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Silica fibres activated by YAG:Nd^{3+} nanocrystals

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Abstract. **We report data on the development of a polymer–salt method for the formation of aluminium yttrium garnet crystals doped with neodymium ions (YAG:Nd) inside the channels of a preform of microstructured fibre based on pure silica glass. The crystals are obtained by impregnating the channels with aqueous solutions of thermally decomposable salts (yttrium nitrate, aluminium nitrate, neodymium chloride) and an organic polymer, followed by drying and heat treatment at a temperature of 1100 °C. The resulting composite structure is drawn into the fibre at a temperature of 2000 °C. Using X-ray diffraction analysis, the presence of oriented YAG:Nd crystals ranging in size from 25 to 37 nm in the silica glass matrix of fibre is established. Measurements of the spectral dependence of optical losses in fibre show the presence of absorption bands of the optical signal, characteristic of Nd^{3+} ions. The shape of the luminescence spectra of nanocrystals is typical of YAG:Nd with a radiation peak at a wavelength of 1064 nm.**

Keywords: *silica glass, optical fibre, microstructured fibre, aluminium yttrium garnet, neodymium, nanocrystal, luminescence.*

1. Introduction

Lasers and amplifiers employing silica optical fibres (SOFs) doped with rare-earth metal ions as an active medium find wide practical application and are subject of intensive research [1–3]. However, despite significant advances in silica glass technology, the formation of active matrices with ions of rare-earth metals with high luminescent characteristics remains a highly demanded task.

Traditional methods for producing active SOFs are based on chemical vapour deposition from the gas phase with the joint doping of silica glass with rare-earth elements and various modifiers (Al_2O_3, P_2O_5, etc.) [4, 5]. The main disadvantage of this approach is the inability to reach the maximum concentration of the activator in the composition of the core glass due to the low solubility of rare-earth ions in silica glass compared to laser crystals, even in the presence of modifiers.

The incorporation of laser crystals with a high concentration of rare-earth elements into the SOF core is only permissible in the form of nanoparticles, which avoids excessive scattering losses on optical inhomogeneities. In this case, due to the potentially high concentration of the activator in the core glass, the operating lengths can be tens or even units of centimetres, and so the level of permissible optical losses can increase up to 10 dB m^{-1}. At the same time, achieving an acceptable level of optical losses requires uniform introduction of nanoparticles into the core material during the preform preparation and the selection of such synthesis regimes that exclude their modification or dissolution in silica glass in the process of SOF drawing, which is an extremely challenging technological problem.

One of the solutions to these problems is a method of direct introduction of nanoparticles with a high activator concentration into the core glass, the essence of which is the simultaneous deposition of amorphous silicon dioxide particles and nanoscale particles of the activator in the liquid phase onto the surface of the silica glass support tube [1, 6]. This approach makes it possible to significantly increase the concentration of rare-earth elements in the SOF core, to reduce the clustering effect, and to use a larger number of activators.

At the same time, the described methods are characterised by excessive consumption of materials, complexity and laboriousness of the process. As an alternative, a technologically simpler method for producing active SOFs has been proposed, based on the modification of silica glass using nanocrystalline inclusions containing rare-earth metal ions [7]. This approach involves the separation of the core material of a certain chemical composition into nanophases, followed by the formation of nanocrystals in the process of heat treatment of the preform or already elongated SOFs. This approach has been used in the present work.

It is known that the arrangement of neodymium ions (Nd^{3+}) in the matrix of aluminium yttrium garnet ($Y_3Al_5O_{12}$) provides excellent spectrally luminescent properties [2], which makes this laser material widely used in practice. However, none of the existing technologies makes it possible to modify the silica glass by means of YAG:Nd^{3+} crystals with the necessary degree of reproducibility. For this reason, the develop-

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ment of SOFs activated with YAG:Nd^{3+} crystals is an urgent problem, the solution of which is important for the development of the industry of high-power fibre lasers and amplifiers.

The aim of this study was to develop an active SOF prototype into the matrix of which high-luminescent YAG:Nd^{3+} nanocrystals are introduced, and to describe its properties. The main idea was to use preforms of microstructured SOFs containing pre-grown small nanocrystals in the channels.

2. Experimental

The technological process of manufacture of optical elements included a number of sequential operations:

1) preparation of a homogeneous film-forming solution with high adhesion to the silica glass surface;

2) impregnation of channels of preliminary prepared preforms of a microstructured SOF at room temperature;

3) drying and calcination of solution-impregnated preforms at a temperature of 1000–1100 °C; and

4) drawing the preforms into SOF at a temperature of 2000–2100 °C.

A method for manufacturing microstructured SOF preforms is described in detail in [8]. A hexagonal system of silica capillaries with a diameter of 1.85 mm was assembled manually inside a silica glass support tube with an internal diameter of 17 mm and a wall thickness of 2 mm. The central capillary was replaced by a micro-rod of the same size to form the light-guiding core. The support tube, capillaries, and micro-rod were made of high-purity synthetic silica glass with a hydroxyl group content of less than 1 ppm. The resulting structure was drawn into a microstructured SOF preform with a diameter of 3.5 mm, while the gaps between the capillaries in the original assembly were melted. Figure 1 shows images of the preform cross section for the formation of coatings inside the channels, based on YAG:Nd^{3+} nanocrystals and a microstructured SOF with nanocrystalline inclusions, drawn from this preform.

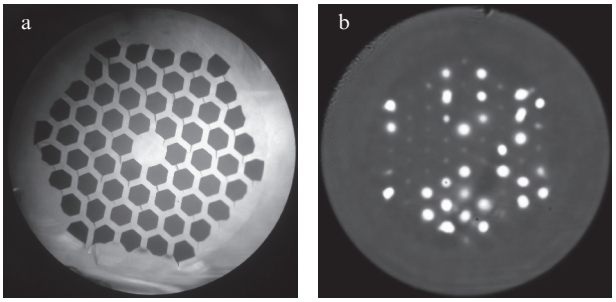

Figure 1. Images of (a) the preform cross section for filling the channels with coatings based on YAG:Nd^{3+} nanocrystals and (b) microstructured SOF with a diameter of 120 μm with nanocrystalline inclusions, drawn from the preform at a temperature of 2000 °C.

For the formation of coatings based on YAG:Nd^{3+} nanocrystals in the channels of the microstructured SOF preform, a liquid polymer–salt method based on the use of solutions of thermally degradable metal salts and soluble organic polymer was used [9]. Aqueous solutions of $Y(NO_3)_2$, $Al(NO_3)_2$, $NdCl_3$ and polyvinylpyrrolidone were selected as precursors for the manufacture of coatings. Specified amounts of these components were intensively mixed for 30 minutes at room temperature to obtain homogeneous and transparent film-forming mixtures. The preform channels were filled with the resulting mixtures at room temperature for 2 hours. After drying *in vivo* for 24 hours, the preform was subjected to heat treatment in an electric furnace at a temperature of 1100 °C.

Additionally, for comparative analysis, silica glass plates with a deposited thin layer of the film-forming solution and nanopowders obtained by grinding a bulk composite material based on a film-forming solution were prepared. These samples were dried at a temperature of 70 °C for 24 hours and heat-treated in an electric furnace at a temperature of 1100 °C for 2 hours.

The crystalline phase composition was determined using a Rigaku Ultima IV X-ray diffractometer. The Debye–Scherrer method was used to estimate the size of individual crystals. The luminescent characteristics of materials were studied in an experimental setup incorporating a solid-state Nd:YAG laser (wavelength 532 nm, pulse duration 10 ns) and an ID-441 photodetector (Acton Research Corporation). To measure the luminescence decay time, the photodetector was connected to an Infinium HP54830 oscilloscope (Agilent Technologies).

3. Discussion of results

The results of X-ray diffraction analysis of nanopowders and coatings applied to silica glass plates obtained on the basis of solutions with a 0.2 at.% neodymium concentration are shown in Fig. 2. The obtained results indicate the formation of aluminium yttrium garnet crystals in the structure of the studied materials and clearly demonstrate the changes caused by heat treatment. Heating the studied materials to a temperature of 550 °C leads to complete decomposition of polyvinylpyrrolidone and inorganic salts. The subsequent temperature rise to 1000–1100 °C provides conditions for the formation of YAG:Nd^{3+} nanocrystals. The number of peaks in the diffractogram of the nanopowders significantly exceeds that in the diffractogram of the coatings applied to silica glass plates. Apparently, this is a consequence of the decrease in the crystallisation process efficiency in the interaction of YAG:Nd^{3+} nanocrystals with the silica glass surface. Apart from the peaks characteristic of $Y_3Al_5O_{12}$ crystals, additional peaks characteristic of Y_2O_3 cubic crystals are present in the nanopowder diffractogram.

Based on the results of X-ray diffraction analysis, we calculated the average size of YAG:Nd^{3+} crystals. The calculation data are presented in Table 1.

Figure 3 shows the presence of YAG:Nd^{3+} nanocrystals in the composition of the elongated SOF. This indicates that nanocrystals preliminarily formed in the preform channels at a temperature of 1100 °C were preserved in a silica glass matrix during repeated heat treatment at a temperature of 2000 °C, which is higher than the melting point of the bulk YAG crystal (1940 °C) [10]. The absence of noticeable changes in the structure of nanocrystals during the SOF fabrication can be explained by the high speed of the drawing process and, accordingly, its short duration. The size of these nanocrystals ranged from 25 to 37 nm, which, given the large difference in the refractive indices of silica glass (n = 1.46) and YAG nanocrystals (n = 1.83), should help minimise light scattering.

Additionally, to confirm the presence of YAG:Nd^{3+} nanocrystals in the composition of the elongated SOF with a neodymium concentration sufficient to amplify the optical signal (0.2 at.% according to Table 1), the spectral dependence of optical losses was measured by the cutback technique (Fig. 4).

Table 1. Average size of YAG:Nd^{3+} crystals in the materials under study as a function of the conditions of their preparation.

Material	Size of YAG:Nd^{3+} crystals (nm) at various neodymium concentrations (at. %) and treatment temperatures						
	0.1; 1100 °C	0.2; 1000 °C	0.2; 1100 °C	0.2; 2000 °C	0.3; 1100 °C	0.6; 1100 °C	1.0; 1100 °C
Nanopowder	25	26	33	–	25	29	28
Coating on a silica glass plate	–	27	37	25*	37	28	–

* Microstructured SOF drawn at 2000 °C.

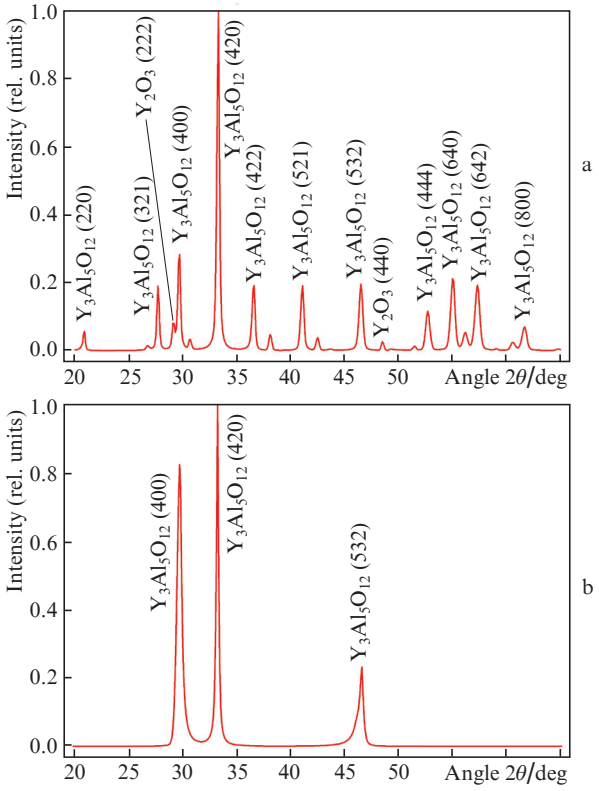

Figure 2. Results of X-ray diffraction analysis of (a) nanopowders and (b) coatings on silica glass plates obtained after processing materials based on YAG:Nd^{3+} with a neodymium concentration of 0.2 at. % at a temperature of 1100 °C.

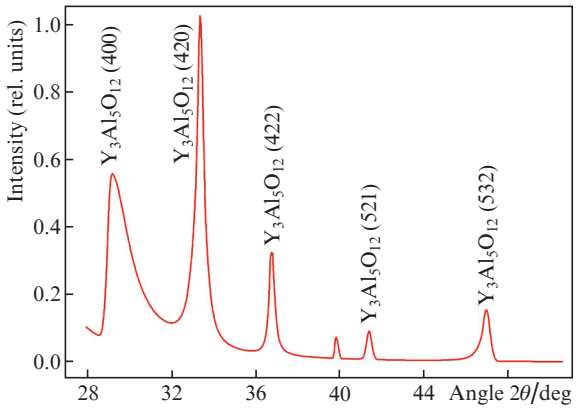

Figure 3. Results of X-ray diffraction analysis of a microstructured SOF with YAG:Nd^{3+} nanocrystals, obtained by drawing the preform at a temperature of 2000 °C.

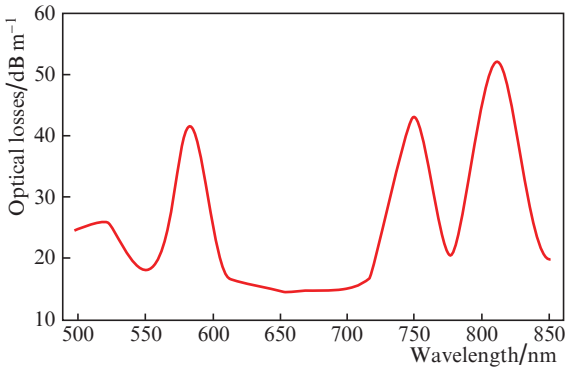

Figure 4. Spectral characteristic of optical losses in the drawn microstructured SOF with YAG:Nd^{3+} nanocrystals, measured at a fibre length of 0.5 m.

As can be seen from Fig. 4, three expressed optical signal absorption bands with maxima near the wavelengths of 580, 750 and 810 nm, characteristic of Nd^{3+} ions, are observed in the studied spectral range [11]. The level of optical losses at a wavelength of 1064 nm, typical for the generation of radiation by YAG:Nd crystals, measured at a fibre length of 3 m, turned out equal to 8.5 dB m^{-1}. In other words, the difference in the levels of optical losses in the absorption and generation regions of radiation constituted more than an order of magnitude, while the power drop in the useful optical signal at the SOF length of about 0.5 m was approximately 60%. In our opinion, the relatively high background level of optical losses is due to partial radiation leakage into the SOF structural cladding due to the uneven spatial distribution of YAG:Nd^{3+} nanocrystals in the silica glass matrix.

Figure 5 shows the luminescence spectra of coatings based on YAG:Nd^{3+} nanocrystals in preform channels and YAG:Nd^{3+} nanocrystalline inclusions in the composition of a microstructured SOF drawn from the preform. In the first case, a preform section of 1.5 cm in length was used for their evaluation, while in the second case, a SOF segment 0.5 m long. The shape of both luminescence spectra is characteristic of YAG:Nd crystals and is almost identical to the shape of bulk materials and nanocrystals obtained by various methods [12]. The main peak of radiation at a wavelength of 1064 nm corresponds to the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ electronic transition. The measured luminescence decay time in the SOF constituted 248 μs, which is comparable to the same parameter for a bulk crystal (292 μs).

4. Conclusions

We have presented data on the development of a polymer–salt method for the formation of YAG:Nd^{3+} crystals inside the preform channels of a silica microstructured optical

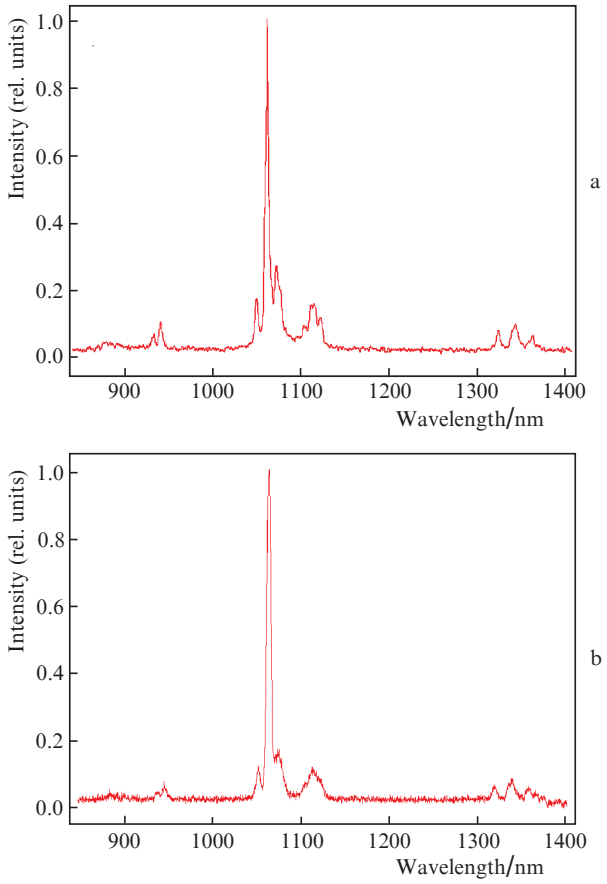

Figure 5. Luminescence spectra of (a) coatings based on YAG:Nd^{3+} nanocrystals in the preform channels and (b) YAG:Nd^{3+} nanocrystals in the composition of a microstructured SOF drawn from the preform. The neodymium concentration is 0.2 at. %.

fibre, distinguishing by technological simplicity and flexibility. The crystals were obtained by impregnating the channels with aqueous solutions of yttrium nitrate, aluminium nitrate, neodymium chloride, and polyvinylpyrrolidone, followed by drying and heat treatment at a temperature of 1100 °C. The prepared composite structure was drawn into the fibre at a temperature of 2000 °C. Using X-ray diffraction analysis, the presence of oriented YAG:Nd^{3+} crystals ranging in size from 25 to 37 nm in the silica glass matrix of fibre was established. The optical signal absorption bands characteristic of Nd^{3+} ions were revealed by measuring the spectral dependence of optical losses in the fibre. It is shown that the shape of the luminescence spectra of nanocrystals is typical of YAG:Nd with a radiation peak at a wavelength of 1064 nm. Further research will be aimed at the development of active optical elements with a uniform spatial distribution of nanocrystals over the fibre cross section and the reduction of optical losses at the operating wavelength.

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