

2. INSTRUMENTATION AND SAMPLE PREPARATION

hence to increase the attainable pressure, which is inversely proportional to the chamber diameter;

- (v) The microbeam can illuminate a small selected portion of the sample chosen for the investigation, which can be used to perform single-crystal diffraction on a selected grain or for X-ray tomography of the sample and its inclusions;
- (vi) The beam diameter is smaller than the diameter of the chamber, which minimizes or even eliminates the effects of beam shadowing;
- (vii) The X-ray wavelength is tuneable down to about 0.3 Å. This considerably increases the data completeness and reduces absorption effects in the sample and DAC.

Owing to these features, synchrotron beams are ideally suited for high-pressure diffraction experiments and some researchers have completely stopped using in-house laboratory equipment with sealed X-ray tubes. Historically, the first use of synchrotron radiation for high-pressure studies was reported by Buras, Olsen & Gerward (1977) and Buras, Olsen, Gerward *et al.* (1977). Conventional diffractometers with sealed X-ray tubes can be effectively used for preliminary powder diffraction experiments. For example, a new high-pressure phase of (+)-sucrose was found in this way (Patyk *et al.*, 2012), although the data were insufficient for any structural refinements.

Diffraction data are collected in single and multiple exposures, and the pressure is controlled remotely by inflating a membrane through a gas system. Currently assembled high-pressure powder diffraction synchrotron beamlines incorporate on-line pressure calibration using ruby fluorescence and, often, Raman spectroscopy.

2.7.10. Sample preparation

Several basic techniques can be used to prepare a sample for a high-pressure experiment, for example:

- (i) A solid sample can be mounted under ambient conditions in the high-pressure chamber together with the hydrostatic fluid, then sealed and pressurized;
- (ii) A solid sample can be mounted under ambient conditions in the high-pressure chamber, condensed gas loaded at elevated pressure (Tkacz, 1995; Rivers *et al.*, 2008; Couzinet *et al.*, 2003; Mills *et al.*, 1980; Yagi *et al.*, 1996; Kenichi *et al.*, 2001) or under cryogenic conditions, and the sample sealed and further pressurized by gasket compression;
- (iii) A liquid sample can fill the whole chamber volume under ambient conditions, or condensed gases or their mixtures can be loaded at elevated pressure, and after sealing the DAC the sample is frozen under isothermal conditions;
- (iv) A crystal of the pure compound or of a solvate can precipitate from the mixture (solution) when compressed isothermally – the crystal can be in the form of a single crystal or a powder, fully or partly filling the DAC chamber;
- (v) Samples completely filling the DAC chamber can be compressed isothermally or undergo isochoric treatment, but strains can be generated in a single crystal or in the grains of a compressed powder conglomerate by anisotropic thermal contraction/expansion; this strain can be avoided by having an excess of the hydrostatic component of the mixture;
- (vi) A solid powdered sample can be mixed with a powder of another compound, which is much softer than the sample and is used as a pseudo-hydrostatic medium (halite and MgO are often used for this purpose) – this technique is mainly used for cubic or isotropic samples in large-volume

presses, where (pseudo)isotropic strain and pseudo-spherical compression minimize the effect of preferential orientation in the sample.

Preferential orientation can significantly hamper the quality of powder diffraction data, and corrections for this effect should be applied in the Rietveld refinement. All Rietveld refinement programs include preferential orientation models, which fit the data with satisfactory results (McMahon, 2004, 2005; Filinchuk, 2010).

2.7.11. Hydrostatic conditions

Hydrostatic conditions in the sample chamber are essential for good-quality high-pressure diffraction data. They are equally important for single-crystal and powder diffraction experiments. To secure hydrostaticity, the sample is submerged in a hydrostatic medium. The pressure and temperature ranges of the planned experiment depend on the hydrostatic properties of the applied medium. Eventually all substances solidify because of crystallization or vitrification (Piermarini *et al.*, 1973; Eggert *et al.*, 1992; Grocholski & Jeanloz, 2005), which can lead to damage of single crystals, anisotropic strain in powder grains and inhomogeneity of pressure across the sample. It is also important to protect a solid sample from dissolution in the hydrostatic fluid. The dissolved sample can lose its required features (such as shape, polymorphic form or chemical composition) and recrystallize at higher pressure in an undesired form. For example, a fine powder may recrystallize into a few large and preferentially oriented grains. Another potential problem can arise from reactions between the sample and the hydrostatic medium. For example, a pure compound can form solvates incorporating molecules of the hydrostatic fluid (Olejniczak & Katrusiak, 2010, 2011; Andrzejewski *et al.*, 2011; Tomkowiak *et al.*, 2013; Boldyreva *et al.*, 2002; Fabbiani & Pulham, 2006). This has also been observed for helium and argon penetrating into the structures of the fullerenes C₆₀ and C₇₀ (Samara *et al.*, 1993) and into arsenolite As₄O₆ (Guńka *et al.*, 2015). High-pressure crystallization of water in the presence of helium leads to an inclusion compound interpreted as ice XII. Therefore, the hydrostatic medium should be carefully chosen for a specific experiment, depending on the sample solubility, the pressure range and the type of investigation, whether a mounted-sample study, or *in situ* crystallization or reaction (Sobczak *et al.*, 2018; Pórolniczak *et al.*, 2018).

Many minerals and inorganic samples hardly dissolve at all and a commonly applied pressure-transmitting medium is a mixture of methanol, ethanol and water (16:3:1 by volume), hydrostatic to over 10 GPa at 296 K (see Table 2.7.1); separately, pure methanol crystallizes at 3.5 GPa, ethanol at 1.8 GPa and water at 1.0 GPa. If a sample dissolves well in methanol, ethanol and water, other fluids can be selected (Piermarini *et al.*, 1973; Angel *et al.*, 2007). Liquids like glycerine (hydrostatic to 3 GPa) and special inert fluids, such as silicone oil (Shen *et al.*, 2004; Ragan *et al.*, 1996), Daphne oil (Yokogawa *et al.*, 2007; Murata *et al.*, 2008; Klotz *et al.*, 2009), or condensed gases, like helium, argon and hydrogen (Tkacz, 1995; Dewaele & Loubeyre, 2007), can be used. Alternatively, a saturated solution of the sample compound, for example in a methanol–ethanol–water mixture, can prevent sample dissolution, but on increasing the pressure the compound can precipitate in the form of a powder or single crystals. One can choose to load an excess of the sample into the chamber before filling it up with the hydrostatic fluid, which would dissolve only some of the sample.

2.7. HIGH-PRESSURE DEVICES

Table 2.7.1

The (pseudo)hydrostatic limits of selected media at 296 K (Holzapfel, 1997; Miletich *et al.*, 2000)

Medium	Freezing point (GPa)	(Pseudo)hydrostatic limit (GPa)	Reference
4:1 Methanol:ethanol	–	9.8	Angel <i>et al.</i> (2007)
16:3:1 Methanol:ethanol:water	–	10.5	Angel <i>et al.</i> (2007)
Anhydrous propan-2-ol	–	4.2	Angel <i>et al.</i> (2007)
Neon	4.7	19	Klotz <i>et al.</i> (2009)
Argon	1.2	9/35	Bell & Mao (1981)/You <i>et al.</i> (2009)
Helium	11.8	70/150	Bell & Mao (1981)/Dewaele & Loubeyre (2007)
Hydrogen	5.7	177	Mao & Bell (1979)
Nitrogen	2.4	13	LeSar <i>et al.</i> (1979)
Glycerol	–	1.4	Angel <i>et al.</i> (2007)
Glycerin	–	3.0	Hazen & Finger (1982)
Glycerin	–	4.0	Tateiwa & Haga (2010)
Fluorinert FC84/87	–	7.0	Klotz <i>et al.</i> (2009)
Petroleum ether	–	6.0	Mao & Bell (1979)
Isopropyl alcohol	–	4.3	Piermarini <i>et al.</i> (1973)
1:1 Pentane:isopentane	–	7.4	Piermarini <i>et al.</i> (1973)
Silicone oil, viscosity 0.65 cSt	–	0.9	Angel <i>et al.</i> (2007)
Silicone oil	–	14	Klotz <i>et al.</i> (2009)
Daphne oil 7373	–	2.3	Murata <i>et al.</i> (2008)
Daphne oil 7474	–	3.7 at 296 K/6.7 at 273 K	Klotz <i>et al.</i> (2009)/Tateiwa & Haga (2010)
Vaseline	–	2.0	Tateiwa & Haga (2010)
NaCl	–	0.05/25	Tateiwa & Haga (2010)/You <i>et al.</i> (2009)

In situ crystallization at high pressure requires good, though not necessarily very good, solvents. Also, co-crystallizations can be performed in the DAC, and in this case the product that is obtained can depend on the solvents used and their concentration. Pressure effectively modifies intermolecular interactions, and new solvates can be obtained depending on the concentration of the substrates. It can be tricky to avoid co-crystallization of some compounds; in these cases a range of hydrostatic fluids has to be tried. A mixture of petroleum ethers, silicone or Daphne oils can be a good choice. Daphne oil, consisting mainly of alkylsilane (Murata *et al.*, 2008), has the rare feature of negligible thermal expansion, which is particularly useful for low-temperature high-pressure experiments: the DAC can be loaded under normal conditions and then pressurized and cooled to the required temperature, *e.g.* in a cryostat, without significant loss of pressure due to contraction of the medium.

The hydrostatic conditions can be checked by inspecting the width of reflections from the sample (full width at half-maximum, FWHM, is usually plotted), the width of the ruby fluorescence R_1 line and the R_1 – R_2 line separation (You *et al.*, 2009). The pressure homogeneity can be checked by measurements for several ruby chips mounted across the DAC chamber. Nonhydrostatic conditions can cause inconsistent results and difficulties in their interpretation, which can prompt the researcher to consider changing the hydrostatic medium.

For hard samples, some departure from hydrostatic conditions is often acceptable. It is assumed that for a hard sample the nonhydrostatic compression component is small in a much softer medium, for example, hard corundum studied in soft NaCl. On the other hand, it may be easier to prepare a sample under normal conditions by uniformly mixing the powder of the specimen with a pseudo-hydrostatic medium, rather than using hydrostatic liquids or gases. The diffraction from the pseudo-hydrostatic medium powder can be used to monitor the pressure and measure non-hydrostaticity effects. Pseudo-hydrostatic solid media are often used for multi-anvil presses, where a solid sample facilitates loading and the uniaxial stress is not as drastic as in the opposed-anvil presses. Also, in high-temperature experiments the process of annealing reduces non-hydrostatic strain.

A relatively low nonhydrostatic effect was reported for argon frozen at 1.9 GPa: its pressure gradient up to 1% only is supported at 9 GPa (Bell & Mao, 1981) and up to 1.5% at 80 GPa (Liu *et al.*, 1990). This illustrates how the pseudo-hydrostaticity limit can be extended depending on the hardness of the specimen, the type of high-pressure device and the acceptance of deviatoric stress in the sample.

At very high pressure, exceeding 60 GPa, no compounds persisting as liquids are known (*cf.* Table 2.7.1). Diffraction data must then be corrected for a deviatoric stress component, causing the broadening of reflection rings and affecting their $2\theta_{\text{Bragg}}$ positions, when the uniaxial stress is not collinear with the incident beam (Singh, 1993; Singh & Balasingh, 1994; Singh *et al.*, 1998; Mao *et al.*, 1998). The effect of uniaxial stress can be reduced or eliminated by sample annealing, which is often applied to improve the hydrostaticity of the sample.

2.7.12. High-pressure chamber and gasket in the DAC

A high-pressure device should be adjusted to the experiments planned, and in particular to the chemical activity of the sample. Gaseous hydrogen penetrates and dissolves in most metals, and therefore special alloys, such as beryllium bronze, have to be used for hydrogen setups. For some experiments non-metallic gaskets can be used, for example amorphous boron, corundum or diamond powders mixed with a resin. Owing to the insulating properties of such a gasket, the pressure dependence of the electric, dielectric and magnetic properties of the sample can be measured. Chemically aggressive samples can interact with the gasket material of the DAC chamber, and even with the diamond anvils, and this effect usually intensifies at high temperature and pressure. Consequently, both the sample and the high-pressure device can be affected. The erosion caused by an aggressive liquid can be considerably slowed down by its crystallization, which freezes the diffusion of molecules into the gasket. For example, *in situ* crystallization of halogen derivatives of acetic acid could only be performed in a DAC chamber with tungsten gaskets (Gajda & Katrusiak, 2009). In these experiments, the gasket was gradually eroded by the acid, but after its crystal-