
Spectral and kinetic luminescence characteristics of emulsion microcrystals AgBr(I) with adsorbed organic dye

¹Tyurin A. V., ^{1*}Zhukov S. A., ¹Bekshaev A. Y. and ²Ternovsky V. B.

¹Physics Research Institute, Odesa I. I. Mechnikov National University, 2 Dvorianska Street, 65082 Odesa, Ukraine

²National University “Odesa Maritime Academy”, 8 Didrikhsona Street, 65023 Odesa, Ukraine

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Abstract. To reveal the structure of tunnel-luminescence centres in AgBr(I) emulsion microcrystals (EMCs), we perform spectro-sensitometric and kinetic studies of their low-temperature ($T = 77$ K) luminescence. The luminescence characteristics depending on the binder, the presence and the nature of sensitizing additions (dyes) and the oxygen treatment are studied quantitatively. Special attention is paid to the comparative studies of the Stokes and dye-induced anti-Stokes luminescence components in the AgBr(I) EMCs. When the dye-sensitized AgBr(I) EMCs distributed in the polyvinyl alcohol are excited by the light photons with the energies corresponding to the intrinsic absorption region of the EMCs ($\lambda_{\max} \approx 460$ nm), the kinetics of the luminescence band centred at the wavelength $\lambda_{\max} \approx 560$ nm is monotonic. On the contrary, upon excitation by the photons corresponding to the absorption region of a J-aggregated dye ($\lambda_{\max} \approx 680$ nm), the kinetics of the anti-Stokes glow ($\lambda_{\max} \approx 560$ nm) is characterized by a rapid ‘flash’ followed by a gradual decrease to a stationary level (a ‘flash enhancement’). These results indicate that a non-equilibrium transfer of charge carriers from the dye, which is adsorbed on the EMC surface, to the EMC volume depends essentially on the binder. If gelatine is the binder, this process is significantly affected by the oxygen adsorption, whereas the resulting effect depends on the aggregate form of the adsorbed dye. Understanding of physicochemical processes that govern the luminescence centres should enable one to control the structural transformations of the donor–acceptor complexes and clusters, which are responsible for the unique photometric properties of AgBr(I), and optimize their parameters for various applications in optoelectronics, holography, photographic materials science, optical sensors and solar energy systems.

Keywords: AgBr(I) microcrystals, low-temperature luminescence, emulsion binders, tunnel-recombination centres, dye sensitization, oxygen treatment, luminescence kinetics

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1. Introduction

Studies of the low-temperature ($T = 77$ K) luminescence in emulsion microcrystals (EMCs) AgBr(I) with adsorbed dye molecules (DMs) play an important role in elucidating the mechanism of spectral sensitization. These studies enable one to disclose the processes occurring in the excited molecules and aggregates of dyes, as well as the processes determining the interactions of excited or ionized dyes with the EMCs. Remarkably, a specific luminescence behaviour is possible in such systems [1]: when a light quantum with an energy $h\nu_1$ is absorbed by the DM adsorbed on the EMC surface, there can appear a luminescence in the AgBr(I) EMCs with the irradiated quantum

*Corresponding author: zhukov@onu.edu.ua

energy $h\nu_2 > h\nu_1$. This phenomenon occurring in silver-halide (AgHal) EMCs is referred to as an “anti-Stokes luminescence of AgHal due to an adsorbed-dye absorption” (ASLADA). Presumably, it can arise as a result of a two-quantum process.

Possible mechanisms of this process have been discussed in a number of works [2–6]. Their authors have suggested the following: if a DM is adsorbed on an AgHal EMC surface, the charge states of surface defects can affect the energy state of the DM, which causes redistribution of its ground and excited energy levels [7, 8]. The absorption of light by the DMs (aggregates), in which the excited level S_1 lies inside the conduction energy band of the AgHal crystals, leads to generation of a free electron. On the other hand, absorption of light by the other molecules (aggregates) of the dye, in which the excited level lies below the conduction band and the ground level S_0 is within the valence band of AgHal, may be accompanied by the appearance of a hole in the valence band [4]. The recombination of an electron from the conduction band and a hole localized at the luminescence centre can result in the ASLADA effect.

This mechanism suggested for the ASLADA effect is reasonable though not unambiguous, since it links the ASLADA exclusively with the surface defects of the AgHal EMCs, thus letting aside the charge state of the DM itself, the presence of silver ions on the EMC surface, the influence of the binder, and the possible effects of the dye self-desensitization. As for the low-temperature ($T = 77$ K) tunnel luminescence in the AgBr(I) EMCs [9, 10], its characteristics should not depend on the Stokes or anti-Stokes way of its excitation.

An interesting though poorly understood problem is related to the nature of the influence of oxygen on sensitivity reduction for the AgBr(I) EMCs upon their sensitization by dyes both in the region of intrinsic AgBr(I) absorption (desensitization) and in the region of DM absorption (self-desensitization) [11, 12]. Various competing hypotheses have been put forward in this context. For example, a self-desensitization mechanism has been suggested in Refs. [13, 14]. According to this mechanism, the transfer of a non-equilibrium electron from a DM to an oxygen molecule, with both being adsorbed on the AgBr(I) EMC surface, results in forming oxygen-radical anions, which change the charge of the AgBr(I) EMC surface. However, in our opinion, the formation of oxygen radical anions has not obtained unambiguous experimental confirmation so far. Accordingly, the influence of oxygen on the desensitization and self-desensitization processes in the AgBr(I) EMCs has not been elucidated in enough detail. Therefore it requires further detailed studies, especially in view of specific effects stimulated by binders.

This problem has been partially addressed in the recent work [15] where the AgBr(I) EMCs distributed in a polyvinyl alcohol are investigated. In such systems, the ASLADA effect has been detected, which is associated with excitation of the dye J-aggregates adsorbed on the charged molecular-silver surface centres. Additionally, the anti-Stokes luminescence process itself has been characterized by the special kinetic and spectral features associated with controllable adsorbed-dye transformations. These observations have stimulated further interest to the similar systems [10]. Here we present the results associated with the low-temperature luminescence characteristics of the AgBr(I) EMCs distributed in various binders, their comparative analysis, and the effects induced by the surface silver and oxygen ions.

2. Problem description and experimental approach

Our object of investigation is the AgBr(I) EMCs distributed in the binder of two kinds: a polyvinyl alcohol (PVA) and gelatine (Gel). For simplicity, the special conditions of EMC environment are indicated in parentheses, so that a notation ‘AgBr(I) EMCs (PVA)’ means the EMCs distributed in PVA, etc. The main features of the EMC structures and the methods of their fabrication have been

described elsewhere [10]. In particular, the binder–EMC interaction manifests itself in the fact that the characteristic size of the EMCs obtained in PVA is 0.1 μm , whereas the EMCs synthesized in Gel are twice as larger.

Spectral sensitization of the AgBr(I) EMCs (Gel, PVA) was performed via a treatment with the alcohol solution of an anionic J-aggregating dye (Pyridine salt of 3,3'-di- γ -sulfopropyl-9-ethyl-4,5,4',5'-dibenzoylbenzene, which will be referred to as simply a 'Dye'). The dye concentration warranting the formation of J-aggregates on the AgBr(I) EMC surfaces [16] was equal to 10^{-4} mol Dye/mol AgBr. A finished spectrally sensitized emulsion was kept at 47°C for 10 min, with continuous stirring in a magnetic stirrer.

During these processes, neither specific chemical interactions nor formation of new compounds were detected in the AgBr(I) EMC systems under inspection. Their features were predominantly mediated by the concentrations of adsorbed dyes or surface silver ions, which indicates a decisive role of the Coulomb forces.

The treatment with oxygen was performed by bubbling a molten spectrally sensitized emulsion during a time interval t_e ($1 \text{ min} \leq t_e \leq 20 \text{ min}$). In the course of this treatment, sampling for the luminescence and spectro-sensitometric tests was carried out, for which the emulsion was poured onto glass plates with the size of $9 \times 12 \text{ cm}^2$. Afterwards, the dried plates were exposed to the light expanded into a spatially variable spectrum (the wavelength range 400–1100 nm) obtained using an ISP-73 high-aperture spectrograph. As a result of such exposure, latent image centres appeared in the AgBr(I) EMCs, which were formed by reduced neutral silver centres with the atomic-molecular degree of dispersity [17]. These centres were developed with a deep developer [18].

The spectral distribution of changes $\Delta D = D - D_0$ in the optical density of the exposed and developed plates, which is proportional to the concentration of developed latent-image centres, was measured with an MF-4 microphotometer according to a standard procedure [19]. The spectra of low-temperature ($T = 77 \text{ K}$) luminescence in the AgBr(I) EMCs and the kinetics of the luminescence intensity as a function of time were measured on alternating-current excitation. The samples were excited by rectangular light pulses with the repetition rate of 800 Hz according to a procedure and using a setup described in Ref. [20]. In this case, a phosphorescence of samples with the relaxation times $\tau > 2.0 \text{ ms}$ was recorded. Actually, the phosphorescence and the anomalously delayed fluorescence of the AgBr(I) EMCs with the adsorbed dye represent the luminescence processes of the main interest in this study.

Under these conditions, the luminescence signal is also alternating but its amplitude evolves gradually, while the amplitude of excitation is constant. Generally, two sorts of the luminescence kinetics were observed: (i) a monotonic increase in the amplitude up to a stationary level I_{st} and (ii) a 'flash enhancement' (FE) or a 'luminescence fatigue' effect, when the amplitude increases rapidly, reaches its maximum value I_{max} and then decreases to a stationary level. These kinetic features are characterized by the numerical coefficient

$$F = (I_{max} - I_{st}) / I_{max} \quad (1)$$

for the monotonic increase, with $I_{max} = I_{st}$ and $F = 0$, or otherwise $0 < F < 1$.

3. Results of experiments

The luminescence spectra observed for the AgBr(I) EMCs are characterized by typical excitation and glow wavelengths and by a specific kind of kinetics (see the paragraph above). Additionally, the spectra depend on the environment conditions including the binder, the temperature and the

content of Ag^+ ions which can be measured by a ‘bromine potential’ parameter pBr [10, 21]. According to these conditions, all the luminescence bands observed are classified as shown in Table 1.

The main properties of the luminescence bands BB1, BB2, BG1 and BG2 have been discussed in Ref. [10]. Here we continue this presentation, with a special emphasis on the changes occurring due to introduction of the dye and the chemical treatment of our samples. Note that in the classification of Table 1, only two bands (BB4 and BG4) reveal a dye-induced anti-Stokes character and thus represent a version of the ASLADA effect.

Table 1. Luminescence spectral bands and conditions for their observation.

Emission-band notation	Binder	Characteristic excitation wavelength λ_{max} , nm	Characteristic glow wavelength λ_{max} , nm	Characteristic temperature range at $\text{pBr} = 4$	Characteristic content of Ag^+ ions (pBr)
BB1	H_2O , PVA	460	560	$77 \text{ K} \leq T \leq 81 \text{ K}$	4
BB2	H_2O , PVA	460	720	$80 \text{ K} \leq T \leq 95 \text{ K}$	$5 \leq \text{pBr} \leq 7$
BB3	PVA+Dye	460	560	77 K	4; 7
BB4	PVA+Dye	680	560	77 K	4; 7
BB5	PVA+Dye	460	720	77 K	4; 7
BB6	PVA+Dye	680	720–780	77 K	4; 7
BG1	Gel	460	580	$77 \text{ K} \leq T \leq 81 \text{ K}$	4
BG2	Gel	460	750	$80 \text{ K} \leq T \leq 95 \text{ K}$	$4 < \text{pBr} \leq 7$
BG3	Gel+Dye	460	580	77 K	4; 7
BG4	Gel+Dye	680	580	77 K	4; 7
BG5	Gel+Dye	460	750	77 K	4; 7
BG6	Gel+Dye	680	750–800	77 K	4; 7

3.1. Influence of dye

The dye-induced spectral sensitization of the AgBr(I) EMCs is accompanied by the adsorption of the DMs on their surface. In cases of either AgBr(I) EMC (H_2O , PVA) or AgBr(I) EMC (Gel) examined at $4 \leq \text{pBr} \leq 7$, addition of the dye entails no qualitative changes in the luminescence spectrum obtained due to excitation with $\lambda_{\text{max}} \approx 460 \text{ nm}$ (the bands BB1, BB2 and BG1, BG2). In the luminescence spectrum of the AgBr(I) EMCs (PVA + Dye), two bands are detected, BB3 and BB5. This is illustrated by Fig. 1a (curve 1) for $\text{pBr} = 4$ and Fig. 2a (curve 1) for $\text{pBr} = 7$. In case of AgBr(I) EMCs (Gel + Dye), the bands BG3 and BG5 are observed (see curve 1 in Fig. 3a for $\text{pBr} = 4$ and curve 1 in Fig. 4a for $\text{pBr} = 7$).

When the silver-ion concentration corresponds to the condition $\text{pBr} = 4$, addition of the dye induces no changes in the glow kinetics for the bands BB3 (see curve k_1 in Fig. 1b) and BB5 (see curve k_3 in Fig. 1b) in the AgBr(I) EMCs (PVA + Dye). This is similar to what is observed for the AgBr(I) EMCs (H_2O , PVA) in the bands BB1 and BB2 [10]. Also, no dye-induced changes are detected in the luminescence band BG5 of the AgBr(I) EMCs (Gel + Dye) (see curve k_3 in Fig. 3b). This situation is similar to that observed earlier for the band BG2 in the AgBr(I) EMCs (Gel) [10].

However, a quite different behaviour is typical for the luminescence kinetics observed in the AgBr(I) EMCs (Gel + Dye) at $\text{pBr} = 4$ and excitation by $\lambda \approx 460 \text{ nm}$. Although the kinetics of the

luminescence increase for the band BG1 shows the FE effect when the dye is absent [10], the FE in the BG3 band is not observed after the dye is introduced (see curve k_1 in Fig. 3b). At the same time, an increase in the content of Ag^+ ions up to $\text{pBr} = 7$ restores the FE in the AgBr(I) EMCs (Gel + Dye) (see curve k_1 in Fig. 4b).

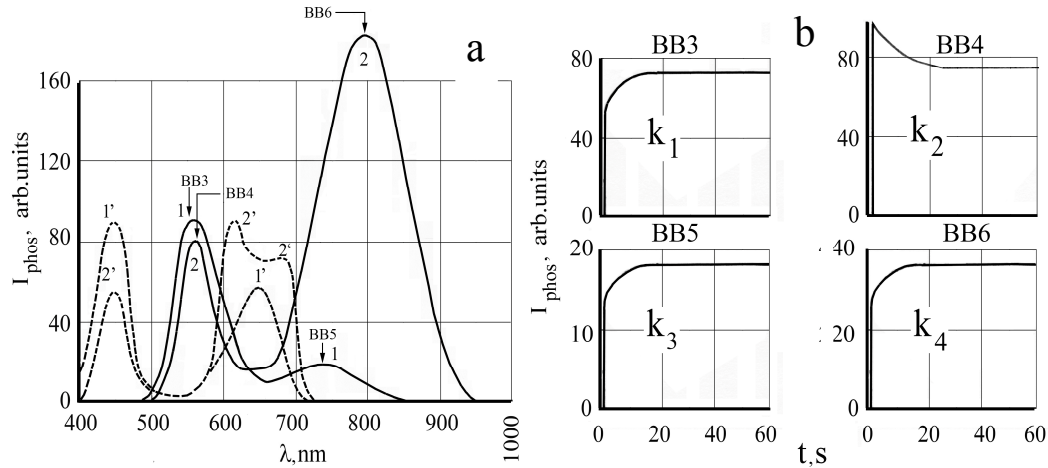


Fig. 1. Spectral and kinetic characteristics of luminescence intensity observed in the AgBr(I) EMCs (PVA + Dye) at $\text{pBr} = 4$ and $T \approx 77$ K: (a) glow spectra (solid curves) obtained upon excitation by the wavelength λ : 1 – 460 nm (BB3 and BB5); 2 – 680 nm (BB4 and BB6); excitation spectra (dashed curves) of the bands with λ_{max} : 1' – 560 nm (BB3 and BB4); 2' – 720 nm (BB5 and BB6); (b) kinetics of establishment of a stationary-value luminescence for the bands BB3 (k_1), BB4 (k_2), BB5 (k_3) and BB6 (k_4) (see Table 1).

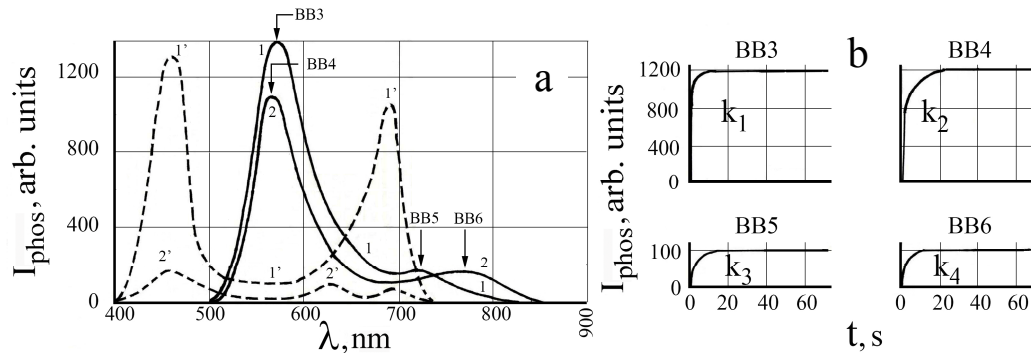


Fig. 2. Spectral and kinetic characteristics of luminescence intensity observed in the AgBr(I) EMCs (PVA + Dye) at $\text{pBr} = 7$ and $T \approx 77$ K: (a) glow spectra (solid curves) obtained upon excitation by the wavelength λ : 1 – 460 nm (BB3 and BB5); 2 – 680 nm (BB4 and BB6); excitation spectra (dashed curves) of the bands with λ_{max} : 1' – 560 nm (BB3 and BB4); 2' – 720 nm (BB5 and BB6); (b) kinetics of establishment of a stationary-value luminescence for the bands BB3 (k_1), BB4 (k_2), BB5 (k_3) and BB6 (k_4) (see Table 1).

For the AgBr(I) EMCs with a higher content of silver ions ($\text{pBr} = 7$), introduction of the dye imposes noticeable changes in the kinetics of the luminescence bands excited by the light wavelength $\lambda \approx 460$ nm. In contrast to a 'no-dye' situation, where the luminescence kinetics for the BB2 band in the AgBr(I) EMCs (PVA) reveals the FE effect [10], no FE is observed in the band BB5 after the dye has been introduced (see curve k_3 in Fig. 2b). For the AgBr(I) EMCs (Gel) at $\text{pBr} = 7$ and the AgBr(I) EMCs (Gel + Dye) at $\text{pBr} = 7$, no qualitative changes in the luminescence kinetics are observed (cf. the behaviours of the band BG1 [10] and the band BG3 in Fig. 4b (curve k_1), as well as those of the band BG2 [10] and the band BG5 in Fig. 5b (curve k_1)).

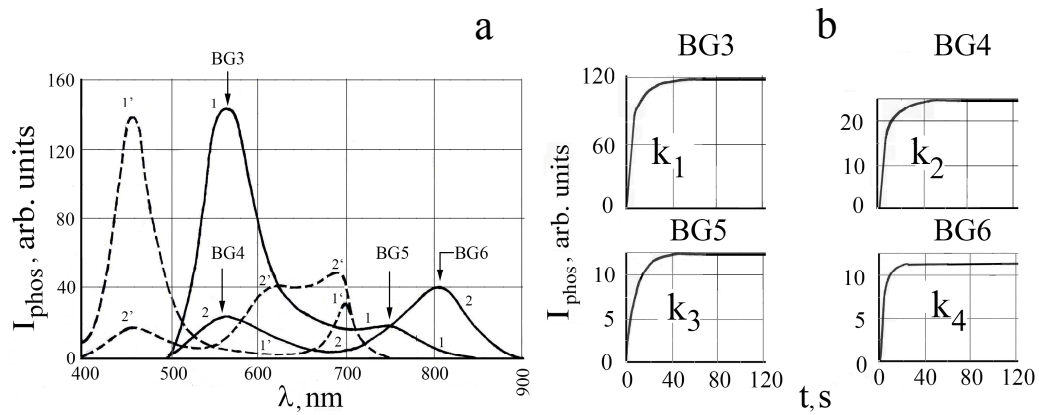


Fig. 3. Spectral and kinetic characteristics of luminescence intensity observed in the AgBr(I) EMCs (Gel + Dye) at $p\text{Br} = 4$ and $T \approx 77$ K: (a) glow spectra (solid curves) obtained upon excitation by the wavelength λ : 1 – 460 nm (BG3 and BG5); 2 – 680 nm (BG4 and BG6); excitation spectra (dashed curves) of the bands with λ_{max} : 1' – 580 nm (BG3 and BG4); 2' – 750 nm (BG5 and BG6); (b) kinetics of establishment of a stationary-value luminescence for the bands BG3 (k_1), BG4 (k_2), BG5 (k_3) and BG6 (k_4) (see Table 1).

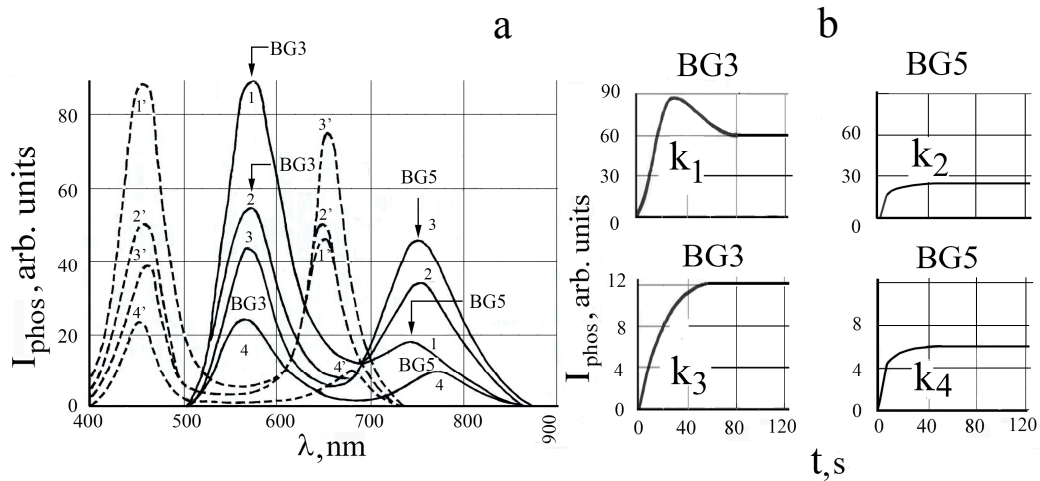


Fig. 4. Spectral and kinetic characteristics of luminescence intensity observed in the AgBr(I) EMCs (Gel + Dye) at $p\text{Br} = 7$ and $T \approx 77$ K: (a) glow spectra (solid curves) obtained upon excitation by the wavelength $\lambda = 460$ nm (BG3 and BG5) and excitation spectra (dashed curves) of the bands with $\lambda_{\text{max}} = 580$ nm (BG3 and BG4; BG4 is described in Fig. 5); duration of O_2 -treatment is equal to $t_e = 0$ min (curves 1 and 1'), $t_e = 1$ min (curves 2 and 2'), $t_e = 2$ min (curves 3 and 3') and $t_e = 4$ min (curves 4 and 4'); (b) kinetics of establishment of a stationary-value luminescence obtained for different luminescence bands and different durations of O_2 -treatment: (k_1) BG3, $t_e = 0$ min, (k_2) BG5, $t_e = 0$ min, (k_3) BG3, $t_e = 2$ min, and (k_4) BG5, $t_e = 2$ min.

The presence of the dye induces notable changes in the excitation spectra, which can be contrasted to the excitation spectra detected in the study [10] for the AgBr(I) EMCs (H_2O , PVA) (the bands BB1 and BB2). Once the dye is introduced, two overlapping bands with $\lambda_{\text{max}} \approx 630$ nm and $\lambda_{\text{max}} \approx 650\text{--}680$ nm appear in the excitation spectrum, in addition to the band associated with the absorption of AgHal ($\lambda_{\text{max}} \approx 460$ nm). Noticeably, this does not depend on the Ag^+ content, since the curves 1' and 2' in Fig. 1a refer to $p\text{Br} = 4$, while the curves 1' and 2' in Fig. 2a refer to $p\text{Br} = 7$. Their spectral positions correspond to the absorption regions of molecular (MDye) and J-aggregated (JDye) dyes [16, 22].

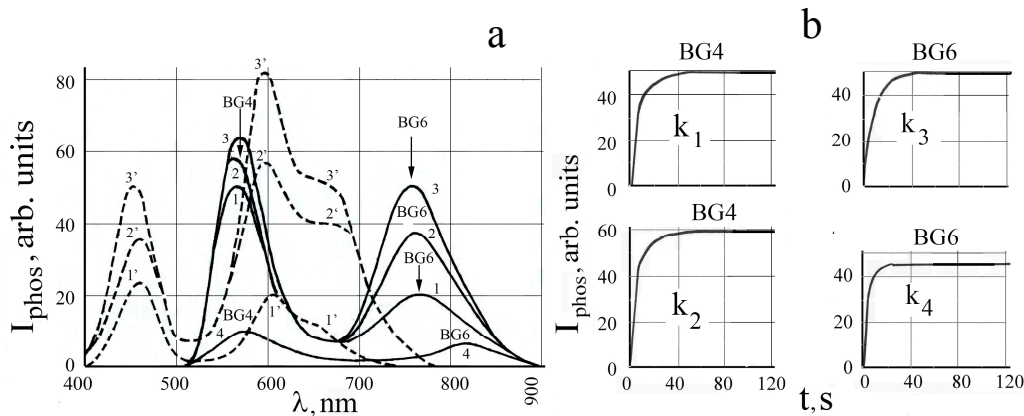


Fig. 5. (a) Spectral and kinetic characteristics of luminescence observed in the AgBr(I) EMCs (Gel + Dye) at $T \approx 77$ K and $pBr = 7$: (a) glow spectra excited by the wavelength $\lambda = 680$ nm (bands BG4 and BG6; solid curves 1–4) and spectra of excitation (dashed curves 1'–3') of the glow with $\lambda = 750$ nm (bands BG5 and BG6; BG5 is described in detail in Fig. 4). Figures corresponding to different curves mark the duration of O_2 -treatment: $t_e = 0$ min (curves 1 and 1'), $t_e = 1$ min (curves 2 and 2'), $t_e = 2$ min (curves 3 and 3'), and $t_e = 4$ min (curve 4); (b) Kinetics of luminescence with $\lambda_{max} = 750$ nm obtained for different bands and different durations of O_2 -treatment: (k_1) BG4, $t_e = 0$ min, (k_2) BG6, $t_e = 0$ min, (k_3) BG4, $t_e = 2$ min, and (k_4) BG6, $t_e = 2$ min (see Table 1).

Upon excitation by the light corresponding to the absorption region of JDye ($\lambda_{max} \approx 680$ nm), four luminescence bands are observed in the glow spectra for the AgBr(I) EMCs (PVA), regardless of the content of silver ions (see curve 2 in Fig. 1a and curve 2 in Fig. 2a). These are the anti-Stokes band BB4 and the closely overlapping Stokes bands. They include the anomalously delayed fluorescence of JDye ($\lambda_{max} \approx 700$ nm), the band BB6 associated with the tunnel recombination at $\{(I_a^- I_a^-) Ag_{i2}^+\}$ centres, and the phosphorescence band of MDye ($\lambda_{max} \approx 800$ nm) [17, 20]. Note that here we use a standard notation for the luminescence centres, where the subscripts 'a' and 'i' imply respectively the node and the interstitial position of atoms, whereas a figure ('2' in our case) means the number of identical atoms combined in a single complex [8, 23].

For the AgBr(I) EMCs (PVA + Dye) at $pBr = 4$, the difference in the kinetics of the Stokes and anti-Stokes luminescences associated with the BB3 and BB4 bands attracts a special attention. While the BB3 intensity increases monotonically from zero to a stationary level (see curve k_1 in Fig. 1b), the increase in the anti-Stokes BB4 luminescence shows the FE effect ($0 < F < 1$). This can be seen from Eq. (1) and the curve k_2 in Fig. 1b. Finally, for the AgBr(I) EMC (PVA + Dye) at $pBr = 7$, the kinetics of both the Stokes BB3 band (see curve k_1 in Fig. 2b) and the anti-Stokes BB4 band (see curve k_2 in Fig. 2b) reveals a monotonic increase in the luminescence intensity up to a stationary level.

Regardless of the content of silver ions, two bands are recorded in the excitation spectrum of the luminescence with $\lambda_{max} \approx 580$ nm (the bands BG3 and BG4) for the AgBr(I) EMCs (Gel + Dye). These are the excitation bands with $\lambda_{max} \approx 460$ nm and $\lambda_{max} \approx 650$ – 680 nm. This is confirmed by curve 1' in Fig. 3a (at $pBr = 4$) and curve 1' in Fig. 4a (at $pBr = 7$). The above excitation wavelengths correspond to the absorptions of AgBr(I) EMCs and JDye, respectively [19, 24]. The excitation spectra of the emission bands with $\lambda_{max} \approx 750$ nm (BG5 and BG6) in this case are characterized by three bands with $\lambda_{max} \approx 460$ nm, 610 nm and 660–680 nm (see curve 2' in Fig. 3a corresponding to $pBr = 4$ and curve 1' in Fig. 5a corresponding to $pBr = 7$). These wavelengths can be referred to the intrinsic absorption region of the AgBr(I) EMCs and the absorption of MDye and JDye, respectively [19, 24].

Upon excitation by the light from the absorption region of JDye ($\lambda_{\max} \approx 680$ nm), the luminescence spectrum detected for the AgBr(I) EMCs (Gel + Dye) still manifests the expressive anti-Stokes band BG4, although the Stokes luminescence band BG6 is transformed due to additional emission with $\lambda_{\max} \approx 800$ nm, which is strongly overlapped with the ‘original’ BG6 band (see curve 2 in Fig. 3a for the case of pBr = 4). The ‘original’ BG6 band and the additional glow originate respectively from the tunnel recombination involving $\{(I_a^- I_a^-)Ag_{12}^+\}$ centres and the phosphorescence of MDye [20, 22, 24–26]. The anomalously delayed fluorescence band of JDye ($\lambda_{\max} \approx 700$ nm) is not observed in this case. For the AgBr(I) EMCs (Gel + Dye) at pBr = 4, no differences are seen between the kinetics of the anti-Stokes BG4 luminescence (see curve k_2 in Fig. 3b) and the Stokes BG3 luminescence (see curve k_1 in Fig. 3b): both kinetic curves have a monotonic character.

3.2. Influence of oxygen treatment

After the emulsion with the AgBr(I) EMCs (Gel + Dye) and the highest content of Ag^+ (pBr = 7) is kept in the atmosphere of gaseous oxygen (O_2), two bands (BG3 and BG5) are still observed in the luminescence spectra (see Fig. 4a, curves 2–4). In this case, the Stokes-luminescence intensity of the BG3 band decreases with increasing duration of O_2 bubbling (see Fig. 4a, curves 1–4). In its turn, the BG5 emission increases at short exposure times given by the inequality $0 < t_e < 2$ min (see Fig. 4a, curves 1, 2 and 3), but decreases with further intensification of O_2 -treatment (see Fig. 4a, curve 4). The emission maximum of the BG5 band shifts from $\lambda_{\max} \approx 750$ nm (see Fig. 4a, curve 1) to $\lambda_{\max} \approx 770$ nm (see Fig. 4a, curve 4). These data agree well with the excitation spectra of the luminescence at $\lambda \approx 580$ nm (the bands BG3 and BG4) which reveal two maxima located at $\lambda_{\max} \approx 460$ nm and $\lambda_{\max} \approx 650$ – 680 nm (see Fig. 4a, dashed curves 1'–4').

For the AgBr(I) EMCs (Gel + Dye) at pBr = 7, the intensity of the anti-Stokes band BG4 reveals the same dependence on the O_2 -treatment duration t_e as the Stokes glow of the BG6 band does. At the durations given by $0 < t_e < 2$ min, the BG4 and BG6 luminescence intensities increase (see Fig. 5a, curves 1, 2 and 3) and then decrease with further increase in t_e (see Fig. 5a, curve 4). Moreover, they become weaker than the initial luminescence intensity level observed before the emulsion has been exposed to O_2 (cf. curves 1 and 4 in Fig. 5a). Additionally, the band BG6 in this case shifts upwards to $\lambda_{\max} \approx 810$ nm (see Fig. 5a, curve 4).

These results also agree completely with the excitation spectra detected for the emission with $\lambda \approx 750$ nm (see Fig. 5a, curves 1'–3'). Interestingly, the most efficient excitation of the BG6 band in this case occurs from the light characterized by $\lambda \approx 600$ nm. This is in contrast, e.g., to the situation observed for the excitation of the BG3 and BG5 bands (see Fig. 4a, curves 1', 2' and 3'). An additional maximum in the excitation spectrum appears because the long-wavelength Stokes BG6 luminescence is a result of overlapping of two bands with $\lambda_{\max} \approx 750$ and 800 nm. According to our data, the second band is associated with the phosphorescence of MDye, which is excited from the absorption regions of both MDye and JDye [25, 26].

Considering the changes occurring in the luminescence kinetics for the AgBr(I) EMCs (Gel + Dye) at pBr = 7, which are induced by the treatment with O_2 , we conclude that these changes are observed only for the band BG3. The BG3 kinetics reveals the FE effect before the O_2 treatment (see curve k_1 in Fig. 4b), whereas the glow intensity increases monotonously up to a stationary level after this treatment (see curve k_3 in Fig. 4b). In all the other cases, the kinetics of the glow increase towards the stationary level is monotonic (see curves k_2 and k_4 in Fig. 4b and curves k_1 – k_4 in Fig. 5b).

3.3. Influence of interstitial silver ions

In order to elucidate the role of interstitial silver ions Ag_i^+ in the light-sensitive properties of the donor–acceptor centres responsible for the luminescence in AgBr(I) at the room temperatures, we have studied the dependence of the optical-density changes $\Delta D = D - D_0$ for the exposed and developed AgBr(I) EMCs (Gel + Dye) on the exposure light wavelength and the O_2 -treatment duration t_e . Originally (at $t_e = 0$), ΔD maxima are observed at $\lambda = 450, 600$ and 690 nm (see Fig. 6a), which correspond to the absorption regions for the AgBr(I) EMCs (Gel + Dye), MDye and JDye, respectively. It follows from Fig. 6a that the ΔD value in the absorption region of MDye is maximal and exceeds that for JDye by the factor of 5. Keeping the emulsion in the O_2 atmosphere during $t_e = 10$ min does not change ΔD in the absorption region of AgBr(I) . On the other hand, ΔD decreases in the absorption region of MDye and increases in the absorption region of JDye (see Fig. 6b). Finally, ΔD in the absorption region of JDye reaches its maximum value at $t_e = 20$ min (see Fig. 6c).

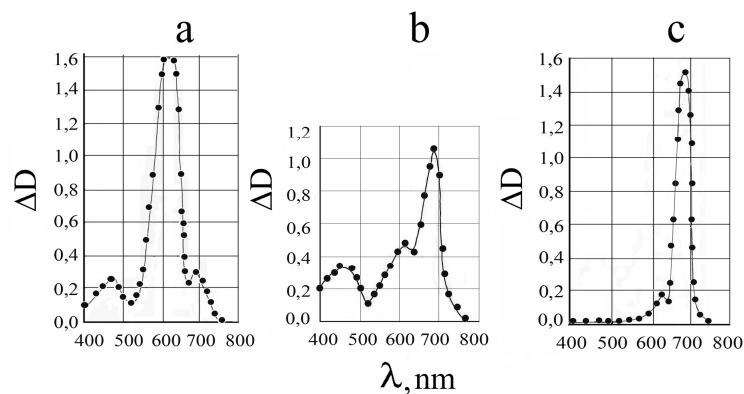


Fig. 6. Changes in optical density $\Delta D = D - D_0$ detected for the AgBr(I) EMC (Gel + Dye) emulsion at $T = 300$ K. Curves show ΔD dependences on the exposing-light wavelength λ at different O_2 -treatment durations t_e : $t_e = 0$ min (a), $t_e = 10$ min (b) and $t_e = 20$ min (c).

As follows from the results obtained above, the dye adsorbed on the AgBr(I) EMC (Gel + Dye) surface interacts efficiently with O_2 . This interaction affects not only the electron–hole subsystem responsible for the tunnelling recombination in the microcrystals at $T = 77$ K but also changes their photosensitivity at $T = 300$ K.

4. Discussion

First, we note the following remarkable consequence of the dye adsorption on the AgBr(I) EMC surface: the BG4 luminescence observed at $\text{pBr} = 4$ exhibits the FE effect upon excitation by the light associated with the absorption region of JDye ($\lambda \approx 680$ nm) (see curve k_2 in Fig. 1b). This effect may occur due to complex processes of excitation transfer from JDye to both AgBr(I) EMCs and MDye, of which contributions are found in the luminescence (see curve 2 in Fig. 1a) and excitation (see curve 1' in Fig. 1a) spectra.

The FE (also called ‘luminescence fatigue’) is a characteristic feature of the luminescence kinetics in the AgBr(I) EMCs, which may appear or disappear depending on different external and internal conditions. This phenomenon has been considered in a series of works [14, 26, 27] for both the Stokes and anti-Stokes luminescences (the band BB4 with $\lambda_{\text{max}} \approx 560$ nm in the AgBr(I) EMCs (PVA + Dye) and the band BG3 with $\lambda_{\text{max}} \approx 580$ nm in the AgBr(I) EMCs (Gel + Dye)). According to the assumptions made in those works, the FE of the Stokes luminescence bands BB3 and BG3, even at $T = 77$ K, is associated either with the formation of silver centres of molecular

dispersion, which localize a hole and create a channel of nonradiative recombination for electrons [26], or with transformation of the silver sub-system. In the latter case, haloid molecules are accumulated, which are capable of creating an additional radiative-recombination channel in the long-wavelength band ($\lambda \approx 750$ nm), which leads to a decreasing the FE intensity for the other luminescence bands [27].

From our point of view, the FE phenomenon for the Stokes luminescence BG3 with $\lambda_{\max} \approx 580$ nm is caused by the presence of deep donor–acceptor electron localization centres with a small capture cross section. As for the anti-Stokes band BB4, the mechanism of the FE in this case has not been considered in Ref. [28].

Moreover, the results presented in this paper show that, contrary to the widespread opinion [28], the influence of O_2 on the spectral sensitization of the AgBr(I) EMCs (Gel + Dye) at pBr = 7 cannot be reduced exclusively to desensitization of the AgBr(I) EMCs. According to our model, MDye adsorbed on the EMC surface interacts predominantly with the interstitial silver ions Ag_i^+ , which can be in their free state and/or constitute a part of $\{(I_a^- I_a^-) Ag_i^+\}$ complexes. This reasoning is supported by the highest concentration of the developed silver observed after the sample has been illuminated by the light corresponding to the absorption region of MDye ($\lambda_{\max} \approx 610$ nm – see Fig. 6a). This interaction does not change the role of Ag_i^+ ions in the generation-recombination processes, so that they remain to be active traps for non-equilibrium electrons. The J-aggregates of the anionic dye (JDye) available on the surface of the AgBr(I) EMCs (Gel) interact predominantly with the silver centres Ag_{i2}^+ with atomic-molecular degree of dispersion, which are both in their free state or in complexes with paired iodine centres $\{(I_a^- I_a^-) Ag_{i2}^+\}$. This interaction results in the formation of complexes $(Ag_{i2}^+ JDye)$ and $\{(I_a^- I_a^-) Ag_{i2}^+ JDye\}$ on the EMC surface. When being excited by the light corresponding to the absorption region of AgBr(I) EMCs or the absorption region of JDye, these complexes are actively involved in the generation-recombination processes.

For the case of AgBr(I) EMCs (Gel + Dye), the treatment with gaseous O_2 , with the duration $t_e < 2$ min, affects the centres Ag_i^+ and $\{(I_a^- I_a^-) Ag_i^+\}$, and the efficiency of localization of non-equilibrium electrons by Ag_i^+ centres decreases. Upon excitation by the light corresponding to the absorption region of the AgBr(I) EMCs (Gel + Dye) ($\lambda \approx 460$ nm), this decreases the BG3 emission intensity (see Fig. 4a, curves 1–4). At the same time, the BG5 luminescence intensity then increases (see the long-wavelength maxima of curves 1–3 in Fig. 4a).

Further treatment with oxygen ($t_e > 2$ min) leads to the interaction of O_2 with the centres Ag_{i2}^+ and the formation of Ag_2O molecules. In its turn, this reduces the luminescence intensity for the BG5 band (see curve 4 in Fig. 4a). This consideration is consistent with the fact that, upon excitation by the light corresponding to the absorption region of JDye, the concentration of developed silver is maximal (see Fig. 6c). Indeed, an electron trapped by the first excited energy level of JDye no longer passes to Ag_{i2}^+ with subsequent excitation to the conduction band (which would enable the anti-Stokes luminescence band BG4 to appear). This electron remains fixed at the Ag_2O molecule (the centre of reductive sensitization), which is located next to JDye. The latter fact increases the number of developed latent-image centres.

5. Conclusions

Upon adsorption of the anionic J-aggregating dye (pyridine salt of 3,3'-di- γ -sulfopropyl-9-ethyl-4,5,4',5'-dibenzoylbenzene) on the surface of AgBr(I) EMCs distributed in PVA or Gel at $T \approx 77$ K, no changes occur in the luminescence spectra of AgBr(I) EMCs excited by the wavelength $\lambda \approx 460$ nm (see the bands BB3, BG3, BB5 and BG5 in Table 1). However, peculiar differences are observed in the luminescence excitation spectra of the AgBr(I) EMCs (PVA + Dye) and in the luminescence-intensity

kinetics. Due to the presence of the dye, supplementary bands in the luminescence excitation spectra appear, of which spectral positions coincide with the absorption regions of the molecular and J-aggregated dyes (in addition to the bands associated with AgHal absorption). The kinetics of the luminescence intensity ($\lambda_{\max} = 560$ nm) exhibits the FE effect [10] before dye is introduced into the AgBr(I) EMCs (H₂O, PVA) at pBr = 7. However, the BB3 luminescence intensity approaches its stationary level monotonically after introduction of the dye (see curve k₁ in Fig. 2b).

Interesting effects accompany of the luminescence by the light corresponding to the absorption region of J-aggregated dye in AgBr(I) EMCs (Gel+Dye). Besides of the anti-Stokes luminescence band BG4 associated with the $\{(I_a^- I_a^-)Ag_{in}^+\}$ centres, the luminescence spectrum then contains the additional bands characteristic for the anomalously delayed fluorescence of the J-aggregated dye, the tunnel recombination of the $\{(I_a^- I_a^-)Ag_{in}^+\}$ ($n = 1, 2$) centres and the phosphorescence of the molecular dye (the BG6 band).

The dye molecules located on the surface of the AgBr(I) EMCs interact predominantly with the interstitial silver ions Ag_i^+ , which are either in their free state or included in the complexes $\{(I_a^- I_a^-)Ag_i^+\}$. In contrast, the J-aggregated JDye interacts with the paired centres Ag_{i2}^+ and the complexes $\{(I_a^- I_a^-)Ag_{i2}^+\}$. In these interactions, the tunnel-recombination centres retain their radiative properties when being excited by the light corresponding to the absorption regions of either the AgBr(I) EMCs or the J-aggregated dye. This difference in the interaction channels of the dye with the silver centres leads to the fact that the O₂ treatment affects differently the luminescent and spectro-sensitometric properties of the AgBr(I) EMCs (Gel). At small enough treatment times ($t_e < 2$ min), the O₂ molecules interact mainly with the interstitial silver ions Ag_i^+ located near the molecular dye. This entails changes in the role of Ag_i^+ ions in the tunnel-recombination centres: the radiative properties of these centres decrease, whereas the luminescence productivity of the centres containing Ag_{i2}^+ increases.

The exposure to O₂ with increasing treatment times ($t_e > 2$ min) imposes chemical transformations of the Ag_{i2}^+ ions located near JDye, with the formation of Ag₂O molecules (reductive sensitization centres) [29]. Accordingly, the rate of the recombination processes in the centres containing Ag_{i2}^+ falls down, while the photosensitivity in a narrow spectral absorption range of JDye increases. This is contrary to the hypersensitization effect (i.e., increased sensitivity in the entire spectral range), which has been observed via the treatment of finished spectrally sensitized AgBr(I) EMCs by hydrogen before exposure [30].

As for the influence of the other physicochemical factors (e.g., the changes in silver-ion content, the efficiency of dye adsorption and the parameters of exciting light) on the kinetics of the luminescence-intensity increase to a stationary level, the above question requires further consideration. It will be examined in our forthcoming works.

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Анотація. Для виявлення структури центрів тунельної люмінесценції в емульсійних мікрокристалах (ЕМК) AgBr(I) проведено спектросенситометричні та кінетичні дослідження їхньої низькотемпературної ($T = 77\text{ K}$) люмінесценції. Кількісно досліджено характеристики люмінесценції залежно від зв'язуючої речовини, від наявності та природи сенсibiliзуючих добавок (барвників) та від обробки киснем. Особливу увагу надано порівняльним дослідженням стоксівської та індукованої барвником антистоксівської компонент люмінесценції в ЕМК AgBr(I). Коли сенсibiliзовані барвником AgBr(I) і розподілені в полівініловому спирті ЕМК збуджуються фотонами світла з енергіями, що відповідають області власного поглинання ЕМК, кінетика смуги люмінесценції з центром на довжині хвилі $\lambda_{\text{max}} \approx 560\text{ нм}$ є монотонною. Навпаки, при збудженні фотонами, що відповідають області поглинання J-агрегованого барвника ($\lambda_{\text{max}} \approx 680\text{ нм}$), кінетика антистоксового світіння ($\lambda_{\text{max}} \approx 560\text{ нм}$) характеризується швидким «спалахом» з наступним поступовим зниженням до стаціонарного рівня («втома люмінесценції»). Ці результати вказують на те, що нерівноважний перенос носіїв заряду від барвника, який адсорбується на поверхні ЕМК, до об'єму ЕМК, істотно залежить від зв'язуючої речовини. Якщо нею є желатин, на цей процес суттєво впливає адсорбція кисню, тоді як результуючий ефект залежить від агрегатної форми адсорбованого барвника. Розуміння фізико-хімічних процесів, які керують центрами люмінесценції, має дозволити керувати структурними перетвореннями донорно-акцепторних комплексів і кластерів, що відповідають за унікальні фотометричні властивості AgBr(I), а також оптимізувати їхні параметри для різних застосувань в оптоелектроніці, голографії та фотоматеріалознавстві, оптичних датчиках і системах сонячної енергетики.

Ключові слова: мікрокристали AgBr(I), низькотемпературна люмінесценція, зв'язуючі речовини, центри тунельної рекомбінації, сенсibiliзація барвниками, обробка киснем, кінетика люмінесценції.