SINGLE CRYSTAL X-RAY DIFFRACTION

Improved data quality for high-energy measurements with the PHOTON III HE detector

Application Note 530

Introduction

High-energy (short wavelength) radiation such as Ag Kα (22.5 keV, 0.56 Å) is advantageous for many applications in crystallography. Using higher X-ray energies, sample absorption is reduced, and the accuracy of scaling and absorption correction is improved for strongly absorbing samples. Shorter wavelengths produce more compact diffraction patterns resulting in more efficient data collection, particularly in high-pressure experiments using diamond anvil cells with limited opening angles. Additionally, shorter wavelengths allow easy access to higher resolution data required in charge density studies.

The IμS 3.0 and IμS DIAMOND II Ag X-ray sources deliver up to 10× higher intensity than conventional microfocus sealed tube sources, and so challenging high-energy measurements can now be consistently performed in a short time.

The PHOTON III HE provides very high Detective Quantum Efficiency (DQE) for high-energy radiation combined with a large active area and photon-counting, making it the ideal detector for use with Ag radiation.

This application note uses data collected on a small crystal of calcium hexafluorosilicate dihydrate ($CaSiF_6 \cdot 2H_2O$) to demonstrate the improved performance of the PHOTON III HE with an Ag IμS 3.0 X-ray source.

Table 1 Selected properties of the PHOTON III and PHOTON III HE

	PHOTON III	PHOTON III HE
X-ray source	IμS 3.0 (Ag Kα 22.5 keV, 0.56 Å)	
Detector area [mm^2]	14 000	
DQE, Ag Kα [%]	69	93

Figure 1
D8 QUEST with Ag and Mo IμS 3.0 X-ray sources and PHOTON III HE detector.

Experimental – Comparison of PHOTON III and PHOTON III HE

A D8 VENTURE equipped with an Ag IµS 3.0 microfocus X-ray source and a FIXEDCHI goniometer was used to compare measurement times and data quality from the new PHOTON III HE with the PHOTON III.

A small crystal of $CaSiF_6 \cdot 2H_2O$ was measured at Ag Kα (22.5 keV). The crystal unit cell parameters were a = 5.7293(3)Å, b = 9.1802(4)Å, c = 10.4773(4)Å, β = 98.947(2)°, and V = 544.36(4) $Å^3$ with space group $P2_1/n$. Identical strategies were used to collect data on both detectors to collect complete data to 0.60 Å.

The large detector area enabled complete data with 6-fold multiplicity to be collected at a single 2-theta setting in just seven minutes.

Figure 2 shows two equivalent frames recorded with the PHOTON III and PHOTON III HE with identical crystal orientation and exposure time. The highlighted reflection on the PHOTON III HE exhibits a peak intensity 40% higher than the same reflection on the PHOTON III. This is directly proportional to the higher DQE of the PHOTON III HE.

The reflection intensities being fully proportional to the DQE nicely demonstrates both the highly linear count-rate and the zero noise of the PHOTON III detectors.

Parameter	Value
Wavelength	Ag Kα (0.56 Å)
Experiment time [min]	7.2
Number of scans	3
Exposure [s]	0.6
Frame width [°]	0.8
Resolution [Å]	0.60
Completeness [%]	100
Multiplicity	6.1

Table 2
Data collection param-etersfor $CaSiF_6 \cdot 2H_2O$. Identical parameters were used for collecting data on both the PHOTON III and the PHOTON III HE.

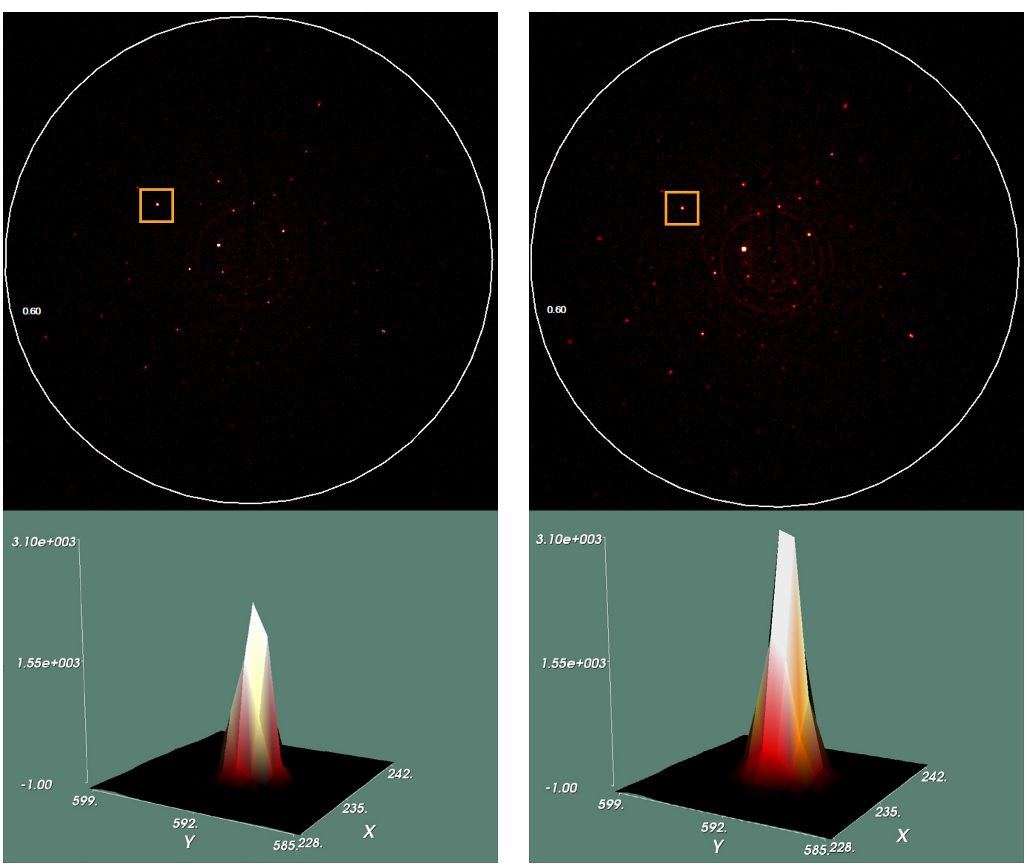

Figure 2
0.6 s diffraction images using Ag radiation recorded with the PHOTON III (left) and PHOTON III HE (right). Both images show excellent signal and near zero noise.
The highlighted reflection (-5,1,13) recorded with the PHOTON III HE has an intensity maximum 40% greater than that recorded under identical conditions with the PHOTON III (insets).

PHOTON III HE - the best data with Ag radiation

Table 3 shows the refinement parameters for the PHOTON III and PHOTON III HE data collections. Data quality from both detectors is excellent, but the new PHOTON III HE yields appreciably better-quality data.

A direct result of the higher DQE of the PHOTON III HE is an overall ~20% higher $I/\sigma(I)$ than the PHOTON III could achieve. This ratio is fully consistent with the expected increase for a noise-free, photon-counting detector.

The improvement in data quality is particularly significant for the weak reflections with the R_{int} for the highest resolution shell reduced by almost 15%.

The higher quality data from the PHOTON III HE consequently, results in a more accurate structure model. Structure residuals R_1 and $wR2$ are reduced by 13%, and 10% respectively.

	PHOTON III	PHOTON III HE
Max. Resolution [Å]	0.60	0.60
R_{int} all / 0.7 - 0.6 Å [%]	9.54 / 21.69	9.18 / 19.33
I/σ all / 0.7 - 0.6 Å [%]	9.25 / 5.01	11.36 / 5.81
Observed reflections ($Fo^2>2\sigma(Fo^2)$) [%]	80.02	82.42
R_1 ($Fo>4\sigma(Fo)$ / all) [%]	4.39 / 6.08	3.84 / 5.32
$wR2$ [%]	15.00	13.59
Residual electron density [e/Å^3]	1.13 / -1.17	1.21 / -1.16

Table 3
Data quality and refinement statistics.

Structure of $CaSiF_6 \cdot 2H_2O$

- This is the first reported single crystal structure of $CaSiF_6 \cdot 2H_2O$. Calcium hexafluorosilicate bishydrate, $CaSiF_6 \cdot 2H_2O$, is a widely used chemical [1], and yet there is no single crystal structure data in the ICSD. An earlier paper reported a structure determined by whole-pattern Rietveld refinement using simulated annealing [2].
- The crystal structure is assembled from individual SiF_6^{2-} octahedra which, together with water, form an 8-fold antiprismatic coordination sphere around the Ca^{2+} ion.
- The high-quality data collected with the PHOTON III HE allows for the anisotropic refinement of all non-hydrogen atoms and provides significantly better atom positions, bond lengths, angles, and related standard deviations.
- The structure features ideal octahedral geometry of the SiF_6 moieties with Si-F bond length of 1.6880(13) Å.
- The high-quality data enabled the free refinement of the hydrogen atom positions with unconstrained isotropic displacement parameters. This is the first atomic description of the O-H-O and O-H-F hydrogen bond networks.

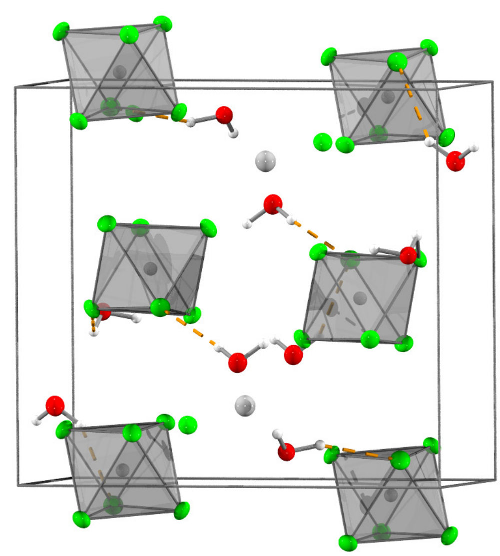

Figure 3
Structure of $CaSiF_6 \cdot 2H_2O$. Data collected in 7 minutes on a D8 VENTURE equipped with Ag IµS 3.0 and PHOTON III HE detector.

Conclusions

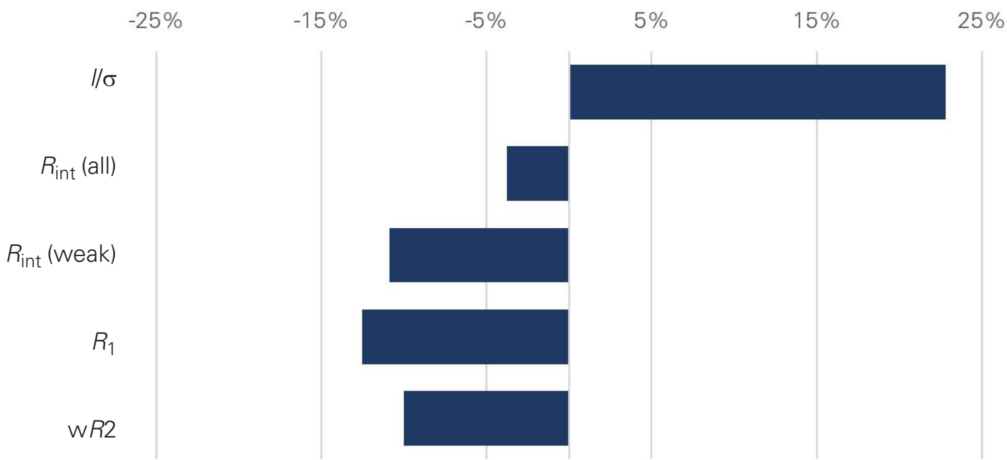

Figure 4
Improvement of data quality and refinement statistics when using the PHOTON III HE versus the PHOTON III.

- **The high-intensity IμS microfocus X-ray sources enable efficient data collection using Ag radiation.**
- **The PHOTON III HE is optimized for high energy applications with a DQE >90% for Ag radiation.**
- **The PHOTON III HE produces significantly better quality data and refinement statistics from crystals measured using Ag radiation.**
- **The PHOTON III HE is the ideal detector for the D8 QUEST and D8 VENTURE equipped with Ag radiation X-ray sources.**

References

[1] CAS 16961-80-1

[2] S. Frisoni, S. Brenna, N. Masciocchi, Powder Diffraction 26(4), 2011.

Bruker AXS

info.baxs@bruker.com

bruker.com

Worldwide offices
bruker.com/baxs-offices

Online information
bruker.com/sc-xrd