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

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**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 $w_{15R} : w_{6H} = 0.002,3(8)$ and $w_{4H} : w_{6H} = 0.000,6(2)$.

**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.

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.

<table>
<thead>
<tr>
<th></th>
<th>pattern #1</th>
<th>pattern #2</th>
<th>pattern #3</th>
</tr>
</thead>
<tbody>
<tr>
<td>diffracted radiation</td>
<td>monochromatic neutrons</td>
<td>pulsed neutrons from spallation source</td>
<td>monochromatized synchrotron radiation</td>
</tr>
<tr>
<td></td>
<td>$\lambda \approx 1.7967$ Å</td>
<td>$\lambda \approx 0.8003$ Å</td>
<td></td>
</tr>
<tr>
<td>instrument; facility</td>
<td>E9; HMI, BENSC</td>
<td>HRPD $^1$; ISIS. RAL</td>
<td>ID31; ESRF</td>
</tr>
<tr>
<td>type of pattern</td>
<td>from a single specimen</td>
<td>from a single specimen</td>
<td>synthesized from the patterns of 10 specimen</td>
</tr>
<tr>
<td>type of specimen</td>
<td>capillary, Ø 16 mm, vanadium</td>
<td>capillary, Ø 8 mm, vanadium</td>
<td>capillary, Ø 1 mm, borosilicate</td>
</tr>
<tr>
<td>specimen rotation</td>
<td>none</td>
<td>none</td>
<td></td>
</tr>
<tr>
<td>mass of specimen</td>
<td>12 g</td>
<td>4 g</td>
<td>80 mg (= 10 • 8 mg)</td>
</tr>
<tr>
<td>total measuring time</td>
<td>17 h</td>
<td>5 h</td>
<td>10 h = (10 • 1h)</td>
</tr>
<tr>
<td>range of d-values</td>
<td>34.0 Å - 0.916 Å</td>
<td>2.4 Å - 0.674 Å</td>
<td>22.9 Å - 0.825 Å</td>
</tr>
<tr>
<td>FWHM $^2$</td>
<td>0.016 Å</td>
<td>0.002 Å</td>
<td>0.001 Å</td>
</tr>
<tr>
<td>signal-to-Bkg $^3$</td>
<td>33</td>
<td>350</td>
<td>650</td>
</tr>
<tr>
<td>noise-to-Bkg $^3$</td>
<td>± 0.125</td>
<td>± 1</td>
<td>± 0.05</td>
</tr>
<tr>
<td>Rietveld programs used</td>
<td>FullProf.2k V.4.30</td>
<td>TOPAS V.4.1</td>
<td>TOPAS V.2.1</td>
</tr>
<tr>
<td></td>
<td>(TOPAS V.2.1)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^1$ 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: Rwp = 6.6 Rexp = 3.2 GoF = 2.03; section 73.0° - 84.6°: Rwp = 4.47 Rexp = 3.51 GoF = 1.27 (see also table 2).](image)

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

<table>
<thead>
<tr>
<th>angular and d-value ranges</th>
<th>GoF</th>
<th>W_{15R}:W_{6H}</th>
<th>W_{4H}:W_{6H}</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 / °</td>
<td>d / Å</td>
<td>only 6H</td>
<td>4H + 6H + 15R</td>
</tr>
<tr>
<td>38.0 - 44.0</td>
<td>2.40 - 2.90</td>
<td>2.41</td>
<td>2.35</td>
</tr>
<tr>
<td>73.0 - 84.6</td>
<td>1.36 - 1.48</td>
<td>1.35</td>
<td>1.27</td>
</tr>
</tbody>
</table>
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


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