Small Crystal Diffraction Experiment with Vacuum Camera for Structure Analysis Beamline

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1.Introduction

Member of the subgruup "Chemical Reaction" collaborated with the other three sub-groups in constructing a bending magnet beamline BL02B1 (Crystal Structure Analysis). Details of the beamline and the diffractometer are described elsewere [1]. On November 1997, X-ray diffrction experiments using the vacuum camera, which was originally designed for laboratory X-rays by K. Tanaka and modified for Spring-8 by Y. Noda and K. Tanaka, were carried out. The vacuum camera is an evacuated cylindrical camera with an imaging plate (IP) attached inside. The camera radius is 75mm and the size of the IP is 440x220mm^2. It enables to measure structure factors under vacuum, that is, extremely low noise and can be used for crystallite structure analysis and electron density measurement. The present article reports the results of our experiments on November 1997 for $KNiF_3$, $Pt_2(dta)_4$,I, Ru complex, a charge transfer complex and an organic small crystals.

2.Experimental

X-rays with energies, 20keV, 30keV, and 50keV monochromated by Si(311) were utilized with the SR beam current from 20mA to 10mA. The incident beam energy was changed by Dr. Yamagata of Spring-8 in a few hours, adjusting parameters for monochromator orientation and platform postitions by a computer controlled system by watching a beam spot with a CCD camera and by counting the beam intensity . XAFS from proper metal foils were measureed to determine the wavelenghs. The vacuum camera is mounted on a off-center 7-axis Huber diffractometer and ϕ-axis permits the rotation of the crystal. The deviation of the orientation of the camera from zero 2θ-position was adjusted by the ω-axis rotation of the diffractometer. The necessary adjustment ranges from 0.1 to 0.3 $^\circ$. Incident X-rays passing through slits 0.5mmϕ or 1.0mmϕ, which comes into the camera passing through a beam paths 50mm long and 3mmϕ at the frontal and rear sides, were used. Once we adjusted the beam position, we did not need to adjust it again. The direct beam-stooper was located outside the camera to avoid high background. The X-rays at 50 keV was intense enough to penetrate through the Al cylinder of 15mm thick and the reflected beam from the beam-stopper penetrate again into the cylinder. Lead plates on both frontal and rear sides of the camera were necessary. However the background intensity recorded on IP were reduced one hundredth of the measured one without evacuating the cmaera. Even zero background area were found on a significant part of an IP plate, when $KNiF_3$ crystal with a diameter of 60μm was attached on a glass capillary with a diameter of 10μm. The oscillation photographs were taken with the overlap of the rotation angle to do the scaling between IP plates. The oscillation and overlap ranges were appropriately determined for each crystal. A program for calculating optimum rotation range for each crystal and incident beam energy was programmed by Takenaka and will be available.

3.Results

a.Electron density mesurement of small crystal with high energy X-rays

Since the electron density of $KNiF_3$ has been extensively studied [2,3], it can be a good smaple to assess the quality of the X-ray beams of BL02B1 and test the performance of the vacuum camera. 50keV SR beam were employed to make the extinction effect minimum. Incident beam slit of 0.5mm wide was used. A $KNiF_3$ crystal was shaped into a sphere with a diameter of 60mm. A total of nine photographs were taken by rotating the crystal by 10 $^\circ$ sixty times.

The scan speed 10° /min was selected so that single scanning is accomplished within a minute to avoid the error due to decay of the incident SR beam intensity. The rotation angle were overlapped by 3° for the scaling of intensities recorded on separate IP plates. Accordingly photographs of rotation angle between 35 and 109° were taken. The position of X-ray beam was stable during the measurement. The orientation matrix was obtained by DENZO [4] using the phtograph rotating ϕ-axis from 0° to 5°. Judging from the shift of the peak positions calculated by DENZO fixing the cell dimensions to those previously determined, the X-ray wavelength was slightly deviated from 50keV within the error of 1%. The intensity data is now being analyzed by HIPPO98 [5] and the detailed results will be presented elsewhere.

b.Small crystallite structure determination

To investigate the physical or chemical properties of the materials, the three-demensional crystal structure is one of the indispensable information. However sub-millimeter single crystals are required in the ordinary laboratory experiment. There are many crystals that show very interesting properties but the structure have not been determined yet since the crystals suitable for the structure determination cannot be obtained. Synchrotron radiation makes it possible to determine structures of micrometer sized crystals. Crystal structure of $[Ru(en)_2(NO)(OH_2)]$ CI_3 (en= $H_2NCH_2CH_2NH_2$) was determined. A single crystal with the size of 85x60x60μm^3 was irradiated by 29.2keV X-rays. Diffraction pattern was collected using the vacuum camera at BL02B1. Indexing and integration of the Bragg diffractions were performed using the program DENZO. The structure was solved by the direct method and refined by the full-metrix least squares method with the program SHELXS97. The structure was successfully solved and was converged to R=0.117 for 61 parameters and 495 observed reflections with $F_{obs} > 4\sigma(F_{obs})$.

Diffraction intensities from a charge transfer complex with dimensions of 30x30x5μm^3 were collected with the vacuum camera. Sufficient diffraction patterns from this crystal were not recorded even with exposures for one hour or more using the IP diffractometer. X-ray beam with energy of 29.2keV monochromatized by Si (311) was narrowed by a slit of 0.5 or 1.0mmϕ. Oscillation photographs recorded for 30 to 60minutes gave diffraction patterns up to $\sin\theta/\lambda$=0.6. Cell constants were successfully determined using DENZO. Unfortunately, the specimen was deteriorated in the course of exposures and the whole diffraction data could not be collected. We can demonstrate, however, that the intensity collection using the vacuum camera system can be utilized for such a small crystal from which diffraction pattern could not be recorded using a laboratory system.

The diffraction intensity of a host-guest compound was measured using the vacuum camera. When this compound is irradiated by light, chiral molecule is created from achiral molecule in more than 90%ee. In order to determine the reaction mechanism of this compound, the crystal structure determination was carried out. The size of the crystal was 200x 50x 20μm^3. The energy of the incident beam was set to 20 keV to avoid the overlap of diffracted peaks on the IP. The crystal was oscillated by 6° twenty times, and 1° of overlap of the oscillation range to adjust the scale of each photograph was permitted. The oscillation speed was 6° /min. It required 12 hours for 16 photographs. The ring current was changed from 15.6 to 10.0 mA during the measurements. An indexing of the photographs were carried our, but the integrated intensities were not accurately determined by the existing computer programs because the peaks are too close to distinguish. The energy of the incident beam was too high for this crystal. The cell parameters were determined for the first time for this crystal by the synchrotron radiation measurement, and the suitable wavelength for the intensity measurement was estimated. But the change of the energy of the incident beam required about a half a day, so it was not possible to measure the diffraction intensity using the most suitable wavelength in the limited beam time.

c.diffuse scattering from a mixed valene complex.

X-ray diffuse streaks from a single crystal

of $Pt_2(dta)_4I$ (dat = dithioacetate) with the size of $120x50x30\mu m^3$ was observed with 29.2keV X-rays under the SR beam current 18 mA using the vacuum camera.

Halogen bridged one-dimensional (1-D) platinum dinuclear mixed-valence complex $Pt_2(dta)_4I$ is crystallized from Pt(II, II) complex with diiodide Pt(III,III) one. The crystal structure analyses has shown no distinction between Pt (II) and Pt (III). An x-ray rotation photograph along 1-D axis using the vacuum camera detected weak diffuse streaks between Bragg diffraction spots. These streaks indicate Pt (II) and Pt (III) are one-dimensionally ordered along the chain. The vacuum camera at BL02B1 with bright x-ray source and low-background area detector was proved to be suitable for detecting such very weak diffuse streaks.

4.Conclusion

The vacuum camera were applied to small crystallite structure determinations, electron density and the diffuse scattering measurements. It enabled us to measure weak diffracted intensities under extremely low background. The background level was two order lower than those measured without evacuating the camera and significant area of the IP plate had no background. The well-collimated parallel beams of SR contribute effectively to reducing the background . The scattering by a capillary supporting the crystal should be reduced as possible as we can by using thin cappillaries.

The software for getting intensities from the measured IP data are not well prepared at present. The programs DENZO and HIPPO for Spring-8 BL02B1 taking care of extremely low background will be avilable in a short time. The other programs such as absorption and multiple diffraction corrections will be prepared.

References

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