

PROPERTIES OF STIMULATED EMISSION OF THE PM567 DYE IN PORES OF ANODIZED ALUMINUM OXIDE

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Properties of the stimulated emission of the PM567 dye in porous aluminum oxide are investigated. It is established that when PM567 molecules are doped into aluminum oxide pores, a small part of dye molecules forms aggregates. The quantum yield of fluorescence of PM567 in Al_2O_3 is $\Phi_f = 0.85$. The stimulated emission of PM567 in the Al_2O_3 film is observed in the short-wavelength maximum of the fluorescence band. The threshold of the stimulated emission is 2 MW/cm^2 . The kinetics of the decay of stimulated emission is measured. It is demonstrated that low- Q lasing of the stimulated emission of PM567 in the film with $Q \geq 1 \cdot 10^2$ is caused by the fact that the geometry of rays in pores does not correspond to that of complete internal reflection, and hence, the radiative losses increase. The efficiency of lasing of PM567 in Al_2O_3 is 0.3%.

Keywords: PM567 dye, stimulated emission, porous aluminum oxide, threshold of stimulated emission, resonator Q-factor, efficiency.

INTRODUCTION

In the optical range, cylindrical microresonators can support high- Q ($\sim 10^5$ – 10^9) modes due total internal reflection of an electromagnetic wave from resonator walls [1]. Because the concentration of the electromagnetic field in the resonator is high, the intensity of radiative processes is amplified. For this reason, the cylindrical microresonators can be used to enhance optical transitions [2].

In this regard, one of the promising materials based on which laser active media can be prepared is porous aluminum oxide. The structure of anode aluminum oxide films represents a system of ordered densely packed pores. The pores are perpendicular to the film surface, and their diameter and spacing can be varied by changing the anodizing conditions [3].

The pores of the cylindrical resonators can be filled by organic dye molecules having high quantum yield and broadband luminescence. The luminescent properties of dyes impregnated into aluminum oxide pores were studied in [4, 5]. In [6] it was demonstrated that the increase in the fluorescence intensity of rhodamine 6G in the porous aluminum oxide matrix in comparison with porous glasses is caused by energy transfer from oxygen vacancies to luminophore molecules. A. V. Kukhta *et al.* [7] demonstrated the possibility of obtaining organic light-emitting devices based on anode porous aluminum oxide films. Membranes made of anode aluminum oxide are a promising material for the development of hi-tech devices operating at elevated temperatures [8]. The anode aluminum oxide structure does not undergo considerable changes and remains stable in a wide temperature interval up to 1000°C . The thermal conductivity of aluminum oxide films is equal to 1.6 W/m/K , which is much higher than the thermal conductivity of polymeric materials and glasses used as solid-state matrices of tunable dye lasers [9, 10]. If Al_2O_3 microresonators are filled with laser dyes, such system can be used as an active medium of a tunable laser. In this case, the use of a porous

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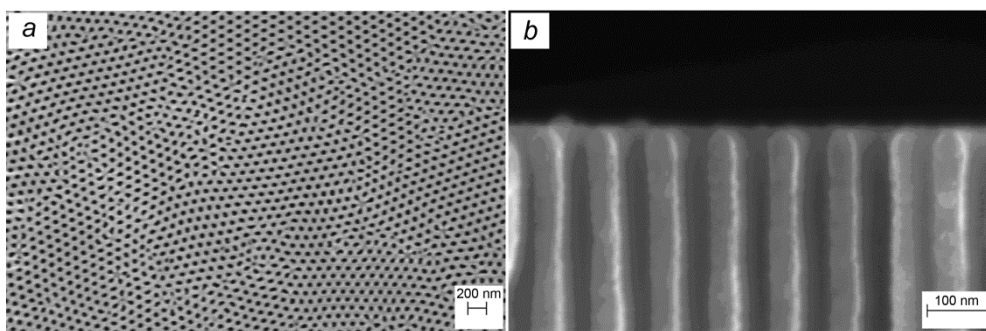


Fig. 1. REM images of the porous film prepared by anode oxidation of Al in 0.3 M $(\text{COOH})_2$ at 40 V.

aluminum oxide matrix will promote fast dissipation of heat liberated due to the absorption of light as a result of processes of internal conversion and vibrational relaxation in dye molecules.

In [11, 12], the stimulated emission was first obtained in anodized aluminum oxide pores filled with rhodamine 6G molecules. Further investigations in this direction were performed in [13]. The present work is a continuation of investigations of the stimulated emission of dyes in Al_2O_3 . As an active medium, the PM567 dye of pyromethene series was chosen. The particular interest to dyes of this class is caused by the fact that they are the effective class of laser dyes with extremely low probability of the induced absorption compared with the induced emission [14].

EXPERIMENTAL PROCEDURE

Porous aluminum oxide was synthesized under *soft* conditions, including two anodizing stages at the voltage $U = 40$ V in 0.3 M solution of oxalic acid [15]. As an initial material, aluminum plates (degree of purity of 99.99%) with a thickness of 0.5 mm and sizes of 3.5×3.5 were used. To increase sizes of aluminum crystallites, to remove microstresses in the sample, and to achieve subsequently the best ordering of pores, the aluminum substrates were annealed in a muffle furnace at atmospheric pressure for 10 h at $T = 500^\circ\text{C}$. To remove surface defects of aluminum, electrochemical polishing in a pulsed regime was performed in CrO_3 and H_3PO_4 solution. After that, the samples were washed out in distilled water and dried in air. Aluminum was anodized in a two-electrode electrochemical cell. The porous aluminum oxide matrices were separated from the aluminum base by selective dissolution of the last in CuCl_2 solution in HCl.

The morphology of the film surface measured with a MIRA 3LMU raster electron microscope (REM) is shown in Fig. 1. Measurements were performed at accelerating voltage of 7 kV and working distance of 7 mm in high vacuum. Pores of identical diameters of ~ 80 nm spaced at 105 nm can be seen on the film surface.

Dye molecules were sorbed in pores by holding aluminum oxide films in ethanol luminophore solution with initial concentration $C = 10^{-4}$ mol/L for 20 h and subsequent drying of films at a temperature of 100°C for 3 h. The film absorption spectra were measured with a Cary UV-VIS (Agilent Technologies), and the fluorescence spectra were measured with a Cary Eclipse (Agilent Technologies).

RESULTS AND DISCUSSION

The absorption and fluorescence spectra of PM567 molecules incorporated into channels of the porous matrix demonstrated that the absorption band of the dye in the matrix had a maximum at the wavelength $\lambda = 524$ nm (Fig. 2). The dye fluorescence was photoexcited in the luminophore absorption band at the wavelength $\lambda = 500$ nm. The fluorescence spectrum had two maxima at $\lambda_{\text{max}} = 547$ and 565 nm.

Figure 2 shows the absorption and fluorescence spectra of the dye molecules in the solution of ethyl alcohol with concentration $C = 10^{-5}$ mol/L. The absorption spectrum of the dye in Al_2O_3 pores was broadened in comparison

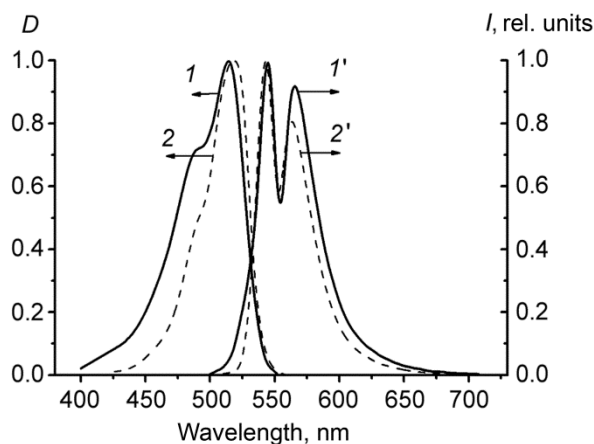


Fig. 2. Absorption (curves 1 and 2) and fluorescence spectra (curves 1' and 2') of PM567 in the porous aluminum oxide matrix (curves 1 and 1') and ethyl alcohol (curves 2 and 2').

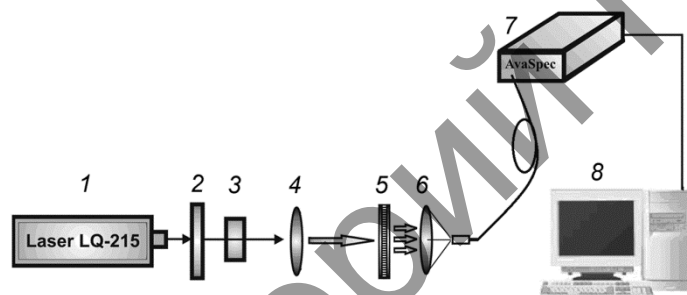


Fig. 3. Block diagram of the setup for investigation of the characteristics of stimulated emission of thin films comprising LQ 215 laser 1, neutral filters 2, diaphragm 3, collecting lenses 4 and 6, examined sample 5, AvaSpec-2048 spectrometer 7, and computer 8.

with the absorption spectrum in ethyl alcohol, and the spectral maximum was shifted by 6 nm toward shorter wavelengths. Along with this, the shoulder ($\lambda_{\text{max}} = 475$ nm) was observed in the short wavelength wing of the absorption spectrum. The shape of the fluorescence spectrum of the dye in Al_2O_3 pores undergoes no changes in comparison with the alcohol solution, and the positions of the spectral maxima do not change.

Since the dye molecules are densely packed in pores, the observed changes of the absorption spectrum in comparison with the alcohol solution testify that a small part of dye molecules forms aggregates. The quantum yield of fluorescence of PM567 in aluminum oxide pores determined by the de Mello method of calculating the absolute quantum yield of mixed systems [16] was $\Phi_f = 0.85$.

The spectral characteristics of the stimulated emission of films were measured using the setup whose block diagram is shown in Fig. 3. The spectral characteristics were investigated for samples excited by the second harmonic of Nd:YAG-laser 1 (SOLAR LQ 215, $\lambda_{\text{gen}} = 532$ nm, $E_p = 90$ mJ, and $\tau = 10$ ns) in the longitudinal configuration. The resonator was formed by two glass plates between which film 5 was inserted. Pump radiation passed field stop 3 by means of lens 4 and was focused onto the film surface in the form of the circle having an area of 0.13 cm².

The pump power density was varied in the range 0.01 – 1 MW/cm² using neutral optical filters 2. The stimulated emission was focused with collecting lens 6 onto the input of the AvaSpec-2048 fiber-optical spectrometer. The lasing

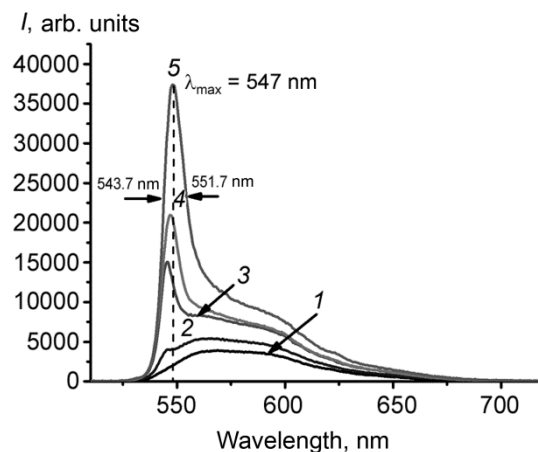


Fig. 4. Lasing spectra of PM567 molecules in anode aluminum oxide for pump power density $P = 1.1$ (curve 1), 2 (curve 2), 3 (curve 3), 4.6 (curve 4), and 7.7 MW/cm^2 (curve 5).

spectra were measured with AvaSpec-2048 7 spectrometer connected to computer 8. The relative error of determining the spectral characteristics was 3%.

The spectra of stimulated emission of PM567 molecules in the cylindrical nanoresonator with the diameter $D = 80 \text{ nm}$ are shown in Fig. 4. The stimulated emission of dye molecules in the anode aluminum oxide film was observed in the short-wavelength maximum of the fluorescence band. As can be seen from Fig. 4, for pump source power density up to 1.1 MW/cm^2 , only the spectrum of laser-induced fluorescence of the examined dye was observed (curve 1).

When the pump source power density reached about 3 MW/cm^2 , a narrow band with a maximum at a wavelength of 547 nm , belonging to laser radiation, arose against the background of the spectrum of laser-induced fluorescence (curve 3). Further increase in the pump source power density led to narrowing of the fluorescence spectrum and developing of the lasing band. As the pump power density achieved 7.7 MW/cm^2 , the stimulated emission component prevailed over the spontaneous emission component (curve 5); however, it was not possible to exclude completely the spontaneous emission component. The Q-factor of the resonator was estimated from the formula

$$Q = \frac{\lambda}{\delta\lambda_{1/2}}.$$

For $\delta\lambda = 8 \text{ nm}$, we obtain $Q \geq 1 \cdot 10^2$ at a wavelength of 547 nm . Such low-Q lasing of stimulated emission is due to the fact that the geometry of rays in pores was not close to the geometry of rays for total internal reflection in the cylindrical resonator with nanoscale dimensions, and hence, the radiative losses increased [1].

The dependences of the half-width of the lasing spectrum and the intensity of the stimulated emission of the film on the pump radiation power density were drawn from the measured emission spectra (Fig. 5), and their threshold values for the film were determined. Narrowing of the emission band with increasing intensity of excitation testifies to the prevalence of the stimulated emission over the spontaneous one, that is, to the system transition to the lasing regime. The lasing threshold was determined from the sharp change of the growth rate of the intensity of film emission. For laser pumping at $\lambda_{\text{las}} = 532 \text{ nm}$, the lasing threshold, on average, was 2 MW/cm^2 (Fig. 5).

The energy characteristics of PM567 in Al_2O_3 pores were measured with an OPHIR NOVA II laser power meter. Investigations demonstrated that for PM567 in aluminum oxide pores, the dependence of the lasing efficiency on the pump source power density was observed (Fig. 6). Based on the results obtained, optimal conditions of excitation of dye in pores can be chosen. A maximal efficiency of 0.3% was obtained for PM567 in Al_2O_3 at pump source power density of $3\text{--}3.5 \text{ MW/cm}^2$. At pump power density higher than 3.5 MW/cm^2 , the dye efficiency decreased.

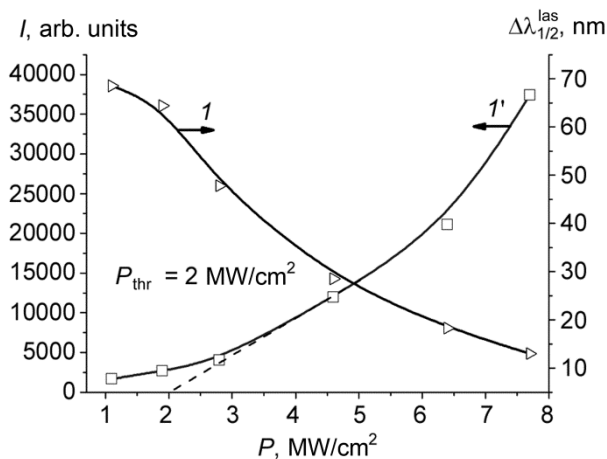


Fig. 5. Dependence of the lasing line half-width (curve 1) and luminescence intensity (curve 1') of PM567 in the porous anode aluminum oxide matrix on the pump power density.

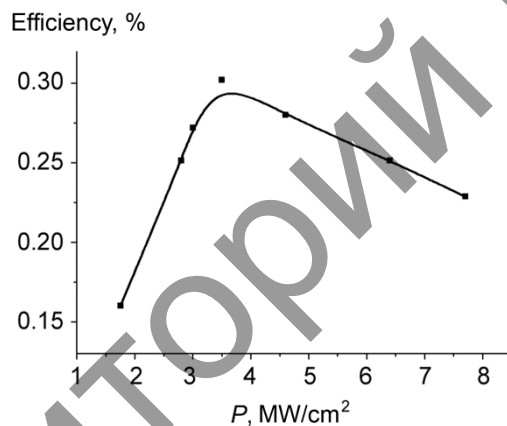


Fig. 6. Dependence of the lasing efficiency of PM567 in aluminum oxide pores on the pump power density.

The kinetics of the stimulated emission of Al_2O_3 films doped with PM567 molecules was measured using a DET025A picoseconds receiver (Thorlabs) and a DSO-X-3102A oscilloscope (Agilent Technologies). The full width of the instrumental function of the measuring system at half maximum was 0.3 ns.

Results of measurements of the kinetics of emission of Al_2O_3 films with PM567 molecules at the indicated pump power densities are shown in Fig. 7. It should be noted that the pulse duration of the stimulated emission of PM567 in the film did not exceed the pump source pulse duration ($\tau_p = 10$ ns). In the regime of spontaneous luminescence, the luminescence duration was ~ 7 ns (curve 1). With increasing pump source power density, an increase in the luminescence intensity was observed (curves 2 and 3). At the same time, the luminescence pulse duration did not decrease. This confirms the fact that the inversed population density in the active medium is formed during the lifetime of the excited state of PM567 molecules. The lasing characteristics of PM567 in the porous anode aluminum oxide film are given in Table 1.

TABLE 1. Lasing Characteristics of PM567 in the Porous Anode Aluminum Oxide Film

$\lambda_{\text{abs}}^{\text{max}}$, nm	$\lambda_{\text{fl}}^{\text{max}}$, nm	Φ_f	$\lambda_{\text{las}}^{\text{max}}$, nm	Efficiency, %	τ_{las} , ns	Q	Lasing threshold, MW/cm ²
475	547	0.85	547	0.3	7	10 ²	2
524	565						

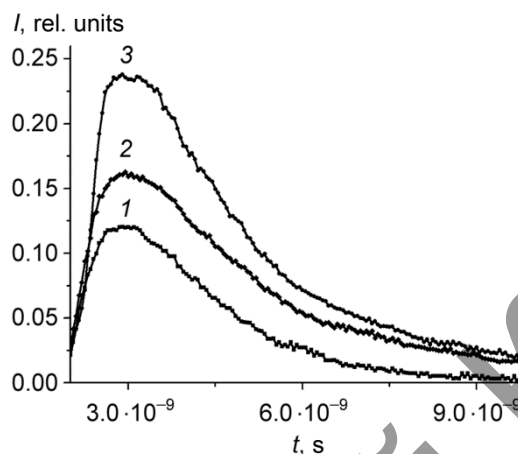


Fig. 7. Kinetics of luminescence of films of anodized aluminum oxide doped with PM567 molecules at the pump power density $P = 1.1$ (curve 1), 3 (curve 2), and 7.7 MW/cm² (curve 3).

CONCLUSIONS

Thus, our investigations have demonstrated that with doping of PM567 molecules in pores of anodized aluminum oxide, a small part of dye molecules formed agglomerates. The quantum yield of fluorescence of PM567 in Al₂O₃ was $\Phi_f = 0.85$. The stimulated emission was observed from PM567 in the film in the short-wavelength maximum of the fluorescence band. The lasing threshold of the stimulated emission, on average, was 2 MW/cm². Low-Q lasing of stimulated emission of PM567 in the film $Q \geq 1 \cdot 10^2$ was due to the fact that the geometry of rays in pores did not correspond to that of rays for the case of the total internal reflection and hence the radiative losses increased. The efficiency of PM567 in Al₂O₃ was 0.3%. The inverse population density of PM567 molecules in the film was formed during the lifetime of the excited state of PM567 molecules (~7 ns).

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