

## Multiple scattering effect on luminescence properties of organic luminophors

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Luminescence properties of the multiple-scattering rhodamina 6G solutions in solid polymers as functions of scattering efficiency and sample thickness have been investigated. It was found that luminescence spectrum (LS) as well as integrated (over the spectrum) intensity observed in the direction backward to the excitation beam depend significantly on the scattering efficiency being varied using changes of the concentration and refractive index of the embedded scattering microparticles. The integrated intensity increases with the particle concentration increase. This increasing is due to spatial redistribution of luminescence radiation when being multiply scattered in the sample as well as to additional absorption of the excitation light. The LS dependence on the scattering efficiency is caused by reabsorption of the luminescence radiation in the sample. Thus, varying the reabsorption allows tuning the LS maximum over the 20 nm range. Two possible methods of the LS tuning using the sample thickness and scattering efficiency variations were investigated. The second tuning method is preferable because energy efficiency of the sample remains unchanged.

Исследованы люминесцентные свойства многократно рассеивающих полимерных растворов красителя родамина 6Ж в зависимости от эффективности рассеяния и толщины образца. Установлено, что спектр люминесценции (СЛ) и интегральная (по спектру) интенсивность люминесценции, наблюдаемые в направлении "на отражение" относительно пучка возбуждения, существенно зависят от эффективности рассеяния, которая варьировалась изменением концентрации и показателя преломления рассеивающих частиц. Интегральная интенсивность возрастает при увеличении концентрации частиц, что обусловлено пространственным распределением излучения люминесценции вследствие рассеяния и возникновением дополнительного поглощения возбуждающего света. Зависимость СЛ от эффективности рассеяния обусловлена перепоглощением излучения люминесценции. Изменение перепоглощения позволяет плавно перестраивать максимум СЛ в пределах 20 нм. Исследованы два метода перестройки СЛ путем изменения толщины образца и эффективности рассеяния. Преимуществом второго метода перестройки есть постоянство энергетической эффективности образца в процессе перестройки.

Recent investigations have demonstrated new possibilities of multiple scattering influence on optical properties of a medium. This concerns, in first turn, the effects of photon localization [1, 2] and resonator-free laser generation [3–5] being possible just

due to strong scattering. Our investigations have demonstrated the multiple scattering effect on luminescence properties of organic luminophors [6]. This makes it possible in principle to vary the luminophor spectrum parameters by scattering efficiency change.

Up to now, the multiple scattering influence on organic luminophor characteristics from the standpoint of their potential future applications has been poorly studied. The results of the investigation could be used to control parameters of the so-called random-lasers [7] and to adjust the spectral and energy characteristics of organic luminophors. The multiple scattering could be provided by embedding fine-disperse (diameter  $d \sim 1 \mu\text{m}$ ) dielectric particles into a luminophor at high concentrations ( $n_p \sim 10^9$  to  $10^{11} \text{ cm}^{-3}$ ). Varying of the particle concentration, size and refractive index of the particle material makes it possible to vary the scattering efficiency within wide limits.

We have investigated the luminescence spectra (LS) of solid polymer (polyvinyl acetate) solution of rhodamine 6G with embedded scattering particles. Powders of  $\text{SiO}_2$  (diameter  $d \sim 0.5 \mu\text{m}$ , refraction coefficient  $n \sim 1.5$ , in the weight concentration  $C_p = 6$  to 30 %);  $\text{Al}_2\text{O}_3$  ( $d \sim 5 \mu\text{m}$ ,  $n \sim 1.7$ ,  $C_p \sim 15$  %); synthetic diamond ( $d \sim 7 \mu\text{m}$ ,  $n \sim 2.4$ ,  $C_p \sim 15$  %) and  $\text{CeO}_2$  ( $d \sim 2 \mu\text{m}$ ,  $n \sim 2.4$ ,  $C_p \sim 15$  %) were used as scattering particles. The number of particles per cubic centimetre is:  $4.2 \cdot 10^{11}$  to  $2.5 \cdot 10^{12}$  ( $\text{SiO}_2$ ),  $7.6 \cdot 10^8$  ( $\text{Al}_2\text{O}_3$ ),  $3.15 \cdot 10^8$  (synthetic diamond), and  $7.75 \cdot 10^9 \text{ cm}^{-3}$  ( $\text{CeO}_2$ ). The samples were made of carefully mixed polyvinyl acetate, alcohol solution of rhodamine 6G, and the particles. The dye concentration was  $\sim 10^{-3} \text{ M}$ . Solid polymer sample on an opaque substrate was obtained by slow alcohol evaporation out of the mentioned composite. The samples of different thickness were cut using the same initial material. The laser pulse excitation was done with the second harmonic ( $\lambda = 532 \text{ nm}$ ) of Q-switch  $\text{Nd}^{+3}\text{:YAG}$  ( $\tau_i = 15 \text{ ns}$ ) or mercury line  $\lambda = 546.1 \text{ nm}$ . The radiation spectra were registered in the opposite direction to the pumping beam (reflected-type experiment). A diffraction monochromator with resolution  $\Delta\lambda = 1 \text{ nm}$  and a PMT were used to record the signal before being processed by a PC.

The effect of the multiple scattering on the luminescence spectrum and backward luminescence intensity of the samples mentioned above was investigated. It is found that particle embedding changes the LS peak wavelength and spectrum shape (Fig. 1a). The LS peak wavelength depends non-monotonically on the particle concentration  $C_p$  (Fig. 1b). The LS is shifted towards short-wavelength region as the particle material refractive index increases (Fig. 2a). The

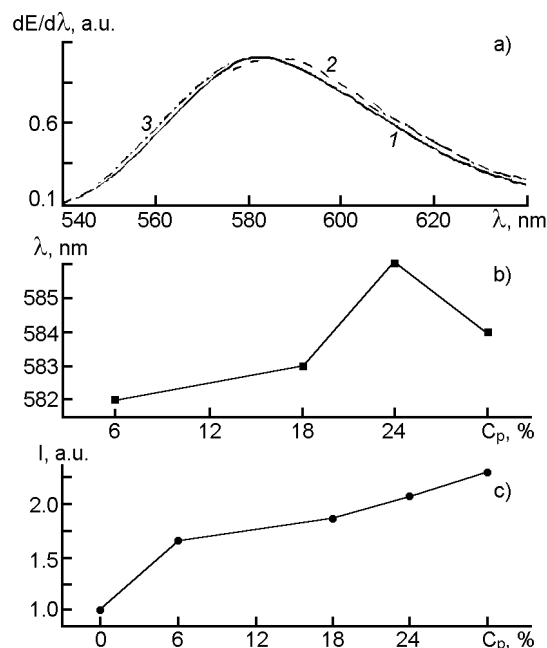


Fig. 1. (a) Luminescence spectra of R6G in solid polyvinyl acetate matrix with different  $\text{SiO}_2$  concentration ( $C_p$ ): 30 % (1), 24 % (2), 6 % (3). (b) LS peak wavelength vs. the  $\text{SiO}_2$  particle concentration. (c) Integrated (over the spectrum) radiation intensity vs. the  $\text{SiO}_2$  particle concentration.

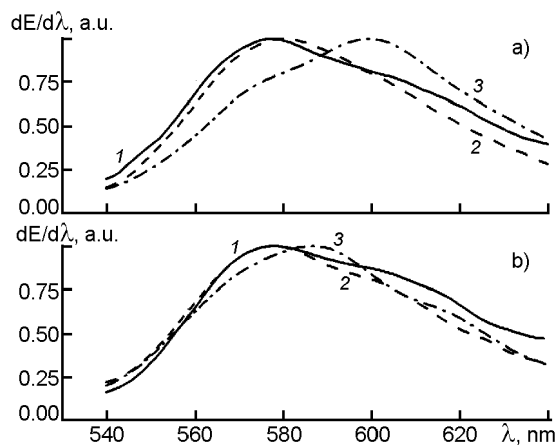


Fig. 2. Luminescence spectra of R6G in the solid polyvinyl acetate matrix with particle of different materials ( $C_p = 15$  %):  $\text{CeO}_2$  (1), synthetic diamond (2),  $\text{SiO}_2$  (3) at the different sample thickness: (a)  $d > 1 \text{ mm}$ , (b)  $d < 0.3 \text{ mm}$ .

particle embedding causes significant increase of the integral luminescence radiation intensity  $I_\Sigma$  (Fig. 1c) as compared to that of non-scattering sample  $I_{\Sigma 0}$ . The integral radiation intensity increases non-linearly as the particle concentration rises. The integral radiation intensity of the least con-

trated sample is approximately  $\gamma = I_{\Sigma}/I_{\Sigma 0} = 1.6$  times higher than that of non-scattering sample. At further increase of the particle concentration, the ratio  $\gamma = I_{\Sigma}/I_{\Sigma 0}$  attains 2 for the sample with 24 % of silica and 2.3 for the sample with 30 % of silica.

The increasing of the integrated radiation intensity in direction backward to excitation beam is accompanied with reduction of the integrated radiation intensity in forward direction. It follows therefrom that the main reason of the "backward" integrated radiation intensity increase with increasing  $C_p$  is a spatial redistribution of the luminescence radiation caused by its multiple scattering. The multiple scattering within the sample volume forms a diffuse reflector effect reversing the luminescence photons to the front sample surface. Thus, the "backward" integrated radiation intensity grows. At the highest particle concentration, almost all luminescence radiation is directed into the hemisphere of the excitation beam incidence and the "backward" radiation intensity grows approximately twice in the high-concentrated sample comparatively to the particle-free one.

Multiple scattering of the exciting light causes the additional increasing of  $I_{\Sigma}$  value, as a result,  $\gamma > 2$  at highest particle concentrations. In this case, the scattering increases the effective path of excitation photons through the sample that is similar to increased optical sample thickness or the additional absorption appearance. The effect increases the fraction of absorbed excitation light that results in increased  $I_{\Sigma}$  value. The additional absorption appearance was proved by direct investigations of the radiation attenuation in the sample versus the SiO<sub>2</sub> particle concentration. It was found that as the scattering particle concentration increases, the scattering coefficient grows approximately linearly while the absorption coefficient of beam reveals a super-linear dependence on the particle concentration. The absorption coefficient increase rate is essentially higher at  $C_{part} > 24$  % than in the low concentration region. Such behaviour evidences the additional absorption to be appeared at high particle concentration is due to the multiple scattering.

The most probable mechanism of the multiple scattering influence on the peak position of the dye LS is the reabsorption of luminescence radiation with unexcited dye molecules. This is confirmed by the dependence of LS position on the sample thickness. As is shown on Fig. 2, the luminescence

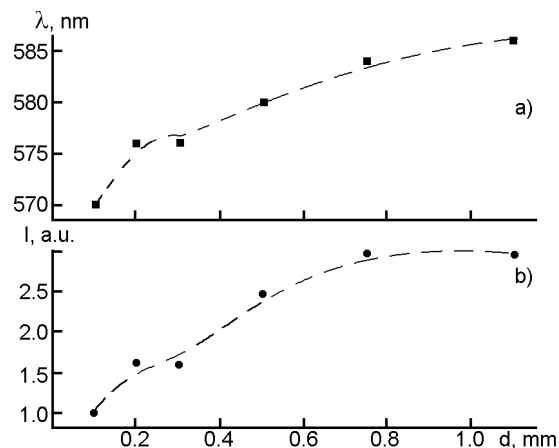


Fig. 3. (a) LS peak wavelength and (b) integrated (over the spectrum) radiation intensity vs. the sample thickness.  $C_p = 30$  % of SiO<sub>2</sub>.

spectra of thin samples become close to each other (Fig. 2b), in spite of being rather different for thick samples (Fig. 2a). This reabsorption is conditioned by significant overlapping of luminescence and absorption spectra of R6G (over 50 nm spectral interval). Unexcited dye molecules could reabsorb the radiation energy with the probability proportional to the radiation path length through the sample. The radiation of the deeper layer passes longer way in the sample, thus, it undergoes more reabsorption. The observed spectrum is a superposition of the spectra radiated in different sample layers. So, the spectrum shape depends on many factors influencing either the luminescence radiation distribution in the sample or the covered radiation path in the sample. The reabsorption redistributes luminescence radiation energy outside the luminescence region and absorption spectra overlapping towards the long-wave LS region. It causes the long-wave spectral shift of the LS. Thus, one can operate the LS position by changing the reabsorption efficiency.

The most influential sample parameters that can change the reabsorption (except for the dye concentration) are the sample thickness and scattering efficiency. As is seen from Fig. 3a, the LS of the sample is shifted within  $\Delta\lambda = 17$  nm as the sample ( $C_p = 30$  %) thickness changes from 0.1 mm to 1.2 mm. The dependence can be used to tune the LS continuously. But drawback of the method is radiation intensity reduction as the sample is thinned (Fig. 3b) due to decreasing of the absorbed excitation energy fraction.

The scattering efficiency could be varied by changing the particle concentration, diameter, and refractive index. As it is shown in Fig. 1a, the scattering efficiency change by means of the SiO<sub>2</sub> particle concentration influences the LS position only slightly. As  $C_p$  changes from 6 to 24 %, the peak wavelength shift is 4.5 nm only, that is, a tenth of the spectrum width. The further non-monotonic dependence of the LS peak wavelength shift on particle concentration (Fig. 1b) is, however, worth to attention. It means that influence of luminescence reabsorption decreases at the further increasing scattering efficiency. The decreasing of the reabsorption influence is caused by reducing of the excitation penetration depth into the sample due to the additional absorption appearance. It results in reduction of the effective path of the luminescence radiation and therefore the LS shifts to the short-wave region. One can expect that further scattering efficiency increasing can shift the LS to the short wavelength region and the shift can achieve a significant value if the LS of homogeneous (non-scattering) luminophor is strongly long-wave shifted owing to high dye concentration.

Since concentration  $C_p = 30$  % is practically a cut-off value, so further scattering efficiency increase can be achieved by using the particles with higher refractive index. It is seen from Fig. 2a that refractive index increase from 1.5 (SiO<sub>2</sub>) to 1.7 (Al<sub>2</sub>O<sub>3</sub>) and 2.4 (synthetic diamond and cerium oxide) shifts the LS within the same limits ( $\Delta\lambda \cong 20$  nm) as the sample thinning from 1.2 to 0.1 mm does ( $\Delta\lambda \cong 17$  nm). Moreover, in contrast to the sample thinning case, the absorbed energy in the sample does not change as the scattering efficiency varies. Thus, the energy efficiency of the sample (defined as the radiated energy ratio to the absorbed one) remains the same. The obtained results demonstrate the principal possibility of the LS shift by means of scattering efficiency variation in the organic dye based luminophors. The method is applicable to all organic luminophors where an overlap region of the LS and absorption spectrum exists (the Stokes shift is small). The quantum yield is desirable to be high

enough because a fraction of energy is lost in the course of reabsorption. The obtained results could be employed to modify the luminescence characteristics of luminophors and to develop continuous tuning methods of the random-laser radiation spectrum.

In conclusion, the multiple scattering caused by embedded fine-scattering particles has been found to influence the luminescence spectrum position and significantly increases the luminescence radiation intensity in the direction backward to the excitation beam. This intensity increase is caused by spatial redistribution of luminescence radiation and by additional absorption of the excitation light appeared due to multiple scattering. In the first case, the sample acts like a diffuse mirror scattering the luminescence radiation toward the registering equipment. In the second case, it increases the absorbed fraction of the excitation light. The reason for the dependence of luminescence spectrum position on scattering efficiency is the luminescence light reabsorption in the sample. This reabsorption influence on the luminescence spectrum could be employed to vary the luminophor spectrum. The reabsorption efficiency could be varied by sample thickness or scattering efficiency varying. The second tuning method offers an advantage over the sample thickness variation, because the absorbed fraction of the excitation energy is less significantly influenced by the scattering efficiency change, thus, the energy efficiency of the sample remains the same.

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## **Вплив багаторазового розсіювання на люмінесцентні властивості органічних люмінофорів**

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Досліджувались люмінесцентні властивості багатократно розсіювальних полімерних розчинів родаміну 6Ж. Встановлено, що спектр люмінесценції (СЛ) та інтегральна (по спектру) інтенсивність люмінесценції, при використаній геометрії спостереження "на відбиття", суттєво залежать від ефективності розсіювання, котра варіювалась зміною концентрації та показника заломлення частинок. Інтегральна енергія зростає при зростанні концентрації розсіювальних частинок, що обумовлено просторовим перерозподілом випромінення люмінесценції внаслідок розсіювання та виникненням додаткового поглинання випромінення збудження. Залежність СЛ від ефективності розсіювання обумовлена перепоглинанням випромінення люмінесценції у зразку. Це дозволяє реалізувати плавну перестроювання СЛ шляхом зміни ефективності перепоглинання. Досліджено два методи такого перестроювання СЛ шляхом варіювання товщини зразка та ефективності розсіювання. Перевагою другого методу є незмінність енергетичної ефективності зразка.