Chapter 9
Taking It to Extremes – Powder Diffraction Under Non-Ambient Conditions

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Abstract Structural studies of materials under elevated pressures provide a fascinating insight into the physical and chemical behaviour of matter under the wide range of conditions experienced throughout the Universe. Both x-ray and neutron powder diffraction techniques play a crucial role in structural studies and are therefore at the forefront of high-pressure research. These notes provide a short introduction to the principles and experimental practice of high-pressure powder diffraction techniques.

9.1 Introduction

Although on the surface of the Earth we rarely experience pressures that deviate significantly from 1 atm, much of the Universe experiences a much wider range of pressures that span the near vacuum of outer space to the pressure at the centre of a neutron star (estimated to be 10^{30} atm). Even on Earth there is a significant variation – at the bottom of the Mariana Trench in the Pacific Ocean at a depth of 11,000 m, the pressure is over 1,000 atm, and the pressure at the centre of the Earth is 3.5 million atmospheres. Under this range of extreme conditions, structural and chemical changes in materials can be dramatic – proteins are denatured; pathogenic bacteria are destroyed; ice melts above 100°C; graphite turns to diamond; and non-metals become metallic. Such conditions also provide a rich regime for geochemical synthesis – diamonds, garnets, and perovskites are just a few of the many minerals produced under extreme conditions within the Earth. The domain of pressure therefore provides an exciting additional dimension to explore structure, chemical

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reactivity, and physical properties. At the same time it provides a powerful way to test computational models, with a particular focus on the validation of the efficacy of intermolecular potentials.

It is for these reasons that high-pressure research attracts such interest across a wide range of disciplines that includes: geosciences; physics; chemistry; materials science; biology; engineering; and astronomy. Since physical properties are intrinsically linked to structure, structural studies are key to understanding how matter behaves under extreme conditions. Both x-ray and neutron powder diffraction techniques therefore play a crucial role in such structural studies. These notes will therefore provide a short introduction to high-pressure powder diffraction techniques.

9.2 Techniques

High-pressure structural science is a particularly good example of an area that relies upon the complementarity of various techniques to achieve the final aim of the structural characterisation of novel materials. The advances in this field are intertwined with the evolution of complex sample environments for experiments at elevated temperatures and/or pressures, as well as the development of techniques for the collection and analysis of spectroscopic and diffraction data under extreme conditions. In particular, developments of high brightness X-ray and neutron sources, coupled with the enhancement of associated detectors, have played a major part in advancing powder diffraction studies at extreme conditions [1].

9.2.1 The Diamond-Anvil Cell

High-pressure X-ray diffraction measurements are generally performed using a gasketed diamond-anvil cell (DAC). The premise for this device is relatively simple; the sample is placed between two diamond faces (culets) and is subjected to high pressures when a force pushes the opposed anvils together (see Fig. 9.1). The DAC utilised in this work was based on developments by Merrill and Bassett in 1974 [2]. The small size ($\sim$5 cm diameter) and relative ease of use make these cells extremely versatile and perfectly suited for high-pressure X-ray diffraction studies. Depending on the size of the culets and the gasket hole, pressures beyond 100 GPa can be obtained. Note that in high-pressure research it is common to find various units used, sometimes interchangeably, as a measure of pressure. Gigapascals (GPa) may be related to other units as follows:

$$1\,\text{GPa} = 10\,\text{kbar} = 9869.2\ \text{atm}.$$

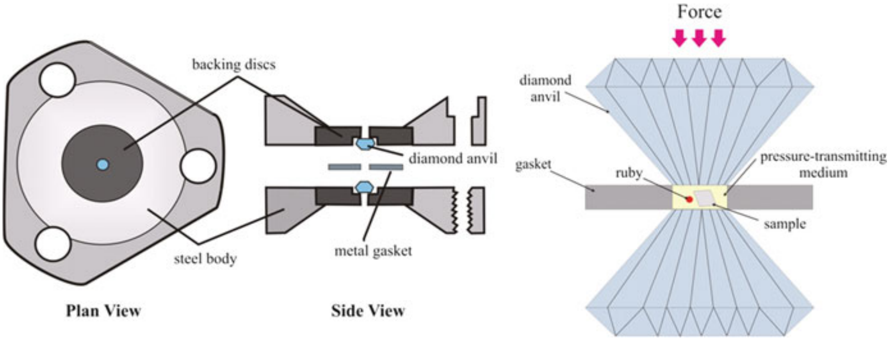

Fig. 9.1 Schematic representation of Merrill-Bassett diamond-anvil cell

The experimental set-up for a typical high-pressure X-ray powder diffraction experiment is represented in Fig. 9.2a. Data are collected on an image plate detector and are generally processed according to the procedure outlined for ambient-pressure powder diffraction, although in some cases it may also be necessary to mask out intense single-crystal reflections arising from the diamond anvils to ensure no anomalies occur in the I_{obs} *vs* 2θ profile. The image can then be integrated to provide the one-dimensional powder diffraction pattern using programs such as Fit2D [3].

It is also possible to mask intense powder diffraction rings due to the tungsten gasket, although should this interfere with sample peaks it is also possible to perform Rietveld refinements in which the tungsten diffraction pattern is incorporated. Finally the data can be integrated to give a plot of diffraction intensity against scattering angle. The large background common to such data collections is due to Compton (inelastic) scattering from the diamonds and can be subtracted prior to data refinement.

9.2.2 Radiation Sources

Whilst in principle it is possible to record powder diffraction patterns on laboratory instruments using conventional sealed sources (e.g. Mo-K_α), far superior results can be obtained using synchrotron sources that combine high flux with tuneable wavelength and low divergence. Beam diameters of less than 30 μm are easily obtained and hence allow one to record diffraction patterns for heterogeneous samples and without contamination from the DAC components. In such studies, however, great care must be taken to ensure effective powder averaging of such a small sample volume. This is typically achieved by ensuring that the DAC is loaded with a very finely ground powder and rocking the DAC through an angle of 5–20°.

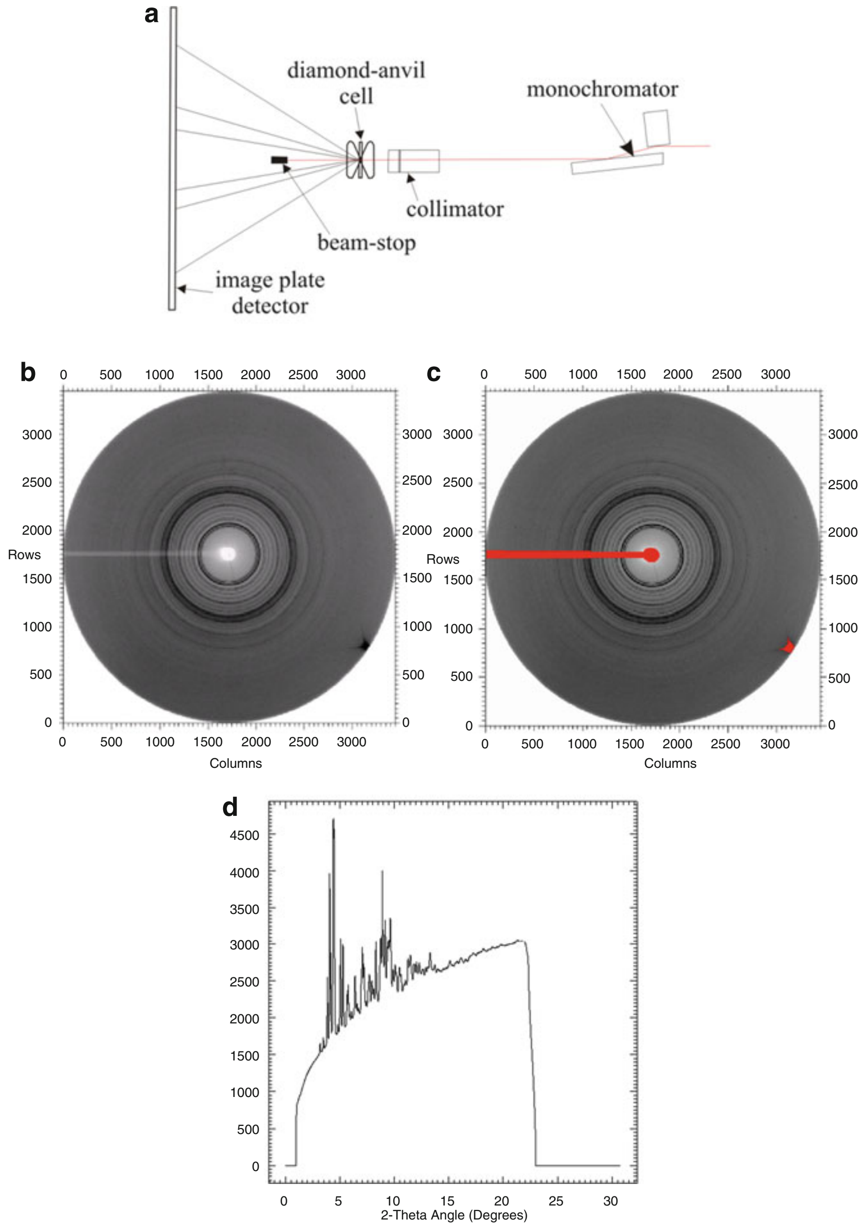

Fig. 9.2 (**a**) Schematic illustrating the key components of a high-pressure X-ray powder diffraction experiment. (**b**)–(**d**) Schematic illustrating the stages of data reduction. The raw image is shown in (**b**). The *concentric rings* correspond to the diffracted intensities from the sample; the *dark spot* at the edge of the image is an intense diamond reflection

9.2.3 Pressure Measurement in the DAC

Direct pressure measurement from the applied force is both inaccurate and impractical. Instead, Piermarini *et al.* demonstrated that a small chip or sphere of ruby (Al_2O_3:Cr^{3+}) could serve as a continuous pressure sensor within the DAC by utilising its laser-induced fluorescence [4]. Indeed the simplicity of the ruby fluorescence method for *in situ* pressure calibration is without question a contributing factor to the widespread application of diamond-anvil cell techniques and, as such, was the subject of an extensive review by Syassen in 2008 [5]. The spectral lines of ruby undergo a pronounced redshift with applied pressure; the R_1 electronic transition shows a linear dependence with pressure up to at least 20 GPa at ambient temperature [4].

9.2.4 The Paris-Edinburgh Cell

Neutron diffraction experiments require sample volumes *ca* 10^6 times larger than those required for X-ray powder diffraction, thus precluding the use of diamond-anvil cells. High-pressure neutron diffraction experiments were therefore severely limited until the advent of the Paris-Edinburgh cell (P-E Cell), developed in 1992, which extended the pressure range to 10–20 GPa [6]. The popularity of the P-E Cell arose from its (relatively) light-weight design and its portability – the Paris-Edinburgh cell weighs ∼50 kg, in contrast to other commercial devices of the time with comparable sample volume that weighed close to 1 tonne. This portability, coupled with the fact that loads can be applied to the cell by a hydraulic ram while it remains *in situ* on the beamline, greatly simplified high-pressure experiments. The P-E Cell is also an opposed-anvil device, like the diamond-anvil cell and the Bridgman cell. In this construction, however, the sample is compressed between anvils made of either tungsten carbide (WC) or sintered diamond, see Fig. 9.3a. Early designs utilised null-scattering TiZr toroidal gaskets located into corresponding grooves machined into the anvil faces to confine the sample and, generally, a solid pressure-transmitting medium. Compression studies using the preferred fluid pressure-transmitting media (methanol:ethanol and iso:n-pentane) were limited to *ca* 2.0 GPa before anvil failure. It was realised that complete encapsulation of the sample and pressure-transmitting medium in two flanged hemispherical caps (TiZr) would prevent the fluid media coming into direct contact with the anvil surface [7]. In this way the anvils were shown to be protected and the available pressure range for hydrostatic studies were extended up to the freezing pressure of methanol:ethanol (*i.e.* ∼10 GPa). The encapsulated gasket is compared to the 'standard' TiZr toroidal gasket in Fig. 9.3b.

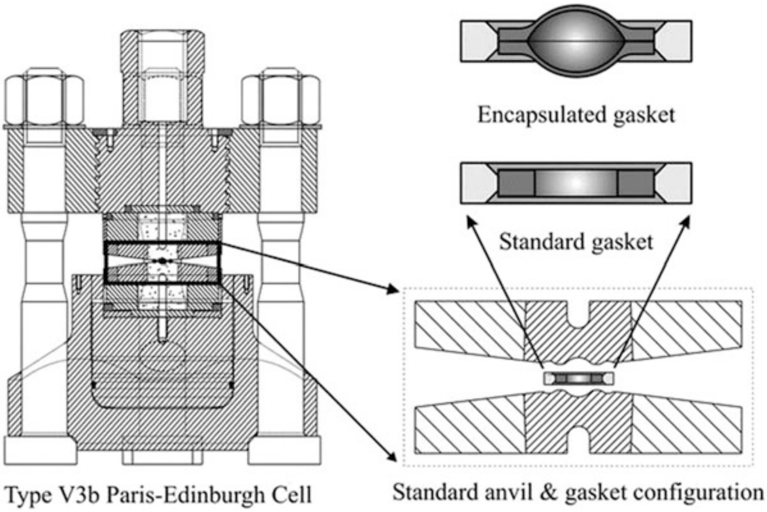

Fig. 9.3 (**a**) Cross-section of the Paris-Edinburgh cell (V3b) and (**b**) a comparison of the standard and encapsulated gaskets [7]

9.2.5 Pressure Measurement in the Paris-Edinburgh Cell

Unlike the diamond-anvil cell, the Paris-Edinburgh cell does not allow optical access to the sample chamber and therefore a method for pressure calibration other than the ruby fluorescence method had to be developed. Instead, small quantities of internal pressure calibrants are used, typically either NaCl(s) or Pb(s). Both materials have clearly defined equations of state which means that the unit cell volume of the chosen calibrant (as determined by Rietveld refinement of the powder diffraction patterns) is directly related to the pressure within the gasket.

9.3 Pressure-Transmitting Media

In most powder diffraction experiments it is desirable to ensure that the stress applied to the sample is homogeneous and that the sample is free of any differential stress or induced shear strain over the entire pressure range of the experiment. In order to achieve these conditions, the powder must be immersed in a medium that displays hydrostatic behaviour. The consequences of a non-hydrostaticity include: inhomogeneous strain in the crystallites leading to broadening of Bragg peaks with associated loss of resolution and signal-to-noise; modification of the relative evolution of unit cell parameters; and difficulties in measuring the pressure using the ruby-fluorescence technique. Non-hydrostatic stresses may therefore adversely affect results from equation of state and elasticity studies, especially those aimed at

Table 9.1 Nominal hydrostatic limits of pressure-transmitting media (From refs. [12] and [13])

Medium	Hydrostatic limit/GPa
4:1 methanol:ethanol	9.8–10.5
16:3:1 methanol:ethanol:water	10.5
Anhydrous 2-propanol (isopropanol)	4.2
Glycerol	1.4
1:1 Pentane:iso-pentane	7.4
Silicone oil (various viscosities)	0.9
Fluorinert	2.0
Argon	1.9
Nitrogen	3.0
Neon	15
Helium	23

obtaining accurate pressure derivatives of elastic moduli. Non-hydrostatic stresses can also promote or suppress phase transitions [8, 9] and they can promote the amorphisation of crystalline samples [10, 11]. Table 9.1 shows the nominal hydrostatic limits of some common pressure-transmitting media. There is considerable variation within the literature about the precise values of hydrostatic limits – this arises because of the different ways that loss of hydrostaticity can be assessed. The onset of line-broadening of the fluorescence spectra of ruby chips immersed in the medium has often been used, but ruby is a relatively stiff material with a bulk modulus of about 254 GPa and is thus intrinsically less sensitive to non-hydrostatic stresses than most minerals or molecular compounds. Furthermore, the fluorescence spectra are intrinsically broad as a result of defects and strains within the ruby crystals, unless the crystallites have been very carefully annealed. More recently a systematic, more sensitive, ruby-fluorescence study has been performed, which monitored values of the pressure gradients across the sample chamber for the pressure-solidified medium [12]. An alternative method for monitoring non-hydrostatic stresses is to measure the widths of the diffraction peaks of quartz single crystals [13]. Quartz is available as gem-quality samples that have intrinsically sharp diffraction peaks and it has a low bulk modulus, which make the peak positions and widths sensitive to small non-hydrostatic stresses. Gigahertz ultrasonic interferometry has also been used to detect the onset of the pressure-induced glass transition in methanol:ethanol mixtures [13].

It should also be noted that neutron experiments require the use of fully deuterated pressure-transmitting media since hydrogen-containing material produces a strong background due to the large incoherent cross section of hydrogen.

9.4 Further Reading

References [14, 15], which represent proceedings of previous Erice Schools, give a flavour of research in the field of high-pressure crystallography. Reference [16] is an informative review of high-pressure chemistry that highlights some of the fascinating structural changes induced by elevated pressures. References [17–21] provide a combination of tutorial and critical reviews that cover a range of high-pressure research from simple metals through molecular compounds to ceramic materials.

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