Fabrication of Transparent Ceramics Using Nanopowders Produced by Laser Evaporation

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Fig. 2

Outline

1. Laser synthesis of nanopowders

- Processing
- Advantages of laser method

2. Nd^{3+}(or Yb^{3+}):Y_2O_3-based ceramics

- Annealing of compacts
- Effect of additives on characteristics of ceramics

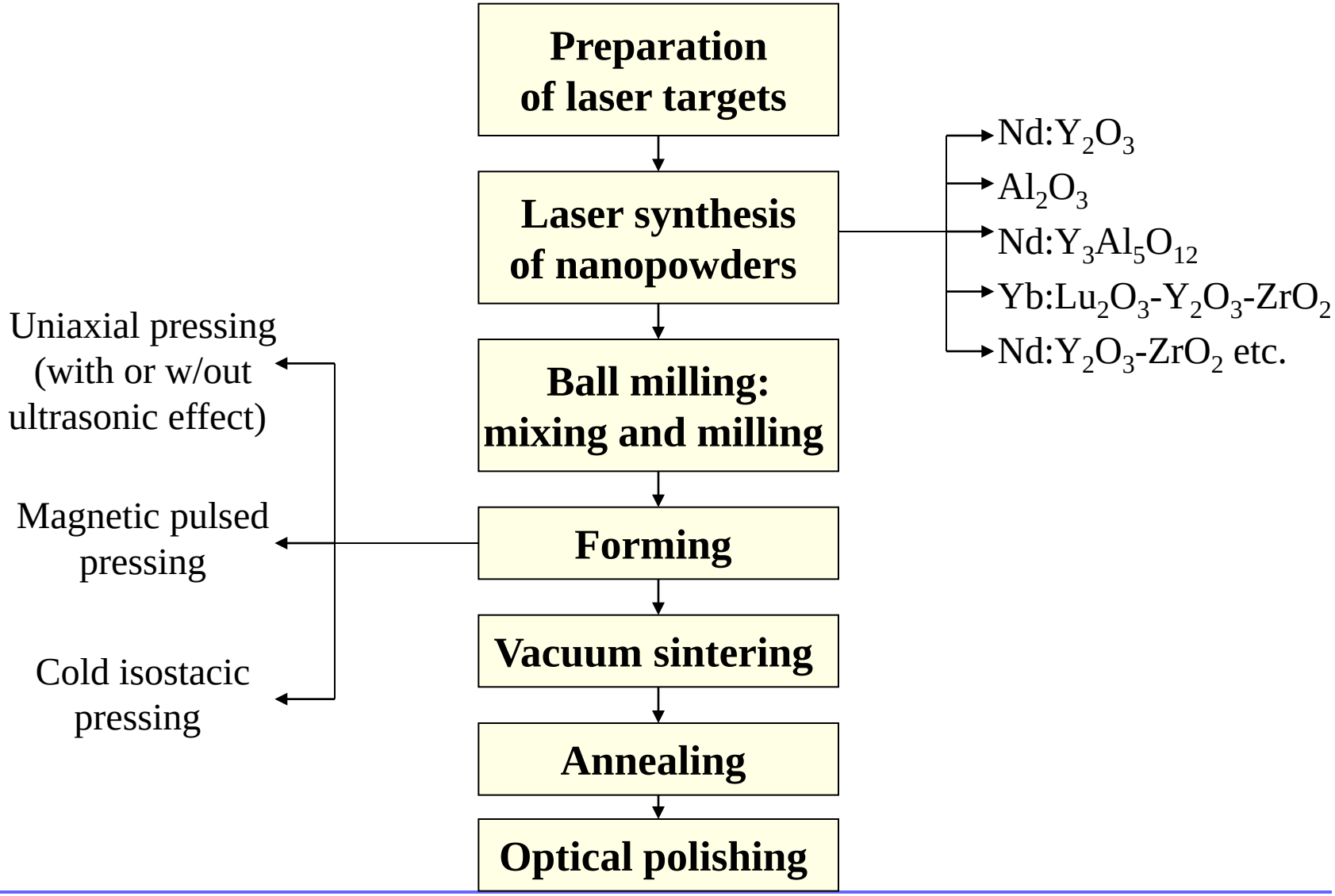
3. Nd^{3+}:YAG ceramics

- Different approaches to synthesis
- Optical and laser characteristics

4. Conclusion

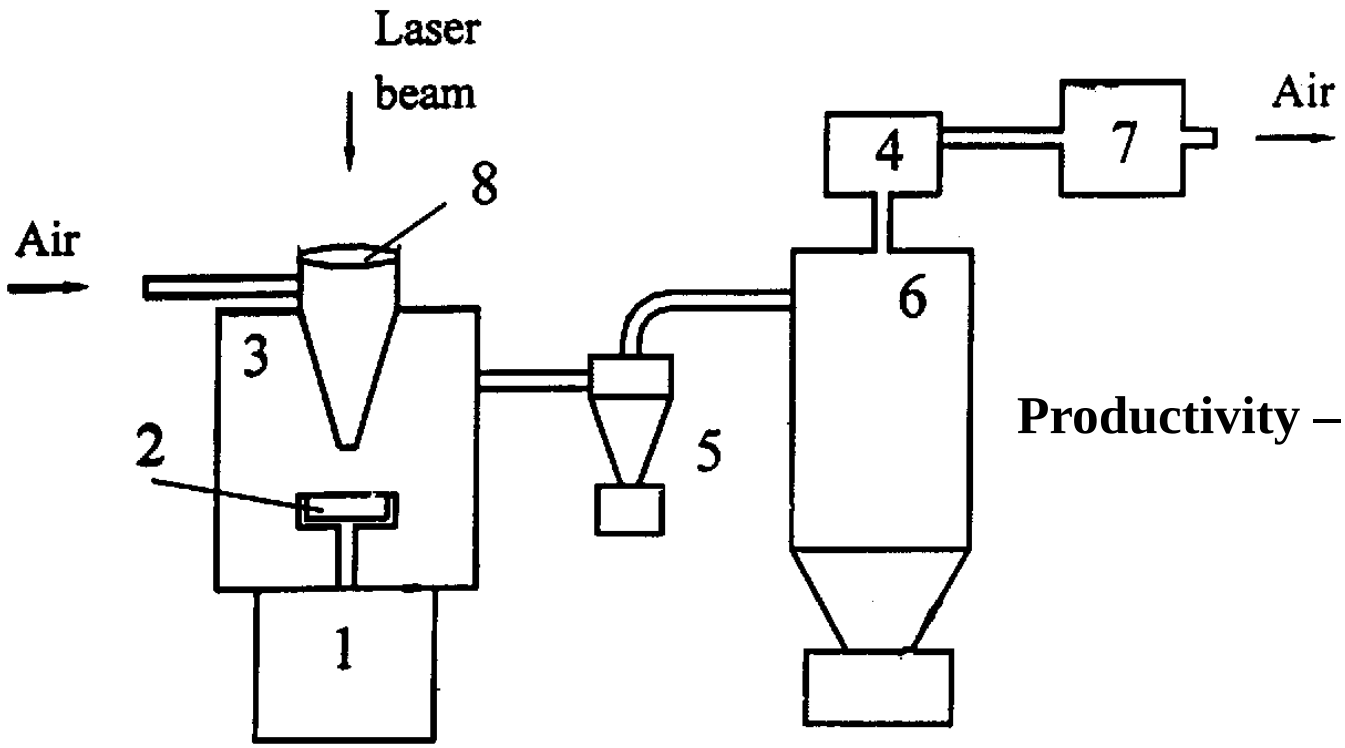
Fig. 3

Fabrication process



Block-scheme of setup for nanopowder obtaining

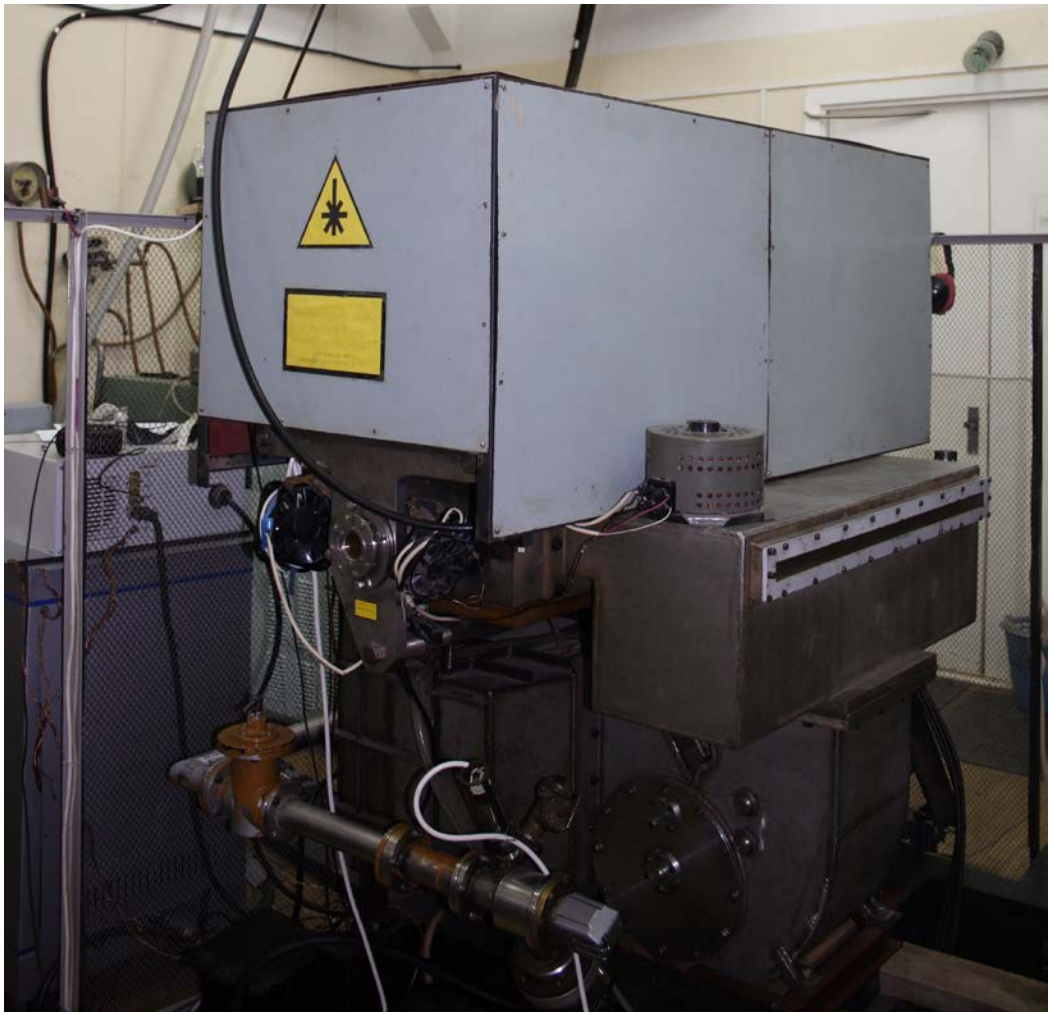
Fig. 4



Productivity – 10-80 g/h

1 - special drive to rotate and move the target linearly in the horizontal plane; **2** – target; **3** - evaporation chamber; **4** – fan; **5** – cyclone; **6** - electrofilter; **7** - mechanical filter; **8** - KCl lens

Fig. 5



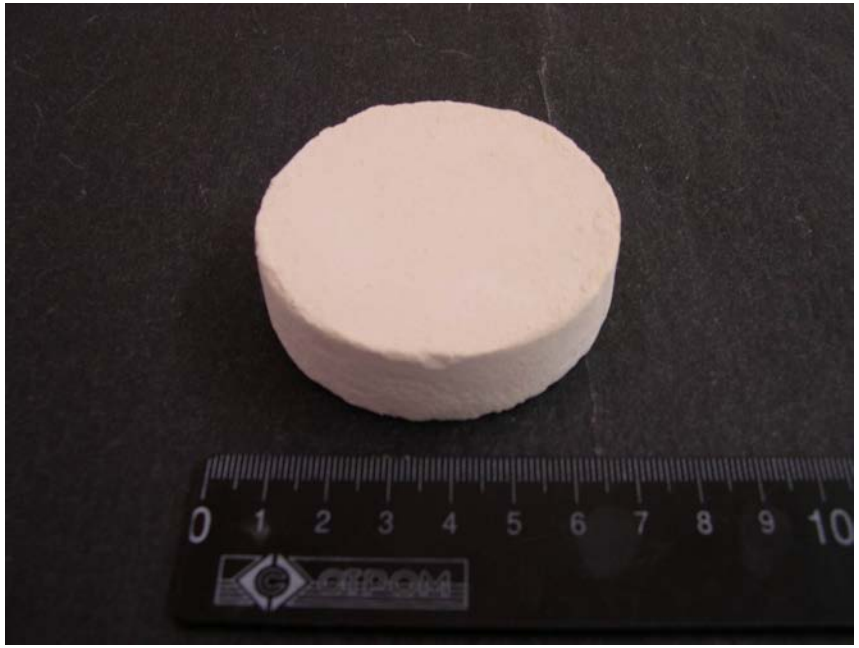
Pulse-repetitive CO_2-laser

- **Wavelength**
  10,6 μm
- **Mean radiation power**
  up to 800 W
- **Peak radiation power**
  8÷11 kW
- **Radiation pulse length**
  140÷250 μs
- **Pulse repetition frequency**
  up to 650 Hz
- **Efficiency**
  ~10%
- **Power consumption**
  10 kW
- **Output rate**
  8÷80 g/h

Fig. 6

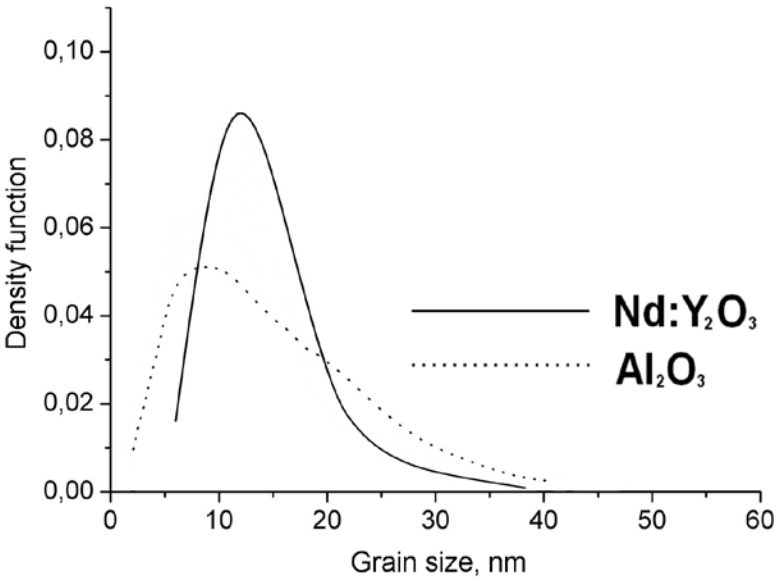
Preparation of laser targets

Coarse powders (4N up purity) → Dry mixing → Uniaxial pressing → Pre-sintering

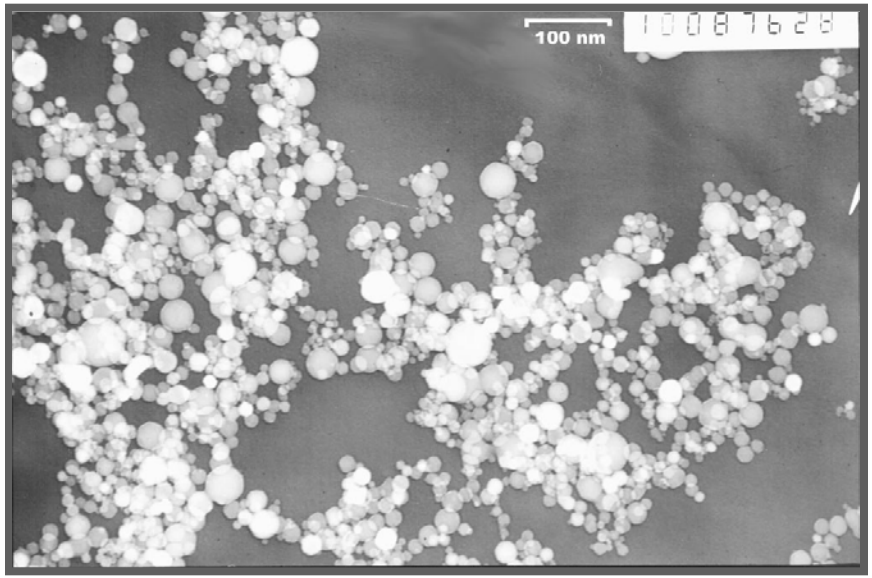


The photos of laser target before and after laser treatment

Fig. 7



Particle size distribution



TEM image of nanoparticles

The characteristics of $Nd:Y_2O_3$ nanopowder after annealing

Average size - 69 nm

Content of cubic phase – 100%

Content of monoclinic phase – 0%

The characteristics of Al_2O_3

Average size - 8 nm

Content of α - phase – 0%

Content of δ - phase – 10-20%

Content of γ - phase – 80%

Fig. 8

Advantages of laser method:

- **Small particle size**, therefore small pore size into compacts, great Laplace pressure and high activity of powders during sintering process;
- **Weak agglomeration of nanopowders**. It is important, because large agglomerates suppress the homogeneous powder packing and produce the defects packing into the green bodies;
- **The purity of nanopowders**, which corresponds to the purity of coarse powders, is obtained easily;
- High evaporation temperature, therefore **high solubility of additional impurities into materials**.

Disadvantage:

- Produced nanopowders have metastable phase.

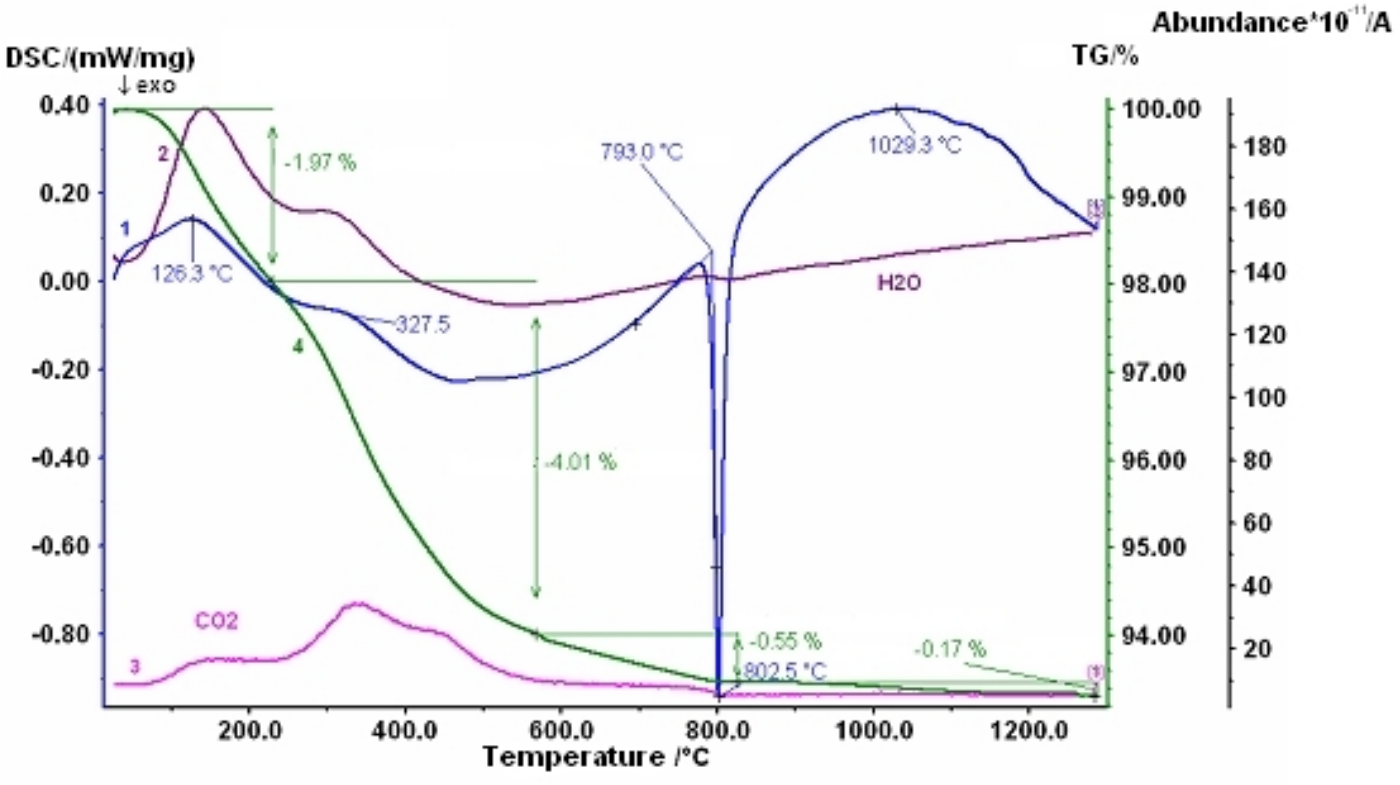
Fig. 9

Main equipment

- Uniaxial static press with ultrasonic effect on nanopowders
- Magnetic pulsed press
- Cold isostatic press
- Air furnace PWK-1,6-5
- Vacuum furnace HTK8W/22-1G HV
- Pulsed cathodoluminescent spectrograph CLAVI
- Scanning electron microscope JEM–2100
- Transmission scanning electron microscope LEO 982 Rentec
- Diffractometer D8 Discover
- Synchronous thermoanalyzer STA449C Jupiter
- Optical microscope OLYMPUS BX51TRF
- High-frequency double-beam spectrophotometer Shimadzu UV-1700
- Spectral system based on monochromator MDR-23 for measurement of luminescent spectra
- Setup for lifetime measurement of excited levels of ions

Annealing of yttria compacts

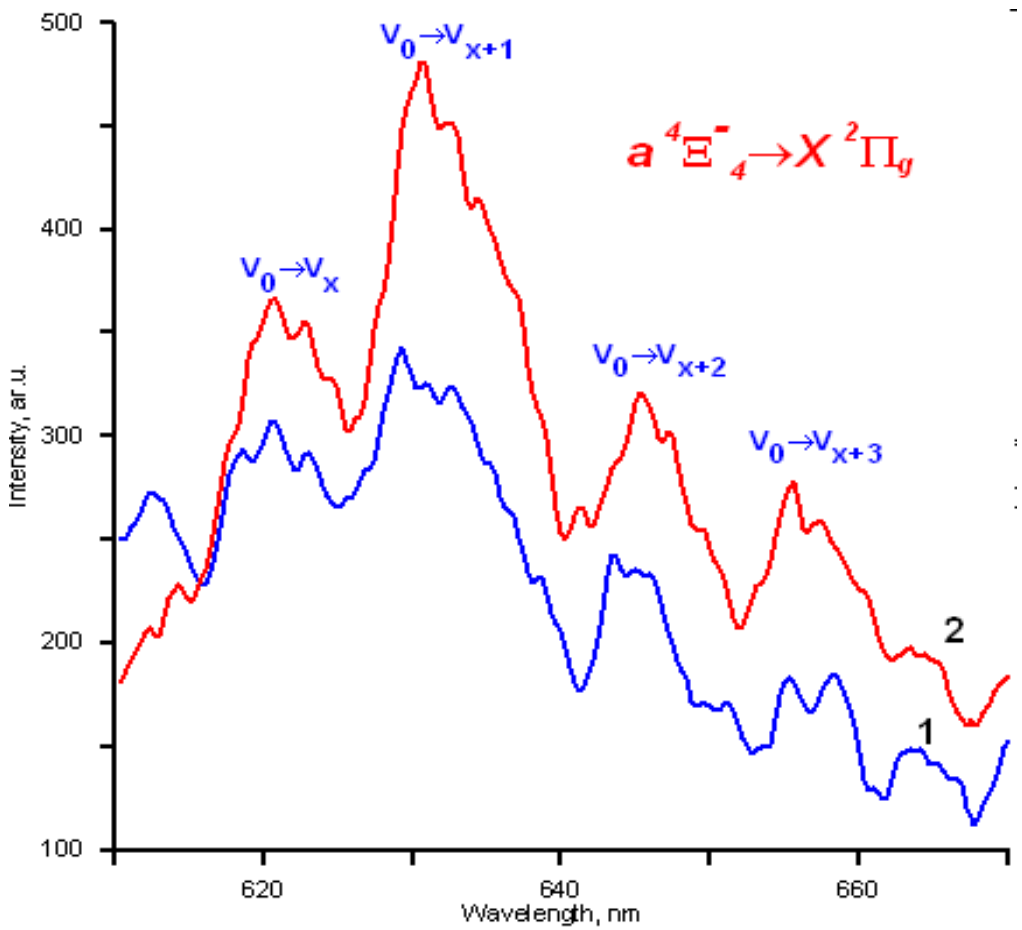
Fig. 10



DSC analysis of $Nd^{3+}:Y_2O_3$ compact

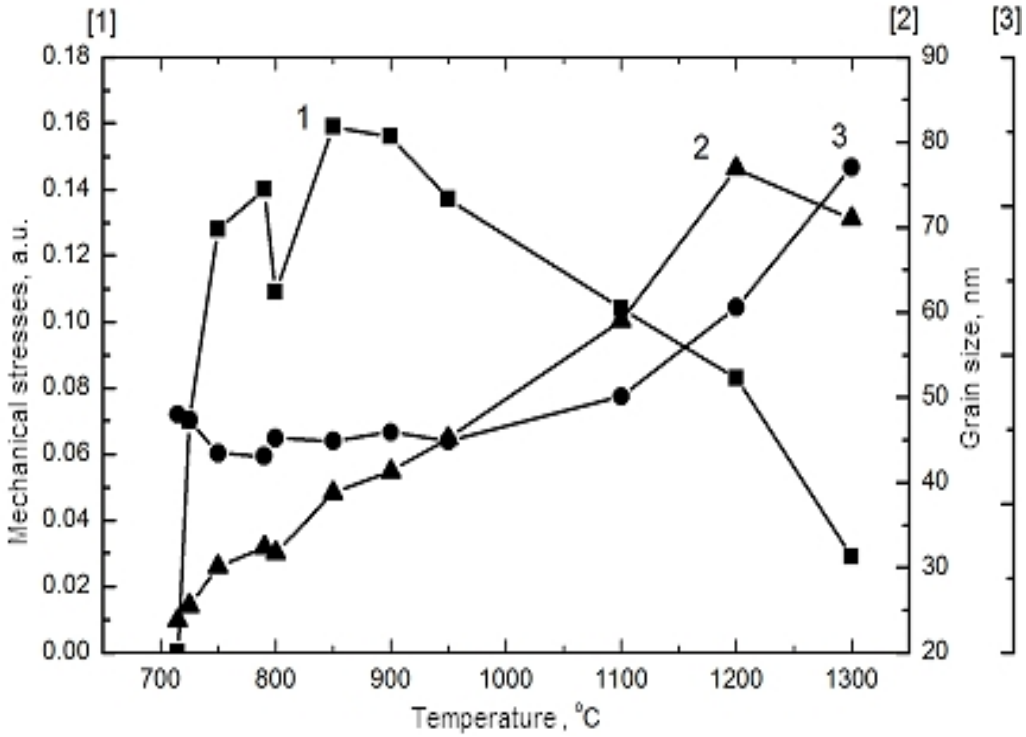
Pulsed cathodoluminescence spectra of O^{2-} molecular ions

Fig. 11



Pulsed cathodoluminescence spectra of Nd:Y_2O_3 compact annealed at 950 ºC (1) and 1300 ºC (2)

Fig. 12



Behavior of mechanical stresses (1), grains size (2) and compact density (3) vs. annealing temperature

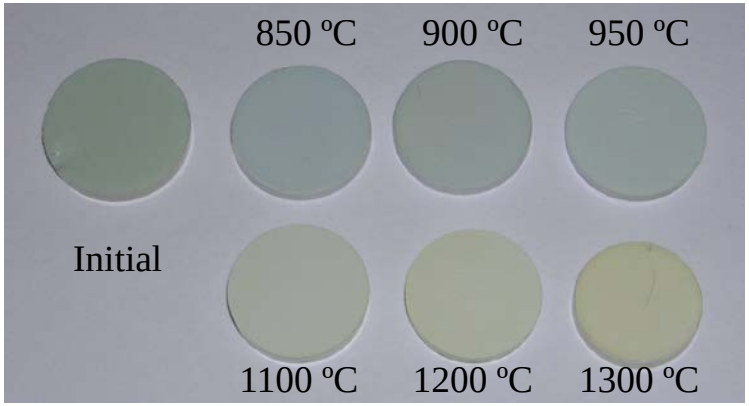


Photo of green bodies annealed at different temperatures

Fig. 13

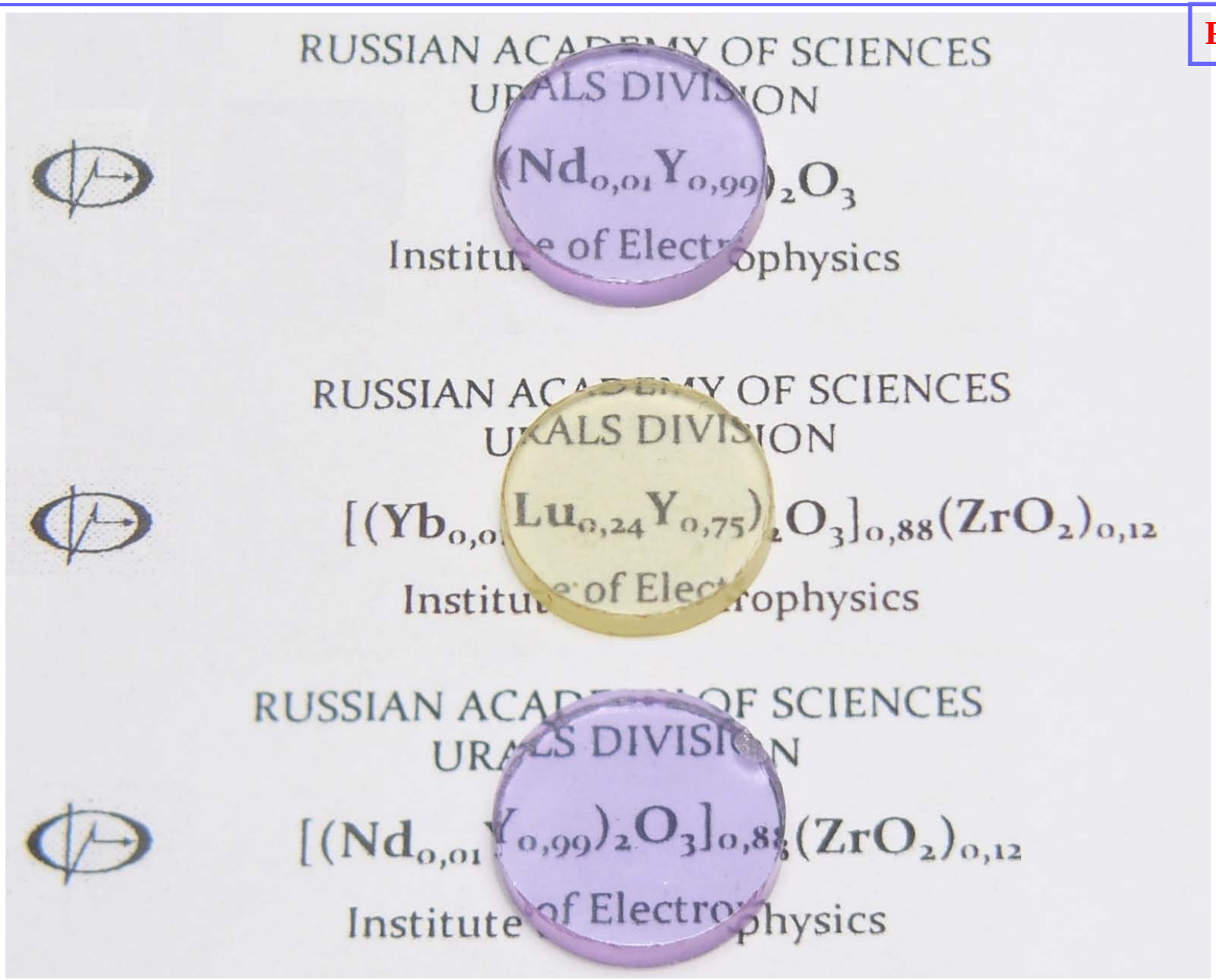


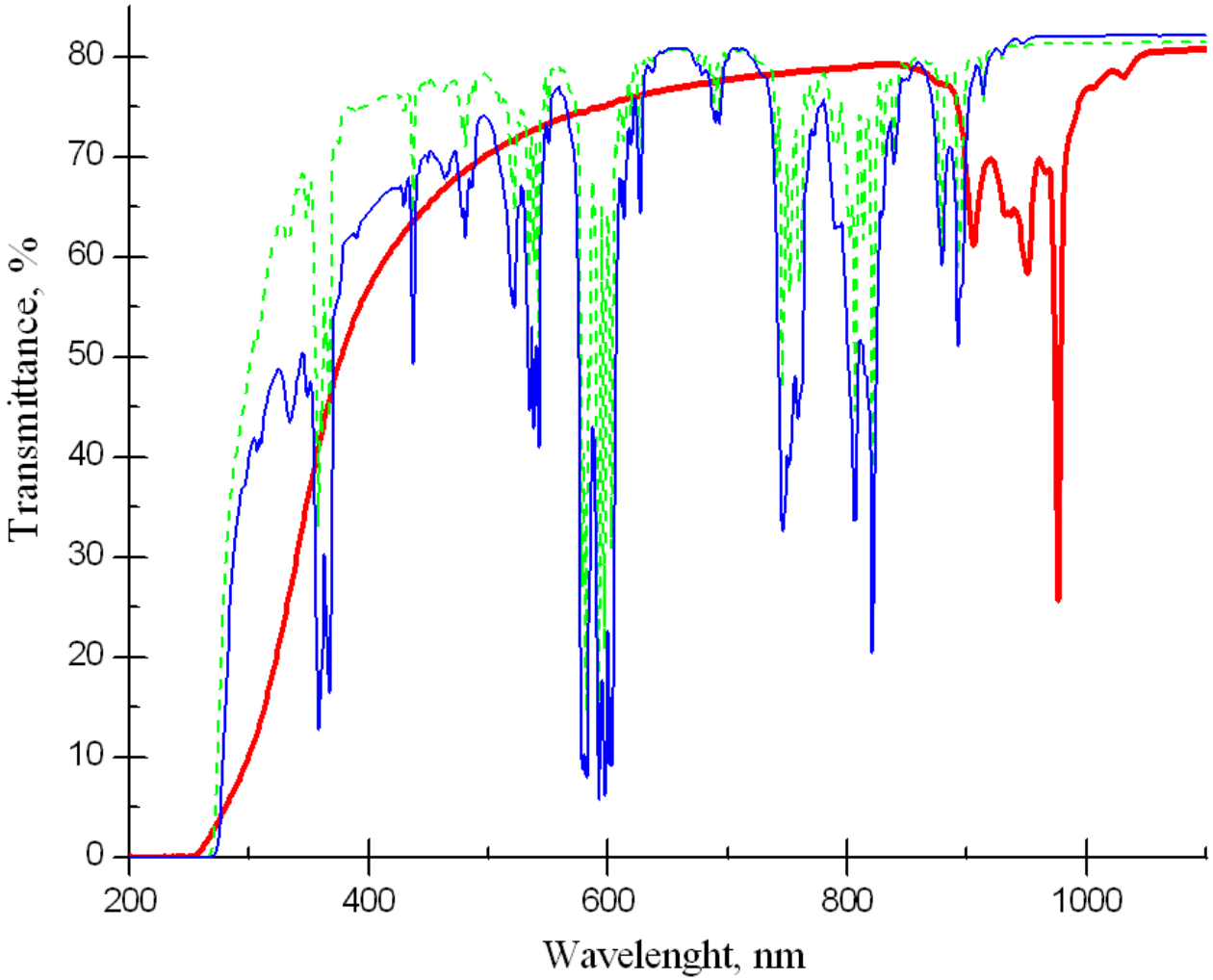
Photo of ceramic samples

Fig. 14

Effect of additives on characteristics of Y_2O_3-based ceramics

Composition	Sintering temperature, ºC	Sintering time, h	Average grain size, μm	Pore content, ppm	Transmittance @ 1,06 μm, %
$Nd:Y_2O_3$	1700 1950 2050	20 20 20	8 60 300	198 20 8	70 76,5 81.34
$[(Nd_{0.01}Y_{0.99})_2O_3]_{0.88}(ZrO_2)_{0.12}$	1900 1950	20 20	20 25	5 1	80.59 81.4
$[(Nd_{0.01}Lu_{0.24}Y_{0.75})_2O_3]_{0.88}(ZrO_2)_{0.12}$	1700	20	1	91	71.14
$[(Nd_{0.01}Sc_{0.24}Y_{0.75})_2O_3]_{0.88}(ZrO_2)_{0.12}$	1700	20	5	94	61.3
$[(Yb_{0.05}Y_{0.95})_2O_3]_{0.94}(ZrO_2)_{0.06}$	1900	20	16	0.33	78.21
$[(Yb_{0.01}Lu_{0.24}Y_{0.75})_2O_3]_{0.88}(ZrO_2)_{0.12}$	1950	10	25	1.03	80.57

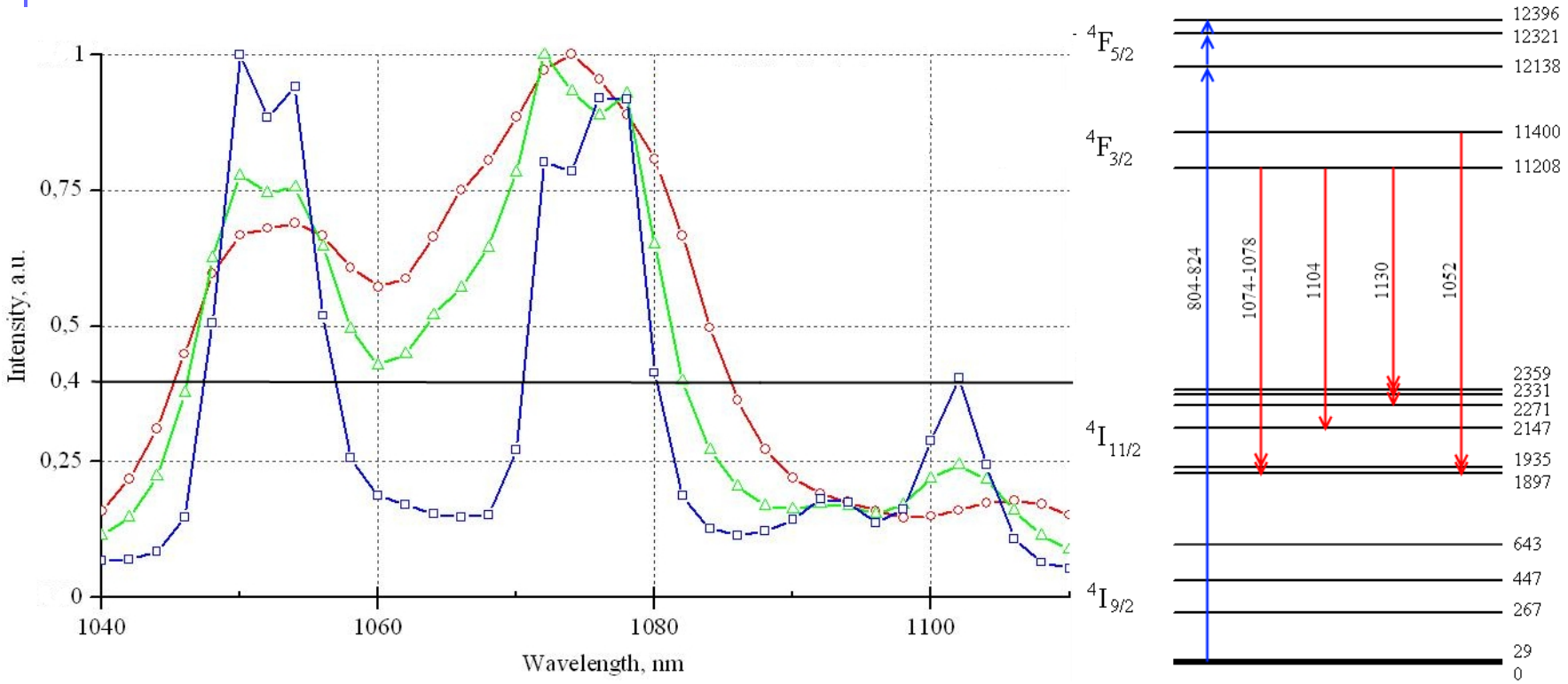
Fig. 15



Transmission spectra of ceramic samples:

$[(Yb_{0,01}Lu_{0,24}Y_{0,75})_2O_3]_{0,88}(ZrO_2)_{0,12}$	**80,57%**
$(Nd_{0,01}Y_{0,99})_2O_3$	**81,34%**
$[(Nd_{0,01}Y_{0,99})_2O_3]_{0,88}(ZrO_2)_{0,12}$	**81,4%**

Fig. 16

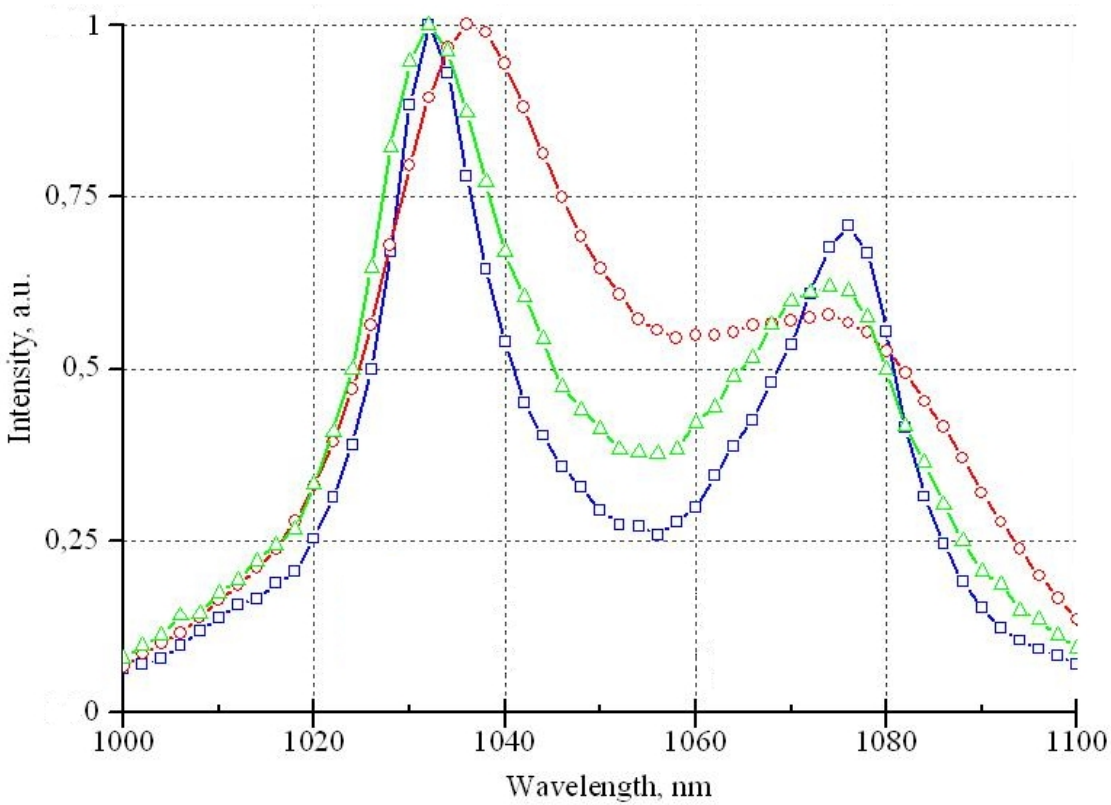


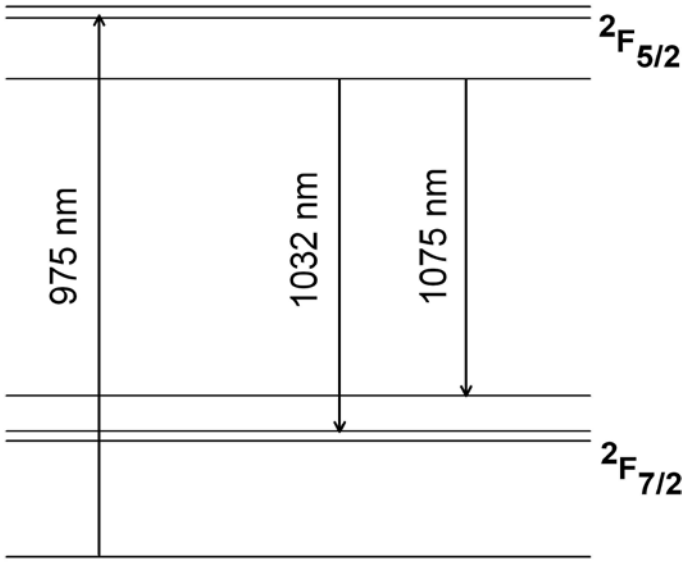
Luminescent spectra of Nd^{3+} activated samples:

- $(Nd_{0,01}Y_{0,99})_2O_3$
- $[(Nd_{0,01}Sc_{0,24}Y_{0,75})_2O_3]_{0,88}(ZrO_2)_{0,12}$
- $[(Nd_{0,01}Y_{0,99})_2O_3]_{0,88}(ZrO_2)_{0,12}$

Blue arrow – excitation
Red arrow - luminescence

Fig. 17



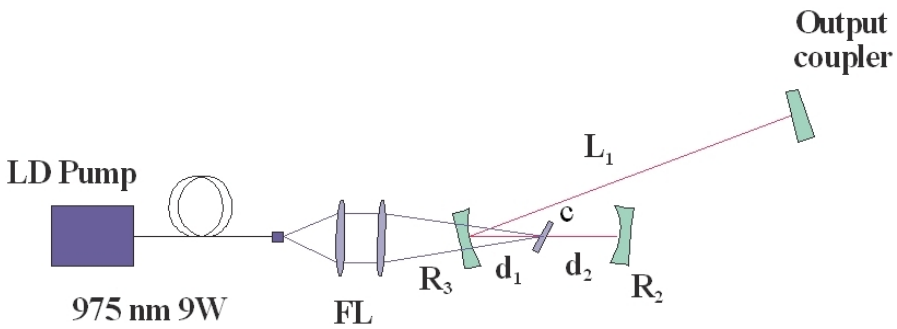


Luminescent spectra of Yb^{3+} activated samples:

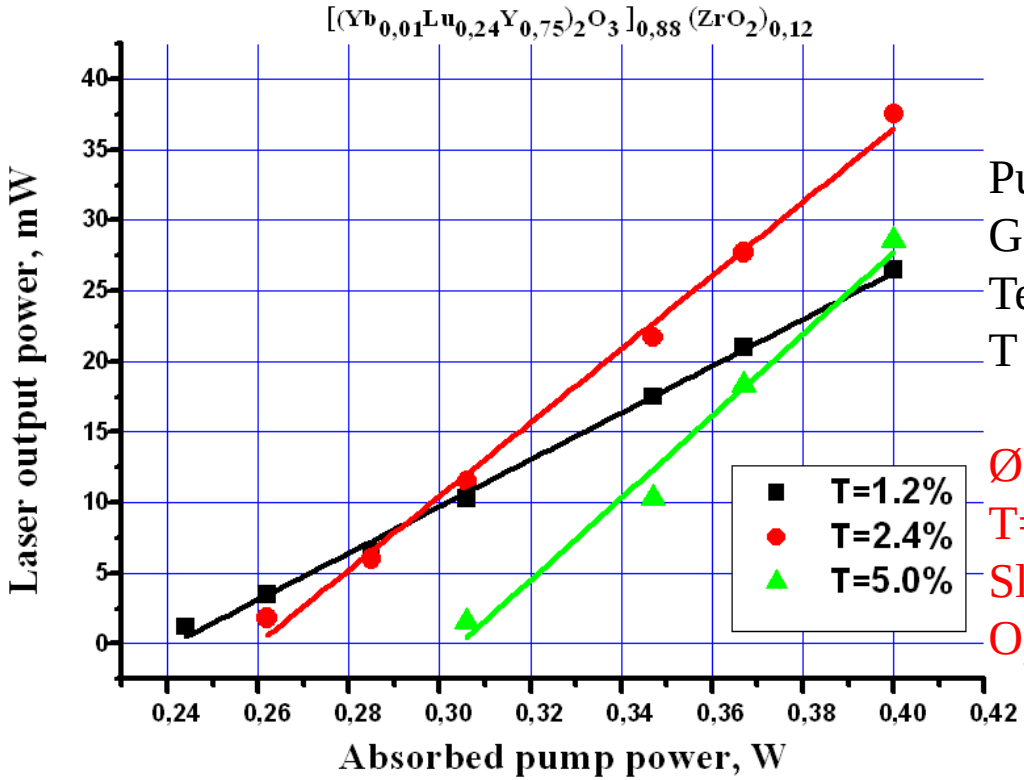
- $(Yb_{0,01}Lu_{0,24}Y_{0,75})_2O_3$
- $[(Yb_{0,01}Sc_{0,24}Y_{0,75})_2O_3]_{0,88}(ZrO_2)_{0,12}$
- $[(Yb_{0,01}Lu_{0,24}Y_{0,75})_2O_3]_{0,88}(ZrO_2)_{0,12}$

Fig. 18

Laser oscillation in $[(Yb_{0.01}Lu_{0.24}Y_{0.75})_2O_3]_{0.88}(ZrO_2)_{0.12}$ ceramics



Scheme of V-shape laser resonator
LD – laser pump diod with fiber output;
FL – focusing lens system;
R_2,R_3 - spherical mirrors with r=100 mm;
L_1 – distance to output coupler;
c – ceramic active element;
Transmission of R_3 ~ 98% at λ=950-980 nm;
Reflection of R_3 ~ 99.9% at λ=1020-1100 nm.



Pumping wavelength – 975 nm;
Generation wavelength – 1034 nm;
Temperature of active element – 300 ºK;
T – transmission of output coupler;

Ø11×1,27 mm

T=5%:	T=2.4%
Slope efficiency – 29.2%;	26.8%
Optical efficiency – 7.0 %	9.4%

Different approaches to fabricate Nd:YAG ceramics

Fig. 19

<u>0 approach.</u> Nd:YAG nanopowders are obtained by the laser evaporation of target. The target are prepared from the oxides mixture where the ratio (Y+Nd)/Al=0.692. Nd:YAG content in nanopowders was not better than 99.8±0.1%. The transparency of samples did not exceed 77%.

V.V. Osipov, V.V. Lisenkov, V.V Platonov. Appl. Phys. B, 2011, vol. 105, №3, p. 583-586.

<u>1 approach (SSR).</u> Phase transformations of Nd_2O_3, Y_2O_3, Al_2O_3 into Nd:YAG occur at the vacuum sintering.

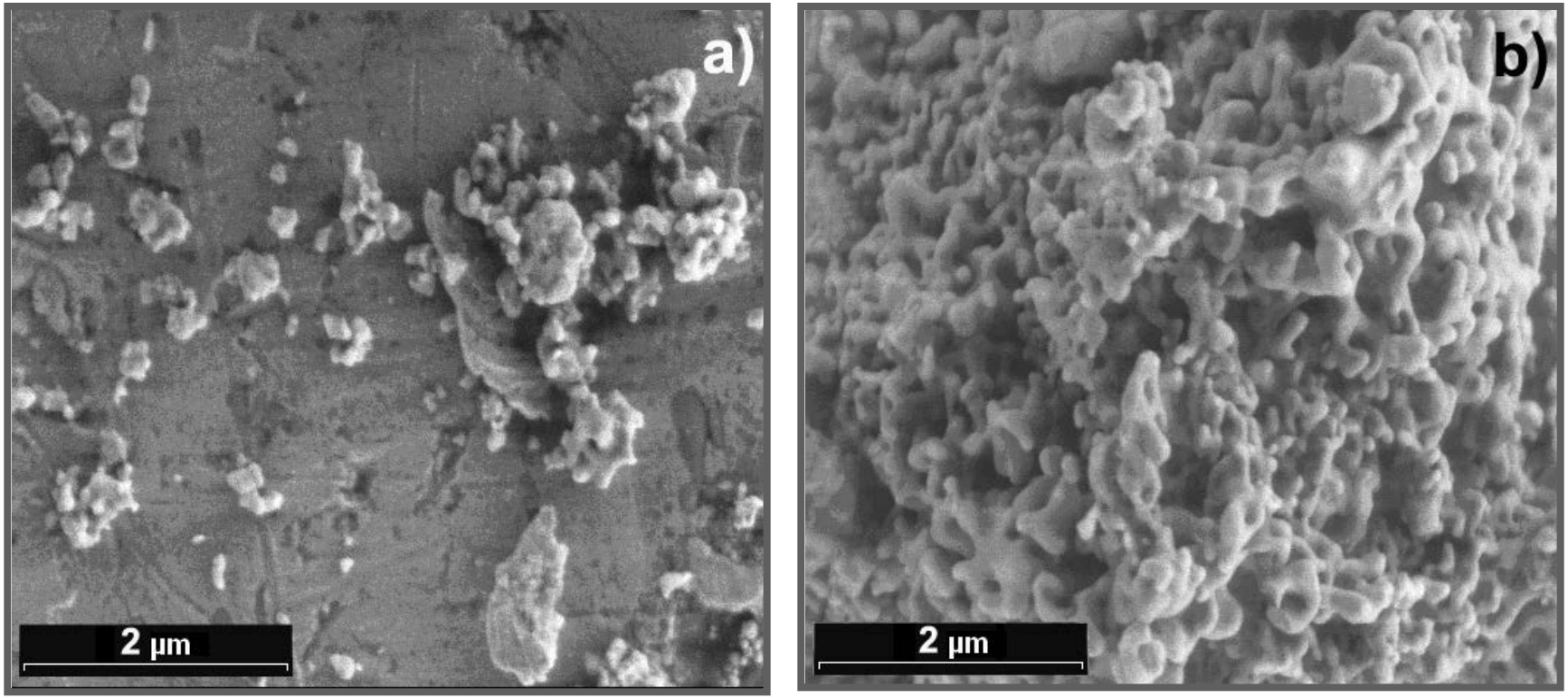
<u>2 approach.</u> Phase transformations of Nd_2O_3, Y_2O_3, Al_2O_3 into Nd:YAG occur at annealing of compacts in air before vacuum sintering.

<u>3 approach.</u> The compact was prepared and sintered from Nd:YAG powders. For preparation of Nd:YAG powder the oxides mixture was compacted into bricket. Then the bricket was annealed in air and ball milled into powder.

S.N. Bagayev, V.V. Osipov et. al. Optical Materials, 34 (2012), 1482-1487

<u>No surface-active additives and sintering aids were used.</u>

Fig. 20



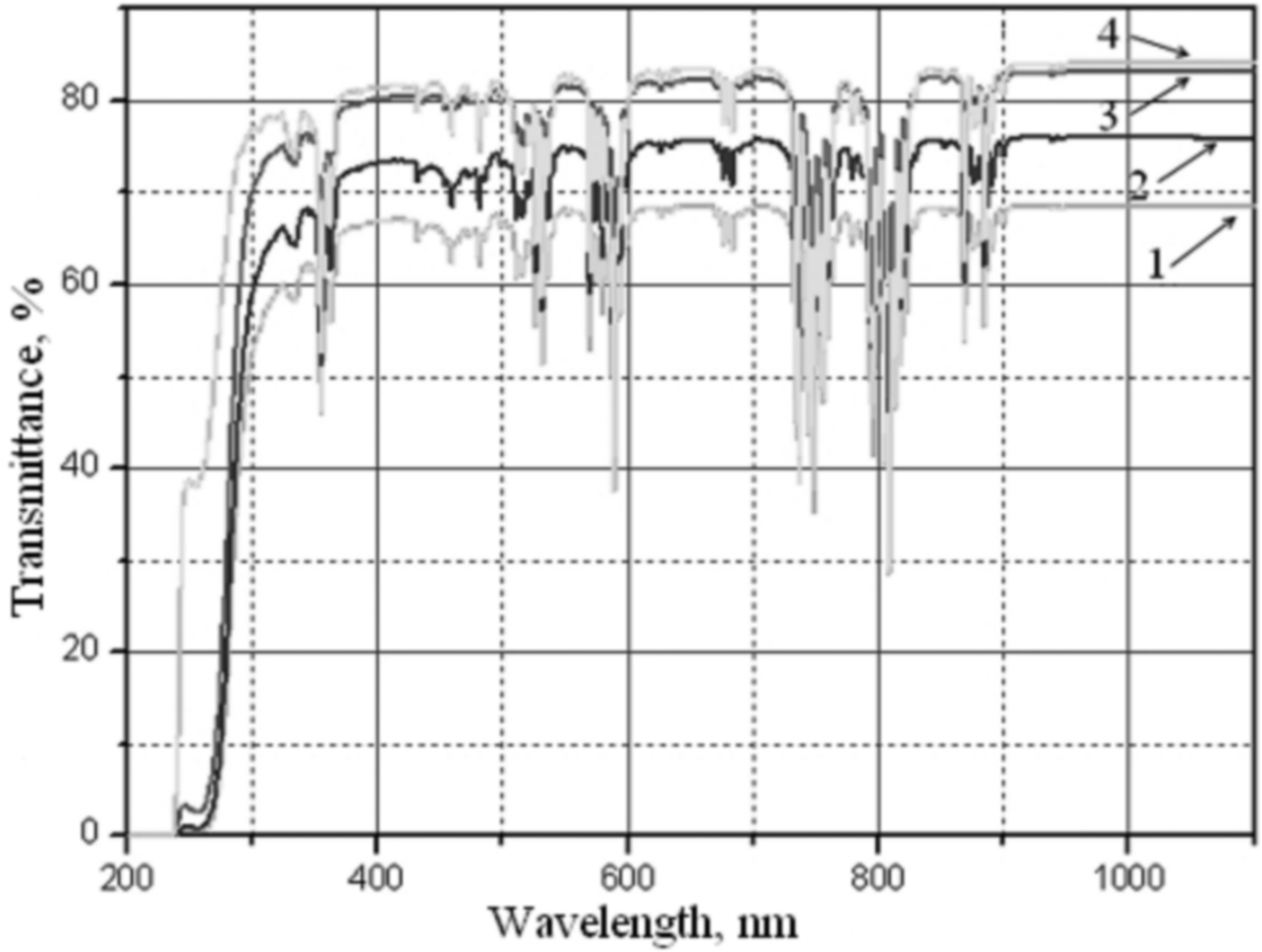
The photo of Nd:YAG particles after ball milling

Fig. 21

The photo of samples fabricated in accordance with the approaches described above are marked as 1,2,3 respectively

Optical transmittance

Fig. 22



Transmission spectra of 1 at.% Nd:YAG ceramic specimens (curves 1 – 3) and single crystal (curve 4).

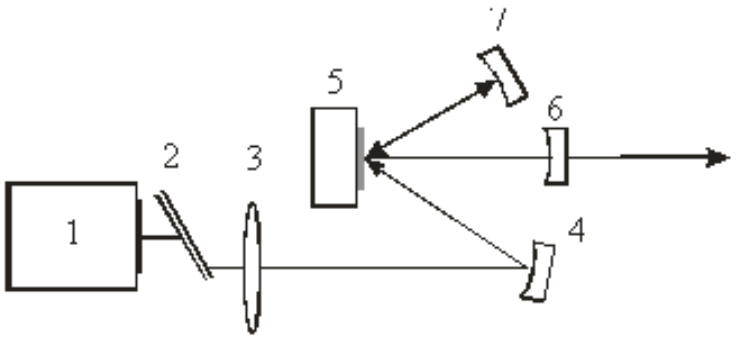
Transmittance at 1.064 μm

1st approach – 68.47%
2nd approach – 75.98%
3rd approach – 83.28%
single crystal – 84.1%

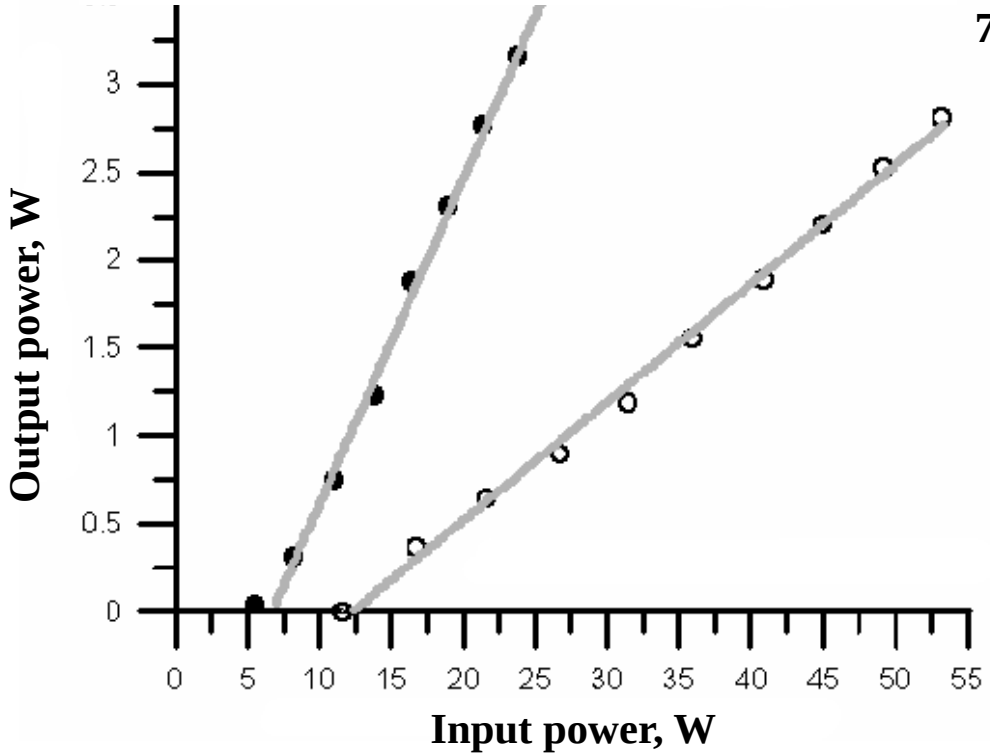
large sample – 80.1%

Laser oscillation in Nd:YAG ceramics

Fig. 23



1. 808 nm laser diode;
2. Two-mirror collimator;
3. Focusing optics;
4. Input spherical mirror, R=30 mm;
5. Heat sink with ceramic disk;
6. Output mirror, R=30 mm, T=3% at 1.064 µm;
7. Return mirror, 30 mm



● Ø11×1 mm
Slope efficiency 19.1%
Transmittance 83.28% at 1.064 µm
Optical efficiency 13.6%

○ Ø46×2.1 mm
Slope efficiency 8.8%
Transmittance 80.1% at 1.064 µm
Optical efficiency 5.4%

Fig. 24

Conclusion

Summary

- Highly transparent Nd:YAG, $(Nd_{0.01}Y_{0.99})_2O_3$, $[(Nd_{0.01}Y_{0.99})_2O_3]_{0.88}(ZrO_2)_{0.12}$, $[(Yb_{0.01}Lu_{0.24}Y_{0.75})_2O_3]_{0.88}(ZrO_2)_{0.12}$ ceramic samples with transmittance of 83.28, 81.34, 81.4 and 80,57% at 1,064 µm were fabricated using nanopowders produced by laser evaporation;
- Doping Nd(Yb):Y_2O_3 with Lu_2O_3 and ZrO_2 reduces the grain sizes (in certain cases to ~1 µm) and pore content up to receiving pore-free ceramics;
- The slope efficiencies of 19,1 and 29,2% were received respectively in Nd:YAG and $[(Yb_{0.01}Lu_{0.24}Y_{0.75})_2O_3]_{0.88}(ZrO_2)_{0.12}$ ceramic samples.

Future works

- Fabrication of Nd:YAG ceramics with additions of TEOS and/or MgO;
- Development of $Yb^{3+}(Nd^{3+})$:Y_2O_3-Lu_2O_3-Sc_2O_3 ceramics with broad emission bandwidth.