Spectral shaping of lasing active medium with agglomerated nanoparticles of metals and dielectrics

Valeriy A. Donchenko[a,b], Alexey A. Zemlyanov[a,b], Mihail M. Zinoviev[a], Vladimir A. Kharenkov[a,b]
[a]Tomsk State University, Tomsk, Russia
[b]Siberian Physical Technical Institute, Tomsk, Russia

ABSTRACT

In this paper presented a series of experiments determine the spectral characteristics of random lasing in lasers with agglomerated nanoparticles metals and dielectrics. The data allowed us to establish that, in the active heterogeneous environment, there are various gain effects of lasing the impact of which is determined nanoparticles concentration.

Keywords: agglomerated nanoparticles, laser active media, spectral shaping of lasing

1. INTRODUCTION

Research of nanomaterials is of interest because of their physical properties different from the properties macroscopic objects. Much attention is paid to the optical properties of nanoparticles, since the introduction nanostructures in optical media leads to an increase in the efficiency their optical processes, such as luminescence, generation, Raman scattering [1,2]. The increase these processes is important in finding new ways to develop components of micro- and nanosystems for the transmission and processing of optical information, creation of ultra-sensitive sensors for diagnostics impurities of various substances.

Letokhov V.S. (1968) theoretically proved the possibility obtain of laser radiation in randomly inhomogeneous media [3]. In his work he presented description of shaping feedback in gain medium due to strong backscatter. This effect was first demonstrated experimentally Markushev V.M. (1986) [4] when working with samples of dielectric powders doped with neodymium ions. In further research lasing was obtained and investigated in randomly inhomogeneous active media on the basis of various nanoparticles. Currently, such studies form a new section of physical optics is called "random lasers" [5,6].

2. PROBLEM DEFINITION

The emission spectra of organic dyes have a number of features. Thus, in [7] reported on the red-shift spectrum of the emission dye R6G due to multiple scattering on nanoparticles TiO_2 which leads to an increase in the optical path. Such spectral shift they explained influenced of reabsorption effect or phenomenon of self-absorption of radiation inside the active medium. This is due to the overlap of absorption spectra dye with a spectrum of its radiation (Fig. 1).

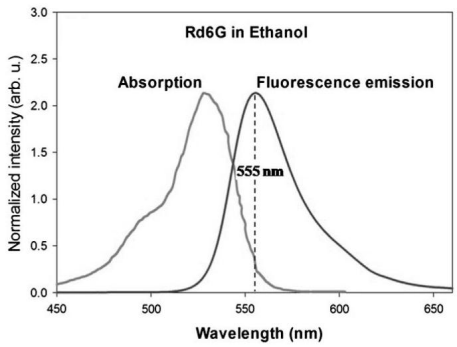

Fig. 1. The overlap of normalized absorption and emission spectra of ethanol solution of the R6G dye without nanoparticles [7]

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Radiation dye undergoes high absorption at shorter wavelengths as the distribution in the luminescent medium. The absorption of photons at the shorter wavelengths leads to the emission of a truncated in comparison with its own luminescence R6G, short-wavelength spectrum wing. Thus, the observed emission spectra are shifted to longer wavelengths. This effect is typical of random lasers.

However, there are a number of works [8,9], which experimentally obtained anomalous blue-shift of emission spectrum of the laser dye relative to the maximum range of its luminescence. In [8] by experiment was obtained lasing in the active medium with Al_2O_3 nanoparticles with spectral response having a blue-shift (Fig. 2). Similar results were also obtained in [10].

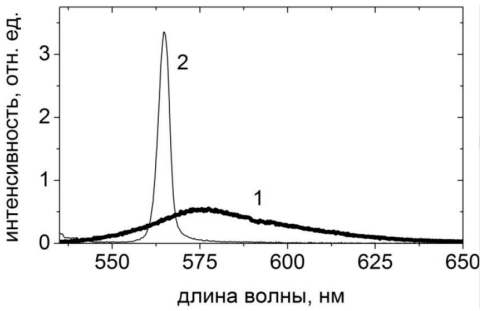

Fig. 2. The luminescence spectra of the dye R6G and lasing in bulk artificial opals. The pumping intensity exceeds the threshold 3 times (1 - luminescence, 2 - laser light) [10]

This feature was explained by the fact that the scattering of light by nanoparticles Al_2O_3 depends on radiation wavelength. That is, the greater efficiency of scattering will have photons shortest wavelength.

In this case, these photons will undergo a greater optical path of the inverted medium, so that when the threshold conditions occur the formation of generation in the blue region of the spectrum (with respect to the spectrum of the spontaneous luminescence). It does not explain the contradiction paintings spectral radiation in random lasers. Since shortwave photons are strongly absorbed by the molecules R6G (Fig. 2).

Our experiments were carried out in active media (ethanol solutions R6G) agglomerated nanoparticles dielectric - TiO_2 and Al_2O_3, metal - Ag and Al. Features lasing a single Ag nanoparticles and TiO_2 are well studied in [8-10]. Lasing with agglomerates of nanoparticles Ag, Al_2O_3, Al and TiO_2 was not investigated, at least we were not able to meet with such work.

In [11], we experimentally demonstrated that the introduction in thin layers (100 microns) of colloidal solutions R6G agglomerated nanoparticles Ag and Al leads to a decrease in the lasing threshold on the order in comparison with solutions doped of single nanoparticles Ag. We explained this decrease of thresholds presence near the surface of the agglomerates fields increased power density compared with the pump field. Then: 1) increasing the number of molecules R6G go into an excited state; 2) according to the Purcell effect [12] the rate of spontaneous emission of molecules R6G increase hence increase the number of photons and stimulated emission. This in turn will lead to lower the lasing threshold, on the one hand, and on the other hand, to the possibility of blue-shift of maximum of the lasing spectrum.

In [13] we have shown theoretically that the deformation of the shape of the spectrum lasing occurs due to the combined action of the effect of enhancing the degree of spatial heterogeneity of inverting the environment and reabsorption, which manifests itself in a shift of the center line of lasing, both the blue and the red region of the spectrum [13].

This work is dedicated to the establishment of laws of change of the radiation pattern of the spectral dispersion media, depending on the concentration and nature of the nanoparticles.

3. RESULTS AND DISCUSSION

In order to obtain the spectral characteristics of colloidal solution of dye laser Rhodamine 6G (Rhodamine 6G) agglomerated nanoparticles was collected installation shown schematically in Fig. 3.

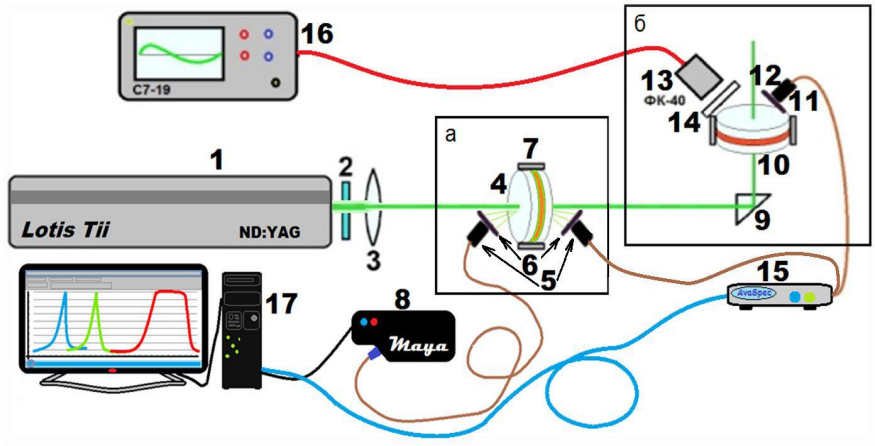

Fig. 3. – The experimental setup (1 – laser YAG:Nd^{3+}(λ = 532 nm), 2 – blue-green glass filter (to reduce background radiation λ = 1064 nm), 3 – focusing lens; A) 4,10 – cuvette, 5,11 – input window of receiving system, 6,12 – orange glass filter (to reduce background radiation λ = 532 nm), 7 – shaker, 8 – spectrometer Maya; Б) 9 – total internal reflection prism, 13 – photocathode, 14 – neutral glass filters ; 15 – spectrometer AvaSpec, 16 – oscilloscope C7-19, 17 – computer)

Focused laser beam laser Lotis TII LS-2132 UTF (λ = 532 nm, pulse duration of 6 ns, pulse repetition frequency of 1 Hz, the laser beam diameter of 2 mm) was directed through the total internal reflection prism perpendicular up and get to the horizontal position of the cell with a solution of the laser dye R6G (concentration of 10^{-3} mol/l) and agglomerates of nanoparticles. This arrangement allowed the cell: 1) to avoid leakage of solutions, 2) avoid the possibility of uneven height deposition of agglomerates nanoparticles.

In addition, the experimental setup was revised for easy study of colloidal solutions in "thick" cuvettes (2 mm), which are installed vertically on a piezoelectric shaker. Using ultrasonic oscillations of shaker supports in cuvette the same absorbance, which was controlled radiation laser He-Ne laser (not shown in figure).

The optical signal passing through the collimator and further fiber diameter of 400 microns, was recorded by the spectrometer Avaspec-ULS2048L-USB2 (450-680 nm) at an angle of 45°. This angle desk provides maximum received signal. For fine adjustment of pump pulse power fixed prisms Glan-Thompson, consisting of two spar prisms.

Obtained of electric explosion method nanoparticle agglomerates have identical morphology and size distribution and are clusters of closely spherical nanoparticles. Fig. 4 shows photomicrographs used agglomerates made with a transmission electron microscope JESP-II.

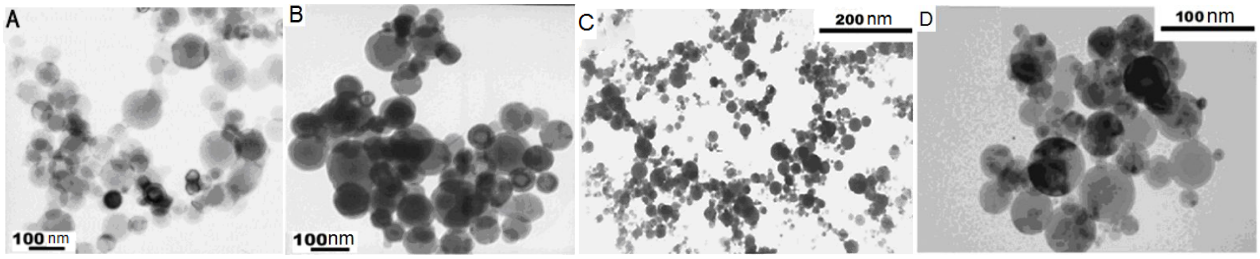

Fig. 4. Photomicrograph of aglomerated nanoparticles: A – silver (Ag); B – aluminum (Al); C – Al_2O_3; D – TiO_2

In the experiment, working colloidal dye solution was placed between two glass slides (active layer thickness was 20 microns) than that used by 2 mm cuvette. Microns layer dye R6G is characterized by the smallest influence reabsorption. According to the results of the experiment were obtained threshold characteristics of the microlayers R6G with different nanoparticles. They are shown in Fig. 5. The lenses were used as agglomerated nanoparticles of Al, Ag, TiO_2 and Al_2O_3.

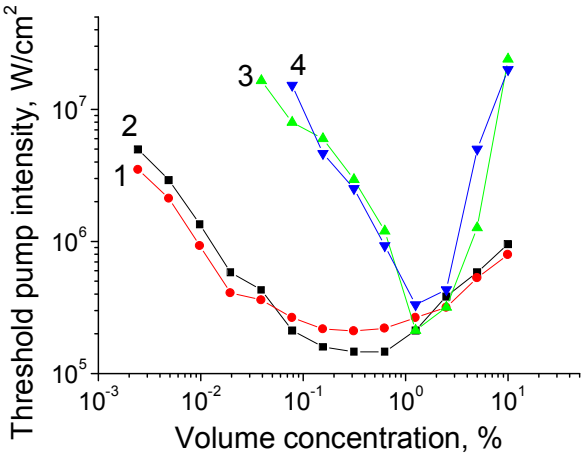

Fig. 5. The dependence of the lasing threshold pump intensity of the solution on the volume fraction of nanoparticles in the solution: 1 – Ag; 2 – Al; 3 – Al_2O_3; 4 – TiO_2

Fig. 5 shows that there is quite a significant range of values for the concentrations of metal nanoparticles (0.01-10 %), which are implemented the minimum thresholds of lasing in composite solutions such as metal nanoparticles-active medium. The magnitude of this range almost identical for Ag nanoparticles and Al. In the case of dielectric nanoparticles, this range is much narrower and is in the range from 1 % to 2,5 %.

This is an interesting dependence of the wavelength of maximum emission spectrum of nanoparticles concentration of used in the experiment (Fig. 6). Red line - lasing wavelength ethanolic R6G (concentration of 10^{-3} mol/l) without the addition of nanoparticles.

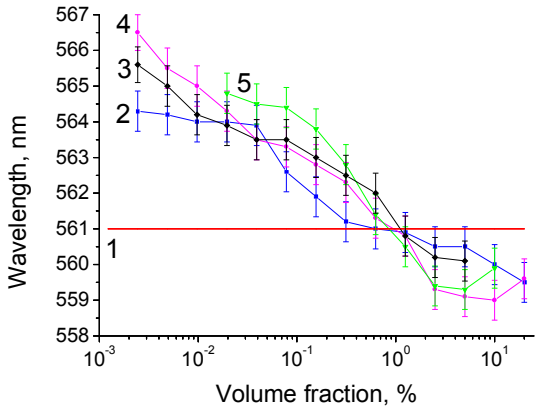

Fig. 6. The dependence of peak wavelength emission spectrum of nanoparticles concentration for cuvette 20 microns (1 – pure dye solution R6G; R6G with agglomerated nanoparticles: 2 – Ag; 3 – TiO_2; 4 – Al; 5 – Al_2O_3)

From the resulting spectral dependence can be seen that at low concentrations and it is < 1 % of the observed red-shift peaks generation spectrum for all working solutions. This suggests that this region dominates multiple scattering effect which leads to an increase in the optical path within the gain medium (ascending role effect reabsorption).

However, with increasing concentrations of nanoparticles we observe the dynamics of blue-shift of emission spectrum [8-10, 14]. This blue-shift is not typical for dye lasers, which due to the reabsorption effect present red-shift.

But how to use a very thin layer of the active medium, we can say that with increasing concentration of generation comes earlier (by volume) in the cell wall layer (from the pump). That is why the impact of reduced reabsorption and the lasing wavelength is shifted to shorter wavelengths.

The dependence of the wavelength on the nanoparticle concentration changes dramatically for TiO_2 and Al_2O_3 using a 2 mm cuvette (Fig. 7).

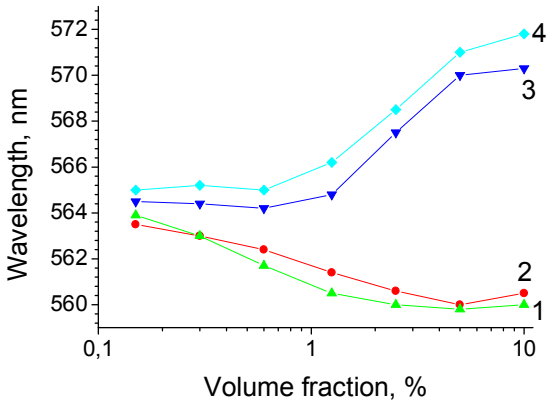

Fig. 7. The dependence of peak wavelength emission spectrum of agglomerated nanoparticles concentration for cuvette 2 mm (1 – Al; 2 – Ag; 3 – TiO_2; 4 – Al_2O_3)

It is evident that a 2 mm cuvette wavelength colloidal solution with nanoparticles dielectrics with increasing concentration shifted to longer wavelengths. This is due to the effect of multiple scattering on nanoparticles, which is the main mechanism for implementing low-threshold lasing in the case of dielectric nanoparticles such as TiO_2 and Al_2O_3.

A different picture when introducing metal nanoparticles, in this case there is a blue-shift. Such spectral behavior due to the presence of high local optical fields near the agglomerates surface of metal nanoparticles Ag and Al. As a consequence is an increase in the rate of spontaneous emission of molecules due to the effect Purcell [11] and increasing the efficiency of stimulated emission or lasing. Since spontaneous photons cause stimulated emission of molecules, this leads to an increase in efficiency of stimulated emission. This can manifest itself in reducing the lasing threshold or an increase in the maximum radiation intensity of the active medium at a fixed pumping energy. The region of the oscillation is reduced significantly, evidenced by a blue-shift.

4. CONCLUSION

Thus, our studies have shown that the introduction of the agglomerated metallic nanoparticles of Ag and Al in a thin layer (thickness about 20 microns) of an ethanol solution of rhodamine 6G concentration of 10^{-3} mol/l results in a significant (more than an order of magnitude) reduction of the lasing threshold in such media. The range of concentrations used agglomerates of nanoparticles of Ag and Al, which can be realized at minimum lasing threshold is sufficiently large and is 0.1% - 1% of volume fraction, for dielectric nanoparticle agglomerates Al_2O_3 and TiO_2 in the range less than 5 times and 1% - 2%. For solutions forming thin layers generation occurs at concentrations of 1% - 10% in the front (with respect to the incident radiation) field generating layer by the action of local field of high power density generated near the surface of the metal nanoparticle agglomerates. This is evidenced by the blue shift of the peak wavelength of the lasing spectrum and its short-wave dynamics during the growth of the concentration of agglomerates. Thus short-wave dynamics of the maximum emission spectrum of metal nanoparticles is observed for Ag and Al in the "thin" (20 microns), and the "thick" (2 mm) cuvettes. At the same time, agglomerates of dielectric nanoparticles Al_2O_3 and TiO_2, the opposite pattern - for “thin” cuvettes observed blue shift with increasing concentration of agglomerates, and for “thick” - on the contrary, the red shift. This spectral shifts are accompanied by a catastrophic increase in the lasing threshold. The red shift can be explained by the influence of reabsorption at low concentrations in the thin cuvettes agglomerates, the dynamics of the red side in the thick cuvettes - also an increase in the optical path for forming the threshold conditions and related reabsorption.

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