ESRF	**Experiment title:** **"Nanocrystalline diamond: Structure of bulk and grain boundary as a function of particle size"**	**Experiment number**: HS-821
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Report:

Materials: We examined four kinds of nanocrystalline diamond powders synthesized by different methods and microcrystalline diamond 0.7/0.3. The nanocrystalline diamonds have similar average grain sizes, around 10 nm, and show similar one dimensional disordering. The samples show different agglomeration and different grain size distributions. The "raw" samples are those as synthesized and routinely purified, "clean" were additionally annealed at 400^{o}C for 4 hrs in vacuum.

Experiment: The diffraction data was taken in transmission geommetry, the flat samples were ~ 0.3 mm thick, beamsize ~ 0.3x2mm, λ ~ 0.2135Å. The patterns were measured in 5 steps with the use of CCD camera covering 12^{o} 2Θ in one step. The subsequent runs overlapped by 3^{o}2Θ . The calibration and integrations were done with the use of FIT2D program (Andy Hammersley, ESRF).
All samples were measured in room-temperature, 3 selected samples were additionally measured at 240, 180 and 120K.

Data elaboration: The sequent parts of the patterns were matched together to get full patterns. Total recorded angular range was up to 45^{o} 2Θ (Q_{max} ≈25 Å^{-1}). The positions of the Bragg lines measured in the overlapping regions of the sequent scans do not match fully. This is probably due to insufficient accuracy of the data callibration and it can result from properties of CCD camera which was calibrated for 0.7 Å wavelength and used for much higher beam energies. This causes severe problems to get a good quality of the fit of the patterns by Rietveld refinement program; typically we get R_{calc} ~ 15-20 for $R_{expected}$ ~ 4-6. In parallel with the Rietveld refinement, we analysed the data based on comparison of singular, isolated reflections.

Lattice parameters: Due to one dimensional disordering the nanocrystalline diamond has not cubic but trigonal structure what leads to lattice anisotropy demonstrated by deviation of *c/a* ratio from that of the cubic structure. Here we calculated the lattice parameters assuming (i) cubic (a_c) and (ii)

trigonal lattices (a_{tr} and c_{tr}). The a_c values were calculated from Rietveld refinement program (c/a = 0.81605), a_{tr} and c_{tr} were calculated from single reflections 404 and 408.

Table 1. Lattice parameters of diamond polycrystals at RT

Sample	a_c [Å]*	a_{tr} [Å]**	c_{tr} [Å]**	c_{tr}/a_{tr}**	V_c [Å^3]
ATM_{raw}	3.5498 (5)	2.5059 (5)	6.2044 (10)	0.8253 (10)	44.72 (1)
ATM_{clean}	3.5511 (5)	2.5161 (5)	6.1303 (10)	0.8121 (10)	44.78 (1)
$DALAN_{raw}$	3.5418 (5)	2.5070 (5)	6.1411 (10)	0.8165 (10)	44.43 (1)
$DALAN_{clean}$	3.5481 (5)	2.5127 (5)	6.1414 (10)	0.8147 (10)	44.67 (1)
$A16_{raw}$	3.5500 (5)	2.5106 (5)	6.1914 (10)	0.8220 (10)	44.74 (1)
$A16_{clean}$	3.5534 (5)	2.5140 (5)	6.1710 (10)	0.8182 (10)	44.87 (1)
microDIA	3.5488 (5)	2.5085 (5)	6.1526 (10)	0.8176 (10)***	44.69 (1)

Note: the calculated values are relative!; *calculated from Rietveld refinement program; **calculated from (404) and (408) trigonal reflections; *** theoretical value for a fcc cubic structure is 0.81605.

From Table 1 it follows that:

1. The lattice of the cleaned materials is expanded compared to the raw powders;
2. The ratio c_{tr}/a_{tr} varies between the materials and it decreases during cleaning the powders.

Internal pressure: Presence of surface tension is demontrated in very small samples by decrease of their lattice parameters. Usually this effect becomes stronger with the decrease of the particle diameter. In the diamond nanocrystals we observe that cleaning of the raw powder leads to an increase of the measured lattice parameters, Table 1. This effect can be related either to compression of single particles or to relaxation of the strain present in the agglomerates of the nanoparticles in the starting material. Considering this effect a property of an individual particle, we calculate the internal pressure using Birch-Murnaghan equation:

$P = 3/2\ K_o \{(V/V_o)^{-7/3} - (V/V_o)^{-5/3}\} \times \{1 - 3/4(4-K_o')[(V/V_o)^{-2/3} - 1] + ...\}$.

For K_o = 550 GPa known for single crystal diamond and assuming $K_o' = 4$ we get the internal pressure P equal 0.7, 1.65 and 3 GPa for A16, ATM and DALAN "raw" samples, respectively. Assuming that the average diameter of the diamond particles is 10 nm, we estimate the surface tension in the "raw" materials equals 4, 8 and 15 N/m, respectively.

Thermal expansion: The expected decrease of the lattice parameter between room-temperature and 240 K should not exceed 0.4×10^{-4}. In microcrystalline and in DALAN samples no changes of the lattice parameter a_c are observed upon cooling. But the decrease of the lattice parameter $\Delta a_c = 3 \times 10^{-3}$ Å from room- to 240 K was observed for ATM sample. This results either from the lattice expansion coefficient $\Delta a_c / a_c = 8.5 \times 10^{-4}$ being property of nano-size (nearly 20 times larger than that of single crystals) or, this is a result of generation of strain upon cooling down the agglomerates present in the starting material.

Interatomic Distance Function (*rdf*): Large Q range of the measured patterns, up to 25 Å^{-1}, gives one a possibility of calculations of *rdf* functions from the measured diffraction patterns with the precision sufficient to see the differences of interatomic distances as small as 1% and less (~ 1.0×10^{-3} Å). Due to relatively poor match of the individual scans and to large background intensity which we obtained only preliminary results which show sensitivity of this method to variation of the interatomic distances, they are not conclusive, c.f. Report of Experiment 01-01-189 at BM01B.