



Welcome
to the Frantsevich Institute for
Problems in Materials Science
Kiev, Ukraine

Frantsevich Institute for Problems in Materials Science



52 years

**of R&TD trials,
achievements
and problems**

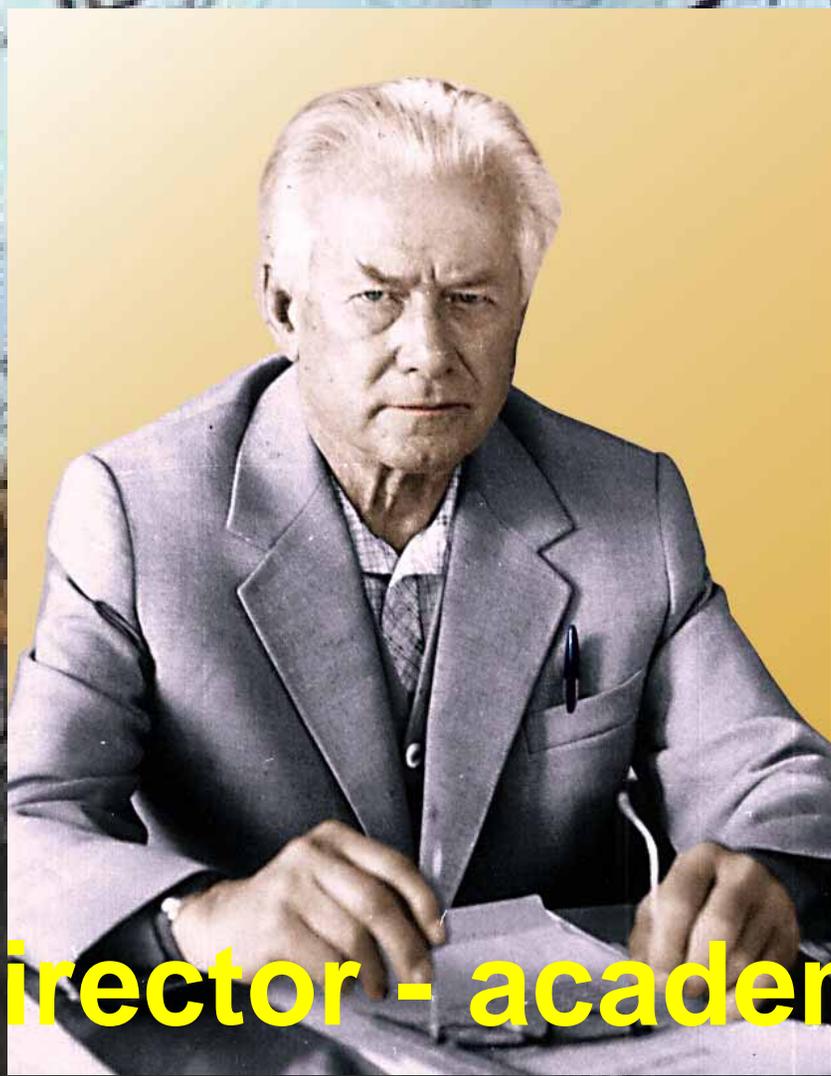


An aerial photograph of the Kiev-Pechersky Monastery. The central focus is a large, ornate church with a prominent golden dome and white columns. The church is situated on a hillside. In the background, a long bridge with multiple arches spans across a wide river. The surrounding area is lush with green trees and some buildings with green roofs.

Founded in

1952

on a territory of Kiev-Pechersky Monastery



**First director - academician
Ivan Frantsevich**

Frantsevich Institute for Problems in Materials Science NAS of Ukraine

I	II	III	IV	V
<p>Division of Physical Chemistry and Materials Science of High-Melting Systems</p> <p>10 depts ~230 researchers & engineers</p>	<p>Division of Materials Science of Particulate & Composite Materials and Coatings</p> <p>8 depts ~190 researchers & engineers</p>	<p>Division of Physical Materials Science and Physics of Strength</p> <p>8 depts ~220 researchers & engineers</p>	<p>Division of Electronic Structure of Matter & Fine Chemical Synthesis of Inorganic Materials</p> <p>8 depts ~130 researchers & engineers</p>	<p>Division of NanoStructured Materials and Thin Films</p> <p>9 depts ~220 researchers & engineers</p>
<p>Head academician V.V. Skorokhod, Director</p>	<p>Head academician A.G.Kostornov, Vice-director</p>	<p>Head D.Sc. S.A. Firstov, Vice-director</p>	<p>Head D.Sc. Yu.M.Solonin, Vice-director</p>	<p>Head D.Sc., A.V.Ragulya, Vice-director</p>

IPMS today - in figures

Institute employs about 1400 people, including >500 researchers in more than 40 departments; among them:

more than 70 D.Sc.;

more than 300 PhD.;

more than 500 engineers;

around 250 young researchers;

Work area 72 000 m²

IPMS today - in figures



Total funding in 2004

a) from budget ~ 16 M UAH

b) from other sources ~ 6.5 M UAH, including 3 M UAH from international grants.

Basic research > 12 M UAH; including 1,6 M UAH from Program “Nanosystems, Nanomaterials & Nanotechnology”

Applied research and contracts > 3 M UAH including 2.5 M UAH of Innovation projects and ~ 0.7 M UAH from Program “Resource”;

Special fund for young researchers and engineers ~ 1 M UAH;

IPMS today - in figures



International cooperation of IPMS in the period 2001-2004

Totally more than 55 international projects :

>30 grants from Science and Technology Center of Ukraine (\$100-300 K, each), primarily with partners from USA;

2 grants of NATO Science for Peace Program (totally \$650 K)

6 grants of Civilian Research & Development Foundation (totally \$370 K)

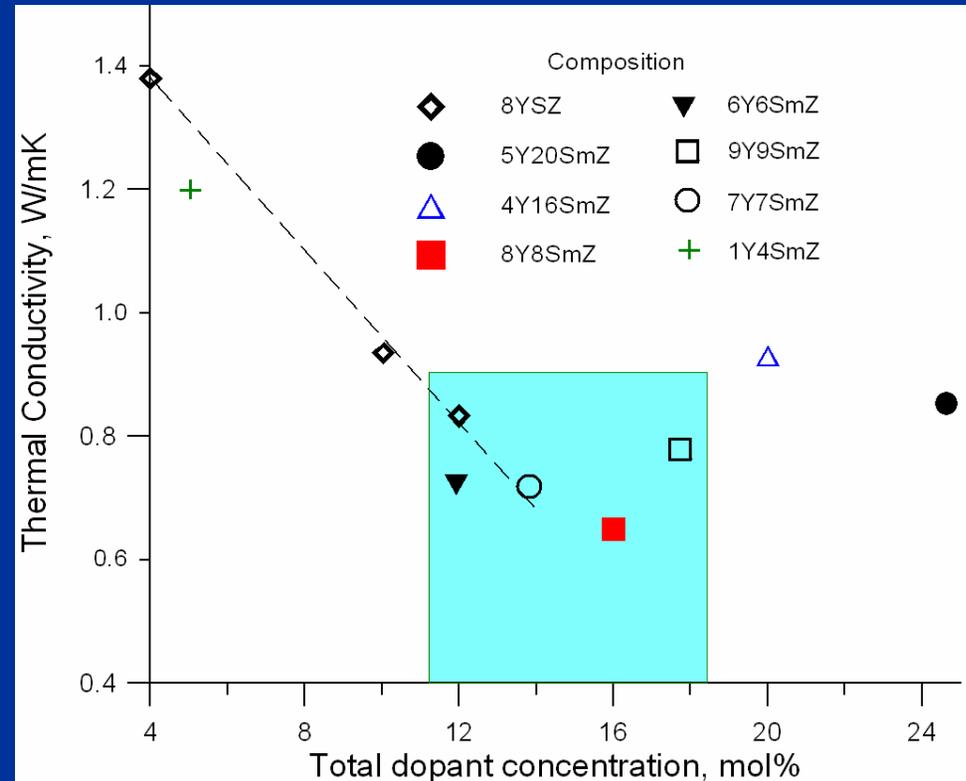
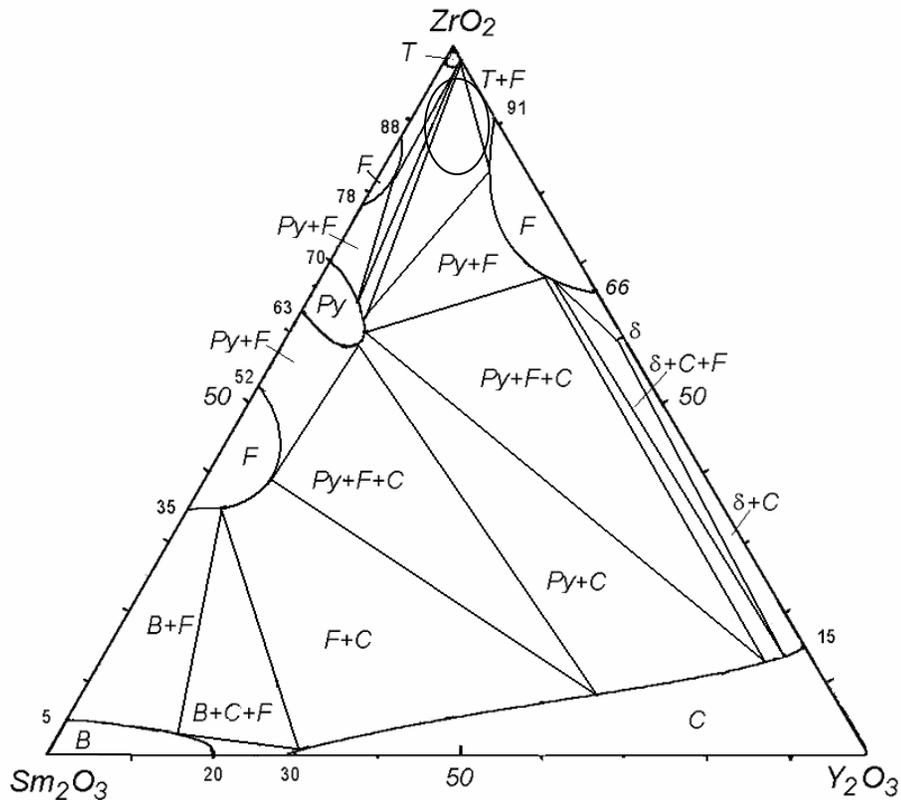
8 grants of INTAS and COPERNICUS

several bilateral grants with partners from France, Italy, Poland, Germany, India, Greece etc.



Achievements on the way of international cooperation

New formulation for TBCs



Tentative phase diagram of the system $ZrO_2-Sm_2O_3-Y_2O_3$ at 1250 C and area for potential TBCs

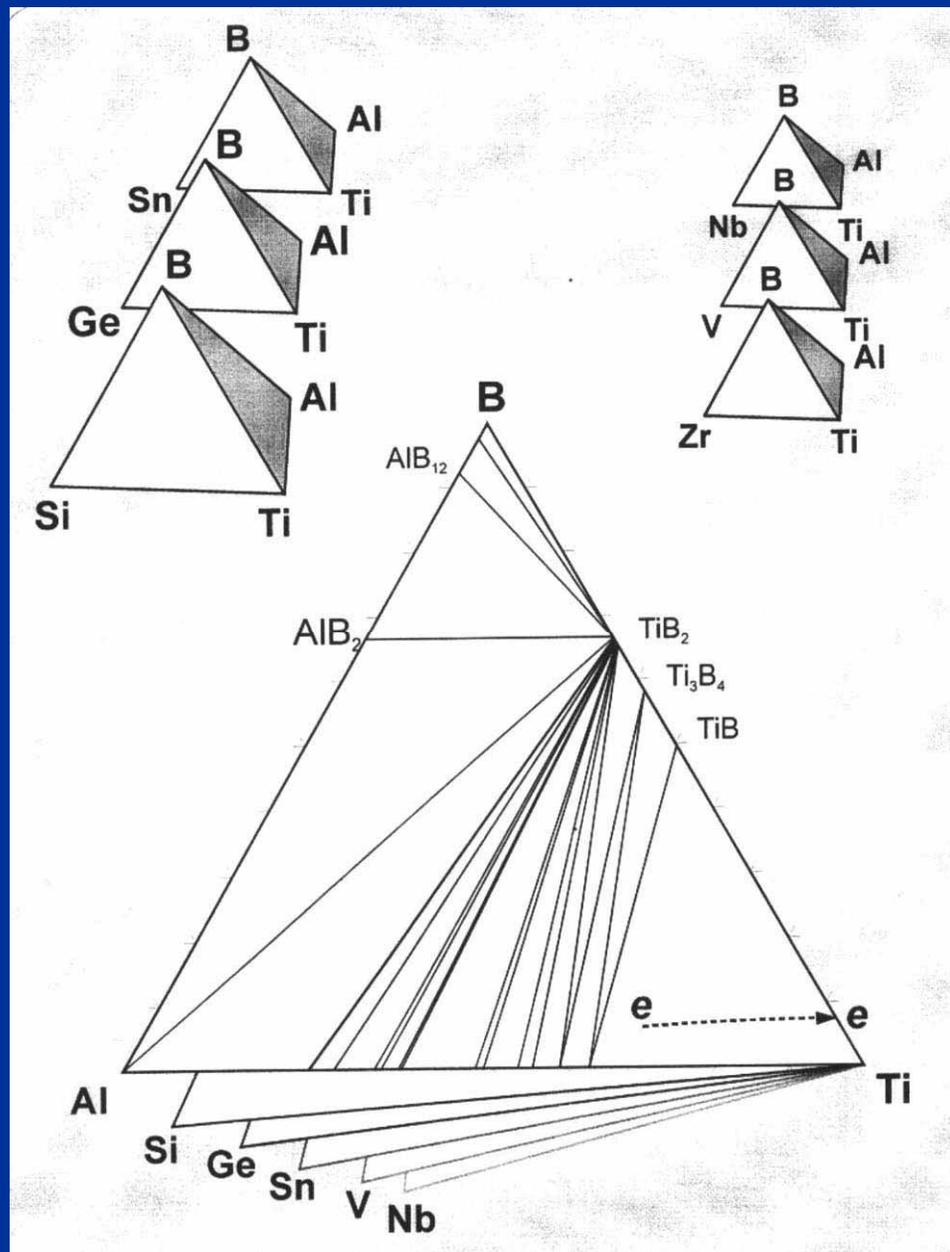
Total dopant concentration dependence of thermal conductivity of selected ceramic compositions and field of most prospective ceramics for TBCs.

New ceramic biomaterials based on hydroxiapatite and nano- ZrO_2



Projects STCU

Dr. O.V. Shevchenko, Dr. V.A. Dubok



Systems Ti-B-Al-Si (Ge, Sn, V, Nb), for new generation of titanium alloys, titanium-based matrix composites reinforced with borides, silicaborides and germanides operating at 650 °C

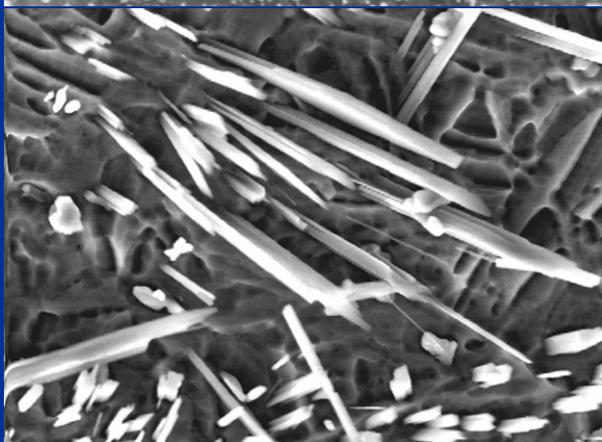
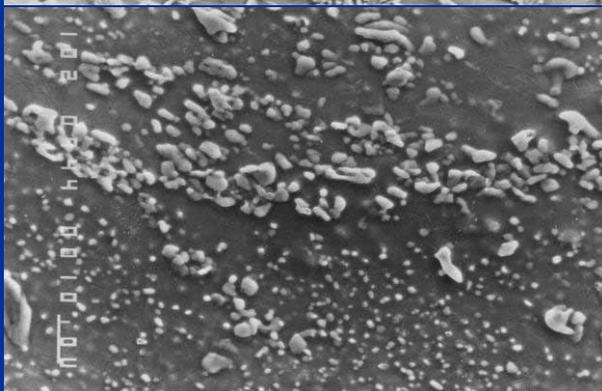
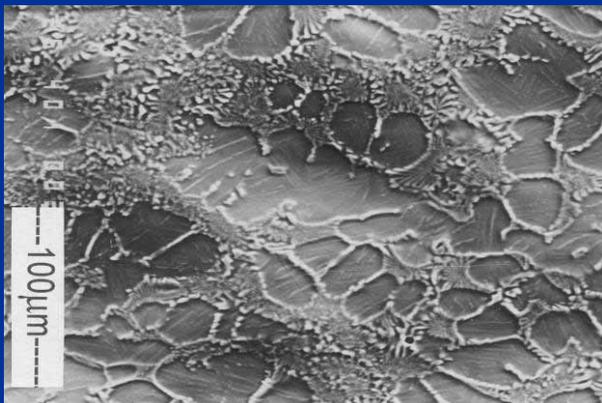
STCU project P-60

Prof. S.A. Firstov, Prof. T.Ya. Velikanova, Dr. M.V. Bulanova



New titanium alloys Ti-Si-X and Ti-B-X

Ti-8Al-1,4Si-2,4Zr



Deformation, $\varepsilon \approx 90\%$		20 °C	600 °C	700 °C
σ_B , MPa	Rolling 1065°C, +800°C, 2 Γ	1182	923	653
δ , %		0,8-1,6	8,4	18,8
K_{1c} , MPa \sqrt{m}		19,2	-	-
σ_B , Mpa	Rolling 970°C +800°, 2 Γ	1234	608	409
δ , %		6,1	18	28,6
K_{1c} , MPa \sqrt{m}		50	-	-
E, GPa		125		

Ti-6,6Al-1,3Si-1,1B-3,3Zr

Deformation, $\varepsilon \approx 90\%$		20 °C	600 °C	700 °C
σ_B , MPa	Rolling 1065°C, +800°C, 2 Γ	1519	590	347
δ , %		1,26	7,8	6,4
K_{1c} , MPa \sqrt{m}		-	-	-
E, GPa		158	-	

STCU P-60

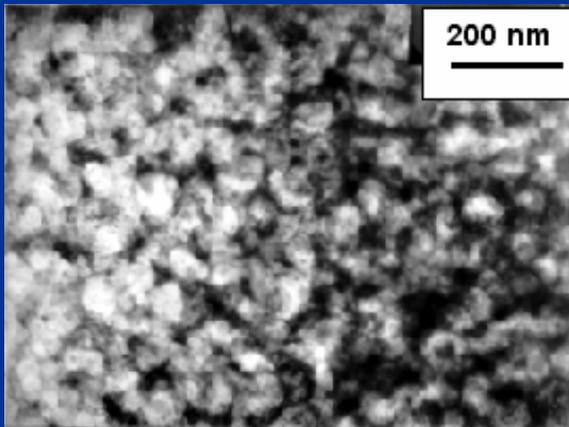
Developed the technology of new aluminum-based alloys stable at high temperatures, hardened with quasicrystals:



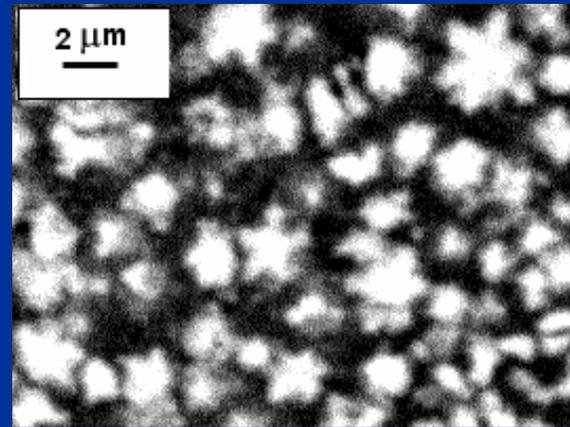
Alloys of the system *Al-Fe-Cr-Ti* respond to the requirements of today's aviation industry

$\sigma_B > 300$ MPa at 300 °C; $\delta > 5$ % at room temperature

2 STCU projects



Aluminum matrix *Al-Fe-Ti-Cr-Sc* with ~30 % nanosize quasicrystalline particles



Quasicrystals within the alloys *Al-Fe-Cr*

Prof. Yu.V. Milman



Achievements in NanoStructured Materials

Direction 2

Functional Nanostructured Materials



- Synthesis of oxide nanoparticles
- Synthesis of non-oxide nanoparticles
- Consolidated oxide nanoceramics and nanocomposites
- Consolidated high-melting nanoceramics and nanocomposites
- Consolidated nanostructured metals and alloys
- Synthesis of carbon and non-carbon nanoclusters
- Physics, chemistry and technology of thin films and quantum dots

Nanostructured particulate oxide-based materials



Wet chemical methods.

Hydrothermal and co-precipitation.

Systems: $\text{ZrO}_2\text{-Y}_2\text{O}_3$, $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-CeO}_2$, $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-Y}_2\text{O}_3$, $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Sc}_2\text{O}_3$, $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-CeO}_2\text{-Al}_2\text{O}_3$, YSZ+ Fe_2O_3 (Co_3O_4) for structural ceramics and components of sensors, SOFC, TBC.

Synthesis in micro/nanoreactors.

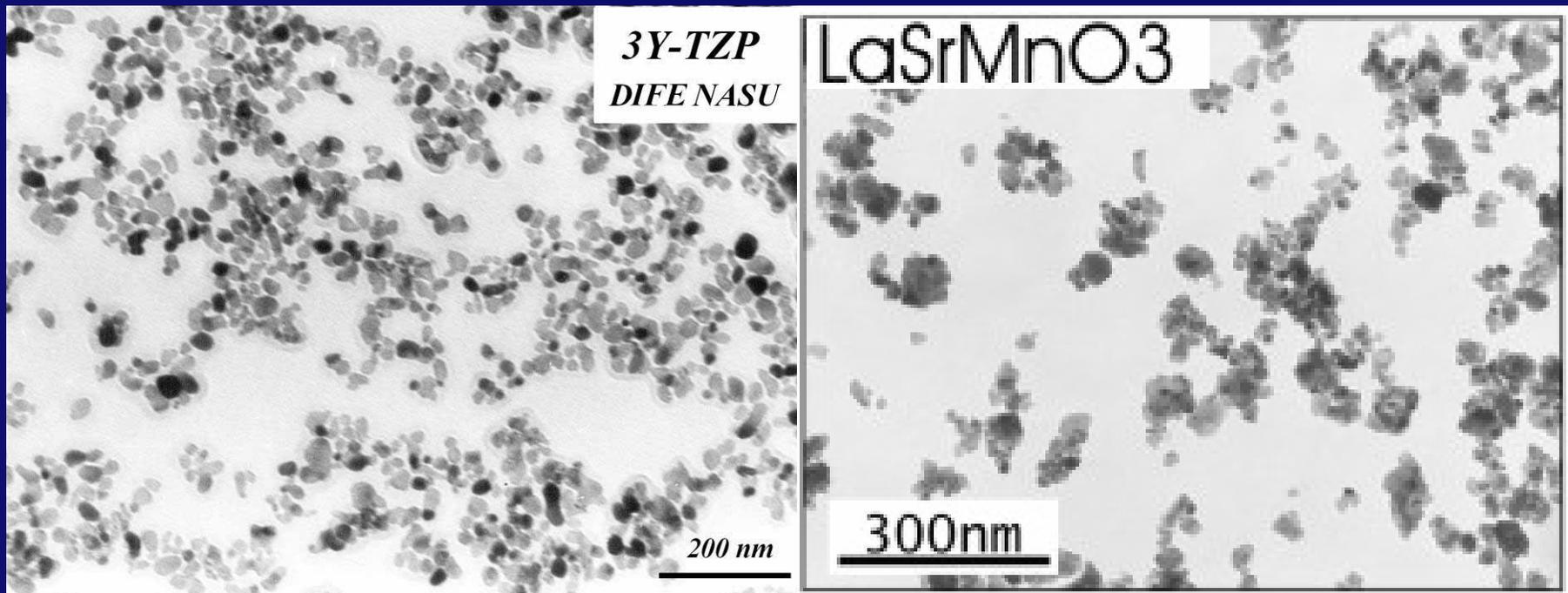
Rate-controlled thermal decomposition of unstable precursors and sonochemical synthesis.

Systems: BaTiO₃-based X7R dielectrics, $\text{ZrO}_2\text{-Y}_2\text{O}_3$, $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Nd}_2\text{O}_3$ (Sm_2O_3) for TBCs, YSZ-Pt, YSZ-Au catalysts, perovskite-type phases like $\text{La}(\text{Nd})\text{SrMn}(\text{Co},\text{Ni})\text{O}_3$ for SOFC.

Combined synthesis



Synthesis combines colloidal processes, microwave treatment and powerful ultrasonication to get unisized nanoparticles



Particle size of 6 to 12 nm

Particle size of 20 to 40 nm

Pilot production developed of both products for SOFC techn.

Dr. Konstantinova et al.

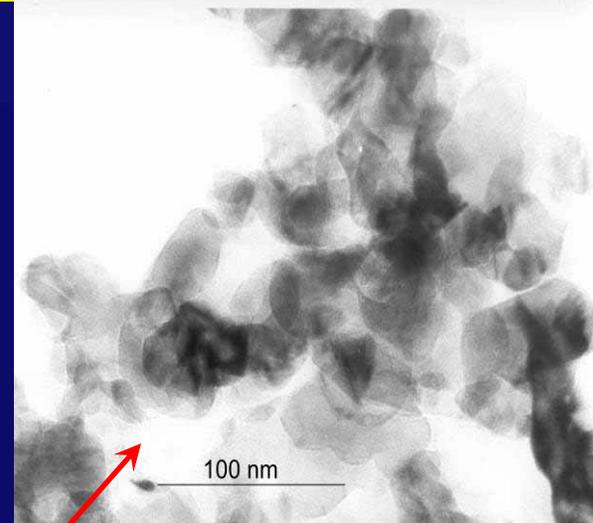
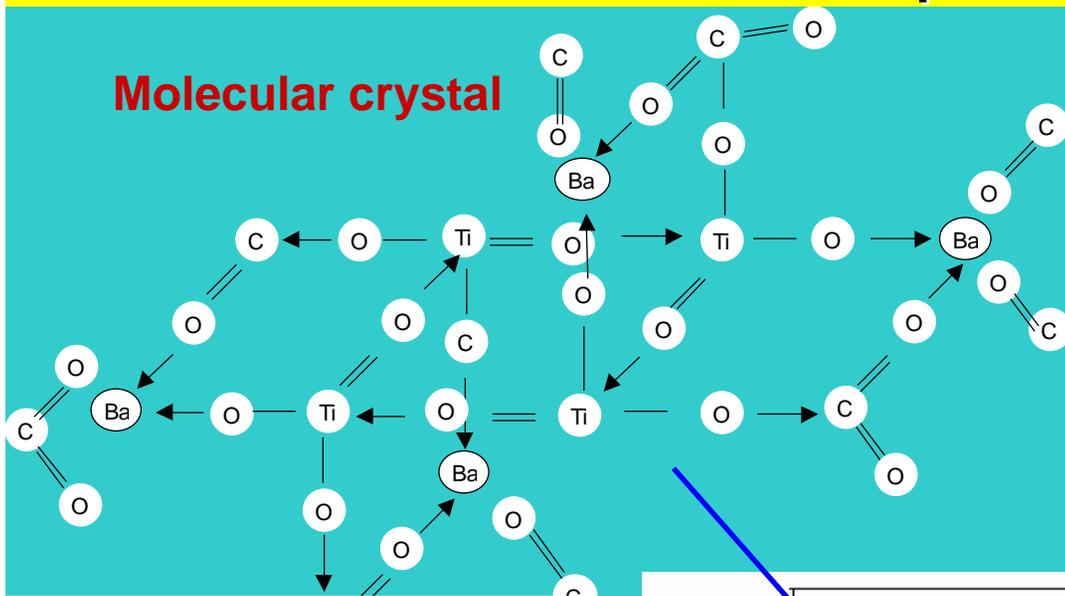
Patent of Ukraine

Synthesis in micro/nanoreactors

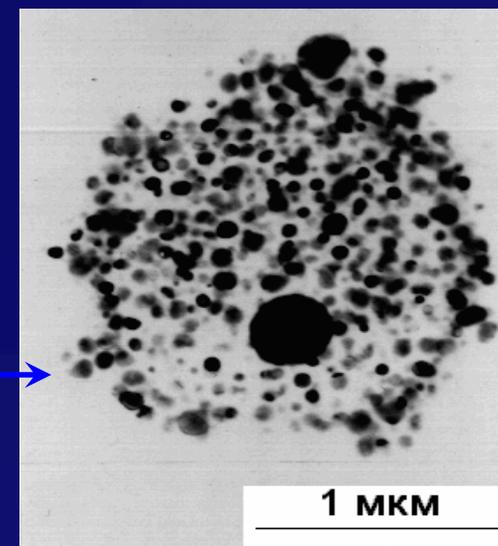
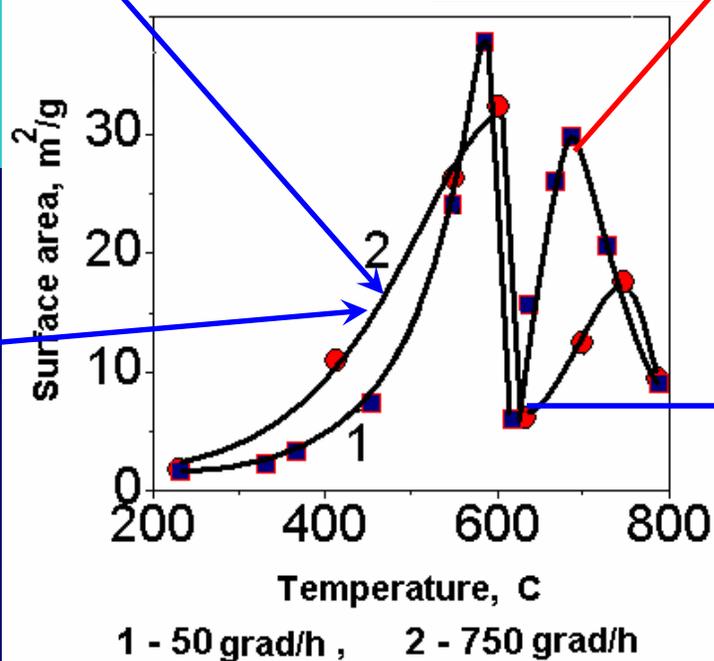
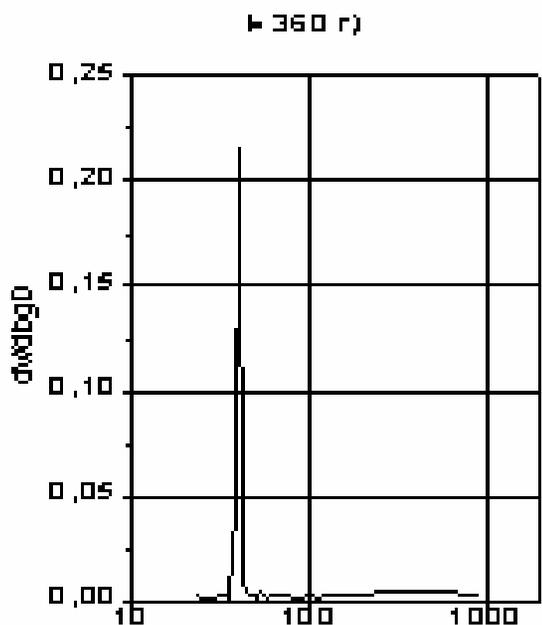
Rate-controlled decomposition of precursors



Molecular crystal



As-prepared powder

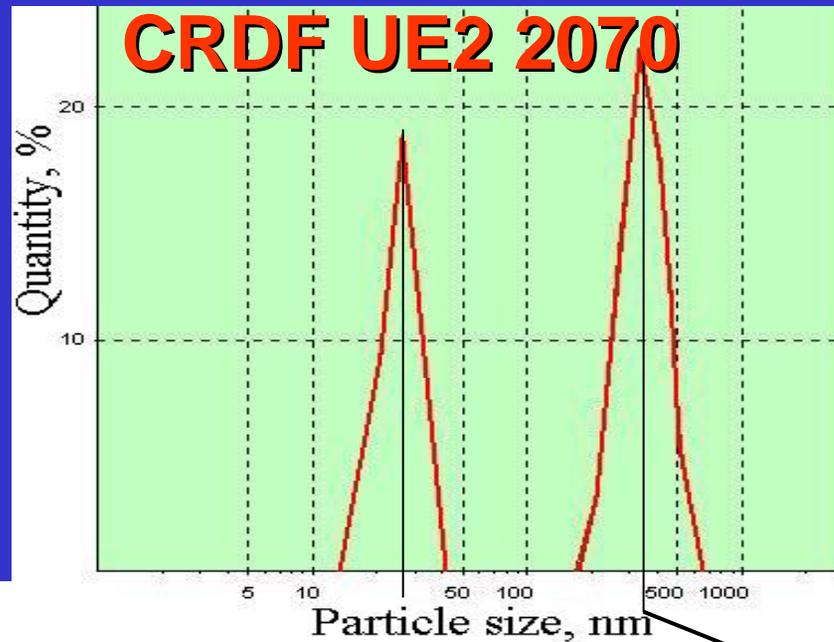


Porous microreactor

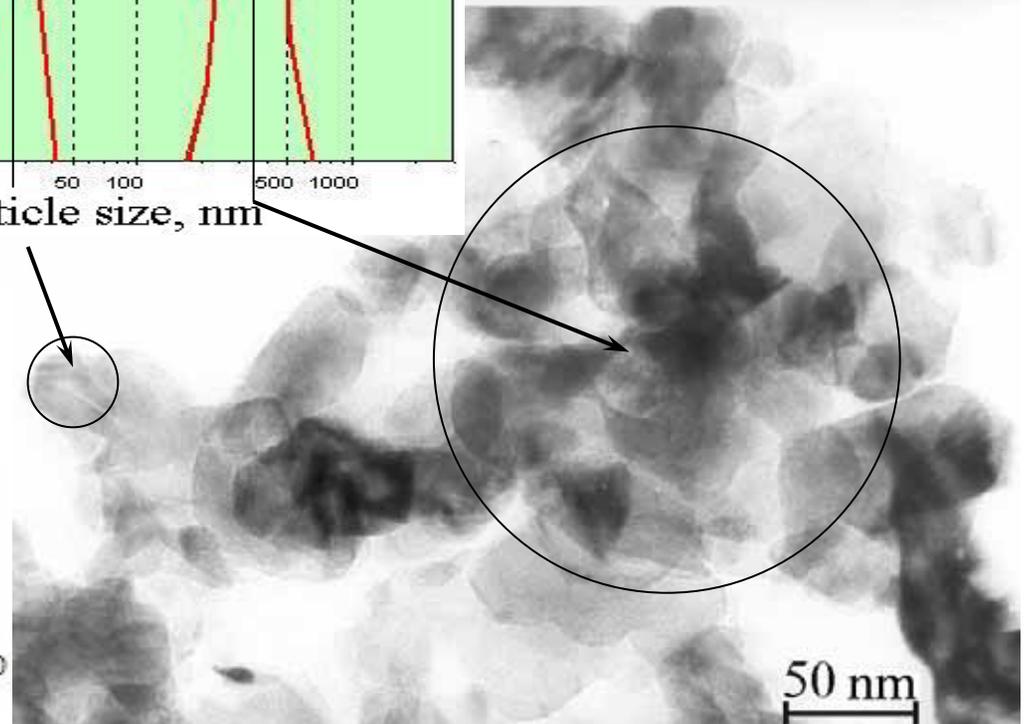
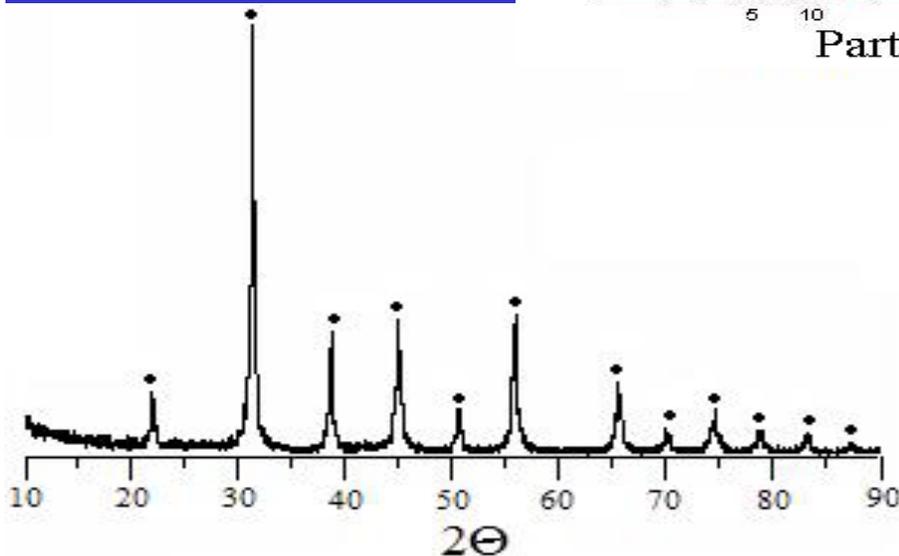
The Nanocrystalline Barium Titanate Powder (in cooperation with Pennsylvania State University)



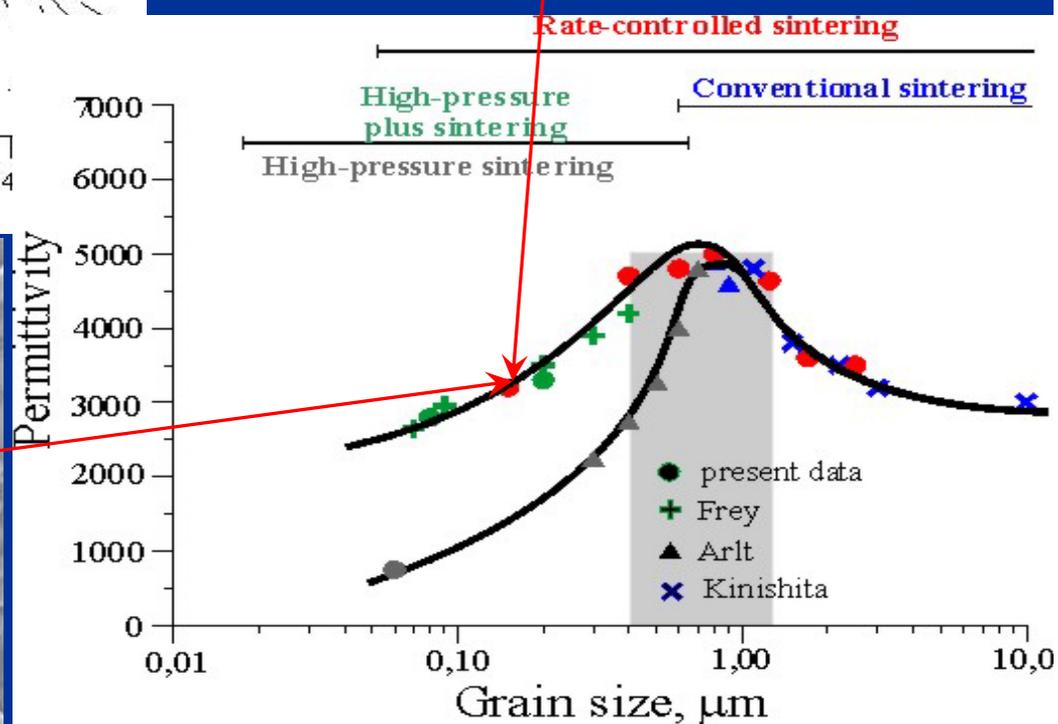
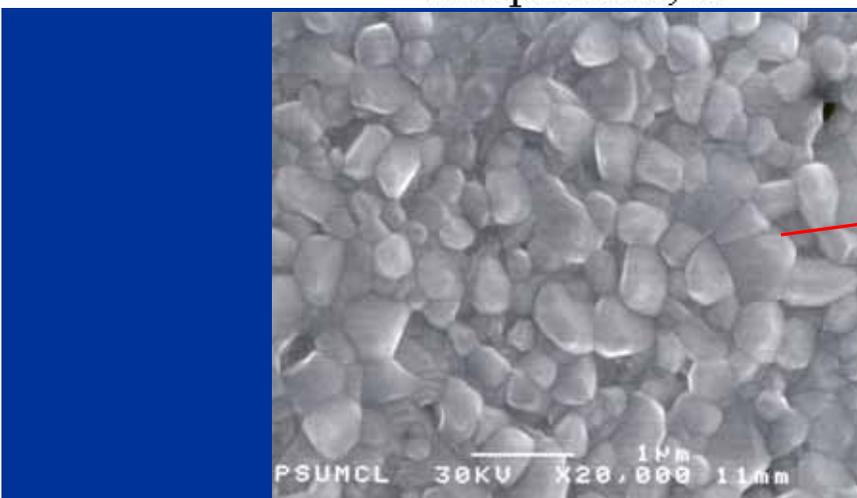
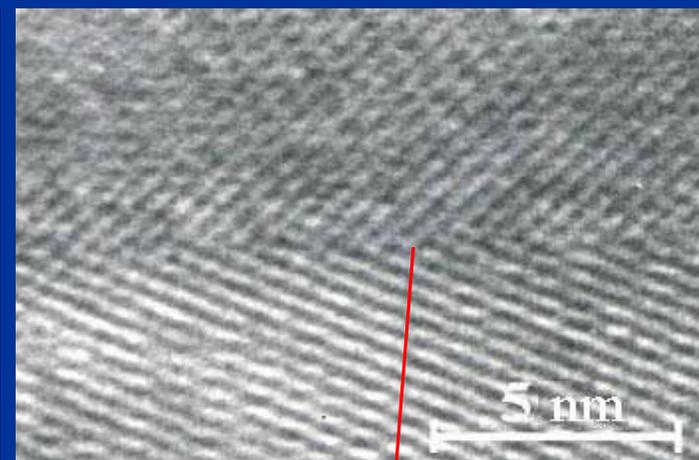
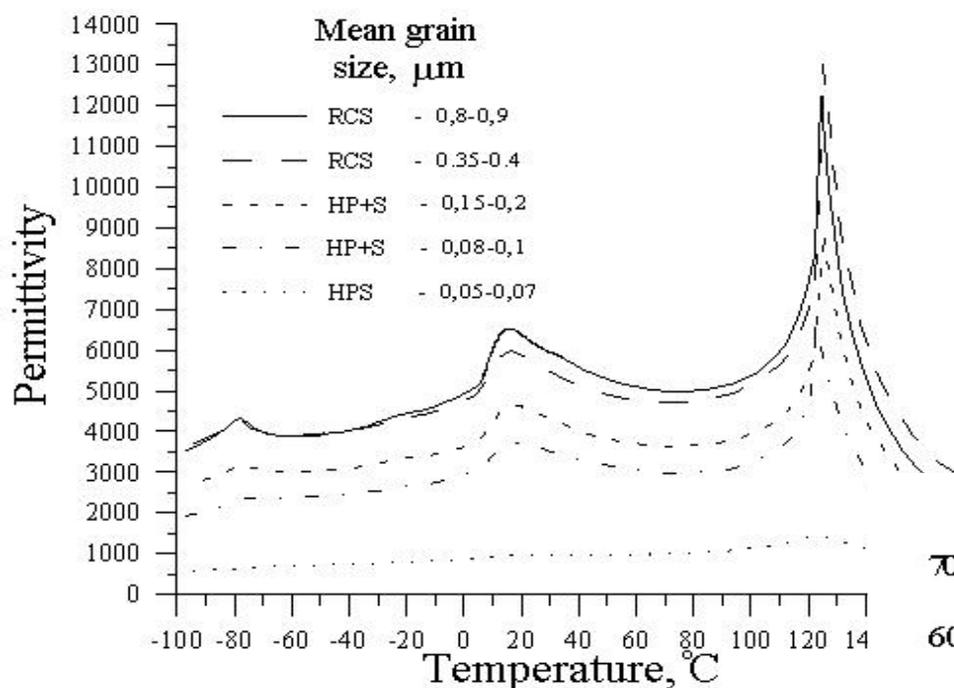
No barium carbonate was revealed in final barium titanate nanosized powder



Mean agglomerate size correlates with the final mean grain size



Dielectric Properties of the fine Barium Titanate Ceramics (CRDF UE2 2070)





Synthesis of nanosize particles based on nitrides, borides and carbides

INTERNATIONAL EFFORTS

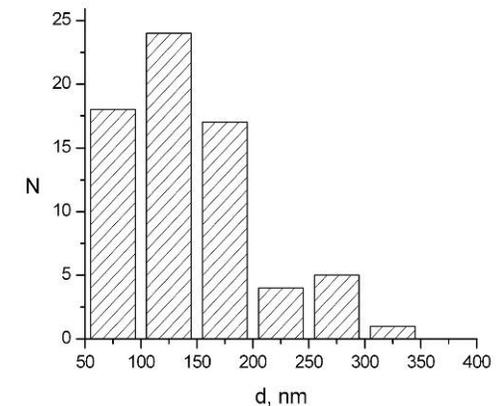
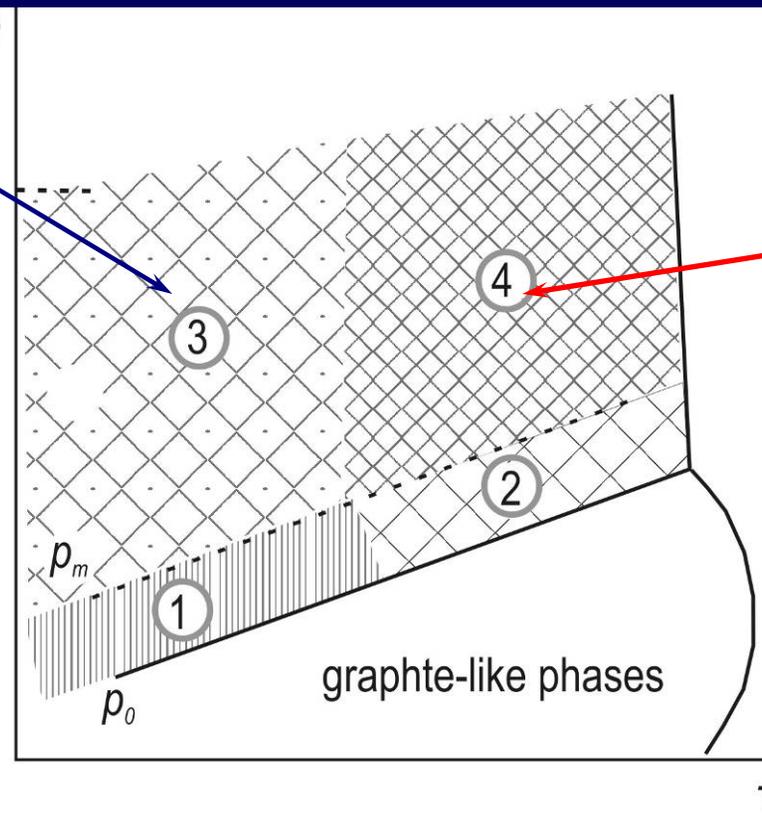
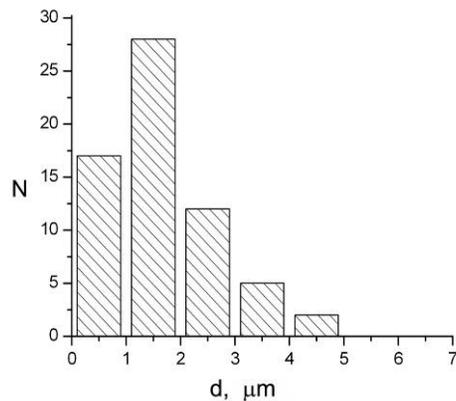
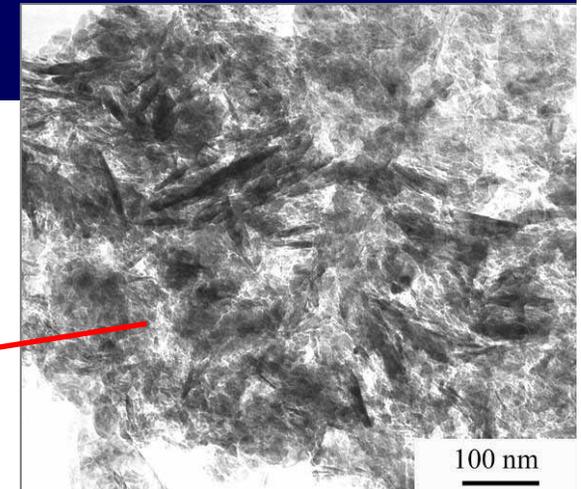
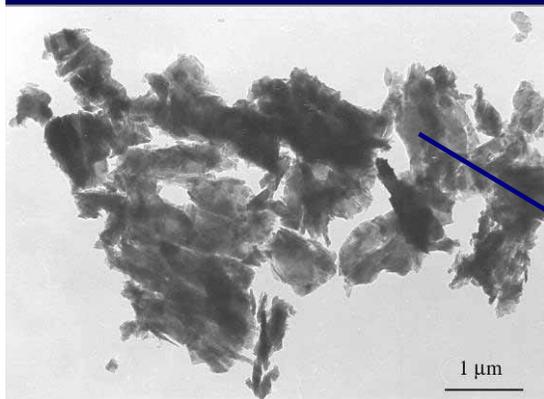
through NATO SfP and 3 STCU projects and 2 contracts with Israel and Sweden

- Detonation synthesis of nanoscale c-BN powders**
- SHS of nanosize SiC-C powders;**
- Plasma-chemical synthesis of single-phase nitrides and nanocomposites ($\text{Si}_3\text{N}_4\text{-TiN}$, $\text{Si}_3\text{N}_4\text{-TiB}_2$, TiN-AlN etc.)**
- Chemical vapor deposition from chlorides**
- Splitting of micron-sized particles of solid solutions Ti-N-C-O with boron additives.**

Shock-wave Synthesis of nano-BN

Fragmentation by martensitic transformation to 50 nm

NEW! Competition of martensitic and diffusion transformations (4).



Size distribution

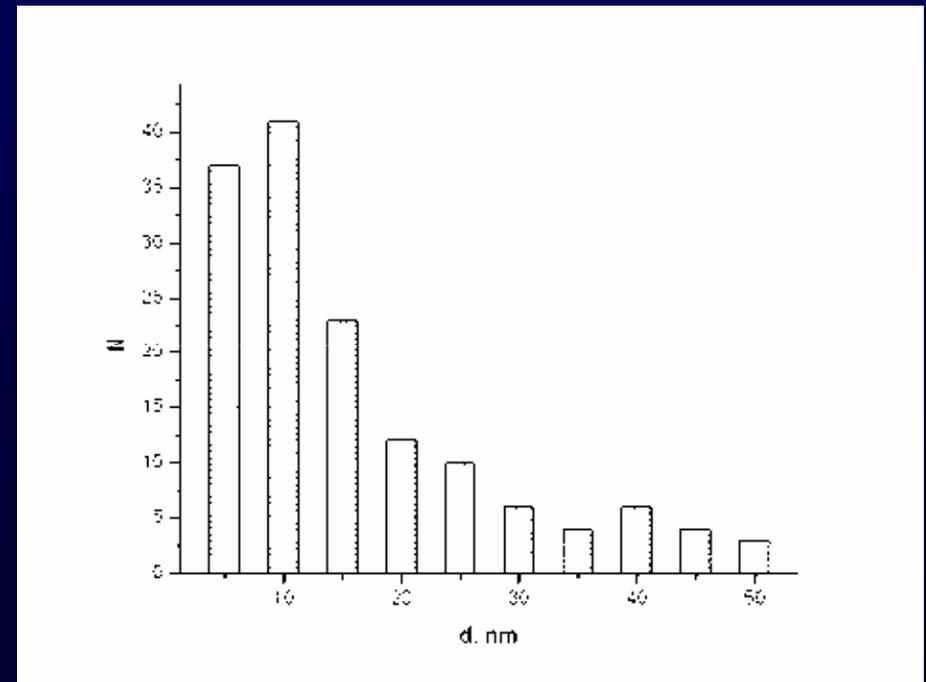
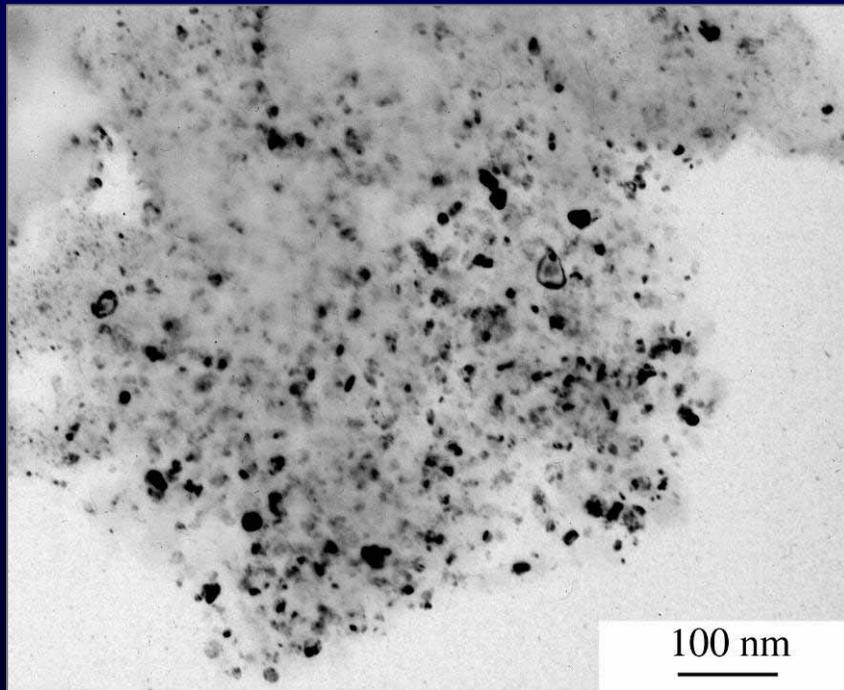
Phase diagram

Size distribution

Shock-wave Synthesis of nano-BN from amorphous Nanoreactors



Usage of disordered precursors (3-D ordering degree $p_3 \approx 0$) allows obtaining the cubic BN phase, in the area of diffusion controlled transformation.



Dark field image of cubic BN phase

Particle size distribution

Patent of Ukraine

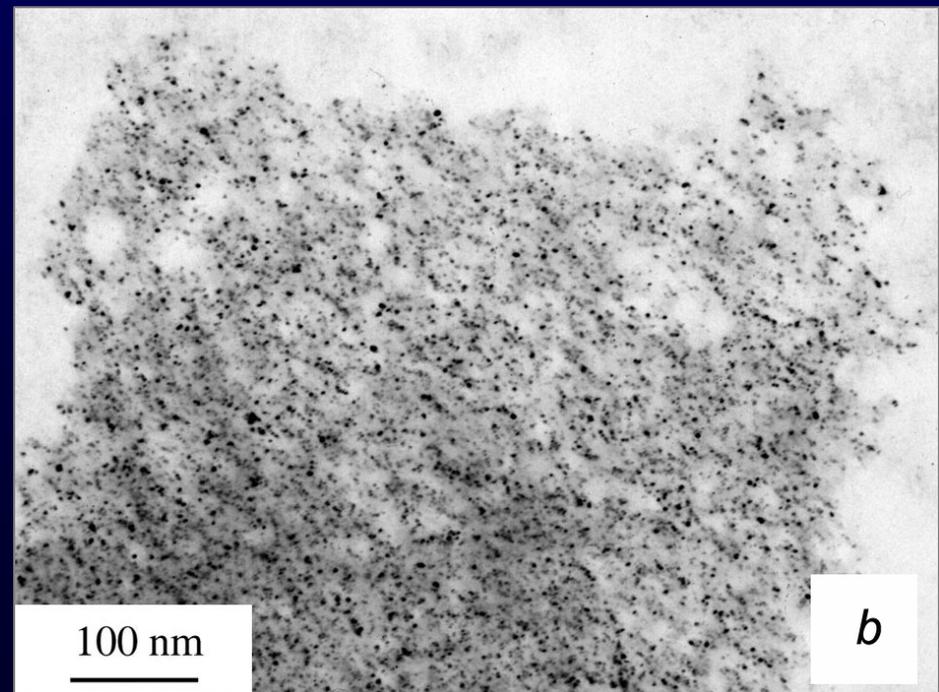
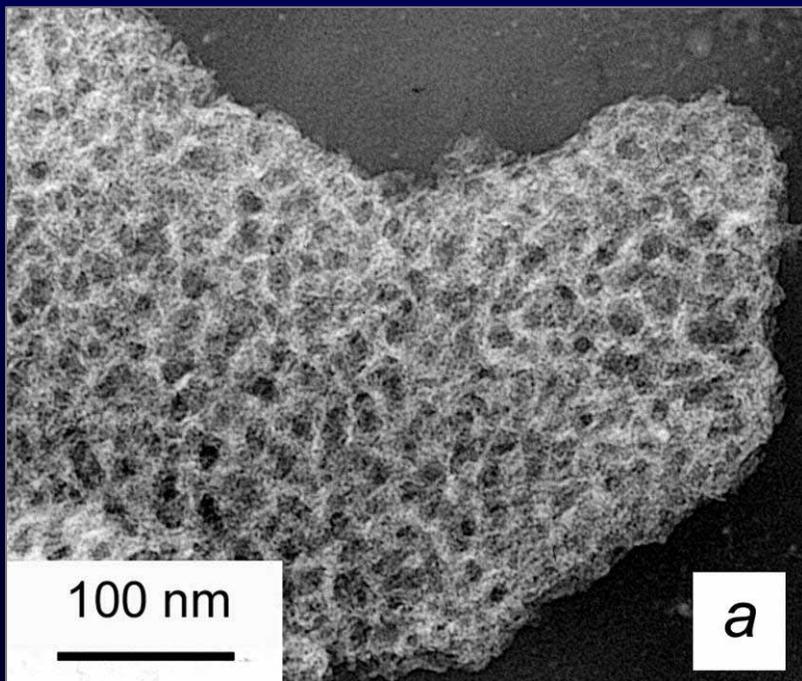
Shock-wave Synthesis of nano-BN



Synthesis of disordered graphite-like BN from unstable precursors. **Patent of Ukraine**

Rate-controlled synthesis gives particles of 1-20 nm in size (we can control the average size).

The best structure of intermediate product consists of crystallites (1-5 nm) divided by pores of 30 nm.



Bright field TEM image of c-BN

Dark field TEM image of c-BN

New structural form of carbon (C_{np})

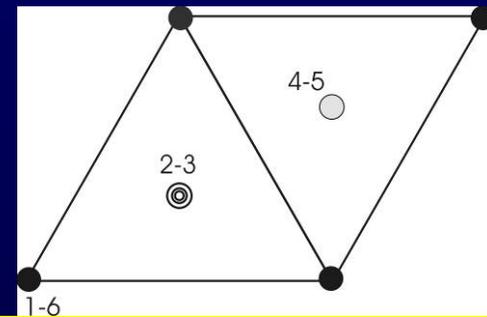
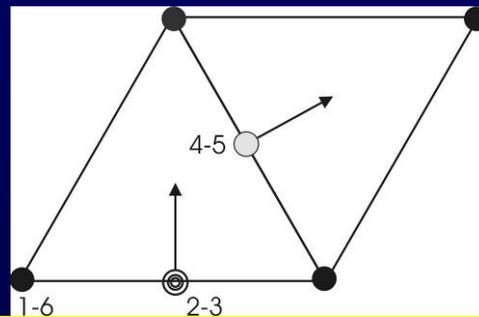
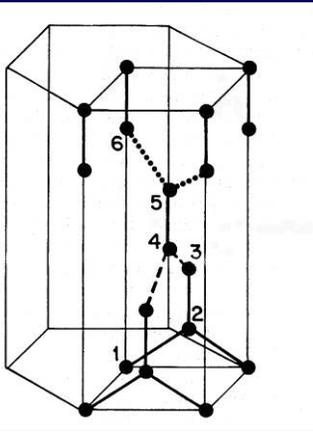
Synthesis from charcoal by high-temperature shock wave compression at:

$P = 30 \text{ GPa}$, $T > 2500 \text{ K}$

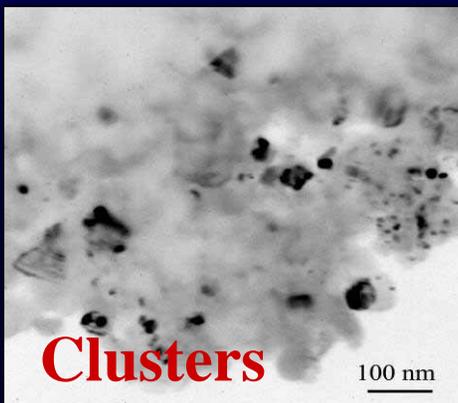
C_{np} shows density of $2,9 \text{ g/cm}^3$ – which is intermediate between one of graphite ($2,2 \text{ g/cm}^3$) and diamond ($3,5 \text{ g/cm}^3$)

The basis of lattice of C_{np} – cubic cell with strong sp^2 bonds ($\kappa = 3$)

Lattice of C_{np} (Cohen model of H-6) easily transforms to diamond lattice ($\kappa = 4$)

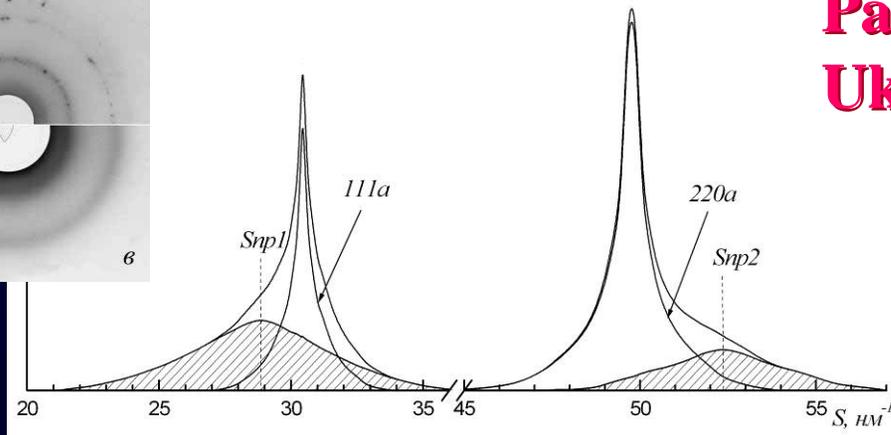
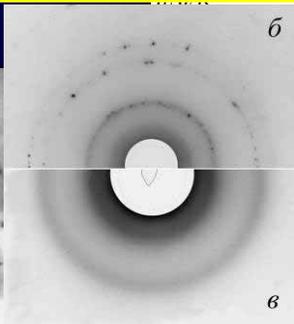


C_{np} forms together with diamond and has a lattice structure



Clusters

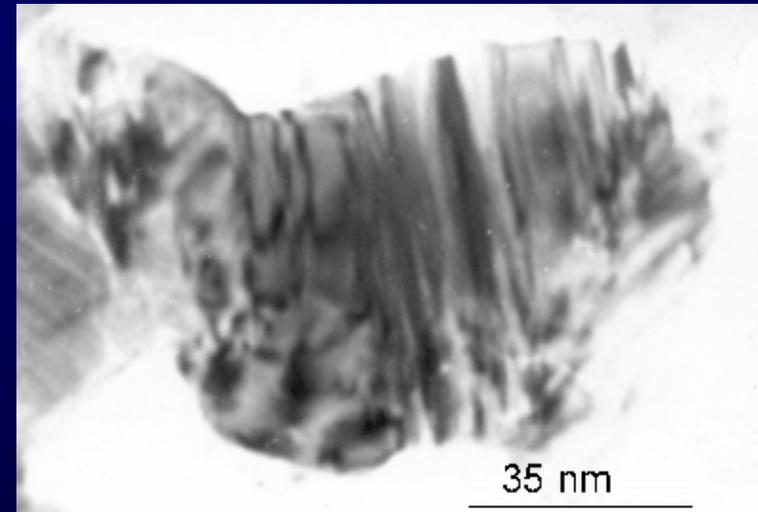
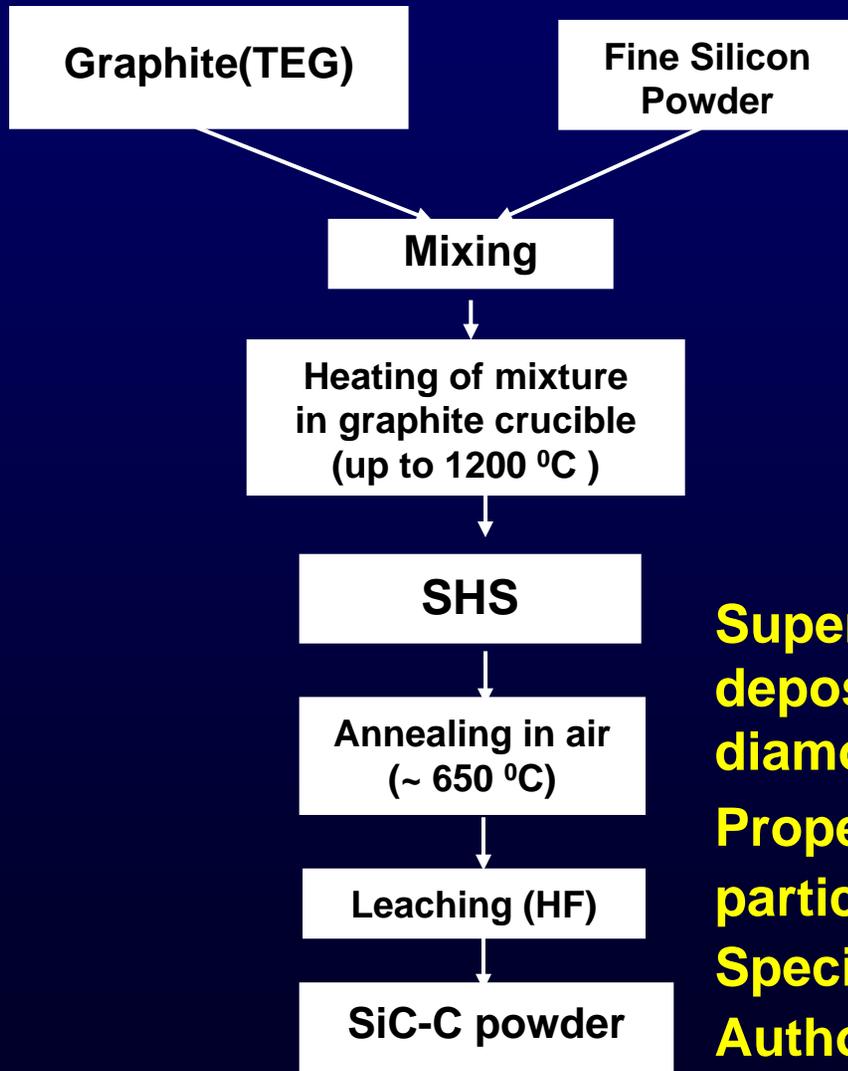
100 nm



**Patent of
Ukraine**

Prognosis of properties: bulk modulus is expected to be C_{np} (390 GPa) close to the bulk modulus of diamond (440 GPa)

SHS of SiC-C nanoparticles in nanoreactors



Superstoichiometric carbon atoms are deposited onto facets of SiC lattice forming diamond-like planar clusters inside SiC.

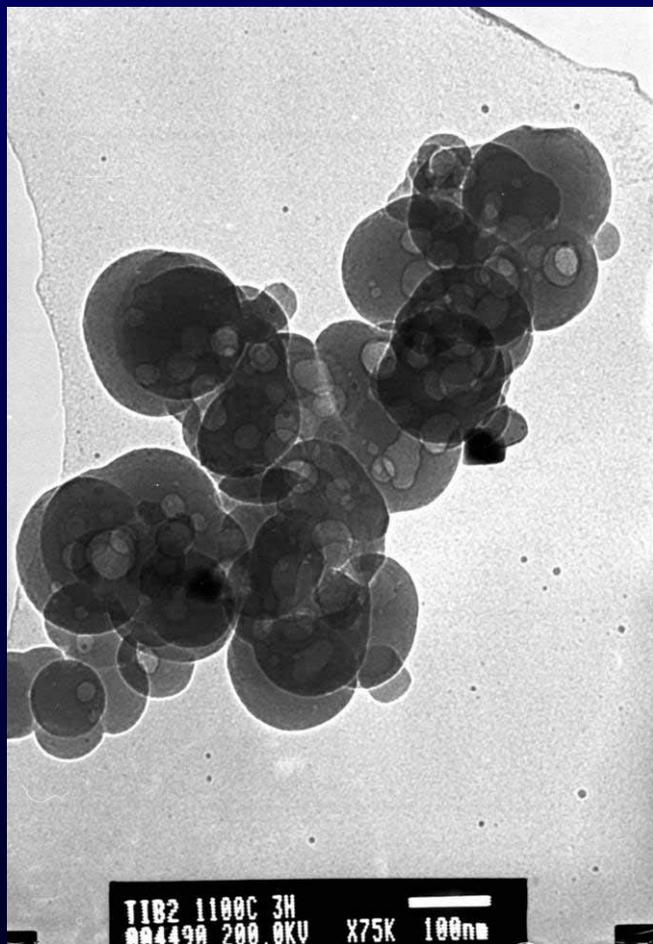
Properties:

particle size 70-200 nm

Specific surface area 17-25 m²/g

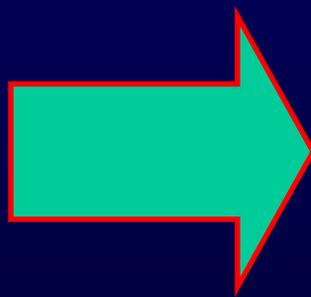
Authored by N. Gadzira and G. Gnesin

Synthesis of TiB_2 and TiB_2 -TiN nanocomposite particles in Ti-O-N-B system

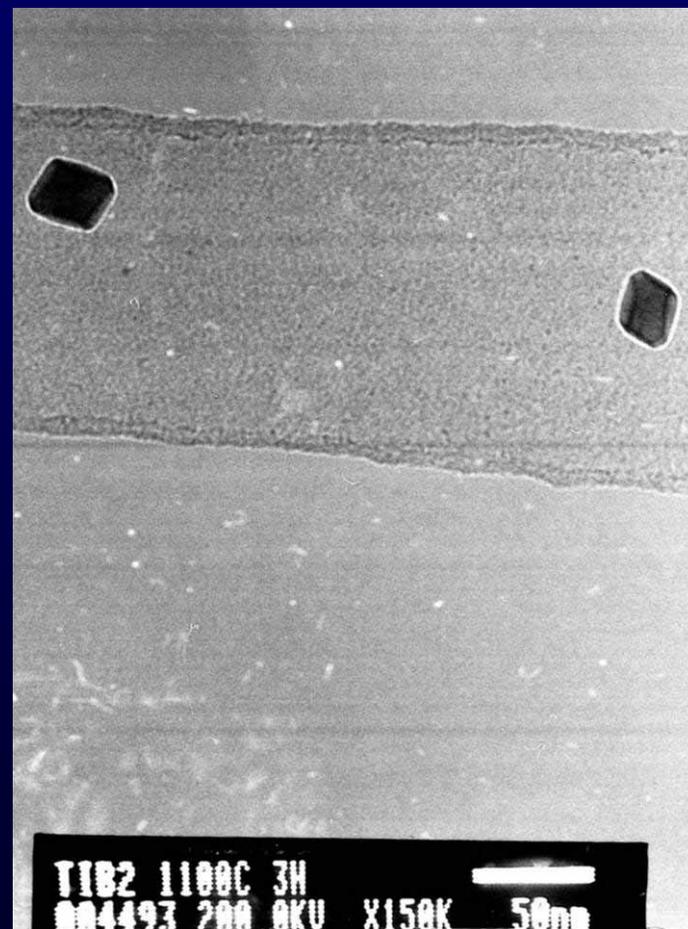


Nano- TiO_2 + B + H_2

Nucleation and growth



in mesopores of TiO_2 and splitting with excess of boron



Nano- TiB_2 particles or nanorods



Synthesis of Nanoclusters

Carbon Onions

Carbon Nanotubes

Non-carbon elongated
nanostructures

H₂-intercalated objects

Core-Shell model of diamond-onion transition

HRTEM
of diamond clusters

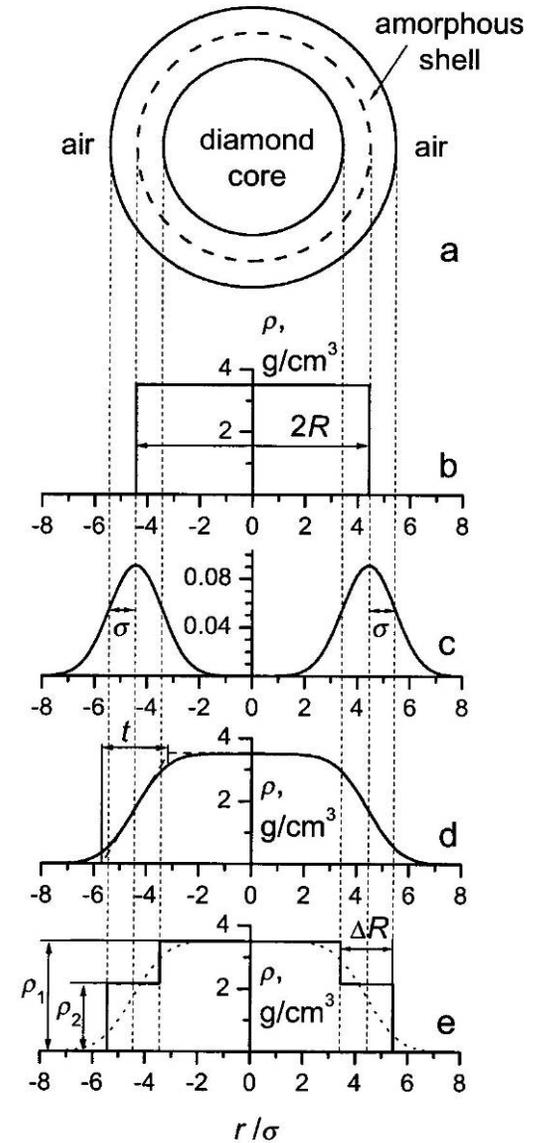
5 nm

5 nm

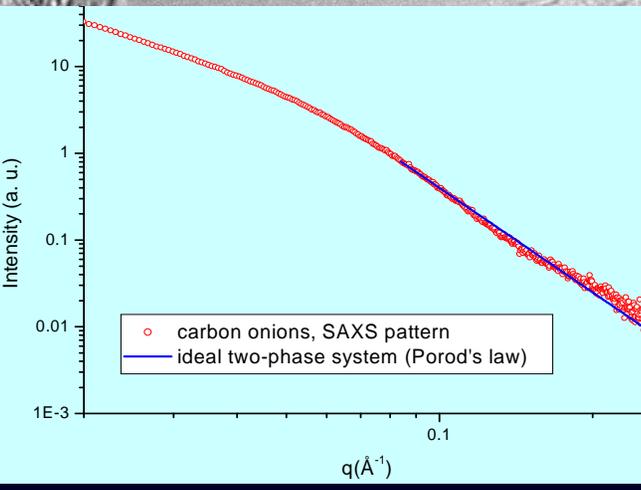
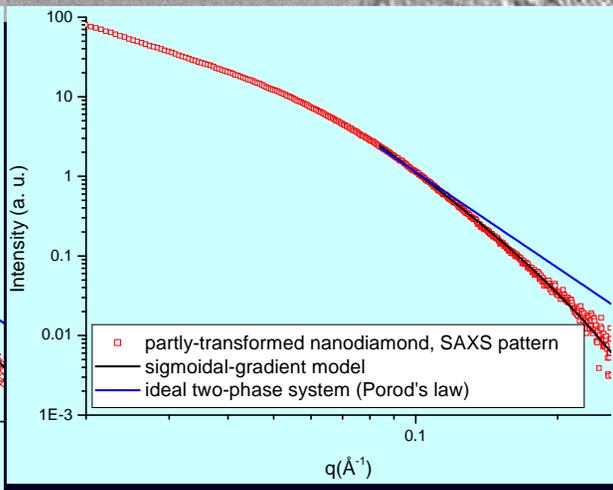
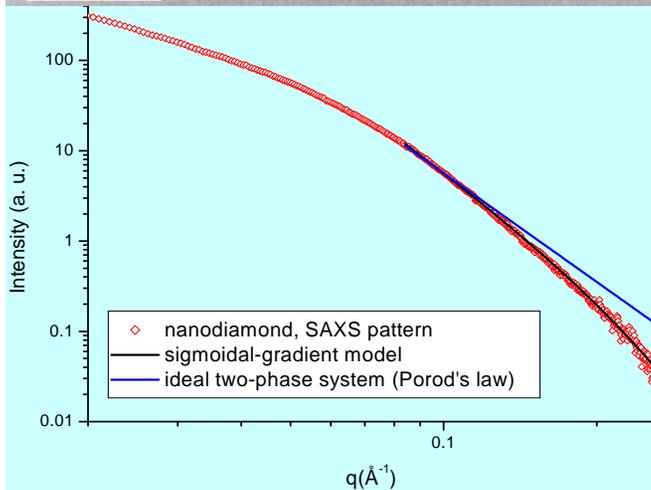
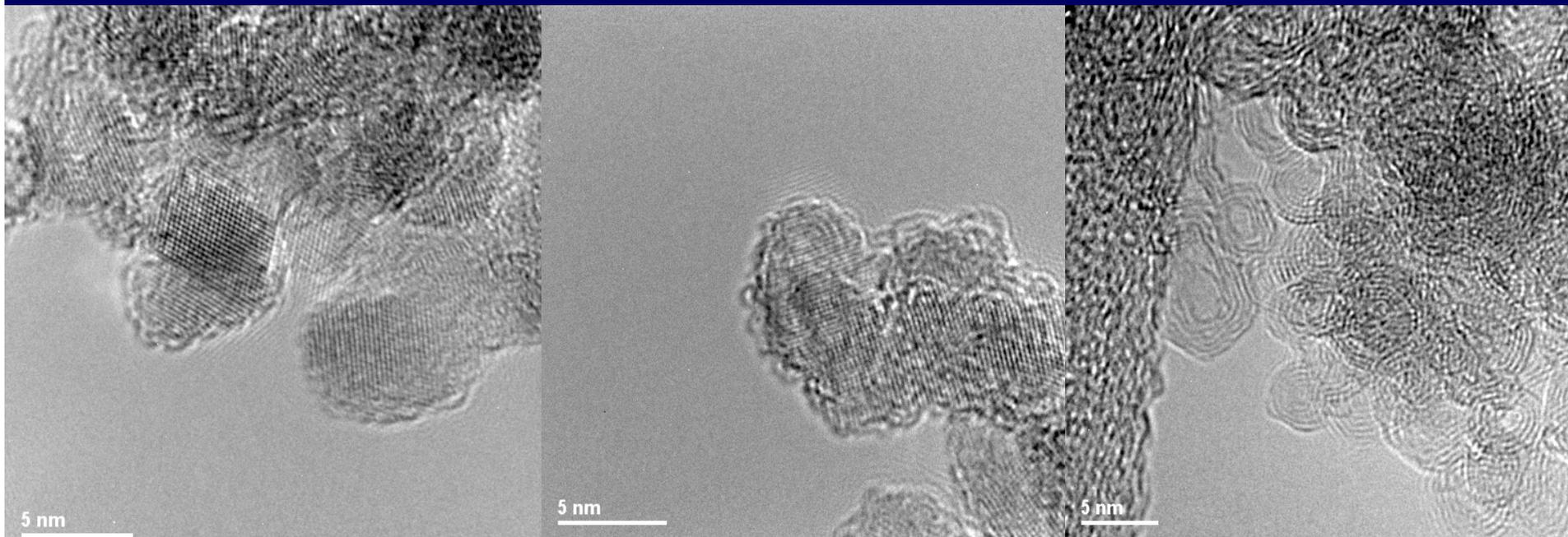
Carbon Onions

5 nm

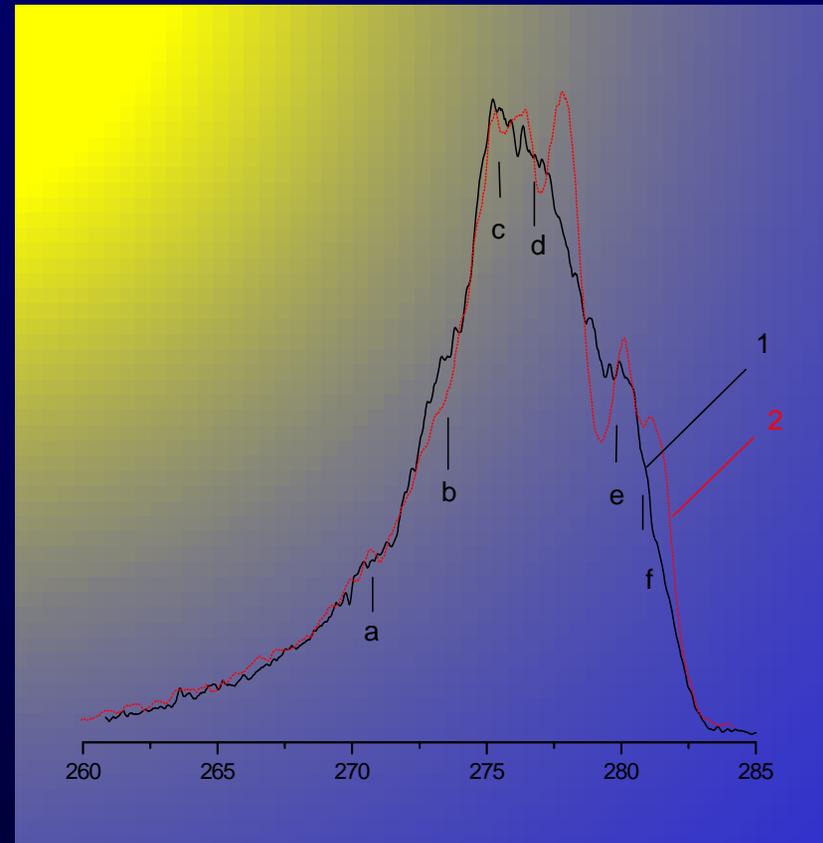
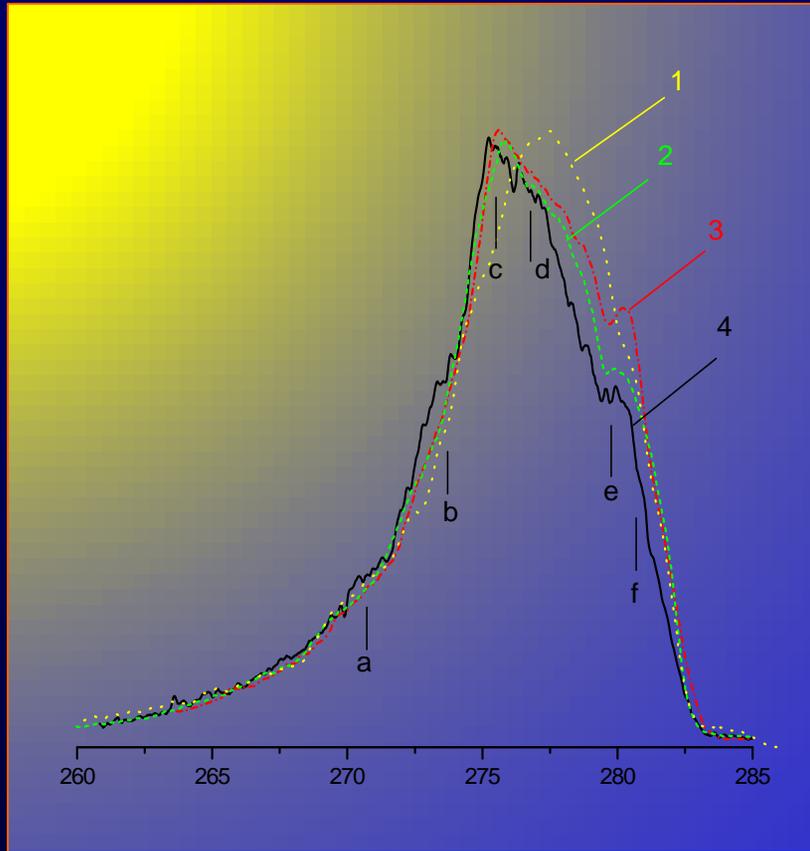
5 nm



Small-angle X-ray Scattering (SAXS)



Carbon onions



Equal intensity peaks $CK\alpha$ -emission:

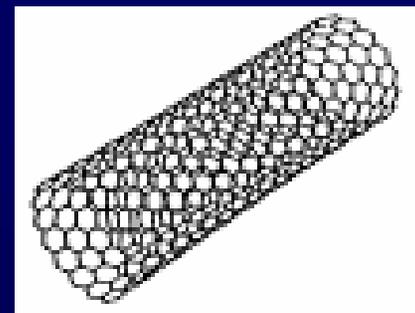
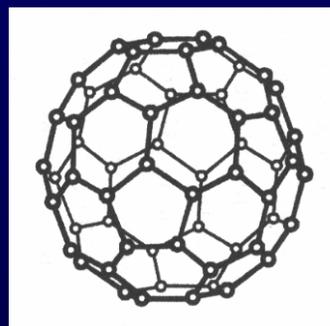
- 1 – nano-diamond,
- 2 – pyrolitic graphite,
- 3 – thermally exfoliated graphite,
- 4 – carbon onion

Photoelectron emission spectra $CK\alpha$ - from:
onions (1) fullerite (2).

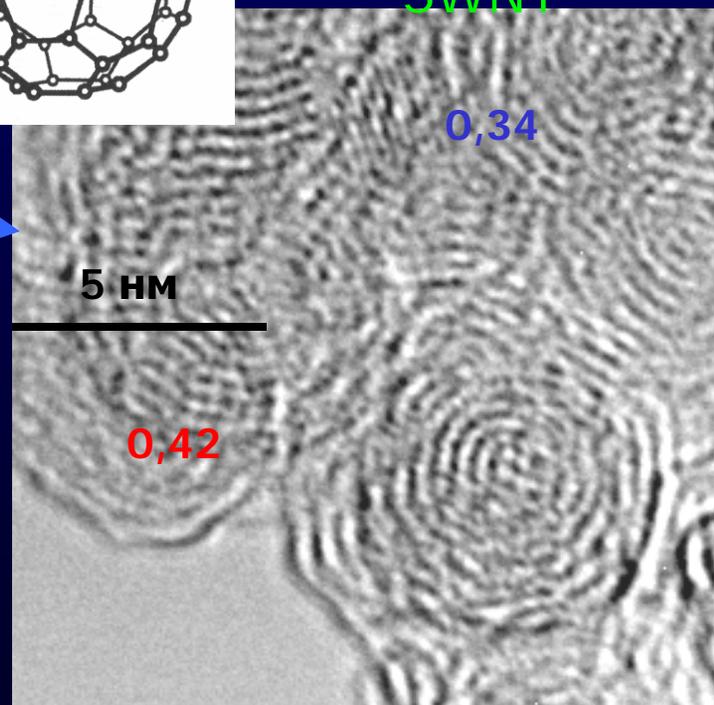
HYDROGEN ADSORPTION BY CARBON NANOMATERIALS

Material	Specific Surface Area m ² /g	Hydrogen , wt.% 77 K, 3 MPa
SWNT	180	1.23
MWNT	18	3.35
Activated:		
C60	3100	3.54
Carbon	3000	5.4
Onions	700	9

C60



SWNT



Carbon onions demonstrate highest physical adsorption capacity
(to 9 wt.%)!

Due capillary condensation of hydrogen in the surface layers of onion particles with increased $d(002)$

Patent of Ukraine



PREPARATION OF MWCNT

SWCNT and MWCNT prepared by CO conversion

- ❖ Method of low temperature (500-600 °C) catalytically conversion of CO results in the creation of carbon nanotubes and onions. Carbon nanotubes and onions prepared do not demand purification from carbon black usually formed in other processes.
- ❖ The weight ratio between nanotubes and onions is about 70...80 / 30...20.
- ❖ A typical nanotube diameter size depends on catalyst particle size and equals to 20...60 nm. The length is commonly about 3...5 μm .

Carbon and noncarbon nanotubes;



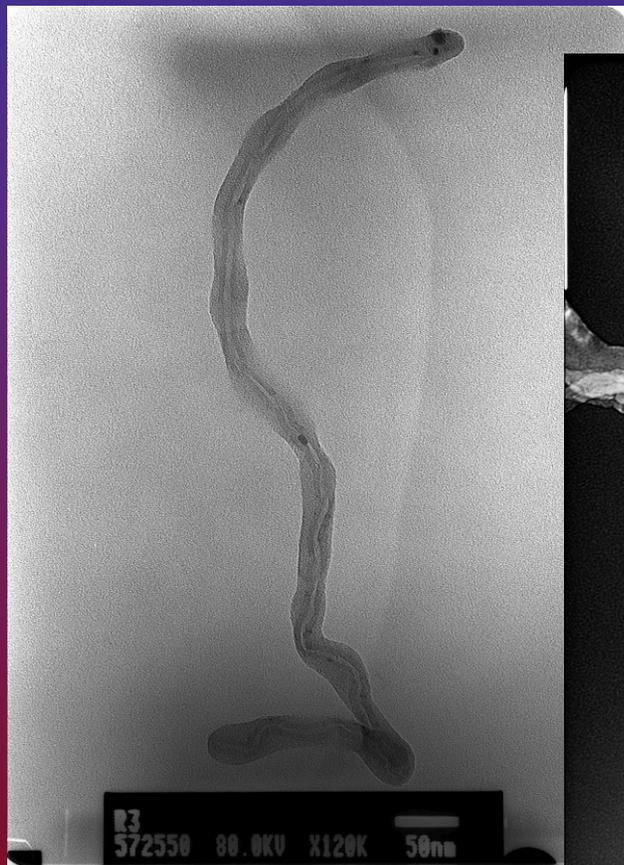
In cooperation with Clarkson University NY,

CRDF UE2-2356

SWCNT and MWCNT prepared by CO conversion

- ❖ **Low temperature preparation of carbon nanotubes and onions free from black carbon.**
- ❖ **Morphology of nanotubes and onions prepared with using of different catalysts.**
- ❖ **HP sintering of nanotubes and onions on Ni catalyst.**
- ❖ **Morphology of powders sintered.**
- ❖ **Nanoindenter tests.**

PREPARATION OF MWCNT with different catalysts



Co

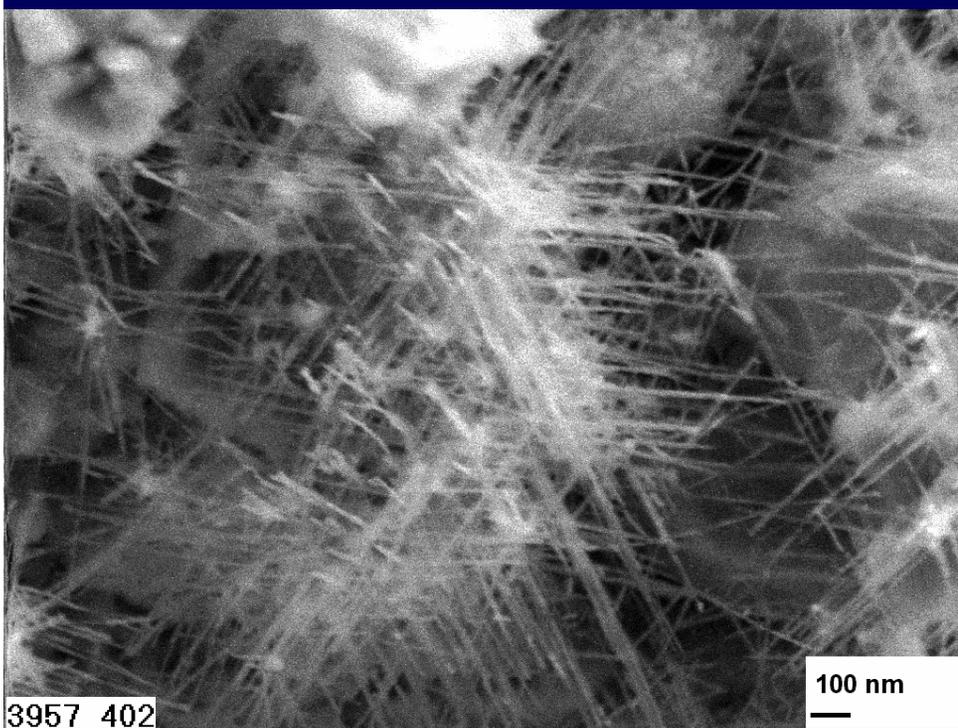


Ni



Fe

Nanorods SiC, prepared by chemical synthesis using Fe – catalyst at 1000 °C for 60 min.



Drs. P. Sylenko, A. Ragulya

Dr. Kharlamov

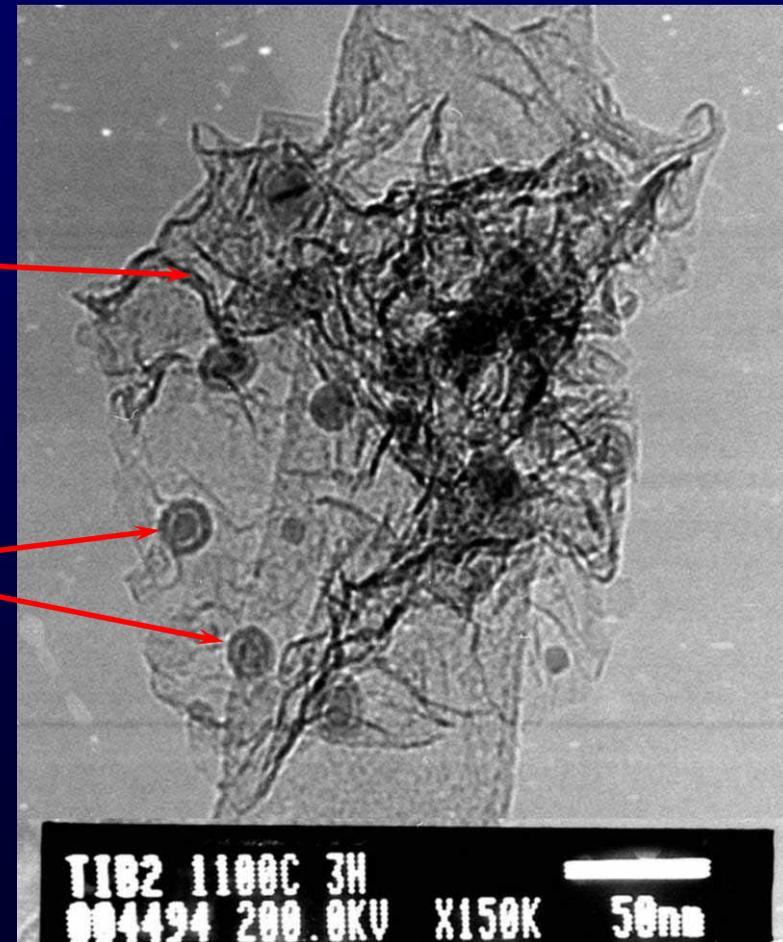
Patents of Ukraine

Nanowires of TiB_2 , synthesized from Ti-C-O-B system at temperature 1100 °C.



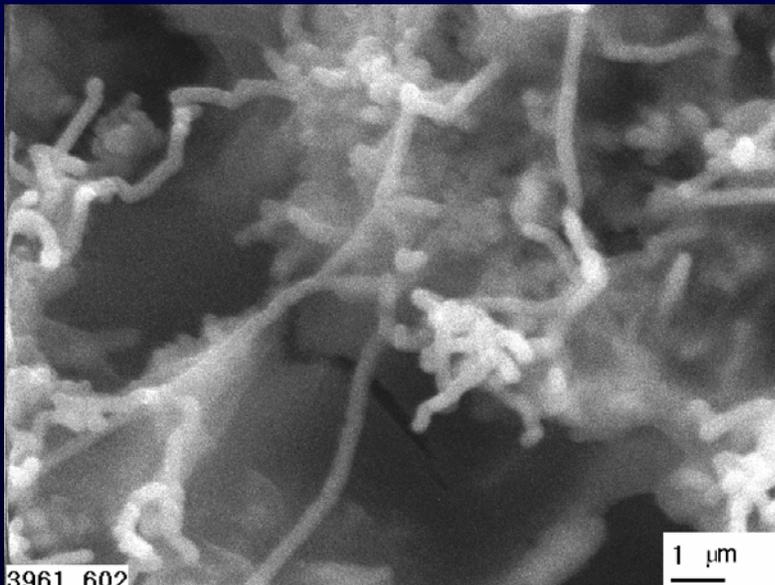
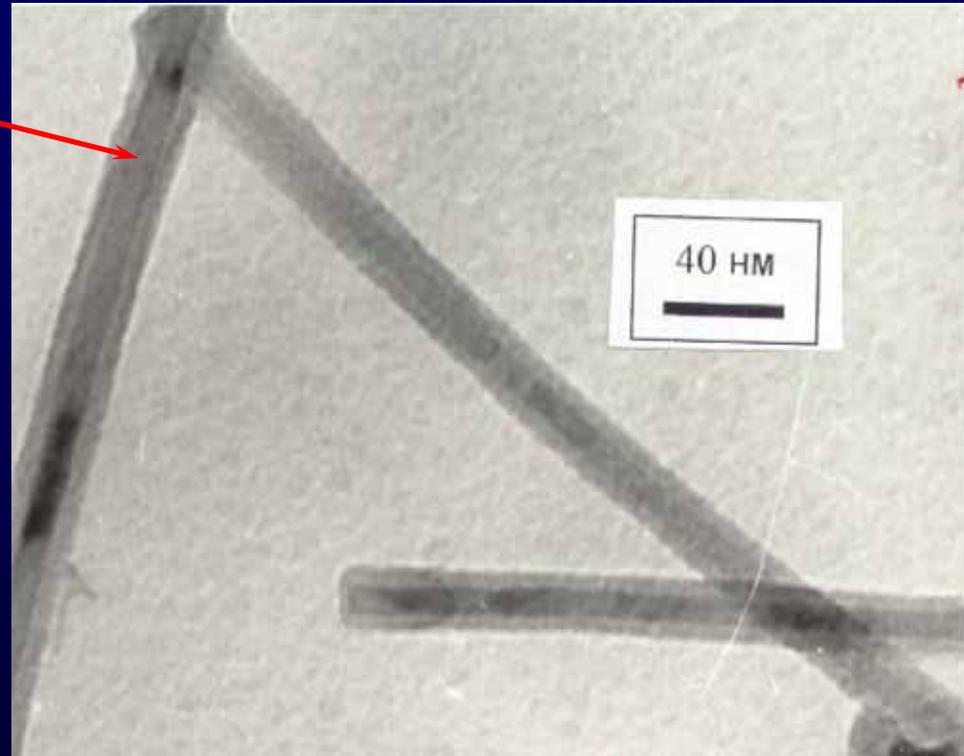
Nanowires TiB_2
6-8 nm in diameter
and 50-100 nm length

Nano-onions TiB_2
10-25 nm in diameter



Developed the technology of synthesis of Si_3N_4 nanorods and nanotubes by CVD technology

Nanotubes of Si_3N_4
15-25 nm in diameter
and up to 1 μm length



Nanorods of Si_3N_4 of
50-75 nm in diameter
and up to 100 μm length

Conclusions

- Tens of particulate substances and compounds had been obtained on laboratory, pilot and industry scales;
- Developed new concept of nanoparticle synthesis in nanoreactor considering wide number of possible reactors;
- Developed rate-controlled synthesis method appropriate for flexible control of nanoparticle size distribution;
- Developed new combined method for synthesis of nano-cubic boron nitride under shock–wave conditions in diffusion-controlled area of transformation from graphite-like BN;
- Developed pilot-scale manufacturing of carbon SWNT and MWNT by carbon oxide conversion reaction
- Developed laboratory synthesis of nanorods, nanowires and other elongated nanostructures based on SiC, Si₃N₄, TiB₂, BN...



THANK YOU



