

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 (Y_2O_3 , 99.99% purity, Polirit (Russia)), scandium oxide powder (Sc_2O_3 , 99.99% purity, Lanhit (Russia)), lutetium oxide powder (Lu_2O_3 , 99.99% purity, Lanhit (Russia)), ytterbium oxide powder (Yb_2O_3 , 99.99% purity, Dalchem (Russia)) nitric acid (99.999% purity), glycine (NH_2CH_2COOH 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:



X-ray diffraction analysis was carried out on a Shimadzu XRD-6000 diffractometer with $CuK\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) 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 Yb^{3+} 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 2Ø 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.

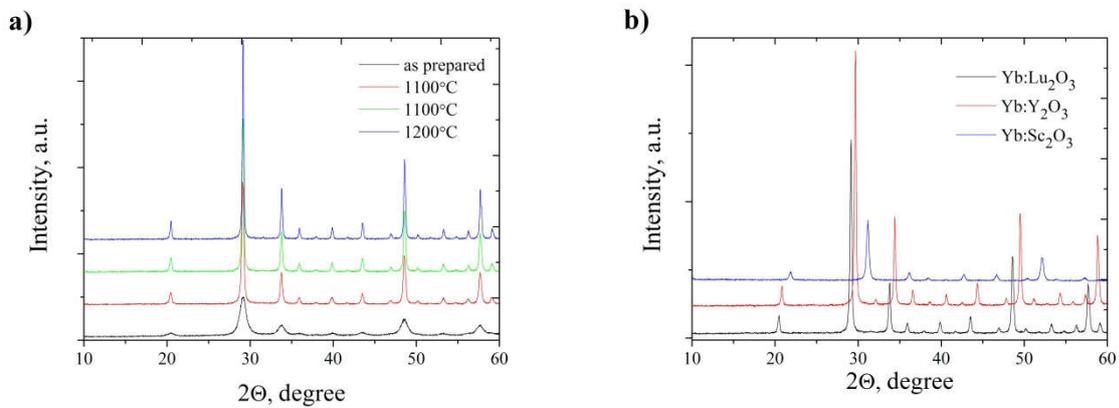


Figure 1. Diffraction patterns of (a) 5%Yb:Y₂O₃ powders as prepared and calcined at different temperatures and (b) 5%Yb:Sc₂O₃, 5%Yb:Y₂O₃ and 5%Yb:Lu₂O₃ powders calcined at 1100°C

3. Results and discussion

3.1. Structural and morphological studies of Yb:RE₂O₃ 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 Ia $\bar{3}$, № 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:Sc₂O₃, 5%Yb:Y₂O₃ and 5%Yb:Lu₂O₃ 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.

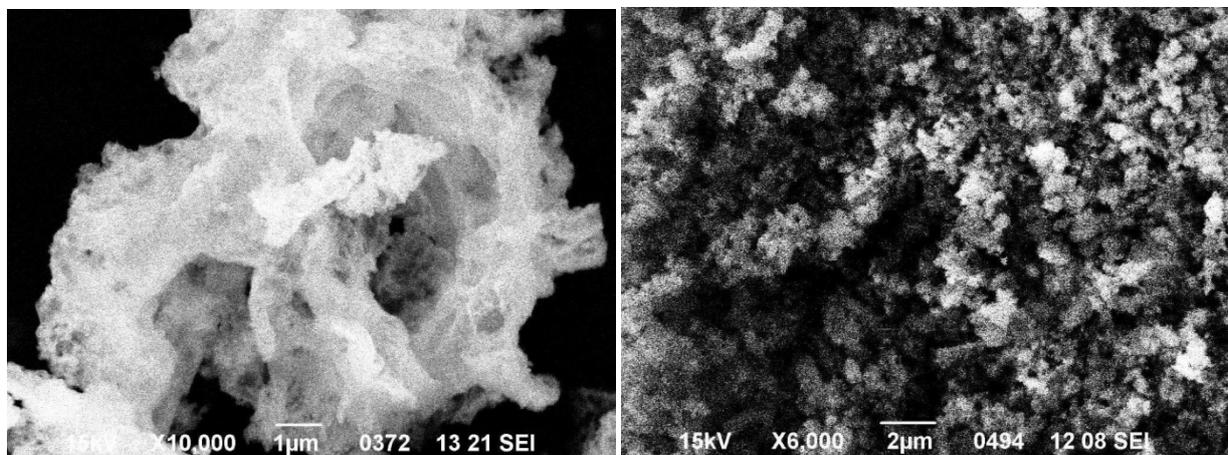


Figure 2. SEM micrograph of the SHS-derived Y₂O₃ nanopowders (a) as-prepared and (b) after attrition milling for 30 minutes

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 Y_2O_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 $Yb:RE_2O_3$ 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% $Yb:Sc_2O_3$, 5% $Yb:Y_2O_3$ and 5% $Yb:Lu_2O_3$ SHS-powders and ceramics .

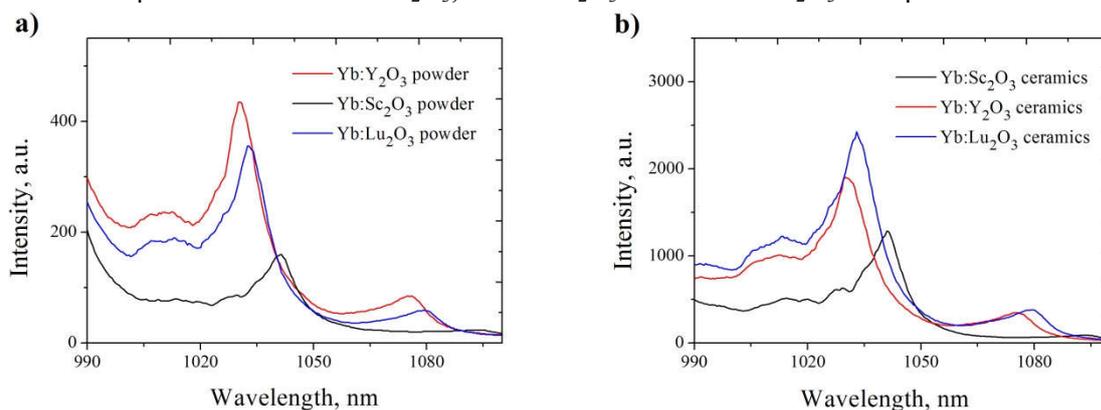


Figure 3. Luminescence spectra of 5% $Yb:Sc_2O_3$, 5% $Yb:Y_2O_3$ and 5% $Yb:Lu_2O_3$ (a) powders and (b) ceramics

The efficiency of the 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.

Table 1. The values of the luminescence most intensive peak maxima, full width at half-maximum (FWHM) and the luminescence decay time of the 5% $Yb:Sc_2O_3$, 5% $Yb:Y_2O_3$, 5% $Yb:Lu_2O_3$ powders

$Yb^{3+}:RE_2O_3$	FWHM, nm	Luminescence peak maximum, nm	τ_1 , μs	τ_2 (ceramics), μs
Y_2O_3	17.0	1031.0	58	677 (950)
Lu_2O_3	18.0	1033.6	26	735 (1150)
Sc_2O_3	16.4	1041.0	6	54 (1000)

The kinetics of decay of the ytterbium ions luminescence in Y_2O_3 , Lu_2O_3 and Sc_2O_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 τ_1 , corresponding to the excitation energy

transfer to closely located acceptors and a much slower decay (τ_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:Sc₂O₃ 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.

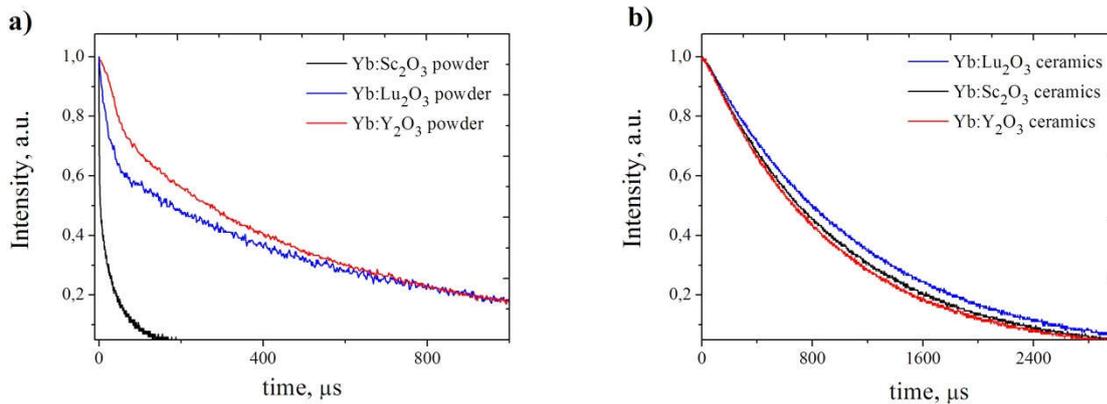


Figure 4. Kinetics of luminescence decay in 5% Yb:Sc₂O₃, 5% Yb:Y₂O₃ and 5% Yb:Lu₂O₃ (a) powders annealed at 1100°C and (b) ceramics sintered at 1750°C

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 Er³⁺ ions. The luminescence spectra of 5% Yb:Lu₂O₃ 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 Er³⁺ impurity ions can lead not only to the appearance of anti-Stokes luminescence bands, but also influence the kinetics of the Yb³⁺ ions IR-luminescence. In this case the Yb³⁺ ions act as sensitizers, and Er³⁺ act as activators in the process of inter-ion excitation transfer resulting in green luminescence. Since ⁴I_{11/2} in Er³⁺ and ²F_{5/2} in Yb³⁺ 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, τ_S^{-1} and τ_A^{-1} are the probabilities of radiative transitions of the sensitizer and activator ions from singly excited states. For Er³⁺ the radiative lifetime of ⁴I_{11/2} level is about 8-9 ms and for ²F_{5/2} level of Yb³⁺ is within 0.5-0.9 ms. Therefore, the presence of Er³⁺ ions in powders and ceramics would increase the observed luminescence decay time according to the formula $\tau_{lum.dec.}^{-1} = \frac{1}{\bar{\tau}} + W_{n/r}$, ($W_{n/r}$ - 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.

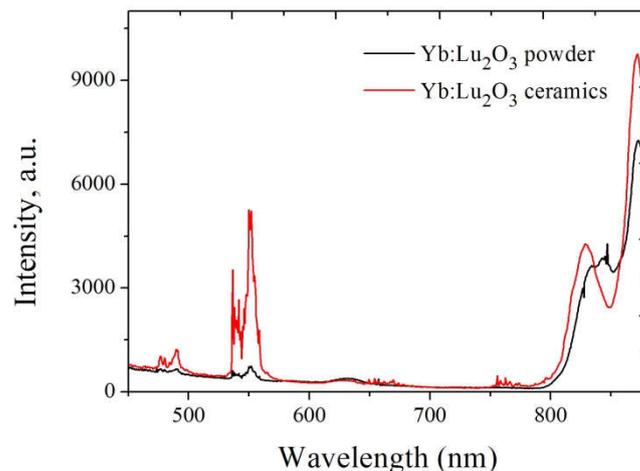


Figure 5. Anti-Stokes luminescence spectra of 5% Yb: Lu₂O₃ ceramic and powder samples

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 Yb³⁺:RE₂O₃ 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.

Acknowledgements

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