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Strategies for reducing preferred orientation and strain in powder samples for high-pressure synchrotron X-ray diffraction in diamond-anvil cells

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Among the many problems associated with high-pressure X-ray diffraction from polycrystalline samples in the diamond-anvil cell are strain and preferred orientation. A method is presented for efficiently reducing preferred orientation of powder samples compressed in diamond-anvil cells to pressures in excess of 20 GPa. This method may be successfully applied to samples of yield strength higher than alkalihalides. In addition, the problem of strain is discussed using ice-VII as an example and as an illustration of the importance of laser heating as a method of minimizing strain.

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1. Introduction

Diamond-anvil cells (DACs) are capable of generating static pressures in the range of several hundred MPa to over 300 GPa (*e.g.* Eremets, 1996; Loubeyre *et al.*, 2002; Hemley & Mao, 1998). The sample size required for reaching tens of GPa in the DAC is restricted by the anvil culet size, usually less than 0.5 mm diameter, requiring samples in the range of 10 μg and 100 ng (Hemley & Mao, 1998). Because of this small sample size the use of highly brilliant X-ray beams from synchrotron sources is almost mandatory for powder X-ray diffraction in DACs. Another important reason for the use of synchrotron radiation is the high flux at energies above 25 keV, which allows for effective sampling of reciprocal space of crystalline materials encased in DACs, where the accessible range of the diffraction cone is rather limited. The availability of third-generation synchrotrons, undulator technology, superconducting wigglers and bending magnets, and focusing optics for X-rays in the energy range of several 10 keV have made the use of monochromatic light for *in situ* powder X-ray diffraction from samples in DACs a common technique over the last five years (*e.g.* Fiquet & Andrault, 1999).

However, several serious problems arise with high-pressure synchrotron X-ray powder diffraction. First, in most experiments the sample is only 10 to 50 μm thick, while grain sizes commonly range between 1 and 5 μm. Since the sample is probed by an X-ray beam of only 10 to 100 μm in diameter, in the absence of extended sample rotation and oscillation during data acquisition only a small number of grains will satisfy diffraction conditions, resulting in inaccurate relative intensities. In this case, interpretation of the observed powder diffraction pattern by means of extracting structure factors is not possible. Second, the diamond cell itself limits the angular accessibility range, requiring the use of higher X-ray energies (>20 keV). The trade-off between higher X-ray energy and lower spatial resolution of area detectors also limits the amount of diffraction data that can be obtained at high pressures. In addition, preferred orientation and textural effects occur in DACs as a result of non-uniform stress fields. While in certain cases they can be used to constrain elastic properties of materials under high pressure (*e.g.* Merkel *et al.*, 2003), the effect of non-uniform stress introduces additional uncertainties on structure modelling. These factors already seem to preclude the extraction of observed structure factors for application of direct methods of structure solution to all but the most trivial structures.

Here we discuss how strain and preferred orientation of samples loaded in DACs can be reduced by means of sample preparation and treatment.

2. Preferred orientation: experimental strategy

Preferred orientation results in the systematic distortion of the intensity ratios of the diffraction peaks. Although preferred orientation can be treated analytically (Bunge *et al.*, 1989; Järvinen, 1993) for samples in the DAC it easily becomes an insurmountable barrier for structure modelling. Corrections for orientation effects add refinement parameters, further reducing the possibility of full model convergence. Above ~10 GPa, all materials are solid or glassy at 300 K and below, implying that the stress field acting on a sample surrounded by a pressure-transmitting medium is no longer hydrostatic. The degree of deviation from uniform stress varies depending on the elastic properties of the pressure medium: the sample

under non-hydrostatic stress may deform elastically or by creep. Softer solid-pressure mediums such as helium (*e.g.* Loubeyre, 1996) can minimize this problem, but require difficult gas-loading procedures. Still, in the case of powder diffraction it may be insufficient to have a polycrystalline aggregate of material embedded in a soft or hydrostatic medium, since the local stress within the sample aggregate can still be highly anisotropic. Ideally, all sample grains are separated by the medium (which is difficult to control during gas-loading procedures). Another serious problem is diffraction from the pressure medium itself; being plastic under the experimental conditions, gas-pressure media tend to form large highly strained crystallites with diffraction that cannot easily be removed from the diffraction image.

We report a strategy for reducing preferred orientation based on the preparation of untextured composites of sample and pressure media, which are characterized by powder diffraction before loading into a DAC and subsequently annealed by CO_2-laser heating at each pressure prior to the diffraction experiment. We used pressure media that are soft, but not fluid, at ambient conditions so that a mixture of sample and medium can be prepared where the sample grains are isolated from each other by the medium. Whereas fine powders tend to lump together when immersed in liquid media, the use of soft highly viscous materials like greases and waxes or plastic solids allows the powdered sample to be intimately mixed prior to loading. The pressure media we tried, alkalihalides and silicon grease, are not very soft at 300 K and high pressure, but become plastic at the annealing temperature. The laser is tightly focused into the sample chamber and the beam is scanned over the absorbing sample while keeping the peak temperature as low as possible for efficient annealing. The tight focusing implies large radial temperature gradients around the hot spot. Thus, grains of sample may re-orient in the plastic regime within this temperature gradient, but there is no overall preferred orientation within the sample chamber, since the hot spot diameter is small in comparison with the chamber diameter and, further, the hot spot is scanned through the sample chamber thus destroying previous preferred orientation. In contrast to this, a broadly defocused laser beam allows for formation of preferred orientation of the sample over a large range of the sample chamber. We notice that stress-induced broadening of sample diffraction peaks may be substantial even after annealing, since the proposed pressure media have higher strength than solidified noble gases. Our concept is therefore suitable for reducing preferred orientation but not for minimizing strain.

3. Experiments

We applied this concept to aluminate-perovskites as sample materials in combination with various media. We used powder material with grain sizes of less than 1 μm to 5 μm. We used a modified Mao-Bell cell with tungsten carbide seats with a 0.8 mm × 4 mm opening at the top and opening angles of 90° and 30° [following a design first used by Yoo *et al.* (1997)]. We used 1/3-carat standard-cut 16-sided diamond anvils of ultralow fluorescence and with culets of diameter 300 μm. Rhenium gaskets were indented to about 70 μm thickness and holes of diameter 160 μm were drilled to contain the samples. At each experimental pressure, the samples were annealed with a CO_2 laser (10.6 μm wavelength) focused into the DAC sample chamber to a hot spot of between 20 and 25 μm in diameter. This focused beam was scanned over the whole sample chamber with a speed of 10 μm min^{-1}. Temperatures in the center of the hot spot were kept at around 2000 K. This implies radial temperature gradients of 1700 K over the whole hot spot (170 K μm^{-1}). The short heating duration and the effective isolation of sample grains from each other by the pressure medium prevents collective recrystallization while micrometer-size grains may break down into smaller ones when experiencing temperature gradients of 170 K μm^{-1}. However, there is no general rule for this breakdown as it depends on the surface energy of the sample material. Generally, the grain size statistics of the sample should be conserved upon annealing or even shift towards smaller grain size. This is very different from annealing homogeneous polycrystalline aggregates of sample which tend to recrystallize to a small number of large grains.

Our initial choice of a pressure medium was high-vacuum silicon grease since it is glassy at high pressure, and chemically rather inert (Haines & Leger, 1997). Compared with Ne or He the overall pressure gradient in a silicon grease pressure medium is substantially higher, but can be relaxed by CO_2-laser annealing. Noble gas media are solid under the experimental conditions discussed here. Hence, $\sigma_{12} = 2s_{1212}\varepsilon_{12}$, where s_{1212} is an independent component of the elastic tensor of the crystalline noble gas (ε_{kl} is the elastic deformation and σ_{ij} is the stress tensor). In elastically truly isotropic media (symmetry $\infty/m\infty$), s_{1212} equals $(s_{1111} + s_{1122})/2$, hence there are no real shear forces. This is the case for silicon grease.

However, it appears that the silicon grease reacted with our sample at high temperature, so we will not discuss further our findings from experiments using silicon grease as medium in combination with laser annealing, but will focus on our results on $LaAlO_3$ in argon and in NaCl. We point out that Haines & Leger (1997) used silicon grease as a pressure medium in combination with NIR laser-annealing successfully for structural studies on rutile-type oxides. Fig. 1 shows the diffraction image of the $LaAlO_3$–NaCl mixture at 27 GPa in a DAC after the described treatment. The $LaAlO_3$:NaCl mixing ratio was around 1:2 as checked by X-ray diffraction of an aliquot of material before loading.

The pattern exhibits uniform intensity along all diffraction fringes. This is very unusual for powder samples loaded in DACs to pressures above 20 GPa and it shows that the described method is successful. The smoothness of the pattern indicates that there were at least 10^4 grains in diffraction position, since the pixel size of the Mar345 image plate detector of 100 μm × 100 μm determines the minimum amount of diffracting grains which yield smooth Debye–Scherrer fringes at the given sample–detector distance rather than a circular array of discrete diffraction spots. The

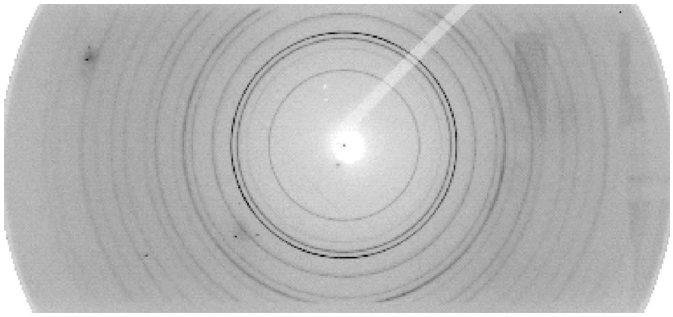

Figure 1
Powder diffraction pattern recorded using a Mar345 image plate on $LaAlO_3$ loaded in NaCl at 27 GPa after annealing with a CO_2 laser. The image shows smooth Debye–Scherrer fringes allowing for straightforward quantitative evaluation of the observed peak intensities. It is very difficult to obtain diffraction patterns of such smoothness at such a high pressure without extensive sample preparation and treatment in advance of the diffraction experiment.

diffraction pattern was collected at the 16ID-B undulator beamline at the High Pressure Collaborative Access Team (HPCAT), sector 16 of the APS-ANL synchrotron, using monochromatic light of 30.93 keV and a Mar345 image-plate detector placed 340 mm away from the sample. The size of the monochromatic micro-focused X-ray beam was 12 µm × 14 µm, achieved by using two Kirkpatrick–Baez mirrors and a 30 µm-diameter Mo clean-up pinhole to eliminate the beam tails. This narrow beam was scanned perpendicular to the beam direction over an area of diameter 100 µm in order to probe a larger amount of sample. We integrated the pattern shown in Fig. 2 and performed a Rietveld refinement using *GSAS* (Larson & von Dreele, 1995) using a pseudo-cubic cell for $LaAlO_3$ and the B1 structure for NaCl. There was no trace of the high-pressure phase of NaCl in this pattern. The initial similarity between calculated and observed pattern was very close and the refinement converged immediately. There is no preferred orientation in the sample, but a slight mismatch between calculated and observed pattern for the pressure medium. We found that often the softer of two phases of a composite develops preferred orientation in a DAC under pressure. We note that these statistical parameters of goodness of fit (wRp − bknd = 0.043, χ^2 = 39.00, RF^2 = 0.22) are not in very good agreement with standard refinements based on data collected under ambient conditions from samples in capillaries. In particular, the scaling factor of 39.1 is large. This, however, is not surprising since the sample is small in comparison with the surrounding diamond anvils. The absorbance in the anvil should increase the scaling factor and this is observed here. The refinement factors are affected by the modulated background (green line in Fig. 2). In the absence of a glassy phase in our sample, this background results from diffuse elastic and from Compton scattering of the diamond anvils and from diffuse scattering in the experimental set-up. Another problem is the increasing mismatch between observed and calculated pattern with increasing angle, which may be an effect of absorption by the diamond anvil downstream. The diffraction peaks of both sample and medium are rather broad (see Table 1). While non-uniform stresses acting

Table 1
Comparison of Cagliotti terms GU, GV, GW, from profile refinements of ice-VII, crystallized from melt at 12.6 GPa, the same ice sample after pressure increase by 3 GPa, $LaAlO_3$ and NaCl (B1).

Obviously ice-VII crystallized from melt exhibits the sharpest profiles. Strain induced in ice-VII by an increased load in the absence of further annealing expresses itself clearly in larger Cagliotti terms. We used profile type 2 in *GSAS* but refined the Cagliotti terms only to allow for direct comparison. We also report the profile parameters for $LaAlO_3$ and NaCl at 27 GPa. The refinement is shown in Fig. 2. The profile parameters show that our method of preventing preferred orientation in samples at high pressure is not efficient in providing sharp peak profiles.

Sample	GU	GV	GW
Ice-VII, crystallized from melt, 12.6 GPa	31.4	21.0	6.56
Ice-VII, strained, 16 GPa	742	66.4	7.32
$LaAlO_3$	2290	−47.2	−1.38
NaCl, B1	6180	−52.5	−31.2

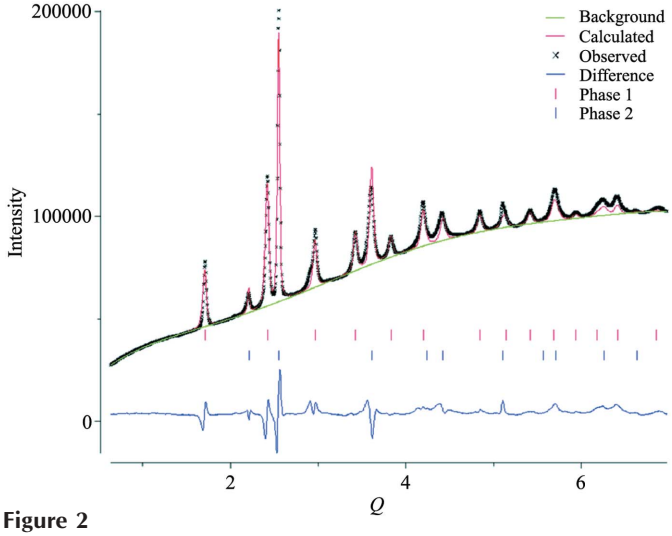

Figure 2
Result of a Rietveld refinement of the pattern shown in Fig. 1 assuming a cubic metric for $LaAlO_3$. Phase 1 is $LaAlO_3$, phase 2 is NaCl in the B1 phase. The statistical measures of goodness are wRp − bknd = 0.043, χ^2 = 39.00, RF^2 = 0.22. The refined cell parameters are 3.6615 (9) and 4.9148 (10) Å. The volume ratio of both phases is 2.07:0.84 (NaCl: $LaAlO_3$). There were 1648 observations and 33 observations in the reflection statistics.

on each sample grain are relaxed by the laser annealing, pressure gradients within the sample chamber are controlled by the yield strength of NaCl and are found to be ∼2 GPa at the experimental pressure of 27 GPa. In the present case the observed diffraction peak width therefore results from contributions of sample grains at slightly different pressures. In sum, our technique of preparing a pressure-medium sample powder composite which is annealed with a scanned focused CO_2-laser beam is successful in preventing preferred orientation of the sample powder and in providing sufficient powder statistics. This is commonly very difficult to achieve at pressures as high as 27 GPa. Our method is conceptually different from common powder diffraction experiments using alkalihalide pressure media. Conventionally, pellets or compact polycrystalline aggregates of sample powder are embedded in a container of neat alkalihalide, which becomes

plastic at experimental pressures in DACs. In this case, preferred orientation in the sample will usually occur already in the prepared pellet or polycrystal. Further, texture increases along with increasing deviatoric stress in the sample. These problems are overcome by our method as illustrated in Figs. 1 and 2.

4. Appearance of strain upon cold compression in DACs

Another important issue of data quality is strain-induced broadening. It has been known for quite a while that laser heating can reduce strain. On the other hand, the high temperatures of the heated sample, which is exposed to a still anisotropic stress field, induces grain growth and preferred orientation. One way to overcome this unwanted effect is heating with tight focus but at low power. Hence, the temperature gradient is large (see §3) while the overall temperature difference is rather small. This method has been applied in our experiments on $LaAlO_3$ (see §3). Obviously, the best way of reducing strain is by crystallization from the melt. In Fig. 3(*a*) we show the pattern of ice-VII which had been directly heated to the molten state with a CO_2 laser in a DAC at 12.6 GPa. The laser beam heated the sample in the middle of the sample chamber which was completely filled with ice. We increased the laser power until 80% of the total sample volume was molten. Then we quenched by closing the laser shutter. Because the gasket did not experienced elevated temperature in the experiment, there is no stress induced by the cooling gasket, which is a common problem when samples are crystallized from melt by external heating of diamond cells and requires extremely low cooling rates to allow for relaxation of the induced stresses without damaging the grown crystals (Schiferl *et al.*, 1983). Water-ice is a material that is extremely sensitive to strain since many of its crystalline phases are ferroelectric or antiferroelectric. Ice-VII is commonly considered as paraelectric, but it has been discussed whether ice-VII could be composed of ferroic nanodomains, thus representing a glassy state of the dipoles (Wolanin *et al.*, 1997). It is to be expected that anisotropic stress has a strong influence on the structure and properties of ice-VII. On the other hand, soft pressure media like He cannot be used for water-ice since they would form clathrates. Fig. 3(*a*) shows a pattern collected immediately after quenching from the melt. The fringes show many small spots lined along the Debye–Scherrer rings like pearls on a necklace. In between these spots we see a smooth ring of much narrower line width. Fig. 3(*b*) shows the sample after a change of pressure by 3 GPa. The fringes are smoother now, but strain-induced peak broadening is substantial and the Debye fringes exhibit noticeable elliptical distortion (Fig. 3*c*). Figs. 4(*a*) and 4(*b*) show the integrated diffraction pattern of both the sample crystallized from the melt and after further cold compression between 18 and 27° 2θ. Clearly peak width and peak asymmetry increase after pressure increase. Fig. 3(*c*) illustrates that this peak asymmetry results from strain-induced ellipticity of the Debye fringes rather than peak splitting owing to a reduction in structure symmetry. For the sample crystallized from melt we achieved wRp − bknd = 0.0852, Rp = 0.0656 and χ^2 = 31.99. There were 1466 observations. The strained sample yielded wRp − bknd = 0.117, Rp = 0.0889 and χ^2 = 11.31 (1464 observations). The refinement was based on weighted structure factors. Interestingly, broadening

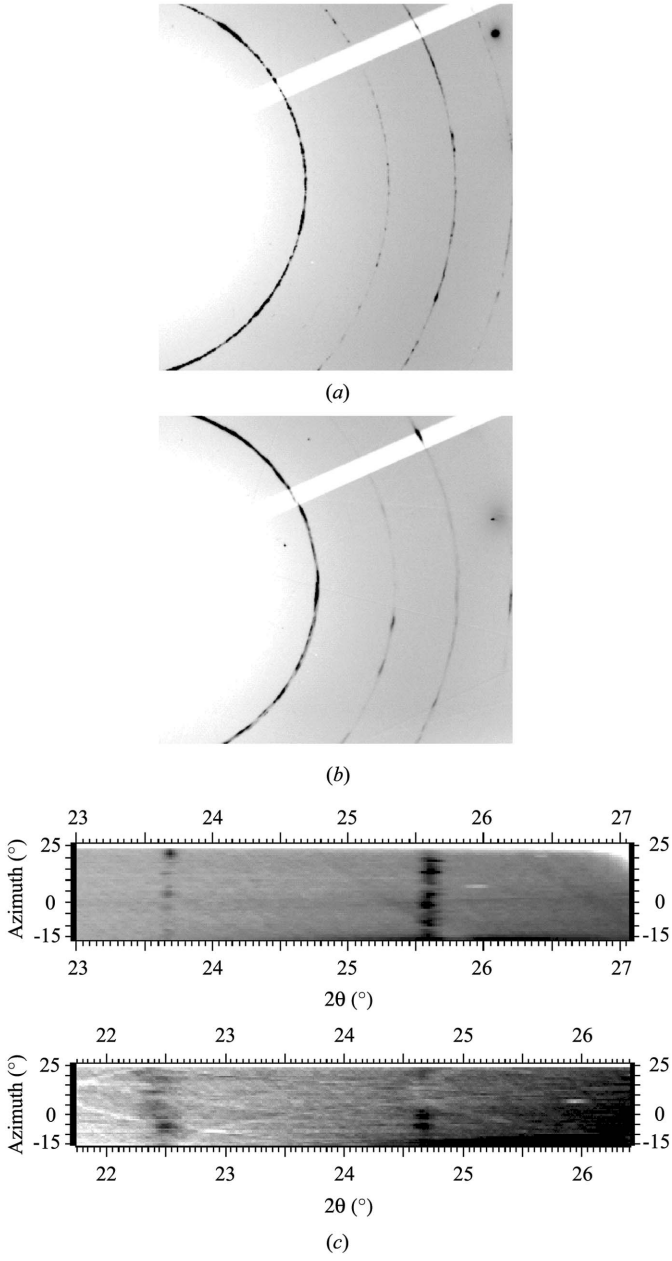

Figure 3
Strain effects in ice-VII at 13 GPa. (*a*) A diffraction image of ice-VII crystallized from melt at 12.6 GPa. Ice is the only phase in the sample chamber. Melting was induced by CO_2-laser heating and the crystallization occurred upon rapid closure of the laser shutter. (*b*) The same sample after increasing the pressure by 3 GPa but before further annealing. The fine spots dominating the image in (*a*) are smeared out while peak widths increase. (*c*) The two patterns after correction for angular distortion. Clearly the Debye fringes in the sample after pressure increase without annealing (lower panel) are broader than those of the heat-treated sample (upper panel) and show ellipticity from anisotropic strain (see text).

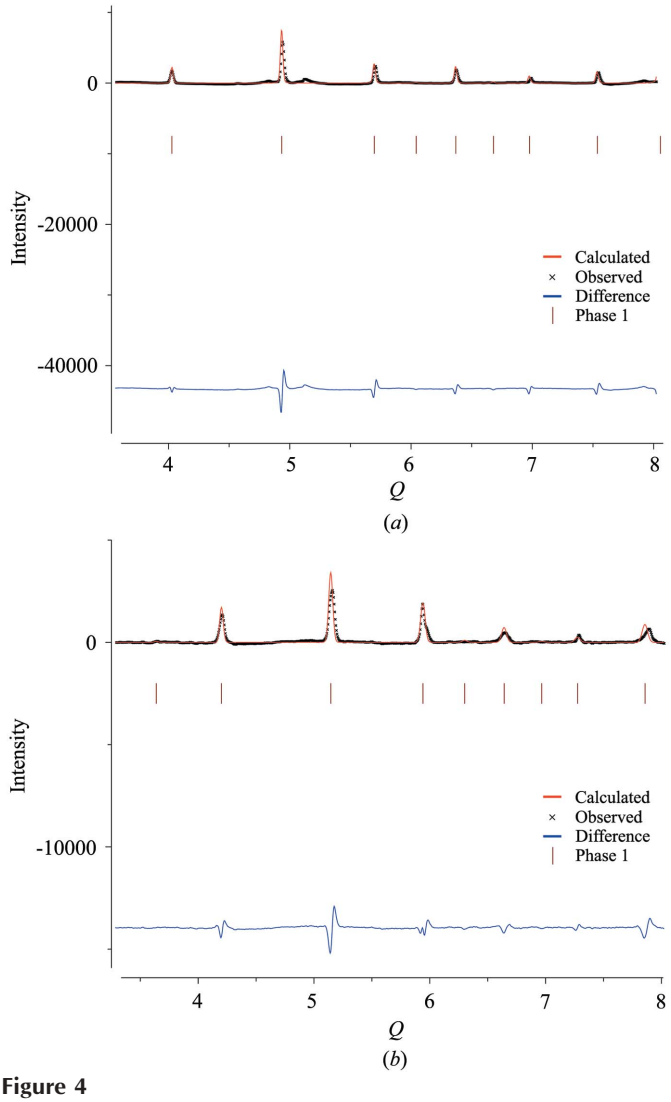

Figure 4
Results of the profile refinement for ice-VII crystallized from melt at 12.6 GPa (*a*) and after further pressure increase by 3 GPa without annealing (*b*). Peak width and peak asymmetry increase are noticeable after pressure increase. Fig. 3(*c*) illustrates that this peak asymmetry results from strain-induced ellipticity of the Debye fringes rather than peak splitting owing to a reduction in structure symmetry. For the sample crystallized from melt we achieved wRp − bknd = 0.0852, Rp = 0.0656 and χ^2 = 31.99. There were 1466 observations. The strained sample yielded wRp − bknd = 0.117, Rp = 0.0889 and χ^2 = 11.31 (1464 observations). The refinement was based on weighted structure factors.

is not equal for all diffraction peaks. Another remarkable feature is the apparent peak splitting of reflection (220) at Q = 6 Å^{-1} in the cold compressed sample. This splitting is apparent in the residual (Fig. 4*b*), since (220) has been fit by a single peak. The origin of the splitting becomes obvious from Fig. 3(*c*) where parts of both patterns are shown after correction for image distortion using *Fit2d* (Hammersley *et al.*, 1996). Even with spots, the sample directly crystallized from melt gives a peak of smaller half width. Furthermore, the unannealed sample shows azimuthal offset of the diffraction signal indicating anisotropic strain (we note that both images were collected along a direction of minimal strain since the primary beam passed through the diamond cell along the cell axis). This offset induces apparent peak splitting and can pretend symmetry reduction by a structural transition. In fact, the peak splitting disappears if we integrate slices of small azimuthal width independently. Symmetry reduction by an induced or spontaneous phase transition in ice implies that peak splitting occurs in all slices of the pattern as an intrinsic feature related to structural change. We refined the integrated patterns shown in Fig. 3 based on the ice-VII structure using *GSAS*. Profile refinement is based only on the three Cagliotti terms in order to allow for a direct comparison. The results of the profile refinement are given in Table 1. The profile parameters in the unannealed ice sample are much larger, thus quantifying the strain broadening.

5. Summary and conclusions

Preferred orientation and strain strongly affect the quality of powder diffraction data collected from samples pressurized in a diamond-anvil cell. We report a novel technique of sample preparation and treatment in advance of the diffraction experiment which is based on composites of sample powder and pressure medium rather than on the conventional concept of embedding sample powder pellets in neat media. The sample–medium composites are annealed by scanning a tightly focused CO_2-laser beam through the sample chamber. Our method improves the quality of the powder diffraction pattern with respect to smoothness and statistics; however, this implies a large diffraction peak width since the sample–medium composites sustain larger pressure gradients than solidified noble gases. Therefore, successful application of this technique may be limited to samples of high yield strength or to high pressure. We further illustrate the importance of laser annealing as a tool for minimizing strain in advance of powder diffraction experiments in DACs by an example of water-ice.

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