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The quantitative calculation of SiC polytypes from measurements of X-ray diffraction peak intensities

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An experimental determination on powder mixtures of SiC–3C and 6H polytypes using an X-ray goniometer system showed the possibility of quantitative determination of polytype fraction directly from peak intensities. In combination with calculated X-ray intensities of 15R and 4H polytype, the method yields a simple equation system for the relative quantities of SiC polytypes 15R, 6H, 4H and 3C in polycrystalline samples and powder mixtures.

1. Introduction

It can be assumed that the type and amount of different SiC polytypes determine the quality of polycrystalline SiC compounds made either by hot-pressing or by pressureless sintering. Experimental determination of amounts of different SiC polytypes by X-ray diffraction in a mixture has always been a problem, which is usually associated with effects such as different degree of crystallinity, particle size and strain associated with the crystals. Another difficulty is the overlapping of diffraction peaks. The most accurate method seems to be the comparison with standard calibration curves generated using pure materials; however, this is not possible in most cases [1].

The purpose of this investigation was to establish a simple technique to determine the amount of the four most common SiC polytypes 3C, 4H, 6H and 15R. The general approach involved calculations of the absolute and relative intensities of the diffraction peaks. The calculations give only a limited accuracy because they cannot account for all factors influencing X-ray intensities such as stacking faults, twinning, particle size effects and textures. Therefore, a combination of calculations and experimental calibration curves seems to provide the most accurate results.

2. Calculation of X-ray diffraction intensities

Intensities reported by Thibault [2], Schaffer [3] and Hannam and Schaffer [4] based on experimental results, could not be used for quantitative phase analysis for only relative intensities were given for each polytype. Calculated intensities for phase analysis were reported by Bartram [5] for selected diffraction peaks in the range $d = 0.266$ to 0.217 nm.

For this work a computer program was used for calculating X-ray diffraction data for a goniometer system with LiF monochromator and Cu$K\alpha$ radiation. Atomic positions parameters for 3C ($F\bar{4}3m$), 4H ($C6mc$), 6H ($C6mc$) and 15R ($R3m$) were taken from Wyckoff [6]. Intensity calculations with atomic scattering factors for Si^0 to Si^{4+} and C^0 to C^{4-} in steps of 1 were carried out. Best agreement between calculated and measured intensities on pure 3C and 6H polytypes was found with scattering factors for Si^{2+} and C^{2-} and therefore used throughout this

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study. These values were obtained by linear extrapolation from tabulated data for Si^0, Si^{3+} and C^0, C^{2+} [7].

The calculations are based on the relation

$$I_n = m|F|^2 \cdot LP \cdot V^{-1},$$

where I_n is the intensity normalized to the unit cell volume V, LP the Lorentz-polarization factor, F the structure factor, and m the multiplicity. The temperature factor was neglected. The resulting X-ray intensities for reflections in the range from d = 0.266 to 0.217 nm are given in Table I, and comparison of selected relative peak intensities, denoted as peaks A to F, from the literature, experiments and calculations are shown in Table II.

The calculated results are in good agreement with those reported by Bartram [5] and those measured on pure 3C and 6H polytype powders. Differences between the calculated and measured intensities [2–4] are obvious from the experimental results for 15R materials. This may be due to the difficulties in preparing pure 15R polytype powders.

X-ray intensities are proportional to the volume fraction of a phase in a mixture of phases with equal absorption coefficients (neglecting extinction effects). The calculated intensities of Table I (last column) were normalized setting I (1 1 1) of 3C polytype to 1 0 0, and were then used to derive the equation system given in Table III for the volume fractions of the different polytypes: *a, b, c* and *d* are the volume fractions of the polytypes 15R, 6H, 4H and 3C respectively, contributing to the intensities of reflections A to F. In order to obtain relative volume fractions, values *a* to *d* are divided by their sum $a + b + c + d$.

3. Experimental calibration on 3C/6H powder mixtures

Powders used for calibration were cubic SiC–3C from H. C. Starck (1-3)* and hexagonal SiC–6H from Elektroschmelzwerk Kempten (4-7)*. Pow-

TABLE I Calculated intensities for X-ray diffraction lines
3C: space group $F\bar{4}3m$, a = 0.436 nm, V = 0.082 256 nm^3

h k l	*d*(nm)	*F*	(*F*/*V*)	*m*	L. P.	I_n
1 1 1	0.251 09	41.73	0.5073	8	18.52	38.132
2 0 0	0.217 45	22.03	0.2678	6	13.3	5.728

4H: space group *C6mc*, a = 0.3073 nm, c = 1.0053 nm, V = 0.082 215 nm^3

h k l	*d*(nm)	*F*	(*F*/*V*)	*m*	L. P.	I_n
1 0 0	0.266 13	14.18	0.1725	6	21.1	3.766
1 0 1	0.257 27	20.70	0.2518	12	19.5	14.834
0 0 4	0.251 33	41.74	0.5077	2	18.56	9.568
1 0 2	0.235 20	21.45	0.2609	12	15.9	12.988

6H: space group *C6mc*, a = 0.3073 nm, c = 1.5079 nm, V = 0.123 32 nm^3

h k l	*d*(nm)	*F*	(*F*/*V*)	*m*	L. P.	I_n
1 0 1	0.262 08	22.78	0.1847	12	20.6	8.435
0 0 6	0.251 32	62.58	0.5075	2	18.5	9.5281
1 0 2	0.250 95	31.29	0.2537	12	18.5	14.292
1 0 3	0.235 20	24.79	0.2010	12	15.9	7.710
1 0 4	0.217 41	16.51	0.1339	12	13.5	2.7861

15R: space group *R3m*, a = 0.3073 nm, c = 3.770 nm, V = 0.308 317 nm^3

h k l	*d*(nm)	*F*	(*F*/*V*)	*m*	L. P.	I_n
1 0 1	0.265 47	30.28	0.0982	6	21.0	1.215
0 1 2	0.263 52	57.16	0.1854	6	20.66	4.261
1 0 4	0.256 12	30.12	0.2920	6	19.33	9.909
0 0 15	0.251 33	156.54	0.5077	2	18.55	9.564
0 1 5	0.250 96	62.52	0.2028	6	18.5	4.564
0 1 7	0.238 59	80.28	0.2604	6	16.5	6.712
0 1 8	0.231 73	68.19	0.2212	6	15.4	4.520
1 0 10	0.217 42	33.11	0.1074	6	13.3	.9230

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* See Appendix.

TABLE II Relative intensities for X-ray diffraction lines

Peak	d(nm)	hkl	a	b	c	d	e	f
15R								
A	0.266	1 0 1 0 1 2	37.3	38.9	44	48	–	–
C	0.257	1 0 4	70.0	70.1	78	78	–	–
D	0.251	0 0 15 0 1 5	100.0	100.0	78	100	–	–
	0.239	1 0 7	51.0	47.5	67	68	–	–
	0.232	0 1 8	36.0	32.0	56	42	–	–
	0.217	0 1 10	7.9	6.6	11	15	–	–
6H								
B	0.262	1 0 1	33.4	35.4	67	39	32.7	33.1
D	0.251	0 0 6 1 0 2	100.0	100.0	78	100	100.0	100.0
E	0.235	1 0 3	35.5	32.4	56	22	30.3	30.0
F	0.217	1 0 4	14.0	12.0	44	11	11.5	11.2
4H								
A	0.266	1 0 0	25.0	25.3	57	19	–	–
C	0.257	1 0 1	100.0	100.0	71	100	–	–
D	0.251	0 0 4	66.0	64.5	57	81	–	–
E	0.235	1 0 2	97.0	87.7	71	89	–	–
3C								
D	0.251	1 1 1	100.0	100.0	100	–	100.0	100.0
F	0.217	2 0 0	17.8	15.0	10	–	15.2	13.1

a Bartram [5] calculated.
b Authors calculated.
c Thibault [2] experimental.
d Hannam and Schaffer [4] experimental.
e Authors experimental, peak areas.
f Authors experimental, peak heights.

ders were pressed in the cavity of a sample holder to give flat powder surfaces. Four goniometer runs were performed with each sample. After each run the sample was rotated 90° within the reflection plane to control texture effects in the surface plane of the specimen. The deviation of the measured intensities from the average value of all four measurements was smaller than the scattering due to counter statistics for small grained powders ($<5\,\mu$m) indicating that texture effects within the sample plane were negligible. Tracings were carried out with a speed of $1/8^\circ$ min^{-1} and a time constant of 4 sec. Peak heights as well as peak areas were determined in the 2θ region between 30 and 45°.

4. Results and discussion

With pure 3C powders a small intensity step was observed at $d = 0.266$ nm but only diffraction lines corresponding to (1 1 1) and (2 0 0) were identified. With pure 6H powders only peaks corresponding to the (1 0 1), (0 0 6, 1 0 2) and (1 0 3) were observed revealing no broadening at the base. This is a strong evidence for the absence of 15R. Half-peak widths of 6H powders of all particle sizes exceeded those of 3C powders by about 10%. The results are shown in Table II (columns e, f), the intensity ratios of $(0\,0\,6, 1\,0\,2)_{6\mathrm{H}}$ to $(1\,1\,1)_{3\mathrm{C}}$ being 0.652 (peak areas) and 0.588 (peak heights), respectively.

X-ray intensities, I, of the powder mixtures (3C, 6H) determined from peak heights are shown in Fig. 1. The measured values were normalized setting $I_{(1\,1\,1)}$ (peak D) to 1 0 0 for pure 3C ($b=0$). By means of least squares fit, the following equations result, b being the volume content of 6H powder.

$$\text{Peak B}: I = 19.34b$$

$$\text{Peak D}: I = 100.00 - 40.77b$$

$$\text{Peak E}: I = 18.06b$$

$$\text{Peak F}: I = 13.08 - 6.61b$$

In the mixtures, contents of 6H as low as $b = 0.01$ could be easily recognized from peaks B and E.

Comparison of the intensity ratios of pure powders measured by means of peak areas shows quite good agreement with calculated values. Our results do not agree well with those of Hannam [4] from carefully prepared SiC–6H powders except for the (1 0 4) diffraction line. Analysing the intensity

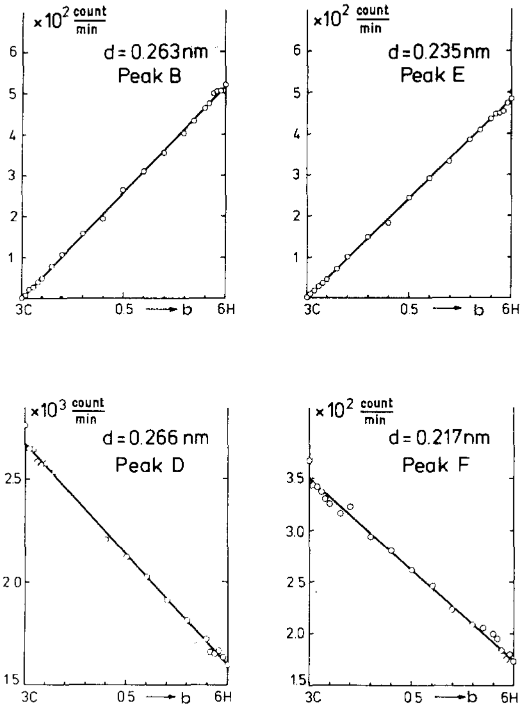

Figure 1 Intensities of SiC powder mixtures (3C, 6H) resulting from peak-height measurements.

ratios of 6H powders, one would expect them to contain significant amounts of 3C. In that case the ratio F/D should be larger, but ratios B/D and E/D should be smaller than the calculated values.

Peak heights measured from pure samples result in comparable intensity ratios owing to nearly identical half-peak widths of a single polytype in the *d* region used. Peak widths can be different for different polytypes, even for a single polytype in the *d* region used. Hence it is necessary to know peak widths for the single polytypes in order to analyse polytype amounts by means of peak heights. Unfortunately, we were not able to obtain pure powders of 15R and 4H polytypes. However, combining our results of intensity measurements of peak heights with calculated ratios for 15R and 4H, the equation system shown in Table IV seems to be the best approximation for SiC-polytype analysis. Further improvement by investigations on pure 15R and 4H powders can easily be made.

Good agreement is observed between the calculated data from Table III for 3C and 6H and measured values from Table IV. This indicates that texture and extinction effects can be ruled out in this case.

Appendix

Average particle sizes of SiC powders used in this investigations:

FSSS = Fisher sub-sieve size method
BET = Specific powder surface measured by gas adsorption

No.	Specification	Phase	Average FSSS (μm)	Particle size BET ($m^2 g^{-1}$)
1	HCST 810	3C	1.6	2.4
2	HCST 1967/V2	3C	1.4	1.8
3	HCST 1967/V3	3C	1.5	2.0
4	ESK 76/1	6H	18	2.0
5	ESK 76/1	6H	8	–
6	ESK 76/1	6H	3	–
7	ESK 77/1	6H	–	5.5

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TABLE III Equation system derived from calculated X-ray intensities

15R		6H		4H		3C		Peak	*d*(nm)
3.19a			+	9.88c			=	A	0.266
11.17a	+	22.12b					=	B	0.263
25.99a			+	38.90c			=	C	0.257
37.05a	+	62.74b	+	25.09c	+	100.00d	=	D	0.251
		20.22b	+	34.06c	+	15.01	=	E	0.235
2.41a	+	7.50b			+		=	F	0.217

TABLE IV Final equation system derived from caluclated and measured data

15R		6H		4H		3C		Peak	*d*(nm)
3.2a			+	9.9c			=	A	0.266
11.2a	+	19.4b					=	B	0.263
26.0a			+	38.9c			=	C	0.257
31.1a	+	59.2b	+	25.1c	+	100.0d	=	D	0.251
		18.1b	+	34.1c			=	E	0.235
2.4a	+	6.5b			+	13.1d	=	F	0.217

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