InForm
Integrating Nanomaterials in Formulations

Formulation Science & Technology Group

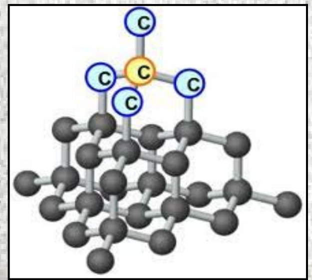
Novel Thermal Interface Materials Based on Ray Nanodiamonds

RAY TECHNIQUES LTD
NANODIAMOND TECHNOLOGIES

30.06.2011

Ray Techniques Ltd (RT)

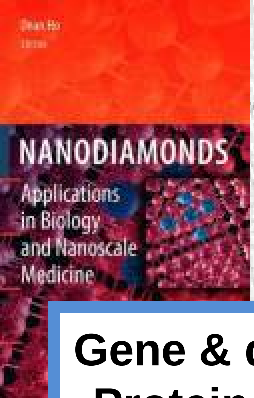
INNOVATIVE TECHNOLOGY FOR CONTROLLED LASER NANODIAMOND SYNTHESIS



CREATION OF NOVEL PRODUCTS BASED ON NANODIAMONDS

A licensed supplier
of the Israel Ministry of Defense

- **Established:** 2009
- **Registration number:** 514305671
- **Address:** Building 4-2, High Tech Village,
  The Hebrew University of Jerusalem, Israel



Nanodiamond Applications

ND

BIO-APPLICATIONS
- Gene & drug delivery
- Protein purification
- Biomarkers

FILLER REINFORCING POLYMERS & RESINS

Water Lapping (Mitsubishi Materials Silicon)

ABRASIVES IN FINE POLISHING & LAPPING

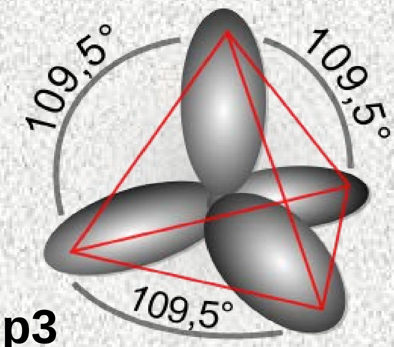
THERMAL MANAGEMENT
- Thermal greases
- Gels
- Adhesives
- Substrates

COATINGS
- Galvanic coatings
- Anodizing
- Electroless coating
- Polymer films
- CVD precursor

ENERGY SOURCE

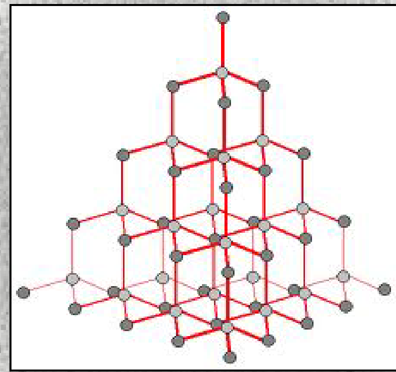
ADDITIVE TO LUBRICANTS

Diamond and its Unique Properties



sp3

A diamond is a transparent crystal of tetrahedral bonded carbon atoms (sp3) collected in the inflexible three-dimensional cubic lattice. a = 0,35668 нм, z = 4



- **Extreme hardness: 98 GPa {111}**
- Highest wear resistance
- Highest Young's modulus: 1223 GPa {111}
- Highest bulk modulus: 442.3 GPa
- Lowest volume compressibility:$18^{x} 10^{-1}$ºm^2/N
- Density: 3.51 g/cm^3
- Toughness: 7.5–10 MPa·m½

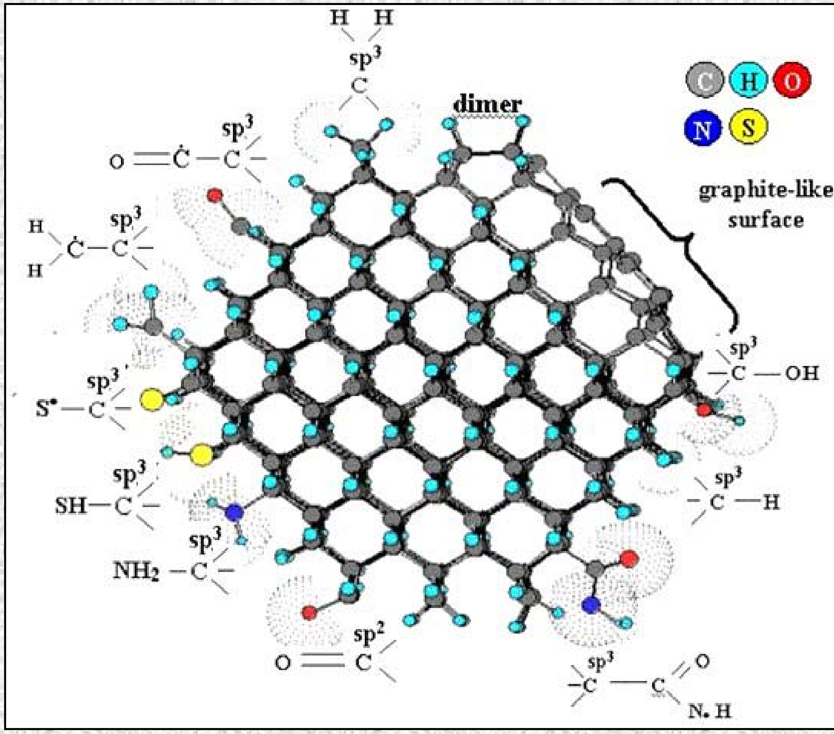
- **Highest thermal conductivity: 2000 W/mK**
- Coefficient of (linear) thermal expansion (20 °C): 1.18 μm m°/C
- Heat capacity: 0.4715 J/g°C

- **High electrical resistivity: 10^{13} Ωcm**
- Dielectric constant: 5.7 {300 K, 1–10 kHz}
- Dielectric strength: 1000 kV mm-1
- Relative permittivity: 5.57
- Wide band gap {300 K}: 5.47 eV

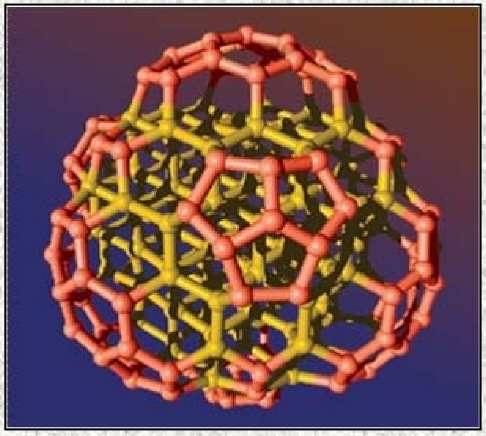
- **Optical transparency from deep UV to far IR**
- Refractive index: 2.419
- **Highest sound propagation velocity: 17.5 km/s**
- Chemical resistance and **highest biocompatibility**

What is Special about Nanodiamonds?

- ND primary particle consists of inert nucleus having unique diamond properties, graphene-like flakes on its surface and chemically active shell of functional groups (carboxyl, carbonyl, methylene, ether and others) with a lot of unpaired electrons.
- This high surface activity defines ND ability to interact with various objects and to influence processes of different kinds.



Functional groups providing outstanding interaction with various molecules and particles



Average size: 4-5 nm

Diamond nucleus
Yellow: cubic diamond structure
Red: graphene-like structure

The model proposed by Dr. O. Shenderova, 2002

Improving Material Properties by Using ND Dispersion

Being dispersed within various media even in small amounts, ND enables significant improvement of functional characteristics of various materials and processes.

ND is usually highly agglutinated which limits its applicability. Thus the development of techniques of surface modification in order to achieve high dispersion within any media is an important part of creation of novel ND-based materials

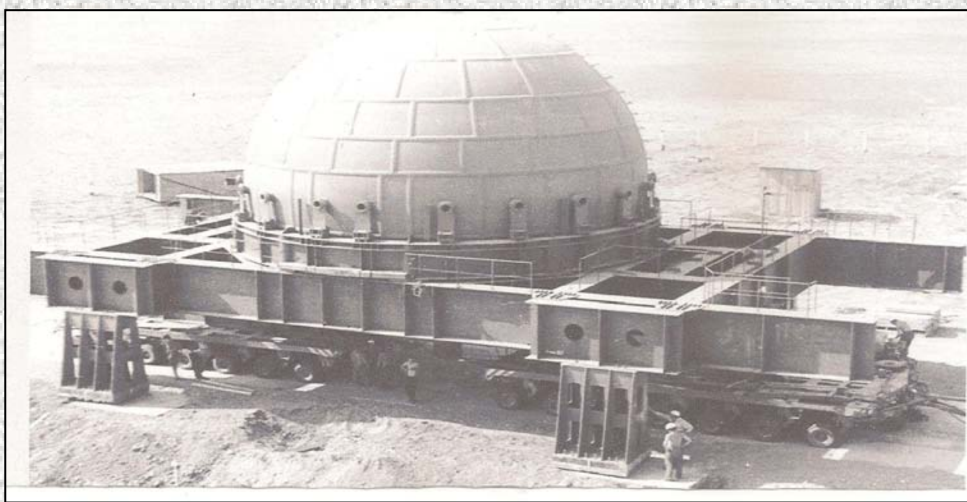
Existing Technology of ND Production

Detonation Synthesis

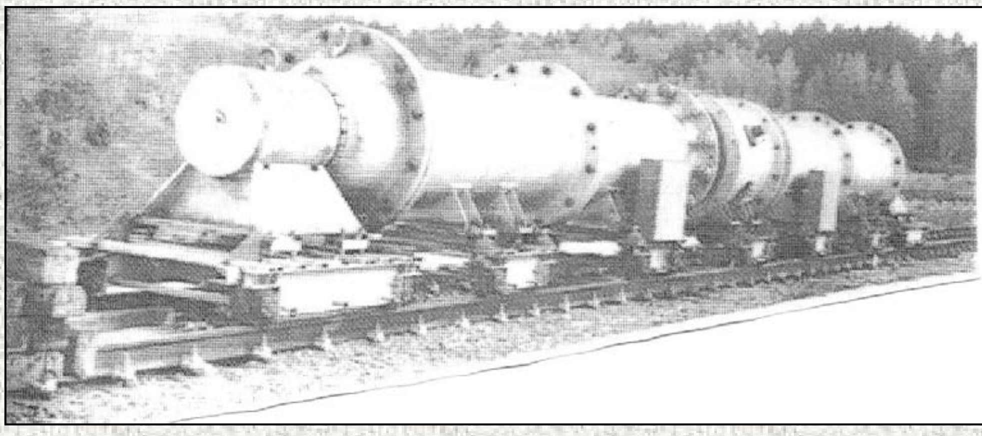
- Preparation of explosive materials mixture containing **TNT and RDX**
- Mixture **detonation** in chambers and obtaining blend containing ND, other carbon structures and metals
- ND separation and purification by **boiling in nitric acid** for a long time and washing

Polluting and Dangerous Technology!

Pictures from the book of Prof. V. Danilenko



ND reactor in Sarov



ND reactor in Snezhinsk

Drawbacks of Detonation Nanodiamonds (DND)

- Due to differences in the synthesis conditions inside the detonation charge volume, DND powder is **polydispersed** and contains primary particles of different sizes, as well as metal impurities from the chamber materials.

- Insufficient levels of purity and homogeneity in DND **limit the applicability** of this unique material in many important fields.

- Insufficient homogeneity **limits the efficiency** of using DND in most applications including Thermal management.

RT Technology Description & Uniqueness

RT developed a unique technology of laser synthesis of nanodiamonds (TLSND).

Our product is monodispersed nanodiamonds (RayND).

- RayND is synthesized using commercially available soot as a carbon source processed by a series of laser pulses of very particular parameters in liquid media at room temperature and normal pressure.
- Contrary to well known detonation technologies of ND production, our TLSND is environmental-friendly and not dangerous. No explosives are needed.
- RayND highly homogeneous in their sizes. The sizes can be controlled. Depending on parameters of laser radiation we obtained ND of 4 nm size and 300 nm size. The size distributions are confirmed by transmission electron microscopy.
- RayND is highly pure.
- Surface termination of ND synthesized with TLSND is mostly graphite-hydrogenated.
- RayND have originally positive Zeta potential. By a rather trivial further processing this Zeta potential can be tuned to any desired value in a very wide range.

TLSND is a scalable technology. Our nearest target is the monthly output of a few kilograms with a production cost of less than 1000$/kg of pure diamond powder.

Ray Techniques' Green Technology

Target Preparation → **Laser Treatment** → **ND Isolation & Washing** → **ND Surface Modification**

Target Preparation: Target preparation from **carbon soot** and binder. In future the soot will be prepared from pure graphite.

Laser Treatment: **Laser treating** of the targets in liquid resulting formation of cubic diamond structure of carbon

ND Isolation & Washing: ND isolation by environment-friendly **flotation** method and washing in deionized water

ND Surface Modification: Modifying ND surface according to further applications or customer's requirements

Every process is unique and patentable.

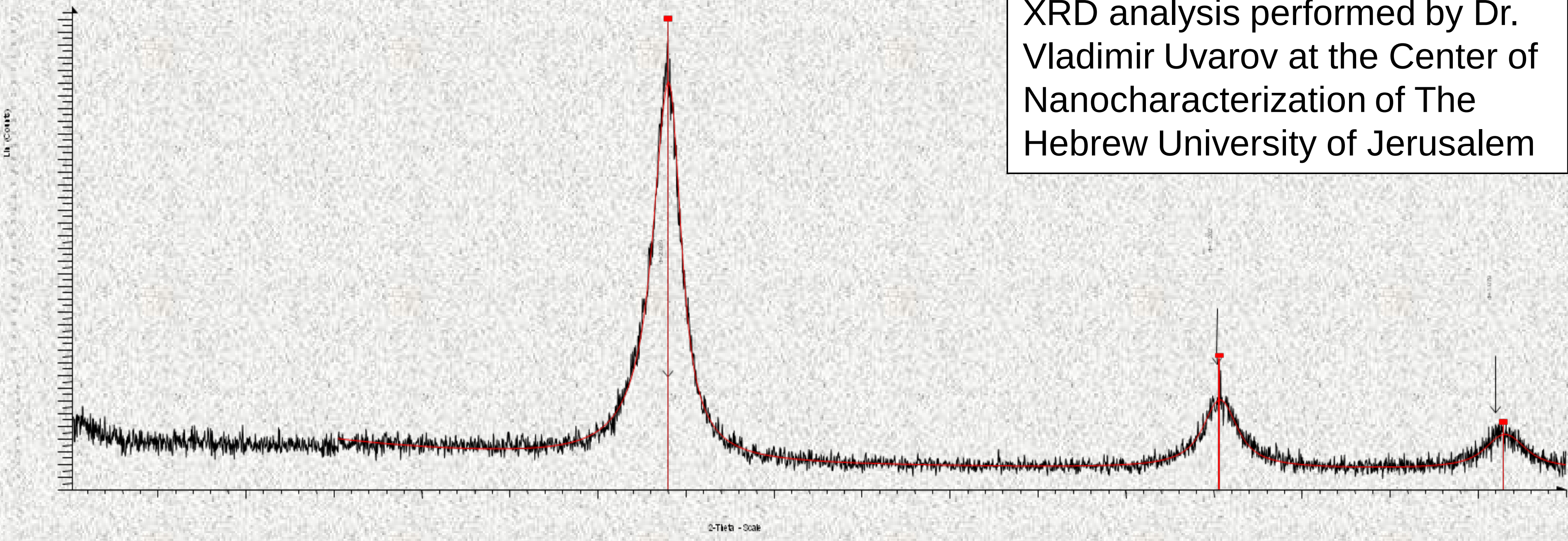
The main product: RayND, Monodispersed ND of high purity!

Advantages of RT Technology

1. **Environment-friendly and non-hazardous**
2. Control the ND crystal dimensions and defects
3. Allows to obtain **monodispersed** ND of much higher quality (RayND):
   - high purity, metal- and graphite-free
   - high homogeneity of ND dimensions
   - high homogeneity of ND surface chemistry
4. **Better results** in most ND applications
5. Wider scope of potential applications
6. Lower cost in mass production

RayND Characterization

XRD analysis performed by Dr. Vladimir Uvarov at the Center of Nanocharacterization of The Hebrew University of Jerusalem

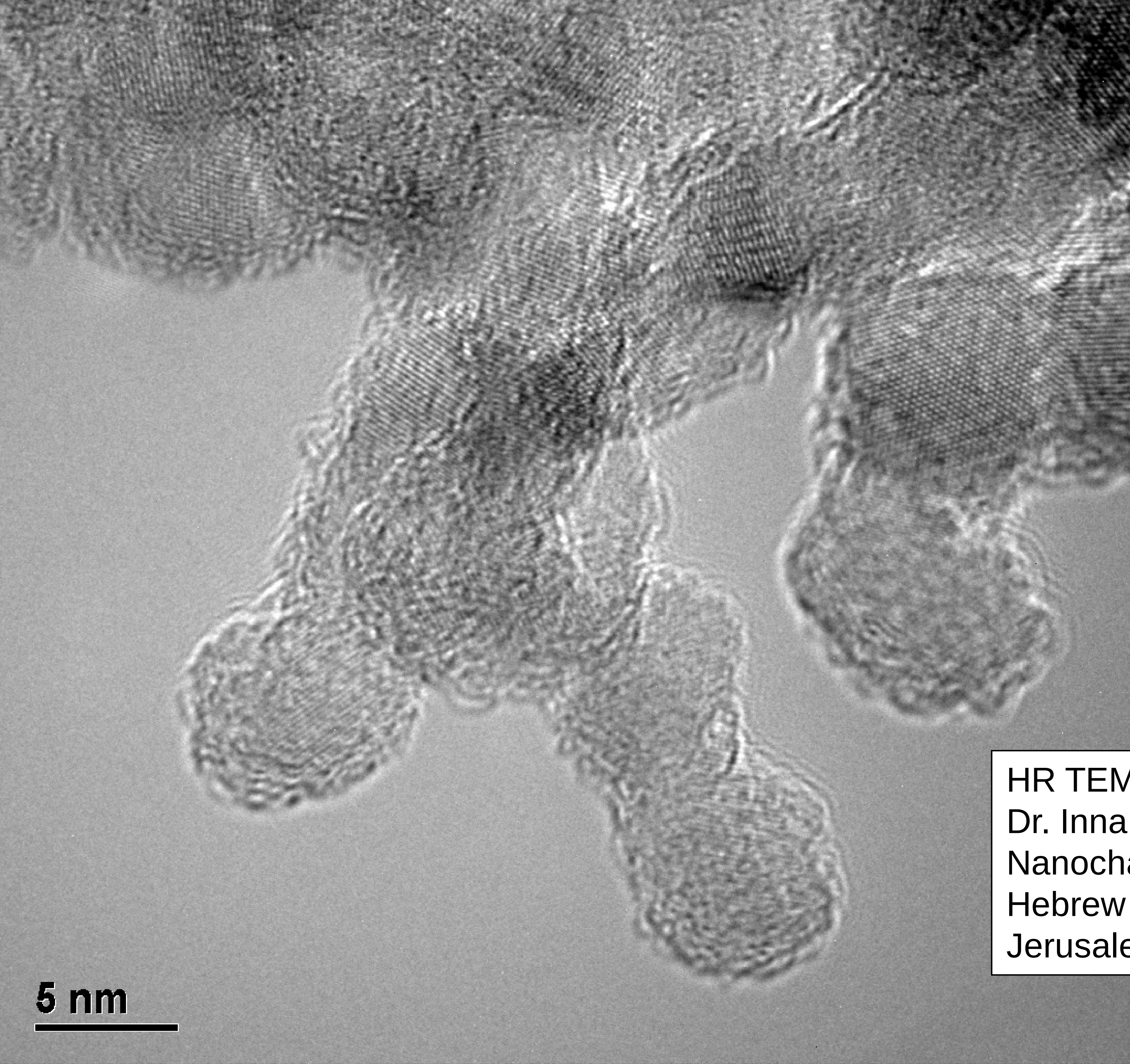


03-065-0537 Diamond, syn; Crystallite Size(Scherrer): 39.7 A; System: Cubic; Space group: Fd-3m (227)

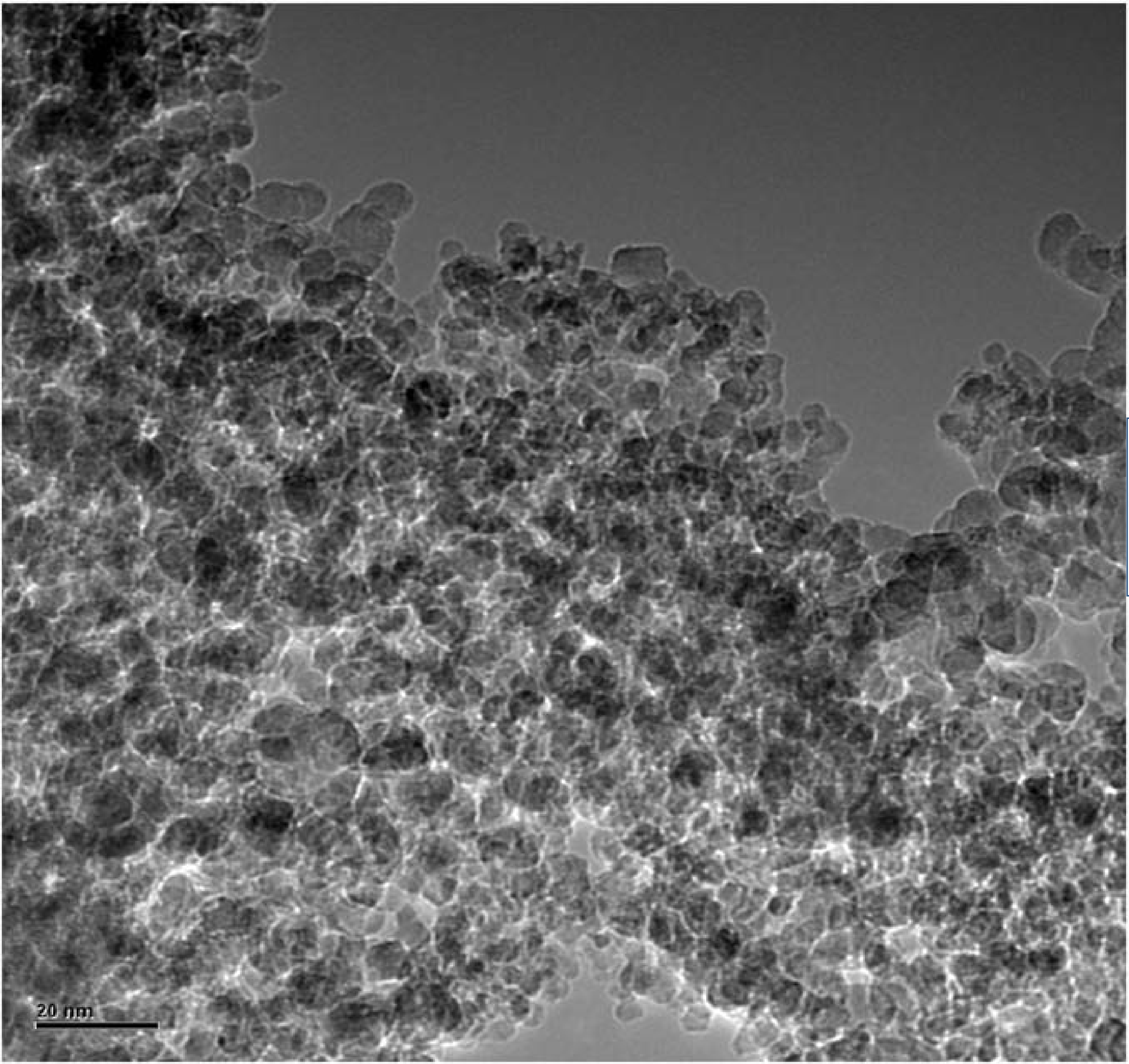
Cell param.:	Initial	Final
a:	3.56703	3.56657

Clear diamond peak at 2 theta = 43.918 ° and the lattice constant of 0.3567 A indicate the absence of cubic diamond structure defects and impurities.

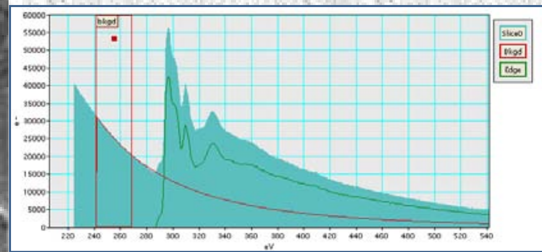
Average crystalline size: 4 nm

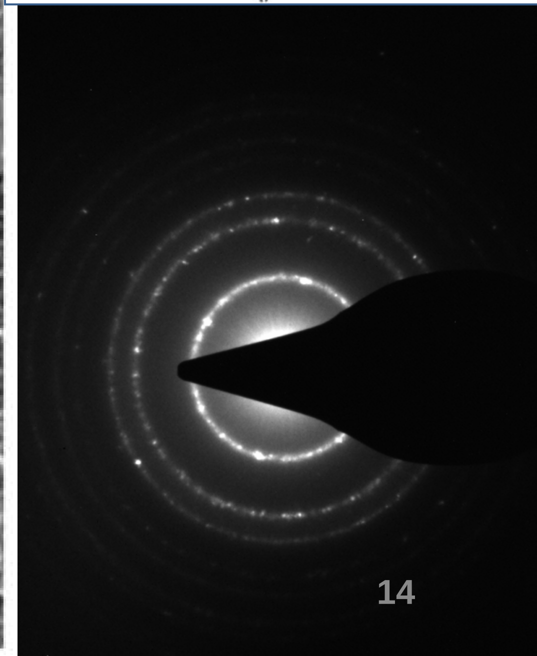


HR TEM Image obtained by Dr. Inna Popov at the Center of Nanocharacterization of The Hebrew University of Jerusalem



HR TEM image demonstrating high homogeneity of RayND





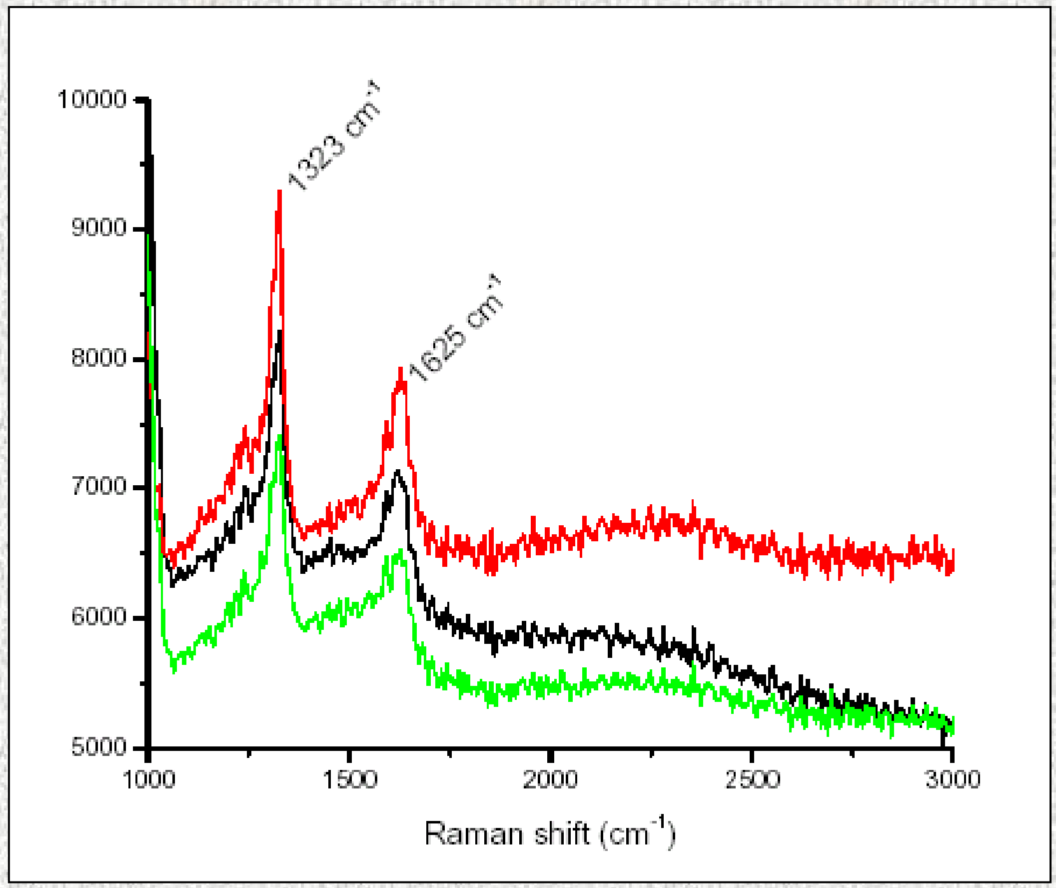
Raman Spectroscopy

Excitation: 488 nm, power: 1 mW (Witec, Germany)

Intensive peak at 1323 cm^{-1} in comparison to weak peak at 1625 cm^{-1} indicates high content of diamond phase in RayND.

The shifts of the diamond peak at 1323 cm^{-1} and G-line at 1625 cm^{-1} confirm that crystallites' size is 4 - 5 nm.

Absence of additional peaks in Raman spectra at 1350 cm^{-1} and 1585 cm^{-1} (which usually present in detonation ND Raman spectrum) indicates the non-existence of graphite and ND particles with sizes 30 – 50 nm.

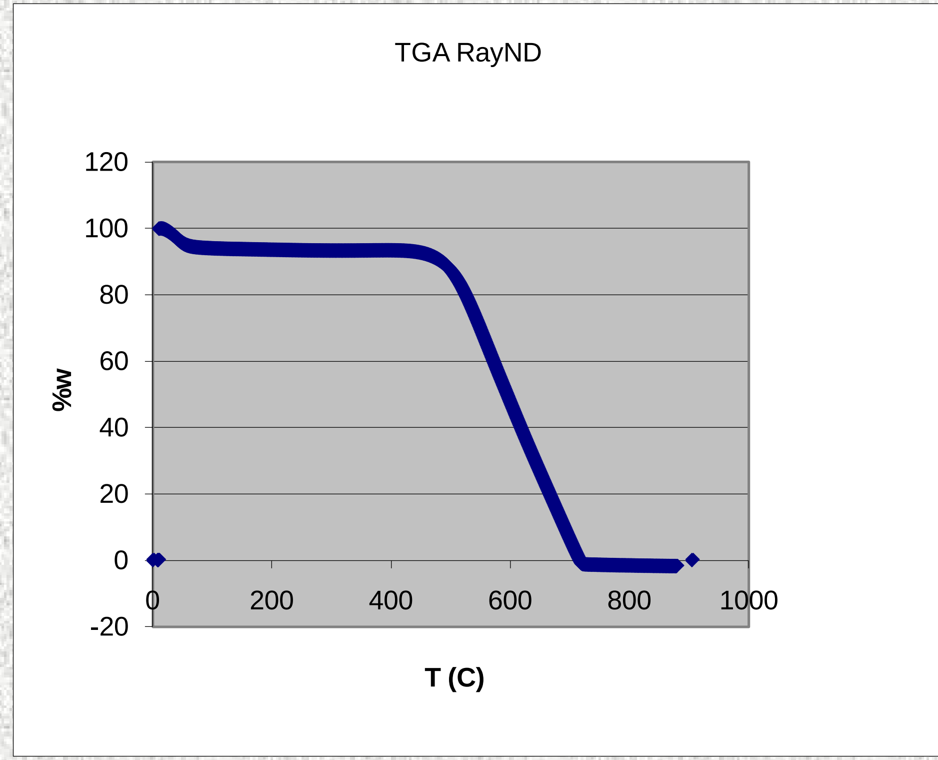


Raman shift (cm^{-1}) was kindly provided by Dr. E. Perevedentseva

Thermo Gravimetric Analysis

TGA results exhibit significantly more narrow temperature range of decomposition: 250 degrees in comparison with 390 **and more** degrees for detonation ND which indicates the high homogeneity of the powder.

In addition, the absence of fracture usually existing in DND graphs indicates homogeneity of RayND.



Analysis performed at the Institute of Chemistry, HU

RayND Specification

- Average crystal size: 4-5 nm
- Crystal lattice constant: 0.3567 nm
- Pycnometric density: 3.25 - 3.4 g/cm^3
- Bulk weight: 0.4 - 0.7 g /cm^3
- **Combustion residue: < 0.005%**

For comparison, combustion residue of DND: 0.2 – 5 %

ICP Analysis (ppm)

	Zn	Co	Ni	Mn	Fe	Cr	Al	V
RayND	44	<1	20	35	45	114	19	<1

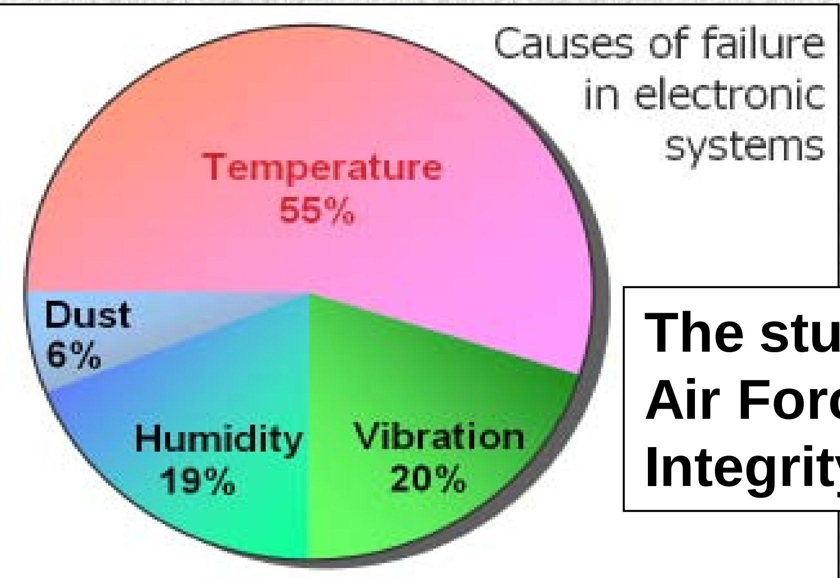
Average of 3 measurements
Testing was conducted at the Hebrew University of Jerusalem using the ICP-OES (Perkin Elmer Optima 3000).

Impurities: < 300 ppm

RT has started R&D project aimed the creation of novel TIM for Electronic Industry

- ND is a state-of-the-art material rapidly finding its way to Thermal Management sector of the electronic industry due to the uniquely high thermal conductivity and electrical resistivity of diamond.
- Being dispersed within polymer matrix, nanodiamonds enable a significant improvement of thermal, electrical and mechanical properties of Thermal Interface Materials (TIM).
- The use of novel TIM will greatly increase heat dissipation from active elements in power- and opto-electronics, improve the performance of electronic devices, as well as increase their reliability and durability.

The Problem of Overheating in Power Electronics



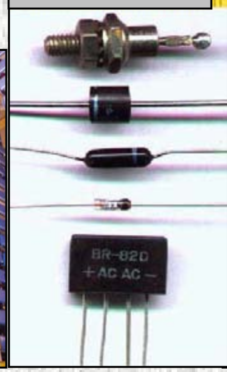
The study of the US Air Force Avionics Integrity Program

Overheating of laptops' motherboards is a serious problem

Overheating is the most common cause why a rear projection TV set won't turn on.

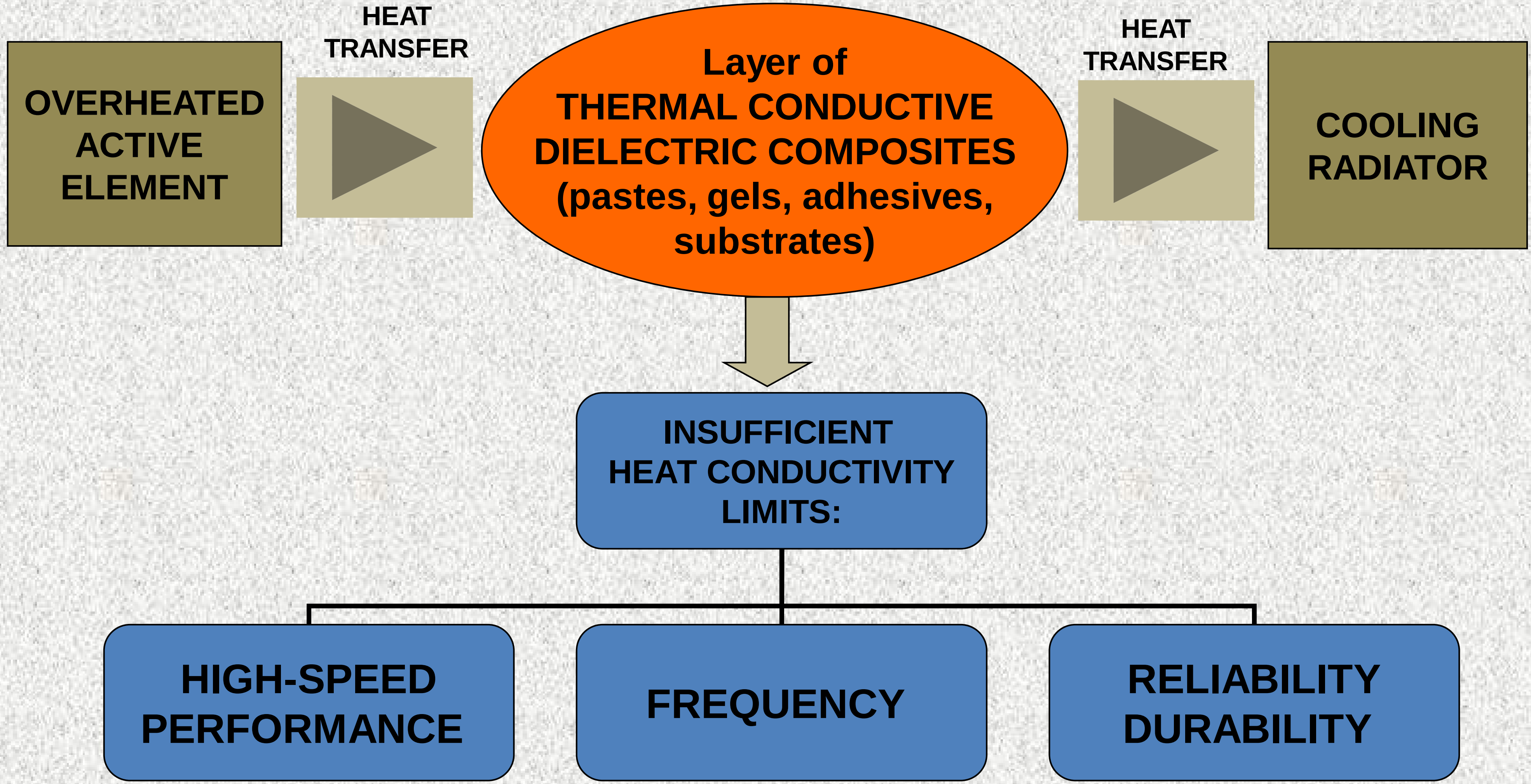
Thyristors

Diodes



Transistors

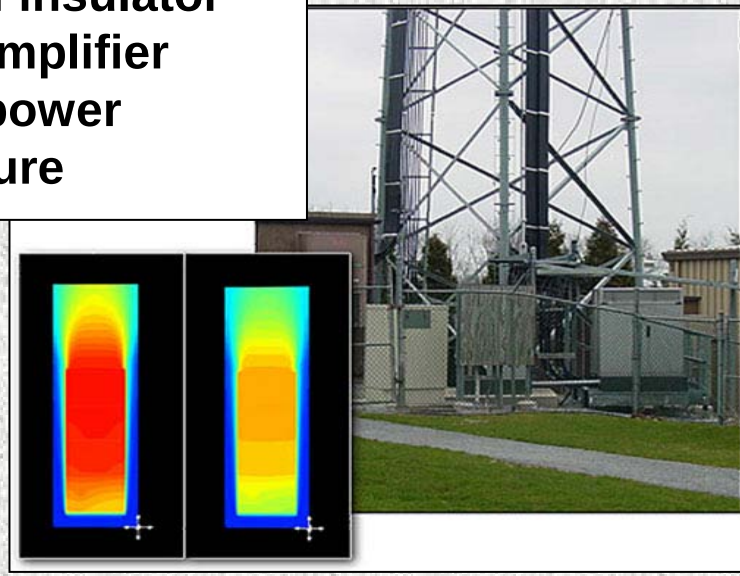
Problem of Overheating of Active Elements in Electronic Industry



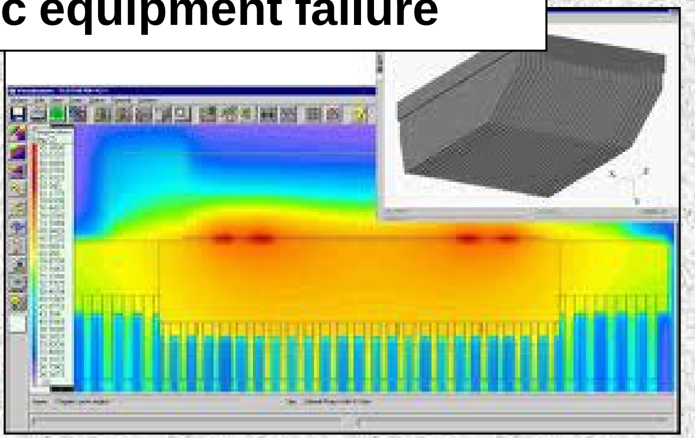
Power Electronics Components Failure

"Hot spots" in plastics can lead to overheat and component failure.

Insufficient thermal conductivity of insulator in 1x1.5-inch amplifier chips causes power equipment failure

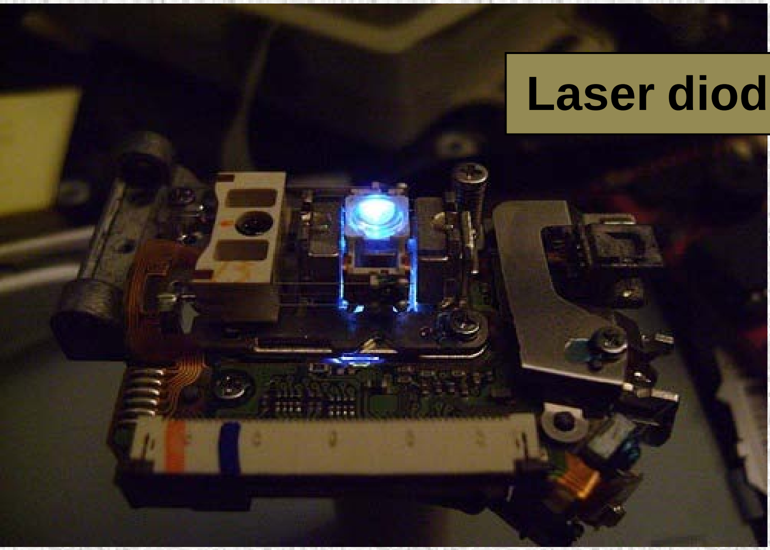


IGBT overheating leads to electronic equipment failure

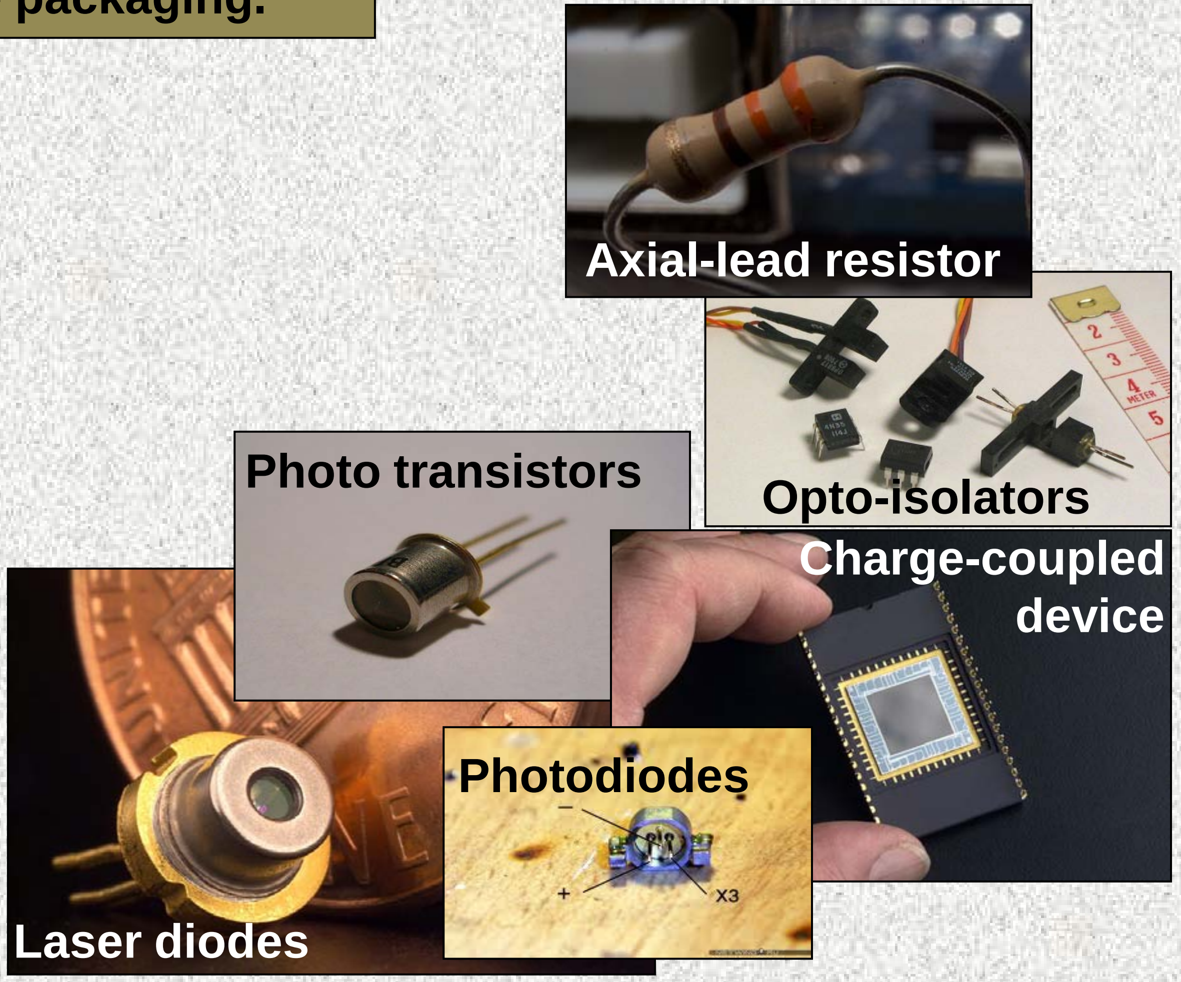


A typical failure mechanism caused by thermal problems is when TIM degrades or delaminates.

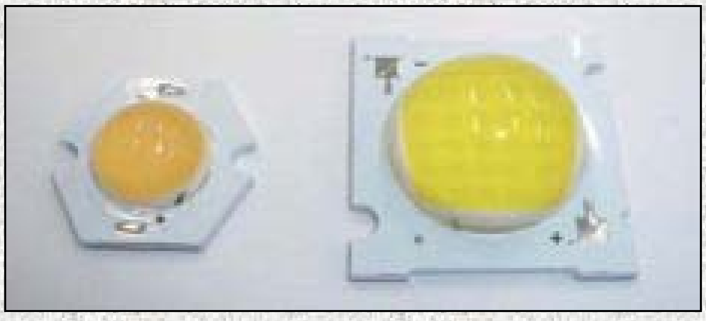
Problem of Overheating in Opto-Electronics

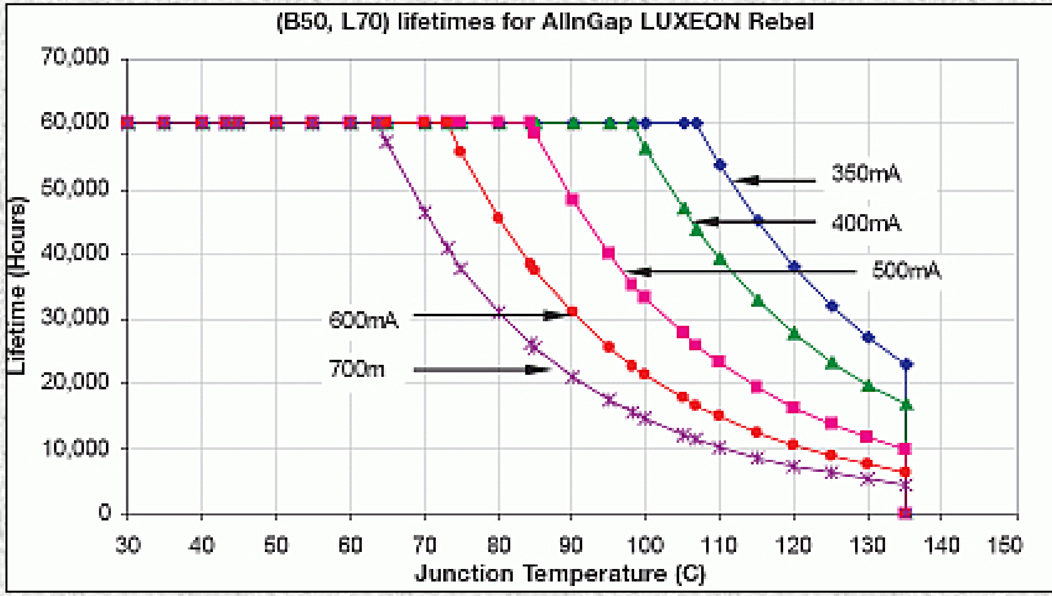


Laser diode packaging.

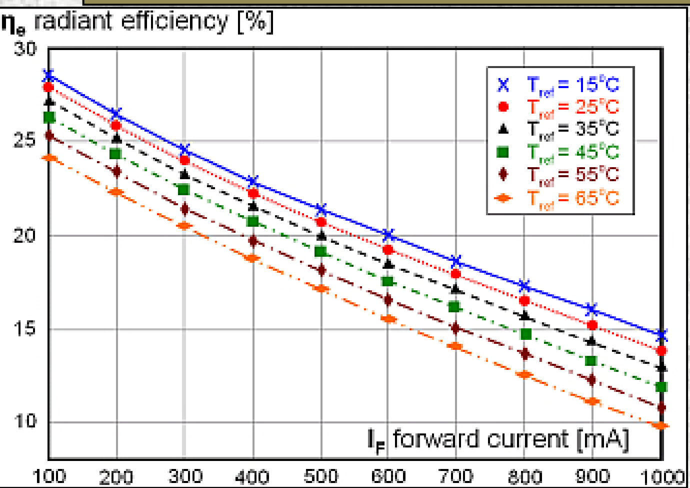


Special Relevance for LED Industry

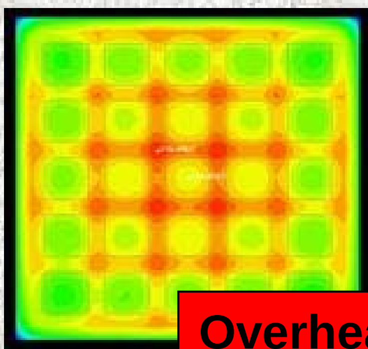


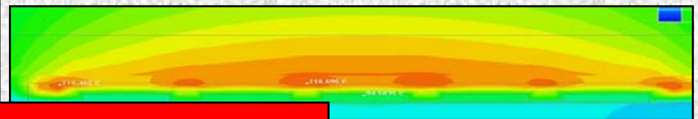


Energy conversion efficiency of LEDs drops with temperature.



Expected lifetime of LEDs also drops with increasing temperature.



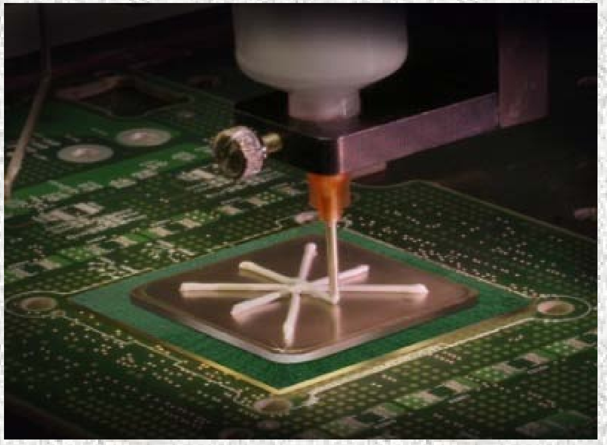


Overheating in LEDs

New Requirements for Thermal Interface Materials

Rapid development of high power electronics presents NEW DEMANDS:

- **Increased thermal conductivity**
- **High insulating properties**
- **High durability**
- **Manufacturability**
- **Cost reduction**

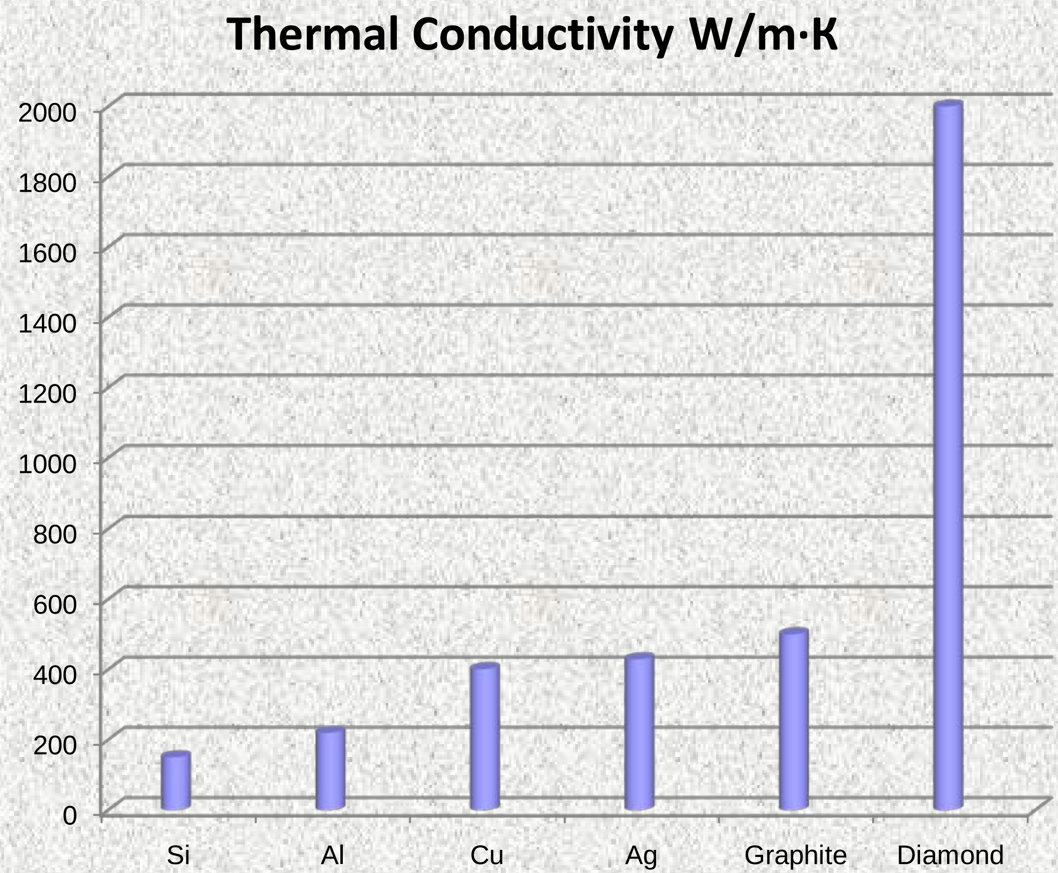


THE GOAL OF THE PROJECT: CREATION OF NOVEL THERMAL INTERFACE MATERIALS THAT MEET THE NEW DEMANDS

Proposed Solution – Using Nanodiamond Filler

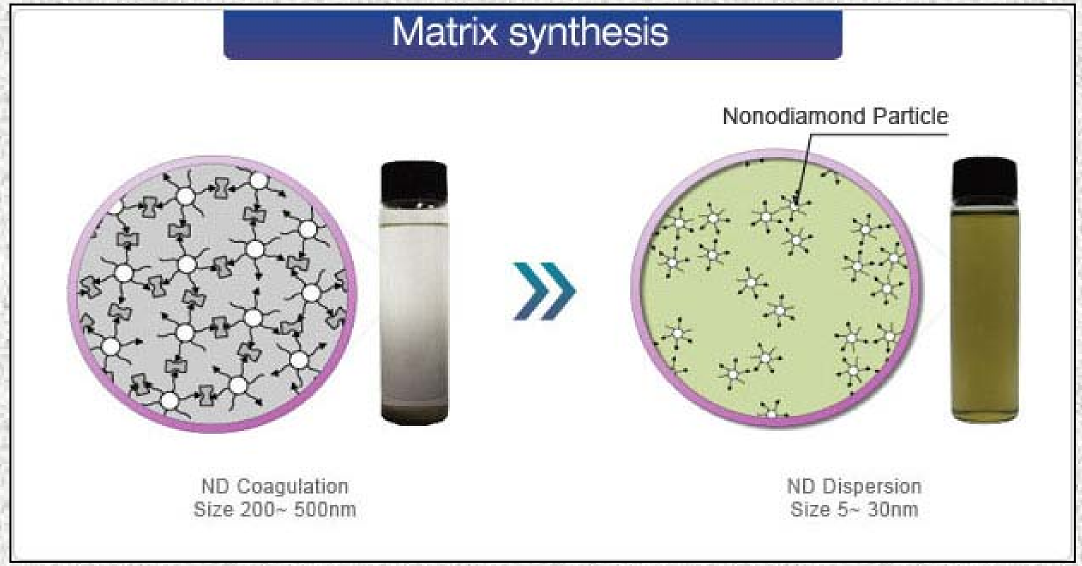
Diamond is the only nature material that combines:
highest thermal conductivity: 2000 W/m·K
lowest specific heat capacity: 6.115 J/m·K
low thermal resistance: 0.25°C-cm²/W
high electrical resistivity: 10^{13} Ω·cm

Alongside with these properties, nanodiamonds have tiny dimensions (average grain size of 4-5 nm) and chemically active crystal shell. Being dispersed within a polymer matrix, ND dramatically improve thermal and mechanical properties of polymer composites.



ND Dispersion within Polymer

High ND dispersion within various polymers provide significant improvement of their ability to heat transfer.



RT is developing unique methods of physical, thermal and chemical **ND surface treatments** for ND disaggregation and obtaining **high dispersion** within various matrixes.

Nanodiamond-Water Suspension

Applications: CVD pre-seeding, bio-medical applications, polishing slurries

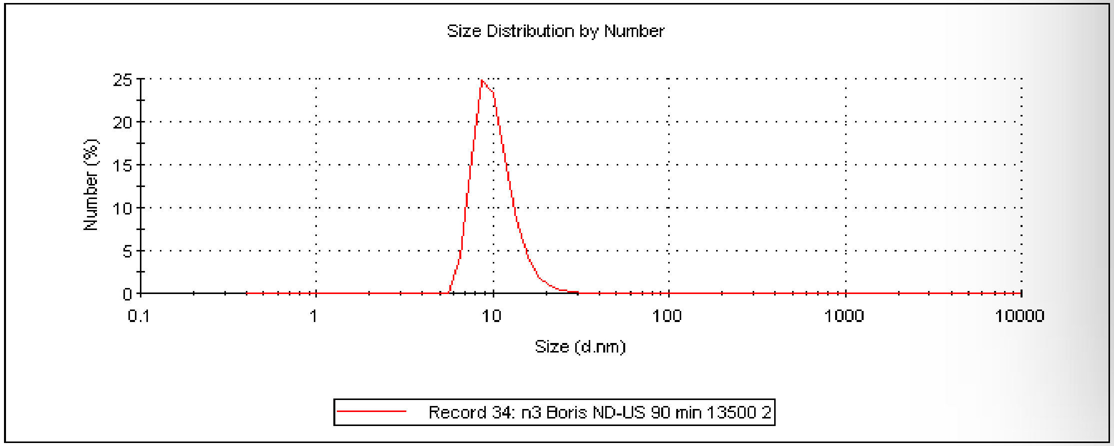
DLS analysis performed by Dr. Priev in HU (Nanosizer of Malvern)

Records View | Intensity PSD (M) | Volume PSD (M) | Size quality rep... | Correlogram (M) | Cumulants Fit (M) | Distribution

Material RI:	2.40	**Viscosity (cP):**	0.8872
Material Absorbtion:	0.01	**Measurement Date and Time:**	16:10:48 2011 יוני 09 יום חמישי
Temperature (°C):	25.0	**Duration Used (s):**	90
Count Rate (kcps):	103.2	**Measurement Position (mm):**	1.05
Cell Description:	Disposable sizing cuvette	**Attenuator:**	3

			Diam. (nm)	**% Number**	**Width (nm)**
Z-Average (d.nm):	34.19	**Peak 1:**	10.35	100.0	3.050
PdI:	0.298	**Peak 2:**	0.000	0.0	0.000
Intercept:	0.942	**Peak 3:**	0.000	0.0	0.000

Result quality : Good



Color: dark-brown transparent
Particle size distribution: 10.35 nm (Nanosizer of Malvern)
ND concentration: 1.7 g/l (Paar 5000 Density Meter).

Using ND as a Filler within Polymers
Preliminary Experiment

The results of the preliminary experiment conclusively prove (for example, silicon oil) that using ND as the filler within a polymer matrix significantly improves the heat dissipation ability of the polymer.

The results also show
a better performance of RT grease
in heat dissipation compared to standard high quality thermal greases including the greases used for Intel CPU cooling.

Comparison of CPU Temperature Using Different Thermal Greases

Paste	t ºC	T ºC (11th min)	T* ºC (20th min)
Deep Cool	40.0	70	82
Zalman TG-2	40.0	69	83
RT5K	38.0	68	81
Silicon oil	54	88	97

Nanodiamond Thermal Grease

RT-Term composition contains:

- silicon oil – 90 wt.%
- pure nanodiamonds – 10 wt.%

Thermal conductivity: 8 W/mK

Electrical resistivity: 10^{10} Ωcm

Permittivity: < 2.8

Density: 1.1 g/cm^3

Color: gray

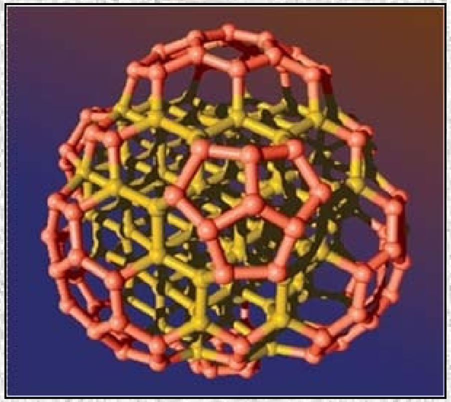
Estimated price: 1.2 $ per gram

Comparison of Thermal Conductivity of Greases with RayND and DND Fillers

ND Grease	Thermal Conductivity, W/m*K
RayND Grease	8.1
DND Grease	6.8

Two grease samples were prepared under the same conditions with the same ND concentration of 10 Wt.% in Silicon oil, one with RayND and the other with DND fillers.
RayND grease has 19 % higher thermal conductivity than DND one.

XPS analysis indicates 12% higher sp2 (graphene-like flakes, marked in red in the figure) on the grain surface in high quality DND sample comparing to RayND.
Does additional sp2 reduces thermal conductivity of the compound?



XPS Results

ND	sp2, %
RayND	22.27
DND	24.90

Prospects

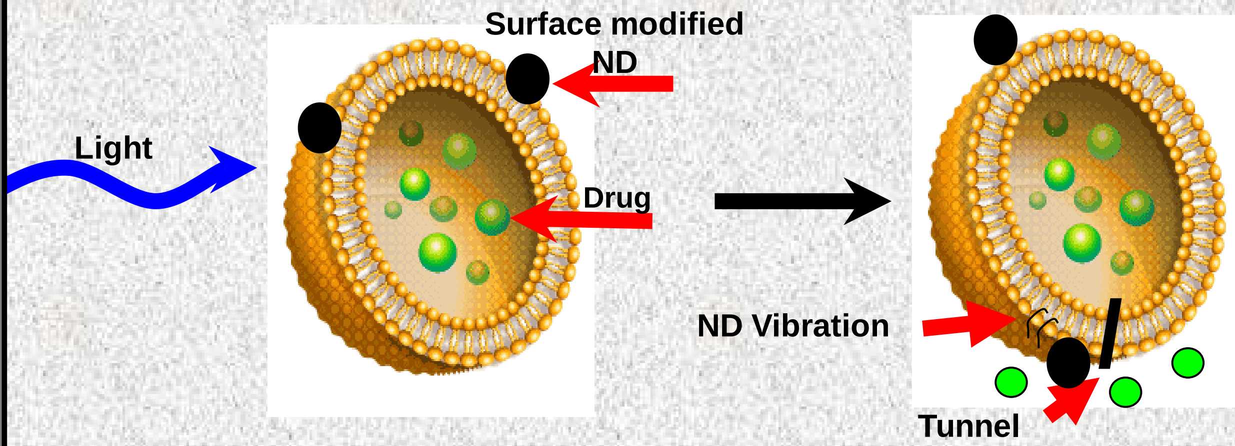
- Further development of special methods of ND surface modification for the achieving high dispersion within chosen polymers and as a result increase TIM ability to heat transfer with low ND concentration
- This approach will enable novel highly effective products in the field of Thermal Management in electronic and LED industry: thermal conductive insulating greases, adhesives and gels

Estimated thermal conductivity: 12-15 W/mK
Estimated TIM price: 1.6 - 2 $/g

P.S. High Potential of RayND Application in Bio-Medicine

A novel ND liposomal biomarker will be used to create a novel method for controlled release from a liposome using light.

- Biocompatibility
- Chemical stability
- Controlled tiny dimensions
- Ability to control the aggregate size
- Large specific surface area and high adsorption potential
- Photoluminescence
- Presence of surface functional groups (carbonyl- C=O, hydroxyl-type COH bonding, and hydrocarbon fragments) and ability to interact with bio-molecules



HU, The Hebrew University of Jerusalem
Membrane and Liposome lab

RT is currently participating in a number of research projects in collaboration with The Hebrew University of Jerusalem:

1.ND-antibody diagnostics for rapid and highly sensitive ultrasonic quality control of water, milk and other fluids.

2.ND-liposome formulation for early-stages cancer diagnostics

3.ND-siRNA system for gene therapy

In these projects, highly promising preliminary results have already been obtained at the membrane and liposome laboratory leaded by Prof. Chezy Barenholz.

Thank you for your attention!

Ray Techniques
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Welcome to Jerusalem!