Precision investigation of modern crystalline material Niobium Carbide by diffraction methods

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Content

- Introduction to diffraction.
- Comparasion of X-ray and neutron diffraction.
- X-ray difraction results from Rietveld refinement.
- Neutron difraction results from Rietveld refinement.
- Williamson-Hall analysis of size and microstrains

Braggs law

- Conects cell parameters with position of interference maxima.
- $N\lambda = 2dsin\theta$, where: λ is wavelenght of the incident wave,

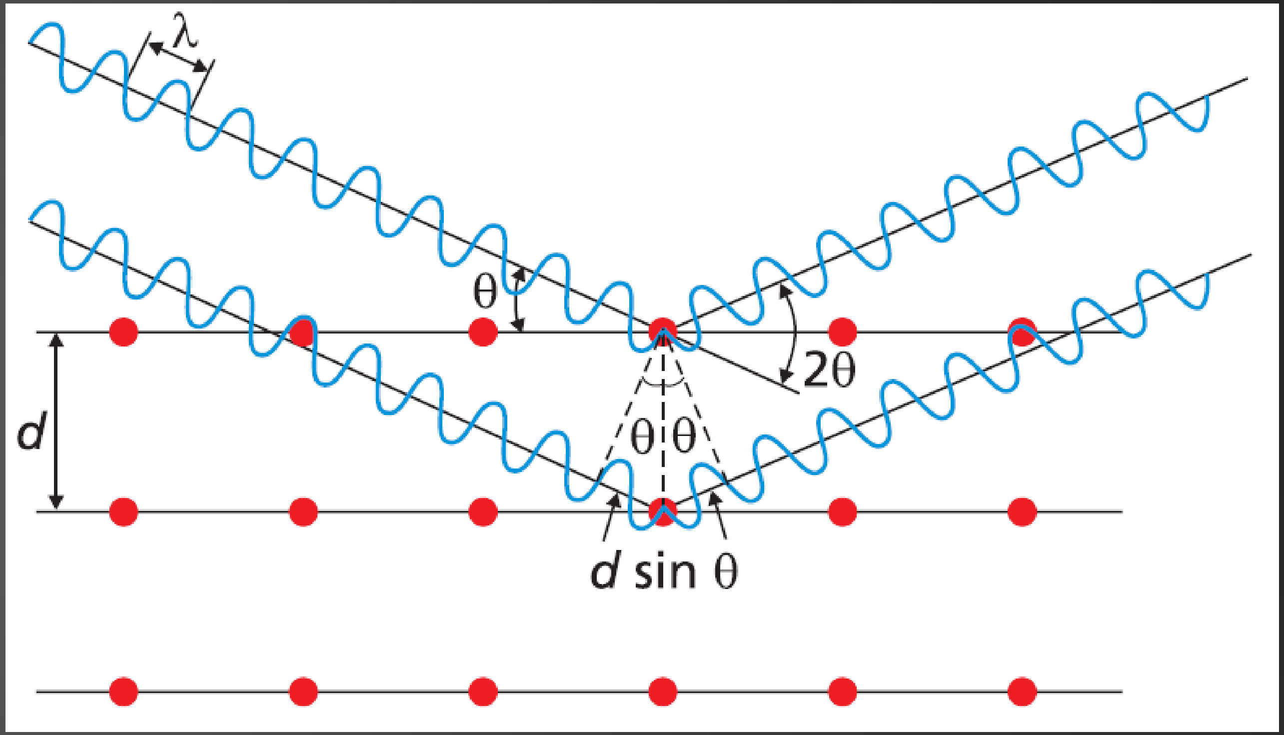
  d is interplanar spacing,

  θ is scattering angle,

  N is an integer.
- For cubic crystal system holds following equation:

$$d^2 = \frac{a}{h^2+k^2+l^2},$$ where: a is cell parameter

h, k, l are Miller idices



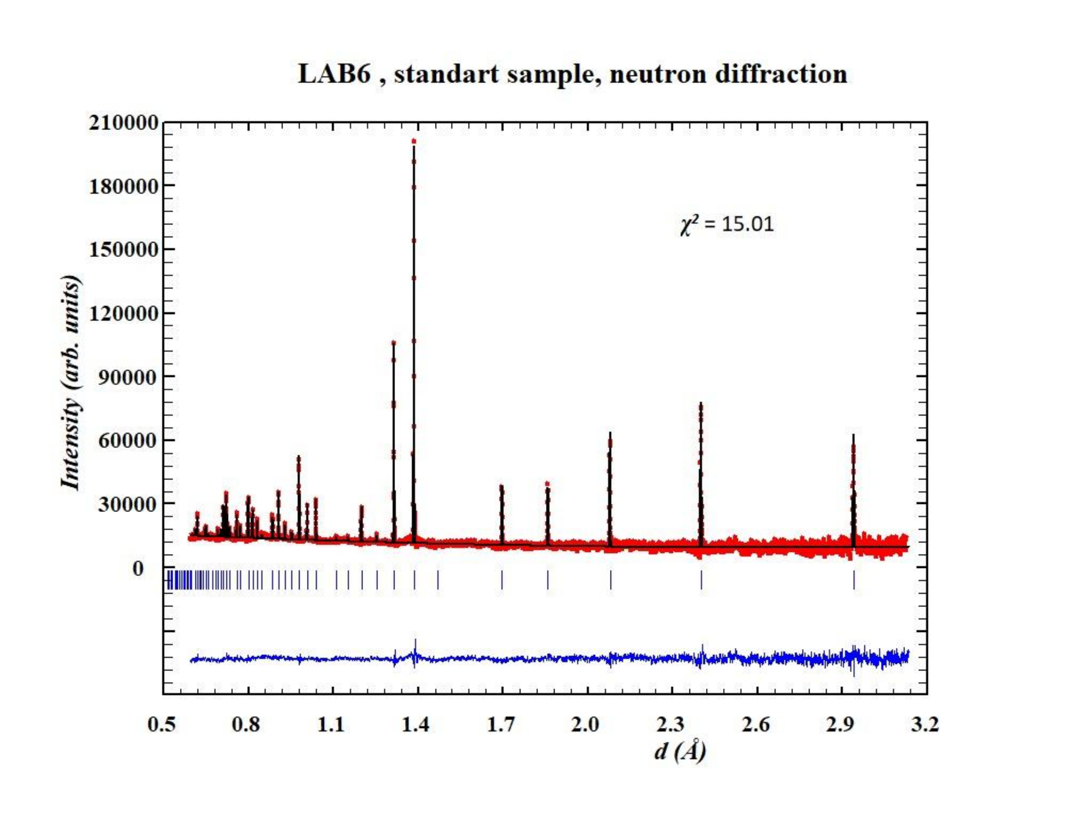
Diffraction

- Diffraction methods are widely used to study the structure of condensed matter.
- Mostly used diffraction methods:
  - X-ray diffraction.
  - Neutron diffraction.
  - Electron diffraction.
- Powder sample diffraction:
  - Used for the phase analysis,

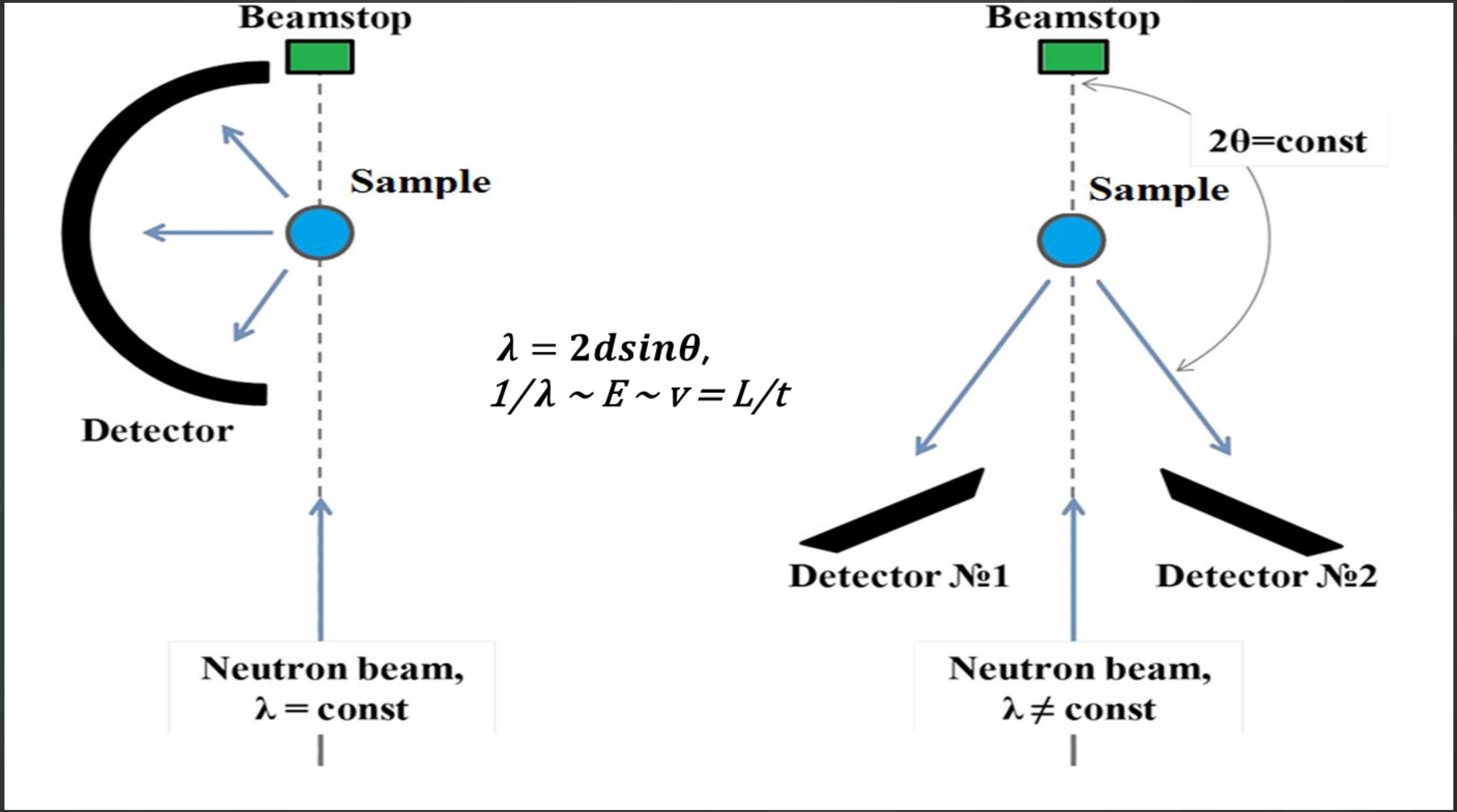
    to determine lattice parameters,

    residual stresses, microstrains

    and crystallite size.



Time of flight and convetional geometry



Neuton diffraction

- Mass, Spin 1/2, Magnetic dipole moment.
- Neutrons interact with the nucleus and magnetic moment of the atom.
- Scattering power independent of 2θ
- Lower absorption.
- Large amounts of sample needed.
- Neighbours and isotopes can be discriminated.
- Light elements can be seen.
- Low availability (nuclear reactor).
- Incoherent scatterers (eg. H) have to be avoided.

X-ray diffraction

- No mass, spin 1, no magnetic dipole moment.
- X-ray photons interact with the electrons.
- Scattering power falls off with 2θ
- Stronger absorption
- Lower amounts of sample needed.
- Neighbours and isotopes cannot be discriminated.
- Light elements hard to detect.
- High availability (lab instrument).

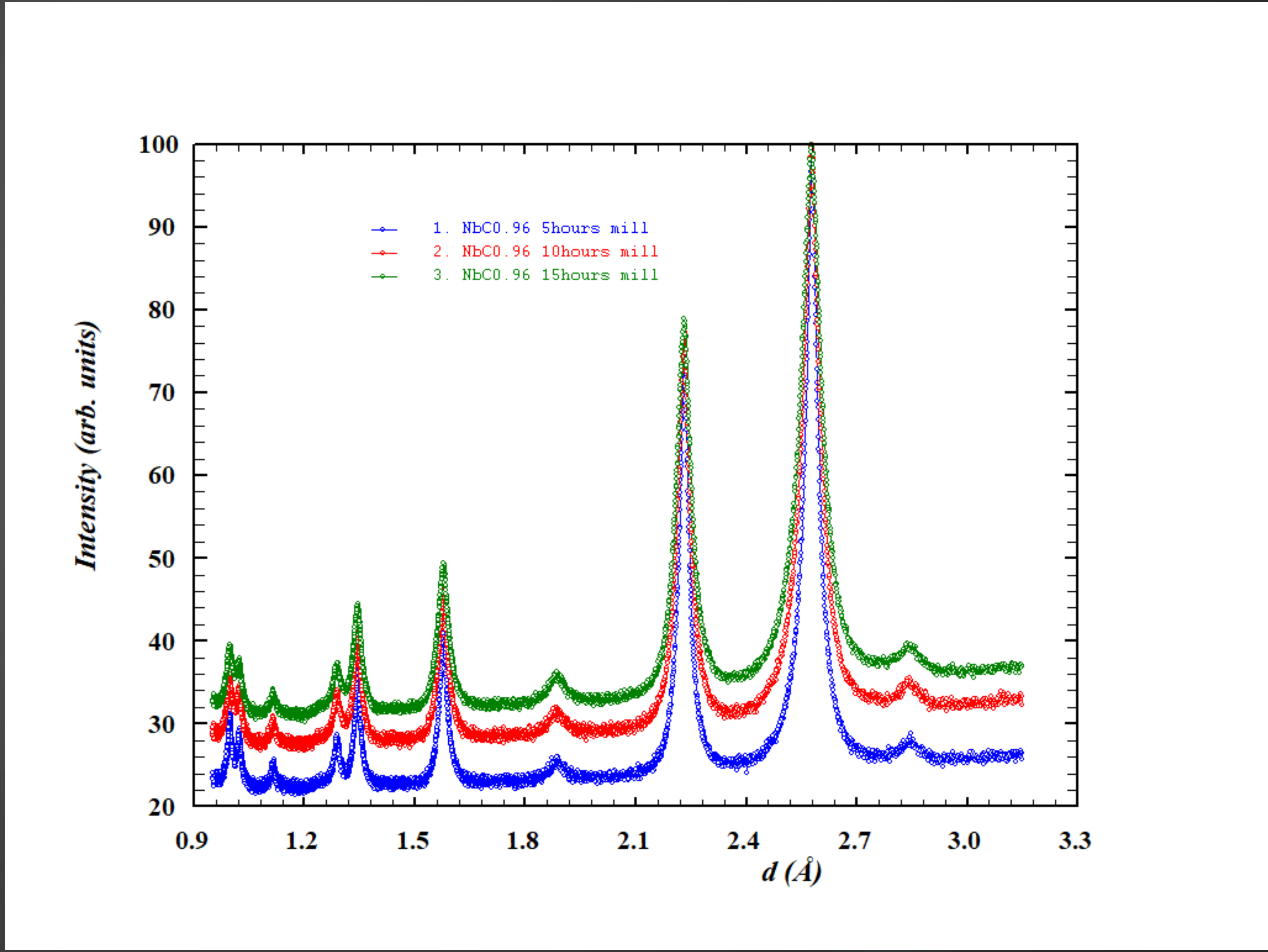
Characterisation of niobium carbide by X-ray diffraction

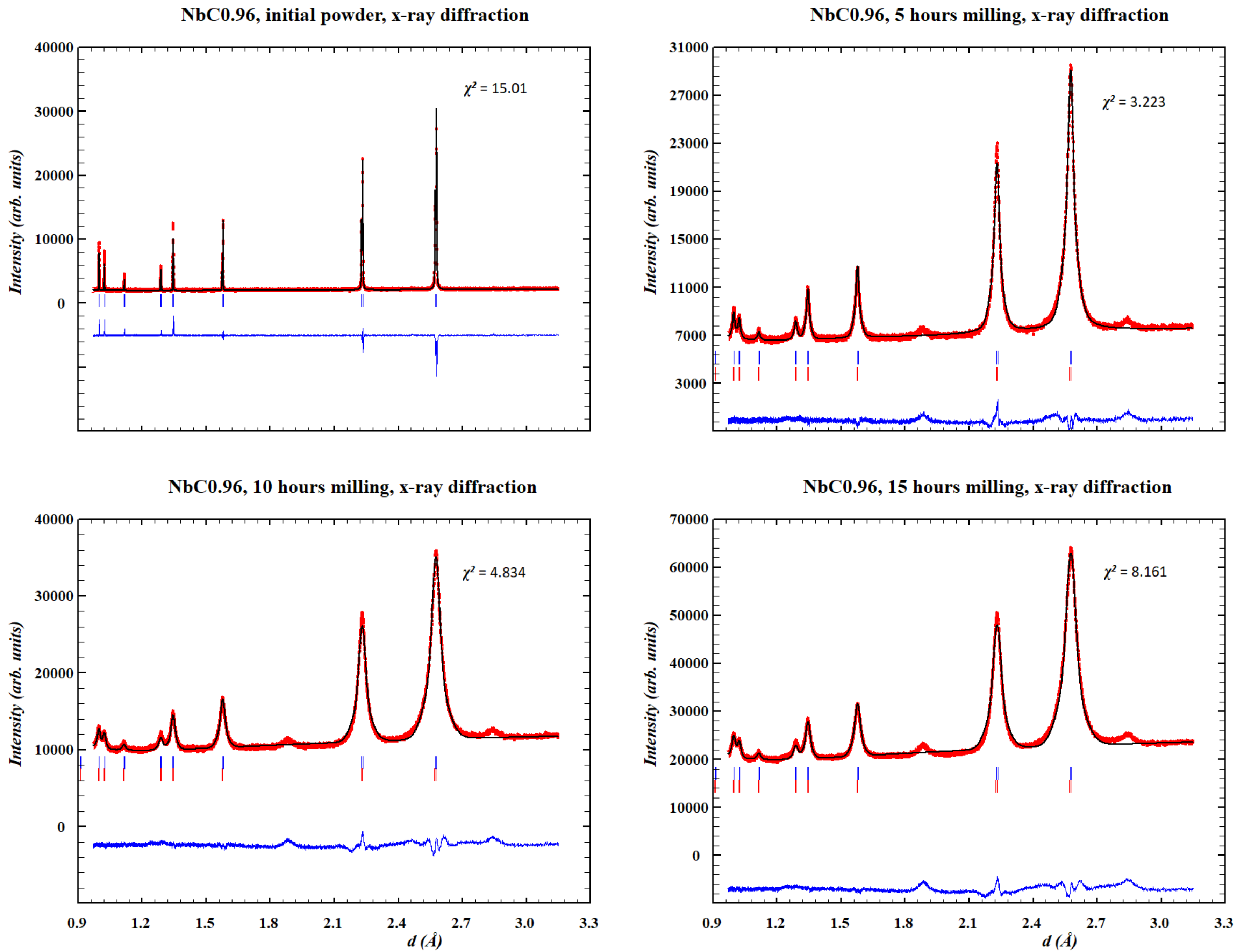
Niobium Carbide

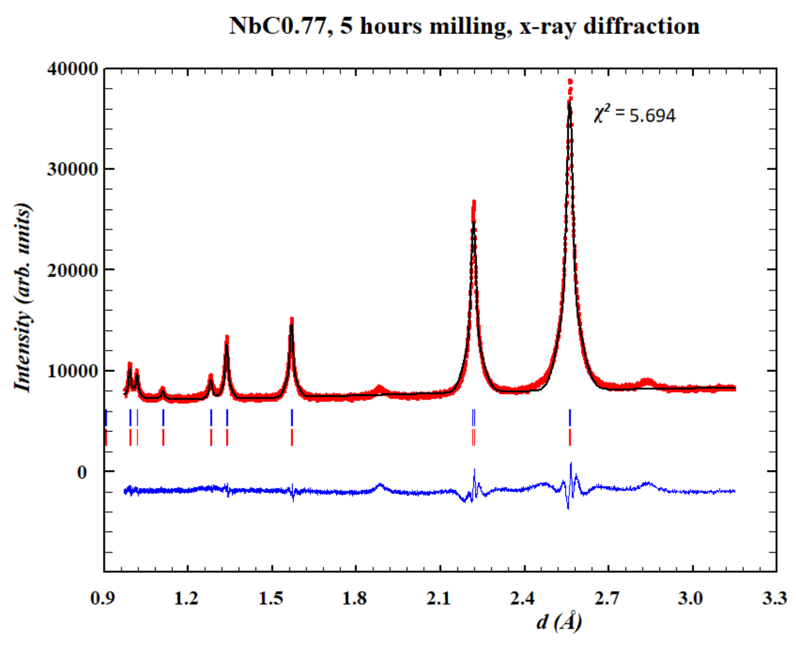
- Extremely hard refractory material.
- Commercial use:
  - tool bits for cutting tools.
- Cubic space group Fm3m
- Studied samples:
  - NbC_x
  - Non-stoichiometries: x = 0.96, 0.84, 0.77.
  - Powder was milled for 0, 5, 10, 15 hours.

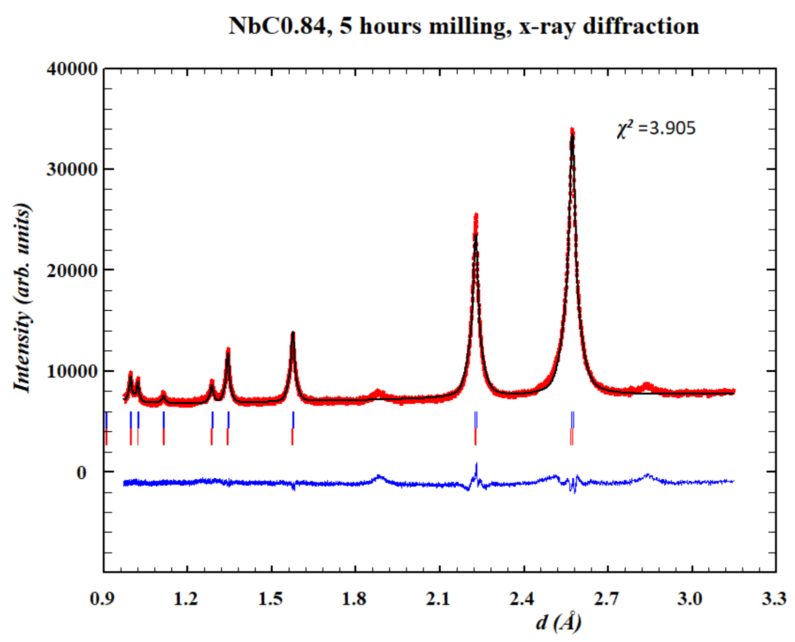
X-ray data for $NbC_{0.96}$

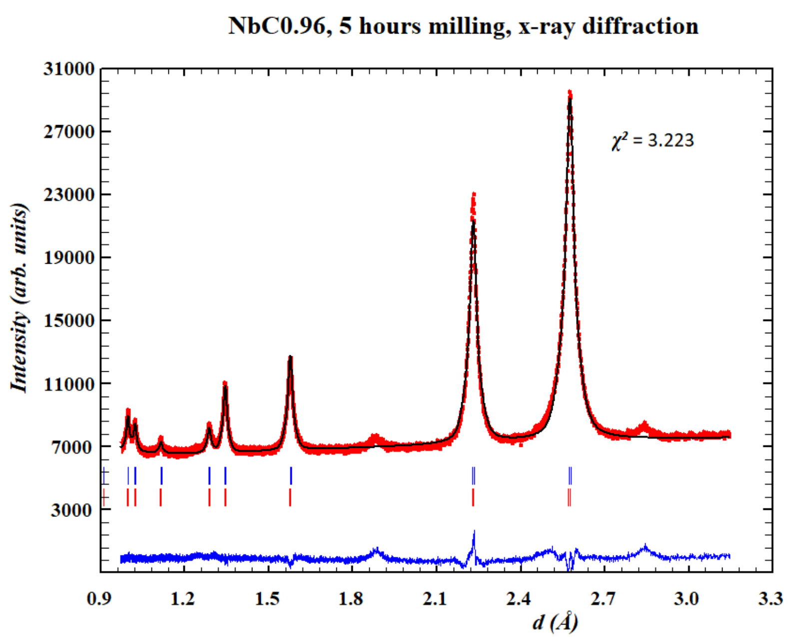
- Backgroung raises, but remains steady.
- Peaks become wider.



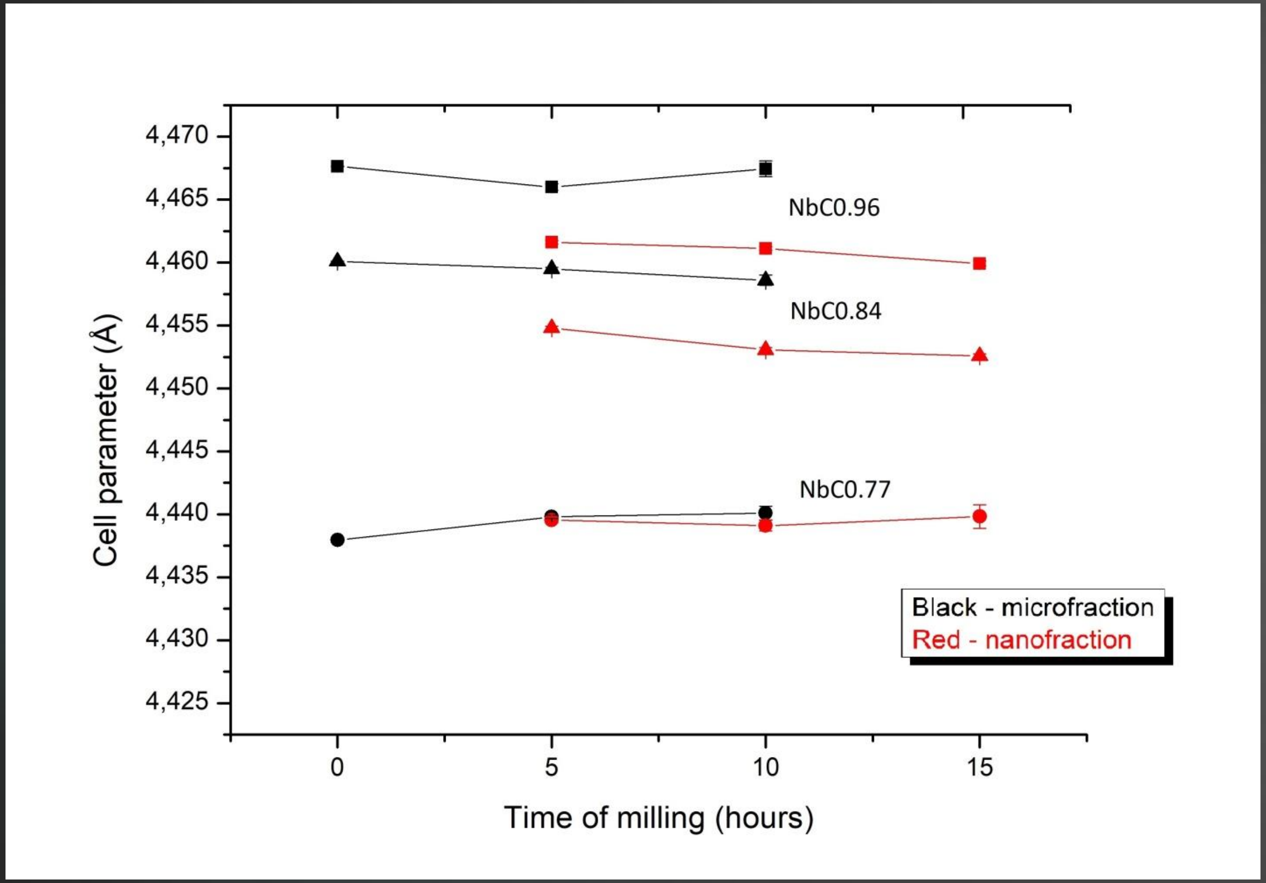

NbC0.96, initial powder, x-ray diffraction
χ² = 15.01
NbC0.96, 5 hours milling, x-ray diffraction
χ² = 3.223
NbC0.96, 10 hours milling, x-ray diffraction
χ² = 4.834
NbC0.96, 15 hours milling, x-ray diffraction
χ² = 8.161
Intensity (arb. units)
d (Å)
40000
30000
20000
10000
0
31000
27000
23000
19000
15000
11000
7000
3000
70000
60000
50000
40000
30000
20000
10000
0.9
1.2
1.5
1.8
2.1
2.4
2.7
3.0
3.3

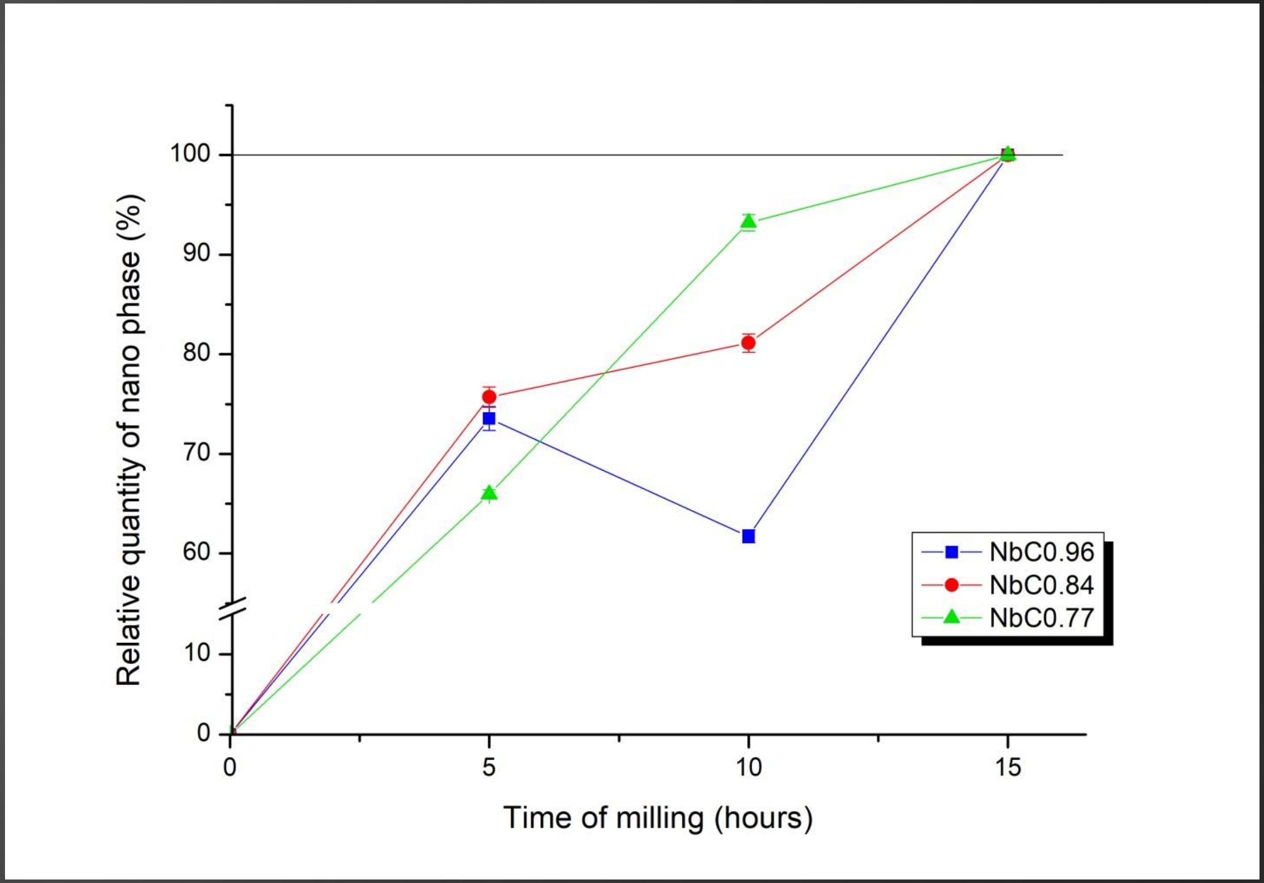

NbC0.77, 5 hours milling, x-ray diffraction
χ² = 5.694
Intensity (arb. units)
40000
30000
20000
10000
0
0.9
1.2
1.5
1.8
2.1
2.4
2.7
3.0
3.3
d (Å)


NbC0.84, 5 hours milling, x-ray diffraction
χ² =3.905
Intensity (arb. units)
40000
30000
20000
10000
0
0.9
1.2
1.5
1.8
2.1
2.4
2.7
3.0
3.3
d (Å)


NbC0.96, 5 hours milling, x-ray diffraction
χ² = 3.223
Intensity (arb. units)
31000
27000
23000
19000
15000
11000
7000
3000
0.9
1.2
1.5
1.8
2.1
2.4
2.7
3.0
3.3
d (Å)

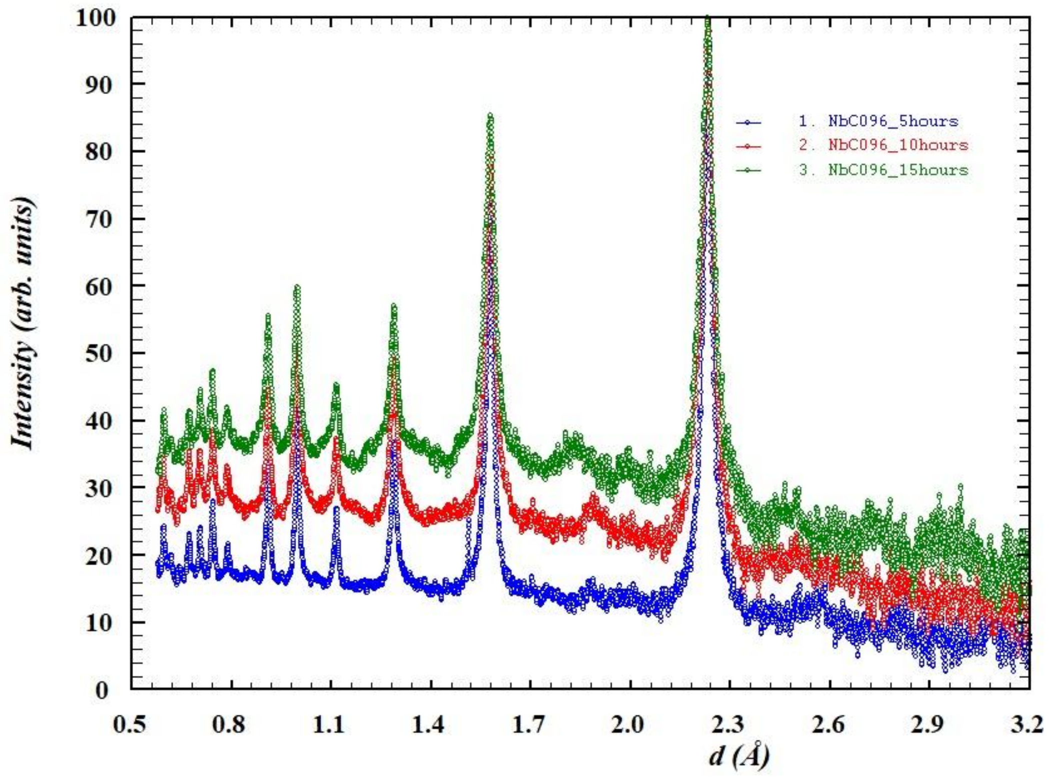
Results


4,470
4,465
4,460
4,455
4,450
4,445
4,440
4,435
4,430
4,425
Cell parameter (Å)
NbC0.96
NbC0.84
NbC0.77
Black - microfraction
Red - nanofraction
0
5
10
15
Time of milling (hours)

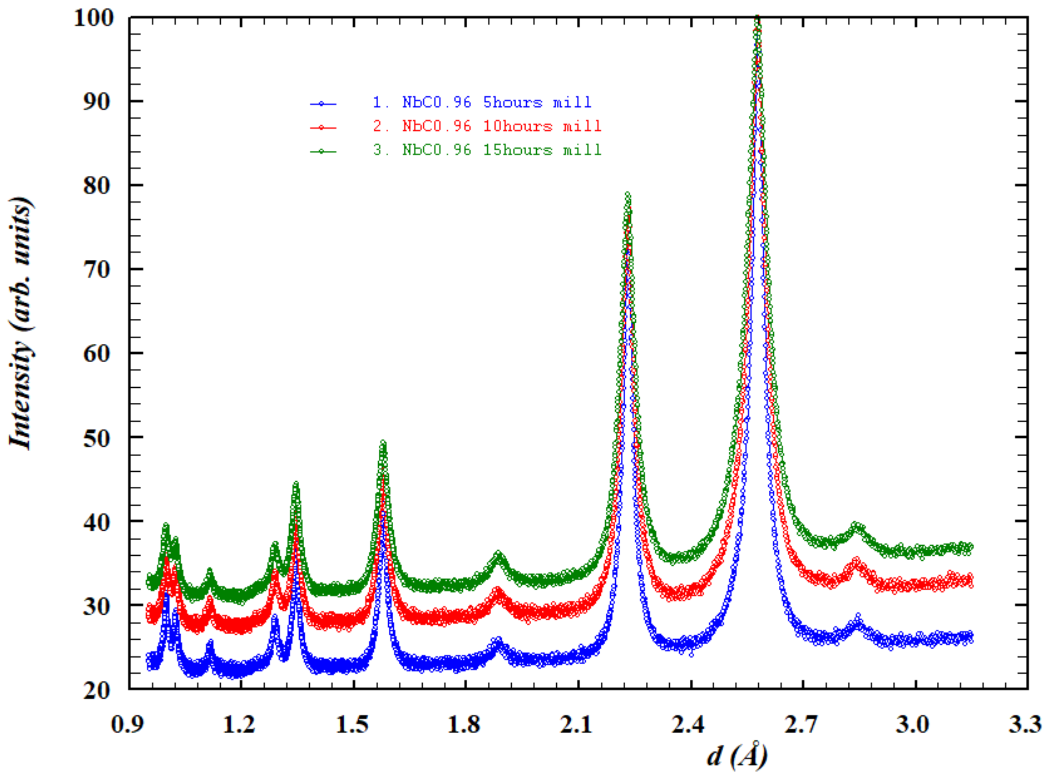

100
90
80
70
60
10
0
Relative quantity of nano phase (%)
NbC0.96
NbC0.84
NbC0.77
0
5
10
15
Time of milling (hours)

Characterisation of niobium carbide by neutron diffraction

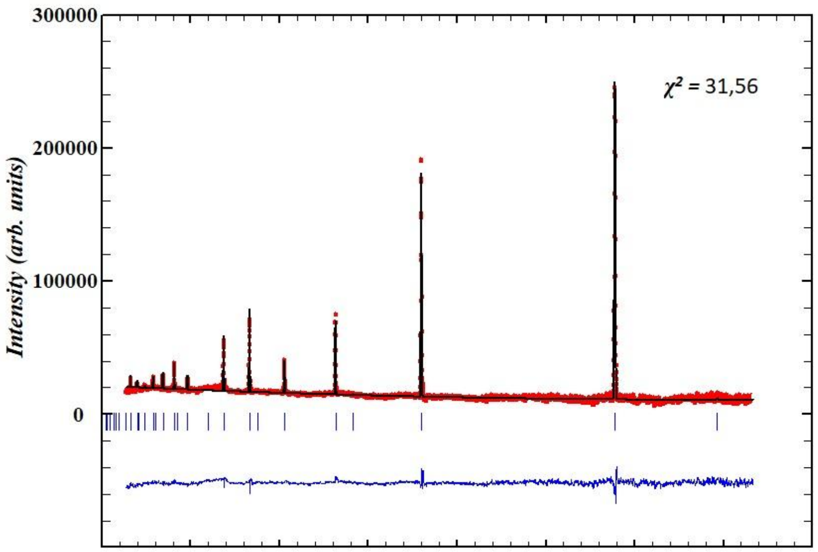
Neutron diffractogram:



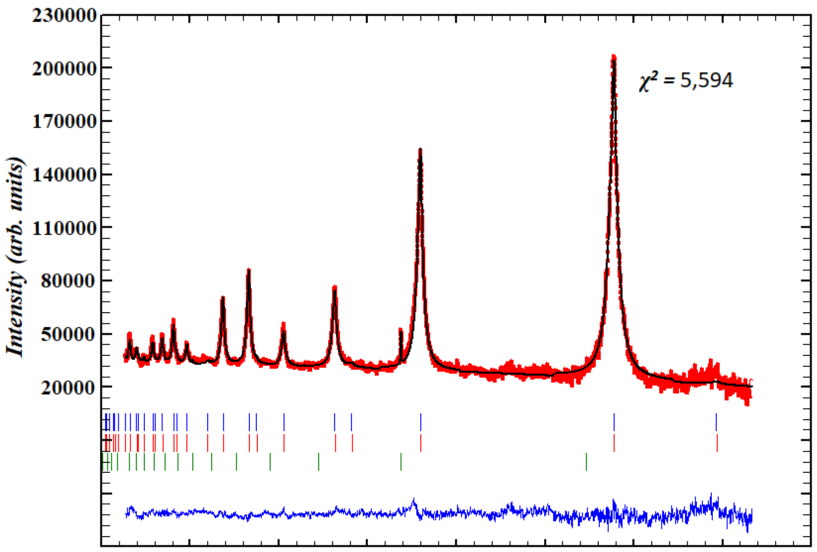
X-ray diffractogram:



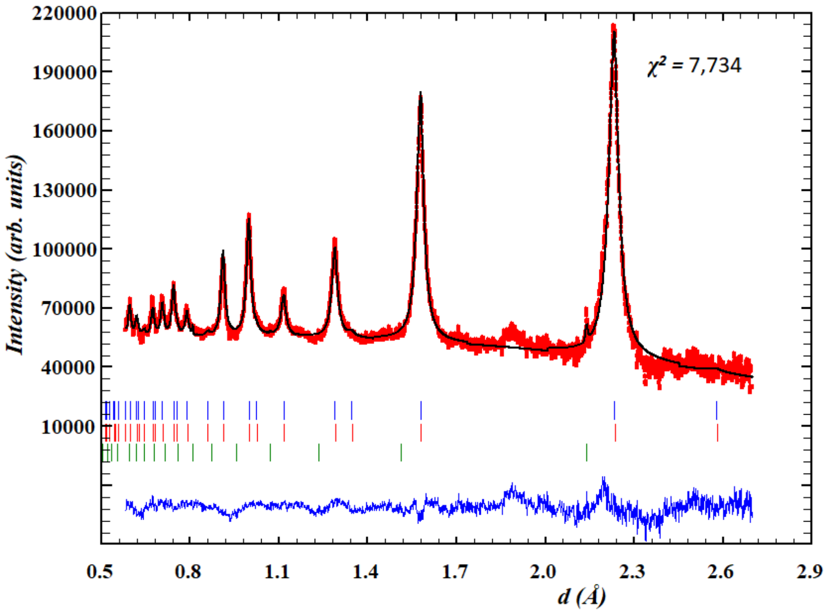
NbC0.96, initial powder, neutron diffraction



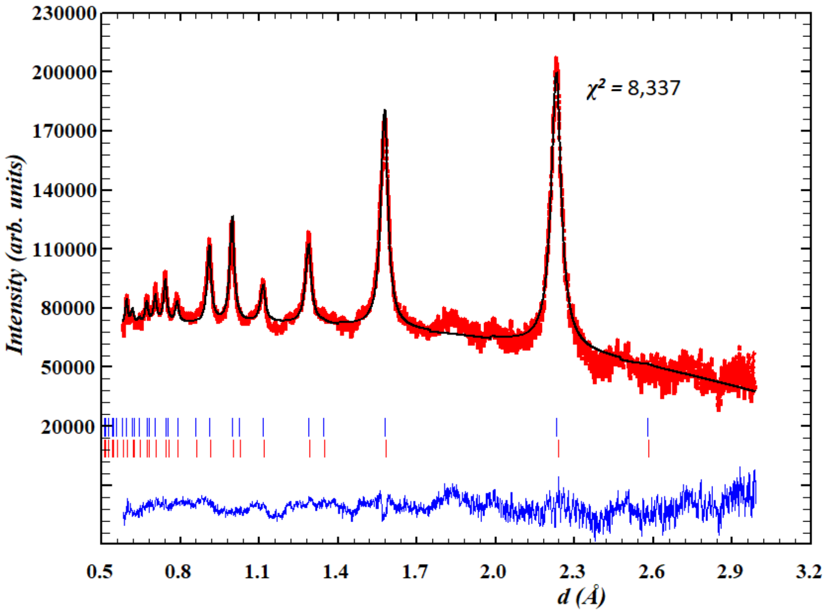
NbC0.96 , 5 hours milling, neutron diffraction

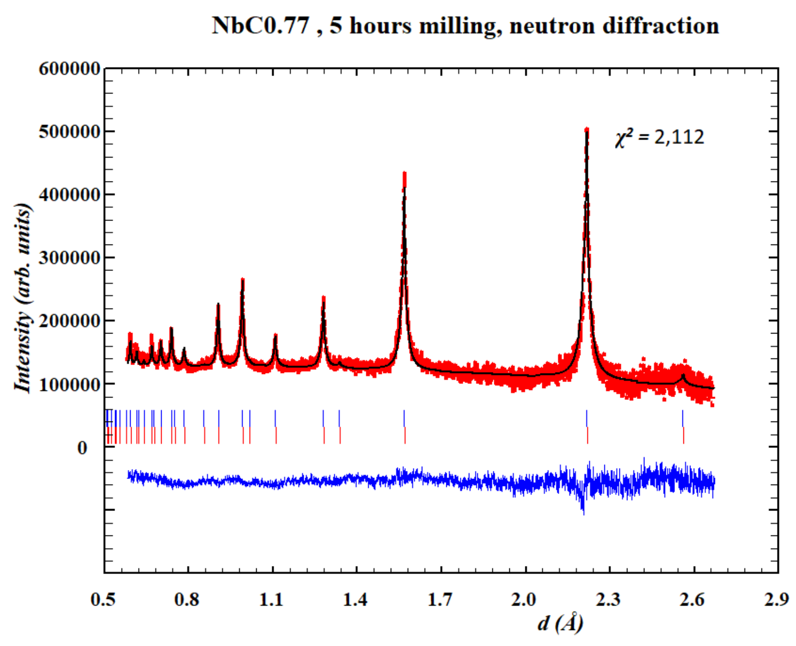


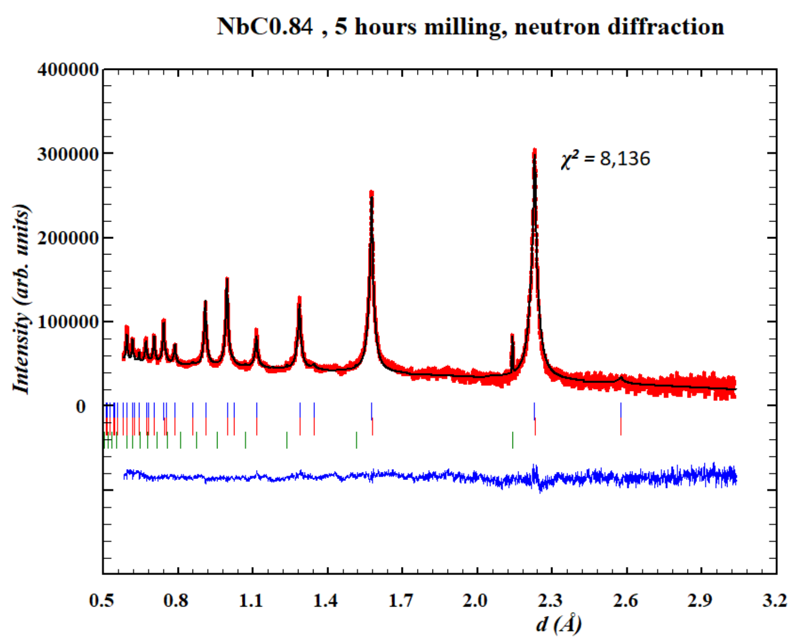
NbC0.96 , 10 hours milling, neutron diffraction

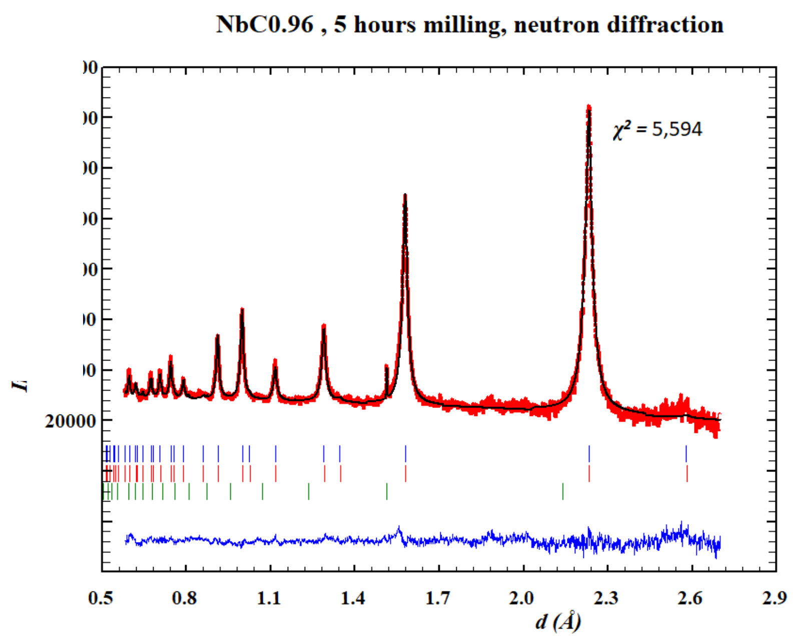


NbC0.96 , 15 hours milling, neutron diffraction

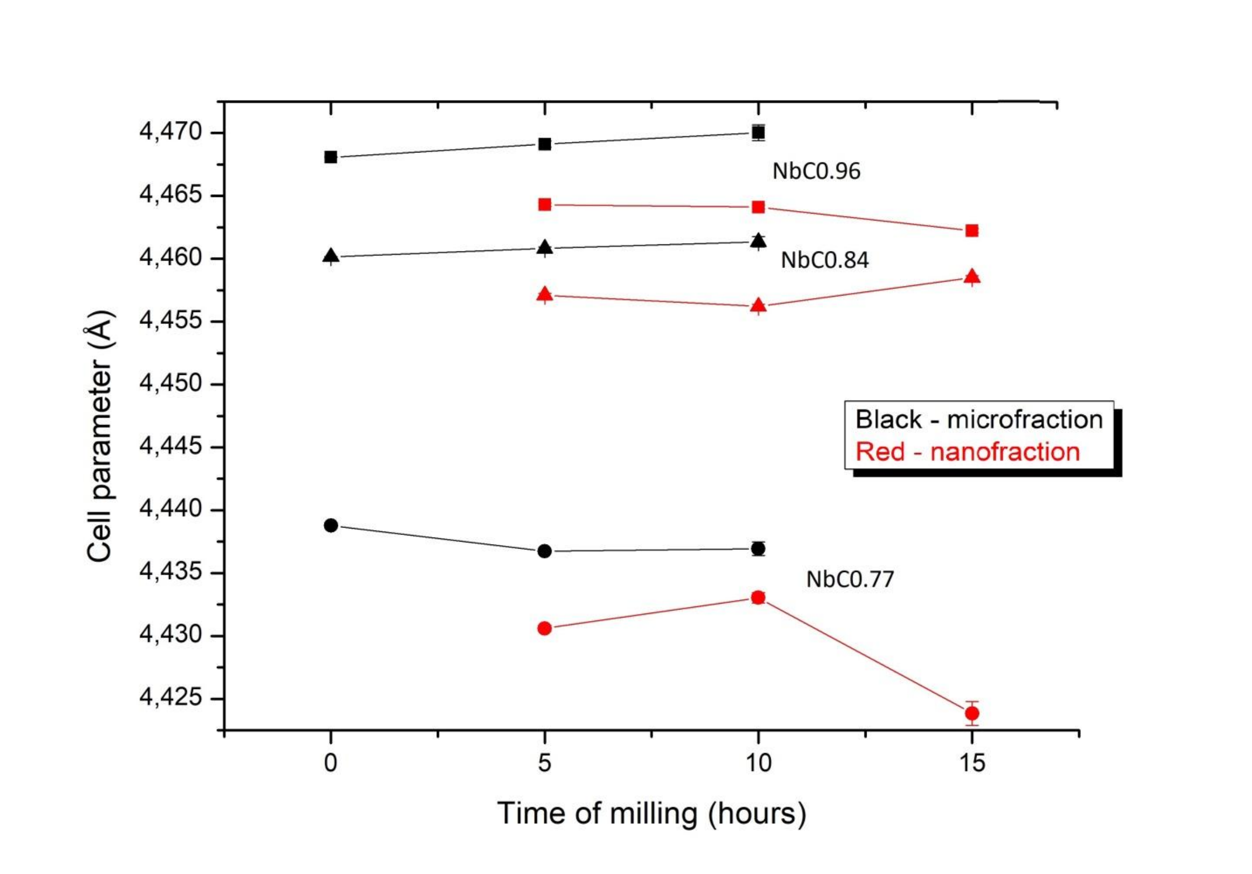



NbC0.77 , 5 hours milling, neutron diffraction
χ^2 = 2,112
Intensity (arb. units)
d (Å)

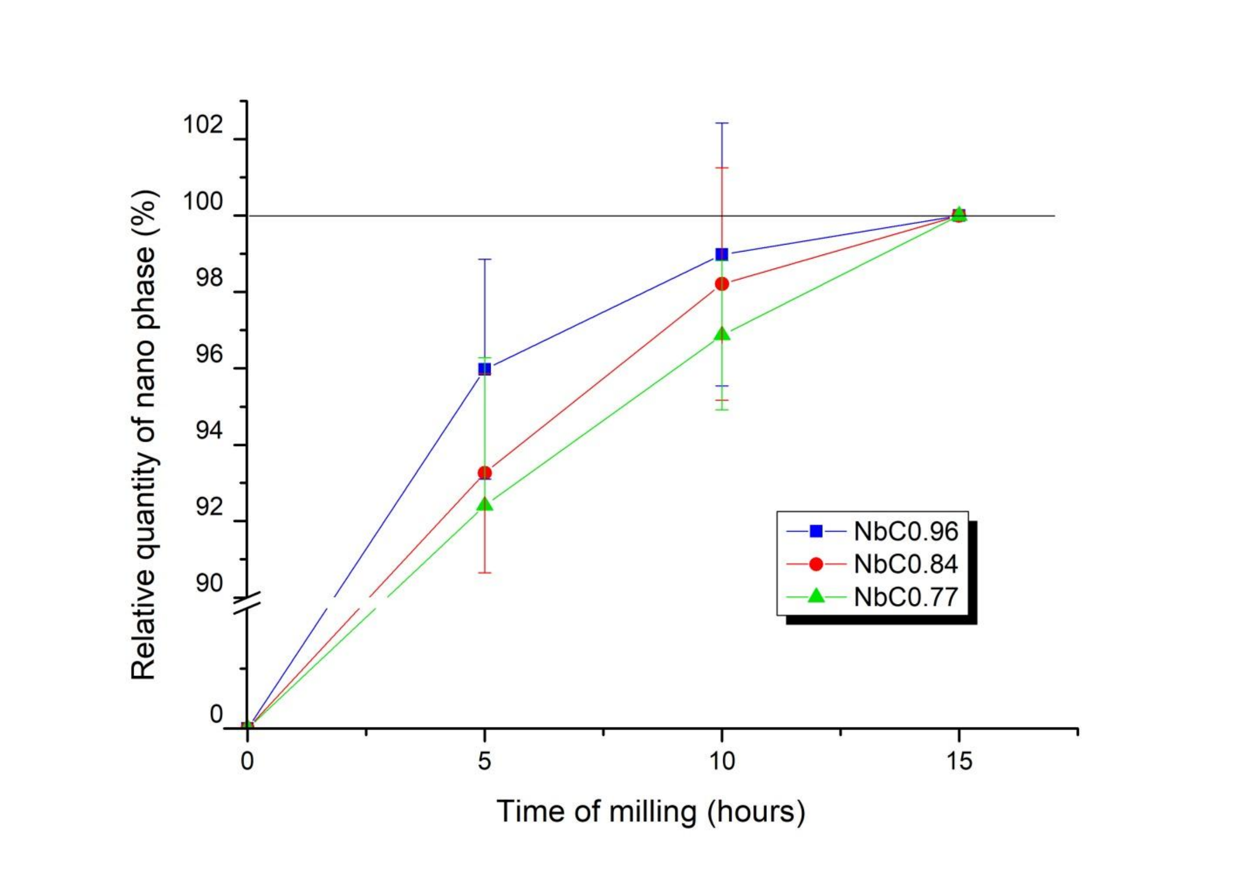

NbC0.84 , 5 hours milling, neutron diffraction
χ^2 = 8,136
Intensity (arb. units)
d (Å)


NbC0.96 , 5 hours milling, neutron diffraction
χ^2 = 5,594
d (Å)

Results



4,470
4,465
4,460
4,455
4,450
4,445
4,440
4,435
4,430
4,425
Cell parameter (Å)
NbC0.96
NbC0.84
NbC0.77
Black - microfraction
Red - nanofraction
0
5
10
15
Time of milling (hours)



102
100
98
96
94
92
90
0
Relative quantity of nano phase (%)
NbC0.96
NbC0.84
NbC0.77
0
5
10
15
Time of milling (hours)

Williamson-Hall analysis of size and microstrains

Williamson-Hall method

- Method for obtaining qualitative information about grain size and microstrains.
- If we assume our crystallites are perfectly isotropic, we can use following simple equation:

$$W^2 = C_1 + C_2 d^2 + C_3 d^2 + C_4 d^4,$$

where W is FWHM of the peak, d peak position and parameters C_1 and C_2 are describing influence of instrument and for C_3 and C_4 following equations are valid:

$$C_3 = 4\epsilon^2,$$

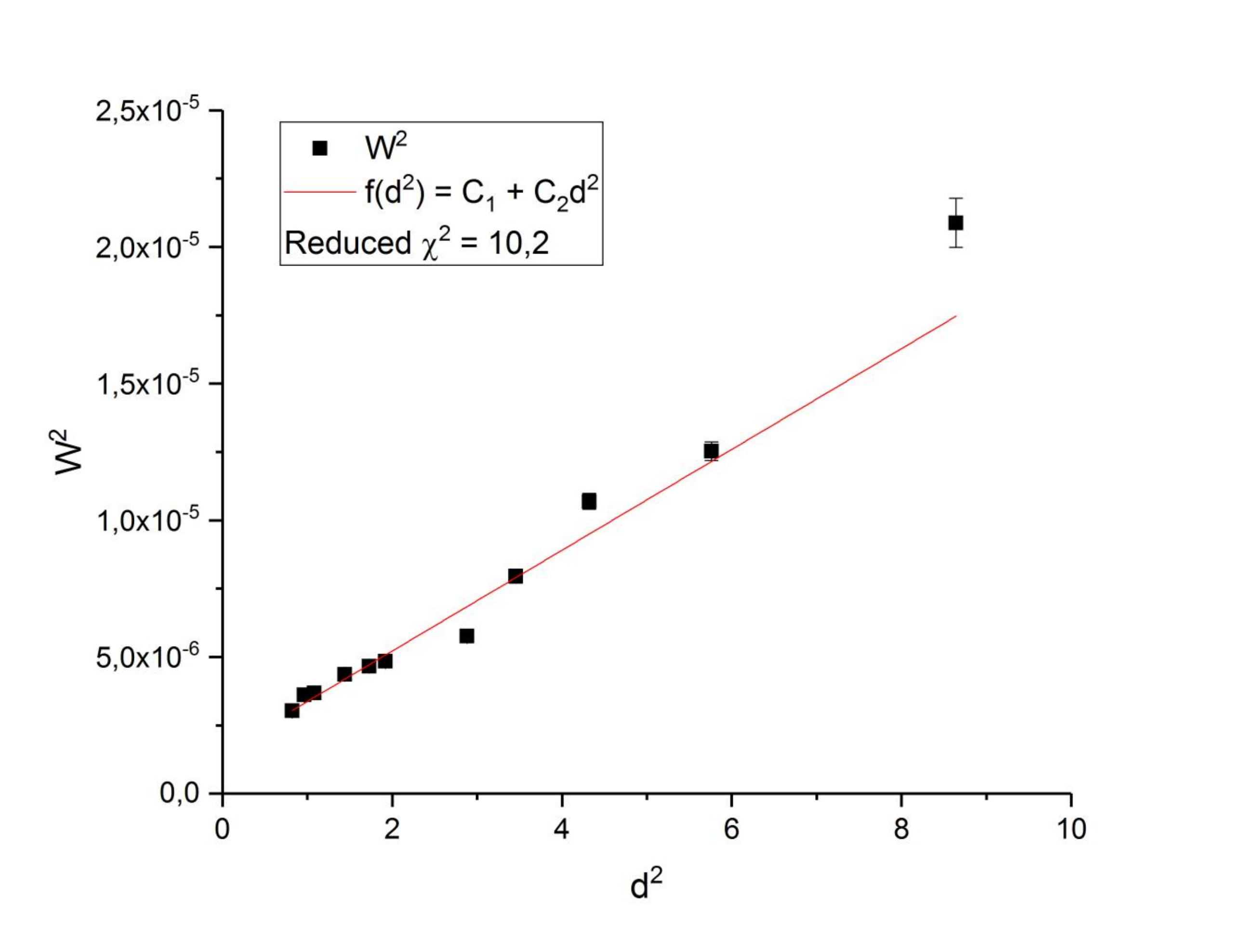
where ϵ are microstrains.

$$C_4 = \left(\frac{K}{L}\right)^2,$$

where K is grain shape parameter and L is size of the grains in Å .

Results of data analysis – Standart sample LaB_6

- Measured by neutron diffraction.
- Peaks were fitted by Gauss funcion.
- C_1 and C_2 are instrumental parameters.
  - $C_1 = (1{,}5 \pm 0{,}3) \cdot 10^{-6}$
  - $C_2 = (1{,}8 \pm 0{,}1) \cdot 10^{-6}$



- Figure 2: Linear fit for obtaining parameters C_1 and C_2

Data refinement - $NbC_{0,96}$ 5 hours

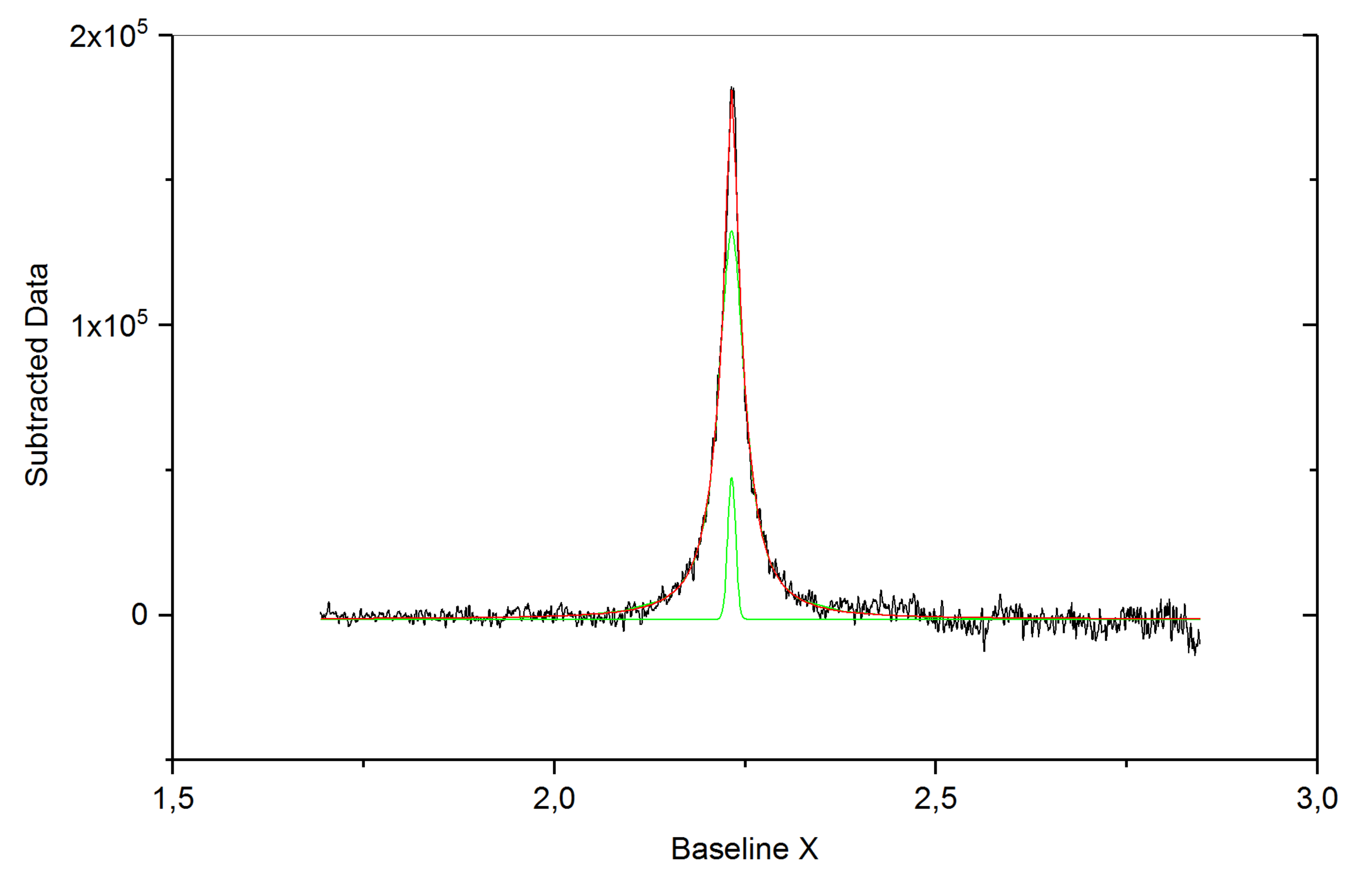
- Two phases fitted with sum of Gauss and Lorentzian.

- Lorentzian - wide phase.

$$L(x) = L_0 + \frac{2A}{\pi}\frac{W}{4(x-d)^2 + W^2}$$

- Gauss - narrow phase.

$$G(x) = G_0 + A\frac{e^{-\frac{2(x-d)^2}{W^2}}}{W\sqrt{\frac{\pi}{2}}}$$



- Figure 2: Refinement of the peak (2 0 0).

Results of data analysis – $NbC_{0,96}$ 5 hours

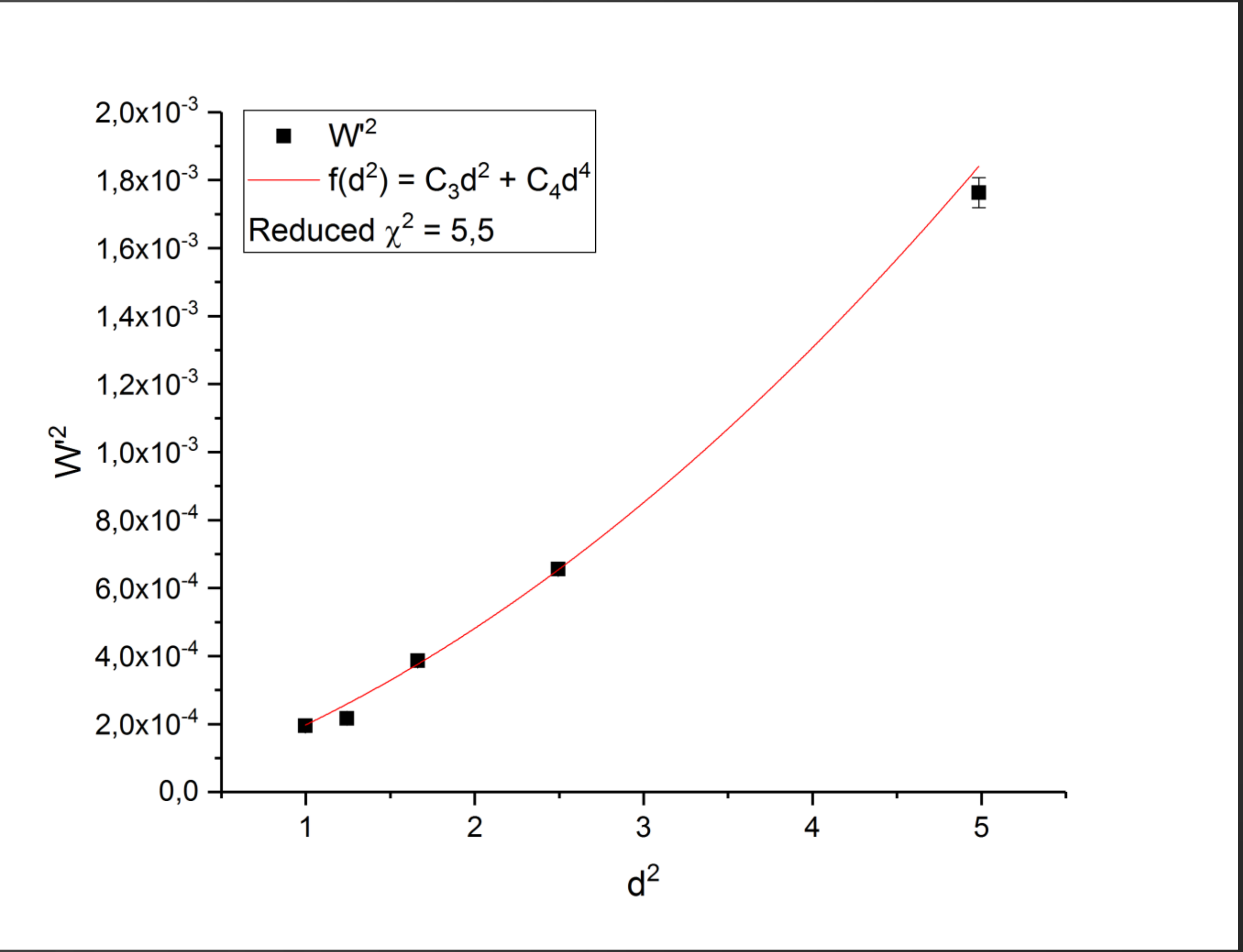
$$f(d^2) = W'^2 = W^2 - C_1 - C_2\ d^2 =$$
$$= C_3 d^2 + C_4 d^4$$

„Micro“ phase:

- $\varepsilon = (1{,}2 \pm 0{,}4) \cdot 10^{-3}$
- $L = (54{,}4 \pm 19{,}6)$ nm

„Nano“ phase:

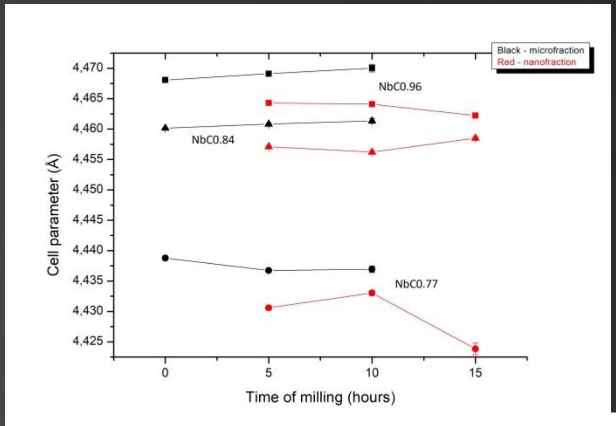
- $\varepsilon = (6{,}0 \pm 0{,}3) \cdot 10^{-3}$
- $L = (15{,}2 \pm 1{,}1)$ nm

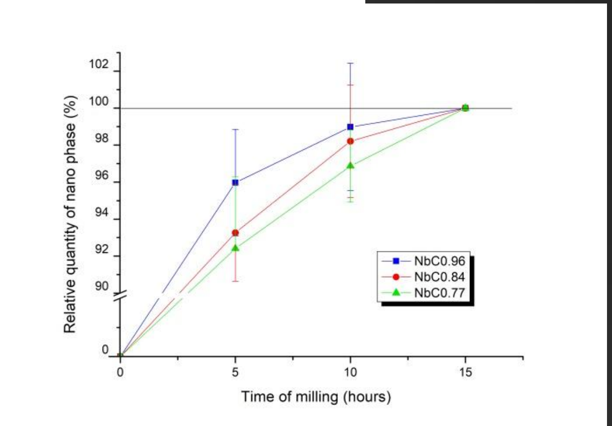


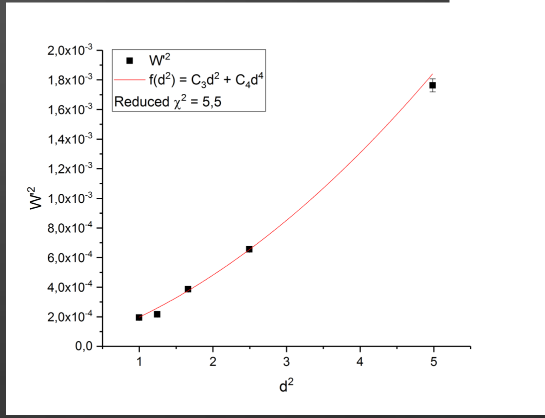
- Figure 3: Parabola fit for obtaining parameters C_3 and C_4

Summarize

- Cell parameters are smaller for „Nano“ phase and are decreasing with decreasing ratio of carbon.
- With increasing non-stoichiometry it is getting more difficult to mill the powder.
- 15 hours is sufficient time to obtain more than 99 % of „Nano“ fraction in our sample.
- The microstrains are higher for „Nano“ phase.
- The size of the „Nano“ phase crystallite is approximately 3 times smaller than of the „Micro“ phase.







Thank you for your attention.

References

[1] http://www.edge-techind.com/Products/Refractory-Metals/Niobium/Raw-Niobium/Niobium-Carbide-Powder-747-1.html (24.7.2018)

[2] ERMRICH, Martin; OPPER, Detlef X-Ray Powder Diffraction. 2011.

[3] BALAGUROV, Anatoly M., et al. High-resolution neutron diffraction study of microstructural changes in nanocrystalline ball-milled niobium carbide NbC0. 93. *Materials Characterization*, 2015, 109: 173-180.