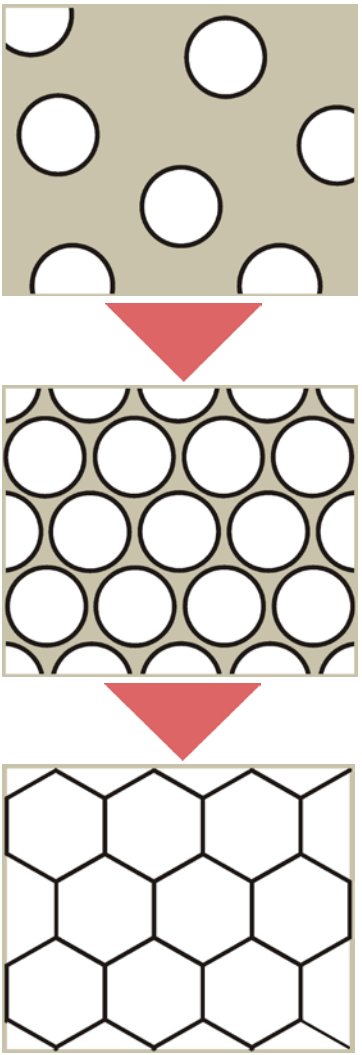

FABRICATION OF YTTRIA NANOGRAINED CERAMICS

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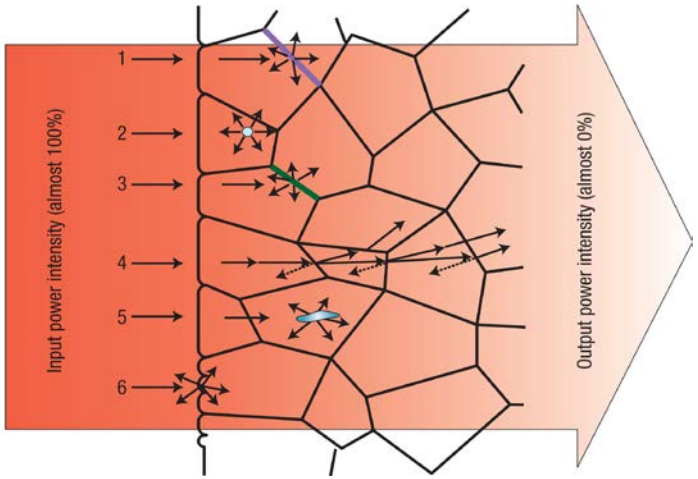
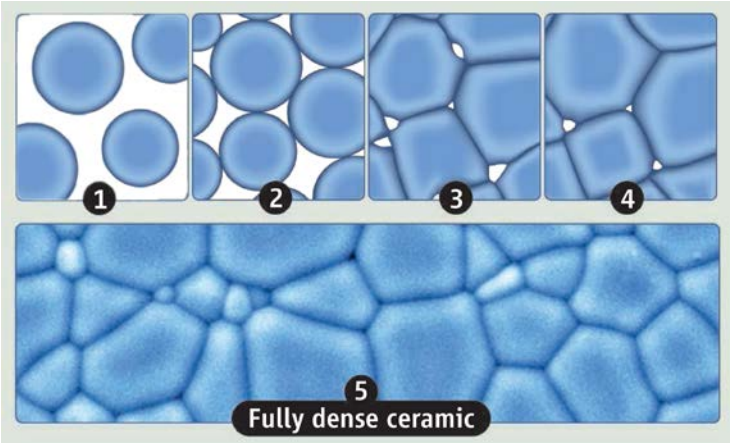
[1] Institute for Single Crystals of NAS of Ukraine, Kharkov, Ukraine;
[2] V. Bakul Institute for Superhard Materials of NAS of Ukraine, Kiev, Ukraine;
[3] Ural Federal University, Yekaterinburg, Russia

Two Approaches to Pore-free Optical Ceramics

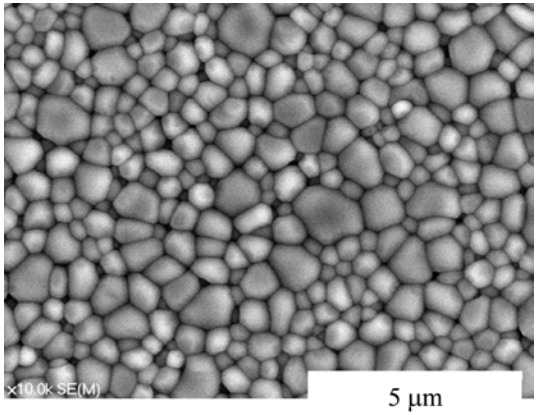


Scattering centers in optical ceramics
[A.Ikesue, Nature Photonics, V.2, 2008, 721]



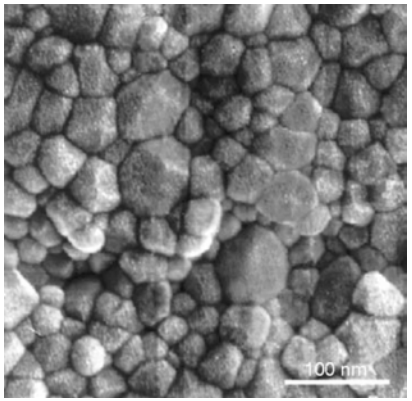
A scheme to obtain optical pore-free ceramics
[G.L.Messing, Science, V.322, 2008, 383]

Decreasing concentration of scattering centers – fine grained ceramics (1-100 μm)



Fine-grained RE_2O_3 laser ceramics
[H.Yagi, LCS-2010]

Decreasing size of scattering centers below critical limit – nanograined ceramics (<100nm)

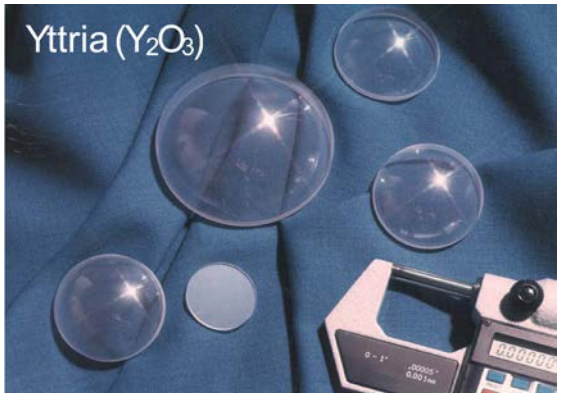


Nanograined Y_2O_3 ceramics
[I.-Wei Chen, Nature, V. 404, 2000, 168]

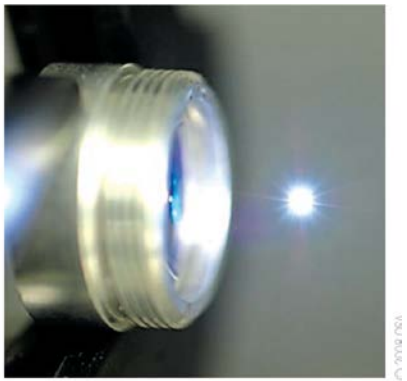
Applications of Optical Ceramics

Lamp Envelopes, Lenses, Windows, etc.

TOTO (Japan)



Raythran, Raytheon (USA)



Institute for Molecular Science, Japan,

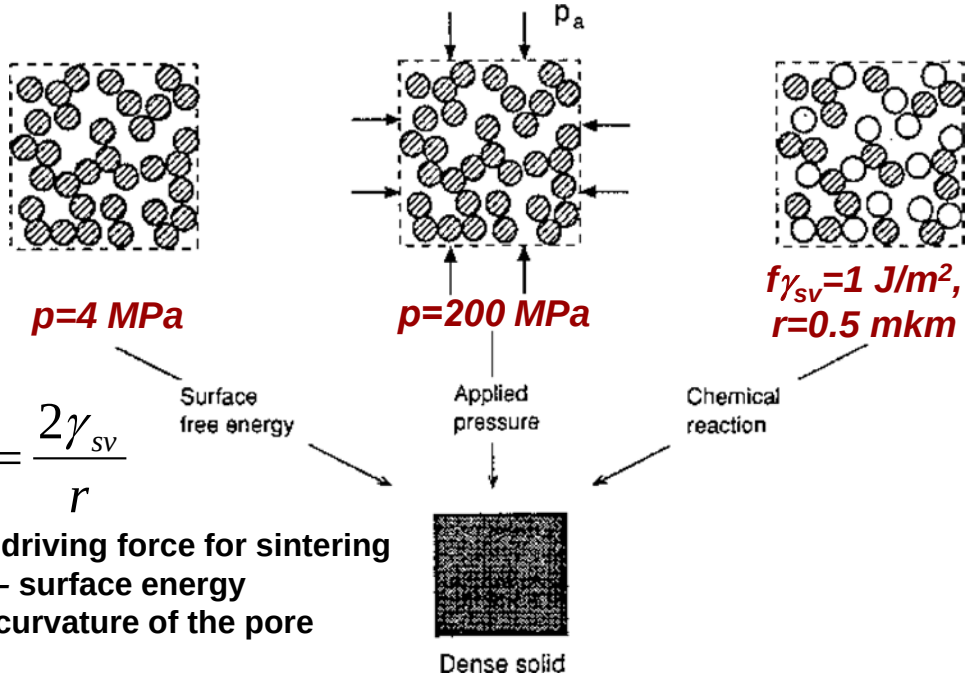
Konoshima Chemical Co. (Japan)

High-power Lasers (100 kW CW already achieved)

Scintillators

LLNL, Livermore (USA)

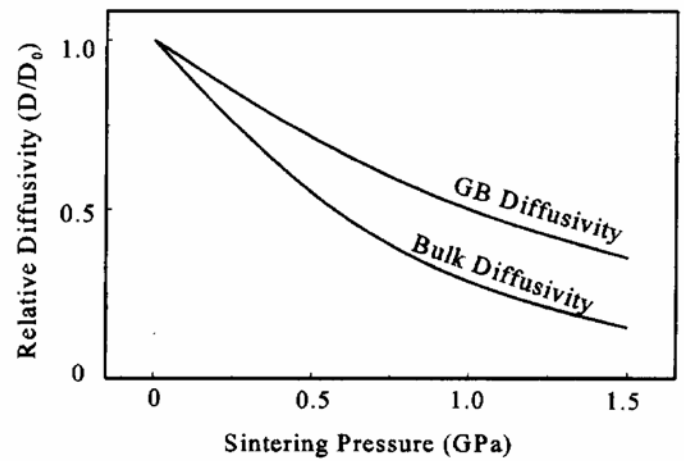
Formation of Optical Ceramics



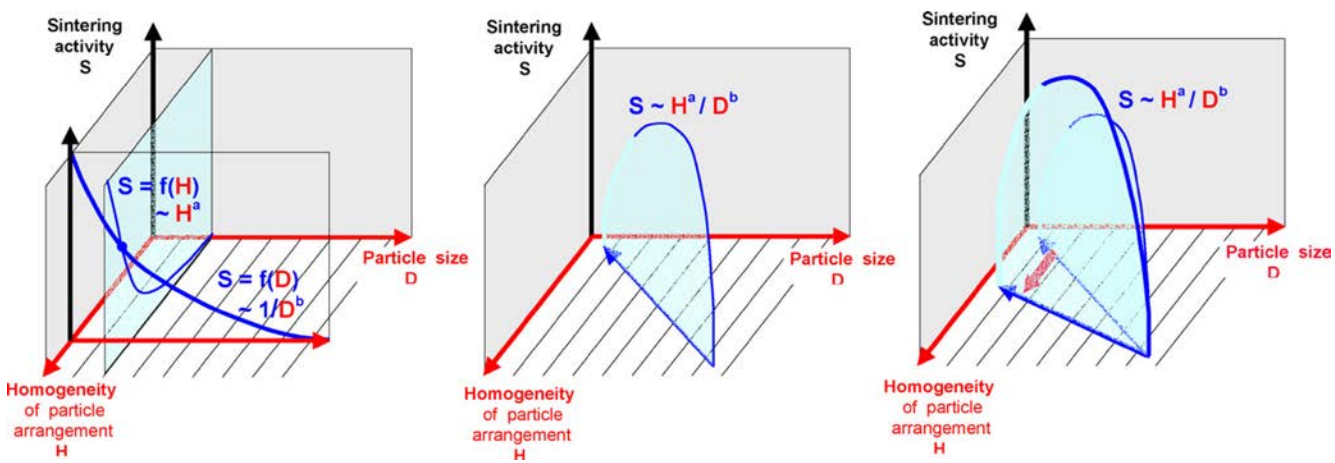
$$p = \frac{2\gamma_{sv}}{r}$$

p – driving force for sintering
γ_{sv} – surface energy
r – curvature of the pore

Schematic diagram illustrating driving forces of sintering



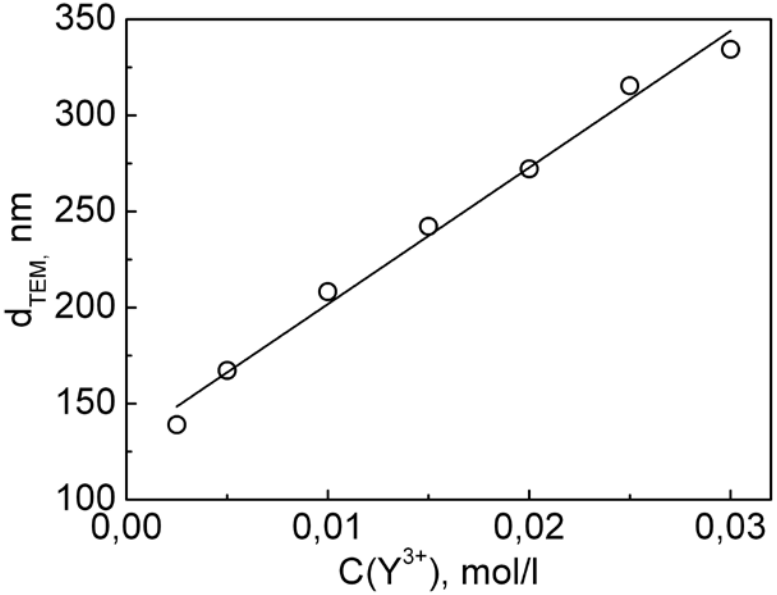
Diffusivity of TiO_2 vs. consolidation pressure
[S.C.Liao et al. Acra mater.,1997. 45,4027]



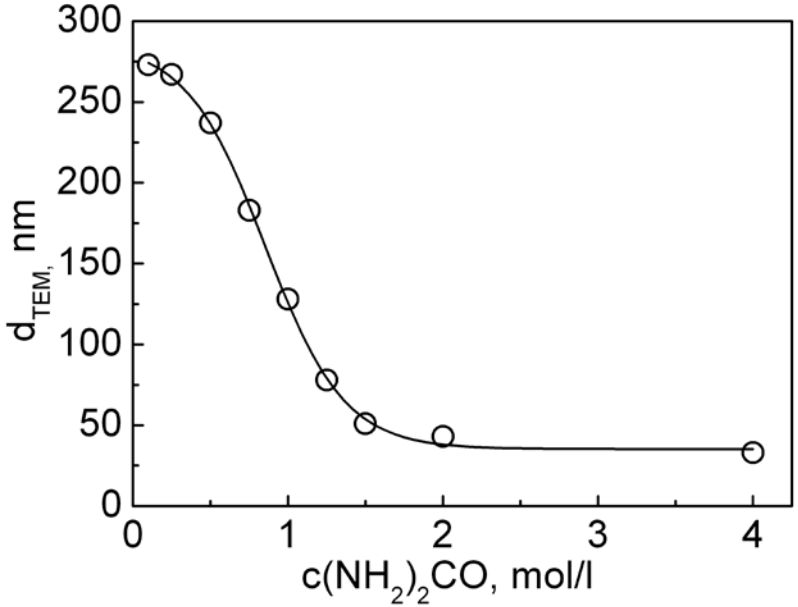
Influence of homogeneity of particle arrangement and particle size on sintering activity of powders
[A.Krell et al. J.Europ.Ceram.Soc. 29, 2009, 207]

Fabrication of Pure and Doped Y_2O_3 Nanospheres

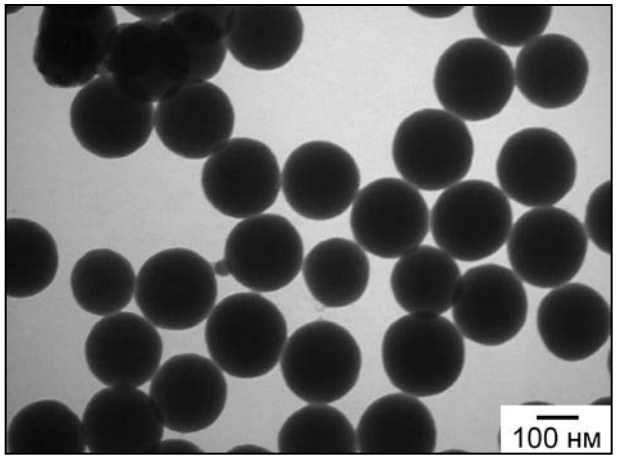
Homogenous chemical co-precipitation method. Starting reagents: Yttrium chloride of nitrate; Precipitant: Urea; T=85-95 C



Average diameter of precursor particles vs. concentration of Y^{3+} ions (C(urea)=0.5 mol/)

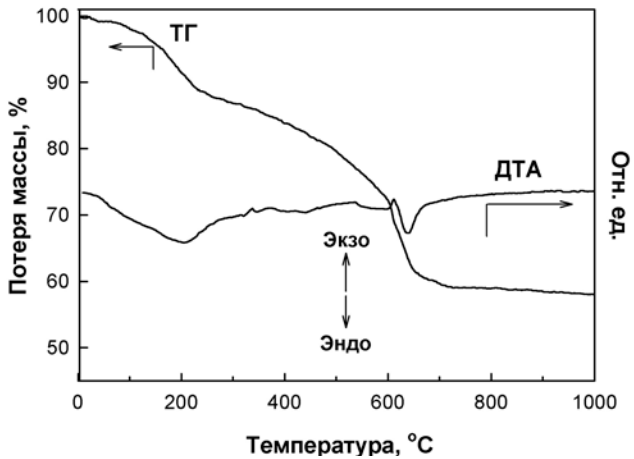


Average diameter of precursor particles vs. urea concentration ($C(Y^{3+})$=0.015 mol/l)

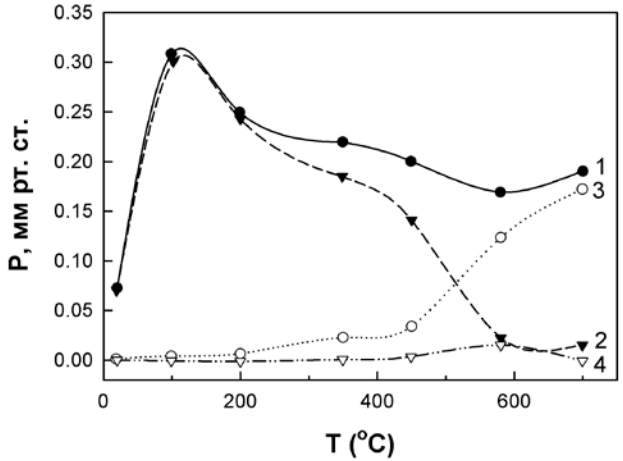


TEM image of yttria precursor

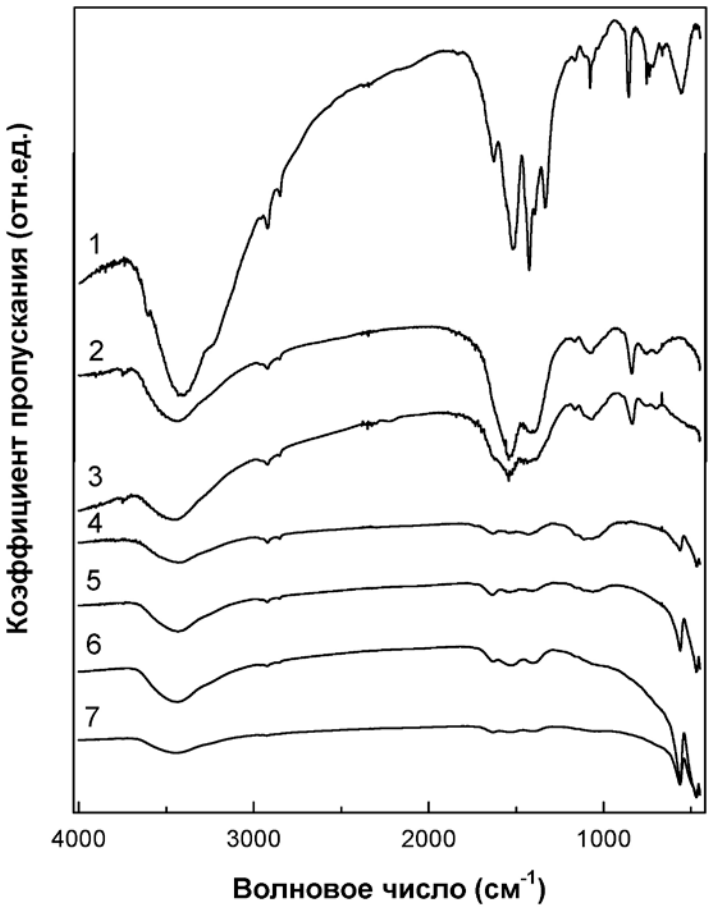
Thermal Decomposition of $Y(OH)CO_3 \cdot nH_2O$ Precursor



DTA/TD traces of then yttria precursor



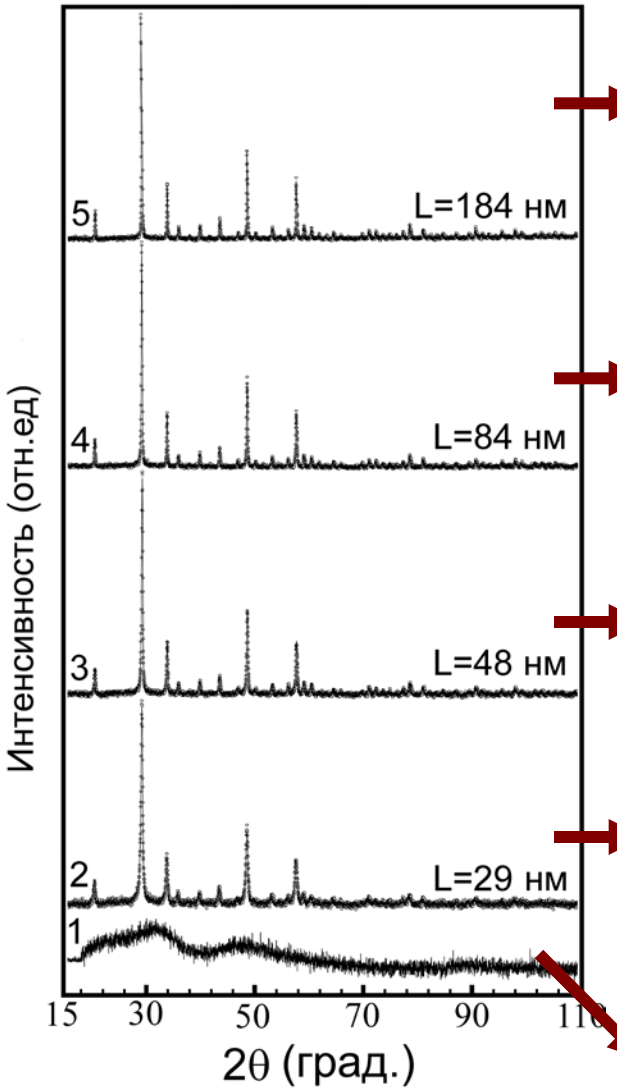
Pressure of the gases releasing during decomposition of yttria precursor: 1 – general, 2 – H_2O, 3 – CO_2, 4 – CO



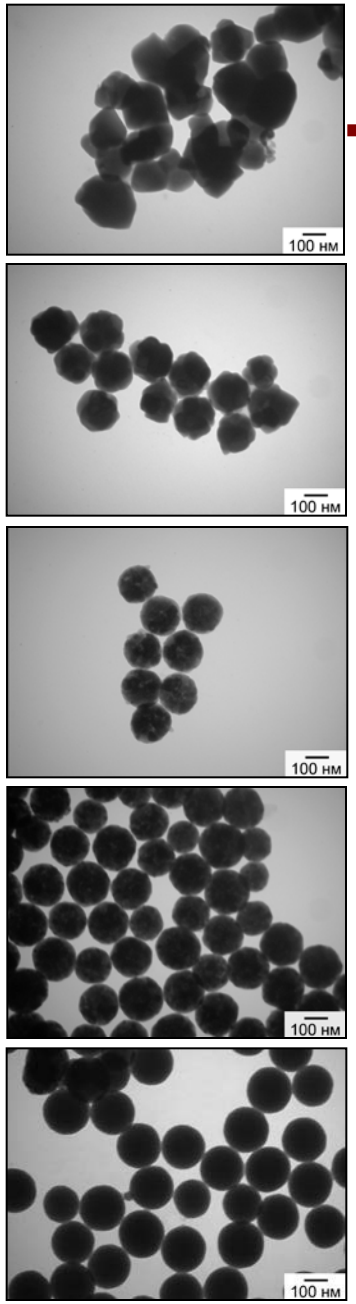
IR spectra of precursor (1) and Y_2O_3 nanopowders calcined at 200 (2); 400 (3); 600 (4); 800 (5); 1000 (6) and 1200°C (7)

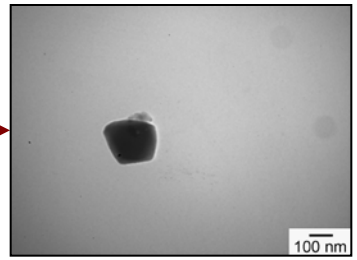
$$(Y_{1-x}Nd_x)(OH)CO_3 \cdot 1.3H_2O \xrightarrow{205\ °C} (Y_{1-x}Nd_x)(OH)CO_3 \xrightarrow{450\ °C} (Y_{1-x}Nd_x)_2O(CO_3)_2 \text{ и } (Y_{1-x}Nd_x)_2O_2CO_3 \xrightarrow{645°C} (Y_{1-x}Nd_x)_2O_3$$

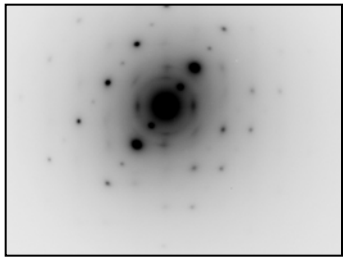
Influence of Calcination Temperature

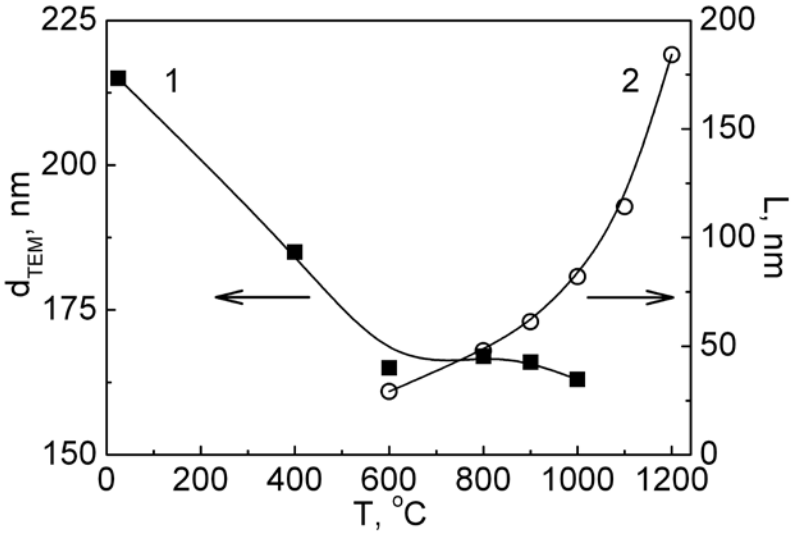


XRD patterns of Y_2O_3 nanopowders calcined at 400 (1); 600 (2); 800 (3); 1000 (4) and 1200°C (5)





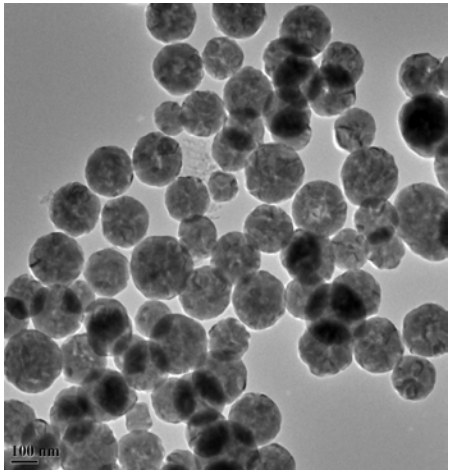


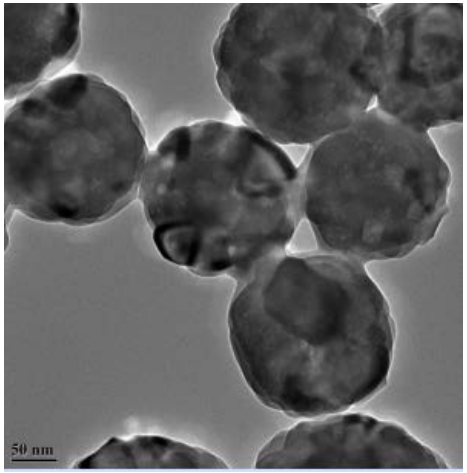


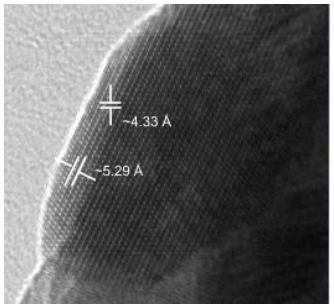
Y_2O_3 particle diameter (1) and average crystallite size (2) vs. calcination temperature

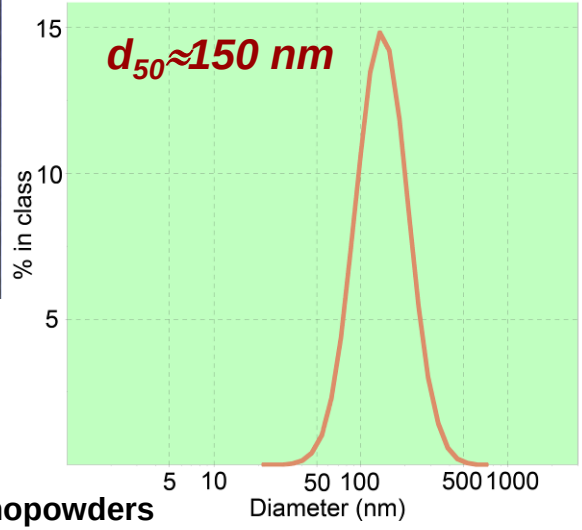
$Y_{1-x}RE_x(OH)CO_3 \cdot nH_2O$ amorphous precursor → intermediate products → porous polycrystalline $(Y_{1-x}RE_x)_2O_3$ spherical particles → aggregated single-crystalline $(Y_{1-x}RE_x)_2O_3$ particles

Consolidation of Y_2O_3 Nanopowders under HP









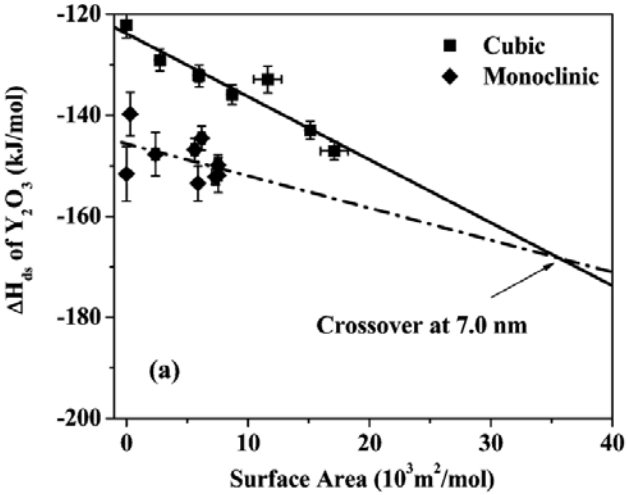
Morphology and granulometric composition of Y_2O_3 nanopowders

Advantages of monosized Y_2O_3 nanospheres:

- Phase stability of nanopowders;
- Possibility to adjust particle size, crystallite size and porosity;
- Possibility to realize close-packed structures;
- Possibility to modify surface and pore subsystems;
- Higher sintering activity of polycrystalline particles
- compared to single crystalline ones

Characteristics of 125 nm monosized Y_2O_3 nanospheres:

- Cubic Y_2O_3 content - 100 %;
- Average particle diameter - 125 nm;
- Standard deviation in particle size ≤10 %;
- Specific surface area - 16 m^2/g (5.1 m^2/g for single-crystalline analogues);
- Average particle size - 37 nm;
- Average pore size – 5-10 nm;
- Porosity – 10-20 %



Entalpy dependence on the specific surface of Y_2O_3 particles [Zhang P, J. Phys.Chem.C 112 (2008) 932]

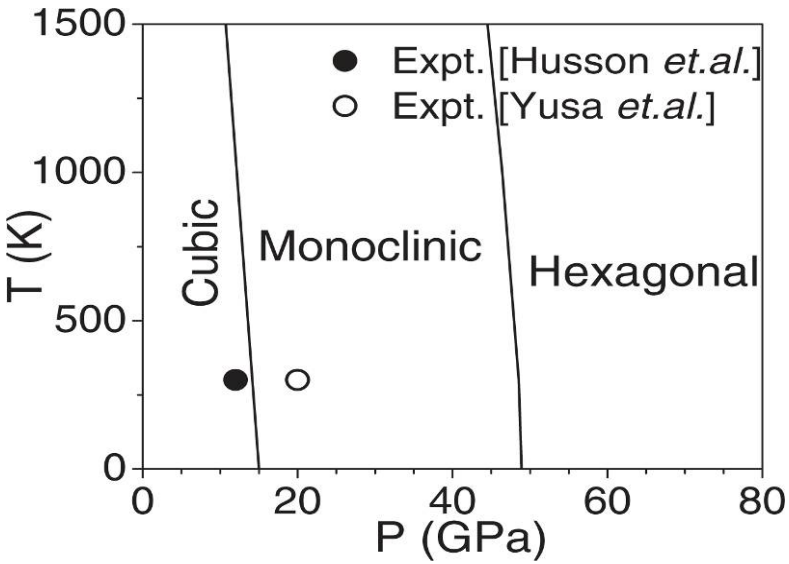
d≤7.0 nm → monoclinic phase
d≥7.0 nm → cubic phase

Transformation-assisted Consolidation of Nanopowders

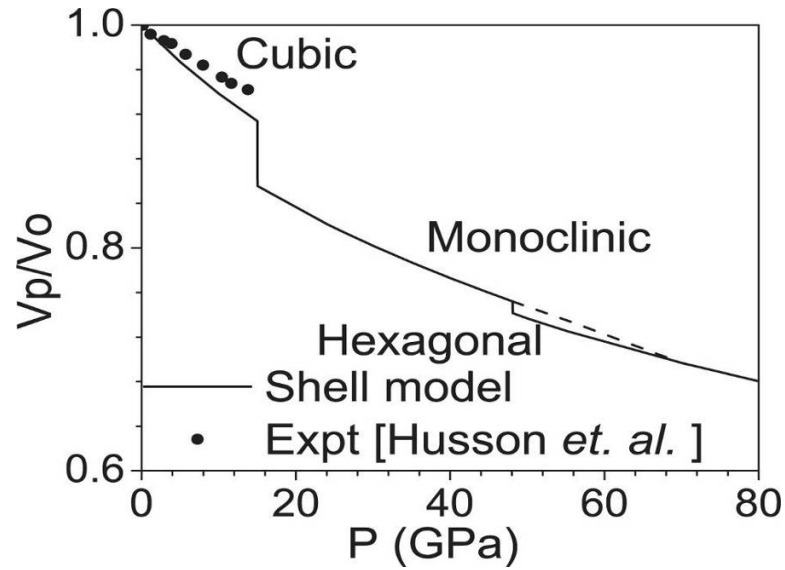
Methods to produce yttria nanograined ceramics:

- **Two step sintering**
- **Spark Plasma Sintering;**
- **Reversible phase transitions;**
- ***Transformation assisted consolidation under high pressures (only TiO_2, Al_2O_3)***

No transparency or translucency achieved at this time



The calculated P-T phase diagram of Y_2O_3 [P.P.Bose, Phys.Rev.B 84, 094301 (2011)]



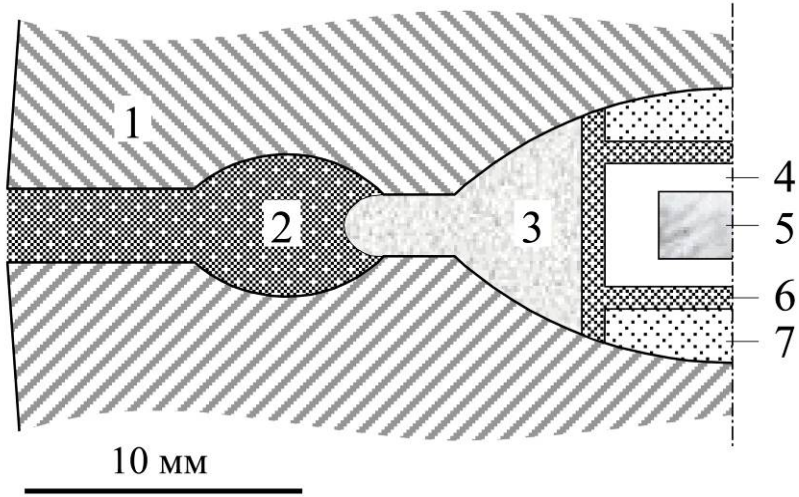
The calculated equation of state for various Y_2O_3 phases [P.P.Bose, Phys.Rev.B 84, 094301 (2011)]

C→B – reconstructive phase transition $\Delta V_{C\to B}$ **= 7 %** **(P=8.6-15 GPa)**

B→A – martensitic phase transition $\Delta V_{B\to A}$ **= 2 %** **(P=12.1-22.5 GPa)**

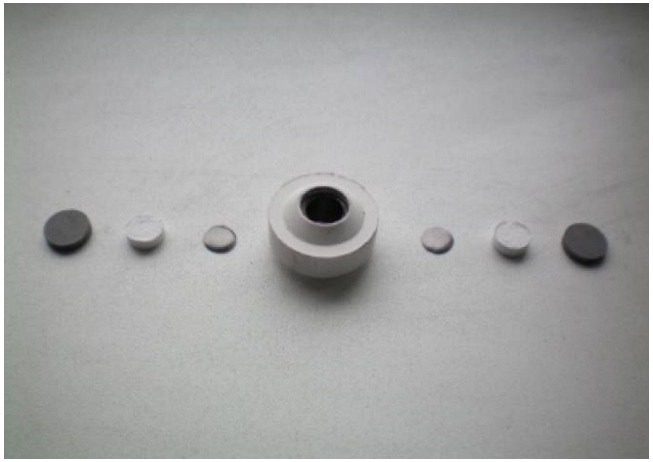
Transformation-assisted Consolidation of Nanopowders

Consolidation conditions: P=0.5-8 GPa; T=25-2000 °C; t=10-1000 s

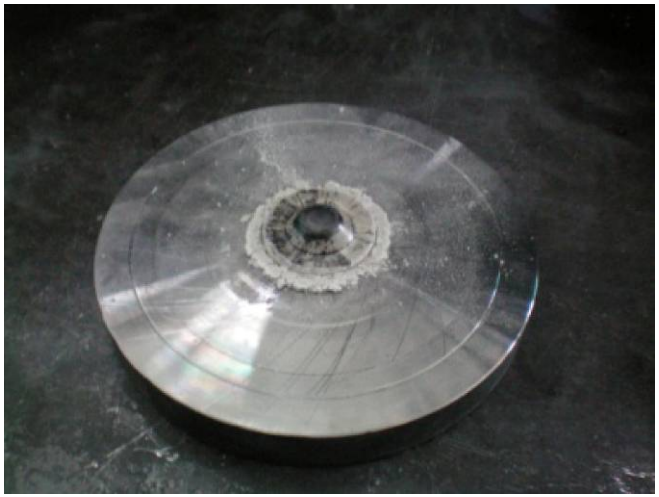


High pressure cell in compressed state (a half of cross section)

1 – toroidal apparatus ; 2 – lithograph stone; 3 – container from lithograph stone; 4 – boron nitride capsule; 5 – sample; 6 – graphite heater; 7 – thermal isolation.

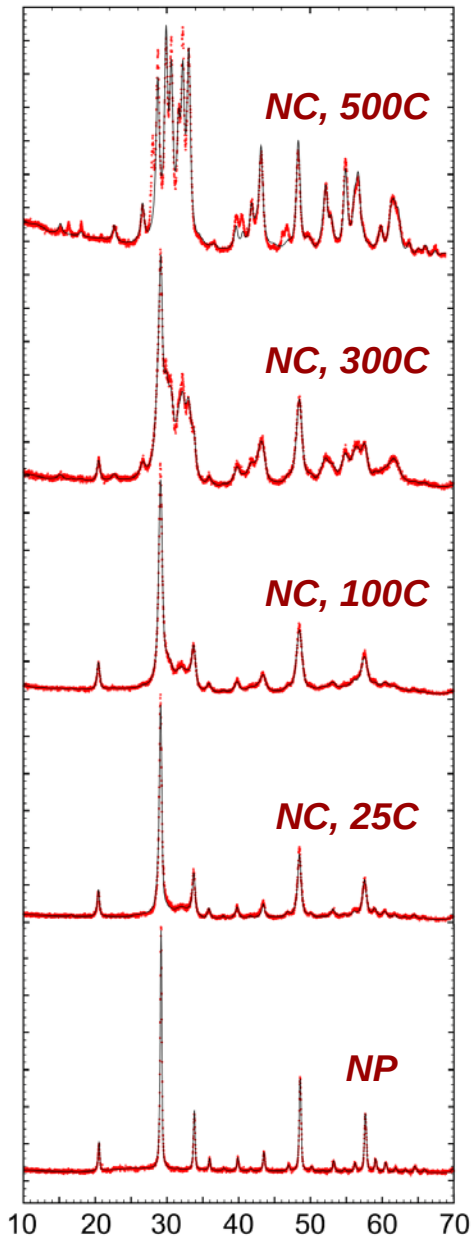


High pressure cell (picture from UNIPRESS)

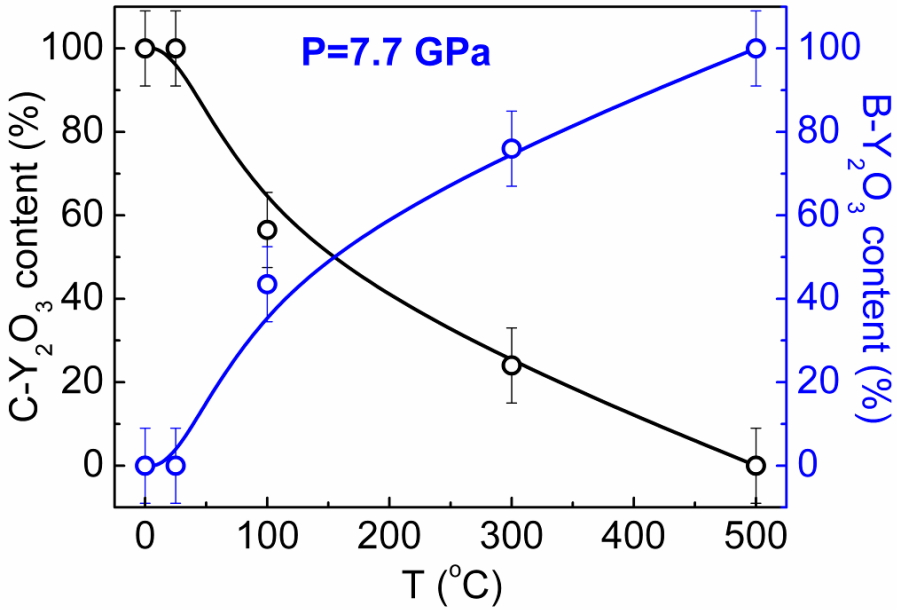


High pressure cell (picture from UNIPRESS)

Phase Composition of Y_2O_3 Nanoceramics



XRD patterns of Y_2O_3 NP and NC



Phase composition of Y_2O_3 nanoceramics vs. consolidation temperature

Lattice parameters

Measured

Cubic (C) Y_2O_3
sp.gr. Ia3, Z=16;
a=10.6190(5) Å;
V=1197.44(1) Å³
ε=0.87 %

Monoclinic (B) Y_2O_3
sp.gr. C2/m, Z=6
a=14,026(5),
b=3,5188(10),
c=8,601(3) Å,
β=100,59(3)°,
V=417,3(3)Å³,
ε=1.7 %

Calculated

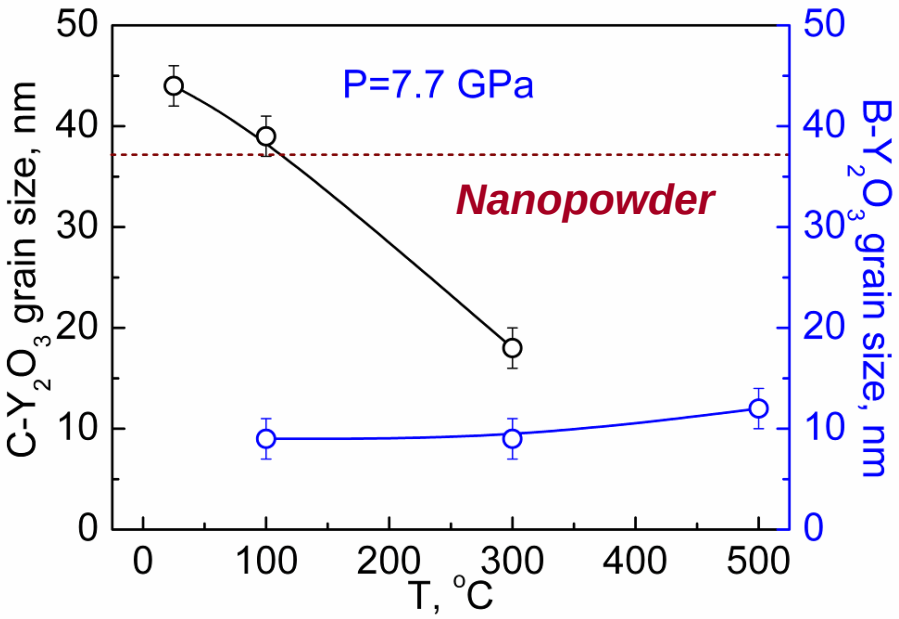
Cubic (C) Y_2O_3
sp.gr. Ia3, Z=16;
a=10.61 Å;
V=1192.36 Å³

Monoclinic (B) Y_2O_3
sp.gr. C2/m, Z=6
a=13,6755,
b=3,4501,
c=8,4878 Å,
β=99,933°,
V=?

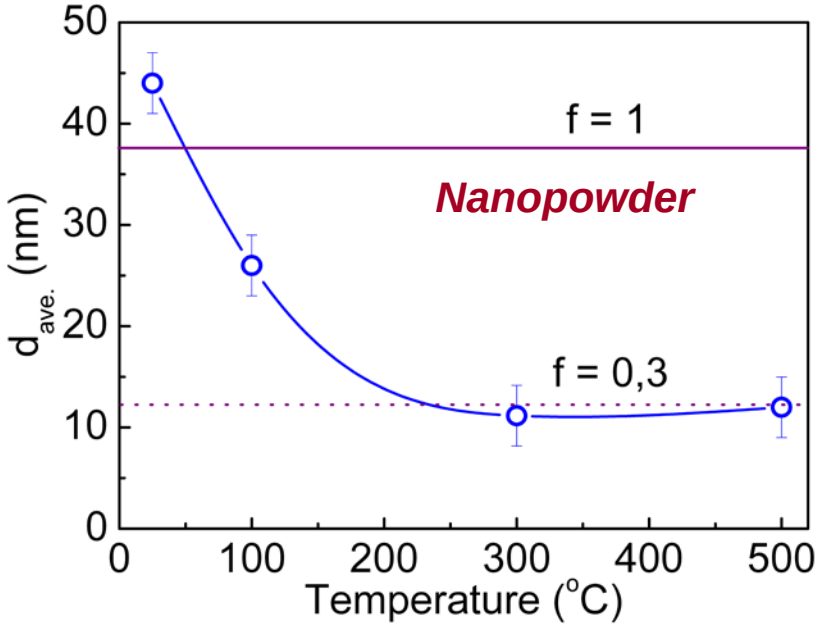
[P.P.Bose, Phys.Rev.B ,2011, 84, 094301]
[H.Yusa, Inorg.Chem. 2010, 49, 4478]

Grain Size of Y_2O_3 Nanoceramics

Consolidation conditions: P=8 GPa; T=25-500 °C; t=30 s



Grain size of Y_2O_3 nanoceramics vs. consolidation temperature

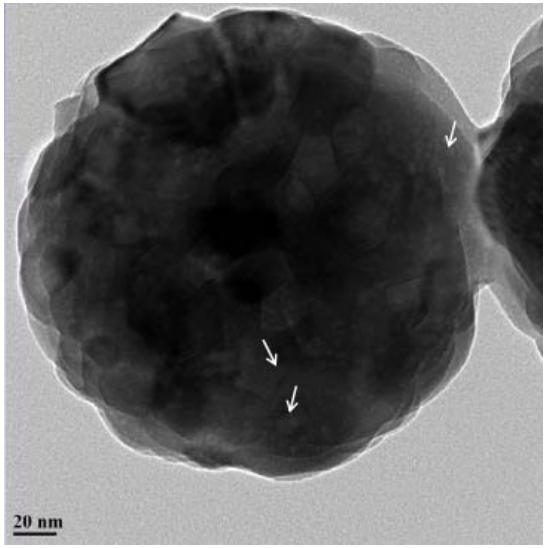


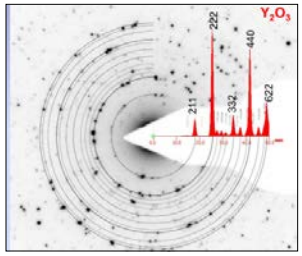
Average grain size of Y_2O_3 nanoceramics vs. consolidation temperature

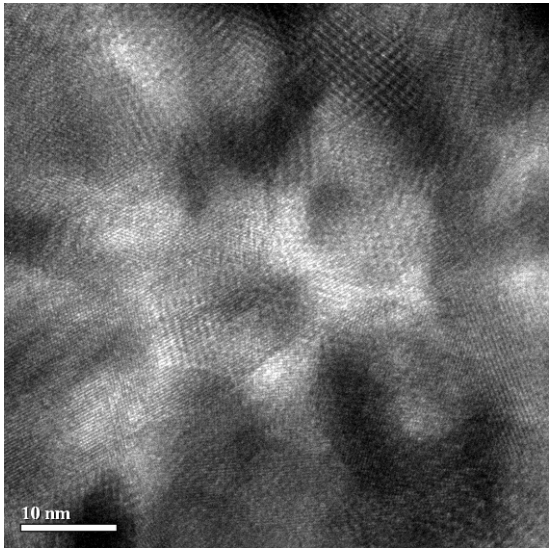
It is possible to obtain nearly full-dense yttria nanoceramics with grain size 3 times lower than that of starting nanopowders by transformation-assisted consolidation under high pressures

HR TEM of Y_2O_3 Nanopowders and Nanoceramics

Nanopowders



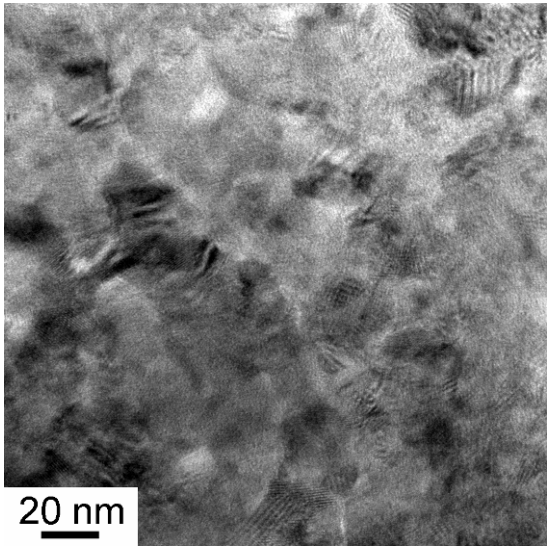


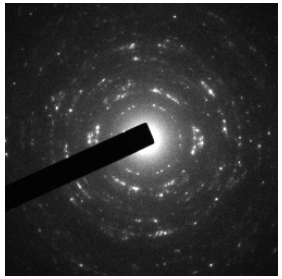


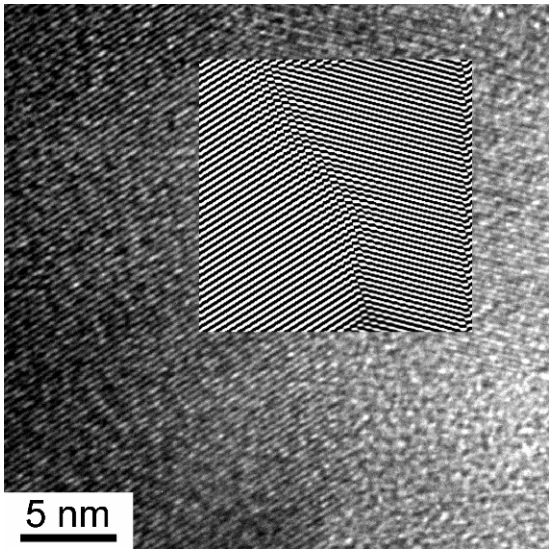
L=37 nm

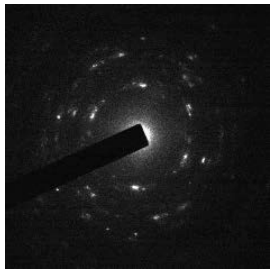
P=8 GPa;
T=(0.1)T_m

Nanograined Ceramics







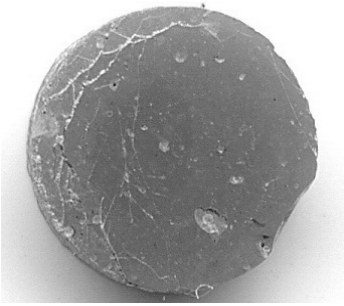


L=14 nm

HR TEM micrographs of Y_2O_3 nanopowders and nanograined ceramics consolidated at P=8 GPa and T=(0.1)T_m

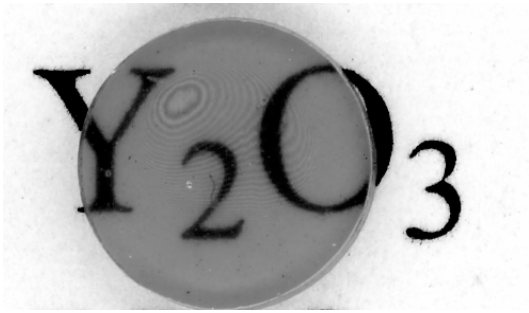
Y_2O_3 Nanograined Ceramics

Cubic (Y_2O_3)



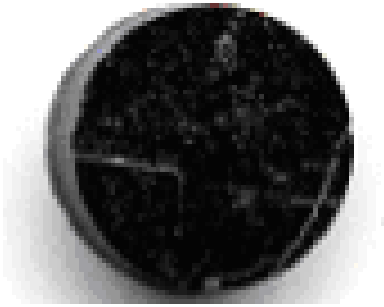
P=8 GPa, T=25°C

Cubic+Monoclinic (Y_2O_3)



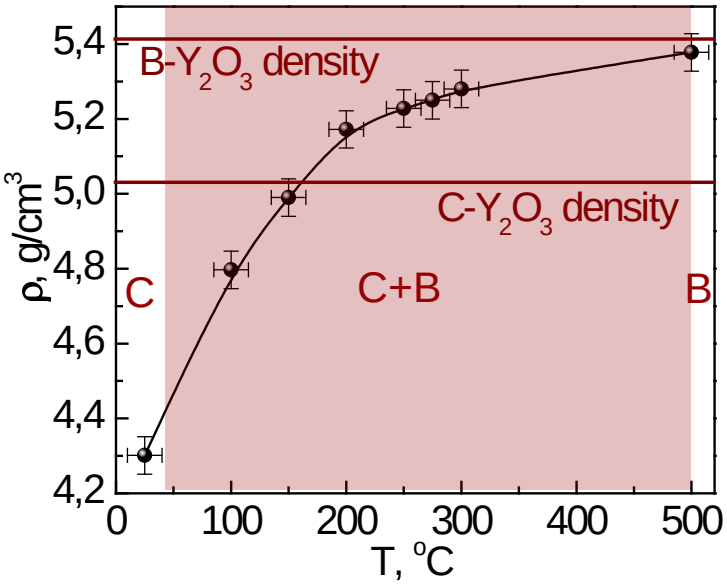
P=8 GPa, T=200°C

Monoclinic (Y_2O_3)

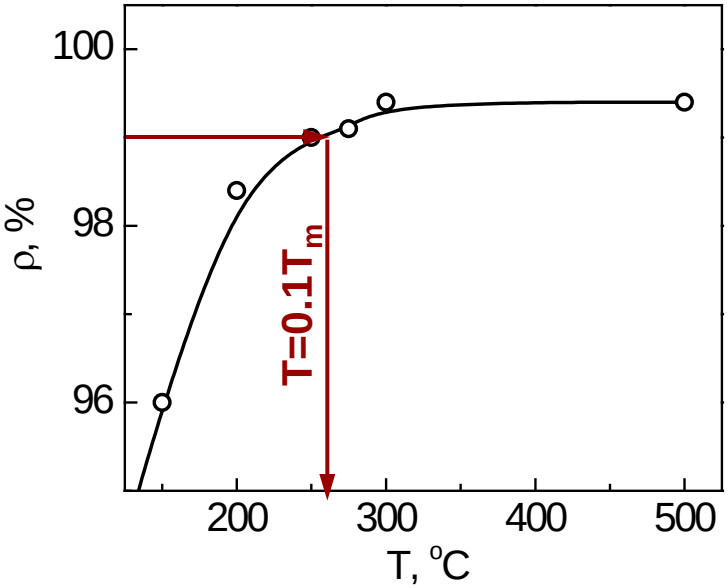


P=8GPa, T=500°C

Appearance of Y_2O_3 nanograined ceramics consolidated at P=8 GPa



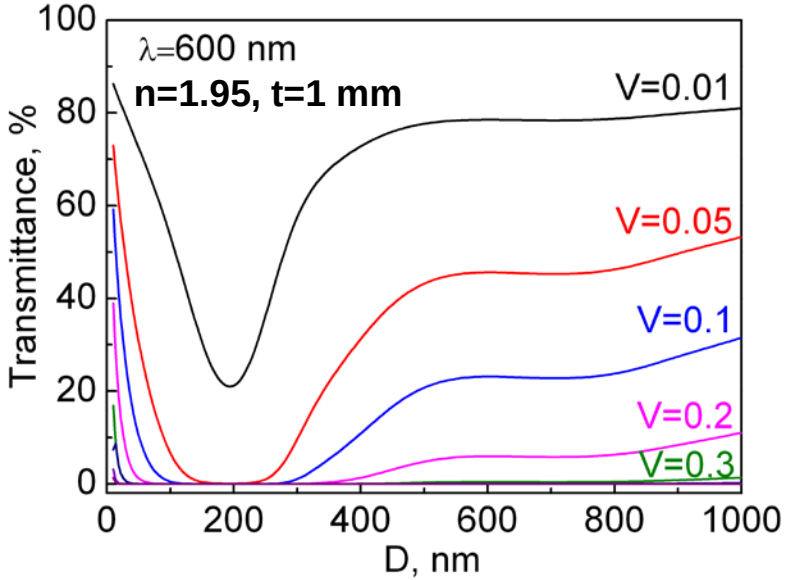
Density of Y_2O_3 nanoceramics vs. consolidation temperature (P=8 GPa)



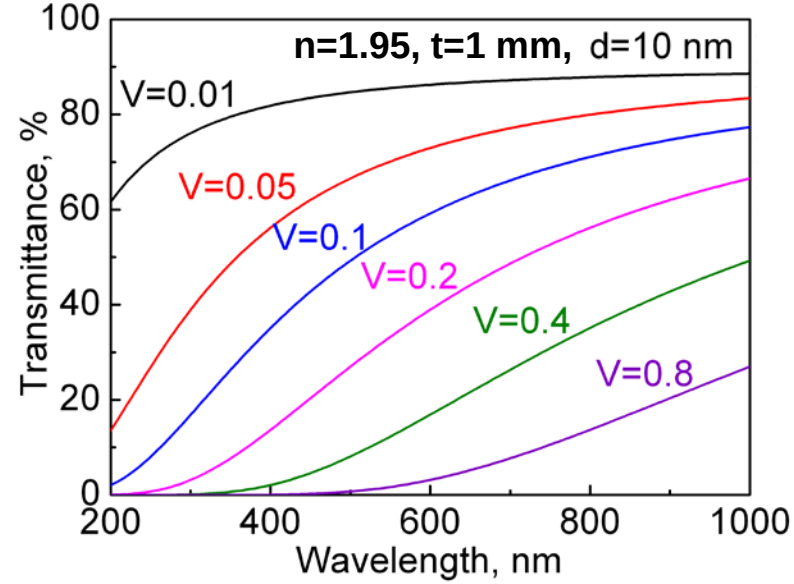
Relative density of Y_2O_3 nanoceramics vs. consolidation temperature (P=8 GPa)

Translucent yttria nanograined ceramics is formed at the temperature of only $0.1T_m$

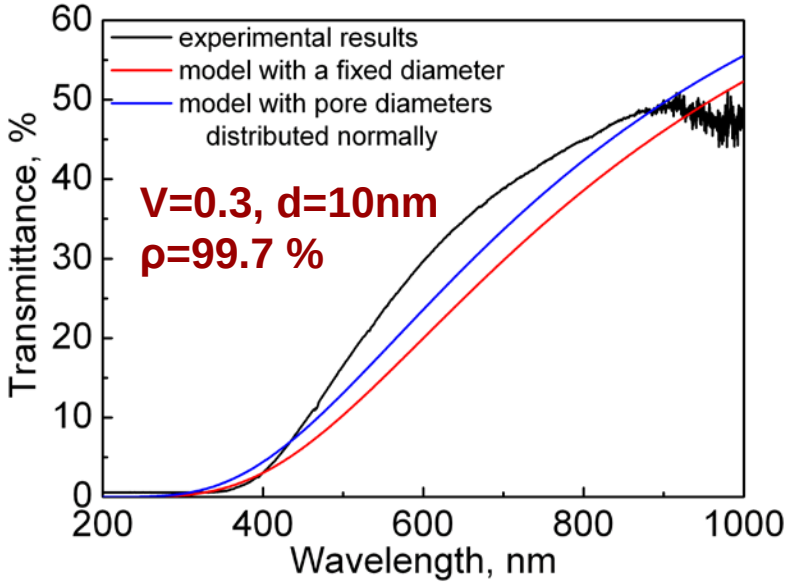
Optical Properties of Y_2O_3 Nanoceramics



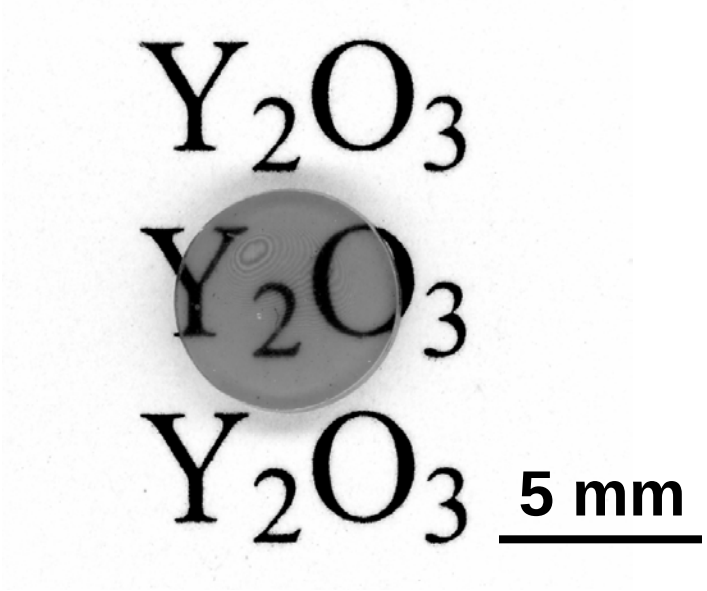
Influence of pore size on relative inline transmission



Influence of porosity on relative inline transmission

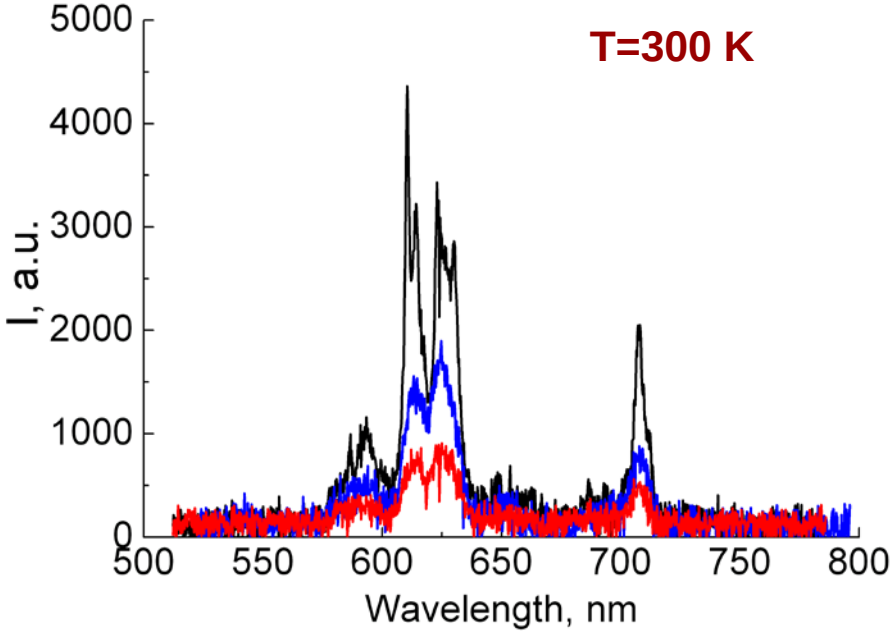


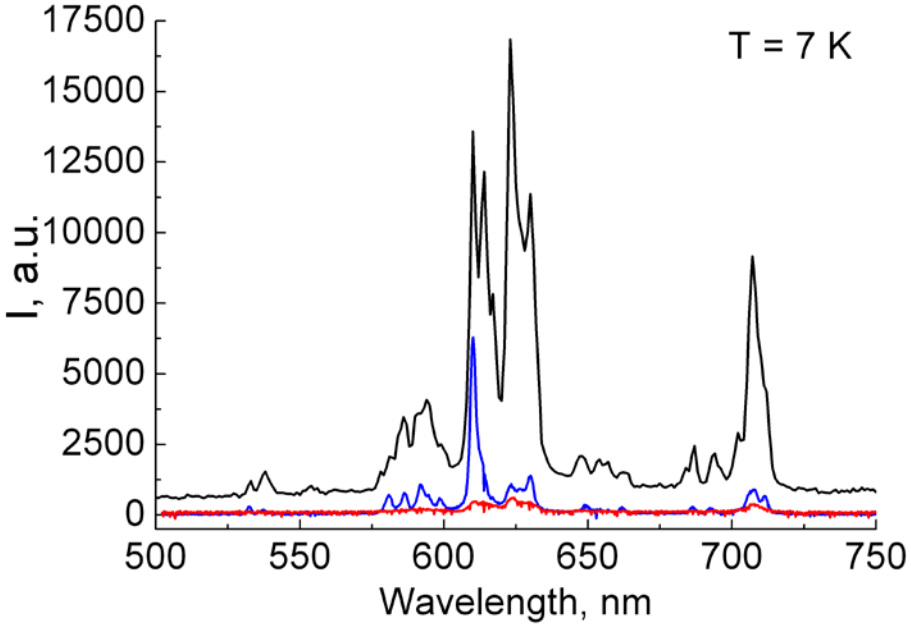
Calculated and measured optical transmittance of Y_2O_3 nanoceramics



Y_2O_3 nanograined ceramics

Luminescence of $Y_2O_3:Eu^{3+}$ Nanoceramics





VUV luminescence spectra of $Y_2O_3:Eu^{3+}$ nanoceramics measured at 300 and 7 K

Luminescence of $Y_2O_3:Eu^{3+}$ nanoceramics is presented by superposition of Eu^{3+} emission from cubic and monoclinic yttria. Wide luminescence band at 575-650 nm is attributed to luminescence from trivalent europium ions placed in perturbed positions (near grain boundaries)

Conclusions

- ***An approach to translucent Y_2O_3 nanograined ceramics by transformation assisted consolidation of isolated nanosphers has been proposed and realized***
- ***We have demonstrated composite translucent nanoceramics with unprecedented low average grain size of 15 nm***