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Relation between spectral and lasing properties for dyes of different classes

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Abstract. **The lasing efficiency and the service life of pyrromethene and phenalemine dyes doped to nanoporous glass-polymer composites are studied upon monochromatic laser pump. The absorption and luminescence spectra of these dyes are investigated. The spectral parameters of the dyes determining their lasing efficiency are found from the analysis of their spectra and lasing characteristics, and the dyes are classified according to their lasing efficiency. A correlation between the lasing efficiency and the service life of laser elements is also established.**

Keywords: *laser dye, pyrromethene, phenalemine, lasing efficiency, service life, absorption, extinction, luminescence, Stokes shift.*

1. Introduction

At present a variety of dyes of different classes lasing in a broad spectral range from the IR to UV region have been studied [1]. Both spectral and lasing properties of the dyes, such as their lasing efficiency and photoinduced degradation, have been investigated in detail. The latter characteristic is especially important for solid-state laser elements (LEs). The problem of dye degradation in liquid elements is solved using the circulation of dye solutions through the pump and lasing regions.

The formulation of requirements to dyes that would provide their high lasing efficiency and photostability in an active medium has been repeatedly attempted [2 – 4]. As a result, a variety of empirical 'rules' for the selection of efficient dyes were proposed. For example, it is assumed that the molecule of a good laser dye should have a rigid planar configuration [2] or that the lasing efficiency of a dye increases with increasing the Stokes shift of the dye luminescence [3], etc. These rules are qualitative, inadequately substantiated, the region of their applicability is usually poorly specified, and there are many exceptions from them. For example, the terphenyl dye, whose molecule is not rigid and not planar, produces efficient lasing.

Numerous theoretical calculations of lasing in organic dyes that have been performed by now also do not allow the rules for selection of efficiently lasing dyes to be formulated.

Therefore, the characteristics of dyes that would permit one to compare their lasing efficiencies and explain their properties observed in experiments have not been determined so far. The aim of this paper is to find the dye characteristics allowing the quantitative comparison of their lasing efficiencies.

2. Formulation of the problem

Because the lasing efficiency of a dye depends on many factors, it is difficult to select the most important of them for comparing the lasing efficiencies of different dyes. These factors are first of all the pump conditions, the type and parameters of the laser cavity, the influence of a medium to which the dye is doped (related to the dye solubility, formation of aggregates, luminescence quenching, etc.), as well as factors caused by the structure and properties of dye molecules. Variations in any of these factors lead to a change in the lasing efficiency and photostability of the active medium.

To compare correctly the lasing efficiencies of the dyes, we will analyse their lasing properties under identical conditions. We assume for definiteness that lasing occurs in dyes longitudinally pumped by nanosecond laser pulses. We also assume that the dye does not form aggregates in a solution or in a solid matrix, and no luminescence quenching occurs. Under such conditions, only the properties of the dye are important.

However, even in such a simplified case, the lasing efficiency of the dyes still depends on many parameters. To determine the most important parameters, we will analyse first the lasing properties for dyes of the same class. Because molecules of such dyes have a similar structure, their optical properties should vary weakly and monotonically in a series of appropriately ordered dyes.

In particular, the lasing efficiency and photostability of the active medium will vary gradually, so that the selection of the most important parameters will be a comparatively simple task. The solution of this problem will form the basis for the comparison of lasing efficiencies for dyes of different classes.

3. Experimental results

We studied the spectral and lasing properties of pyrromethene (PM567, PM580, PM597, PM650) and phenalemine

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(P510, P512, P640) dyes impregnated into a nanoporous glass-polymer (NGP) composite or dissolved in a monomer mixture used for the composite preparation.

Laser elements of size $20 \times 15 \times 3$ mm made of the composite were fabricated by the method described in [5, 6].

The spectral studies of the dyes were performed by the method used in Ref. [7]. The concentration of dyes in the monomer mixture was varied from 10^{-5} M up to the solubility limit of the order of 10^{-2} M (the solubility of the dyes is presented in Table 1). The absorption and luminescence spectra of one of the dyes are shown in Fig. 1.

Table 1.

Dye	C_s/M	C_q/M	C_{ex}/M
PM567	2×10^{-2}	10^{-2}	10^{-3}
PM580	2.2×10^{-2}	10^{-2}	10^{-3}
PM597	2×10^{-2}	10^{-2}	10^{-3}
PM650	10^{-2}	0.5×10^{-2}	10^{-5}
P512	10^{-2}	2.5×10^{-3}	10^{-3}
P510	0.5×10^{-2}	10^{-3}	10^{-3}

Note: C_s, C_q, and C_{ex} are the dye solubility limit, the luminescence quenching concentration, and concentration at which a shoulder appears in the luminescence band, respectively (1M = 1 mol L^{-1}).

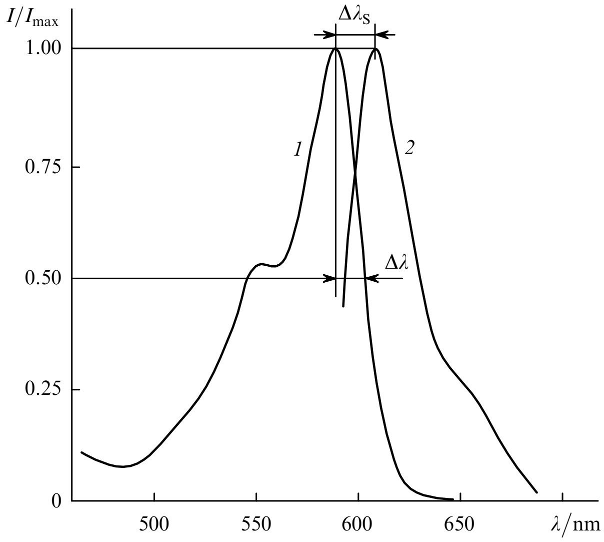

Figure 1. Absorption (1) and luminescence (2) spectra of the PM650 dye solution in a monomer composite ($\Delta\lambda_S$ is the Stokes shift, $\Delta\lambda$ is the half-width of the absorption band from the long-wavelength side).

The shape of the absorption bands of the dyes remains invariable for any concentrations studied. The optical density $D(\lambda)$ satisfied the relation $D(\lambda) = \varepsilon(\lambda)CL$, where $\varepsilon(\lambda)$ is the extinction, λ is the wavelength, C is the dye concentration, and L is the layer thickness. This means that no dye associates were formed in the monomer mixture up to the dye solubility limit.

Unlike the absorption spectrum, the luminescence spectrum depends on the dye concentration in solution. At high concentrations exceeding C_{ex} (Table 1), a 'shoulder' appears in the long-wavelength region of the luminescence spectrum, which shifts to the red with increasing dye concentration. This probably indicates to the formation of excimers at high concentrations of the dye [8]. When the the dye concentration in the monomer mixture exceeds 10^{-3} M (Table 1), the concentration quenching of luminescence is observed.

Table 2.

Dye	λ_a/nm	λ_f/nm	$\Delta\lambda$/nm	$\varepsilon(\lambda_a) \times 10^{-3}$	$\varepsilon(\lambda_p) \times 10^{-3}$	$\varepsilon(\lambda_f) \times 10^{-3}$
PM567	518	536	10	96	28	14
PM580	520	537	10	89	32	16
PM597	524	561	16	80	64	3
PM650	590	607	14	45	14	14
P510	524	593	46	22	21	1.5
P512	533	578	24	25	25	2
P640	590	616	16	30	8.5	5.5

Note: λ_a, λ_f, and λ_p are the wavelengths of the main absorption band and of the luminescence and pump bands, respectively; $\varepsilon(\lambda)$ is the dye extinction (in L mol^{-1} cm^{-1}).

The shape of the absorption and luminescence spectra of dyes in the composite was the same as that in the monomer mixture within the measurement accuracy. However the luminescence spectrum shifted to the red by 3 – 5 nm and the luminescence intensity increased.

Spectral parameters of interest to us are listed in Table 2.

The lasing parameters of LEs were studied upon pumping them longitudinally by the second harmonic from a *Q*-switched single-mode Nd^{3+} : YAG laser. The LE was placed into a resonator formed by a plane dichroic mirror with the transmission coefficient 98 % at a wavelength of 532 nm and the reflectivity 98 % in the spectral range from 550 to 660 nm, and the output mirror with the reflectivity 62 %. The pump-beam diameter on the LE was 1.3 mm. The pulse duration τ_p, energy E_p, and intensity I_p were 5 ns, 2 mJ, and 30 MW cm^{-2}, respectively. The energy of the pump and output pulses was measured with an accuracy of 10 %.

We studied the lasing efficiency η and the service life $N_{0.7}$ of the dyes. The lasing efficiency η was measured for a pulse repetition rate of $3\frac{2}{3}$ Hz as the ratio of E_g/E_a, where E_g is the output-pulse energy and E_a is the absorbed pump-pulse energy. The parameter $N_{0.7}$, defined as the number of pump pulses after which the lasing efficiency decreases down to the 0.7 level of its initial value, was measured at the pump-pulse repetition rate of 33 Hz. We neglected in the calculation of η the radiation losses due to Fresnel reflection from the LE surface.

Figure 2 shows the dependence of $\eta(D)$ for the PM 597-doped LE. One can see that the dependence of the lasing

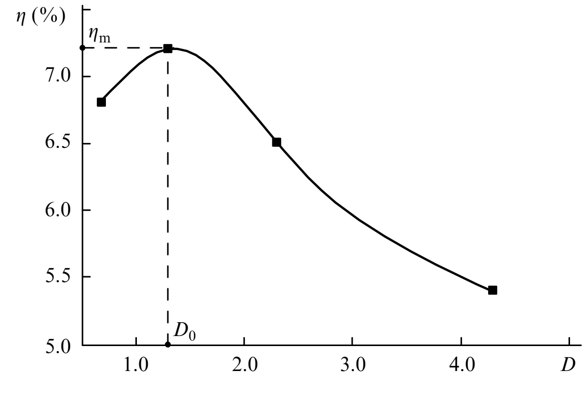

Figure 2. Dependence of the lasing efficiency η of the PM597-doped NGP LE on the optical density D. The LE was pumped by the second harmonic from a single-mode Nd^{3+} : YAG laser with the pulse power density $I_p = 30$ MW cm^{-2}; D_0 is the optimal optical density; η_m is the maximum lasing efficiency.

efficiency on the optical density of the LE at the pump wavelength is nonmonotonic and has a maximum $\eta_m = \eta(D_0)$ at a certain optical density D_0.

The values η_m and $N_{0.7}$ corresponding to the optical density D_0 are of most interest for the following discussion. These data for the LEs doped with the dyes studied are presented in Table 3.

Table 3.

Dye	λ_g/nm	D_0	η_m (%)	$N_{0.7} \times 10^{-3}$
PM567	562	8.8	55	40
PM580	561	12	55	51
PM597	570	13	72	340
PM650	625	1.6	33	8
P512	595	5.8	42	30
P510	614	10	30	14
P640	642	4.3	35	16

Note: λ_g is the lasing wavelength.

The values of $N_{0.7}$ presented in Table 3 were obtained for a pulse repetition rate of 33 Hz. When the pulse repetition rate was decreased, the service life of LEs increased by 2–3 times due to the reduction in the LE heating.

4. Lasing efficiency: key parameters

The existence of the optimal density for the dependence $\eta(D)$ (Fig. 2) is caused by the inhomogeneity of the LE excitation. The inversion of laser energy levels upon longitudinal pump decreases from the input end of the LE to its output end. If $D > D_0$, the region of the output end remains 'unpumped', and reabsorption of laser emission dominates in this region, resulting in the reduction of η. If $D < D_0$, the pump radiation saturates the $S_0 \rightarrow S_1$ laser transition (where S_0 and S_1 are the ground and the first excited singlet states, respectively) in the entire LE region interacting with radiation, resulting in the LE bleaching. In this case, the pump radiation is either absorbed due to the $S_1 \rightarrow S_n$ transitions (S_n is the excited electronic state lying above the S_1 state) or propagates through the LE without appreciable absorption. Each of these processes reduces the lasing efficiency η. For $\eta_m = \eta(D_0)$, the absorption of pump radiation and the reabsorption of laser emission are in balance.

Because the value η_m is determined by a balance between the absorption of pump radiation and the reabsorption of laser emission, it is natural to assume that there exists the parameter $\bar{\xi}$ characterising the lasing efficiency of the dye, which is related to the absorption parameters of the dye and is equivalent to η_m. The lasing efficiency increases with $\bar{\xi}$:

$$\bar{\xi} = [\varepsilon(\lambda_p)/\varepsilon(\lambda_f)]k(\lambda_p, \lambda_f, I), \tag{1}$$

where $\varepsilon(\lambda_p)$ and $\varepsilon(\lambda_f)$ are the dye extinction at the pump wavelength and the luminescence maximum, respectively and $k(\lambda_p, \lambda_f, I)$ is the dimensionless coefficient taking into account the contribution of induced absorption. The validity of this assumption will be confirmed by the analysis of the experimental data. There is no need to specify the form of $k(\lambda_p, \lambda_f, I)$ for a further consideration. Note, however, that because induced absorption always causes energy losses, then $k(\lambda_p, \lambda_f, I) \leqslant 1$ and $k(\lambda_p, \lambda_f, I) \rightarrow 1$ with decreasing radiation intensity.

The calculation of $\bar{\xi}$ requires the knowledge of the values of $\varepsilon(\lambda_p)$, $\varepsilon(\lambda_f)$, and $k(\lambda_p, \lambda_f, I)$, which are, as a rule, unknown. However, these quantities can be expressed in terms of the spectral parameters of dyes, which can be quite easily measured. Assuming that the absorption band is described by a Gaussian, we write $\varepsilon(\lambda) = \varepsilon_a \exp[-\ln 2(\lambda - \lambda_a)^2/(\Delta\lambda)^2]$, where ε_a is the extinction in the maximum of the absorption band; $\Delta\lambda = \lambda_{1/2} - \lambda_a$ is the half-width of the absorption band (Fig. 1); $\lambda_{1/2} > \lambda_a$; and $\varepsilon(\lambda_{1/2}) = (1/2)\varepsilon(\lambda_a)$. Then, by introducing the parameter $\xi = \ln\bar{\xi}$, we obtain

$$\xi = (\Delta_S^2 - \Delta_p^2)\ln 2 + \xi_{nl}, \tag{2}$$

where $\Delta_S = (\lambda_f - \lambda_a)/\Delta\lambda$ and $\Delta_p = (\lambda_p - \lambda_a)/\Delta\lambda$ is the relative Stokes shift and the detuning of the pump wavelength, respectively; $\xi_{nl} = \ln k(\lambda_p, \lambda_f, I)$ is the term describing induced nonlinear absorption. The quantity $\xi_{nl} \leqslant 0$ because $k(\lambda_p, \lambda_f, I) \leqslant 1$ and its form is determined by the shape of the induced absorption band.

The parameter ξ is equivalent to the parameter $\bar{\xi}$ (i.e., the increase in both these parameters corresponds to the increase in the lasing efficiency of the dyes studied here) if ξ is calculated from the exact value of $\varepsilon(\lambda)$. We assume here that pumping is performed into the main absorption band of the dye, so that the parameter ξ (2) is equivalent to (1) only in this case. This requirement is fulfilled for all the dyes studied here.

5. Classification of dyes according to their lasing efficiency

An account of induced absorption in the estimate of the lasing efficiency of dyes from equivalent parameters ξ and $\bar{\xi}$ is the most complicated problem. However, as mentioned above, the properties of dyes of the same class vary only slightly from dye to dye. For this reason, the parameters $\bar{\xi}_1 = \varepsilon(\lambda_p)/\varepsilon(\lambda_f)$ и $\xi_1 = (\Delta_S^2 - \Delta_p^2)\ln 2$ vary monotonically (Table 4) and, hence, $k(\lambda_p, \lambda_f, I)$ and ξ_{nl} also should vary monotonically for dyes of the same class. This means that $\bar{\xi}$, ξ, $\bar{\xi}_1$ and ξ_1 are equivalent for dyes of the same class.

Table 4.

Dye	$\bar{\xi}_1$	ξ_1	Δ_S	η_m (%)
PM567	2.0	0.89	1.8	55
PM580	2.0	1.0	1.7	55
PM597	21	3.5	2.3	72
PM650	1.0	−1.0	1.2	33
P512	13	1.36	1.9	42
P510	14	2.4	1.5	30
P640	1.5	−0.9	1.6	35

Table 4 also demonstrates that the relative Stokes shift Δ_S is equivalent to $\bar{\xi}$ for many dyes of the same class. By using $\bar{\xi}$ for the classification of dyes according to their lasing efficiency, we obtain the result shown in Fig. 3.

The data presented in Table 4 show that the parameters $\bar{\xi}$, ξ, $\bar{\xi}_1$ and Δ_S for dyes of the same class are equivalent to η_m, and the set of dyes is partially ordered. According to the Zermelo theorem [9], any partially ordered set can be completely ordered, so that, using the spectroscopic data, dyes of different classes can be in principle classified according to their lasing efficiency. It follows from the

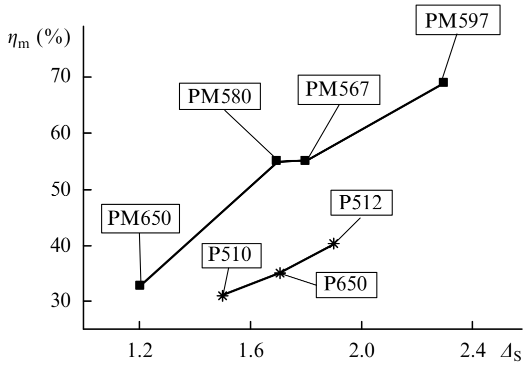

Figure 3. Dependence of the lasing efficiency η_m of pyrromethene and phenalemine dyes doped into the NGP composite on the relative Stokes shift Δ_S.

Zermelo theorem that, depending on the problem being solved, the ordering can be performed differently. For example, the parameter Δ_S classifies dyes according to their lasing efficiency for the optimal pump wavelength ($\Delta_p = 0$) and moderate radiation intensity, when induced absorption can be neglected.

The data presented in Fig. 3 show that lasing efficiencies of dyes belonging to different classes differ due to the influence of induced absorption. To take induced absorption into account, it is sufficient to compare the lasing efficiencies for two dyes of different classes. Indeed, assuming that η_m is proportional to $\bar{\xi}$, we obtain for the difference $\delta\xi_{nl}$ of induced absorption parameters for dyes of classes 1 and 2, under the condition $\Delta_p = 0$ and taking into account (1) and (2),

$$\delta\xi_{nl} \simeq \ln(\eta_{m1}/\eta_{m2}) + (\Delta_{S1}^2 - \Delta_{S2}^2)\ln 2. \tag{3}$$

By using the data for PM650 and P640 presented in Table 4, we obtain $\delta\xi_{nl} \simeq 0.8$. The classification of the dyes according to the parameter $\xi^* = (\Delta_S)\ln 2 + \delta\xi_{nl}$, taking into account the estimate of $\delta\xi_{nl}$ (3), is presented in Table 5.

Table 5.

Dye	ξ^*	η_m (%)
PM597	4.2	72
PM567	2.6	55
PM580	2.3	55
P512	2.0	42
P640	1.3	35
PM650	1.2	33
P510	1.0	30

6. Discussion

A specific feature of organic dyes used in lasers is a strong overlap of their absorption (excitation) band with the luminescence band. This results in considerable losses due to reabsorption of laser emission. We have taken above this circumstance into account as the main factor determining the lasing efficiency of active media doped with dyes. Note that in the case of crystals or glasses doped with transition-metal ions, the dominating process of absorption of laser emission is different and, therefore, the relation between spectral and lasing parameters should be also different.

The classification of dyes according to their lasing efficiency performed above was based on the analysis of experimental data obtained upon the longitudinal pump of active media by nanosecond pulses. However, these results can be also used for other experimental conditions. This is explained by the fact that the lasing efficiency substantially depends on absorption and reabsorption of light. Of course, the key parameters should be corrected according to the lasing conditions. For example, when an active medium is pumped by broadband radiation, the parameter $\bar{\xi}$ should be averaged over the excitation spectrum. By neglecting induced absorption, the averaged classification parameter is $\bar{\zeta} = \langle\varepsilon(\lambda)\rangle/\varepsilon(\lambda_g)$ (angle brackets denote averaging over the pump spectrum). Because the averaging takes the pump parameters into account, the parameter $\bar{\zeta}$ will classify dyes differently than $\bar{\xi}$. A change in the classification is not a peculiarity of broadband pumping. In the case of the monochromatic pump, the lasing efficiency also depends on the pump wavelength, as shows the term Δ_p in (2) representing the detuning of the pump wavelength from the absorption band maximum.

It is important that the spectral parameters calculated by neglecting induced absorption classify dyes of the same class. This allows one to predict the lasing efficiency of these dyes on the basis of spectral data. Thus, using spectral data [1] for coumarins, we obtained a series (in the order of decreasing lasing efficiency): C152, C522, C152A, C153, C151, C30, C307, C102, C120, C47, C2, C4, C314, C334, C7, C6.

Thus, we have related the lasing efficiency of dyes to their spectral parameters, thereby taking the influence of the environment into account. The role of the environment in the absence of aggregates and quenching of luminescence is manifested in the shift and change in the width (and possible shape) of absorption and luminescence bands. It is accepted that an increase in the Stokes shift leads to an increase in the lasing efficiency, while the inhomogeneous broadening of the spectrum results in a decrease in the lasing efficiency (see, for example, Ref. [4]). One can see from (2) that the relative Stokes shift, which takes into account changes in the Stokes shift itself and in the width of the spectral band, adequately reflects the influence of the environment. If the absorption and luminescence spectra of a dye do not change upon a change in the environment, the lasing efficiency should not vary. In particular, the lasing efficiency of dyes in a solid matrix should not be lower than that in a liquid solution. This is confirmed by the example of phenalemines [7].

An important parameter of a solid LE, along with the lasing efficiency, is the service life. Numerous experimental data demonstrate the correlation between these characteristics. For example, Table 6 demonstrates such a correlation for the NGP LE.

It does not follow, however, from Table 6 that spectral

Table 6.

Dye	η_m (%)	$N_{0.7}$
PM597	72	3.4×10^5
PM567	57	4×10^4
PM580	55	5.1×10^4
P512	42	3×10^4
P640	35	1.6×10^4
PM650	33	8×10^3
P510	30	1.4×10^4

parameters considered above also classify dyes according to their service life. These parameters are not related to the destruction mechanism of dye molecules. The service life of dyes can be adequately classified only based on the mechanism of their destruction.

At the same time, the correlation between the lasing efficiency and the service life of the LE, which is demonstrated in Table 6, can be qualitatively explained based on simple energy considerations. Indeed, the higher the lasing efficiency, i.e., the higher the conversion efficiency of pump radiation into output radiation, the lower the probability of the photochemical destruction of the dye.

The existence of this correlation makes it possible to fabricate LEs with the long service life and high lasing efficiency. It is obvious that the concentration of a dye with the high relative extinction and the large relative Stokes shift can be increased without a substantial increase in the absorption of pump radiation. Among the dyes studied here, PM597 has such parameters ($\Delta_S = 2.3$, $\bar{\xi}_1 = 21$). The 3.5-mm thick LE made of the NGP doped with this dye had the optical density of 23 and the lasing efficiency of 65% for the pump intensity of 30 MW cm^{-2}. The service life of this LE exceeded 10^6 pulses upon irradiation of a fixed region at a pulse repetition rate of $3\frac{2}{3}$ Hz. When the optical density of the LE was reduced down to 13, the lasing efficiency increased up to 72 % and the service life slightly decreased.

7. Conclusions

We can make the following conclusions from the analysis performed in the paper:

(i) The lasing efficiency of dyes is determined by their spectral parameters. The key parameter of the dye is its relative extinction $\bar{\xi}$ (or the equivalent spectral parameter ξ), which classifies the dyes according to their lasing efficiency (the value of $\bar{\xi}$ increases with η).

(ii) The difference in the lasing efficiency of dyes of different classes is caused by induced absorption.

(iii) The service life of solid LEs correlates with their lasing efficiency.

The results obtained in the paper can be used for predicting the lasing efficiency of dyes and interpreting the lasing properties of dyes of different classes in liquids and solids.

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