Squeezing the Best Data out of Your High-Pressure Experiment

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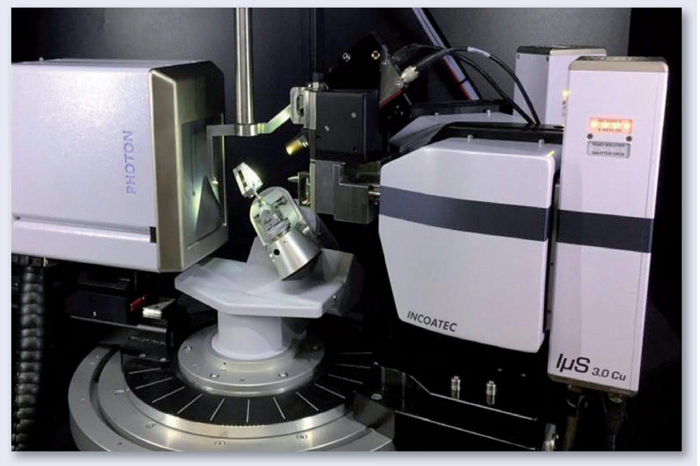
Over the last decade, high-pressure studies have received a significant increase in interest. Typical applications [1-3] range from the investigation of high-pressure polymorphism of solid-state organics as part of the pharmaceutical drug development to the study of rocks and minerals with an applied pressure of up to 50 GPa [4] and beyond [5]. A major challenge in the field of high-pressure crystallography is the acquisition of data of sufficient quality and completeness for a successful structure determination [6]. Here, we will be reviewing recent advances in hardware development, such as X-ray detectors and X-ray sources for higher energies, and highlight the latest improvements in software for data acquisition and reduction in high-pressure experiments.

Experimental Challenges in High-Pressure Crystallography

Due to the design of even the smallest diamond anvil cell (DAC), a high-pressure data collection imposes several challenges to the experimental setup:

- Special collimator and beamstop allowing free rotation of the DAC
- Reliable collision prevention taking into account even relatively large DACs
- Very flexible goniometer to provide access to all data not shadowed by the DAC
- High brightness X-ray source with harder radiation (Mo-Kα, Ag-Kα, In-Kα) to increase the accessible reciprocal space and reduce background as well as absorption
- Small X-ray beam cross-section to avoid parasitic diffraction from the gasket
- Sensitive X-ray detector with high efficiency for harder radiation



Bruker D8 VENTURE DUO with two IμS 3.0 X-ray sources and PHOTON II detector, ready to take on the challenges of high-pressure crystallography.

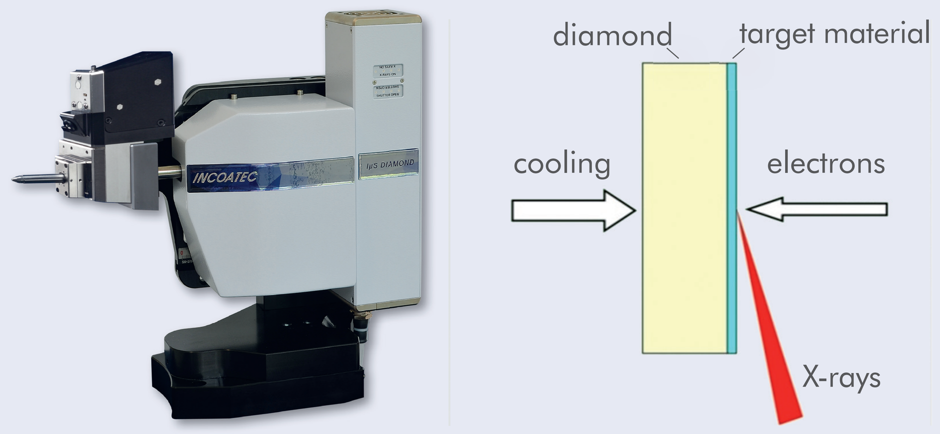
X-ray Detectors for Harder Radiation

The recently introduced PHOTON III CPAD detector series combines photon-counting and charge-integration (mixed-mode detection) for highest sensitivity and best dynamic range. With no gaps and no noise (no charge-sharing noise, no read-out and dark-current noise), the PHOTON III detector family delivers the ultimate data quality for crystallography in the home lab. For X-ray energies > 20 keV, dedicated PHOTON III detectors are available with optimized phosphors, improving the quantum yield significantly. Mixed-mode detection allows for very long exposure times that are crucial for high-pressure experiments with harder radiation due to the relatively weak interaction, especially when very small crystals are studied.

Hard Radiation X-ray Sources

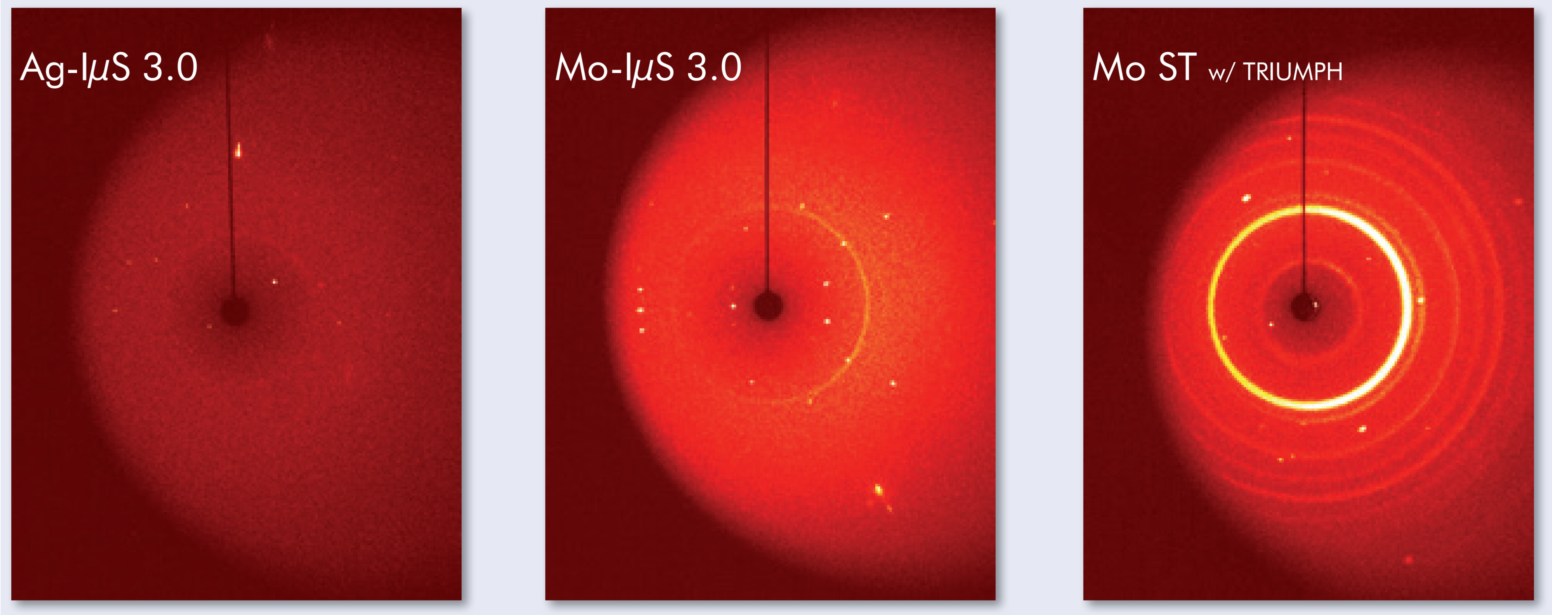
Over the years, Incoatec has improved the performance of the IμS by optimizing critical parameters in the X-ray tube, such as take-off angle and electron beam focusing. As a result, the IμS 3.0 is the first and only microfocus sealed tube source that is fully optimized for X-ray diffraction applications, combining a superb intensity with a new beam path design and a high-precision mounting concept (quicklock concept) which allows for a true downstream alignment and swappable optics for maximum user friendliness.

The latest development of Incoatec's X-ray tube factory is the IμS DIAMOND, a new microfocus sealed tube with a unique anode technology - the diamond hybrid anode. It uses an industrial diamond substrate as a heat sink, taking advantage of the exceptionally high thermal conductivity of diamond, which is about 5 times higher than that of copper and the highest known conductivity of all bulk materials. This allows for a higher power density in the focal spot on the anode, and, hence, yields a higher intensity. It comprises the latest generation of Montel multilayer optics to form the most intense microfocus X-ray sealed tube source currently available. The IμS DIAMOND combines the performance of a low power microfocus rotating anode with the reliability, low maintenance, low cost of ownership and high uptime of a conventional microfocus sealed tube source with a bulk copper anode, and is now available for Cu-Kα, Mo-Kα and Ag-Kα radiation.



The IμS DIAMOND and working principle of the diamond hybrid anode.

Why Using a Microfocus X-ray Source for High-Pressure Crystallography?



The IμS 3.0 and IμS DIAMOND not only give intensities that are significantly higher than the intensity from standard sealed tubes. The small beam cross-section of the focused beam from the multilayer optics results in a dramatic reduction of the parasitic scattering at the gasket, as shown below in typical diffraction patterns from a Ylid crystal in a DAC.

Typical diffraction images of a monoclinic Ylid crystal in a diamond anvil cell, recorded with different X-ray sources (Ag-IμS 3.0, Mo-IμS 3.0 and 2kW Mo sealed tube with monochromator) and with the goniometer at comparable angular settings.

References

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[4] D. R. Allan, R. Miletich, R. J. Angel, *Rev. Sci. Instrum.*, (1996), 67, 840-842.
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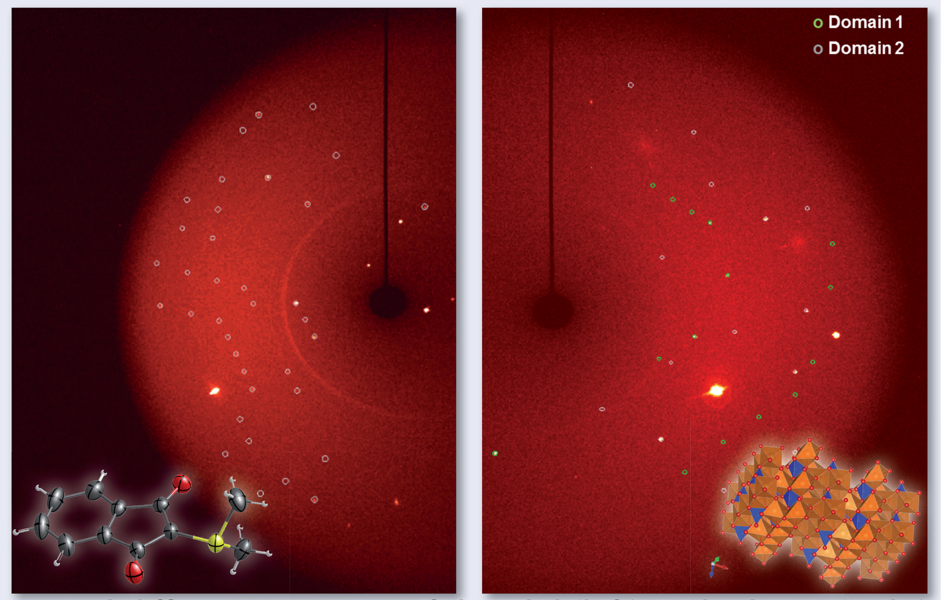
High-Pressure Crystallography Studies using a Bruker D8 VENTRUE

To demonstrate the capabilities of a Bruker D8 VENTURE, data of a monoclinic sulfonium ylid crystal (0.05×0.05×0.12 mm^3) in a DAC were collected and compared to a standard data collection under ambient conditions using the same crystal. Further, a pressurized two domain Olivine sample (0.02×0.02×0.02 mm^3) was investigated to highlight how multiple crystal handling can help to increase the data completeness and, thus, improve the data quality.

Crystal Centering and Data Aquisition

In the first step, the crystals encapsulated in a DAC were aligned optically. Then, based on two subsequent short omega scans, the APEX3 *Crystal Centering Refinement* plug-in was used to determine the actual crystal position and to perfect the crystal alignment. Data sets were acquired using multiple sets of omega and phi scans optimized for the DAC's opening angle. Because the angular range of the scan is limited by the DAC's opening angle, the cell was first oriented perpendicular to the conical opening and then scanned in both positive and negative directions by one-half of the opening angle; this allows for the best data processing. Due to the limited accessibility of diffraction data imposed by the geometry of the DAC, it is, in general, advisable to collect as much data of the reciprocal space as possible regardless of the sample's symmetry, as high multiplicity will be improving the data quality.



Typical diffraction images of the Ylid (left) and Olivine (right) data collections showing shaded areas and diffuse rings resulting from the DAC.

Data Reduction and Results

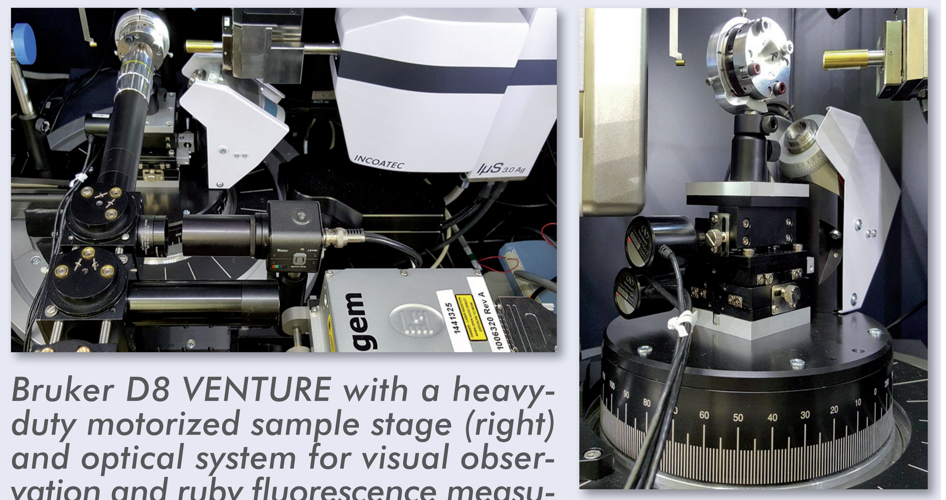
The APEX3 software suite offers advanced tools tailored to the requirements of high-pressure experiments. All tools are fully implemented in the user interface to guaranty an intuitive data processing and analysis work flow. APEX3's *Determine Unit Cell* and *View Reciprocal Lattice* plug-ins allow for the quick and easy indexing of all sample and diamond domains. Multi-Bravais integration with SAINT using dynamic image masks calculated "on-the-fly" and "best-plane" background determinations yield the best sample intensity data, stripped of all artefacts from DAC shading or diamond reflection overlaps. Both the crude single crystal (Ylid) and the two domains (Olivine) hkl data were further processed using the APEX3 *Scale* plug-in. For the Olivine data, both equally strong domains were used to increase the data completeness. Structure solution and (twin-)refinement were performed using the *Solve* and *Refine Structure* plug-ins of APEX3.

	Ylid			Olivine	
Source	Mo IμS 3.0	Mo IμS 3.0	Ag IμS 3.0	Mo IμS 3.0	Mo IμS 3.0
Experiment	Ambient	DAC	DAC	DAC	DAC
Exp. time [h]	2.51	13.3	50.0	13.96	13.96
Exposures [s/°]	10/0.5	10, 20/0.5	30, 120/0.5	10/0.5	10/0.5
Completeness [%]	99.9	35.2	41.9	57.5	79.4
Multiplicity	7.5	20.3	22.8	17.7	19.4
HKL format	4	4	4	4 (one domain)	5 (two domains)
Unique / Observed Refl.	2142 / 1950	753 / 666	905 / 751	187 / 176	312 / 286
R_{int} [%] [Å]	2.25	2.88	5.32	2.60	2.60
R1 [%]	2.93	3.01	3.20	1.79	1.92
Diff.Density [e$^-$/Å^3]	0.24/-0.24	0.10/-0.09	0.10/-0.11	0.21/-0.29	0.26/-0.36

The comparison of the ambient condition data and the DAC Ylid data impressively shows that the sophisticated data processing functions of APEX3 eliminate systematic experimental features introduced by a DAC, resulting in a quality of the high-pressure data that is comparable to ambient single-crystal experiments. The investment of longer exposures using Ag radiation clearly pays off in higher data completeness. Good residual values were also obtained for the pressurized two domain Olivine sample. The intuitive multi-domain handling implemented in the APEX3 user interface allows to significantly increase the completeness achievable in a single high-pressure experiment.

Advanced Accessories for Cutting-Edge High-Pressure Crystallography

Over the last two decades, the great majority of high-profile crystallographic studies in mineral physics have been performed at synchrotron facilities. Besides the most obvious advantages of much higher incident beam intensity, small focal spot size, and adjustable energy, synchrotron instruments were the only ones to provide the accuracy of motorized sample positioning and the availability of on-line pressure measurements based on ruby fluorescence. All of these components make the experiments with tiny mineral crystals enclosed in diamond anvil cells more reliable and dramatically increase the data quality. Now, some of these features have been made available for the home-lab, turning a Bruker D8 VENTURE instrument into "a little synchrotron at home".



Bruker D8 VENTURE with a heavy-duty motorized sample stage (right) and optical system for visual observation and ruby fluorescence measurements (left) (courtesy of P. Dera).

Conclusion

Modern D8 QUEST and D8 VENTURE instrumentation equipped with a Mo- or Ag-IμS microfocus source, a PHOTON CPAD detector, and APEX3 software is an optimum setup for home-lab high-pressure experiments, providing high-pressure data that yield structures comparable in quality to standard single-crystal experiments. Advanced accessories offer cutting-edge functionalities, which before were only available at synchrotrons.