

Video Article

Synthesis and Microdiffraction at Extreme Pressures and Temperatures

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Abstract

High pressure compounds and polymorphs are investigated for a broad range of purposes such as determine structures and processes of deep planetary interiors, design materials with novel properties, understand the mechanical behavior of materials exposed to very high stresses as in explosions or impacts. Synthesis and structural analysis of materials at extreme conditions of pressure and temperature entails remarkable technical challenges. In the laser heated diamond anvil cell (LH-DAC), very high pressure is generated between the tips of two opposing diamond anvils forced against each other; focused infrared laser beams, shined through the diamonds, allow to reach very high temperatures on samples absorbing the laser radiation. When the LH-DAC is installed in a synchrotron beamline that provides extremely brilliant x-ray radiation, the structure of materials under extreme conditions can be probed *in situ*. LH-DAC samples, although very small, can show highly variable grain size, phase and chemical composition. In order to obtain the high resolution structural analysis and the most comprehensive characterization of a sample, we collect diffraction data in 2D grids and combine powder, single crystal and multigrain diffraction techniques. Representative results obtained in the synthesis of a new iron oxide, Fe₄O₅¹ will be shown.

Video Link

The video component of this article can be found at <https://www.jove.com/video/50613/>

Introduction

Pressure can fundamentally change the properties and bonding of matter. The Earth's topography, composition, dynamics, magnetism and even the atmosphere composition are profoundly tied to processes occurring at the interior of the planet which is under extremely high pressure and temperature. Deep Earth processes include earthquakes, volcanism, thermal and chemical convection, and differentiation. High pressure and temperature are used to synthesize super-hard materials like diamond and cubic boron nitride. High PT synthesis combined with *in situ* x-ray diffraction allows researchers to identify the crystal structures of the new materials or high-pressure polymorphs of extreme technological importance. The knowledge of high-pressure structures and properties allows interpretation of the structure and processes of planetary interiors, modeling of the performance of materials under extreme conditions, synthesis and design of new materials, and achievement of a broader fundamental understanding of materials' behavior. The exploration of high pressure phases is technically demanding due to the twofold challenges of controllably generating extreme environmental conditions and probing small samples within bulky environmental cells.

A range of materials and techniques may be used to perform synthesis at extreme conditions^{2, 3}. The most suitable equipment for each particular experiment depends on the material investigated, the target PT, and the probing techniques. Among high pressure devices, the LH-DAC has smallest sample size, but is however capable of reaching the highest static PT (above 5 Mbar and 6,000 K) and allows the highest resolution x-ray structural analysis. The protocol described below led to the discovery of Fe₄O₅¹ and is applicable to a wide range of materials and synthesis conditions. The LH-DAC is best suited for materials efficiently absorbing the laser wavelength of ~1 μm available at high pressure synchrotron beamlines (e.g. 16-IDB and 13-IDD stations at the Advanced Photon Source, Argonne National Lab), for synthesis pressures up to 5 Mbar and for temperatures greater than about 1,500 K. Fairly complex structures and multiphase samples can be characterized with the x-ray microdiffraction strategies presented here. Other techniques, such as whole DAC heating⁴ and local resistive heating, are suitable for lower synthesis temperatures. CO₂⁵ laser heating, with wavelength of about 10 μm, is suitable for the heating of materials transparent to the infrared YLF laser but absorbing the CO₂ radiation. Other devices, such as multi-anvil, piston-cylinder and Paris-Edinburgh presses, provide larger volume samples necessary for neutron diffraction experiments, for instance.

In the LH-DAC, invented in 1967^{6, 7, 8}, high pressure is generated on a small sample placed between the tips of two opposed diamond anvils. In the laser heating systems installed at synchrotron experimental stations^{9, 10, 11}, laser beams are delivered on a sample from both sides through the diamond anvils while a brilliant x-ray beam is focused on the heated spot. Samples absorbing the laser light are heated while x-ray diffraction is used to monitor the progress of the synthesis. The thermal radiation emitted by the laser heated sample is temperature dependent.

Thermal emission spectra collected from both sides of the sample are used to calculate the sample temperature by fitting the spectra to the Planck radiation function assuming black body behavior⁸.

The crystal structure analysis of products of synthesis in a LH-DAC is carried out using the brilliant synchrotron x-ray beam, high precision motorized stages and the fast x-ray detectors available at dedicated synchrotron experimental stations. We collect x-ray diffraction data in a 2D grid and customize the data collection strategy according to the grain size. This approach allows to: i) map the sample composition; ii) obtain robust data analysis of a complex multiphase sample by combining single crystal, powder and multi-grain diffraction techniques.

Protocol

1. Diamond Anvil Cell and Gasket Preparation

1. Select a pair of diamond anvils with conical design¹² and matching culet size. The conical anvil design is chosen for the wide angular x-ray windows it provides, allowing to collect relatively high resolution x-ray microdiffraction data. The culet (flat or beveled tip of a diamond anvil) is selected according to the maximum target pressure. The diameter of the flat part of the culet ranges from about 1-0.07 mm for target pressures from 10 to more than 200 GPa, respectively.
2. Position a diamond anvil in the matching conical housing of a tungsten carbide seat and place the two in a mounting jig. Make sure that the bottom cone of the diamond anvil is firmly sitting in the tungsten carbide seat by rotating the anvil with tweezers.
3. Apply load (few kg) on the diamond. No gap should remain between the diamond and the seat. Apply a small amount of glue around the anvil outer circumference.
4. Cure for 1 hr at 120 °C. Repeat the operation for the second diamond and seat.
5. Insert the pair of seats with glued diamonds in the two parts of a diamond anvil cell. Bring the diamond tips (culet) in close proximity (about 30 μ m distance).
6. Using a stereoscopic microscope and inspecting the anvils sideways, align the flat tips of the diamond anvils (culets) laterally using the DAC lateral set screws (**Figure 1a**).
7. Gently, bring the diamond tips in contact. Use the interference fringes (**Figure 1b**), visible in axial stereoscopic view, to monitor the anvils relative tilt.
8. Rock the top anvil using the DAC top screws. Fringes becoming wider and "moving out of the culet" (**Figure 1c**) indicate that the diamonds relative tilt is decreasing. In axial view, adjust the horizontal alignment (**Figure 1d**) using the DAC lateral set screws. Aligned diamonds show no interference fringes and overlapping edges (**Figure 1e**). Clean the diamonds thoroughly using acetone.
9. Position a small metal foil, acting as gasket, between the tips of two aligned diamonds and attach the foil to the DAC body with waxy material. Suggested gasket materials include high yield strength metals such as rhenium, stainless steel or tungsten. Typical foil size is about 5 mm x 5 mm square with a thickness of 0.15-0.25 mm. The gasket should have fine texture and be free of cracks.
10. While monitoring the total thickness of the DAC with a micrometer, turn the DAC bolts evenly and in small steps producing an indentation of a thickness that varies with the culet size in the range of about 80-20 μ m (**Figure 2a**).
11. Drill a hole in the center of the indentation of diameter between 1/2 and 1/3 of the culet size using a laser drilling system (**Figure 2b**) or an EDM machine¹³. The gasket-hole should be centered in the indentation and be perpendicular to it.
12. Carefully clean the gasket using a needle and ultrasonic bath for about 5 min in ethanol.
13. Clean the diamond tips carefully using sandpaper first and then acetone dipped wipes. Reposition the gasket firmly, using waxy material, on one anvil tip.

2. Sample and Gas Loading

1. The ruby fluorescence spectral shift^{14, 15, 16} and the gold compressibility¹⁷ are used as secondary pressure gauges. Using a fine tip tungsten needle, handpick one or two ruby spheres (~10 μ m in diameter) and place them on the walls of the gasket-hole, repeat the operation for a small amount of fine gold powder (**Figure 2c**). The pressure standards positioned on the gasket should not come in contact with the sample to avoid unwanted reactions and parasitic scattering effects. Perform all sample loading operations without the aid of bonding materials, small grains adhere weakly to the needle, the gasket or the diamond by electrostatic forces.
2. Using an electronic balance, weigh the pure reagents, mix thoroughly appropriate proportions using a mortar.
3. Place a small amount of the mixture between the tips of two aligned diamonds of a second DAC. Press the sample squeezing the cell by hand. The powder will be compacted in a foil about 10 μ m thick. Due to the small size of the sample, if the starting material is a powder mixture, as in the case of Fe₄O₅, it is difficult to load exact proportions, it is therefore essential that the starting powders are very fine (below 1 μ m) and very well mixed.
4. Carefully, with the fine tip tungsten needle, break the foil of compacted powder into pieces. Select a flake about 40 μ m large. Note: The size of the loaded sample should be smaller than the size of the sample chamber at the target pressure. The sample chamber shrinks according to the assembly design and materials, and the compressibility of the materials filling the sample chamber, which is very high for the Ne and He media we use. A sample chamber starting 40 μ m thick and 120 μ m large loaded with pressurized Ne (see below) shrinks to about 15 μ m thickness and 70 μ m diameter at 20 GPa.
5. Transfer the flake on the center of the diamond culet in the first DAC. Reassemble the two parts of the DAC (**Figure 2c**).
6. Besides the absorbance of the particular laser wavelength used, the sample heating efficiency crucially depends on the sample preparation. In particular it is important to load a sample with uniform thickness that should be well insulated from diamonds and gasket. It is crucial to ensure that the sample does not adhere to the thermal conductive diamonds, which would dissipate the heat. Few grains of loose powder that almost inevitably end up around the pressed flake are usually sufficient to keep the sample lifted from the anvils. The pressure-transmitting medium will then provide a thermal insulating layer.
7. Fill the sample chamber with a pressure-transmitting medium. Recommended media include pre-pressurized (1.7 kbar) Ne or He as these two inert media provide quasi-hydrostatic conditions to very high pressure in addition to thermal insulation. Perform the gas loading using the COMPRES/GSECARS gas loading system, described in detail elsewhere¹⁸.

3. Laser Heating and High Temperature X-ray Diffraction

Heating of a sample inside a DAC is achieved by applying infrared lasers to the sample through diamond anvils. Samples are heated to high temperatures by absorbing the laser radiation. Samples that don't absorb the 1,063 nm radiation can be mixed with absorbing and chemically inert material (example: Pt black powder) for indirect laser heating. Since diamond is a superior thermal conductor, a preferred practice is to use thermal insulation layers (example: NaCl, MgO or Al₂O₃) to separate the sample from the anvil surface. Absorbing and insulating materials will, however, cause additional parasitic scattering and might react with the sample.

The online laser heating systems installed in the experimental stations 16IDB of HPCAT and of 13IDD of GSECARS^{9, 10, 11} of the APS are designed to perform heating and x-ray diffraction on samples loaded in the DAC. Typical energies of the x-ray beam are about 30 keV and the size at the focal spot is about 5x5 μm FWHM. Infrared lasers (YLF, wavelength = 1,063 nm) are used for heating samples in the DAC. A fast x-ray area detector such as MARCCD and XRD 1621 xN ESPE is utilized.

1. Secure the DAC in the water cooled copper holder. Use the offline system (a remotely controlled motorized stage and a microscope) to determine the rough sample positional coordinates. The x-ray beam and the laser beams are pre-aligned to the sample position on the rotation axis of the sample stage.
2. Mount the holder on the sample stage (**Figure 3**), exit and close the experimental station following the laboratory safety procedures (these are specified in the mandatory trainings required to perform experiments in the laboratory).
3. Remotely operate the laser heating and x-ray diffraction systems from inside the experimental station, equipped with computers and monitors. Position the sample on the rotation axis of the sample stage using x-ray absorption profiles of the sample measured with an x-ray photodiode.
4. Move the upstream and downstream laser heating optical components in the x-ray beam path.
5. Focus the optics for clear sample viewing and adjust heating mirrors to compensate the tilting of diamond anvils.
6. Turn on the lasers and slowly increase the laser power delivered to the sample.
7. When the sample starts to glow (**Figure 4a**), collect the thermal radiation spectrum using an imaging spectrograph.
8. Use the available software to fit the observed spectrum to the Plank radiation function assuming black body behavior to determine the sample temperature^{19, 20}. Adjust the laser power delivered on the two sides of the sample, together or separately, to achieve the target temperature as measured on both sides of the sample.
9. While heating the sample, collect diffraction patterns to monitor the disappearance of the starting material characteristic peaks (usually smooth Debye rings) and the appearance of the new phase peaks (usually spotty patterns). The heating time depends on the temperature and the kinetics of the particular synthesis performed. In case of the synthesis of Fe₄O₅ briefly described below, the synthesis is faster than this detection system (seconds).
10. Move the sample in the plane perpendicular to the x-ray beam in steps of a few micrometers, heating the sample as uniformly as possible. Turn off the lasers and move the optical components out of the x-ray beam path.

4. X-ray Diffraction Data Collection after Synthesis

If the synthesized phase is stable after temperature quenching, diffraction data may be collected after heating. The x-ray diffraction data are collected in transmission geometry (through the anvils). Still diffraction patterns and rotation diffraction patterns (ω-scan) are collected. The latter are collected as single rotation images (wide scan), sets of fine step scan images (one degree or less), or large step scans images (5-10°). The data collection strategy is adjusted according to the available beamtime, exposure time and detector readout speed. When using very fast detectors, fine step-scan data can be collected at each point of the 2D grid in less than an hour. This allows a complete and objective sampling of the reciprocal space across the whole sample.

1. Collect a set of still diffraction images in a 2D grid distribution covering the sample area with step size similar to the x-ray beam size, about 5 μm. In **Figure 4b** the grid of 8 x 8 = 64 images collected in a 40 μm sample is shown. Typical exposure time ranges between 3-20 sec, depending on the x-ray flux and the sample scattering power.
2. Inspect the diffraction images, select a set of locations best suited for single crystal (or multi-grain) and powder diffraction analysis. Diffraction images showing few spots are likely generated by one or few crystals that might provide good single crystal diffraction patterns. The corresponding sample locations, defined as Ay,z (with y and z being the horizontal and vertical coordinates in the plane perpendicular to the beam), are suitable for single crystal or multigrain analysis. Patterns showing smooth or, more commonly, "spotty" Debye rings, defined as location By,z, are suitable for powder diffraction analysis.
3. Using the sample stage translation motors, move to the first Ay,z location. Collect a wide angle diffraction image and a set of fine step ω-scan diffraction images (with omega step size of 1 degree or less). Use these patterns for single-crystal or multigrain data analysis.
4. Repeat for each selected Ay,z location.
5. Using the sample stage translation motors, move to By,z locations. Collect wide step ω-scan diffraction images, i.e. 7 images with 10° step size for 70° total opening. Collect rotation images for powder diffraction analysis to compensate for the low grain statistics typical of LH-DAC samples.

Representative Results

We show representative microdiffraction data obtained from the high pressure and temperature synthesis of Fe₄O₅ from a mixture of hematite and iron according to the reaction:



15 GPa, 1700 K

Figure 5 illustrates powder diffraction patterns from B locations. Although they were collected a few microns apart, the patterns are remarkably different. In a particular spot (**Figure 5a**) the synthesis of Fe_4O_5 did not occur, instead we obtained wüstite (FeO). The locally high Fe/O ratio is presumably caused by a slightly higher local iron/hematite ratio or by a thermally induced chemical gradient. In addition to Fe_4O_5 and neon, the pattern in **Figure 5b** shows smooth Debye rings of fine grained non-recrystallized hematite, here the reaction is incomplete most likely due to non-homogeneous heating. The pattern in **Figure 5c** is representative of a spot where the reaction was complete and produced nearly pure Fe_4O_5 . Data were processed using FIT2D²¹ and Jade²².

Figure 6 shows the single crystal diffraction pattern that led to the discovery of Fe_4O_5 . The pattern is indexed using GSE_ADA²³ (**Figure 6a**) and RSV (**Figure 6b**). Like powder diffraction data, single crystal diffraction data suffer from low resolution and intensity reliability limitations when measured in a DAC. Nonetheless, the three dimensional nature of the data allows for more robust interpretation.

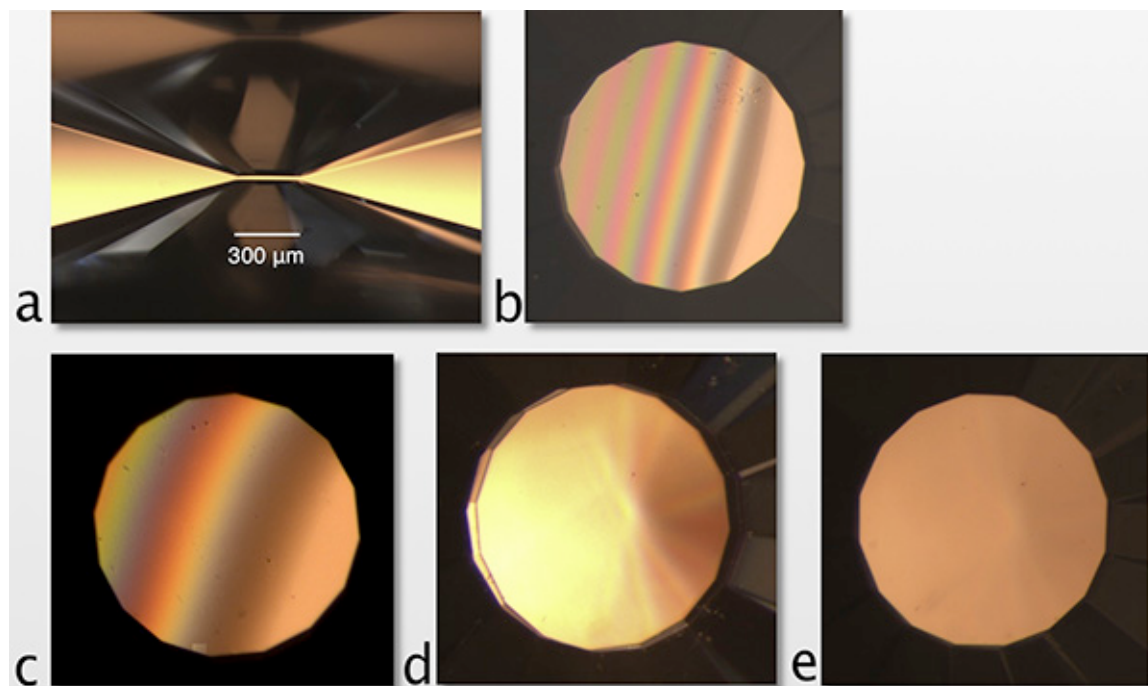


Figure 1. Microphotographs taken at different steps of diamond anvils alignment. The side view of the diamond tips shows laterally roughly aligned tips (a). The axial views show interference fringes in tilted culets (b, c), laterally misaligned anvils (d), and aligned diamonds (e). [Click here to view larger image.](#)

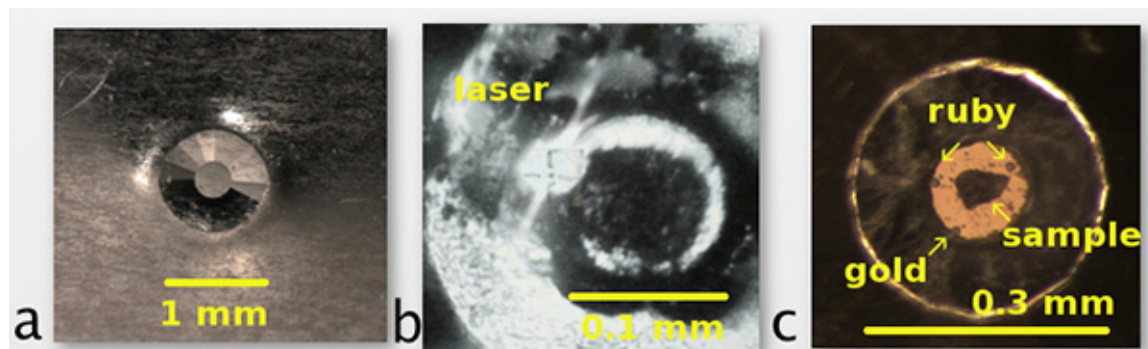


Figure 2. Microphotographs of indented gasket (a), laser beam drilling a hole in the gasket (b), sample chamber with sample and pressure markers (c). [Click here to view larger image.](#)

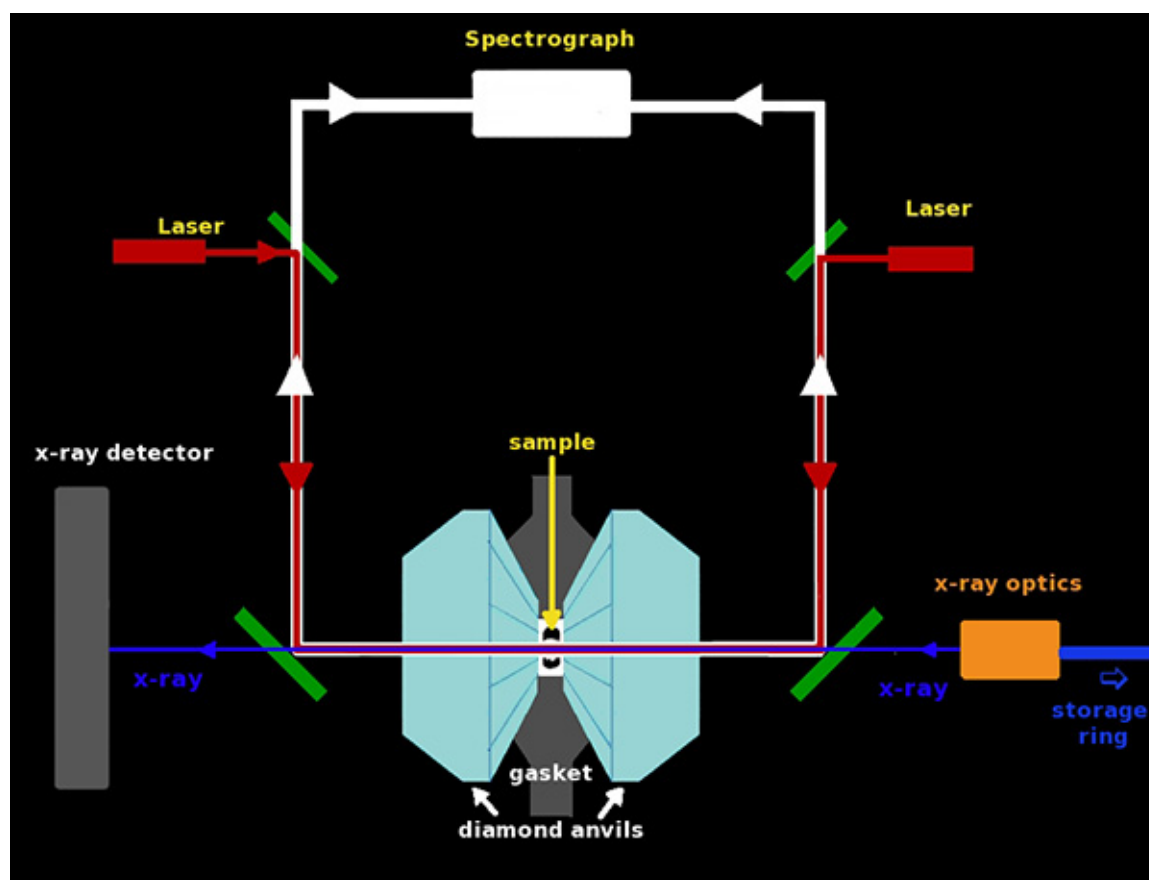


Figure 3. Cartoon representation of a LH-DAC system combined with micro-focused x-ray diffraction. Laser beams (red) are delivered to the sample through two opposed anvils. The heated sample emits thermal radiation (white) from both sides that is collected by the spectrograph for temperature determination. The synchrotron beam (blue), aligned with the laser beam, allows collecting x-ray diffraction data from the center of the heated spot. [Click here to view larger image.](#)

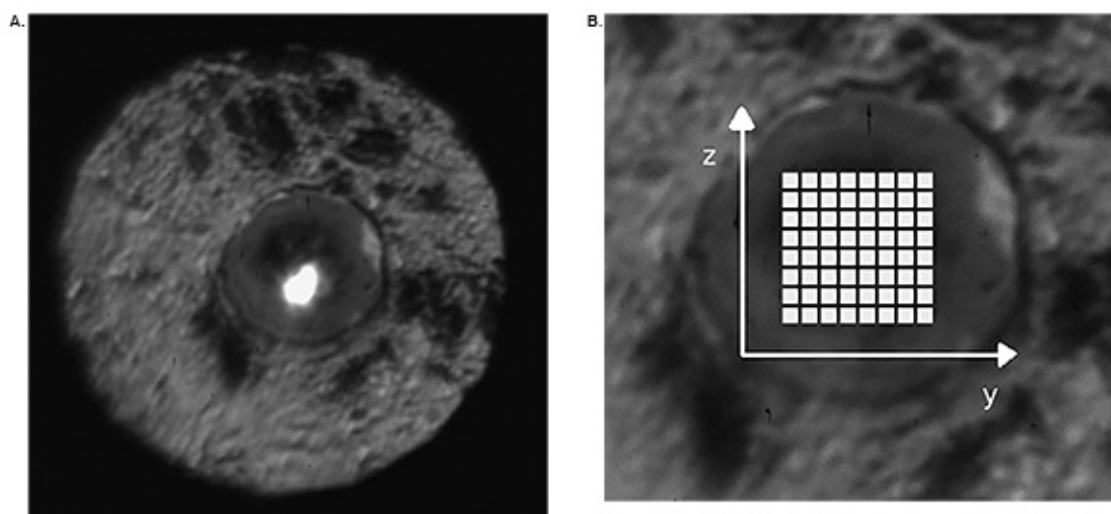


Figure 4. The glowing sample in a DAC emitting thermal radiation in the visible range while heated with IR laser (a) and the grid of x-ray data collected across the sample area (b). [Click here to view larger image.](#)

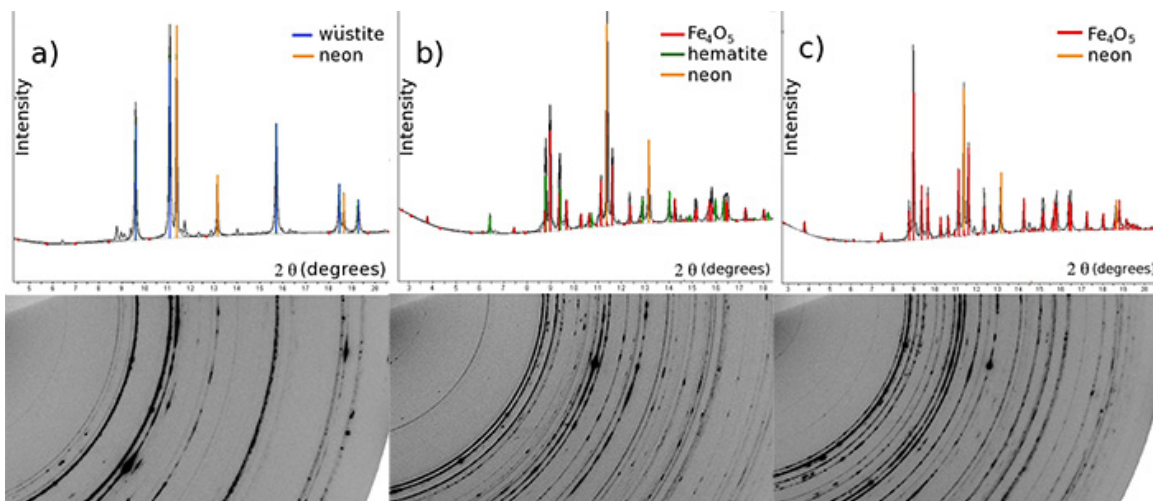


Figure 5. Selected powder diffraction patterns collected from different locations of a mixture of iron and hematite loaded at 14 GPa and after heating at about 1,700 K. As indicated by color-coded diffraction lines, major phases in the three patterns are: a) neon and wüstite; b) Fe_4O_5 , neon and hematite; c) Fe_4O_5 and neon. [Click here to view larger image.](#)

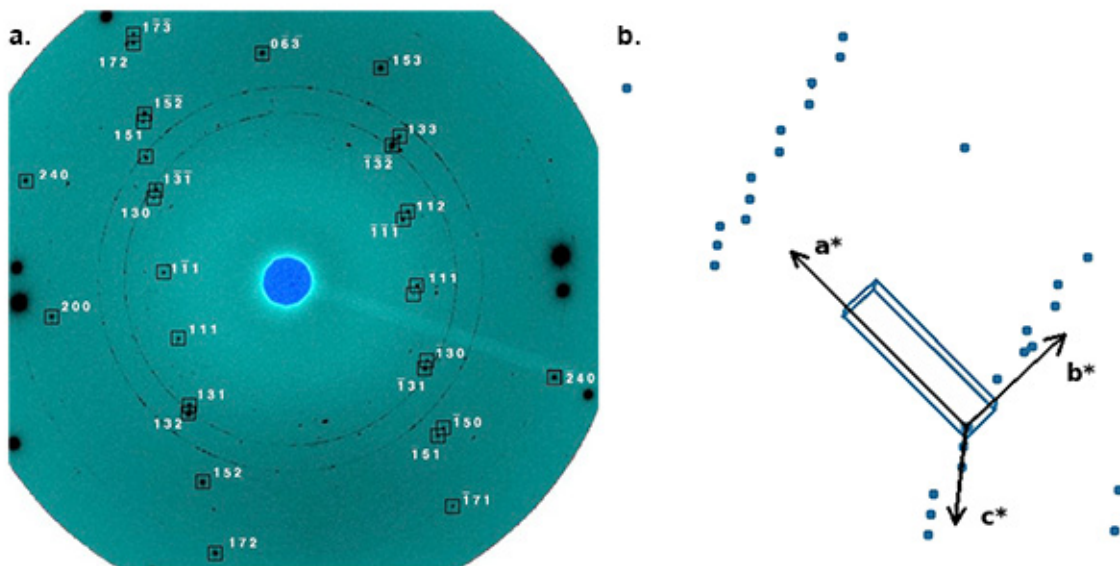


Figure 6. Indexed single crystal diffraction pattern of Fe_4O_5 ¹ (a). Diffraction peaks in the reciprocal space and unit cell (b). [Click here to view larger image.](#)

Discussion

Every step of the described protocol must be performed with great care to avoid risks of experimental failure via catastrophic shatter of the anvils, gasket instability and loss of pressure, inability to achieve target temperature, sample contaminations, severe non-hydrostaticity, *etc.*

The greatest challenge of high P-T synthesis is the interpretation of x-ray diffraction data, a problem too extensive to be summarized here. While structural solution is inherently a non-trivial problem^{24, 25, 26}, high pressure data suffer from very high background, presence of parasitic scattering, absorption effects, peak broadening and overlapping, poor grain statistics, multiphase samples, *etc.* It is therefore important to collect diffraction patterns with the highest possible resolution and redundancy.

Until recently, due to technical limitations and time constraints, most high pressure synthesis products were characterized using a single still diffraction pattern. Such an approach is suitable for the characterization of simple structures and homogeneous samples. By fine mapping the samples with a highly focused beam and using a multi-technique approach, we properly account for, and even take advantage of, the spread in grain sizes of a sample synthesized in the LH-DAC. The characterization of the structural properties of each phase composing heterogeneous samples is performed in selected patterns, preferably single-phase and better approaching an ideal powder and/or single crystal diffraction pattern. Once the structural parameters of each phase are well defined, they can be used to interpret the most complex multiphase patterns. Mapping the sample composition greatly enhances our understanding of the processes occurring in the LH-DAC. While requiring significant

efforts in data collection and processing, the described approach leads to a robust and complete structural analysis of relatively complex samples and structures.

Disclosures

The authors declare no conflict of interest.

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