Polymer-salt synthesis of Gd$_2$O$_3$:Nd$^{3+}$ nanophosphors

N K Kuzmenko$^1$, S K Evstropiev$^{1,2}$, V A Aseev$^1$, D P Danilovich$^2$, N V Nikonorov$^1$, A I Ignatiev$^1$, A S Matrosova$^{1,3}$, V V Demidov$^3$, A V Emerson$^2$, I M Sevastyanova$^1$

$^1$ITMO University, St. Petersburg 197101, Russia
$^2$Saint-Petersburg State Institute of Technology, St. Petersburg 190013, Russia
$^3$R&P Association Vavilov State Optical Institute, St. Petersburg 192171, Russia

Abstract. The paper describes aspects of Gd$_2$O$_3$:Nd$^{3+}$ phosphors synthesis by the liquid polymer-salt method. The double role of polyvinylpyrrolidone as an organic solvent was revealed in the process of highly-luminescent cubic nanocrystals formation. The developed technique was applied for modification of a hollow-core anti-resonant optical fiber by thin films based on the synthesized material without any structural and phase transformations of Gd$_2$O$_3$ nanocrystals after the fiber drawing process.

1. Introduction
Many oxide-based phosphors are characterized by excellent luminescent properties in the visible and near IR spectral ranges and widely used in different practical applications. Modern nanotechnologies allow obtaining nanoscale phosphors based on metal sesquioxides due to their narrow emission spectra, long lifetimes, high Stokes shifts and low toxicity [1].

Gadolinium sesquioxide (Gd$_2$O$_3$) is a well-known inorganic compound which is extensively used as a host matrix for nanoscale phosphors fabrication because of its high chemical durability, thermal stability and low phonon energy [2-5]. Such nanophosphors with Gd$^{3+}$ ions substituted by rare earth metal ions have been applied in lighting and display technologies [1, 6], multicolor reporters [7], as contrast agents [8] and upconversion materials [4, 9].

Europium (Eu$^{3+}$) ions are the most commonly used doping material for fabrication of Gd$_2$O$_3$-based nanophosphors which exhibit high-intensity emission in the red part of the visible spectrum under UV excitation [1, 6, 10-20]. However, utilizing Neodymium (Nd$^{3+}$) ions may be equally or even more promising, especially for various sensing applications such as optical thermometry [21, 22]. The effectiveness of Nd$^{3+}$-containing oxide nanoscale particles (for example, Y$_2$O$_3$ [23], YVO$_4$ [24]) for photoluminescence nanothermometry has already been demonstrated experimentally [23-25]. These nanoparticles have luminescence bands in the near IR spectral range and can operate in the optical windows of biological tissues. Moreover, combination of high magnetic properties of Gd$_2$O$_3$ and emission properties of Nd$^{3+}$ ions may allow producing a highly sensitive magnetic field controlled photoluminescence nanothermometer.

Gd$_2$O$_3$-based nanophosphors doped with rare earth metal ions are usually prepared by different techniques among which are hydrothermal method [18, 26], sol-gel method [4, 10, 11, 13, 20, 27], polyol process [28], co-precipitation method [12, 29], spray pyrolysis process [1, 6, 17], combustion process [9, 14, 17, 20, 30, 31]. Typically, crystal structure and luminescent properties of oxide nanoscale particles strictly depend on fabrication method. Particularly, Gd$_2$O$_3$-based nanophosphors prepared by low-temperature processes (sol-gel, polyol) have cubic structure which is stable at
temperatures up to 1200 °C while nanoparticles synthesized by high-temperature processes (spray pyrolysis, combustion) are monoclinic [32]. Liquid phase methods (sol-gel, polyol, co-precipitation) are preferred over others because they utilize high-purity precursors and inexpensive equipment and allow obtaining homogeneous starting solutions at relatively low processing temperatures [33].

The paper discusses aspects of Gd₂O₃:Nd³⁺ nanophosphors synthesis by the polymer-salt method using polyvinylpyrrolidone (PVP) as a solvent and stabilizing agent [34, 35], morphological, structural and luminescent properties of powders fabricated under different temperature conditions and modification of a hollow-core anti-resonant optical fiber by thin films based on the synthesized material.

2. Materials and Methods
High-purity aqueous solutions of Gd(NO₃)₃ and NdCl₃ were applied as precursors for Gd₂O₃:Nd³⁺ phosphors synthesis. Predetermined volumes of these solutions along with the solution of high-molecular PVP (PVP 10, average molecular weight 10000, Sigma-Aldrich) were mixed while being vigorously stirred for 30 minutes at room temperature. The addition of PVP was intended not only to increase the homogeneity of the mixture, but also to provide high adhesion of the obtained powders and thin films to the surface of silica glass. After drying under normal conditions for 24 hours, the homogeneous mixture was heat-treated in an electrical furnace with treatment temperatures of 550 °C, 900 °C and 1000 °C for 2 hours. Content of Nd³⁺-ions in the prepared materials varied in the range 0.1±2 at. %.

Crystalline phase composition of the produced Gd₂O₃:Nd³⁺ phosphors was determined by X-ray diffraction (XRD) analysis using a high-resolution diffractometer Ultima IV (Rigaku). The average crystal size was calculated from the Scherrer equation: \( d = k\lambda/(\beta \cos \theta) \), where \( d \) is the crystal size; \( k \) is a dimensionless shape factor (\( k = 0.9 \)); \( \lambda \) is the X-ray wavelength (\( \lambda = 0.15406 \) nm) for Cu Ka; \( \beta \) is the full width at half maximum of the X-ray diffraction peak; \( \theta \) is the Bragg angle.

Morphology of the powders prepared under different temperature conditions was studied by SEM analysis using a microscope VEGA3 (TESCAN ANALYTICS).

For luminescent properties measurements, the second harmonic of a pulsed diode-pumped Nd:YAG laser (\( \lambda = 532 \) nm, \( \tau \sim 10 \) ns, \( E \sim 30 \) mJ) was applied to excite the luminescence. The emission spectra were registered using a monochromator (Acton-300, Acton Research) and InGaAs photodetector (ID-441, Acton Research). 532 nm radiation was used to record the emission spectra as well as the luminescence decay time under the same experimental conditions. To measure the luminescence decay time, the photodetector was connected to an oscilloscope (Infinium HP54830, Agilent Technologies). During experiments, the powder samples 150-µm-thick were fixed firmly between two identical polished plane-parallel plates made of silica glass. The laser radiation was focused into a \( \sim 130 \) µm spot on the surface of the powder samples. In the case of optical fiber, the radiation was focused into a spot with a size of 30 µm corresponding to the diameter of the fiber core.

3. Results and Discussions
Figure 1 presents the XRD patterns of Gd₂O₃:Nd³⁺ powders prepared under different heat-treatment conditions for 2 hours. Particularly, it can be seen from Figure 1a that the initial mixture of metal nitrates and PVP completely decomposed after heat treatment at 550 °C, which is typical for the method we applied to synthesize phosphors [36]. According to this method, oxide nanoscale particles and gases are products of the chemical reaction and the powder is a loose substance with voids and pores formed by escaping gases during the combustion process. Diffraction peaks in the XRD pattern (Figure 1a) correspond to Gd₂O₃ crystals with the cubic structure however intensities of the peaks are relatively low due to small amount of crystals grown at 550 °C.

The XRD patterns of Gd₂O₃:Nd³⁺ powders heat-treated at 900 °C (Figure 1b) and 1000 °C (Figure 1c) reveal diffraction peaks characteristic to cubic Gd₂O₃ crystals. The observed peaks tend to be more intense and narrower upon increasing treatment temperature that can be related to higher crystallinity and larger size of particles.
Figure 1. XRD patterns of Gd$_2$O$_3$:Nd$^{3+}$ powders with Nd$^{3+}$-ions content 0.4 at.% heat-treated at temperatures of 550 °C (a), 900 °C (b) and 1000 °C (c) for 2 hours

Based on calculations from the Scherrer equation, the average size of the crystals grown in the prepared Gd$_2$O$_3$:Nd$^{3+}$ phosphors with Nd$^{3+}$-ions content 0.4 at.% was estimated to be 12-14 µm for the powders heat-treated at 550 °C and 30-42 µm for the powders heat-treated at 900-1000 °C. Additional calculations taking into account the positions of the diffraction peaks in the XRD patterns showed the absence of the crystal lattice strains with Gd$^{3+}$ ions substituted by Nd$^{3+}$ ions. Ionic radii of Gd$^{3+}$ ions (1.4 Å) and Nd$^{3+}$ ions (1.44 Å) are close to each other. For this reason, replacement of Gd$^{3+}$ ions by Nd$^{3+}$ ions in an oxide matrix proceeds without significant crystal lattice deformations.

Thus, the data collected by XRD analysis testifies that the main part of the produced Gd$_2$O$_3$ crystals has the cubic structure. However, detailed consideration of the XRD patterns presented in Figures 1a and 1b reveals the presence of a few small peaks at θ = 27-33° which could not be assigned to cubic Gd$_2$O$_3$ crystals. The position of these peaks and their relative intensities between each other allow suggesting the existence of small amounts of monoclinic Gd$_2$O$_3$ crystals in the powders heat-treated at 550 °C and 900 °C. The formation of both cubic and monoclinic Gd$_2$O$_3$ nanocrystals was observed earlier for treatment temperature ranges 500÷1000 °C [37] and 800÷900 °C [38]. In our case, this phenomenon can be related to high heat generation during the combustion of the initial mixture and strong local heating at the very first stage of Gd$_2$O$_3$ nanocrystals formation.

Figure 2 demonstrates SEM image of the Gd$_2$O$_3$:Nd$^{3+}$ powder prepared at 1000 °C. As can be seen from the image, the synthesized material consists of small particles having a size of less than 100 nm and exhibits no larger particles or aggregates. This circumstance can be attributed to the influence of PVP addition on morphological properties of the powder. Particularly, generation of large amounts of gaseous products during the initial mixture decomposition and PVP combustion leads to spatial separation of the forming oxide nanoscale particles that, in turn, contributes to production of the non-aggregated powder.

Figure 2. SEM image of Gd$_2$O$_3$:Nd$^{3+}$ powder with Nd$^{3+}$-ions content 0.4 at.% heat-treated at 1000 °C for 2 hours
Figure 3 presents the photoluminescence (PL) spectra of Gd$_2$O$_3$:Nd$^{3+}$ powders prepared at 550 °C and 1000 °C. Generally, the shapes of the Nd$^{3+}$-ions luminescence peaks are almost identical regardless the intensity. The main emission peak at the wavelength of 1064 nm corresponds to the electron transition $^4F_{3/2}$-$^4I_{11/2}$. Side luminescence bands with the peaks near the wavelengths of 900 nm and 1340 nm which correspond to the transitions between energy levels $^4F_{3/2}$-$^4I_{9/2}$ and $^4F_{3/2}$-$^4I_{13/2}$ respectively are also observed. An increase in treatment temperature accelerates the crystallization process and leads to a significant growth of the luminescence intensity.

![Figure 3. PL spectra of Gd$_2$O$_3$:Nd$^{3+}$ powders with Nd$^{3+}$-ions content 0.4 at.% heat-treated at 550 °C (curve 1) and 1000 °C (curve 2)](image)

The experimental data on the luminescence decay time in the produced nanophosphors revealed the values of $\tau$ up to 190 µs which is comparable with $\tau$ reported for transparent Y$_2$O$_3$:Nd$^{3+}$ ceramics [39] and slightly lower than $\tau$ in YAG:Nd$^{3+}$ ceramics [40].

The developed technique for the highly-luminescent Gd$_2$O$_3$:Nd$^{3+}$ nanophosphors fabrication was applied to modify a silica-based hollow-core anti-resonant optical fiber. This type of fiber was chosen because of its architecture providing a relative simplicity of impregnating host matrix with a mixture of composite materials and subsequent treatment at high temperatures. According to modification, the preform comprising of six cladding capillaries around one central core capillary was filled with the mixture of metal nitrates and PVP, dried at room temperature for 24 hours, heat-treated in an electrical furnace at 1000 °C for 2 hours followed by the formation of Gd$_2$O$_3$:Nd$^{3+}$ thin films on the inner surfaces of the capillaries and drawn into the optical fiber at 1850 °C for 30 minutes. The fiber cross-section obtained by an optical microscope with high-resolution imaging system Nikon Eclipse Ni-U (Nikon Instruments) is presented in Figure 4a.

![Figure 4. Cross-section (a) and transmission spectrum (b) of hollow-core anti-resonant optical fiber modified by Gd$_2$O$_3$:Nd$^{3+}$ nanophosphors](image)
The basic requirement for a chosen hollow-core anti-resonant optical fiber modified by Gd$_2$O$_3$:Nd$^{3+}$ nanophosphors was the functionality simultaneously in two separate spectral ranges ("transmission windows"), i.e. with the luminescence excitation wavelength (λ$_{ex}$) inside the one window and with the luminescence emission wavelength (λ$_{em}$) inside the other. To record the transmission, the experimental setup including halogen lamp 64642 HLX (OSRAM), programmable monochromator ANDO, silicon photodiode (λ = 400-900 nm), germanium photodiode (λ = 900-1300 nm), optical amplifier eLockIn (Anfatec Instruments) and optical power meter ANDO AQ-1135E was applied. During measurements, the fiber sample of ~ 40 cm in length was almost straightened in order to exclude the influence of bending on optical signal.

Figure 4b illustrates the transmission spectrum of the fiber. As can be seen from the curve, the optical element satisfies the condition of having several transmission windows, namely in the visible part of the spectral range with the luminescence excitation wavelength (λ$_{ex}$ = 532 nm) inside the third window and in the near IR part with the luminescence emission wavelength (λ$_{em}$ = 1064 nm) inside the first window. This disposition was achieved by choosing properly the silica wall thickness at the core-cladding boundary which was equal to 0.8 µm. With a view to prevent changes of the shape or even collapsing of the capillaries as well as silica walls resizing during the fiber drawing process an excess gas pressure was supplied into the voids of six cladding capillaries. Based on the measured transmission and length of the fiber, attenuation level was estimated to be more than 10 dB/m at the wavelength of 532 nm and 3-5 dB/m in the wavelength region ~ 1100 nm.

The main technological task during the additional heat-treatment while drawing the optical fiber at 1850 °C was to avoid significant structural and phase transformations of Gd$_2$O$_3$ nanocrystals which cause a decrease in the luminescence intensity. To evaluate this, a piece of the fiber was ground into powder and subjected to XRD analysis. The results revealed the presence of cubic Gd$_2$O$_3$ crystals with an average size not exceeding 50 nm. This indicates the absence of any crystal structure transformations, despite the closeness of the temperatures of drawing and melting of the crystals.

PL spectrum of the modified optical fiber repeats the spectrum registered for the Gd$_2$O$_3$:Nd$^{3+}$ powder prepared at 1000 °C. However, the luminescence kinetics of the fiber is described by two exponential dependencies with decay times $\tau_1$ = 12 µs and $\tau_2$ = 233 µs. According to the authors, this phenomenon is due to the cubic structure of Gd$_2$O$_3$ nanocrystals and $\tau_2$ is almost the same as for transparent Y$_2$O$_3$:Nd$^{3+}$ ceramics [39].

4. Conclusions
The aspects of Gd$_2$O$_3$:Nd$^{3+}$ nanophosphors fabrication by the liquid polymer-salt method were studied in detail. It was found out that polyvinylpyrrolidone as an organic solvent, on the one hand, stabilizes the process of Gd$_2$O$_3$ crystals formation prohibiting their growth and aggregation and, on the other hand, plays the role of a fuel during the combustion increasing the reaction temperature and thereby affecting structural and luminescent properties of the obtained nanophosphors. Drying of the initial mixture containing Gadolinium and Neodymium salts and polyvinylpyrrolidone at room temperature followed by heat-treatment at 1000 °C allow obtaining highly-luminescent Gd$_2$O$_3$:Nd$^{3+}$ cubic crystals with an average size of 40 nm. The developed technique is suitable for modification of a hollow-core anti-resonant optical fiber by thin films based on the synthesized material without any structural and phase transformations of Gd$_2$O$_3$ nanocrystals.

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