Multiple scattering effect on luminescence of the dyed polymer matrix

E. Tikhonov[1], V. Yashchuk[2], O. Prygodjuk[2], V. Bezrodny[1], Yu. Filatov[3]

[1]Institute of Physics, National Academy of Sciences of Ukraine, 46, prospect Nauky, 03028 Kyiv, Ukraine
[2]Kyiv T.Shevchenko University, 6,Glushkov av., 03680 Kyiv, Ukraine
Phone: +380 (44) 259-04-76, E-mail: yavasil@ukr.net,
[3]Institute of Superhard Materials, National Academy of Sciences of Ukraine, 2, Avtozavodska str., 04074 Kyiv, Ukraine

Abstract. The luminescence properties of the Rodamine 6G in strongly scattering matrix in dependence of the medium parameters were examined. The luminescence spectrum of this object was found to be dependent on the scattering particle concentration, particle material and sample thickness. It was shown that the main reason of the dependencies is an enhanced reabsorption of luminescence radiation in the light scattering sample caused by manifold light scattering.

Keywords: multiple light scattering, reabsorption, luminescence, dye, polymer, rhodamine 6G.

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1. Introduction

Stimulated emission phenomenon in the strongly scattering active medium is of great interest and importance owing to possibility to obtain specific lasing sources on the basis of these media and due to some fundamental questions to the nature of this phenomenon [1–3] as well. Such lasing is possible due to multiple scattering of light "keeping" photon trajectories within active medium. To produce lasing (stimulated radiation), the active media must have amplifying coefficient g higher than α_{loss} factor loss determined by leakage losses owing to light leaking out of the active region, absorption *etc*.: $g > \alpha_{loss}$. The minimal characteristic size of active volume is defined in a complicated way by the diffusion coefficient, amplification coefficient, shape of the active medium volume, and particle size [4]. The first investigations of strongly scattering active media, according to literature, were carried out using liquid dye solution with suspended particles [1, 2]. But progressive sedimentation of the particles in such liquid suspension restricts both the possibility of comprehensive investigations, and practical use of such lasing media. So the next papers have reported about solid polymer solutions [3] and nanocrystalline films [4].

Fabrication of the polymeric multiple scattering media with organic dye is rather simple. In contrast to semi-conductor films, this fabrication technology allows varying of the active medium parameters in a simple way. Due to high quantum yield of dye in solid polymer matrix [5] such objects are very effective and promising. Multiple scattering may be provided by embedding of the fine dispersed particles having refraction coefficient different from the matrix one. Light scattering parameters can be varied within wide region by means of change of the scattering particle concentration (up to $C_{part} \sim 10^{10}$–10^{12} cm^{-3}) and their refraction coefficient. The amplifying factor can be changed by dye molecule concentration or pump intensity varying.

Our previous investigations proved the possibility of lasing in such solid media [6]. The luminescence and lasing spectra of these objects were proved to depend on the parameters defining the light scattering in the media. Particularly, it was found that peak wavelength both of luminescence and lasing spectra depend on particle concentration and material [6,7]. It is known that in the case of ultra strong scattering when photon localisation phenomenon prevails over the diffusion regime, the edge of absorption band can shift [8]. To determine the nature of these and the other possible scenario of luminescent spectra behavior, the investigations presented below were carried out.

2. Experimental

In this paper we present the results of the investigations of luminescence spectra (LS) and excitation spectra (ES) of solid polymer (polyvinyl acetate) solution of rhodamine 6G with embedded fine scattering particles. The powders of SiO_2 (particle diameter $d \sim 0.5$ m, refraction coefficient $n \sim 1.5$, weight concentration C_p in the samples was varied from 6 to 30%), Al_2O_3 ($d \sim 5$ μm, $n \sim 1.7$, $C_p \sim 15\%$), and synthetic diamond ($d \sim 7$ μm, $n \sim 2.4$, $C_p \sim 15\%$) were used as scattering particles.

Therewith the dependence of the coefficient of radiation attenuation in the sample on scattering particle concentration was analyzed. This coefficient was determined in the conventionally accepted manner as relation of the transmitted beam intensity to the incident beam intensity. The radiation used in this experiment was monochromated with double monochromator DMR-4 with spectral line width of 5 nm. The luminescence was excited with green band of Hg lamp ($\lambda = 546.1$ nm) or by $\Delta\lambda = 5$ nm spectral bands of incandescent lamp selected with the same monochromator. The luminescence was registered in backward direction to the excitation beam (reflected-type experiment).

Spectral resolving for LS and ES registration was 2 and 5 nm, respectively. The ES were registered for the observation luminescence spectral bands of 2 nm width. The bands were selected by diffraction monochromator MDR-2.

3. Results and discussion

The investigations of the scattering medium parameter influence on the LS of the sample were carried out. It was found that particle embedding shifts the LS to the long-wave region (Fig. 1a). But the value of the shift depends non-monotonically on the embedded particle concentration (Fig. 1b). Under increasing of refraction coefficient of material n the LS shifts to the short wave region (Fig. 1c).

Besides this the radiation spectra reveal typical features of inhomogeneous spectral broadening: the LS depends on the excitation wavelength λ_{ex} (Fig. 2a), and ES depends on observation wavelength of luminescence λ_{lum} (Fig. 2b). Moreover these dependencies are observed both for sample with embedded particles and without ones.

The observed dependencies in luminescence spectra behavior can be caused by two appropriate reasons. The first one is based on inhomogeneous spectral broadening probably caused by several luminescent centers existence. The probable centers aside from singular molecules (monomers) can be dimers and molecule associates of higher degree formed at dye molecule concentration $C_{dye} \geq 10^{-4}$M [9]. Contrary to the solid solutions, in the liquid ones these associates do not luminescence. They absorb excitation light and thus cause the suppression of luminescence. But in the case of solid dye solution the dimers and higher associates having high luminescence yield can make a contribution into the observed LS. So
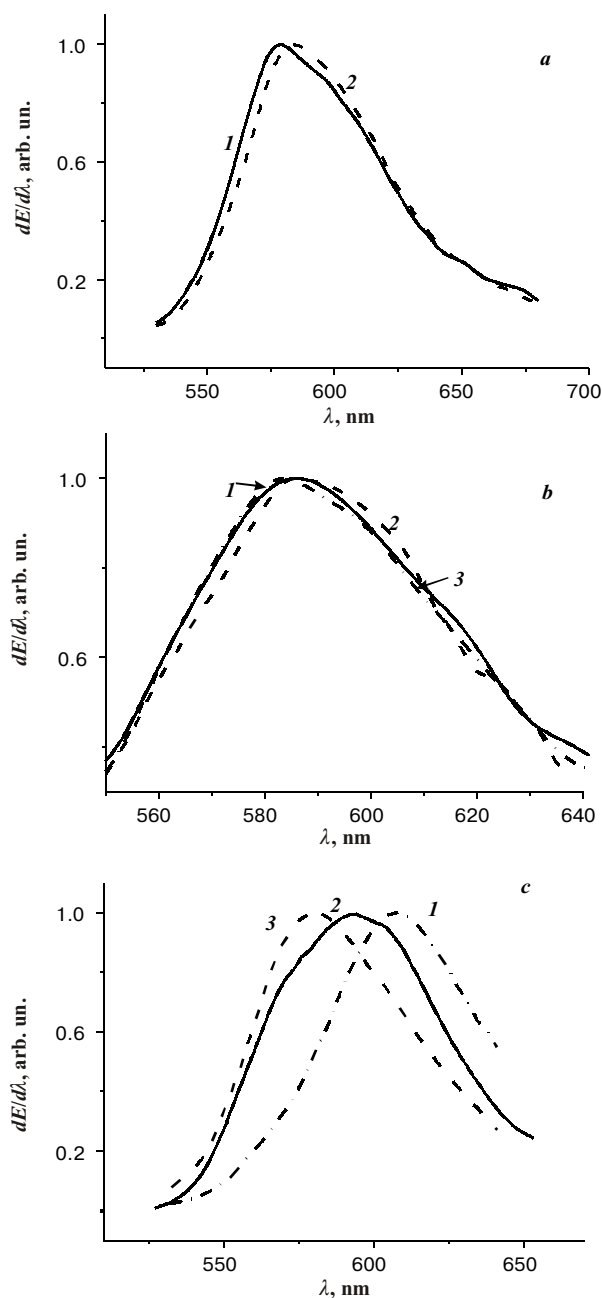

Fig. 1. Luminescence spectra of R6G (the dye concentration is $C_{R6G} = 10^{-3}$ M) in the solid polyvinyl acetate matrix:
a) *1* – sample without scattering particles, *2* – sample with $C_{part} = 30\%$ of SiO_2; the samples thickness is $d_s = 1$ mm;
b) samples ($d_s = 0.9$ mm) with different SiO_2 concentration: *1* – $C_{part} = 18\%$, *2* – $C_{part} = 24\%$, *3* – $C_{part} = 30\%$;
c) samples ($d_s > 1.5$ mm) with particle of different materials ($C_{part} = 15\%$): *1* – SiO_2, *2* – Al_2O_3, *3* – synthetic diamond.

the resulted luminescence spectrum consists of several elementary components (they are spectra of monomer, dimer and associates of higher degree), and thereby it behaves as inhomogeneously broadening one even in the absence of scattering particles. The embedded particles
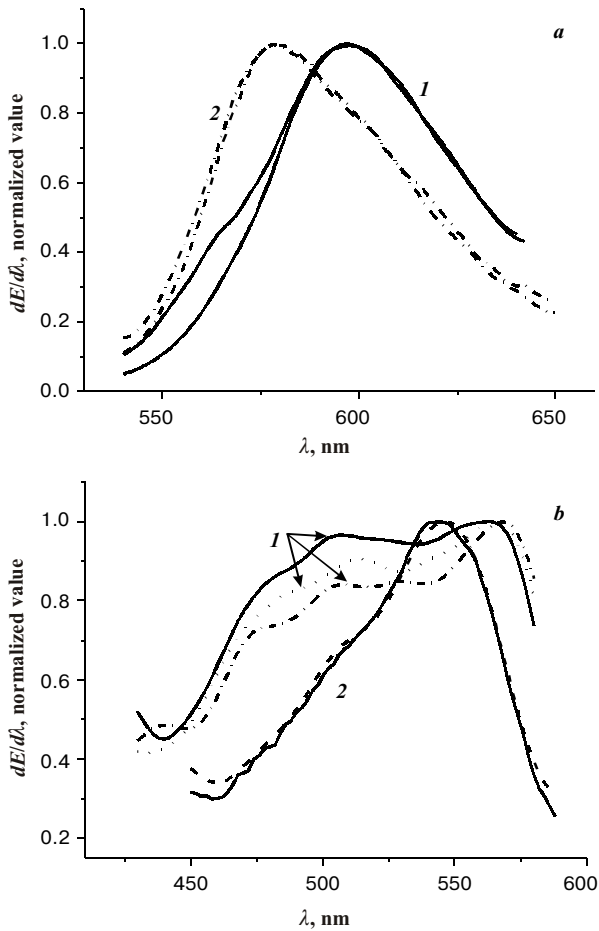
points of emission, the luminescence spectra emitted in the different sample layers differ from each other on the sample surface due to passing different paths through the luminescence medium (Fig. 3). The reabsorption redistributes energy within total luminescence spectrum out of the overlapping region to the long-wave LS part. It results in long-wave shift of observed LS. The observed luminescence spectrum of the sample is a superposition of the luminescence spectra obtained from different layer, thus the envelope of LS depends on each factor, which causes luminescence radiation redistribution within the sample and radiation path through the sample. The most evident factors are the scattering of luminescence radiation, the scattering of exciting radiation, the exciting radiation wavelength and sample thickness.

Scattering of the luminescence light lengthens the path of radiation through the sample and consequently increases the LS deformation and long-wave shift. Therefore, the particle embedding causes long-wave shift of the observed LS.

On the other hand scattering of the exciting radiation decreases its penetration depth into the sample. It results in decreasing of deep sample layer contribution into the total LS, consequently LS shifts to the short-wave region.

The ability of exciting radiation to penetrate into the sample depends on the radiation wavelength. Because of the reabsorption makes LS observed from different layers as non-equivalent, it causes the LS dependence on exciting radiation wavelength and ES dependence on observation wavelength of luminescence. So, the reab-

Fig. 2. a) Luminescence spectra of the samples (C_{part} = 30% of SiO_2) with different thickness ($1 – d_s$ > 1mm, $2 – d_s$ ~ 0.05mm) under different excitation wavelengths: $\lambda_{ex} \cong 530$nm (above lines), 482 nm (below lines);

b) excitation spectra of the samples with two different thickness under different luminescence observation wavelengths: $1 – d_s$ > 1mm, λ_{lum} = 600nm, 615nm, 630nm (from above to below lines), $2 – d$ ~ 0.05mm, λ_{lum} = 600nm, 630 nm.

can influence the process of molecule association. So the relative concentrations of these centers and, consequently, relative intensities of their spectra as well can be changed. Since the absorption spectra of different luminescence centers differ from each other, the luminescence spectrum depends on the excitation wavelength, and excitation spectrum depends on observation wavelength of luminescence.

The second reason that can cause the obtained results is based on reabsorption of radiated emission. It is known that luminescence and absorption spectra of the dye are overlapped over the significant spectral region ($\delta\lambda$ > > 50 nm). Unexcited dye molecules can reabsorb radiation emitted by other dye molecules within this overlapping spectral region. The probability of this reabsorption is proportional to the path length of radiation through the luminescence medium. So, despite being equal in the
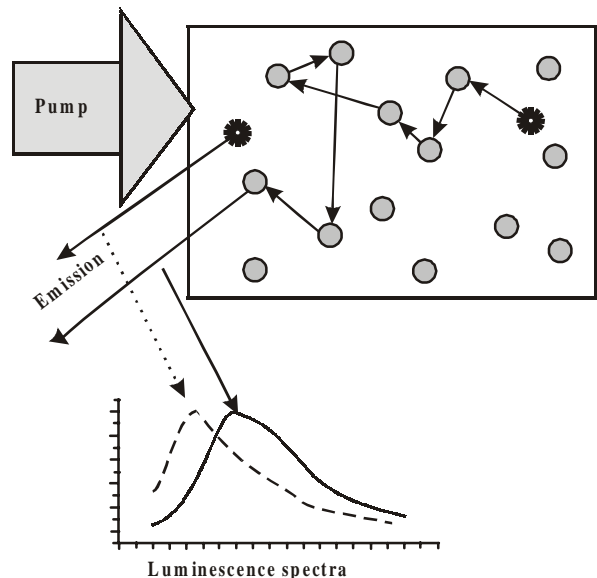
Fig. 3. The figure demonstrates that LS emitted in the different sample layers are different due to different paths through the sample. Radiation from the deeper layer is more reabsorbed, so the corresponding spectrum is long-wave shifted.

sorption reveals itself like mechanism of inhomogeneous spectral broadening.

Since the reflected type geometry of registration was used, the decreasing of sample thickness eliminates the contribution of radiation of the deep sample layers. As a result, LS shifts to the short-wave region.

LS dependence on the sample thickness is appropriated to reabsorption only, because the inhomogeneous spectral broadening influence is independent of the sample thickness. So, the investigation of sample thickness-dependency allows defining the actual mechanism. According to Fig. 4, LS reveals short wavelength shift under sample thickness decreasing. It proves that predominant mechanism of particle influence on LS is reabsorption.

The same conclusions can be done while analyzing Fig. 2a. As it is seen from the figure, only short-wave part of the LS depends on the excitation wavelength, unlike the long-wave one that remains invariable. Namely, all changes are within the region of luminescence and absorption spectra overlapping. Moreover, the excitation wavelength dependency of LS gradually disappeared under sample narrowing. As for ES (Fig. 2b), they significantly differ from each other only at the observation wavelengths corresponding to different reabsorption efficiency of luminescence. This difference between ES virtually disappeared for thin samples.

To define the reasons of non-monotonic dependency of LS peak position on particle concentration, we investigated the behaviour of the coefficient of radiation attenuation for two radiation wavelengths (λ_1 = 520 nm and λ_2 = 648 nm) versus the particle concentration. The wavelengths of the attenuated beams were chosen in such a manner that the first one is within the absorption band (Fig. 5 insertion), and the second one is out of absorption region.

According to Bouguer's law, intensity of light passing distance x through the sample decreases exponentially:

$$I(\lambda) = I_0(\lambda)*\exp(-K(\lambda)*x), \tag{1}$$

where $K(\lambda)$ is a total attenuation coefficient, that conditioned by light scattering as well as absorption. In the case of multiple scattering, the law can be applied only approximately, because attenuation coefficient depends on the order of scattering, and thereby, on thickness x. Thus, in the considered case the law is proved only for enough thin samples, when order of scattering is close to unity. Under sample thickening, the deflection from the law increases. However, this declination is not principal for qualitative conclusions, so we use Bouguer's law as the first approximation. According to the law the attenuation coefficient is:

$$K(\lambda) = -\frac{1}{x}\ln\frac{I(\lambda)}{I_0(\lambda)}. \tag{2}$$

Then attenuation of radiation at λ_1 wavelength to be within absorption band is conditioned by absorption as well as scattering:

$$K(\lambda_1) = K_A^m + K_S^m + \Delta K_A^p + K_S^p, \tag{3}$$

where K_A^m and K_S^m are coefficients of absorption and of scattering, respectively, in the sample without scattering particles. Coefficient ΔK_A^p characterises additional absorption conditioned by lengthening of the radiation path through the sample due to scattering on the particles; K_S^p -scattering coefficient caused by particles. The first items define losses in the sample in the absence of scattering particles, so they can be found as initial points of the plot on Fig. 5. These points correspond to zero particle concentration C_{part} = 0.

The beam attenuation at the second wavelength λ_2 is caused mainly by scattering. Thus corresponding attenuation coefficient contains the scattering coefficients only:

$$K(\lambda_2) = K_S^m + K_S^p. \tag{4}$$

Using these results one can estimate an additional absorption caused by scattering on the particles, and coefficient of particle scattering depending on the particle concentration.

It is seen from the calculated data (Fig. 5), both scattering and additional absorption coefficients increase similarly at low particle concentration. But the additional absorption coefficient grows faster than scattering one at highest particle concentration.

Scattering coefficient growth influences the propagation both of luminescence and excitation radiation. Growth of the scattering efficiency of luminescence radiation lengthens its path through the sample and causes long-wavelength shift of LS. Growth of the excitation light scattering as well as additional absorption of excitation light causes the reduction of penetration depth of excitation radiation and thereby causes short-wavelength shift of LS. This results in the particle concentration dependency of LS. At low particle concentration the first
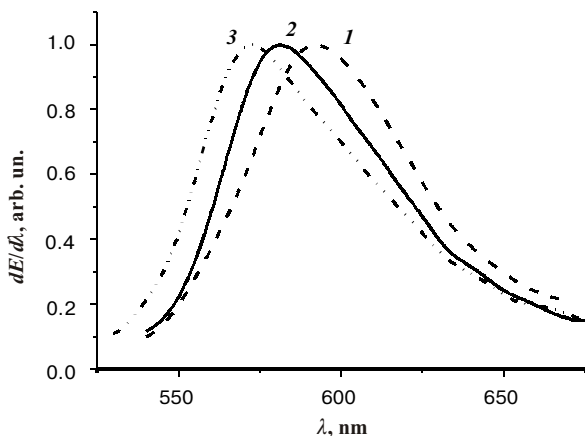

Fig. 4. Luminescence spectra of the samples with different thicknesses: *1 – dₛ = 1 mm, 2 – dₛ = 0.2 mm, 3 – dₛ ∼ 0.05 mm.*
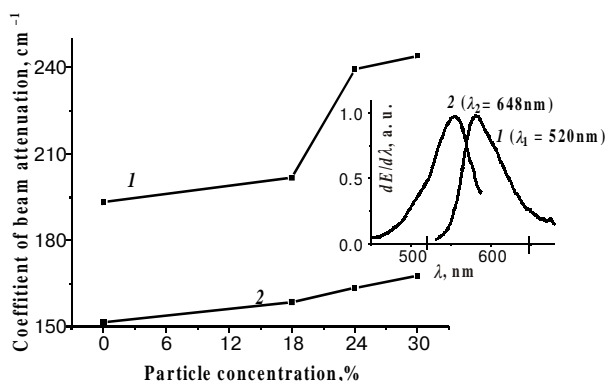
Fig. 5. Coefficients of beam attenuation versus the particle concentration $1 - K(\lambda_1)$, $2 - K(\lambda_2)$. Insertion: luminescence (1) and absorption (2) spectra of R6G overlapping, the positions of the used wavelengths $\lambda_1 = 520$nm and $\lambda_2 = 648$nm are depicted.

4. Conclusions

The luminescent properties of R6G in solid polymer matrix under multiple scattering conditions were investigated. As it was found, multiple scattering provided by embedded fine scattering particles influences the luminescence spectra of solid polymer solution of dye. The reason of such influence is mechanism of luminescence radiation reabsorption. It results in particle concentration and sample thickness dependencies of luminescence peak wavelength.

The reabsorption is a reason of LS dependency on excitation wavelength and ES dependency on luminescence observation wavelength as well.

It was found that in the multiple scattering sample the additional absorption arises, when the particle concentration is rather high. This absorption is conditioned by radiation path lengthening due to scattering on the particles.

effect predominates and LS shifts to the long-wave region under concentration increasing. At high particle concentration, the additional absorption is predominant, and therefore LS reveals short-wavelength shift under the concentration increase.

The mechanism of reabsorption can explain the dependency of LS on particle material (Fig.1*b*), because the scattering of excitation radiation increases with the increasing particle refraction coefficient. It causes the reduction of the penetration depth of excitation radiation, and then short-wave LS shift. This shift is observed when silica particles ($n_{silica} = 1.5$) are displaced with corundum ones ($n_{corundum} = 1.7$), and synthetic diamond ones ($n_{diamond} = 2.4$). In the last case excitation light is absorbed in the nearsurface layer and the LS is mostly short-wave shifted. From the standpoint of light scattering, particle refraction index increasing is equivalent to the particle concentration increasing, which causes the short-wave shift of the LS under multiple light scattering, as it was stated above.

The adduced interpretation of the results is useful to define the mechanism of dependence between lasing spectrum parameter and scattering parameters of the medium. As we have obtained earlier [6, 7], the dependencies of lasing and luminescence spectra on the scattering parameters correlate with each other. It testifies that these changes are conditioned by the same physical reasons. Determining of the physical reasons of the dependency between lasing spectrum and scattering medium parameters gives the possibility to control and operate on the lasing spectra parameters in the investigated media.

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