Powder Diffractometry at the Tsukuba Photon Factory*

R. Uno,^A H. Ozawa,^A T. Yamanaka,^B H. Morikawa,^C M. Ando,^D K. Ohsumi,^D A. Nukui,^E K. Yukino^E and T. Kawasaki^F

^A College of Humanities and Sciences, Nihon University,

3-25-40 Sakurajosui, Setagaya, Tokyo, Japan.

^B College of General Education, Osaka University,

Machikaneyama, Toyonaka, Osaka, Japan.

^C Research Laboratory of Engineering Materials,

Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama, Japan.

^D Photon Factory, National Laboratory for High Energy Physics,

Oho-machi, Tsukuba-gun, Ibaraki-ken, Japan.

^E National Institute for Research in Inorganic Materials,

Sakura-mura, Niihari-gun, Ibaraki-ken, Japan.

^F Rigaku Corporation, Haijima Plant, Matsubara-cho,

Akishima, Tokyo, Japan.

Abstract

Powder diffractometry at the Photon Factory has been carried out with a diffractometer specially designed for measurements on molten salts, liquids, amorphous solids and polycrystalline materials. The main work done with the diffractometer has been structure analysis, and the study of phase transitions at high pressure and high temperature on GeO_2 . In 1986 a new powder diffractometer was designed and constructed. The aims of the new diffractometer are to allow easy alignment and provide sufficient accuracy for measurements taking advantage of anomalous dispersion and also to provide for energy dispersive diffractometry. The basic features are described.

1. Introduction

Powder diffractometry at the Photon Factory has been carried out with a diffractometer specially designed for measurements on molten salts, liquids, amorphous materials and polycrystalline solids. In 1986 a new powder diffractometer was designed and constructed, and a new age of powder diffractometry at the Photon Factory was opened. This report will be divided into two parts. The first deals with investigations carried out with the old goniometer and the second describes the basic characteristics of the new goniometer.

The first part includes Rietveld analysis on GeO_2 and investigations on the phase transitions of GeO_2 at high temperature and high pressure. The second part is mainly devoted to the design of the new diffractometer, reproducibility of the wavelength selected by the monochromator and the accuracy of monitoring.

* Paper presented at the International Symposium on X-ray Powder Diffractometry, held at Fremantle, Australia, 20–23 August 1987.



Fig. 1. Pattern of profile fitting in the Rietveld analysis of GeO_2 in the angle dispersive method.

		SOR + SC	SOR + SSD	Cu tube	Single ^A
		L	attice constant (Å)		
	a	4.9963(2)	4.9929(3)	4.9858(1)	4.987
	c	5.6542(2)	5.6509(3)	5.6473(1)	5.652
		Fi	ractional coordinate		
Ge	x	0.451(2)	0.451(2)	0.451(1)	0.4513(1)
0	x	0.385(7)	0.389(10)	0.392(6)	0.3909(5)
U	v	0.296(6)	0.298(8)	0.303(5)	0.3021(5)
	z	0.094(6)	0.093(8)	0.092(5)	0.0909(4)
		Isotropi	c temperature factor (.	Å ²)	
R(Ge)	0.406(3)	0.532(7)	0.428(6)	0.537
B(O)	,	0.802(3)	1.024(8)	0.930(7)	1.061

Table 1.	Lattice	constants	and	structure	parameters	of	GeO	Ż
----------	---------	-----------	-----	-----------	------------	----	-----	---

^A Smith and Isaacs (1964).

2. Investigations on GeO_2

(a) Rietveld Analysis of GeO_2

The α -quartz type structure of GeO₂ (P3₁2, z = 3) has been investigated by Rietveld structure refinement. The sample was prepared by annealing a commercial GeO₂ powder at 1050°C for 49 hours. The collection of the diffraction intensity data was carried out by three methods: (1) using a monochromatised synchrotron orbital radiation (SOR) beam with a scintillation detector, (2) using the same SOR beam with a Ge solid state detector (SSD) and (3) using a conventional Cu X-ray tube with a scintillation counter (SC). The wavelength of the SOR beam was 0.6654 Å. The result of a profile fitting procedure with the pseudo-Voigt profile function for the Rietveld analysis in the case of the first example is shown in Fig. 1. The *R* factor for profile fitting was 0.119. It was 0.154 in the second method because of the asymmetry of the line profile. In the third method the gaussian fraction was about 0.41 in contrast to more than 0.9 in the other two methods. The structure parameters refined by the Rietveld method are all in good agreement with the results obtained from the single crystal structure analysis by Smith and Isaacs (1964), as shown in Table 1.



Fig. 2. Pattern of profile fitting in the Rietveld analysis of trigonal GeO_2 in the energy dispersive method.

(b) Energy Dispersive Diffraction Spectra of GeO₂ at High Pressure and Temperature

The diamond anvil cell used in the present study was originally designed by Yamaoka *et al.* (1979). Pressure and temperature can be generated easily up to 20 GPa and 550°C. NaCl powder was placed in the cell as an internal standard for the pressure calibration. The sample temperature was measured with a thermocouple close to the surface of the diamond. An example of an energy dispersive pattern is shown in Fig. 2. The crystal was trigonal at 29 kb (1 kb \equiv 0.1 GPa) and 220°C. The lattice constants obtained from the pattern fitting analysis are a = b = 4.9924 Å, c = 5.6529 Å, $\alpha = \beta = 90.0^{\circ}$ and $\gamma = 120.0^{\circ}$.



Fig. 3. Diffraction pattern of GeO_2 in the phase transition from a trigonal form to a tetragonal one.

The kinetics of the phase transition were studied taking advantage of the short measuring time permitted by the energy dispersive method. GeO₂ is known to have a phase transition from a trigonal form to a tetragonal one at high pressures and temperatures. Under a constant pressure of about 30 kb and varying temperature, a phase transition was observed at 29 kb and 220°C, as shown in Fig. 3. The mass ratio of the two phases was estimated from the peak ratio obtained in the profile fitting. The rate constant k and order n of the reaction of the transition in the kinetic equation, $x(t) = 1 - \exp(-kt^n)$, were estimated from the observed bulk fractions x(t) at 15 minute intervals. The values of k and n were 0.0302 per hour and 1.056 respectively. A phase transition was also observed at 31 kb and 315°C and at 29 kb and 380°C. Hence, we can derive the Arrhenius activation energy E of the transition from the equation, $\log k = C - E/2.303 RT$; this was found to be ~16 kcal mol⁻¹.

3. A Newly Designed X-ray Powder Diffractometer

A newly designed powder diffractometer for the Photon Factory has as an objective (1) the alignment of the diffractometer assembly should be as easy as possible, because the experimental hutch is also used by other groups with different apparatus. Other objectives are (2) the wavelength of the incident beam can be changed simply in order to take advantage of anomalous dispersion, (3) the intensity of the diffracted beam can be measured with sufficient accuracy for Rietveld analysis and (4) energy dispersive diffractometer.

We designed a special slit system for the alignment, which will be discussed in detail in a later section. As for changes of the wavelength, we adopted a fixed exit position monochromator which was specially designed by Spieker et al. (1984) in order to make re-adjustment of the heavy diffractometer unnecessary unless a precise alignment is required. Several improvements were made to achieve the necessary accuracy for the intensity measurements. The first was that the angles of counter scanning and specimen rocking were measured by means of rotary encoders directly attached to the goniometer axes to eliminate errors due to gears. The second is that the intensity of the monochromatised incident beam of the goniometer is monitored by the intensity of fluorescent and scattered X-rays from an Al foil in the X-ray path. The third is that the X-ray path is evacuated by a rotary pump in order to reduce the tail part of the diffraction profiles which are usually difficult to fit in the profile analysis. The fourth is that a powder specimen can be rotated at a higher speed than one revolution per second to average out the intensity of diffracted beams from crystallites with different size and different orientation. In the case of the energy dispersive method, the monochromator can be removed from the incident SOR beam path and a guide tube with an incident slit is set in place of the monochromator. The goniometer should be displaced about 50 mm from the position used for the angular dispersive method. A portable-type SSD is fixed on the counter arm in place of the scintillation counter.



Fig. 4. Side view of the new powder diffractometer for the Photon Factory.

(a) Outline of the Diffractometer

A side view, a plan and a rear view are given in Figs 4, 5 and 6. The system consists mainly of a vertical-type goniometer, a monochromator with slits and monitor,



Fig. 5. Plan of the new powder diffractometer.



Fig. 6. Rear view of the new powder diffractometer.

and a special slit system for alignment. Other attachments include a high speed specimen spinner, a counter monochromator with a graphite crystal and a specimen heating apparatus.

The camera radius of the goniometer is 300 mm and the detector is an NaI(Tl) scintillation counter. The range of angles for detector scanning is from -40° to $+150^{\circ}$ and for specimen rocking from -20° to $+190^{\circ}$. Both angles are measured by rotary encoders directly attached to the goniometer axis. The resolution of the

encoder is 5×10^{-4} °. A sample holder and the specimen spinner can both be set in a vacuum chamber at about 1 Pa.

The fixed exit position monochromator has a monolithic silicon crystal with a (111) reflecting plane. The range of wavelengths is from 0.76 to 3.6 Å from this reflection, but the intensity of X-rays longer than 2.3 Å will be reduced very much by windows in the vacuum X-ray path. The position of the outgoing beam is 50 mm higher than the incident SOR beam. The crystal is also placed in a vacuum chamber at about 1 Pa. The monochromator system with incident slit, exit slit and monitor can be moved vertically, that is, at right angles to the SOR beam. The distance of movement can be controlled with a minimum step of 1 μ m. The intensity of the fluorescent and scattered X-rays from an Al foil, placed in the outgoing beam path of the monochromator at an angle of 45°, is measured with an NaI(T1) scintillation counter to monitor the beam intensity.

The slit system for alignment has eight slits, of which four are before the incident slit of the monochromator and form the first composite collimation slit. The rest are after the goniometer, at a distance of 1650 mm from the first slit. The second slit has a stage for an ionisation chamber (IC) to measure the intensity of X-rays passing through each slit. The four slits of the first and the second slit are separated vertically by 50 mm and horizontally by 140 mm. The lower pair (ADM slit) is used for alignment in the angle dispersive method, while the upper one (EDM slit) in the energy dispersive method.

The whole system of goniometer, monochromator and collimation slit is on the same stage which can be moved horizontally by 140 mm at right angles to the incident SOR beam and can be fixed at both ends.



Fig. 7. Example of the intensity distribution of the SOR beam through the first collimation slit observed with an ionisation chamber after the second collimation slit.

(b) Alignment of the Goniometer

The alignment of the goniometer is done in two stages; the first is alignment using the collimation slit and the second is a more precise alignment by displacing the monochromator vertically. In the first operation a stage on a rack with four legs is fixed at the left end in the rear view (Fig. 6) at the beginning. The outside ADM slit of the first collimation slit is placed just in the centre of the SOR beam. The same slit of the second collimation slit is moved to the centre of the beam passing through the first slit. The position of the second slit is finely adjusted at the centre of the SOR beam through the first slit, according to the vertical intensity distribution measured by the ionisation chamber after the second slit. An example is shown in Fig. 7, where the widths of the first and the second slit were 100 and 50 μ m respectively, and the length of the rear legs was changed by 10 μ m. Now the height of the second slit can be adjusted within 10 μ m, so that the optical axis of the diffractometer system is parallel to the SOR beam within 3×10^{-4} °. Then the stage was moved to the right end by 140 mm and fixed. By this adjustment the centre of the monochromatised beam will pass through the goniometer axis within 50 μ m if the position of monochromator is adjusted according to a previous measurement.



Fig. 8. Estimate of the distance between the centre of the incident beam and the goniometer axis from the scattering angle of a diffraction line at the lower and upper sides of the incident beam.

If more precise alignment is necessary, the vertical position of the monochromator should be finely adjusted. If the scattering angle of the same diffraction line can be measured on the lower and the upper side of the incident monochromatised beam, the distance δ between the centre of the beam and the goniometer axis can be estimated as $\delta = R \sin \eta$, where R is the camera radius and η is half the difference in the two scattering angles, as shown in Fig. 8. Then the monochromator is displaced by a distance δ in order to bring C to P in Fig. 8. In estimating δ , it is assumed that the goniometer axis lies on the surface of the specimen.

4. Basic Characteristics of the Diffractometer

The minimum controllable angle of the goniometer and the monochromator was 0.001° and the vertical distance of the monochromator was $1 \,\mu m$. The length of the

legs of the rack is controlled only by the number of pulses sent to the driving motors and this can be controlled relatively to 1 μ m, but absolutely only to about 20 μ m. When the angle of the goniometer is scanned by a constant number of pulses sent to a motor to reduce the time of scanning, the reproducibility of the angle was $\pm 0.0015^{\circ}$. This error was neglected in the intensity measurement with θ -2 θ scanning. The basic characteristics of the monochromator and the monitor were found as follows.

Materials	λ _K (Å)	May 15		June 7		July 3	
	(K edge)	$\theta_{\rm m}$ (deg.)	λ _{cal} (Å)	$\theta_{\rm m}$ (deg.)	λ _{cal} (Å)	$\theta_{\rm m}$ (deg.)	
SrCO ₃	0.76973			5.294	0.76988		
Zn foil (50 μm) (12 · 5 μm)	1.2834	10.065	1.28324	10.057	1.28355	10.063	
Cu foil (100 μm) (50 μm) (15 μm)	1.38059	10.975	1.38056	10.966	1.38074	10.973 10.972 10.971	
Ni foil (100 μm) (10 μm)	1.48807	11.985	1.48816	11.976	1.48821	11.981	
Fe foil (100 μ m)	1.74346	14·399	1.74341	14.394	1.74361		
Ti foil (50 μm)	2.49734			21.719	2.49748		
Mo foil [333] (100 μm) [444]	0.61978	15·505 21·546	0∙61976 0∙61979		1		
Zr foil [333] (100 μm) [444]	0.68883	17·497 24·322	0∙68879 0∙68882				
Diffraction	λ_{obs} (Å) 0.95236 1.19645 1.19784 1.48858	9·260	1 · 19687 1 · 48816	6.980 9.244	0·95233 1·19632		
Si: <i>d</i> (111) (Å) Error	1.40030	3.13522 ± 0.00027	1.40010	3 · 13403 ±0 · 00059			
$\Delta \theta_{\rm m}$ (deg.) Error		1 · 744 ±0 · 0009		1.759 ±0.0023		-	

Table 2. Wavelength of beam from the monochromator over extended period in 1987

(a) Basic Characteristics of the Monochromator

The position of the outgoing beam shifted about 300 μ m when the Bragg angle was changed from 7.0° to about 35°. The wavelength of the outgoing beam was calibrated against the angle of incidence read at the absorption edges of several materials. The main calibration was carried out twice. The results are listed in Table 2. The wavelength λ is assumed to be given by

$$\lambda = 2d(111)\sin(\theta_{\rm m} + \Delta\theta_{\rm m}),$$

where θ_m is the angle of incidence as read and $\Delta \theta_m$ is the difference between the Bragg angle and θ_m . The values of d(111) and $\Delta \theta_m$ were estimated by a least-squares method. The results are shown in Table 2 along with the calculated values of the wavelength. The differences obtained for θ_m show that the reproducibility of θ_m was



Fig. 9. Characteristics of the monochromator.

about $\pm 0.005^{\circ}$ and that of λ was about 0.0005 Å. The calibration curve obtained in June 1987 is shown in Fig. 9. The vertical position Z of the monochromator was estimated from the result that Z = 9.990 mm at $\theta_m = 9.244^{\circ}$. The results for the wavelength estimated from the scattering angles of the high angle diffraction lines from an NBS standard sample of Si powder 640b are also shown. The measured wavelengths were slightly greater than the calculated values, but the first four digits agree.

(b) Normalisation by the Monitor Intensity

The 111 reflection of NBS Si 640b was measured for three different widths of the incident slit of the monochromator and for different divergences of the Soller slits with a receiving slit of 0.2 mm. Unsmoothed data from this experiment are shown in Fig. 10. The integrated intensity obtained from data normalised by the monitor intensity is shown in Table 3. In the normalisation the monitor intensity was smoothed linearly against the scattering angle. The results for slit widths of 0.2and 0.3 mm show that the normalisation is effective to about three digits in spite of the differences in the raw data. The result for the 0.5 mm slit (dashed curve) shows



Fig. 10. Diffraction profiles of the 111 line from a sample of NBS Si powder 640b for three different widths of the incident slit of the monochromator assembly. The wavelength was 1.48816 Å.

Width of incident slit (mm)	Divergence of Soller slit (deg.)	2θ (deg.)	<i>I</i> _r ^A	
0.2	1	27.452	236 ^B	
0.3	1	27.451	236 ^B	
0.5	1	27.450	293	
0.2	2	27.449	377	
0.3	2	27.448	378	
0.2	Without	27.445	568	

 Table 3. Integrated intensity and scattering angle for Si(111) against width of the incident slit of monochromator and divergence of the Soller slits normalised to monitor intensity

^A Relative integrated intensity calculated from a fitted gaussian function, except first two data. ^B Relative integrated intensity obtained by numerical integration, where the background could be estimated fairly well.

that the efficiency of fluorescence and scattering seems to change slightly owing to a decrease in the purity of wavelength of the beam.

5. Discussion

Only basic characteristics have been obtained for the newly designed powder diffractometer. Although the intensity of the incident beam of the goniometer was not so high, its accuracy was better than expected. The most interesting investigations with the new diffractometer are expected to be those taking advantage of anomalous dispersion. Energy dispersive diffractometry has also been started with the new diffractometer.

References

Smith, G. S., and Isaacs, P. B. (1964). Acta Crystallogr. 17, 842-6.

Spieker, P., Ando, M., and Kamiya, N. (1984). Nucl. Instrum. Methods 222, 196-201.

Yamaoka, S., Fukunaga, O., Shimomura, O., and Nakazawa, H. (1979). Rev. Sci. Instrum. 50, 1163-4.

Manuscript received 21 August, accepted 6 October 1987