

## 5.2. X-RAY DIFFRACTION METHODS: POLYCRYSTALLINE

 Table 5.2.10.6. *Fluorophlogopite 00l standard reflection angles* [NIST SRM 675,  $d(00l) = 9.98104(7) \text{ \AA}$ ,  $T = 298 \text{ K}$ ,  $\lambda = 1.5405929 \text{ \AA}$ ]

$l$	$2\theta$ (°)
1	8.853
2	17.759
3	26.774
4	35.962
5	45.397
6	55.169
7	65.399
8	76.255
10	101.025
11	116.193
12	135.674

 Table 5.2.10.7. *Silver behenate 00l standard reflection angles* [ $d(00l) = 58.380(3) \text{ \AA}$ ,  $\lambda = 1.5405929 \text{ \AA}$  (Huang, Toraya, Blanton & Wu, 1993)]

$l$	$2\theta$ (°)
1	1.512
2	3.024
3	4.537
4	6.051
5	7.565
6	9.081
7	10.599
8	12.118
9	13.640
10	15.164
11	16.691
12	18.221
13	19.754

The forward reflections have been used in parallel-beam synchrotron-radiation lattice-parameter studies (Parrish *et al.*, 1987).

- (3) The profile shape has a strong influence on the accuracy of the angle measurement. The geometrical aberrations produce asymmetries that reduce the accuracy; the effects can be minimized by a proper selection of slit sizes. In most cases, it is inadvisable to use  $K\beta$  radiation to avoid  $K\alpha$ -doublet splitting, as the intensity is reduced by a factor of seven. Symmetrical profiles are obtained with parallel-beam optics, but it is usually necessary to use synchrotron radiation to achieve sufficient intensity.

- (4) The largest and commonest source of systematic error in focusing geometry is the specimen-surface displacement. Several remountings of the specimen in the diffractometer and measurement of some low-angle reflections may be helpful in determining and minimizing the error. This aberration does not occur in parallel-beam geometry unless a receiving slit is used.

- (5) The precision of the diffractometer gears (or the equivalent) may be the limiting factor in high-precision measurements. The use of an electromagnetic encoder mounted on the  $2\theta$ -output shaft can increase the precision considerably. It is not normally included in commercial diffractometers because of its cost, but it is essential for adequate accuracy when the  $2\theta$  angles must be determined to better than  $0.001^\circ$ . The various types of mechanical error have been described by Jenkins & Schreiner (1986).

The diffractometer must be carefully adjusted to avoid mechanical problems. The effect of backlash can be minimized by slewing beyond and then returning to the starting angle, and by always scanning in the same direction. It is essential to avoid over-tight worm-and-gear meshing, as it causes jerky rather than smooth movement.

- (6) The beam must be precisely centred, the slits and monochromator (if used) must be parallel to the line focus of the X-ray tube, and the scanning plane must be perpendicular to the line focus.

- (7) The use of standard specimens with accurately known lattice parameters (Section 5.2.10) and ideally free of line broadening is strongly recommended as a test of the overall precision of the instrumentation and method.

- (8) For a given total time available for an experiment, it is necessary to strike a balance between numerous short steps with short counting times and fewer longer steps with longer counting times. The former alternative may give a better definition of the line shape; the latter may give lower calculated standard uncertainties (formerly called estimated standard deviations) in any derived parameters. Obviously, the step length must be considerably shorter than the width of any feature of the profile that is considered to be of importance.

- (9) Least-squares refinement is discussed in Subsection 5.2.3.2. The programs and the methods of handling the data should be carefully checked, as various programs have been found to give slightly different values from the same experimental data (see, for example, JCPDS – International Centre for Diffraction Data, 1986; Kelly, 1988).

- (10) Specimen preparation is very important; the particle size should preferably be less than  $10 \mu\text{m}$ , and a flat smooth surface normal to the diffraction vector is essential. The linearity of the detector and the temperature of the

 Table 5.2.11.1. *NIST intensity standards, SRM 674*

Standard	Crystal system	$a_0$ (Å)	$c_0$ (Å)	$I_{\text{rel}} \text{ } hkl$		$I_1/I_c(113)$
				2	3	
$\text{Al}_2\text{O}_3$ (corundum)	Trigonal	4.75893 (10)	12.9917 (7)	92.5 (26) 116	87.4 (19) 104	—
ZnO	Hexagonal	3.24981 (12)	5.20653 (13)	57.6 (11) 100	40.2 (14) 002	5.17 (13) 101
$\text{TiO}_2$ (rutile)	Tetragonal	4.59365 (10)	2.95874 (8)	56.9 (28) 211	44.0 (17) 101	3.39 (12) 110
$\text{Cr}_2\text{O}_3$	Trigonal	4.95916 (12)	13.5972 (6)	94.5 (22) 116	87.1 (23) 110	2.10 (5) 104
$\text{CeO}_2$	Cubic	5.41129 (8)	—	53.5 (20) 220	43.4 (23) 311	7.5 (2) 111