Nanodiamonds for photonics, biomedical and radiochemical applications: structure and defects

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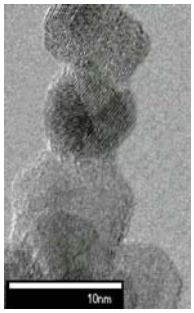
Outlook

- **Nanodiamonds: properties and synthesis**
- **Luminescing nanodiamonds: Structure and defects**
- **Sorption of radionuclides on nanodiamonds**
- **Conclusions**

Synthetic nanodiamonds: Production methods and properties I

Detonation of O-poor explosives (TNT/hexogen…) in a closed volume

- Discovered at least three times (1963-1988) in the USSR.
- Narrow size distribution 4-5 nm (XRD/TEM)
- Strong tendency of aggregation of primary nanodiamond particles into larger very stable clusters (100-200 nm)
- Very fast process (microseconds) at high PT-conditions. The charge must be cooled at extremely high rates to reduce graphitisation.
- Main chemical impurities: N, O, H
- Mass production – 100's kg/year for various industrial and biomedical applications



Iakoubovskii et al., 2008

Synthetic nanodiamonds: Production methods and properties II

Shock wave processing of C-containing materials

- First realised in 1959 by DeCarli in USA: shock compression of graphite.
- Grains up to several microns in size could be obtained. Very different P-T-t paths in comparison with the detonation synthesis.
- Graphite to diamond transition may be martensitic (diffusion-less) or displacive depending on orientation of the shock wave and graphite planes.
- One may live without graphite precursor (e.g. shock transformation of soot, hexane etc), but the efficiency of the diamond formation is lower.

Synthetic nanodiamonds: Production methods and properties III

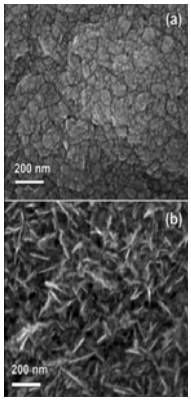
Grinding of macroscopic diamonds

- It is possible to mechanically grind mAcroscopic diamond crystals to nano sizes.
- Usually the crystals are irradiated/annealed prior to grinding. The main idea is to create luminescing ND's.
- The process is very labour- and time-consuming and (at present) very expensive.

Synthetic nanodiamonds: Production methods and properties IV

Chemical Vapour Deposition (CVD)

- In mid 90-ies it was found *(Gruen et al., 1994)* that use of some types of microwave reactors permits to obtain thin (few microns) diamond films with nanosized grains: UNCD or Ultra NanoCrystalline Diamond. The growth units are, possibly, C_2 molecules.
- Growth is very slow.
- Grain boundaries are graphitic.
- Huge influence of gas composition on grain morphology: possibility to make diamond nanowires!



Vlasov et al., 2007

Detonation nanodiamonds

Advantages:

- Small (4-5 nm) and uniform size;
- Mass production and relatively low price;
- Very bright and efficient (high quantum yield) luminescence;
- Some defects (e.g., the Nitrogen-Vacancy (NV) complex) are paramagnetic => applications for (nano)magnetometry;
- Biological compartibility (virtually nontoxic);
- Surface radicals could be controlled relatively easily (surface functionalisation).

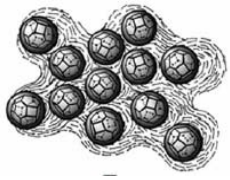
Problems:

- Very strong aggregation of nanograins: difficult (but possible!) to separate individual particles;
- Very problematic control of luminescing properties (difficult to make abundant NV defects);
- Difficult to achieve single-photon emission.

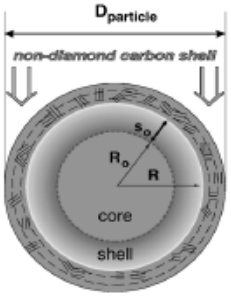
Structure of dispersed nanodiamonds

After synthesis and purification detonation nanodiamonds form aggregates of diamond grains, bounded by (semi)amorphous carbon.

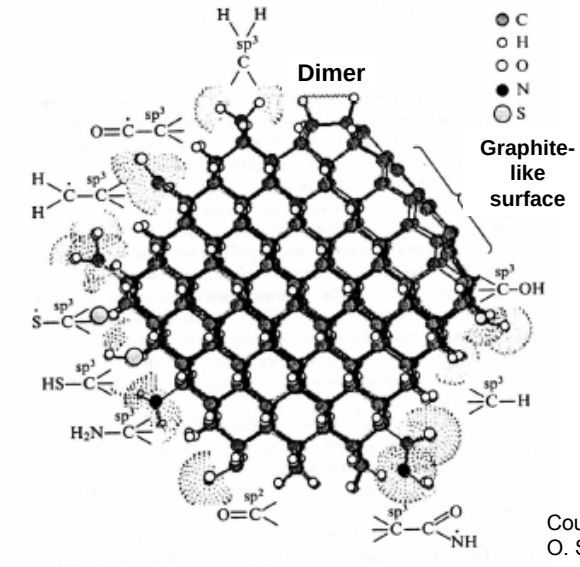
Separation of individual diamond grains is notoriously difficult.



The most probable structure of grains of detonation nanodiamonds *(Aleksenskii et al., SSP, 1999; Palozs et al., DRM, 2006)*.

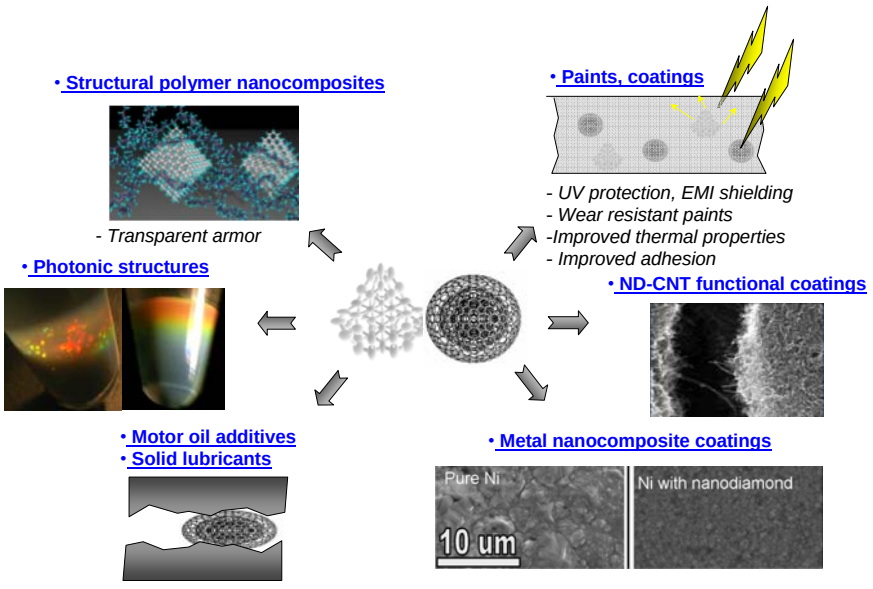


Structure of dispersed nanodiamonds



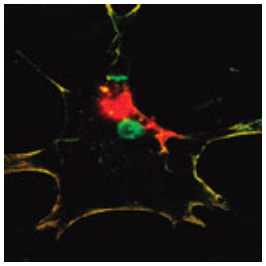
Courtesy by
O. Shenderova

Applications of Detonation Nanodiamonds & Onion-like Carbons

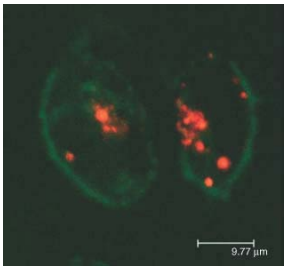


Some applications of Detonation Nanodiamonds

- Luminescing nanoparticles for biomedicine
- Sorbent of radionuclides



Nanowerk.com

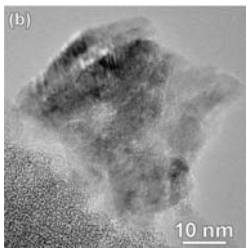


Ohulchanskyy et al., 2010

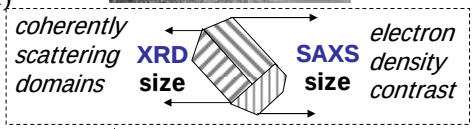
Structure

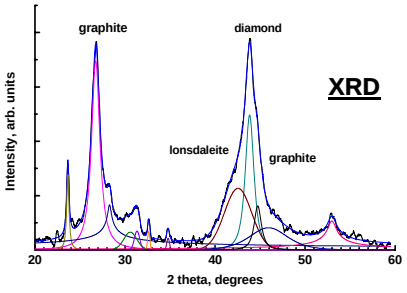
Nanodiamond produced by a shock wave conversion of graphite

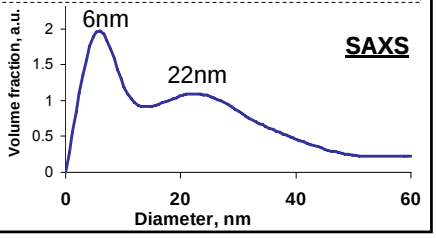
- Presence of graphite
- Presence of lonsdaleite (hexagonal diamond)
- **N<0.5 wt%** (from CHN analysis)
- Particle size from Dynamic Light Scattering: 25nm
- Crystal size from XRD:
  8 nm (111 reflection, Diamond),
  2.4 nm (002 reflection, Lonsdaleite)



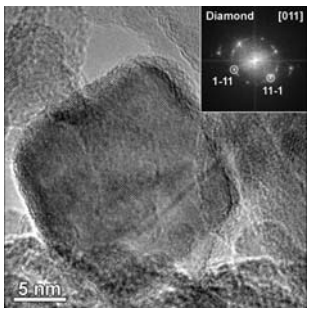
Mypolex™

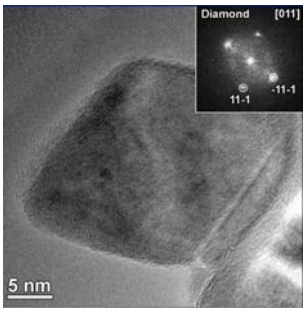


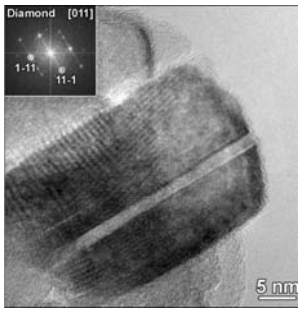




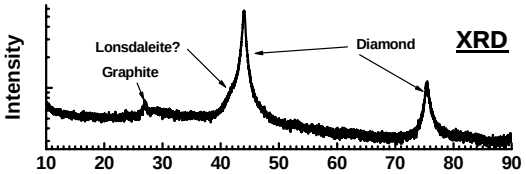
Nanodiamond from graphite/hexogen

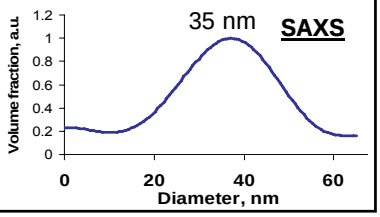




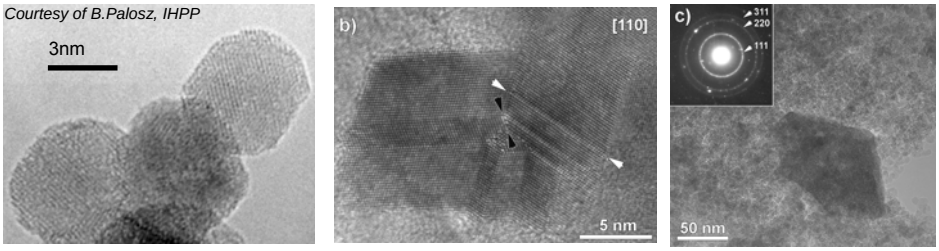


- **N <0.5 wt% (from CHN analysis)**
- **Graphite is not abundant**
- **Crystal size from XRD: 14.8 nm (<111>), 9.6 nm (<110>)**
- **Crystal size from SAXS: 35 nm**

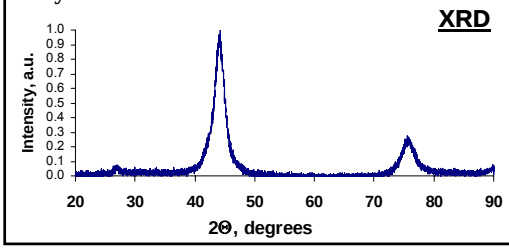


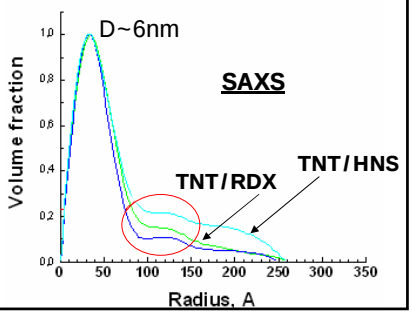


Detonation Nanodiamond

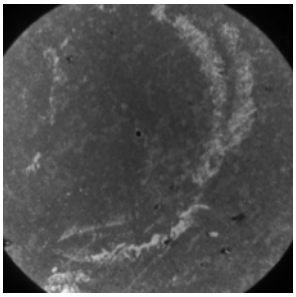


- N ~2.4 wt% (CHN analysis) – from TNT\RDX (21 at% of N in 50\50)
- N <1 wt% (CHN analysis) – from TNT\HNS (hexanitrostilbene) (15 at% of N)
- Graphite is not abundant
- Crystal size from XRD: 4 nm
- Crystal size from SAXS: 6 nm





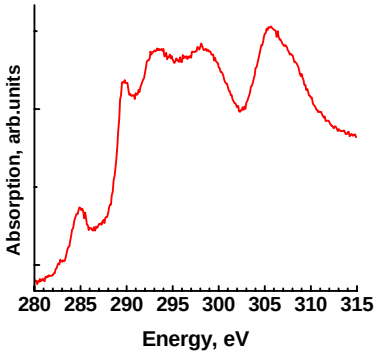
Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy



Photoemission (PEEM) image at the C absorption edge of a Si wafer with precipitated nanodiamond.

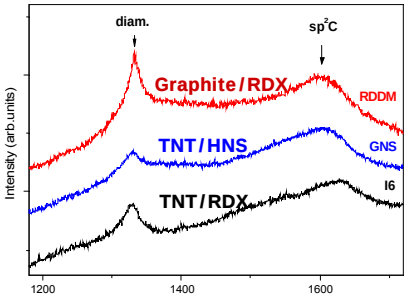
The field of view is 37 microns.

Absorption spectrum at carbon K-edge is typical for diamond

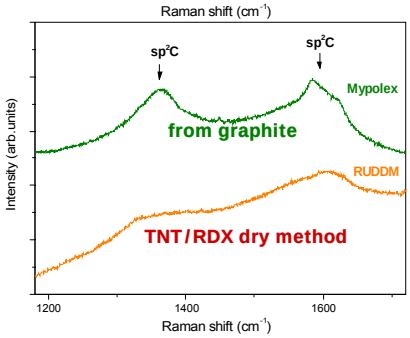


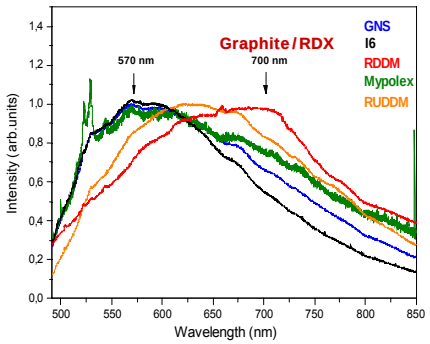
Lattice defects

Raman & PL Spectra of Nanodiamonds

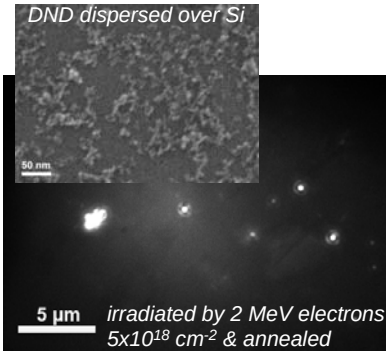


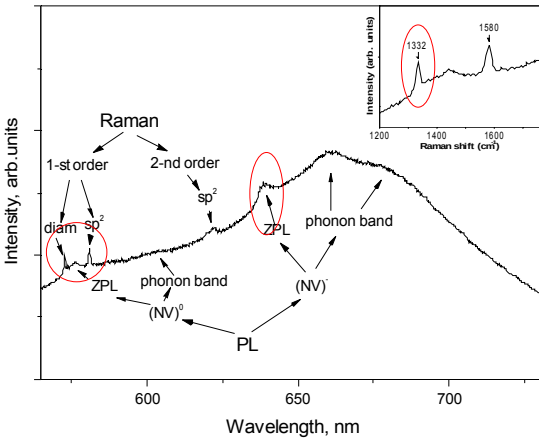
Sample	Crystal Size (nm)	Diamond Peak pos. (cm^{-1})
Graphite/RDX	35	1332.5
TNT/RDX	6	1328.5
TNT/HNS	6	1330.5





Nitrogen-Vacancy Centers in Detonation ND





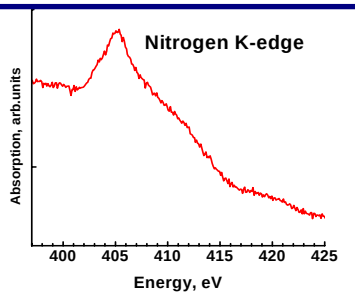
• edge filter with wavelength >630 nm

Intense and stable emission from the NV centers in large DND crystallites (>20-30 nm)

I. Vlasov et al., ***Small****, 2010*

Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy of N in nanodiamond

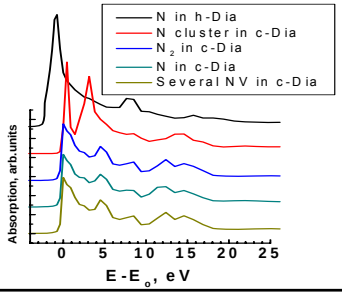
N spectra are similar for dispersed (detonation and meteoritic) nanodiamonds and for UNCD *(Shiryaev et al., 2011; Zapol et al., 2003)*.



N is clearly NOT in substitutional position (modeling by feff8.2)!

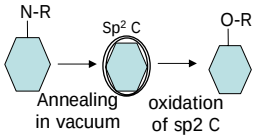
Most likely N is present in extended defects such as twin boundaries *(Vlasov et al., Small, vol. 6, 2010).*

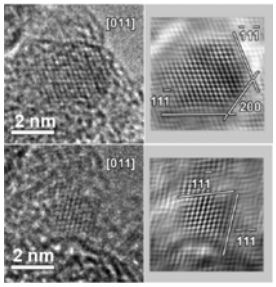
Spectroscopic manifestations of N in ND must differ from macrocrystals!!



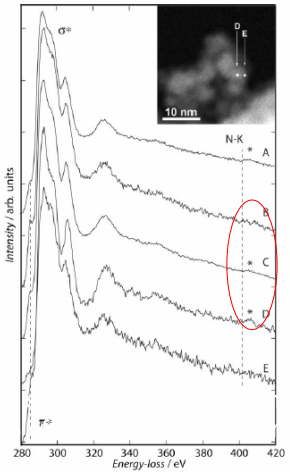
Nitrogen state in Detonation Nanodiamond: “small” particles

Elimination of contribution of N from surface groups:



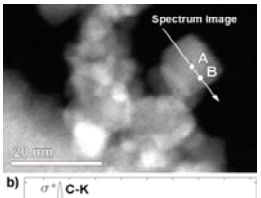


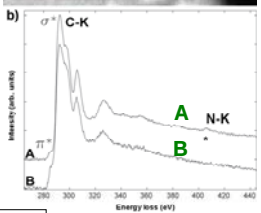
spatially resolved EELS



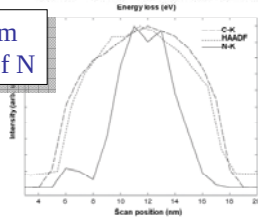
S. Turner, et al. ***Adv. Funct. Mater****. 2009, 19, 2116–2124*

Nitrogen state in “large” particles of DND

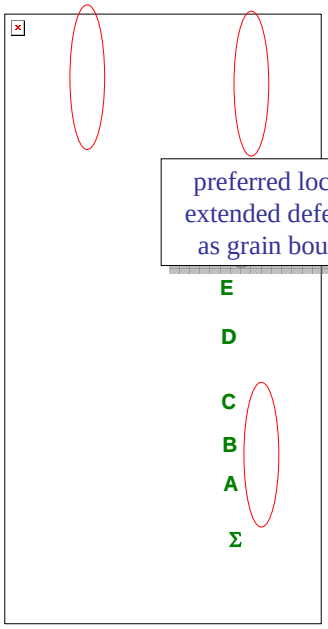




non-uniform distribution of N



I.Vlasov et al., ***Small****, 2010*

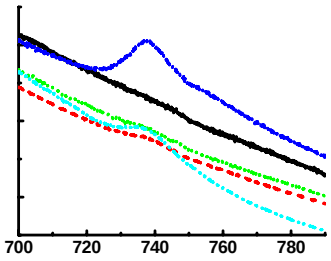


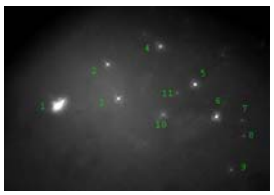
Other luminescing defects in nanodiamonds

In our recent study of nanodiamonds from meteorites *(Shiryaev et al., 2011)* we have shown that nanodiamond particles 1-2 nm in size may contain a bright luminescing center: the silicon-vacancy (Si-V).

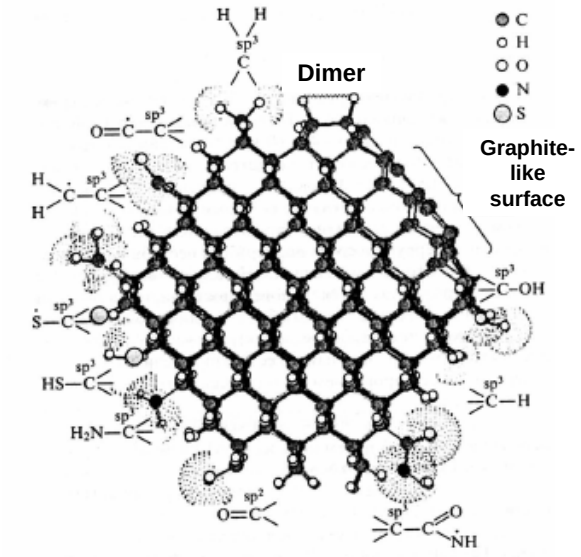
The PL line is very narrow for nanoparticles.

New promising applications!

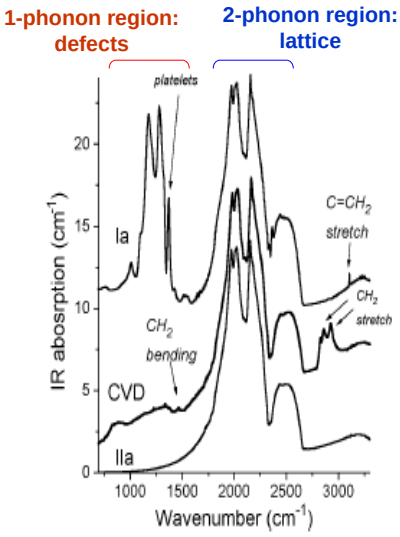




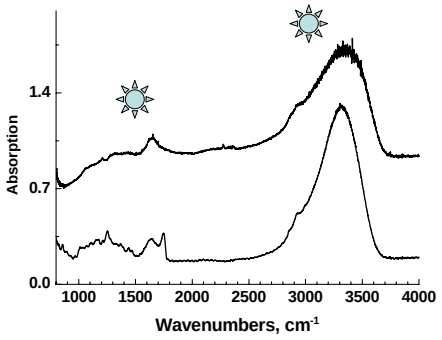
Surface of dispersed nanodiamonds



Surface of nanodiamonds



Rich surface chemistry
Surface groups could be modified by oxidation/hydrogenation/amination etc.

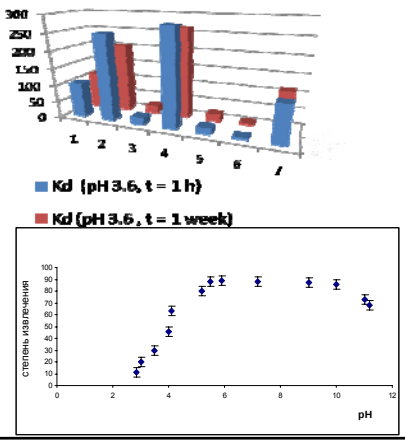


IR spectra of sintered nanodiamonds
(Shiryaev et al., JPCM, 2006)

Nanodiamonds as sorbents of radionuclides

Some examples:

- **Sorption of Cs** *(Chukhaeva and Cheburina, 2000)***: up to 0.5 mmol/g**
- **Sorption of Technetium** ***(see poster 6P.3 by Obruchnikova et al. today).***
  Partition coefficients are comparable to the best anionites
- **Sorption of Uranium.**
  Degree of U extraction from solution exceeds 90% in broad pH range.



Nanodiamonds as efficient sorbents of radionuclides

Main advantages:

- High temperature stability (400 °C is feasible)
- High chemical and radiation stability
- High density
- Negligible swelling
- It is possible to adjust surface chemistry to increase sorption of target elements
- Labeling with radionuclides

- Efficient *de*sorption is possible => repeated use of the sorbent

Conclusions

- Our study shows that it is possible to control nitrogen content of detonation nanodiamonds by proper choice of explosives
- We have observed the NV and Si-V defects in small and large nanodiamond particles
- Nitrogen in nanodiamonds is largely confined to extended defects such as grain boundaries
- Nanodiamonds are efficient sorbents of radionuclides

Future works:

- Further tuning of luminescing properties of nanodiamond
- In-depth studies of functionalisation of nanodiamond surfaces

Some related publications:

Shiryaev et al., *J.Phys.: Cond.Mat.*, vol. 18, L493-L501 (2006)
Davydov et al., *JETP Letters*, vol. 90(12), 763-767 (2009)
Shiryaev et al., *J. Phys.: Condens. Matter*, Vol. 22, 045801-06 (2010)
Shiryaev et al., *Geochim.Cosmochim.Acta (2011)*
Shenderova et al., *J. Phys.Chem.C* (2011)
Vlasov et al., *Small*, Vol. 6(5), 687-694 (2010)