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Highly transparent ytterbium doped yttrium lanthanum oxide ceramics

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Abstract: To prepare ytterbium doped lanthania yttria nanopowder a method of laser evaporation of mixed oxides was used. After calcinations of the powder at 1200 °C a pure single-phase solid solution Yb^{3+}:$(La_xY_{1-x})_2O_3$ was formed in the nanoparticles. Influence of lanthanum oxide as an isovalent additive on the yttria structure was investigated. The lanthanium ions were proved to be a good aid to sinter yttria ceramics doped with Yb^{3+} at moderate temperatures about 1650 °C. The ceramics with relative density higher than 99.99% and grain size about 40 μm were fabricated. Full transmittance of 1.8 mm thick $Yb_{0.11}La_{0.23}Y_{1.66}O_3$ ceramics reached 82.5% at 800 nm. This material could be a good gain medium for ytterbium high power pulse lasers.

Keywords: RE-doped ceramics; nanopowders; ytterbium oxide; transparency

For the time being, active laser mediums doped with Yb^{3+} are used more and more often to fabricate high power CW and pulse lasers. First of all it is caused by the fact that high-power and high-efficient laser diode to pump these mediums at wavelength of 900–1000 nm where Yb^{3+} has absorption maximums were developed[1,2]. Besides, Yb^{3+} ion has some advantages in comparison with Nd^{3+}. In lasers doped with neodymium ions heat losses mount to ten percent of pumping power[3,4], for the large quantum defect and parasitic absorption from exited states, cross-relaxation and so on[5]. There are a small quantum defect (~9%) and no absorption from exited states in the case of ytterbium ions[6,7]. In spite of a relatively low peak power of pumping diodes quite a long life time of Yb^{3+} exited states gives a chance to store up energy comparable with Nd^{3+} pumped with lamps. Owing to allowable high doping the ytterbium laser can be effective in disks geometry. Efficient cooling of the disk surface and high concentration of ytterbium ions provide high gain. For its turn the small thickness of the disk gives a chance to avoid self-focusing in high power pulse lasers[8].

As for a host material for such lasers transparent yttria ceramics are among the most promising ones because of high thermal conductivity, good optical, chemical and mechanical properties[9]. But fabrications of laser grade both Y_2O_3 single crystal[10] and ceramics[11] are extremely difficult. Phase transformation close to melting temperature complicates tremendously growth of yttria single crystal from the melt. For its turn highly transparent yttria ceramics could hardly be sintered without a sintering aid. There are several most-used additives to improve the ceramics transparency: ThO_2, ZrO_2, HfO_2 [12,13]. All of them are heterovalent and vastly reduce laser efficiency when the ceramics are used as a host to rare-earth ions. Recent investigations revealed a potential of La_2O_3 to serve as an isovalent aid to sinter yttria ceramics both undoped[14] and doped with either Nd^{3+} [15] or Yb^{3+} [16,17].

This paper dealt with fabrication and investigation of highly transparent Yb-doped yttrium lanthanum oxide ceramics. To sinter the ceramics we used a technology, which consists of several consecutive steps: (a) laser synthesis of weakly agglomerated Yb^{3+}:$(La_xY_{1-x})_2O_3$ nanopowder, (b) compacting of green body with either magnetic pulsed press or cold isostatic pressing (CIP), (c) sintering in vacuum at the temperature up to 1750 °C for 13 h. This work investigated laser synthesized Yb^{3+}:$(La_xY_{1-x})_2O_3$ nanopowder used for the ceramics sintering, crystallite structure and transparency of the ceramics produced.

1 Experimental

1.1 Synthesis

The ytterbium doped Y_2O_3 nanopowders with different contents of La_2O_3 (from 10.5 mol.% to 13.5 mol.%) were synthesized by material evaporation with an ytterbium fiber laser. The evaporation setup was described in detail in Refs. [18–21]. The material to evaporate was made of

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mixed La_2O_3 (99.99% REO), Yb_2O_3 (99.99% REO) and Y_2O_3 (99.99% REO) commercially available powders. The ytterbium fiber laser YLR-1000 (IPG Photonics) worked in modulated mode, modulation frequency was 5 kHz, laser pulse duration – 100 μs, average laser power – 450 W. The intensity of laser radiation in the focal spot was about 10^6 W/cm^2, distribution – close to Gaussian. Average output rate of the nanopowder production was about 28 g/h[20].

The nanopowders were calcined in air in a camber furnace LHT 02/18 (Nabertherm), ball milled for 10 h with zirconia balls and compacted into disk-shaped green bodies (15 mm diameter, 1.5–3 mm thickness) with the help of an uniaxial magnetic pulsed press[17]. The amplitude of the applied pressure was up to 1.2 GPa, duration of the pulse 300–500 μs. The green body density was about 68%. The nanopowders were compacted with the help of cold isostatic pressing (Shanghai Institute of Ceramics, CAS) as well (diameters – 20 and 30 mm, thickness – 4–7 mm). The applied pressure was 250 MPa. In this case the green body density was about 53%–54%.

The green bodies were densified by pressureless sintering at different heating rates (0.5–5 °C/min) and different temperatures either in a camber furnace with graphite heaters and tungsten insulation (Institute of Radioengineering and Electronics of RAS) or in a camber furnace with tungsten heaters and insulation (Shanghai Institute of Ceramics, CAS).

Disk specimens to be used for measuring optical transmittance were ground and optically-polished on both surfaces with Phoenix Beta Grinder/Polisher (BUEHLER, Germany).

1.2 Characterization

Analysis of chemical composition of the produced nanopowders was made from solutions by the atomic-emission method with high stable inductively coupled plasma (ICP) (iCAP 6300, Thermo scientific). Phase structure and composition of the nanopowders were characterized with X-ray analysis. The XRD was made with the help of D8 DISCOVER (Bruker AXS) in Cu radiation diffracted beam with carbon monochromator. The XRD data treatment was made with the help of TOPAS 3 software (BRUKER AXS) with Ritveld's algorithm to specify structure parameters by Scherrer's method with regard to diffraction lines broadening (compensation factor k=0.89). The specific surface area (S_{BET}) of the nanopowders was measured by nitrogen adsorption according to the BET method (TriStar 3000, Micromeritics). Adsorbates content and exo/endothermal reactions that take place during heating up to 1400 °C were analyzed by simultaneous thermo analysis (TG-DSC) with NETZSCH-STA409PC. The particle size and morphology were investigated by transmission electron microscopy (TEM) (JEM-2100, JEOL Ltd.). The green body density was calculated from the size of the samples. The shrinkage of green bodies was investigated with the help of a high-temperature dilatometer (NETZSCH DIL 402 C) both in vacuum (10^2 Pa) and in air (gas flow – 100 L/h) at the temperature up to 1500 °C.

After sintering, the samples were characterized with respect to their final density and grain size. Average crystalline size of the samples was determined by atomic-force microscopy (AFM) of the sintered samples with "Solver 47p" (NT-MDT) and scanning electron microscopy (SEM) (LEO982). Defects inside the samples were analyzed with optical microscope OLYMPUS BX51. Full transmittance of polished ceramics was measured over the wavelength region 200–1700 nm with the help of a spectrophotometer (UV-1700, Shimadzu Corp.).

2 Results and discussion

As a result of the laser evaporation of powder mixture weakly agglomerated Yb^{3+}:$(La_xY_{1-x})_2O_3$ nanopowders with different contents of ytterbium and lanthanum were produced. The nanopowders consisted of weakly agglomerated spherical particles[17]. The average size of the particles was 16 nm, 98% of them were less than 40 nm. The specific surface area (S_{BET}) of the powders was 62 m^2/g. A characteristic XRD spectrum of Yb^{3+}:$(La_xY_{1-x})_2O_3$ nanopowder is shown in Fig. 1(a).

XRD analysis revealed that all the samples are monoclinic B-type Y_2O_3 (Base-centered monoclinic, S.G: *C*2/*m*, PDF No. 047-1274), which is typical for Y_2O_3 condensed from a vapor phase[22]. The phase characteristics for $Yb_{0.12}La_{0.27}Y_{1.61}O_3$ nanopowder are: a=1.396 nm, b= 0.3516 nm, c=0.865 nm, β=100.2º, coherence area (crystallite size) 18 nm. This spectrum displays high value of relative variance parameter $\Delta d/d$=0.5% – an evidence of considerable inequality of elemental composition among the nanoparticles. A small amount (less

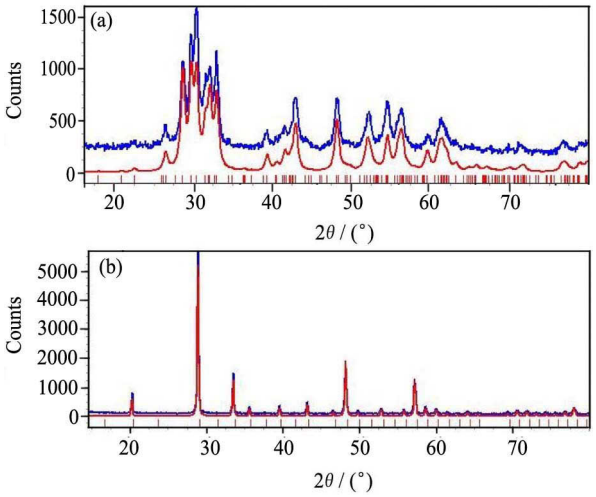

Fig. 1 XRD spectrum of $Yb_{0.12}La_{0.27}Y_{1.61}O_3$ nanopowder: as prepared (a) and after calcination in the air 1200 ºC/3 h (b) (Blue curve – measured data; red – calculated one)