Проведены исследования по влиянию температуры термического оксидирования пленок NiO_x, полученых методом spin-coating из раствора гексагидрат нитрата никеля на их электрофизические свойства. Измерены спектры электрического импеданса пленок NiO_x, отоженных при разных температурах. Показано, что сопротивление внешних электродов прилегающих к NiO_x увеличивается с ростом температуры отжига в то время как сопротивление рекомбинации на границе NiO_x/электрод уменьшается. Наблюдаемое возрастание сопротивления пленки R_1 при повышении температуры отжига связано с уплотнением пленки а уменьшение сопротивления R_2 связано с усилением рекомбинации дырок на границе разделе NiO_x/электрод.

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INFLUENCE OF THE CHEMICAL STRUCTURE OF POLYMETHINE DYE ON SPECTRAL – FLUORESCENT AND GENERATION PROPERTIES

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The present study examines the spectral-luminescent properties of a cationic polymethine dye in ethanol solutions at two concentrations (10^{-5}

mol/L and 2·10^{-4} mol/L). The absorption and fluorescence spectra were analyzed under conditions of low molecular aggregation and at the threshold concentration for stimulated emission. The results demonstrate that increasing the dye concentration leads to spectral broadening, a hypsochromic shift of the absorption maximum, and a bathochromic shift of the fluorescence maximum. Additionally, at 2·10^{-4} mol/L, stimulated emission is observed. These findings provide insights into the optical behavior of polymethine dyes under different aggregation conditions and their potential applications in laser technologies.

Keywords: polymethine dye, absorption spectra, spectral-luminescent properties, stimulated emission, concentration.

Introduction

Polymethine dyes are unique light energy converters due to their extensive photophysical and nonlinear optical properties compared to other organic chromophores [1–3]. They are widely used as active media [1, 4] and passive Q-switches [1, 5]. In particular, symmetrical polymethine dyes are promising for laser applications, as they exhibit significantly narrower absorption bands and smaller fluorescence Stokes shifts compared to their asymmetrical counterparts [6, 7]. Narrow absorption bands make them more efficient for specific wavelength applications, while small Stokes shifts simplify working with visible light in laser systems. Additionally, their predictable optical characteristics allow for precise tuning in various laser technologies.

Experimental

Two working concentrations of the dye in ethanol solutions were selected. The first concentration (10^{-5} mol/L) provides information on the spectral-luminescent properties under low aggregation conditions. The second concentration (2·10^{-4} mol/L) is the minimum concentration at which stimulated emission generation is observed for the selected dye. Figure 1 presents the absorption spectra of dye K1 (curves 1, 2) and fluorescence spectra (curves 3, 4) at concentrations of 10^{-5} mol/L (1, 3) and 2·10^{-4} mol/L (2, 4).

The absorption and fluorescence spectra of the cationic polymethine dye K1 exhibit a pronounced vibrational structure (Figure 1). An increase in the dye concentration in solution results in a blue shift of the absorption spectrum maximum and a red shift of the fluorescence intensity maximum.

With increasing dye concentration, the half-width of both the absorption and fluorescence spectra also increases (Table 1). The spectra significantly broaden and distort due to enhanced aggregation processes in the ionic dye K1. The absorption spectra data for K1 suggest that the second harmonic of a neodymium laser (λ_gen = 532 nm) can be employed for stimulated emission generation. The main spectral and luminescent properties of dye solution are shown in Table 1.

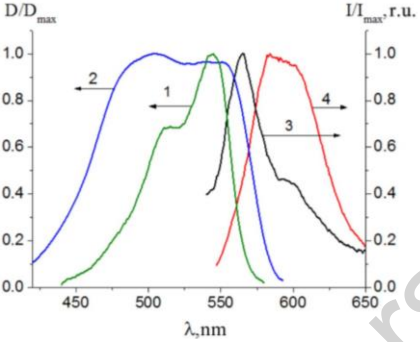


Figure 1 - Absorption (1, 2) and fluorescence (3, 4) spectra of ethanol solutions of dye K1 at concentrations C=10^{-5} mol/L (1, 3) and C=$2\cdot10^{-4}$ mol/L (2, 4).

Table 1 - Absorption and fluorescence characteristics of PD in ethanol solution at various concentrations

Dye (concentration)	$^a\lambda_1$ max, nm	$\Delta\lambda_{1/2,}$nm	$^f\lambda$ max, nm	$\Delta\lambda_{1/2,}$nm	ε, l/moL,cm ($^a\lambda_{Max}$)	ε, l/moL, cm ($^a\lambda$ =532 nm)
K1 (10^{-5} l/moL)	545	59	573	38	134000	128000
K1 ($2\cdot10^{-4}$ l/moL)	503	112	583	58	48000	48000

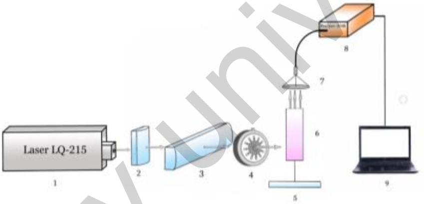
For the selected dye concentrations, the molar extinction coefficients (ε) were determined (Table 2). The maximum extinction coefficient was observed at C = $2\cdot10^{-4}$ mol/L. At this concentration, Beer's law is not obeyed. However, the extinction coefficient at this concentration allows for the evaluation and comparison of the dye's light absorption capacity in the solution used for stimulated emission. The quantum yields (Φ_f) of dye fluorescence are presented in Table 2.

Table 2 - Quantum yields (Φ_f) and lifetime (τ_{fl}) of dye K1 fluorescence at dye concentrations in ethanol of 10^{-5} mol/L and $2{\cdot}10^{-4}$ mol/L.

Dye	K1	
C, mol/L	10^{-5}	$2{\cdot}10^{-4}$
Quantum yield, Φ_f	0,03	0,02
Lifetime τ_f, ns	0,30	0,30

An increase in the dye concentration in solution to $C = 2{\cdot}10^{-4}$ mol/L does not affect the fluorescence lifetime (τf) (Table 2).

For measuring the characteristics of laser generation, the experimental setup shown in Figure 3 was used. It includes an optical resonator formed by a blind mirror (6) and the front face of a cell containing the dye solution (7) (Figure 3). The distance from the center of the cell to the mirror was 70 mm. The pump radiation, after passing through the aperture (3), was focused by cylindrical lenses (4, 5) onto the side face of the cell, forming a strip with an area of 0.07 cm².



1 - LQ 215 laser; 2 - neutral filters; 3 - diaphragm; 4,5 - cylindrical lenses; 6 - blind mirror; 7 - the test sample; 8 - converging lens; 9 - AvaSpec-2048 spectrometer; 10 - computer

Figure 3 - Experimental setup for studying the generation characteristics of dye solutions

The emission generation occurred in a narrow near-wall region on the side of the entrance wall of the cell. Glass or quartz cuvettes were used in the experiment. The dye-containing cell was securely fixed using a steel holder. The pump power density was adjusted using neutral filters (2) within the range of 1–300 MW/cm². The emitted radiation was focused by a converging lens (8) onto the optical fiber input of the AvaSpec-2048 spectrometer (9).

The relative error in determining the spectral characteristics was 3%. Figure 4 presents the emission spectra of dye solutions at different laser pump power densities (P). The length of the active medium in the cell was 10 mm. As shown in Figure 4, with an increase in P, a narrow band of laser emission emerges against the background of the fluorescence spectrum.

For the K1 dye, both spontaneous and stimulated luminescence are observed in the emission spectra. A further increase in the pump power density leads to an increase in the intensity of the generation band and a decrease in its half-width. The narrowing of the emission band with increasing excitation intensity indicates the predominance of stimulated emission over spontaneous emission, signifying the transition of the system into the generation mode.

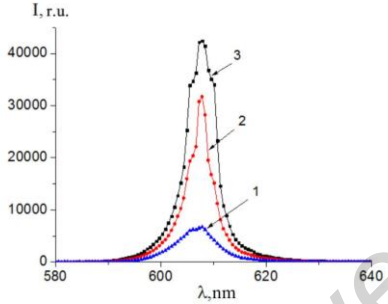


Figure 4 – Generation spectra of the K1 dye solution at different pump power densities (MW/cm²): 1 – 4.6, 2 – 6.6, 3 – 7.03.

For the obtained dependences of the emission spectra of dye solutions on the power density of laser pumping, graphs of the dependences of the radiation intensity and the half-width of the dye luminescence spectra on the pump power density were constructed (Figure 5).

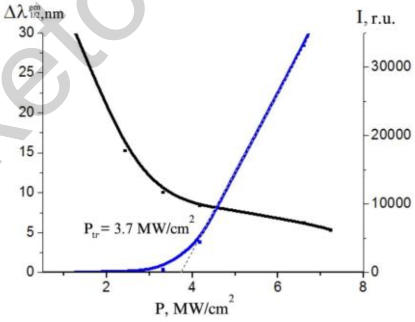


Figure 5 – Dependence of the intensity of generation and the half-width of the emission spectrum of the dye K1 in ethanol on the pumping power density

Thresholds of generation of stimulated emission of dye molecules were determined from the obtained graphs (Table 3).

Table 3 – Main generation characteristics, absorption and fluorescent properties affecting the generation of stimulated emission of dye K1

Dye	Threshold gen. (P_{tr}), MW/cm^2	$\Delta\lambda_{1/2,}$ nm	ε, (λ_a =532 nm)	Φ_f,($2 \cdot 10^{-4}$ mol/L)	τ_f, ns
K1	3,7	5	48000	0,02	0,3

As seen from the data, the K1 dye has a low threshold for generating stimulated emission. Its generation threshold is 3.7 MW/cm². The values of ε, Φ_f, and τ_f (Table 3), which influence the generation of stimulated emission, were compared with the generation threshold (P_{tr}).

Conclusion

Spectral-luminescent properties of PD K1 in ethyl alcohol at concentrations of 10^{-5} mol/L and $2=10^{-4}$ mol/L were explored. An increase in the concentration of the studied dyes in the ethanol solution leads to the observation of molecular aggregation of dyes, a decrease in the extinction coefficient and a decrease in the quantum yield of fluorescence. The lifetime of the dye fluorescence does not change with increasing dye concentration. The stimulated emission of the K1 dye in ethanol was obtained at the maximum of the fluorescence band.

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