phys. Lett.*, 2000, **76**, 3706; E. Soignard, M. Somayazulu, H.-k. Mao, J. Dong, O. F. Sankey and P. F. McMillan, *Solid State Comm.*, 2001, **120**, 237; M. Schwarz, A. Zerr, E. Kroke, G. Miehe, I.-W. Chen, M. Heck, B. Thybusch, B. T. Poe and R. Riedel, *Angew. Chem. Int. Ed.*, 2002, **41**, 788; W. Schnick, *Angew. Chem Int. Ed.*, 1999, **38**, 3309.

12 S. Nakamura, *MRS Bull.*, 1997, **22**, 29; F. A. Ponce and D. P. Bour, *Nature*, 1997, **386**, 351.

13 S. Horstmann, E. Irran and W. Schnick, *Z. Anorg. Allg. Chem.*, 1998, **624**, 620; S. Horstmann, E. Irran and W. Schnick, *Angew. Chem. Int. Ed.*, 1997, **36**, 1873; K. Landskron, H. Buppertz, J. Senker and W. Schnick, *Angew. Chem. Int. Ed.*, 2001, **40**, 2643; J. Dong, A. A. Kinkhabwala and P. F. McMillan, *Phys. Rev. B*, 2003.

14 H. Sumiya, N. Toda and S. Satoh, *J. Crystal Growth*, 1997, **178**, 485; T. Taniguchi, *Jpn. J. Appl. Phys.*, 2002, **241**, L109; J. C. Angus and C. C. Hayman, *Science*, 1988, **241**, 913; C.-S. Yan and Y. K. Vohra, in *Science and Technology of High Pressure*, ed. M. H. Manghnani, W. J. Nellis and M. F. Nicol, Universities Press, Hyderabad, India, 2000, p. 885; S. T. Weir, J. Akella, Y. K. Vohra, S. A. Catledge, C. Ruddle and K. Ghandehari, *ibid*, 2000, p. 82; J. R. Patterson, *J. Nanosci. Nanotechnol.*, 2001, **1**, 143.

15 V. L. Solozhenko, S. N. Dub and N. Novikov, *Diamond and Related Materials*, 2001, **10**, 2228; H. T. Hall and L. A. Compton, *Inorg. Chem.*, 1965, **4**, 1213; T. Endo, M. Sato and M. Shimida, *Japan Tokai Tokyo Koho, No 60-21812*, 1985; T. Endo, M. Sato and M. Shimida, *J. Mat. Sci. Lett.*, 1987, **6**, 683; M. P. Grumbach, O. F. Sankey and P. F. McMillan, *Phys. Rev. B*, 1995, **52**, 15807; H. Hubert, L. A. J. Garvie, K. Leinenweber, P. Buseck, W. T. Petuskey and P. F. McMillan, *MRS Symp.*, 1996, **410**, 191; H. Hubert, L. A. J. Garvie, P. R. Buseck, W. T. Petuskey and P. F. McMillan, *J. Solid State Chem.*, 1997, **133**, 356; H. Hubert, B. Devouard, L. A. J. Garvie, M. O′Keeffe, P. R. Buseck, W. T. Petuskey and P. F. McMillan, *Nature*, 1998, **391**, 376; P. F. McMillan, H. Hubert, A. Chizmeshya, L. A. J. Garvie, W. T. Petuskey and B. Devouard, *J. Solid State Chem.*, 1999, **147**, 281.

16 L. A. J. Garvie, H. Hubert, P. Rez, P. F. McMillan and P. R. Buseck, *J. Alloys Compounds*, 1999, **290**, 34; D. M. Teter and R. J. Hemley, *Science*, 1996, **271**, 53; T. Malkow, *Mat. Sci. Eng. A*, 2001, **302**, 309; J. Kouvetakis, A. Bandari, M. Todd, B. Wilkens and N. Cave, *Chem. Mat.*, 1994, **6**, 811; G. Demazeau, H. Montigaud, B. Tanguy, M. Birot and J. Dunogues, *Rev. High Pressure Sci. Technol.*, 1998, **7**, 1345; Z. Zhang, K. Leinenweber, M. Bauer, L. A. J. Garvie, P. F. McMillan and G. Wolf, *J. Am. Chem. Soc.*, 2001, **123**, 7788.

17 U. Schwarz, A. Grzechnik, K. Syassen, I. Loa and M. Hanfland, *Phys. Rev. Lett.*, 1999, **83**, 4085; R. J. Nelmes, D. R. Allan, M. I. McMahon and S. A. Belmonte, *Phys. Rev. Lett.*, 1999, **83**, 4081; M. I. McMahon, O. Degtyareva and R. J. Nelmes, *Phys. Rev. Lett.*, 2000, **85**, 4896; M. I. McMahon, R. J. Nelmes and S. Rekhi, *Phys. Rev. Lett.*, 2001, **87**, 25502; M. I. McMahon, S. Rekhi and R. J. Nelmes, *Phys. Rev. Lett.*, 2001, **87**, 5501; M. I. McMahon, R. J. Nelmes, J. R. Loveday and S. Rekhi, *Phys. Rev. Lett.*, 2002, **88**, 155503.

18 O. Mishima, L. D. Calvert and E. Whalley, *Nature*, 1984, **310**, 393; O. Mishima, L. D. Calvert and E. Whalley, *Nature*, 1985, **314**, 76; C. A. Angell, *Science*, 1995, **267**, 1924; E. G. Ponyatovsky and O. I. Barkalov, *Mat. Sci. Rep.*, 1992, **8**, 147; P. F. McMillan, *Proc. Enrico Fermi School of Physics on ‘High Pressure Phenomena’*, Italian Physical Society, 2003.

19 P. H. Poole, T. Grande, C. A. Angell and P. F. McMillan, *Science*, 1997, **275**, 322; Y. Katayama, T. Mizutani, W. Utsumi, O. Shimomura, M. Yamakata and K.-I. Funakohi, *Nature*, 2000, **403**, 170; M. C. Wilding and P. F. McMillan, *J. Non-Cryst. Solids*, 2001, **293**, 357; S. K. Deb, M. C. Wilding, M. Somayazulu and P. F. McMillan, *Nature*, 2001, **414**, 528.