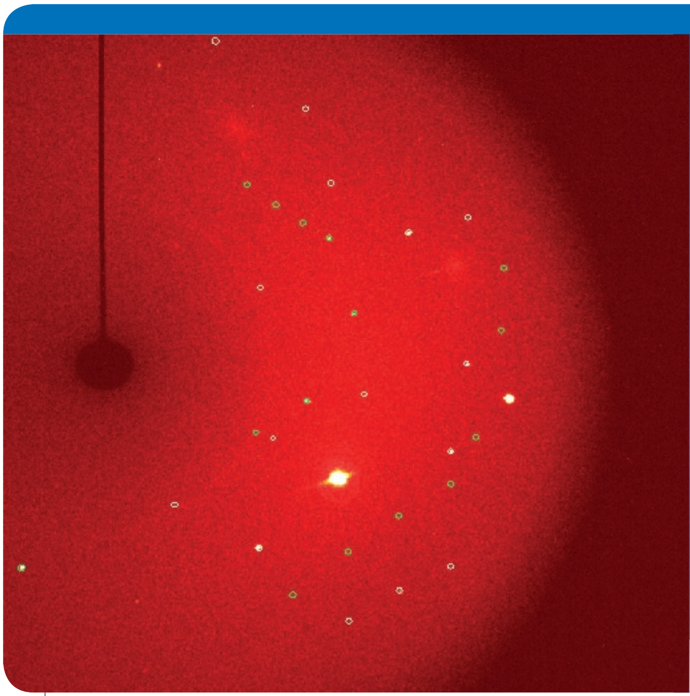


Application Note SC-XRD 516

When one crystal is not enough

- Better Completeness with Multiple-Crystal High-Pressure Experiments

Introduction

This Application Note explores a method for increasing the completeness of high-pressure experiments by mounting multiple samples in a Diamond Anvil Cell (DAC) and measuring and processing data concurrently. Two small olivine crystals were investigated: first independently, and then in a multiple-crystal DAC experiment. These experiments were then compared.

One of the challenges of high-pressure experiments is the limited accessibility of reciprocal space caused by geometrical limitations. The vises, backing plates, and gaskets used with DACs restrict accessibility to about 30% of the reflections in a triclinic sphere. Especially for lower-symmetry samples, the smaller number of reflections available for structure refinement can reduce the structure quality and require restraints or even constraints. Recent enhancements in hardware and software design have brought dramatic improvements in data acquisition and data processing quality both for high-pressure and multiple-domain-sample experiments.

Figure 1: D8 VENTURE dual microfocus source instrument.

Experiment

Data was collected on two small olivine crystals. First, data was acquired on the two crystals individually at ambient conditions. Data was collected with a D8 QUEST equipped with a Mo sealed tube, TRIUMPH monochromator, FIXED-CHI goniometer, and PHOTON II detector (Experiments 1 and 2). Then, both crystals were mounted in a Diacell Bragg-Mini Diamond at ambient conditions without applying pressure. Data was collected on a D8 VENTURE equipped with a Mo IμS microfocus sealed source, KAPPA goniometer, and PHOTON II detector (Experiments 3 and 4, Figure 1).

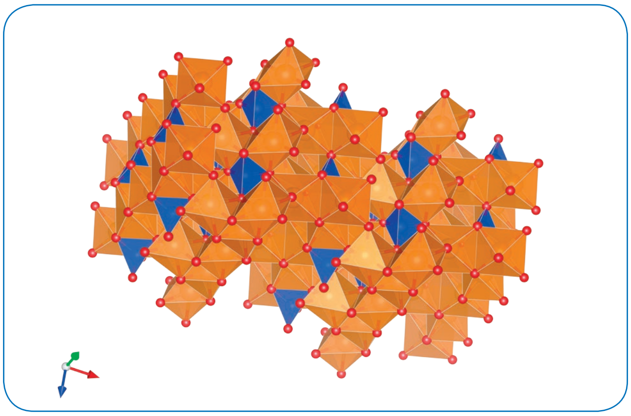


Figure 2: Olivine structure.

Olivine is a magnesium iron silicate with a ratio of magnesium to iron (for the samples used) of about 8:1 with an approximate formula of $(Mg_{0.89}Fe_{0.11})_2SiO_4$. Olivine crystalizes in the orthorhombic space group Pnma with a unit cell of a = 10.2297(2), b = 5.9952(1), c = 4.7618(1) (Experiment 1). SiO_4 tetrahedra cap voids in the zigzag chains of Mg/Fe octahedra (Figure 2).

The cell used for the experiment was a Merrill-Bassett diamond anvil cell, the Diacell Bragg-Mini purchased from Almax easyLab Inc. The Diacell Bragg-Mini is small and light and can be easily mounted on a standard goniometer head (Figure 3, part number A30B48). The pale green crystals were prepared by crushing a larger crystal between two glass slides. Two similar-sized crystals with dimensions of about 15 × 20 × 20 micrometers were chosen for the experiment.

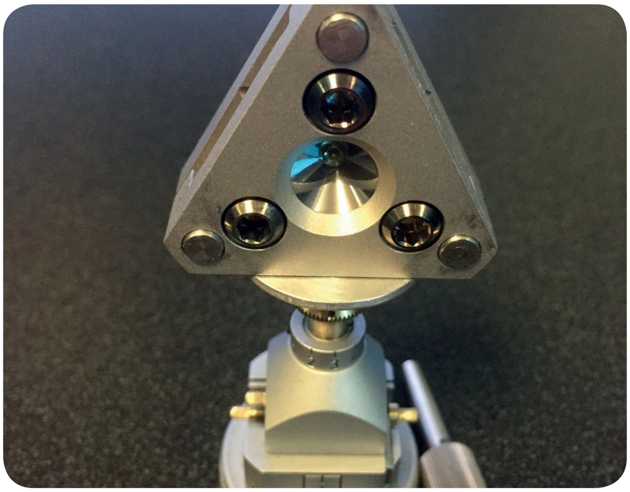


Figure 3: Diacell Bragg-Mini on XYZ goniometer head.

Data Collection and Processing

The data collection strategies for Experiment 1 and 2 (i.e., the control experiments) were determined using APEX3, based on the samples' orientation matrices determined from a fast scan for each. Data was collected with a combination of phi and omega scans and processed using standard methods in APEX3 for data integration, scaling, structure solution, and refinement. Table 1 shows a summary of data collection and processing parameters. Both experiments delivered very good reliability criteria for the refined structures with $R1$ = 1.50% for Experiment 1 and $R1$ = 1.73% for Experiment 2.

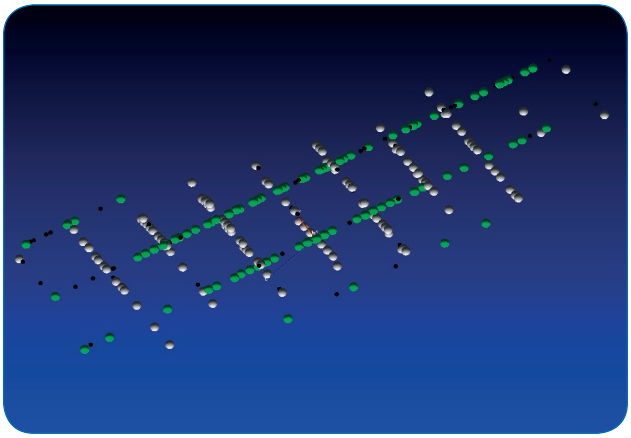
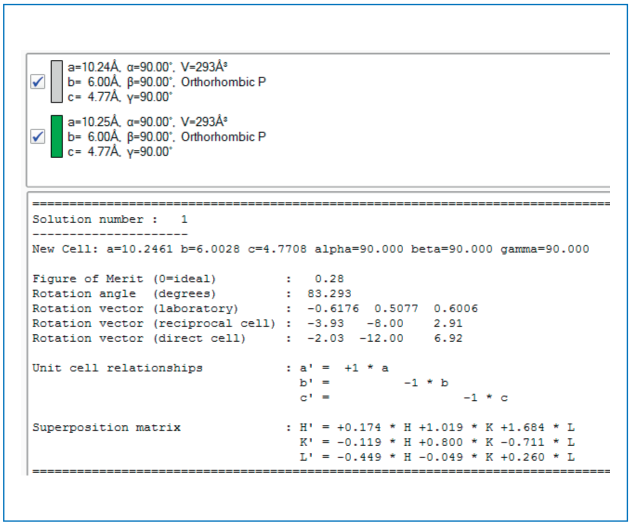


Figure 4: The reciprocal space viewer shows both Olivine diffraction patterns nicely separated.

Experiments 3 to 6 shared the same frame data. With limited accessibility to diffraction space due to the geometry of the DAC, it is sensible to collect as much of the reciprocal sphere as possible regardless of the sample's symmetry. While the overall data collections time significantly increases, high multiplicity is advantageous during data processing, as it will help improve data quality. Data was acquired using the KAPPA goniometer, with sets of omega and phi scans optimized for the DAC's opening angle. The IµS microfocus source was chosen to keep the increase in data acquisition time within reasonable limits.

Because the scan's angular sweep 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 the opening angle; this allowed for the best data processing. Data was basically treated like a twinned sample. With two olivine crystals and two diamonds contributing to the diffraction pattern, it was first necessary to identify the domains of both olivine samples.



☑ ⬜ a=10.24Å, α=90.00°, V=293Å³
b= 6.00Å, β=90.00°, Orthorhombic P
c= 4.77Å, γ=90.00°

☑ 🟩 a=10.25Å, α=90.00°, V=293Å³
b= 6.00Å, β=90.00°, Orthorhombic P
c= 4.77Å, γ=90.00°

```
==========================================================================
Solution number :   1
---------------------
New Cell: a=10.2461 b=6.0028 c=4.7708 alpha=90.000 beta=90.000 gamma=90.000

Figure of Merit (0=ideal)          :   0.28
Rotation angle  (degrees)          :  83.293
Rotation vector (laboratory)       :  -0.6176  0.5077  0.6006
Rotation vector (reciprocal cell)  :  -3.93   -8.00    2.91
Rotation vector (direct cell)      :  -2.03  -12.00    6.92

Unit cell relationships            : a' =  +1 * a
                                     b' =          -1 * b
                                     c' =                  -1 * c

Superposition matrix               : H' = +0.174 * H +1.019 * K +1.684 * L
                                     K' = -0.119 * H +0.800 * K -0.711 * L
                                     L' = -0.449 * H -0.049 * K +0.260 * L
==========================================================================
```

Figure 5: Compare Unit Cells output provides details on the relative orientation of the sample.

APEX3's Reciprocal Space Viewer plug-in was used to separate the olivine domains for indexing. Typical for randomly-oriented crystals, the diffraction pattern shows little overlap. (Figure 4). The Compare Unit Cells plug-in calculated the relative orientation of the domains to be a favorable 83 degrees (Figure 5). The Integrate Images plug-in was used to integrate both domains concurrently (Figure 6), and the Scale plug-in was used to deconvolve hkl data and produce hkl format 4 data for structure solution and initial refinement (Experiments 3, 4 and 5), as well as hkl format 5 data for final structure refinement (Experiment 6) with SHELXL. Experiment 3 is data from domain 1 and experiment 4 is data from domain 2. Experiments 5 and 6 contain data from both domains.

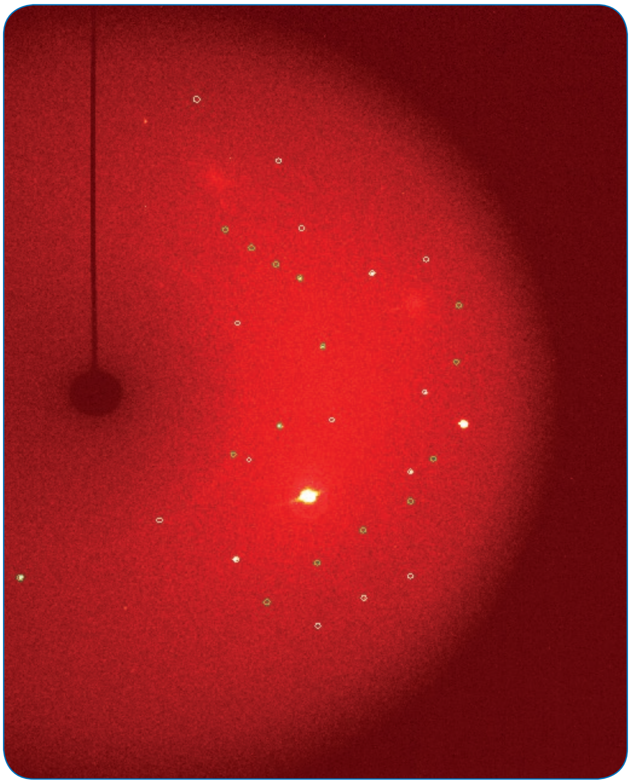


Figure 6: Concurrent integration an of both patterns with SAINT.

Single domain Experiments 3 and 4 illustrate the problem with low completeness (57.5% for experiment 3 and only 35.1% for experiment 4). For experiment 4, the very low completeness severely impacts the quality of the structure refinement with the highest *R*1 of 4.63% and the highest residual densities. This is even more remarkable, as a smaller number of reflections (lower parameter-reflection ratio) from a theoretical point of view results in lower residuals (*R*-factors).

Both Experiments 5 and 6 rival the data quality of Experiments 1 and 2 (i.e. the control experiments), with reliability criteria below 2%: *R*1 = 1.82% for Experiment 5 and *R*1 = 1.92% for Experiment 6. The extraordinary fact is that, although the DAC only allows access to about 30% of reciprocal space, Experiments 4 and 5 have high completeness (79.4%). Data from two crystals (combined with a favorable orientatvion of about 83 degrees relative to each other) provided a nearly complete data set for a high-pressure experiment.

Conclusion

This example, combining specialized techniques for both high pressure and twins, showcases Bruker's advances in X-ray hardware and software. Bruker's sophisticated tools for data acquisition and processing can make even the most difficult experiments yield superb results.

Author

Dr. Michael Ruf, Bruker AXS Inc, Madison, WI, USA

		Experiment					
		1 Domain 1	2 Domain 2	3 Domain 1	4 Domain 2	5 Domains 1+2	6 Domains 1+2
Setup	Source	Mo TRIUMPH	Mo TRIUMPH	Mo IμS	Mo IμS	Mo IμS	Mo IμS
	Experiment type	<control>	<control>	DAC	DAC	DAC	DAC
	Goniometer type	FIXED-CHI	FIXED-CHI	KAPPA	KAPPA	KAPPA	KAPPA
	Experiment time (h)	3.42	2.58	13.96	13.96	13.96	13.96
	Exposure (s/°)	3/5/10	3/5/10	20	20	20	20
	HKL format	4	4	4	4	4	5
Results	Resolution (Å)	0.8	0.8	0.8	0.8	0.8	0.8
	Completeness (%)	99.4	99.4	57.5	35.1	79.4	79.4
	Mean multiplicity*	14.5	11.3	17.72	22.77	19.38**	19.38**
	Unique reflections	324	324	187	114	258***	312***
	Observed	294	289	176	110	246	286
	R_{int} (%)	3.57	4.25	2.60**	2.60**	2.60**	2.60**
	R1 (%)	1.50	1.73	1.79$^{\#}$	4.63$^{\#}$	1.82	1.92
	Difference density (e$^-$/Å^3)	0.263/-0.252	0.268/-0.289	0.205/-0.287	0.649/-0.531	0.221/-0.328	0.261/-0.364

*Multiplicity of measured reflections, **Values derived from Scale plug-in (TWINABS), ***The number of unique reflections in experiment 6 is higher because identical hkl reflections from the 2 domains are kept separate in the hkl format 5 file, whereas they are combined in the hkl format 4 file, # The incomplete data set leads to artificially low R-factors.

Bruker AXS GmbH

info.baxs@bruker.com

www.bruker.com

Worldwide offices

bruker.com/baxs-offices

Online information

bruker.com/sc-xrd