Self-propagating high-temperature synthesis and luminescent properties of ytterbium doped rare earth (Y, Sc, Lu) oxides nanopowders

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Abstract. This paper describes a comparative study of structural and luminescent properties of 5%Yb-doped yttrium, scandium, and lutetium oxides (Yb:RE₂O₃) powders and ceramics fabricated by self-propagating high-temperature synthesis. According to X-ray diffractometry and electron microscopy the chosen method ensures preparation of low-agglomerated cubic C-type crystal structured powders at one step. No crucial differences in luminescence spectra were found the Yb:RE₂O₃ powders and ceramics. It was shown that the emission lifetimes of the Yb:RE₂O₃ powders are lowered by crystal structure defects, while its values for ceramics samples are compared to that of monocrystals and more influenced by rare earth impurities.

1. Introduction

In recent years, ytterbium doped rare-earth sesquioxide (RE₂O₃, RE=Y, Sc, Lu) materials have been paid attention because of interesting properties of those materials which are promising for laser applications [1-4]. At that it is very difficult to produce them by melt-growth process (conventional single crystal technology). Ceramic approach seems to be preferable to achieve highly transparent RE₂O₃ media due to several advantages, such as cost-effectiveness, large-scale production, feasibility of shape controlling and better mechanical properties.

Ceramics transparency is determined by the absence of scattering centers – pores, secondary phases, thick grain boundaries. Such an ideal microstructure can be achieved by using powders that meet a number of requirements. They include high dispersity and chemical purity, narrow size distribution and low agglomeration degree.

Respectively several methods have been developed to synthesize powders for transparent ceramics. The most commonly used method is the co-precipitation [5-8]. But there are also some alternative approaches allowing making high quality transparent ceramic material. Different scientific groups use laser sublimation method [9,10], flame-spray pyrolysis [11], sol-gel technology [12], as well as self-propagating high-temperature synthesis (SHS) [13,14]. The last one is a very promising approach, since it does not require any complicated equipment, high energy consumption and is characterized by sufficiently high productivity.

Usually in the case of high-disperse powders synthesis metal nitrate acts as an oxidant and crystalline organic substances serve as a fuel. Earlier transparent ceramics of different rare earth
oxides were obtained by sintering of SHS-powders derived with the metal acetate [15], citric acid [16] and glycine [14,17].

The aim of this study was to establish basic structural and luminescent properties of the ytterbium doped yttrium, lutetium and scandium oxide powders and ceramics prepared by self-propagating high-temperature synthesis.

2. Experimental
Among all types of fuel, glycine is the most commonly used for the synthesis of highly disperse powders by the SHS method. Moreover, only with the use of glycine it was possible to obtain optical ceramics based on all three target RE oxides. In this connection yttrium oxide powder (Y₂O₃, 99.99% purity, Polirit (Russia)), scandium oxide powder (Sc₂O₃, 99.99% purity, Lanhit (Russia)), lutetium oxide powder (Lu₂O₃, 99.99% purity, Lanhit (Russia)), ytterbium oxide powder (Yb₂O₃, 99.99% purity, Dalchem (Russia)) nitric acid (99.999% purity), glycine (NH₂CH₂COOH 99.9% purity) were used as the starting materials.

To prepare nitrate solutions a portion of the oxides of the respective metals was dissolved in a stoichiometric amount of dilute nitric acid at heating. Solutions of metal nitrates and glycine were mixed in a 1:1 molar ratio in a quartz flask, which was placed in an oven preheated to 500 °C to initiate the SHS reaction. At the end of the reaction a white foam-like bulk product was formed.

The corresponding scheme of proceeding chemical reactions can be written as follows:

\[
6\text{RE(NO}_3\text{)}_3 + 10\text{NH}_2\text{CH}_2\text{COOH} \rightarrow 3\text{RE}_2\text{O}_3 + 20\text{CO}_2 \uparrow + 14\text{N}_2 \uparrow + 25\text{H}_2\text{O} \uparrow
\]

X-ray diffraction analysis was carried out on a Shimadzu XRD-6000 diffractometer with CuKα radiation (\(\lambda = 1.54178 \text{ Å}\)) in the 2θ range of 10-60 deg to study the structural properties of the powders. The scanning step for 2θ was 0.02 deg., the scanning rate was 2 deg/min. The diffraction patterns were refined by the Rietveld method using the Rietan-98 software. The coordinates of the atoms and the unit cell parameters of the corresponding rare earth oxides were used as the basic model. The ICSD/Retrieve and PCPDF2 databases were used in the analysis. The morphology of the powders was studied by the scanning electron microscopy method using JEOL JSM-6390 LA microscope.

Disks with a diameter of 15 mm and a thickness of 3-5 mm were produced from the calcined powders by uniaxial pressing at a pressure of about 10 MPa to measure the luminescence spectra and the decay time of luminescence. The luminescence was excited by the emission of a semiconductor laser Latus with fiber output at a wavelength of 975 nm (FWHM is about 3 nm). The laser radiation was focused on the sample using an optical condenser and a short-focus lens (\(F = 50 \text{ mm}\)). Then the image was transferred to the entrance slit of the double monochromator M833 using the system of wide-aperture lenses. The radiation passed through the monochromator was detected by high-sensitivity InGaAs photodiode FGA10 operating in a synchronous detection circuit (synchronous detector Stanford Research Systems SR810).

Luminescence decay of Yb³⁺ ions was studied under excitation of a semiconductor laser diode with a center of the radiation band at a wavelength of about 975 nm, operating in a pulse generation mode with a 5 ms repetition period. The lens system focused the luminescence emission at the entrance slit of the monochromator. The radiation passed through the monochromator was converted to an electrical signal using the photoelectric multiplier FEU-62, which was then fed to the input of a digital oscilloscope.

Deagglomeration of the powders was carried out on an attrition mill LDU-3MPR (Labotex, Russia) with 2\(\odot\) mm yttria-stabilized zirconia balls in isopropyl alcohol medium for 30 minutes.

The synthesized powders were uniaxially pressed at 300 MPa to prepare ceramic samples. The resultant green compacts in the form of disks 15 mm in diameter and 2 mm in thickness were sintered in an SNVE 1.3.1 vacuum furnace with tungsten heaters at a residual pressure of 10⁻³ Pa and temperatures up to 1750°C for 3 h at a heating rate of 10°C/min. After that samples were additionally
calcined in air at a temperature of 1300°C for 2 h to eliminate oxygen vacancies (forming at the vacuum sintering stage) and then polished on both sides with diamond slurry.

![Figure 1](image1.png)

**Figure 1.** Diffraction patterns of (a) 5%Yb:Y$_2$O$_3$ powders as prepared and calcined at different temperatures and (b) 5%Yb:Sc$_2$O$_3$, 5%Yb:Y$_2$O$_3$ and 5%Yb:Lu$_2$O$_3$ powders calcined at 1100°C

3. Results and discussion

3.1. Structural and morphological studies of Yb:RE$_2$O$_3$ SHS-powders

Figure 1 shows the results of XRD analysis of the SHS products. In each case the synthesized powders represent respectively yttrium, scandium and lutetium oxide with a cubic C-type crystal lattice (space group Ia3, No 206, Z = 16). As can be seen from figure 1a powders after the synthesis are noticeably amorphized, calcination of the powders leads to a decrease in the number of defects and an increase in the crystallite size, which results in the increase of reflections intensity on the X-ray diffraction pattern.

Figure 1b shows X-ray diffraction patterns of 5%Yb:Sc$_2$O$_3$, 5%Yb:Y$_2$O$_3$ and 5%Yb:Lu$_2$O$_3$ powders calcined at 1100 °C. The highest intensity of reflections is observed for lutetium oxide. A possible explanation for this is the higher density of lutetium oxide, which provides a more intense reflection of X-radiation. According to the calculations by Rietveld method, the largest crystallite size (320 nm) was observed for lutetium oxide, for yttrium oxide and scandium oxide powders the corresponding values amount to 165 and 45 nm.

![Figure 2](image2.png)

**Figure 2.** SEM micrograph of the SHS-derived Y$_2$O$_3$ nanopowders (a) as-prepared and (b) after attrition milling for 30 minutes
The prepared powders are similar in morphology and consist of loose agglomerates with a porous structure. For example, a typical SEM micrograph of SHS-derived $\text{Y}_2\text{O}_3$ powder is shown on the figure 2a. The microstructure of the powders is determined by the mechanism of the particle formation upon combustion. The propagation of the reaction front first causes foaming of the precursor, followed by the onset of the combustion reaction, which is accompanied by the evolution of a large amount of gaseous products. As can be seen from figure 2b, during attrition milling large particles are destroyed to submicron particles of rounded shape, which proves a low agglomeration degree.

Vacuum sintering of these high-disperse low-agglomerated powders make it possible to achieve a material with 97-99% density of theoretical value at temperatures even as low as 1650-1700°C, which is ~ 700 °C below the melting points of the corresponding materials. However, obtaining highly transparent materials based on synthesized powders requires the use of sintering additives and special temperature regimes to control the grain growth and removal of residual porosity.

3.2. Luminescent properties of $\text{Yb}^3+:\text{RE}_2\text{O}_3$ SHS-powders and ceramics

To study the luminescent properties, powders calcined at 1100°C for one hour and ceramic samples sintered in vacuum at 1750 °C and further calcined in air at 1300°C were chosen. Figure 3 presents luminescent spectra of the 5% $\text{Yb}:\text{Sc}_2\text{O}_3$, 5% $\text{Yb}:\text{Y}_2\text{O}_3$ and 5% $\text{Yb}:\text{Lu}_2\text{O}_3$ SHS-powders and ceramics.

![Figure 3. Luminescence spectra of 5%$\text{Yb}:\text{Sc}_2\text{O}_3$, 5%$\text{Yb}:\text{Y}_2\text{O}_3$ and 5%$\text{Yb}:\text{Lu}_2\text{O}_3$ (a) powders and (b) ceramics](image)

The efficiency of the $\text{Yb}^3+$ ions emission for ceramic samples is much higher compared to respective powders. Nevertheless peak positions and their intensity relations are the same. The calculated characteristics for the most intensive luminescence band (at 1030-1050 nm region) are given in the table 1. The position of the peaks maxima corresponds to the literature values [21], the width of the bands for variety oxides differs insignificantly.

| $\text{Yb}^3+:\text{RE}_2\text{O}_3$ | FWHM, nm | Luminescence peak maximum, nm | $\tau_1$, $\mu$s | $\tau_2$ (ceramics), $\mu$s |
|----------------------|-------|-----------------|--------|------------------|
| $\text{Y}_2\text{O}_3$ | 17.0  | 1031.0          | 58     | 677 (950)        |
| $\text{Lu}_2\text{O}_3$| 18.0  | 1033.6          | 26     | 735 (1150)       |
| $\text{Sc}_2\text{O}_3$| 16.4  | 1041.0          | 6      | 54 (1000)        |

The kinetics of decay of the ytterbium ions luminescence in $\text{Y}_2\text{O}_3$, $\text{Lu}_2\text{O}_3$ and $\text{Sc}_2\text{O}_3$ powders and ceramics is shown in figure 4. The luminescence decay in powder samples can be divided into two stages: a rapid decay in the beginning with a characteristic time $\tau_1$, corresponding to the excitation energy.
transfer to closely located acceptors and a much slower decay ($\tau_2$), forming a long tail on the oscillogram and corresponding to energy transfer between distant ions [18]. The luminescence decay time of synthesized powders (see figure 4a) is somewhat lower than the literature values [1, 19], which can be attributed to the imperfection of the crystalline structure and the presence of intermediate products of the starting components interaction, as was previously noted by other authors [20]. This influence is mostly typical for 5%Yb:Sc$_2$O$_3$ powders. Apparently, the residual carbon- and hydrogen-containing groups (hydroxyl OH-, carboxylic COO-) do not only remain in the powders after the precursor combustion, but also are not being removed during high-temperature annealing.

![Figure 4](image)

**Figure 4.** Kinetics of luminescence decay in 5% Yb:Sc$_2$O$_3$, 5% Yb:Y$_2$O$_3$ and 5% Yb:Lu$_2$O$_3$ (a) powders annealed at 1100°C and (b) ceramics sintered at 1750°C

Quite different picture is observed for ceramic samples (figure 4b). The luminescence decay is approximated by one exponent, and the obtained luminescence lifetime values are higher than the literature values for single crystals [21]. Such effect can be explained by two factors. On the one hand, the vacuum sintering conditions at high temperatures facilitate the removal of impurity groups that introduce defects into the crystal lattice of rare-earth element oxides and increasing the crystalline structure ordering.

When the samples are illuminated by laser radiation at a wavelength of 975 nm, green glow is observed in all the studied samples, and the relative intensity of this glow for ceramics is noticeably higher than for powders. Analysis of the anti-Stokes luminescence spectra of the studied samples in the optical range shows the presence of luminescence bands typical for Er$^{3+}$ ions. The luminescence spectra of 5% Yb:Lu$_2$O$_3$ ceramic and powder samples are presented in figure 5, which clearly shows the increase in the intensity of green luminescence in ceramics compared to the powder. The presence of Er$^{3+}$ impurity ions can lead not only to the appearance of anti-Stokes luminescence bands, but also influence the kinetics of the Yb$^{3+}$ ions IR-luminescence. In this case the Yb$^{3+}$ ions act as sensitizers, and Er$^{3+}$ act as activators in the process of inter-ion excitation transfer resulting in green luminescence. Since $^4I_{11/2}$ in Er$^{3+}$ and $^2F_{5/2}$ in Yb$^{3+}$ levels are very close, it will not be mistakenly to assume that the energy transfer coefficients from the sensitizer to the activator and back for the singly excited states are the same. Then, according to [22], the IR-luminescence of both ion types will decay with the same time constant:

$$\frac{1}{\bar{\tau}} = \frac{\tau_{S}^{-1}C_S + \tau_{A}^{-1}C_A}{C_S + C_A}$$

where $C_S$ and $C_A$ are the total ion concentrations of the sensitizer and activator, $\tau_{S}^{-1}$ and $\tau_{A}^{-1}$ are the probabilities of radiative transitions of the sensitizer and activator ions from singly excited states. For Er$^{3+}$ the radiative lifetime of $^4I_{11/2}$ level is about 8-9 ms and for $^2F_{5/2}$ level of Yb$^{3+}$ is within 0.5-0.9 ms. Therefore, the presence of Er$^{3+}$ ions in powders and ceramics would increase the observed luminescence decay time according to the formula $\tau_{\text{lum.dec.}}^{-1} = \frac{1}{\bar{\tau}} + W_{n/r}$, ($W_{n/r}$ - non-radiative transition probability) which we observe in the experiment.
The difference in the intensities of anti-Stokes luminescence in powders and ceramics can be explained by the fact that on the one hand the crystalline structure of the powders is strongly disordered, and on the other hand, the average interionic distance in ceramics is somewhat smaller, and since the probability of the interionic interaction is proportional to $1/R^6$, the effect of increasing anti-Stokes luminescence in ceramics can be significant. A detailed study of the proposed mechanisms of the influence of rare-earth element impurities on the IR-luminescence kinetics will be further considered.

![Graph](image.png)

**Figure 5.** Anti-Stokes luminescence spectra of 5% Yb: Lu$_2$O$_3$ ceramic and powder samples

### 4. Conclusion

In this work, the self-propagating high temperature synthesis of ytterbium doped rare earth (Y, Sc, Lu) oxides powders and comparative study of their structural and luminescent properties are reported. The results show that particles of the SHS-derived powders exhibit cubic crystalline structure and combined in loose agglomerates which can be crushed down to submicron size via attrition milling.

Crystal structure defects in the Yb$^{3+}$:RE$_2$O$_3$ powders are highly affected on the emission efficiency and luminescence lifetime. This influence disappears during high-temperature sintering of the obtained powders into dense ceramics. In this connection it can be concluded, that the developed SHS techniques for the synthesis of rare earth oxide powders are promising for the producing of new optical ceramic materials of visible and near-IR ranges.

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### References

[1] Lupei V, Lupei A and Ikesue A 2005 Transparent Nd and (Nd, Yb)-doped Sc$_2$O$_3$ ceramics as potential new laser materials *Appl. Phys. Lett.* **86** 111 – 18

[2] Sanghera J et al 2011 10% Yb$^{3+}$-Lu$_2$O$_3$ Ceramic Laser with 74% Efficiency *Opt. Lett.* **36** (4) 576 – 78

[3] Snetkov I L, Mukhin I B, Balabanov S S, Permin D A and Palashov O V 2015 Efficient lasing in Yb:(YLa)$_2$O$_3$ ceramics *Quant. Electronics* **45** (2) 95

[4] Tokurakawa M, Shirakawa A, Ueda K, Yagi H, Yanagitani T, Kaminskii A, Beil K, Kränkel C
and Huber G 2012 Continuous wave and mode-locked $\text{Yb}^{3+}:\text{Y}_2\text{O}_3$ ceramic thin disk laser Opt. Express 20 (9) 10847

[5] Li J G, Ikegami T and Mori T 2005 Fabrication of transparent, sintered $\text{Sc}_2\text{O}_3$ ceramics J. Am. Ceram. Soc. 88 817–21

[6] Li J G, Ikegami T, Mori T and Yajima Y 2003 Monodispersed $\text{Sc}_2\text{O}_3$ precursor particles via homogeneous precipitation: synthesis, thermal decomposition, and the effects of supporting anions on powder properties J. of Materials Research 18 1149–56

[7] Liu W, Kou H, Li J G, Jiang B and Pan Y 2015 Transparent $\text{Yb}$: ($\text{Lu}_x\text{Sc}_{1-x})_2\text{O}_3$ ceramics sintered from carbonate co-precipitated powders Cer. International 41 6335–39

[8] Nengli W 2010 Synthesis of $\text{La}^{3+}$ and $\text{Nd}^{3+}$ co-doped yttria nanopowder for transparent ceramics by oxalate precipitation method J. of Rare Earths 28 (2) 232

[9] Khasanov O, Osipov V, Dvilis E, Kachaev A, Khasanov A and Shitov V 2011 Nanoscaled grain boundaries and pores, microstructure and mechanical properties of translucent $\text{Yb}:[\text{Lu}_x\text{Y}_{1-x})_2\text{O}_3$ ceramics J. of Alloys and Compounds 509 (1) S338 – 42

[10] Ivanov M, Kalinina E, Kopylov Yu, Kravchenko V, Krutikova I, Kynast U, Li J G, Lezmina M and Medvedev A 2016 Highly transparent $\text{Yb}$-doped ($\text{La}_x\text{Y}_{1-x})_2\text{O}_3$ ceramics prepared through colloidal methods of nanoparticles compaction J. of the European Ceram. Soc. 36 4251–59

[11] Baker C, Kim W, Sanghera J, Goswami R, Villalobos G, Sadowski B and Aggarwal I 2012 Flame spray synthesis of $\text{Lu}_2\text{O}_3$ nanoparticles Materials Lett. 66 (1) 132–34

[12] Balabanov S S, Yavetskiy R P, Belyaev A V, Gavrishchuk E M, Drobotenko V V, Evdokimov I I, Novikova A V, Palashov O V, Permin D A and Pimenov V G 2015 Fabrication of transparent $\text{MgAl}_2\text{O}_4$ ceramics by hot-pressing of sol-gel-derived nanopowders Ceram. International 41 (10) 13366–71

[13] Linsheng W, Suqin L, Kelong H, Xinyu Y, Youming Y and Zhi Z 2011 Characterization and photoluminescence of $\text{Lu}_2\text{O}_3$-Eu$^{3+}$ nano-phosphor prepared by modified solution combustion method J. of Rare Earths 29 (11) 1049 – 52

[14] Zou X, Yi H, Zhou G, Chen S, Yang Y and Wang S 2011 Highly Transmitting $\text{ZrO}_2$-Doped $\text{Lu}_2\text{O}_3$ Ceramics from Combustion Synthesized Powders J. Am. Ceram. Soc. 94 (9) 2772 – 74

[15] Balabanov S S, Gavrishchuk E M, Kut’in A M and Permin D A 2011 Self-propagating high-temperature synthesis of $\text{Y}_2\text{O}_3$ powders from $\text{Y(NO})_3\text{(CH}_3\text{COO})_{3(1-x)nH}_2\text{O}$ Inorg. Mat. 47 (5) 484 – 88

[16] Chen W et al 2014 Luminescence of $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ nanostructured scintillators Opt. Lett. 39 (19) 5705 – 08

[17] Permin D A, Novikova A V, Gavrishchuk E M, Balabanov S S and Sorokin A A 2017 Self-propagating high-temperature synthesis of $\text{Lu}_2\text{O}_3$ powders for optical ceramics Inorg. Mat. 12 1330 – 35.

[18] Zhang H, Yang Q, Lu S and Shi Z 2012 Structural and spectroscopic characterization of $\text{Yb}^{3+}$ doped $\text{Lu}_2\text{O}_3$ transparent ceramics Opt. Materials 969 – 72

[19] Osipov V V, Solomonov V I, Spirina A V, Vovkotrub E G and Strekalovskii V N 2014 Raman scattering and luminescence of yttria nanopowders and ceramics Optics and Spectroscopy 116 (6) 946 – 55

[20] Zych E 2001 On the reasons for low luminescence efficiency in combustion-made $\text{Lu}_2\text{O}_3$:Tb Opt. Materials 16 (4) 445 – 52

[21] Peters V 2001 Growth and spectroscopy of Ytterbium-doped sesquioxides (Hamburg: University of Hamburg, Shaker)

[22] Kazaryan K A, Timofeev Yu P and Fok M V 1986 Antistoksovo preobrazovanie izlucheniya v lumofoforah s redkozemelnymi ionami (Tr. FIAN) 175 (in Russian)