

NRC Publications Archive Archives des publications du CNRC

Structural Characterization of a Coarsegrained Transparent Silicon Carbide Powder by a Combination of Powder Diffraction Techniques

Peplinski, B.; Fitch, A. N.; Evans, A.; Ibberson, R. M.; Többsens, D. M.; Cranswick, L. M. D.; Dörfel, I.; Emmerling, F.; Matschat, R.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

<https://doi.org/10.1524/zksu.2009.0009>

Zeitschrift für Kristallographie Supplements, 30, pp. 61-66, 2009-09-01

NRC Publications Archive Record / Notice des Archives des publications du CNRC :

<https://nrc-publications.canada.ca/eng/view/object/?id=f0b4230c-2863-4b91-b057-0a4ecdb71578>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=f0b4230c-2863-4b91-b057-0a4ecdb71578>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

Structural characterization of a coarse-grained transparent silicon carbide powder by a combination of powder diffraction techniques

B. Peplinski^{1,*}, A. N. Fitch², A. Evans², R. M. Ibberson³,
D. M. Többsens⁴, L. M. D. Cranswick⁵, I. Dörfel¹,
F. Emmerling¹, R. Matschat¹

¹ BAM Federal Institute for Materials Research and Testing
Richard-Willstätter-Str. 11, D-12489 Berlin, Germany

² European Synchrotron Radiation Facility (ESRF), BP 220, F-38043 Grenoble, France

³ ISIS Facility, Rutherford Appleton Laboratory (RAL), Chilton, Didcot, OX11 0QX, UK

⁴ Hahn-Meitner-Institute (HMI), SF2, Berlin, Germany, now Institute of Mineralogy and Petrography, University of Innsbruck, Innrain 52, A-6020 Innsbruck, Austria

⁵ National Research Council of Canada, Canada, Chalk River ON, Canada, K0J 1J0

* burkhard.peplinski@bam.de

Keywords: silicon carbide, polytypes, phase quantification, reference material

Abstract. Diffraction of hard synchrotron radiation as well as constant-wavelength and time-of-flight neutron diffraction were used for the structural characterization of a silicon carbide powder having extremely low levels of chemical impurities, high perfection of the crystalline lattice and a grain size of up to 150 μm . The presence of three polytypes was ascertained and the ratios of their mass fractions were determined to be $w_{15\text{R}} : w_{6\text{H}} = 0.002,3(8)$ and $w_{4\text{H}} : w_{6\text{H}} = 0.000,6(2)$.

Introduction

Silicon carbide powders having chemical impurity levels as low as a few mg per kg or even less, high perfection of the crystalline lattice and a crystallite size exceeding several tens or even hundred μm show not only high hardness but also exceptional chemical resistance (insolubility in acids), as well as unique electronic and optical properties. One of the main challenges to a reliable structural characterization of such a material is its rather large crystallite size considerably exceeding the value acceptable for reliable X-ray powder diffraction measurements. Any grinding bears a high risk of changing/destroying the original real structure characteristics of the sample, e.g. the degree of stacking disorder and their polytype composition. Thus, grinding can significantly distort the outcome of the structural investigation and,

therefore, should be avoided. Consequently, highly penetrating radiation has to be used for any quantitative diffraction analysis and measures have to be taken to reduce the unfavourable influence of insufficient crystal orientation statistics as much as possible.

Sample

The element composition of the sample was extensively examined mainly by atomic absorption spectrometry (AAS) and by inductively coupled plasma optical emission spectrometry with electrothermal evaporation of the sample (ETV-ICP OES). The content of the following trace elements were determined: Al, B, Ca, Cr, Cu, Fe, Mg, Na, Ni, Ti, V, Zr. The mass fraction of the Al component incorporated into the bulk of the material is about 44 mg/kg, and that of B about 4 mg/kg. The other trace metals are mainly adhered to the surface of the particles. For that part of their mass fractions that is dissolved in the silicon carbide crystals values below 1 mg/kg were determined.

According to SEM the most frequently occurring particle size is about 20 μm . The smallest particles are ca. 8 μm while a considerable number of particles have dimensions between 100 and 180 μm (see figure 1). TEM in combination with the FIB preparation technique showed that the powder particles are quite perfect single crystals. Dislocations were found only in a surface layer less than 1 μm thick but not in the interior of crystals.

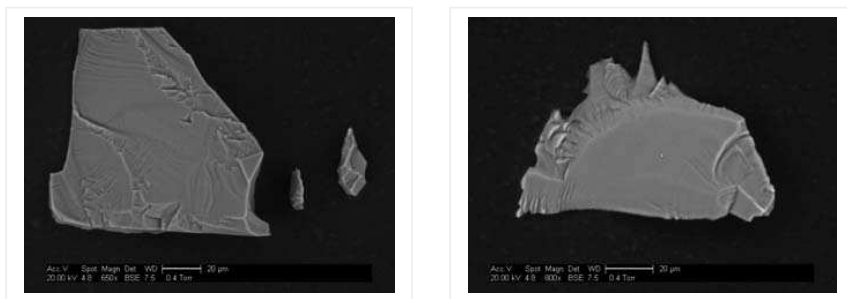


Figure 1. SEM pictures of individual crystallites of the silicon carbide powder sample. The largest dimensions in the 2D-projection of the displayed crystallites are ca. 140 μm (left) and 110 μm (right).

Data collection and data analysis

Instrumentation and conditions of data collection used in the present diffraction investigation as well as computer programs applied for data evaluation are summarized in table 1.

Results and discussion

All three diffraction patterns have FWHM values very close to the instrument contributions to the line profiles, see figure 2. The three patterns were evaluated by the Rietveld method [1-2] describing the sample as 6H-SiC, either completely pure or with traces of other SiC

Table 1. Characteristics of the three diffraction patterns of the silicon carbide material.

	pattern #1	pattern #2	pattern #3
diffracted radiation	monochromatic neutrons $\lambda \approx 1.7967 \text{ \AA}$	pulsed neutrons from spallation source	monochromatized synchrotron radiation $\lambda \approx 0.8003 \text{ \AA}$
instrument; facility	E9; HMI, BENSCH	HRPD ¹ ; ISIS. RAL	ID31; ESRF
type of pattern	from a single specimen	from a single specimen	synthesized from the patterns of 10 specimen
type of specimen	capillary, Ø 16 mm, vanadium	capillary, Ø 8 mm, vanadium	capillary, Ø 1 mm, borosilicate
specimen rotation	none	none	3000 rpm
mass of specimen	12 g	4 g	80 mg (= 10 • 8 mg)
total measuring time	17 h	5 h	10 h = (10 • 1h)
range of d-values	34.0 Å–0.916 Å	2.4 Å - 0.674 Å	22.9 Å - 0.825 Å
FWHM ²	0.016 Å	0.002 Å	0.001 Å
signal-to-Bkg ²	33	350	650
noise-to-Bkg ³	± 0.125	± 1	± 0.05
Rietveld programs used	FullProf.2k V.4.30 (TOPAS V.2.1)	TOPAS V.4.1	TOPAS V.2.1 TOPAS V.4.1
¹ pattern #2 was collected before the major upgrade of the neutron guide in 2007			
^{2,3} FWHM and signal-to-background ratio for the 103 reflection of 6H-SiC at ~ 2.36 Å; noise-to-background ratio near that line.			

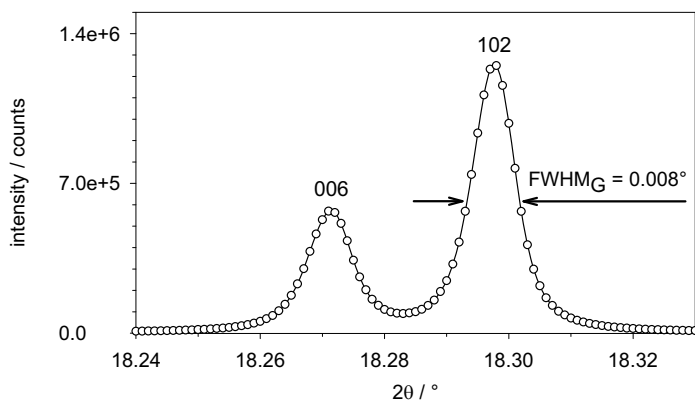


Figure 2. Section of diffraction pattern #3 displaying two reflections of 6H-SiC illustrating the exceptional high angular resolution.

polytypes, see figures 3 and 4. The values of the goodness-of-fit (GoF) achieved with each of these three observed SiC patterns are significantly higher than those resulting from the refinements of a standard silicon powder measured under identical instrument conditions. This discrepancy between the agreement indices might partly be caused by a very low, but non-zero content of planar disorder (stacking faults) that is known to cause (hkl)-dependant line

shifts as well as distortions of line profiles and of the background [3]. Another factor to be considered is extinction, as the goodness-of-fit for the two neutron diffraction patterns improves when changing from Rietveld to Pawley refinements (from 2.55 to 2.29 and from 1.57 to 1.47 for pattern #1 and #2, respectively).

Pattern #3 has superior angular resolution and signal-to-background ratio. Comparing it to the calculated diffractions patterns of the pure SiC polytypes it clearly shows that there are - besides the reflections of the main 6H-SiC component - well discernible 21 isolated reflections of 15R-SiC and 6 isolated reflections of 4H-SiC, see figure 4. This proves that the sample does not consist of completely pure 6H SiC, but contains traces of 15R and 4H SiC.

Phase quantification should consider two main specifics of the present sample: the occurrence of *systematic coincidences* of diffraction lines of symmetry-related polytypes and the *extremely* different phase abundance of the main and minor components. Consequently, for reliable phase quantification *only isolated diffraction lines* should be evaluated. This was done by applying the Rietveld method to several angular ranges of pattern #3 that include all isolated reflections of the two minor phases as well as 23 isolated and intense reflections of

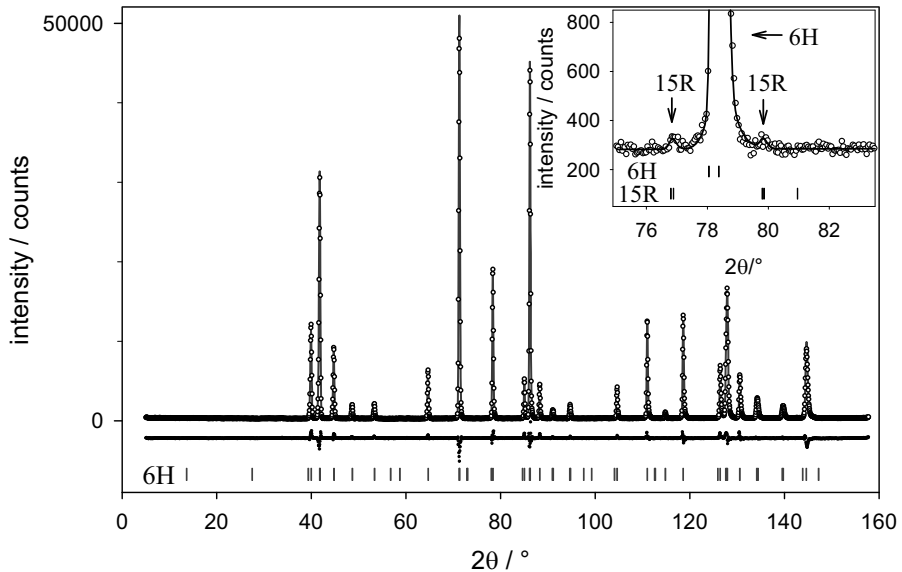


Figure 3. Rietveld plot for diffraction pattern #1;
whole angular range: $R_{wp} = 6.6$ $R_{exp} = 3.2$ $GoF = 2.03$;
section $73.0^{\circ} - 84.6^{\circ}$: $R_{wp} = 4.47$ $R_{exp} = 3.51$ $GoF = 1.27$ (see also table 2).

Table 2. Results of the Rietveld analysis of two selected sections of diffraction pattern #1.

angular and d-value ranges		GoF		$W_{15R}:W_{6H}$	$W_{4H}:W_{6H}$
$2\theta / ^{\circ}$	$d / \text{\AA}$	only 6H	4H + 6H + 15R		
38.0 - 44.0	2.40 - 2.90	2.41	2.35	0.002,7(19)	0.001,7(12)
73.0 - 84.6	1.36 - 1.48	1.35	1.27	0.002,9(6)	-

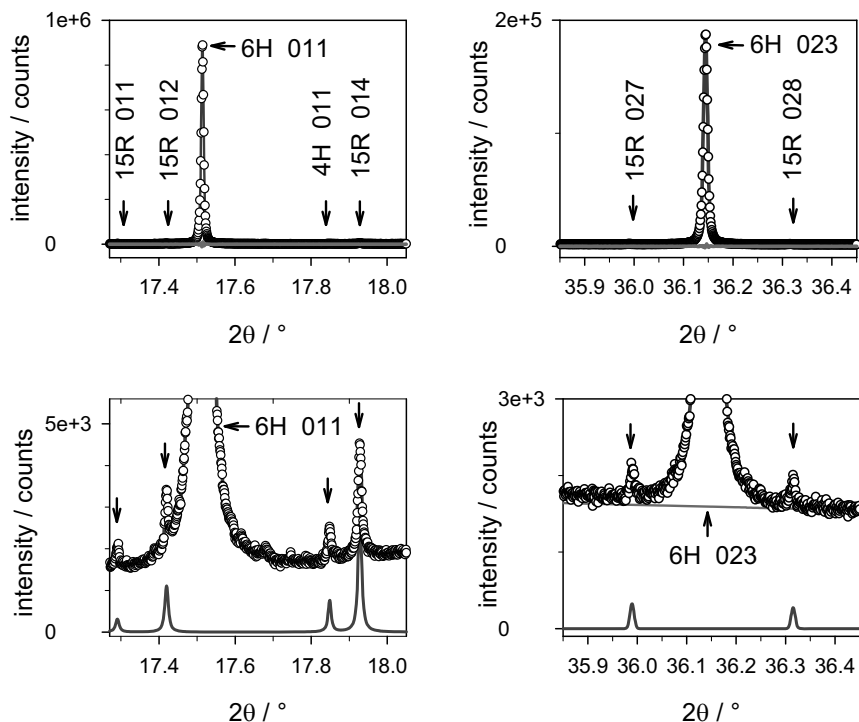


Figure 4. Rietveld plots for the two displayed angular ranges of diffraction pattern #3;
top left: full intensity scale, $R_{wp} = 1.93$, $R_{exp} = 0.84$, $GoF = 2.30$;
bottom left: Same as previous but reduced intensity scale. The lower curve shows the calculated contributions of the 15R- and 4H-SiC components, i.e. of the two minor phases. Ratios of the mass fractions from this refinement $w_{15R} : w_{6H} = 0.003,88(20)$ and $w_{4H} : w_{6H} = 0.000,643(58)$;
top right: full intensity scale, $R_{wp} = 1.66$, $R_{exp} = 1.39$, $GoF = 1.19$;
bottom right: Same as previous but reduced intensity scale. The lower curve is the calculated contribution of the 15R-SiC component, i.e. of one of the minor phases. Ratio of the mass fractions from this refinement $w_{15R} : w_{6H} = 0.003,0(3)$.

the 6H-SiC main component. In the result the following values for the ratios of the mass fractions were determined (numbers in parentheses are estimated standard deviations): $w_{15R} : w_{6H} = 0.002,3(8)$ and $w_{4H} : w_{6H} = 0.000,6(2)$.

The angular resolution in pattern #1 is considerably lower than in pattern #3, see FWHM values in line 10 of table 1, and there are only two narrow angular ranges in pattern #1 where

isolated reflections of the minor components might be detected if their phase abundance is sufficiently high. Visual inspection, search/match routines and Rietveld analyses carried out on these two sections as well as on the whole pattern #1 support the finding derived from pattern #3 by showing that the sample is an unusually pure 6H silicon carbide and that the mass fractions of possible traces of the 15R- and 4H-polytypes of silicon carbide are far below the 1% level, see table 2 and figure 3. It is this huge difference in the phase abundance of the major and minor polytypes – together with the extreme size and lattice perfection of the SiC crystallites - that distinguishes the SiC material investigated in the present work from those analyzed in previous powder diffraction investigations, see e.g. [4], which had reported in detail on the phase quantification of micron-sized, commercial SiC powders by applying the Rietveld method to diffraction patterns collected with *conventional* X-ray powder diffraction instrumentation – an analytical technique rather unsuited for the *given* SiC material.

Summary

A coarse-grained silicon carbide powder was analysed ‘as received’ by two neutron powder diffractometers and one synchrotron radiation powder diffractometer. These three investigations complete each other very nicely as the mass of the analysed specimen and the representativeness of the results of the diffraction analysis for the whole material are very large in the case of the two neutron diffraction data sets while the synchrotron radiation data provide superior values of the background level, the angular resolution and of the detection limit for minor constituents. The outcome of these three diffraction experiments concurrently confirmed the exceptional high phase and polytype purity of the investigated 6H silicon carbide powder. In addition to this important finding, the outstanding performance of the ESRF instrument allowed to detect in the diffraction pattern of this silicon carbide powder 27 well discernible, isolated and indexed reflections of the 15R and 4H polytypes of silicon carbide thus proving that this material contains very minor mass fractions of the 15R and 4H SiC polytypes. The ratio of the mass fractions of these polytypes to the mass fraction of the main polytype was determined to be $w_{15R} : w_{6H} = 0.002,3(8)$ and $w_{4H} : w_{6H} = 0.000,6(2)$.

References

1. Rietveld, H.M., 1969, *J. Appl. Cryst.*, **2**, 65.
2. Young, R.A., 1995, *The Rietveld Method*, International Union of Crystallography, Monographs on Crystallography (Oxford University Press).
3. Ustinov, A.I., 1999, in *Defect and Microstructure Analysis by Diffraction*, edited by Snyder, R.L., Fiala, J. & Bunge, H.J. (Oxford: Oxford University Press), IUCr Monographs on Crystallography, **10**, 264–317.
4. Ortiz, A.L., Cumberra, F.L., Sanchez-Bajo, F., Guiberteau, F., Xu, H. & Padture, N.P., 2000, *J. Am. Ceram. Soc.*, **83**, 2282.

Acknowledgments

One of the authors (B.P.) would like to thank D. Schulz, Leibniz Institute for Crystal Growth (IKZ), Berlin, for helpful discussions, as well as G. Kley and H.-E. Maneck, both BAM.