

Stimulated emission from aluminium anode oxide films doped with rhodamine 6G

N.Kh. Ibrayev, A.K. Zeinidenov, A.K. Aimukhanov, K.S. Napolskii

Abstract. The spectral and luminescent properties of the rhodamine 6G dye in a porous matrix of aluminium anode oxide are studied. The films with a highly-ordered porous structure are produced using the method of two-stage anodic oxidation. By means of raster electron microscopy it is found that the diameter of the pores amounts to nearly 50 nm and the separation between the adjacent channels is almost 105 nm. The thickness of the films is equal to 55 μm , and the specific surface area measured using the method of nitrogen capillary condensation is 15.3 $\text{m}^2 \text{g}^{-1}$. Fluorescence and absorption spectra of rhodamine 6G molecules injected into the pores of the aluminium anode oxide are measured. It is found that under the excitation of samples with the surface dye concentration $0.3 \times 10^{14} \text{ molecules m}^{-2}$ by the second harmonic of the Nd:YAG laser in the longitudinal scheme with the pumping intensity 0.4 MW cm^{-2} , a narrow band of stimulated emission with the intensity maximum at the wavelength 572 nm appears against the background of the laser-induced fluorescence spectrum. A further increase in the pumping radiation intensity leads to the narrowing of the stimulated emission band and an increase in its intensity. The obtained results demonstrate the potential possibility of using the porous films of aluminium anode oxide, doped with laser dyes, in developing active elements for quantum electronics.

Keywords: aluminium anode oxide, rhodamine 6G, fluorescence, stimulated emission.

1. Introduction

Polymer matrices [1, 2], sodium-borosilicate porous glasses [3] and glasses obtained using the sol–gel method [4, 5] are widely used as active media in solid-state lasers. The drawback of polymer media is the radical reactions involving dye molecules that lead to the destruction of matrices [6]. In addition, the porous glass manufacturing is labour-consuming.

At the present time intense studies are carried out to obtain laser oscillation in nanostructured materials doped with laser dyes [7–10]. The dye molecules are deposited on the surface of nanoparticles [11, 12] or are introduced into nanoscale porous structures [13, 14]. In cylindrical microreso-

nators such structures can support the modes with a high Q -factor due to the effect of total internal reflection of the electromagnetic wave from the resonator walls [15]. Due to the high-efficiency concentration of the electromagnetic field inside the microresonator, the rates of the radiation processes are essentially increased [16]. Filling the microresonators with laser dyes yields a system that can be used as an active medium for a tunable laser.

The porous aluminium anode oxide doped with laser dyes is one of the promising materials that can serve as an active medium. The structure of the films of the aluminium anode oxide presents a system of ordered densely packed pores. The pores are arranged perpendicular to the surface of the film, and their diameter and the separation between them can be varied by changing the anode oxidation conditions [17].

The porous aluminium oxide has a number of advantages, e.g., chemical and thermal resistance, transparency in the visible range of the spectrum, perfect adsorption properties caused by the large volume of pores with branched surface [18, 19]. The films of aluminium anode oxide are widely used as matrices in fabricating different nanostructures by means of the template method [20–22]. The available initial substances for the synthesis of such matrices and the simplicity of their fabrication process allow one to expect that the resulting laser-active media will have relatively low cost in comparison with other lasing elements.

It is known that in porous films of the aluminium anode oxide the photoluminescence in the blue spectral region occurs, the properties of which are largely dependent on the composition of the electrolyte used in the anode oxidation [23–25]. The spectral composition of the radiation emitted by the aluminium anode oxide is caused by the production of F-centres in different charged states.

The study of the fluorescence properties of dyes, introduced into the pores of the aluminium oxide, was carried out in Refs [26, 27]. The authors of these papers attribute the increase in intensity of the rhodamine 6G fluorescence in the aluminium oxide matrix in comparison with the intensity of the rhodamine 6G in porous glasses to the energy transfer from the oxygen vacancies to the luminescent molecules. In Ref. [28] the optical and lasing properties of the sol–gel aluminium oxide films doped with laser dyes rhodamine 6G, rhodamine B and oxazine 4 are studied. The laser oscillation was observed under the Förster energy transfer from rhodamine 6G to rhodamine B in sol–gel Al_2O_3 films [29]. The dependences of the efficiency of the pump energy conversion into the energy of stimulated emission and the maximum of its intensity on the donor concentration in the films were studied. The maximal efficiency amounted to $\sim 2.1\%$ in both cases.

N.Kh. Ibrayev, A.K. Zeinidenov, A.K. Aimukhanov Institute of Molecular Nanophotonics, E.A. Buketov Karaganda State University, ul. Universitetskaya 28, 100028 Karaganda, Republic of Kazakhstan; e-mail: asyl-zeinidenov@mail.ru;

K.S. Napolskii Department of Chemistry, M.V. Lomonosov Moscow State University, Vorob'evy Gory, 119991 Moscow, Russia

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One of the main disadvantages of the existing laser active elements based on the stained polymer materials is the fast degradation of their functional properties due to the low heat conduction and insufficient thermal stability of the polymer. For example, in widely used polymethylmethacrylate the heat conduction coefficient is equal to $0.19 \text{ W m}^{-1} \text{ K}^{-1}$ [30], which is by an order of magnitude smaller than in the porous aluminium oxide ($1.6 \text{ W m}^{-1} \text{ K}^{-1}$ [31]). In Ref. [31] it was shown that the membranes of the aluminium anode oxide are a promising material for designing high-technology devices operating at high temperatures. The porous structure of the aluminium anode oxide does not undergo significant changes and remains stable in a wide temperature interval up to 1000°C . This is also one of the advantages of using porous aluminium oxide in fabricating solid-state active elements for tunable dye lasers. The use of a porous aluminium oxide matrix will facilitate fast dissipation of heat resulting from the internal conversion in the dye molecules.

In the present paper we report the results of the studies of the transformation of spontaneous fluorescence into the stimulated emission of rhodamine 6G molecules embedded in a porous matrix of aluminium anode oxide.

2. Preparation of samples and experimental technique

The aluminium oxide synthesis was implemented under 'mild' conditions, including two stages of anodic treatment at the voltage of $U = 40 \text{ V}$ in the solution of oxalic acid (0.3 M) [32]. The source material was aluminium plates (the degree of purity 99.99%) with the thickness 0.5 mm and the dimensions $3.5 \times 3.5 \text{ cm}$. To increase the size of aluminium crystallites, to remove the microstresses in the sample and to achieve better ordering of the obtained pores, the aluminium substrates were annealed in the muffle furnace in air during 10 hours at the temperature $T = 500^\circ\text{C}$. To remove the surface defects of the aluminium, it was electrochemically polished in the pulsed regime in the solution of CrO_3 in H_3PO_4 . After that the samples were washed in distilled water and dried in air.

The anode treatment of the aluminium was implemented in a two-electrode electrochemical cell using an MPS-7081 direct current source. A platinum plate served as an auxiliary electrode, and the polished aluminium foil was used as a working electrode. The electrolyte was prepared on the basis of water, double-filtered and deionised using an AquaMax 360 Basic water purifier. The specific resistance of the water amounted to $18.2 \text{ M}\Omega \text{ cm}^{-1}$. The resulting matrices of aluminium oxide were separated from the non-reacted aluminium as a result of the selective dissolving of the latter in the solution of CuCl_2 in NCl .

The sorption of the molecules of the rhodamine 6G dye into the pores was implemented by keeping the aluminium oxide films in the ethanol solution of the luminophor with the initial concentration $C' = 10^{-4} \text{ mol L}^{-1}$ during 5 h with subsequent drying of the films in the drying box at the temperature 100°C during 1 h.

The number of adsorbed luminophor molecules (the surface concentration*) was determined by measuring the change of the solution optical density as a result of sorption using the expression

$$C = \frac{N_A C' V}{MS} \left(1 - \frac{D_2}{D_1}\right), \quad (1)$$

where V is the solution volume; C' is the concentration of the dye solution; D_1 and D_2 are the optical densities before and after the sorption; S is the specific surface of the porous aluminium oxide; N_A is the Avogadro number ($6.022 \times 10^{23} \text{ mol}^{-1}$); and M is the molar mass of the dye (479 g mol^{-1}).

The specific surface of the film was determined using the BET (Brunauer–Emmet–Teller) method by measuring the nitrogen adsorption using a Sorbi MS measuring system. The specific surface area of the obtained aluminium oxide membranes amounted to $15.3 \pm 0.2 \text{ m}^2 \text{ g}^{-1}$.

The absorption and fluorescence spectra of rhodamine 6G were measured using a CM2203 spectrophotometer (Solar). The fluorescence decay kinetics of rhodamine 6G was measured using the spectrofluorimeter with picosecond resolution operating in the time-correlated photon counting mode. The fluorescence of the samples was excited by the radiation of semiconductor lasers with the oscillation wavelengths $\lambda = 375$ and 488 nm and the pulse duration at the intensity half-maximum level $\tau = 40 \text{ ps}$. The relative error of the spectral measurements using a CM3303 spectrophotometer does not exceed 2%. The precision of measuring the absorption spectra was $\pm 2 \text{ nm}$, and the precision of measuring the fluorescence spectrum equals $\pm 1 \text{ nm}$.

The spectral characteristics of the stimulated emission from the films were measured using the setup, schematically presented in Fig. 1. The spectral characteristics were studied under the excitation of the samples with the radiation of the second harmonic of an Nd:YAG laser (1) (Solar LQ 215, $\lambda = 532 \text{ nm}$, $E_p = 90 \text{ mJ}$, $\tau = 10 \text{ ns}$) in the longitudinal geometry. The cavity was formed by two glass plates, between which a film (5) was placed. The pumping radiation, passed through an aperture (3), was focused by a lens (4) onto the film surface to produce a circular spot with the area of 0.13 cm^2 .

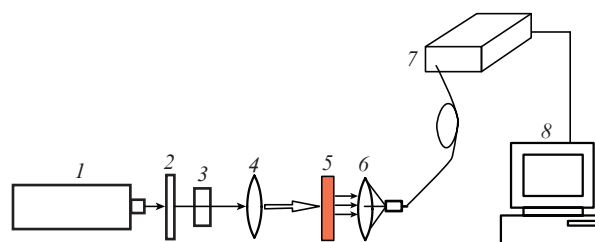


Figure 1. Schematic diagram of the setup for studying the characteristics of stimulated emission by thin films: (1) LQ215 laser; (2) neutral optical filters; (3) aperture; (4, 6) focusing lenses; (5) sample under study; (7) AvaSpec-2048 spectrometer; (8) computer.

The intensity of pumping radiation was varied by means of neutral optical filters (2) and amounted to $0.01\text{--}1 \text{ MW cm}^{-2}$. The stimulated radiation was focused with a collecting lens (6) onto the input optical fibre of an AvaSpec-2048 spectrometer (7), connected to a computer (8). The relative error in determining the spectral characteristics was equal to 3%.

The quantum yield Φ_{fl} of the fluorescence of the dye molecules was measured in the absolute units by means of an AvaSphere-50-REFL reflectometry sphere (Avantes BV). The error of Φ_{fl} determination was no greater than 5%.

* Hereafter, we use the term 'concentration' is used.

3. Results and discussion

The images of the surface and the transverse cleavage of the samples, obtained using a Leo Supra 50VP scanning electron microscope (SEM), are shown in Fig. 2. The measurements were carried out at the accelerating voltage 7 kV and the working distance 7 mm under the high-vacuum conditions. At the surface of the film the pores are observed having a similar diameter ~ 50 nm, separated by a distance ~ 105 nm (Fig. 2a). At the transverse cleavage of the sample (Fig. 2b) one can see straight parallel channels, perpendicular to the surface.

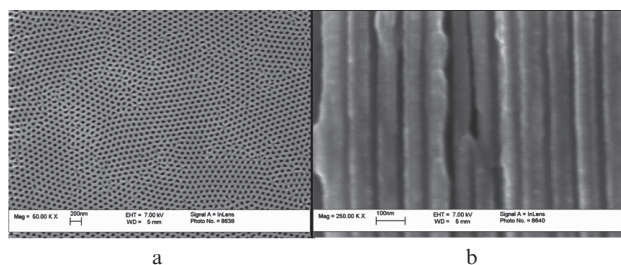


Figure 2. SEM images of the porous film of aluminium anode oxide, obtained using the method of two-stage anode treatment in the oxalic acid solution (0.3 M) under the voltage of 40 V; the lower side of the oxide film after the removal of the barrier layer (a) and the transverse cleavage (b).

Figure 3 presents the absorption and fluorescence spectra of rhodamine 6G molecules, adsorbed in porous matrix channels. It is seen that the absorption band of the dye in the matrix has a maximum at the wavelength $\lambda = 524$ nm. The photoexcitation of the dye fluorescence was implemented in the luminophor absorption band at $\lambda = 520$ nm. The fluorescence spectrum had a maximum at $\lambda = 572$ nm.

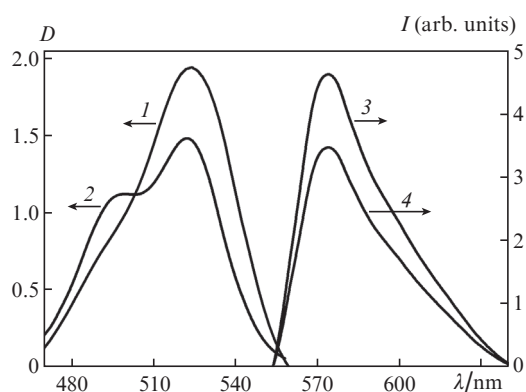


Figure 3. Spectra of (1, 2) absorption and (3, 4) fluorescence of rhodamine 6G in the matrix of porous aluminium oxide for the dye concentration (1, 3) 0.3×10^{14} and (2, 4) 0.46×10^{14} molecules m^{-2} .

When the concentration of rhodamine 6G molecules is increased, one can observe the reduction of the optical density in the absorption band of monomers. Alongside with this, a new maximum appears at the short-wavelength wing of the spectrum [curve (2)], associated with the formation of dye dimers. The absorption by dimers also leads to the broadening of the absorption spectrum. For monomers the half-

width of the absorption spectra is $\Delta\lambda_{1/2}^{\text{abs}} = 42$ nm. With the growth of dye concentration the absorption band is broadened up to $\Delta\lambda_{1/2}^{\text{abs}} = 54$ nm. The dye concentration increase leads also to rhodamine 6G fluorescence quenching [curve (4)]. The obtained data are typical for high-concentration liquid and solid solutions of rhodamine 6G and agree with the results obtained by other authors [33].

Thus, the observed changes in the absorption and fluorescence spectra under the increasing number of adsorbed molecules in the pores of the aluminium oxide confirm the molecular aggregation of the dye.

Figure 4 illustrates the dependence of the luminophor fluorescence intensity on the number of dye molecules, adsorbed in aluminium oxide pores. It is seen that the dye fluorescence intensity ($\lambda = 572$ nm) increases to a certain critical value with the growth of the dye concentration in the pores, and after attaining a critical value the fluorescence intensity begins to decrease. The optimal time of the dye sorption, corresponding to the maximal fluorescence intensity, amounted to 5 h. In this case the number of molecules in the aluminium oxide pores was 0.3×10^{14} molecules m^{-2} . The reduction of fluorescence intensity for the concentrations exceeding the critical one is due to the aggregation of dye molecules [Fig. 3, curves (2, 4)].

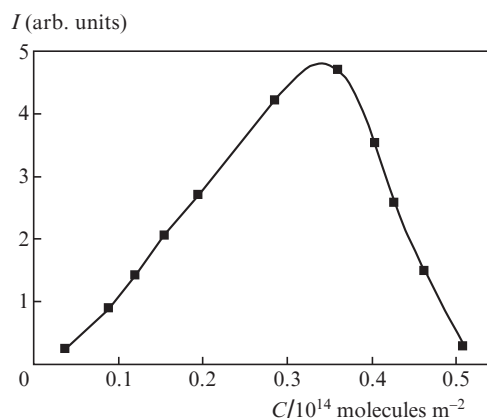


Figure 4. Dependence of dye fluorescence intensity at $\lambda = 572$ nm on the concentration of adsorbed molecules.

Inside the aluminium oxide pores the quantum yield Φ_f of rhodamine 6G fluorescence, determined using the de Mello method for calculating absolute quantum yields of mixed systems [34], amounted to 0.52. The obtained value is comparable to the quantum yields of the dye fluorescence in the matrices of methyl methacrylate (0.53 [35]) and epoxy polymer (0.67 [36]).

The fluorescence decay kinetics of rhodamine 6G molecules in the porous aluminium oxide film and the fluorescence of the porous aluminium oxide film itself are presented in Fig. 5. The lifetimes of the excited states, calculated using the exponential parts of the decay curves, amounted to 1.7 and 3.3 ns for rhodamine 6G and the porous aluminium oxide, respectively. Rhodamine 6G in the porous aluminium oxide was excited at the wavelength $\lambda = 488$ nm, and the intrinsic luminescence of the aluminium oxide was excited at $\lambda = 375$ nm.

The stimulated emission from the dye molecules in the aluminium anode oxide film was observed in the maximum of

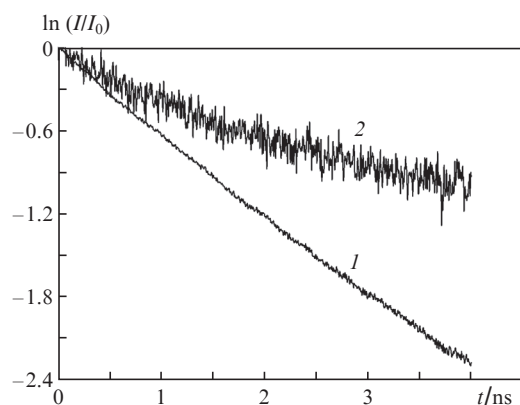


Figure 5. Decay kinetics for the fluorescence of rhodamine 6G in the film of porous aluminium oxide (1) and the fluorescence of porous aluminium oxide itself (2).

the fluorescence band (Fig. 6). From Fig. 6 it is seen that at the pumping radiation intensity $P \leq 0.2 \text{ MW cm}^{-2}$ only the spectrum of laser-induced fluorescence of dye is observed [curves (1, 2)]. At $P \sim 0.4 \text{ MW cm}^{-2}$ a narrow band of stimulated emission appears against the background of this spectrum with the maximum at the wavelength 572 nm [curve (3)]. A further increase in the pumping radiation intensity leads to an increase in the stimulated emission intensity and reduction of its spectral bandwidth. At $P = 0.8 \text{ MW cm}^{-2}$ the integral intensity of the stimulated radiation exceeds the intensity of the spontaneous one [curve (4)]; however, it is not possible to suppress the spontaneous radiation completely.

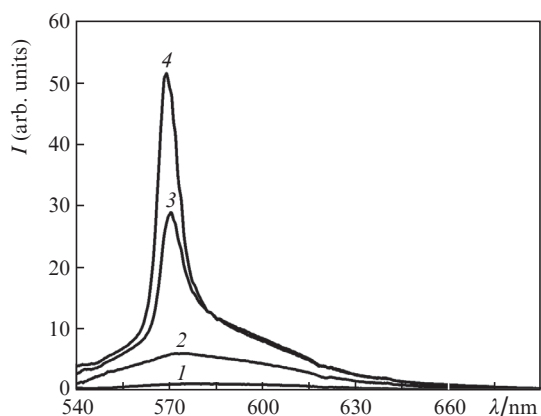


Figure 6. Emission spectra of rhodamine 6G molecules in the aluminium anode oxide at the pumping radiation intensity $P = (1) 0.04$, (2) 0.2, (3) 0.4 and (4) 0.8 MW cm^{-2} . The dye concentration in the film amounts to $0.3 \times 10^{14} \text{ molecules m}^{-2}$.

The appearance of the stimulated radiation, when using a low- Q -factor resonator formed by two glass plates, is related to the fact that, besides the Fresnel reflection from them, in the studied system the reflection occurs from the walls of the cylindrical pores of the matrix that serve as microresonators. Due to the total internal reflection of the electromagnetic wave from the microresonator walls, the energy density of the electromagnetic field accumulated in the pores becomes very high, which facilitates a considerable increase in the radiation intensity from the dye molecules in the pores.

From the spectra of stimulated emission the dependences of the radiation band half-width $\Delta\lambda_{1/2}$ and the intensity of the film glow on the pumping intensity were found (Fig. 7). When the pumping intensity varies from 0.1 to 0.8 MW cm^{-2} , the radiation intensity in the maximum of the spectrum increases almost by 50 times, and $\Delta\lambda_{1/2}$ decreases by 7.4 times. The reduction of the radiation bandwidth with the growth of the excitation intensity confirms the dominance of the stimulated emission over the spontaneous one.

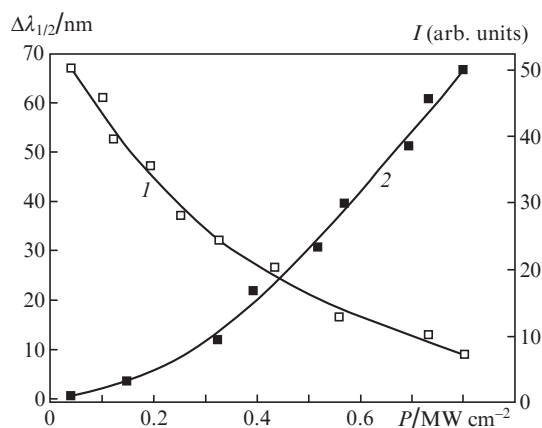


Figure 7. Dependence of the stimulated emission spectrum half-width (1) and intensity (2) on the pumping intensity.

4. Conclusions

In the present work we have studied the spectral and luminescence properties of aluminium anode oxide films having a highly-ordered porous structure doped with the molecules of the rhodamine 6G dye. The quantum yield of the dye fluorescence in the aluminium oxide matrix is equal to 0.52. At the pumping intensity $P = 0.1 \text{ MW cm}^{-2}$ only the spectrum of laser-induced fluorescence of the dye is observed. When the intensity reaches $P = 0.4 \text{ MW cm}^{-2}$, a narrow band of stimulated emission with the maximum at the wavelength 572 nm appears against the background of this spectrum. With increasing pump intensity from 0.1 to 0.8 MW cm^{-2} the intensity of radiation in the spectral maximum increases by almost 50 times, and $\Delta\lambda_{1/2}$ decreases by 7.4 times. The obtained results demonstrate the potential possibility of using the porous films of aluminium anode oxide doped with laser dyes in laser-active elements.

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