

Structure refinements of a GeO_2 rutile single crystal at 6GPa using hard x-rays of 25 and 50 keV

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To determine the pressure dependency of each atomic distance is important. For example, the compression behavior of the octahedral shared edge and the unshared edge in a rutile structure is strongly related with the repulsive force between the cations. To clarify those, we are challenging to analyze the electron density under pressures. Generally a diamond anvil cell (DAC) limits the measurable reciprocal space by angular dispersive method because of its geometry. Therefore, high energy x-ray source is desirable especially for the single-crystal diffraction study under high pressure. The beamline facility at BL02B1 designed for the single-crystal X-ray diffraction in the energy range from 5 to 50 keV is useful for this purpose.

This study were performed using hard x-ray radiation of 25 and 50 keV, which was-monochromatized by silicon 311 double crystals. The energies were calibrated by the Nd K-edge (43.5806keV) and Ag K-edge (25.517keV), respectively. A single crystal of GeO_2 rutile with the size of $100 \times 80 \times 40 \mu\text{m}^3$ was synthesized by a flux method, which was compressed in the 4:1 mixture of methanol:ethanol pressure medium using a DAC. The pressure was determined by a conventional ruby R1 fluorescence method. X-ray diffraction intensities were measured using a seven-circle diffractometer installed at BL02B1, in which a distance from the goni center to a scintillation counter is 500mm. The intensity data were collected with the bisecting setting by a ω -scan mode in order to distinguish diffraction peaks of sample with those of Be & gasket. The scan-width and scan-step were 0.4° and 0.005° , respectively. The scan speed was $0.25^\circ/\text{min}$. The size of an incident hole slit and the opening angle of a receiving slit were $0.2\mu\text{m}\phi$ and 1° , respectively.

The cell parameters at 25, 50keV and $\text{MoK}\alpha$ were shown in Table 1, which were calculated by 17 and 27 reflections at 25keV and 50keV, respectively. Cell parameters were not fixed as a tetragonal system in order to check the accuracy of cell refinements. The

α, β and γ -angles indicate that cell parameters were well determined at each energy, though which have relative large e.s.d. This is because the centering of some peaks was not well successful due to the unexpected poor crystallinity of a sample. Especially the crystallinity of a sample largely effects on the centering procedure in the case using highly monochromatized synchrotron radiation source. Diffraction profiles of the 002 reflection using synchrotron radiation at 25, 50 keV and using a conventional Mo rotating anode X-ray generator are shown in Fig.1. Profiles taken by synchrotron radiation are quite sharp compared to those at our laboratory. The S/N ratios for 002 diffraction peak are about 150 at 25keV, 21 at 50keV and 15 at $\text{MoK}\alpha$, respectively. In this study we succeeded to collect the diffraction peak intensities with small d-values up about $0.80\text{\AA}$ at both energies in spite of the geometrical restriction of DAC, which indicates that synchrotron radiation is very useful to analyze the electron density under pressures.

Fig.1 002 diffraction profiles at 25,50keV and $\text{MoK}\alpha$

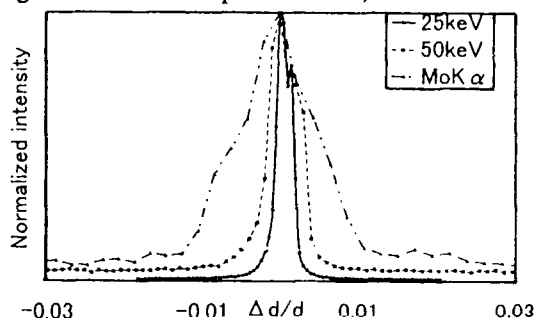


Table 1 Cell parameters at 25,50keV and $\text{MoK}\alpha$.

	25keV	50keV	$\text{MoK}\alpha$
a/ $\text{\AA}$	4.3590(30)	4.3616(70)	4.3683(23)
b/ $\text{\AA}$	4.3616(47)	4.3568(91)	4.3623(25)
c/ $\text{\AA}$	2.8544(12)	2.8539(23)	2.8548(10)
$\alpha/^\circ$	89.995(73)	89.910(147)	90.102(46)
$\beta/^\circ$	89.990(59)	89.846(133)	89.994(45)
$\gamma/^\circ$	90.014(39)	89.978(104)	90.002(45)

Acknowledgment: We are grateful to members of Prof. Noda's group, Chiba University for their technical assistance in the experiments.