ESRF

ESRF	Experiment title: "Nanocrystalline silicon carbide: Structure of bulk and grain boundary as a function of particle size"	Experiment number: 01-01-189
Beamline: BM01B	Date of experiment: from: 9-June 1999 to: 11 June 1999	Date of report: 8-Nov-1999
Shifts: 9	Local contact(s): Emerich Hermann	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Hans-Peter Weber* **SNBL at ESRF, PO Box 220, F-38043 Grenoble**

Bogdan Palosz* **High Pressure Research Center UNIPRESS, Warsaw, POLAND**

Svetlana Stel'makh ***as above***

Stanislaw Gierlotka ***as above***

Roman Pielaszek ***as above***

Report:

Materials: Four kinds of nanocrystalline SiC powders were examined. The samples K1, K2 and K9 with the average particle diameters 8, 10 and 30 nm were synthesized in flame. The samples K1 and K9 show one- and K2 bi-modal grain size distribution functions. The sample EW3G with 3-4 nm diameter particles was synthesized from organic precursors

Experiment: The diffraction data was collected in transmission geommetry with application of scintillation counter and secondary beam monochromator. Flat samples were ~ 0.3 mm thick, beamsize ~ 0.3×6 mm, λ~ 0.7963Å. The patterns were measured at room-temperature up to 90° 2Θ.

Data elaboration: The structure of nanocrystalline SiC is one-dimensionally disordered, similarly in all K-type samples (≈20-25%h), it is a bit larger in the 3-4 nm SiC sample EW3G. Presence of disordering leads to broadening of individual Bragg reflections and to diffuse scattering at the background. For this reason the Rietveld refinement program gives typically R_{calc} ~ 12 for $R_{expected}$ ~ 4, what is sufficient however, for the determination of lattice parameters.

Lattice parameters: The crystallographic structure of one dimensionally disordered SiC is trigonal with the *c/a* ratio always larger than the ideal value 0.81605. We calculated the lattice parameters of nanocrystalline SiC assuming both cubic (described by one prameter a_c) and trigonal lattices (hexagonal parameters a_{tr} and c_{tr}). The calculated values for 4 samples are given in Table 1:

Table 1. Lattice parameters of SiC nanocrystals at room-temperature

Sample	a_c [Å]	a_{tr} [Å]	c_{tr} [Å]	c_{tr}/a_{tr}*
K9	4.3582 (5)	3.0805 (5)	7.5516 (10)	0.8171 (10)
K2	4.3545 (5)	3.0810 (5)	7.5335 (10)	0.8150 (10)
K1	4.3549 (5)	3.0820 (5)	7.5252 (10)	0.8139 (10)
EW3G	4.3517 (5)	3.0635 (5)	7.5973 (10)	0.8266 (10)

* the c/a ratio for a perfect cubic lattice is 0.81605

Table 1 shows that:

1. The cubic lattice parameter a_c decreases with the decrease of the grain size,
2. The c_{tr}/a_{tr} parameter decreases with the decrease of the grain size except the smallest grain nanocrystals which show alongation of the lattice in c direction.

The decrease of the lattice parametrs with the decrease of the particle size suggests presence of compressive internal pressure. This can originate from the stress generated by the surface tension and the effective internal pressure should depend on the particle size.

Internal pressure: The sample K9 with 30 nm grains shows the lattice parameter and the c/a ratio close to that of a cubic structure and we assume that in this case the effect of the surface tension on the core-lattice of the SiC grains is negligible. Considering that the compression of SiC lattice is the property of a single particle, we can calculate the internal pressure using Birch-Murnaghan equation: $P = 3/2\ K_o \{(V/V_o)^{-7/3} - (V/V_o)^{-5/3}\} \times \{1 - 3/4(4-K_o')[(V/V_o)^{-2/3} - 1] + ...\}$. By taking $K_o = 230$ GPa measured for single crystal SiC and assuming $K_o' = 4$ we get the internal pressure P equal 0.6 GPa for 8 nm grain powder K1 and between 2 and 3 GPa for 3-4 nm grain powder EW3G. The surface tension can be calculated from the relationship $P = 2\gamma/r$ what gives the surface tension $\gamma = 6$N/m for 8 nm material K1 and 2-3 N/m for 3-4 nm sample EW3G. The difference between the calculated surface tensions is probably result of different methods of synthesized of these two materials and their different surface structures. (We do not calculate the internal pressure of K2 material because this powder shows bimodal grain size distribution and there is no unique size parameter which we could associate to this material).

Interatomic Distance function (*rdf*): Calculation of *rdf* functions from powder diffraction patterns is potentially a strong tool for determination of the interatomic distances. Information on the interatomic bonds combined with the lattice parameters can serve for identification of origin of relaxation (deformation) of the crystal lattices of nanocrystals with varying size and shape parameters. In Fig.1 we present an example of *rdf* analysis applied for the present data. Although the Q range is only 12Å^{-1}, changes of the interatomic distances with the particle size are clearly seen in Fig.1. To improve resolution of *rdf* functions good quality diffraction data measured for large Q's is necessary.

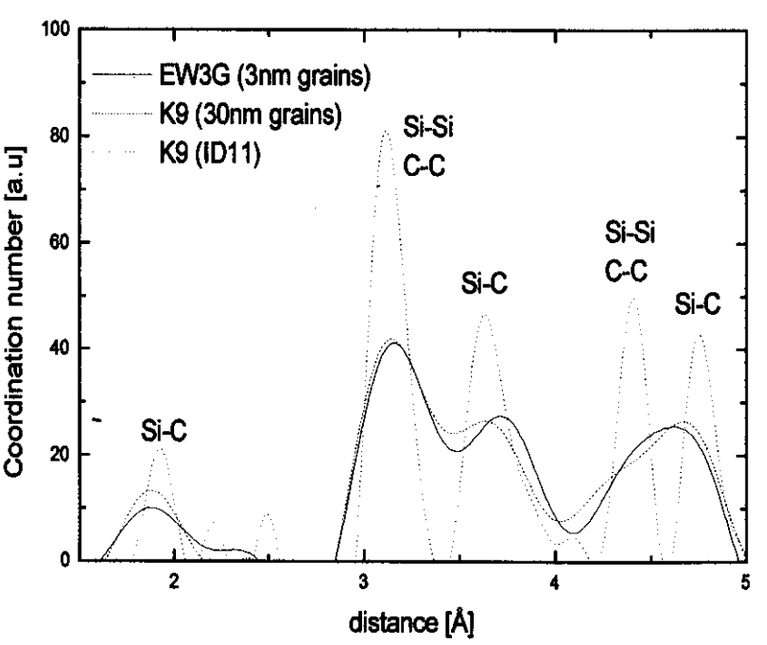

Fig.1 Plot of *rdf* functions calculated for the present data (Q_{max}= 12 Å^{-1}) for EW3G (3-4 nm) and K9 (30 nm) samples. The *rdf* function calculated for K9 sample measured at ID11 for Q_{max}= 25 Å^{-1} is given for comparison.