

Grain-size control *in situ* at high pressures and high temperatures in a diamond-anvil cell

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The grain-size distribution and the character of individual grain boundaries in microcrystalline networks play a significant role in material properties, such as melting temperature, diffusion coefficients, resistivity, optical absorption, elastic constants, phase transformation pressure, and so on. In this study, the grain size of NaCl, SiO₂ and FeC₃ is controlled *in situ* at high pressures over the entire range of the length scale of crystallinity: single-crystal, micro-/nanocrystalline and amorphous materials within a volume commensurate with the size of the probing X-ray beam. The structure refinement of high-pressure samples from X-ray diffraction data can be significantly improved by controlling grain size by selecting the structure of starting materials and following certain high pressure–temperature–time paths.

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1. Introduction

Single-crystal X-ray diffraction is the most powerful technique for crystal structure determination under ambient conditions. In high-pressure studies, however, the single-crystal technique is restricted by limited angular access to the sample in the diamond-anvil cell (DAC) and by the requirement of having a high-quality thin crystal (thickness usually less than 10 µm) sustained in the desired pressure range. Therefore, so far, powder diffraction is still the most routinely used technique for structure solution under extremely high pressure and high temperature conditions.

X-ray powder diffraction is a superposition of Bragg reflections from randomly oriented single crystals. However, in practice the macroscopically observable powder diffraction pattern is more complicated than a simple orientation averaging of the reciprocal lattice of the irradiated individual crystallites. Intensities, profiles and positions of powder diffraction lines essentially depend on the type of the lattice-disorder statistics and the microscopic architecture of the sample (Warren, 1990). Any factor which results in a modification of the *d*-spacing distribution will change the shape, particularly the width and intensity, of the peak (excluding instrumental broadening): the finite size and shape of crystals, deformation, thermal oscillations of the atoms at their regular lattice sites, vacancy and impurity, element concentration gradient *etc.* (Klimanek, 1991).

The length scale of the periodic structure in the finite volume of a solid is the fundamental parameter for the

microscopic description of that solid: single crystal (periodic across the entire volume), polycrystalline (periodic across each grain) and amorphous (non-periodic). Over the last two decades, a new subclass of polycrystalline material with unique chemical and physical properties has been developed: nanocrystalline materials (Gleiter, 2000). There is no exact boundary to distinguish nanocrystalline from microcrystalline material. In general, the specific behavior of materials defines the nanocrystalline state, with phenomena that cannot be seen at smaller or larger grain size (Navrotsky, 2001). Typical nanocrystalline materials have a grain size of less than 100 nm (Gurin *et al.*, 2001; Dubrovinskaia *et al.*, 2005).

The boundary separating grains of crystals having different crystallographic orientation plays a significant role in controlling the properties and the behavior of polycrystalline materials. Although the importance of grain boundaries has long been recognized, many fundamental aspects of grain boundary behavior remain poorly understood, especially under extreme conditions.

In most crystalline solids, a grain boundary is typically only one to three atoms in thickness. However, as grain size decreases, the volume percentage of grain boundaries with respect to bulk crystallites increases. Assuming an average grain interface thickness of 0.3 nm, an equant grain of 10 nm consists of 20 vol% grain interface. Grain boundaries have a distorted structure unavoidable for geometrical reasons, resulting in a large excess of free energy (Sutton & Balluffi, 1995). The structural arrangement within a grain boundary is non-uniform in composition, average coordination number of

atoms and bond lengths compared with the single-crystal structure. Hence, the large number of atoms associated with the grain boundaries can significantly change the physical and chemical properties of polycrystalline materials: melting temperature, diffusion coefficient, resistivity, optical absorption, elastic constants, phase transformation path *etc* (Thornton *et al.*, 2003).

Thus, grain size and grain boundaries are important parameters that should be taken into account in high-pressure research and particularly in diffraction studies. In this study, the effects of pressure, temperature and quench rate on crystal growth from different starting materials have been studied in a diamond-anvil cell using synchrotron X-ray diffraction techniques.

2. Experiment details

Various types of DACs (membrane, symmetrical and four-pin) were used for pressure generation up to ~ 60 GPa. The samples were loaded into the 100–150 μm holes in stainless steel or rhenium gaskets, pre-indented to a thickness of 20–40 μm . NaCl samples were dried for 24 h in a vacuum furnace at ~ 400 K before loading in the DAC. A high-resolution scanning electron microscope (Hitachi S-4700-II) was used to analyse the grain size of the quenched samples.

Amorphous silica with a highly disordered network was synthesized by the sol–gel technique (Prokopenko *et al.*, 2001). In order to absorb laser radiation, the SiO_2 powder was mixed with boron powder (~ 3 at%) and loaded into a symmetrical DAC. Gold powder compressed into a foil of thickness 5 μm was used as a pressure marker (Anderson, 1995). The Fe_3C sample was synthesized in a large-volume press at 4 GPa and ~ 1600 K and ground prior to loading into the DAC. NaCl was used as a thermal insulator and pressure marker (Sata *et al.*, 2002). High-resolution angle-dispersive X-ray diffraction experiments were performed using online area detectors (MAR345 or MAR-CCD) and high-energy (37.077 keV, 0.3344 \AA) X-radiation focused to 6 $\mu\text{m} \times 6 \mu\text{m}$ at the GSECARS beamline of sector 13 at the Advanced Photon Source, USA. A double-sided laser-heating system (Shen *et al.*, 2001) was used with simultaneous temperature control and X-ray diffraction measurements.

The natural monoclinic tridymite (SiO_2) from San Cristobal (Mexico) used in this experiment was provided by Dr P. Nysten (Uppsala University, Sweden). The sample was loaded into a membrane DAC (300 μm -diameter diamonds culet size) with a stainless steel gasket without a pressure medium. A gold wire of diameter 5 μm was used as a pressure marker. Powder diffraction data were collected at beamline ID30 of the ESRF with a MAR345 imaging plate using a 0.3738 \AA -wavelength X-ray beam focused to 10 $\mu\text{m} \times 15 \mu\text{m}$.

3. Results and discussion

The pressure effect on the NaCl grain size is illustrated in Fig. 1. The sample was quenched from different pressures: 24 GPa (Fig. 1a) and 36 GPa (Fig. 1b). The same starting

material was used in both cases with an average grain size of $\sim 3 \mu\text{m}$. It is clear that pressure-induced phase transformation at room temperature, $\text{B1} \rightarrow \text{B2}$, at ~ 30 GPa can drastically reduce the NaCl grain size to less than $\sim 1 \mu\text{m}$, while sample quenching from 24 GPa (still B1 phase) shows a larger grain size distribution, from $\sim 1 \mu\text{m}$ to $\sim 5 \mu\text{m}$.

The high-resolution angle-dispersive X-ray diffraction technique is one of the routine methods for probing structural properties of materials *in situ* at high pressures and temperatures. However, experience shows that, as pressure is increased in a DAC at room temperature, the diffraction peaks become broader owing to complex stress (Funamori *et al.*, 1997; Dubrovinsky & Dubrovinskaia, 2004). High-temperature annealing is required to release the stress (Wenk *et al.*, 2004). The high-temperature heating often causes crystal growth, resulting in ‘spotty’ diffraction patterns when the grain size of the material is comparable with the X-ray beam size (typically 5–15 μm for a focused synchrotron beam). In this case, without sample scanning, reciprocal space cannot be completely covered, and reliable intensity required for Rietveld refinement cannot be obtained. One of the ways of solving this problem is to synthesize microcrystalline samples *in situ* at high pressures. A small grain size compared with the X-ray beam size can be obtained by heating amorphous

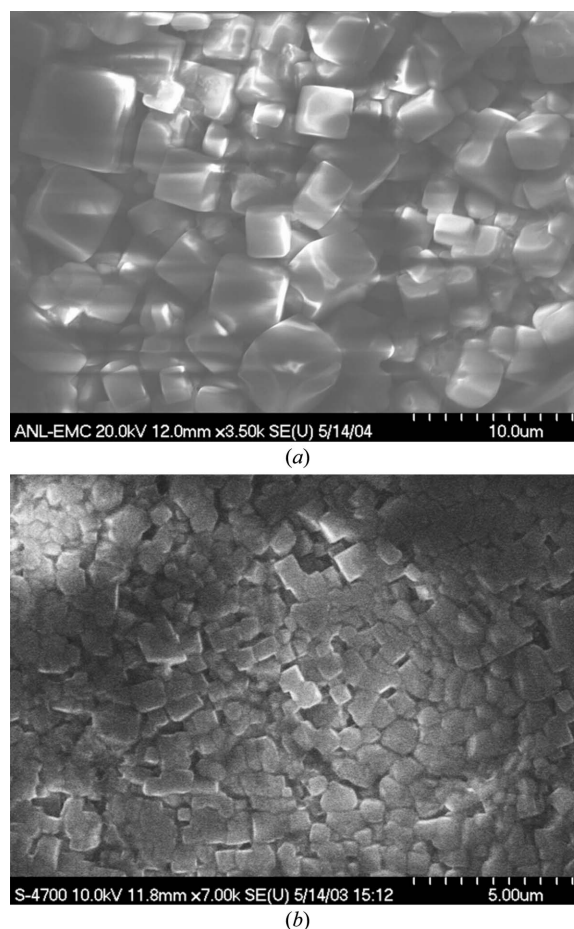


Figure 1
SEM images of NaCl samples quenched from different peak pressures: (a) 24 GPa and (b) 36 GPa.

SXD at Mbar pressures

materials at relatively low temperature and at high pressure. Fig. 2 shows the result of double-side laser heating of amorphous SiO_2 at ~ 1200 K and 53 GPa for 60 s (Prakapenka *et al.*, 2004). The relatively low heating (typically in the range 1000–1400 K for silicates) for a short time (10–60 s) induces crystallization of the amorphous solid but limits grain growth, resulting in smooth microcrystalline powder diffraction patterns, as shown in Fig. 2(b). However, extensive heating at higher temperatures may provoke significant crystal growth, leading to a spotty diffraction pattern unsuitable for Rietveld refinement.

Another way to synthesize microcrystalline materials in order to improve structure refinement from X-ray diffraction data is to use fast quenching of molten materials, a well established method in material science. However, it is very challenging to keep samples at temperatures above their melting point for any length of time in the DAC because of the drastically increased mobility and reactivity of the molten samples with surrounding materials such as pressure medium, gasket and diamond anvils (Prakapenka *et al.*, 2003/2004). Melting temperatures in the DAC are often reached with the

laser-heating technique. Special care must be taken to load the sample into the DAC between layers of low-thermal-conductivity material of equal thickness to insulate the sample from the highly conductive diamonds.

To test this approach, we performed experiments on Fe_3C samples. Melting of Fe_3C at 58 GPa was observed at ~ 3100 K, determined by the appearance of diffuse scattering from the molten sample. Fig. 3(a) shows a typical X-ray scattering pattern from Fe_3C liquid collected for 10 s. The corresponding integrated spectrum is shown in Fig. 4(a). After gradual temperature reduction to ambient conditions within 1 s, a very ‘spotty’ diffraction pattern appeared (Figs. 3b and 4b) owing to the grain growth. In the case of fast temperature quenching (in less than 1 ms) of the molten sample, achieved by closing the laser beam shutter, very smooth powder diffraction lines were

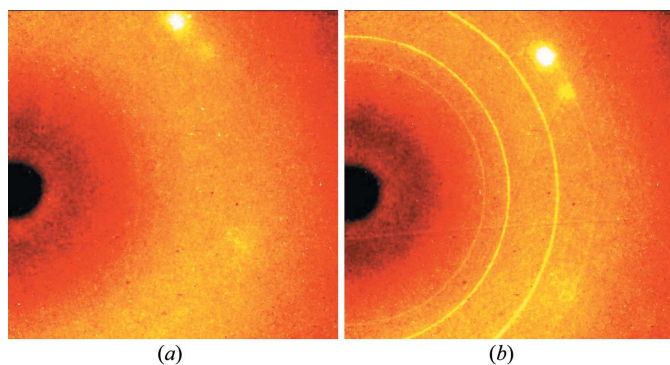


Figure 2 Diffraction patterns collected from amorphous SiO_2 at 53 GPa (a) before and (b) after laser heating at ~ 1200 K. The sharp continuous reflections in (b) correspond to the d-NiAs phase of silica described by Prakapenka *et al.* (2004). Boron powder was used as a laser absorber. This figure is in colour in the electronic version of the paper.

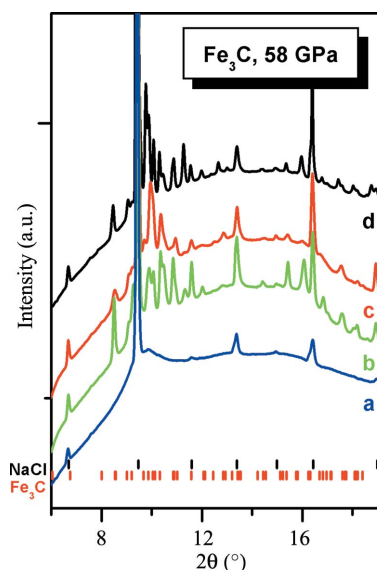


Figure 4 Integrated X-ray diffraction pattern collected at 58 GPa from an Fe_3C sample at ~ 3100 K (a) and quenched from melt in ~ 1 s (b), ~ 0.001 s (c) and after additional annealing of (c) at ~ 1600 K (d). This figure is in colour in the electronic version of the paper.

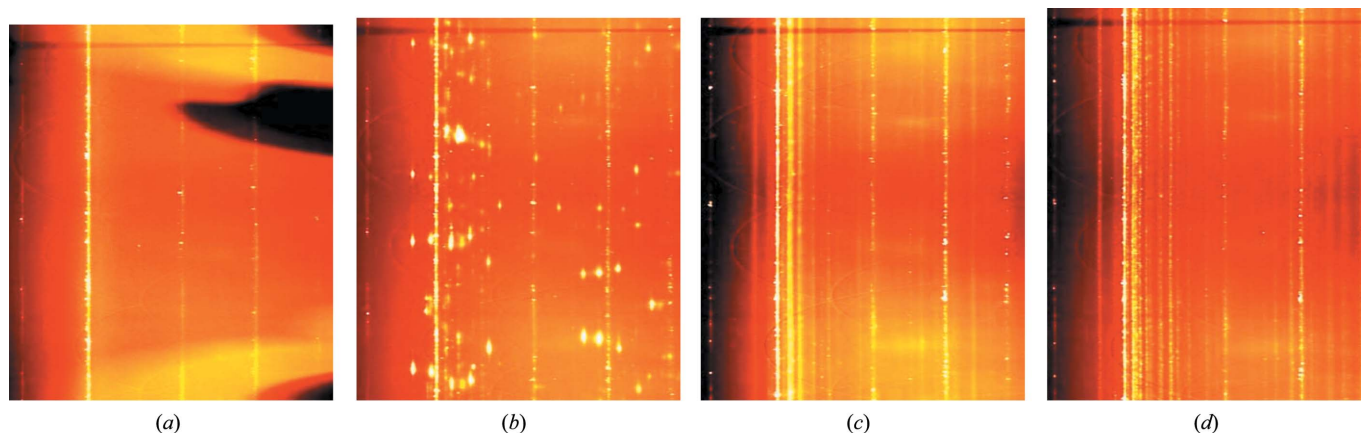


Figure 3 Two-dimensional X-ray diffraction patterns showing azimuth angle (vertical axis, 0 – 360°) versus 2θ (horizontal axis) collected at 58 GPa from an Fe_3C sample at ~ 3100 K (a) and quenched from melt in ~ 1 s (b), ~ 0.001 s (c) and after additional annealing of (c) at ~ 1600 K (d). This figure is in colour in the electronic version of the paper.

recorded (Figs. 3c and 4c). We also note that the width of the diffraction peaks from the Fe_3C are broader than for the NaCl pressure medium collected under the same conditions. The non-hydrostatic stress in the DAC at high pressure can cause the peak broadening (Weidner *et al.*, 1998; Funamori *et al.*, 1997; Dubrovinsky & Dubrovinskaia, 2004). The elastic distortion of the sample owing to applied stress results in the

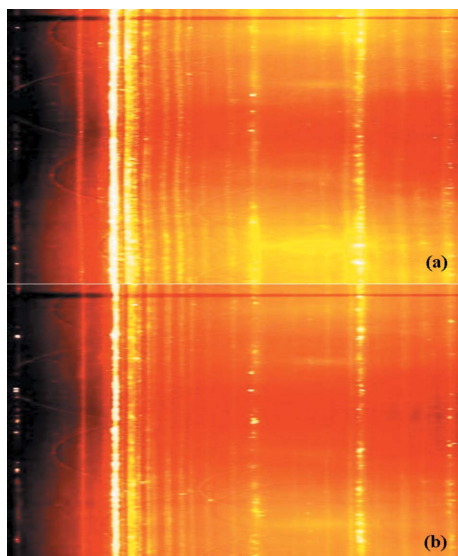


Figure 5
Two-dimensional X-ray diffraction patterns showing azimuth angle (vertical axis, $0\text{--}360^\circ$) versus 2θ (horizontal axis) collected from an Fe_3C sample decompressed from 58 GPa to 50 GPa at room temperature (a) and after additional annealing at ~ 1650 K (b). This figure is in colour in the electronic version of the paper.

transformation of the Debye–Scherrer rings to ellipses. Any non-circularity of diffraction rings collected with an area detector can be analysed routinely using option ‘cake’ in the *fit2D* program (Hammersley *et al.*, 1996). Fig. 5(a) shows an example of stress-induced sinusoidal peak shifts on a ‘caked’ diffraction pattern collected from the Fe_3C sample after decompression from 58 GPa (Fig. 3d) to 50 GPa (Fig. 5a). Further high-temperature annealing at ~ 1650 K for 60 s converts the wavy diffraction reflections into straight lines (Fig. 5b) owing to strain releasing (Wenk *et al.*, 2004). This suggests that broadening of the diffraction peaks of the fast-temperature-quenched sample Fe_3C at 58 GPa (Fig. 3c) is mostly a result of the grain size effect. Simple estimation of the peak broadening using the Scherrer equation (Bartram, 1967) gives an average grain size of ~ 12 nm for the Fe_3C sample at 58 GPa (Figs. 3c and 4c). We have observed similar phenomena at lower pressures (Fe_3C sample) and for other materials (such as Pt, Fe). The nanocrystalline Fe_3C synthesized *in situ* is not suitable for bulk lattice structure refinement owing to the grain size effect on diffraction peak positions, intensities and widths (Palosz *et al.*, 2004). To provoke grain growth, we heated the sample at moderate temperatures, ~ 1600 K, for 1 min, resulting in sharp diffraction lines (Figs. 3d and 4d). After annealing, the two-dimensional diffraction pattern from the sample still showed an even intensity distribution within each reflection that was suitable for Rietveld refinement and structure determination. Thus, by varying the heating procedure, it is possible to control the grain size *in situ* at high pressures in the range from nano-sized to micro-sized materials, thereby optimizing diffraction

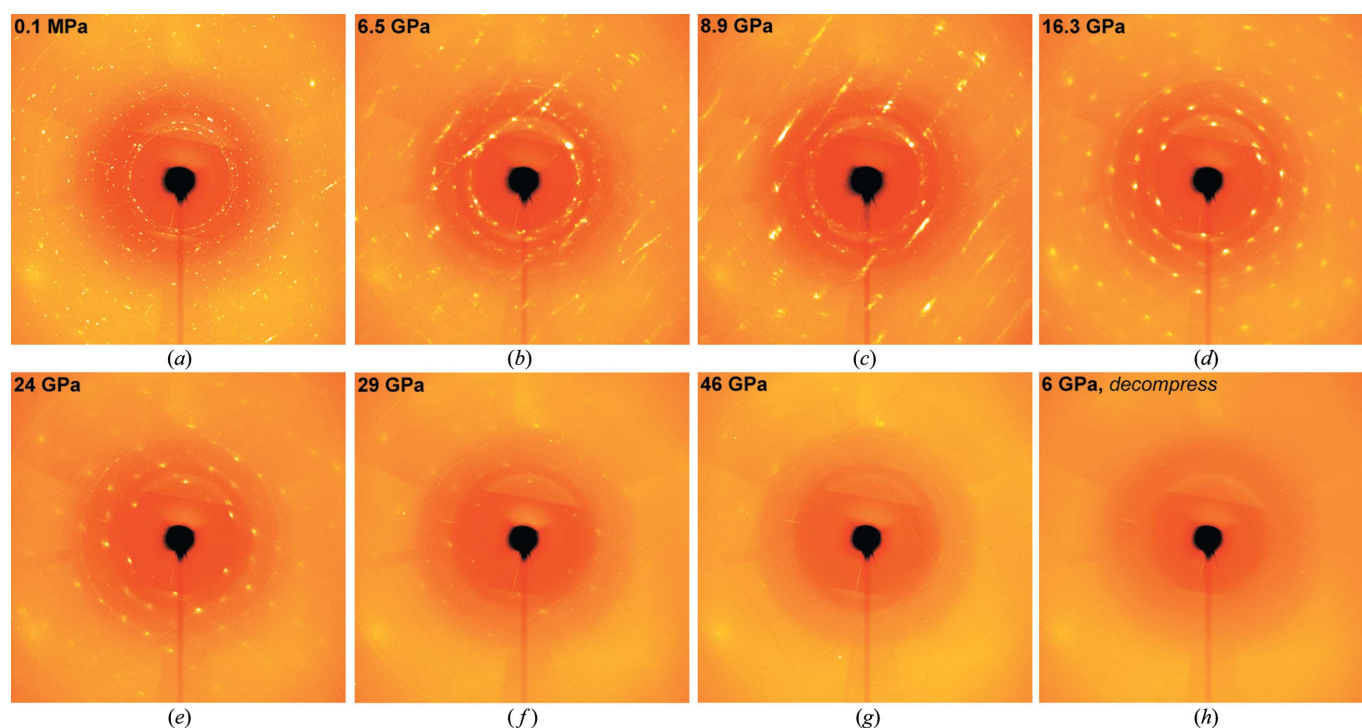


Figure 6
Selected row images of X-ray scattering from the tridymite phase of SiO_2 compressed to different pressures at room temperature. This figure is in colour in the electronic version of the paper.

patterns from materials at high pressure for improved Rietveld refinements.

In contrast to the grain-size reduction methods described above, we have observed pressure-induced growth of single crystals from polycrystalline samples at ambient temperature under non-hydrostatic conditions. Fig. 6 shows a selected set of diffraction patterns collected at each step of the pressurization. The polycrystalline sample at ambient pressure gradually transforms to a single crystal at a pressure of ~ 16 GPa as evidenced by the diffraction patterns (Fig. 6). Further compression resulted in the disordering of the crystalline lattice. Only diffuse X-ray scattering from an amorphous sample was detected at a maximum pressure of 46 GPa and on decompression to 6 GPa. We used gold wire to define the sample position relative to the X-ray beam. It is interesting to note that, during transformation from the polycrystalline to the single-crystal phase (within a volume defined by the X-ray beam size), the process of atoms long-range ordering is accompanied by the appearance of diffuse streaks in the diffraction patterns, indicating atomic displacements resulting from non-uniform stress and grain rearrangement. The pressure-induced amorphization of tridymite above 16 GPa is characterized by a gradual disappearance of diffraction spots without visible stress-induced single-crystal deformation. Structure determination of the new high-pressure crystalline phase is still underway.

Novel transformation from the polycrystalline to the single-crystal phase at room temperature under compression can be explained in terms of sample grains and their boundaries behaviour. On the one hand, the atomic mismatch at the grain boundary commonly produces an excess of free volume. The energy of grain boundaries is higher, and the transport properties of grain boundaries are faster than in single crystals. On the other hand, the tridymite phase of SiO_2 is metastable under ambient conditions and has a highly open low-density structure (compared with the stable α -quartz phase of SiO_2 , for example). During compression, the open structure of tridymite may transform to the new dense high-pressure phase through recrystallization of grain boundaries, resulting in the change of shape (aggregation of grains) and reorientation of individual crystallites under uniaxial stress. This suggestion is confirmed by the appearances of diffuse streaks in the diffraction patterns with increasing pressure.

The diffraction pattern collected at ~ 16 GPa can also be explained by a polycrystalline sample in which all grains were aligned along at least one unit-cell axis perpendicular to the X-ray beam (otherwise, in the diffraction pattern the spots will be converted into rings). In this experiment the X-ray beam was parallel to the loading axis of the DAC. The load in the DAC is radially symmetric, and therefore no pressure gradient in any radial direction can induce the formation of grains aligned along a particular radial direction. At the same time, uniaxial stress in the DAC and pressure-induced phase transformations might cause grain reorientation and further recrystallization of random-oriented grains in the starting material into a single crystal in preferred orientation along the loading axis.

Our understanding of pressure-induced transformation of polycrystalline material to the single-crystal phase at room temperature under compression is still preliminary. Further study of this interesting phenomenon is required to validate, understand and use this effect in high-pressure research.

Based on our experience with grain-size modification *in situ* at high pressure, it may be possible to grow previously unavailable single-crystal samples that are stable only at high pressure (e.g. Fe-hcp, NaCl-B2 *etc.*). One way is to provide a nucleation center (seed) with the same structure as the desired phase, but with a higher melting temperature than the sample. To promote single-crystal growth, the temperature of the melted sample should be reduced to below freezing point, forming an unstable super-cooled liquid. After complete crystallization of the entire liquid surrounding the nucleation center, the sample could be cooled down to room temperature. The crystal size can be increased by repeating (or cycling) these melting–freezing steps a few times. In this case the growing crystal could serve as a nucleation center since smaller crystallites usually melt at lower temperatures than larger ones. At each step of the single-crystal growing process the high-resolution angle-dispersive X-ray diffraction technique should be used *in situ* to monitor sample behaviour. Near real-time analysis of crystal growth at megabar pressures is possible only at synchrotron facilities where diffraction data on micrometer-sized samples can be obtained within seconds.

4. Summary

We have presented a few examples of grain size changes that can occur at high pressure. Pressure-induced structural phase transformations at room temperature can produce different phenomena: single-crystal growth (SiO_2), grain size reduction (NaCl) and amorphization (SiO_2). At ambient temperature, grain size is difficult to control because it mostly depends on the type and structure of the starting materials and weakly on high-pressure parameters (hydrostaticity, compressibility *etc.*). However, using high-temperature heating (annealing and/or melting), grain size can be controlled *in situ* at high pressure. For example, by varying the cooling speed (quench rate) of a molten sample at high-pressure, nanocrystalline (quenching in less than 1 ms) or microcrystalline (cooling rate under 10000 K s^{-1}) materials can be synthesized. Thus, structure and physical/chemical properties of materials, which significantly depend on the grain size distribution, can be modified *in situ* at high pressures in diamond-anvil cells.

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