
Structure and transformations of tunnel-luminescence centres in emulsion microcrystals AgBr(I)

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Abstract. It is known that the tunnel luminescence in emulsion microcrystals (EMCs) of AgBr(I) at the temperatures $T \geq 77$ K is determined by donor–acceptor complexes with a specific structure. Such a complex includes a paired iodine centre, which combines two neighbouring sites of anionic sublattice, and an interstitial silver ion Ag^+ located nearby. If the AgBr(I) EMCs are distributed in a binder of which molecules do not interact with Ag^+ ions, the centres are characterized by a luminescence band with the characteristic wavelength $\lambda_{\text{max}} \approx 560$ nm. Modifications of the content of silver ions in the emulsion produce an additional luminescence band with $\lambda_{\text{max}} \approx 720$ nm. If the AgBr(I) EMCs are distributed in gelatine, its molecules interact with clusters of silver ions and form specific complexes with the characteristic luminescence bands located at $\lambda_{\text{max}} \approx 580$ nm and $\lambda_{\text{max}} \approx 750$ nm. In both cases, two sorts of luminescence-glow kinetics can be observed, depending on the temperature and the Ag^+ concentration: a monotonic intensity increase from zero to a maximum stationary level or a rapid ‘flash enhancement’ followed by a gradual decrease to a lower value. Remarkably, the additional luminescence ‘flash’ stimulated by infrared radiation is detected whenever the monotonic growth is observed. On the contrary, no infrared-stimulated glow occurs in the luminescence band when the ‘flash enhancement’ is detected in this band. All of these results are interpreted in terms of structural transformations taking place with the tunnel-recombination centres in the AgBr(I) EMCs.

Keywords: AgBr(I) microcrystals, low-temperature luminescence, emulsion binders, tunnel-recombination centres, infrared radiation, luminescence kinetics

UDC: 535.37

1. Introduction

In this paper we study a low-temperature ($77 \text{ K} \leq T < 120 \text{ K}$) luminescence in AgBr(I) emulsion microcrystals (EMC) which are inserted in a binder [1, 2]. Being excited by the radiation corresponding to the intrinsic-absorption region of the EMCs (the optical wavelength $\lambda \approx 460$ nm), such a luminescence occurs due to localized traps for the charge carriers existing in a crystal structure [3]. According to this scheme, the AgBr(I) EMCs involve paired iodine centres ($\text{I}_a^- \text{I}_a^-$), where the symbols I_a^- denote the iodine ions located in the neighbouring anionic sites of a crystal lattice. Such a centre acts as an acceptor which forms a molecular centre $(\text{I}_2^-)_{\text{aa}}$ whenever a hole is localized, similarly to the known V_k centres in alkali-halide crystals [4]:



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In Eq. (1), p means the hole which is transferred to the valence energy band. Recombination of the localized hole with the free electron results in a ‘green’ luminescence band ($\lambda_{\max} \approx 560$ nm). Moreover, a similar luminescence (termed also as a ‘green flash’) appears under the action of infrared (IR) radiation.

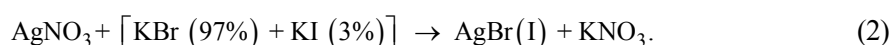
These considerations provide a reasonable explanation of the luminescence phenomena occurring in both macroscopic AgBr(I) crystals and the AgBr(I) EMCs distributed either in water (H₂O) or in polyvinyl alcohol (PVA) [5]. However, they seem to be invalid for the AgBr(I) EMCs distributed in gelatine (Gel) where the luminescence spectrum is noticeably shifted ($\lambda_{\max} \approx 580$ nm) and the IR-stimulated ‘flash’ is not observed [6]. Additionally, a peculiar transient temporal behaviour of the luminescence occurs there: instead of a gradual monotonic increase of the glow intensity up to a stationary level, the luminescence increases abruptly in the initial moment (a ‘flash enhancement’), with a subsequent gradual decay to a smaller though nonzero stationary value (a ‘luminescence fatigue’).

To interpret these discrepancies, a number of ionic processes characteristic for the AgBr(I) EMCs have been discussed in the literature, which can lead to associated channels of non-radiative recombination. To the best of our knowledge, a still more relevant mechanism has been suggested in Ref. [6]. According to Ref. [6], a surface of the AgBr(I) EMCs can play a significant role in the effects mentioned above. In particular, if Gel serves as a binder, its molecules are adsorbed at the EMC surface and form electron traps, thus providing the conditions for radiative recombination of the localized electrons and holes. In this respect, the authors [6] consider that the low-temperature ($T = 77$ K) glow observed in the AgBr(I) EMCs in Gel appears due to a tunnel recombination of the hole localized on the paired iodine centre, with the electron localized on the EMC surface.

Still, the assumption made in Ref. [6] has received no theoretical or experimental substantiation. Currently there are no reliable data that would establish unambiguously the nature and the properties of the centres of electron localization. To fill this gap, a series of experimental works has been undertaken, with detailed studies of the low-temperature luminescence in the AgBr(I) EMC and, in particular, its spectral and temporal features under the action of various physicochemical factors [1, 7–10]. In the present work, we report the data that illustrate the influences of such factors as the temperature, the emulsion-binder nature and properties, the content of silver ions and the additional IR radiation. The results obtained and their interpretation enable us to refine the structure of the tunnel-recombination centres in the AgBr(I) EMCs and disclose their specific behaviour and transformations caused by the external influences mentioned above.

2. Problem description and experimental methods

We used EMCs AgBr_{1-x}(I_x) ($x = 0.03$) for our luminescence studies. From now on, these EMCs will be referred to as the AgBr(I) EMCs – without special indication of the iodine molar concentration x . Additionally, special conditions of the EMC environment will be indicated in parentheses, so that ‘AgBr(I) EMC (H₂O)’ means that the EMCs are distributed in water as a binder, ‘AgBr(I) EMC (PVA)’ implies that the binder is PVA, etc. The AgBr(I) EMCs (Gel) were obtained in a 5% solution of Gel, using a method of controlled two-jet emulsification [11] according to the double-exchange reaction



The AgBr(I) EMCs (H₂O) (or so-called ‘sol’ EMCs) were obtained by instant emulsification of 1N solutions of AgNO₃ and (KBr + KI) at 70°C. The sol was formed during 2 s and a

sedimented powder was repeatedly washed with demineralized water to remove soluble salts. The content of silver ions in the emulsion was monitored by an EV-74 ion-meter. In the finished emulsion, the content of silver ions was adjusted by adding AgNO_3 or KBr solutions. The crystalline structure and the dimensions (i.e., the characteristic size d) of the AgBr(I) EMCs synthesized in the above manner were controlled using an electron microscope UMV-100K and observing their carbon replicas shaded with platinum. Typical electron-microscopic photographs of the AgBr(I) EMCs synthesized in Gel, PVA and H_2O are shown in Fig. 1.

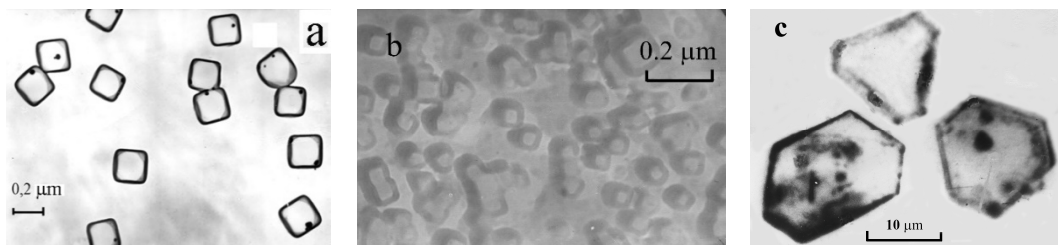


Fig. 1. Electron-microscopic photographs of carbon-platinum replicas of the AgBr(I) EMCs distributed in different binders: (a) Gel ($d \approx 0.2 \mu\text{m}$), (b) PVA ($d \approx 0.1 \mu\text{m}$), and (c) H_2O ($d \approx 15 \mu\text{m}$).

The content of silver ions was characterized by a ‘bromine potential’ parameter $\text{pBr} = -\lg([\text{Br}^-])$. Then the true $[\text{Ag}^+]$ ion concentration can be determined with the relation $-\lg([\text{Ag}^+]) = 12.28 - \text{pBr}$ [12] and a linear pBr increase would mean an exponential increase in the $[\text{Ag}^+]$ concentration. The low-temperature luminescence spectra of the AgBr(I) EMCs and the kinetics of luminescence intensity were detected upon excitation by rectangular-shaped light pulses with the repetition rate 800 Hz. The appropriate procedures and an experimental setup have earlier been described in Ref. [13]. In our case, only the phosphorescence of the luminescence centres was measured, with the relaxation times $\tau > 2.0 \text{ ms}$. It is just these relaxation processes associated with photo-excitation of the AgBr(I) EMCs that are of our main interest.

The kinetics, i.e. the temporal evolution of the luminescence intensity $I(t)$ to a stationary level I_{st} , is characterized by the numerical coefficient

$$F = (I_{max} - I_{st}) / I_{max}. \quad (3)$$

We observed two sorts of the luminescence kinetics. In case of a monotonic increase we have $I_{max} = I_{st}$ and $F = 0$, whereas in case of a ‘flash enhancement’ the intensity increases strongly at the initial moments, after which it decreases gradually (which is sometimes treated as a ‘luminescence fatigue’ effect [14–16]), so that we have $I_{max} > I_{st}$ and $0 \leq F < 1$. Note that in the context of current discussion, the ‘flash enhancement’ is always accompanied by the ‘luminescence fatigue’ so that both terms describe two sides of the same phenomenon.

The luminescence ‘flashes’ of the AgBr(I) EMCs in different spectral ranges under IR irradiation were measured as follows. The AgBr(I) EMCs were excited by light during 1 min. Then the IR radiation with $\lambda_{\text{IR}} > 1000 \text{ nm}$ was switched on (an IKS-3 filter or germanium light filter with the thickness 1.5 mm were used) after a ‘dark’ interval of 30 s, when the afterglow was practically absent. A luminescence ‘flash’ at a given wavelength was detected by a cathode storage oscilloscope C8-12. The IR-radiation influence was characterized by the maximal change in the luminescence intensity occurring during the ‘flash’, $I_{flash} = I_{max} - I_0$, with I_{max} being the maximal value of the ‘flash’ intensity, I_0 the afterglow intensity at the wavelength at which the ‘flash’ was studied. The dark interval was chosen such that the effect of IR radiation began when $I_0 \approx 0$.

3. Experimental results

Our experimental investigations testify that in all the situations considered, the luminescence spectra can be classified according to their spectral characteristics and the conditions of observation (see Table 1). The results presented in Fig. 2 show that the luminescence spectra of the AgBr(I) EMCs (H₂O and PVA; pBr = 4), which are obtained upon excitation with $\lambda \approx 460$ nm in the temperature range $77 \text{ K} \leq T \leq 86 \text{ K}$, are characterized by a broad ‘green’ emission band BB1 with $\lambda_{\text{max}} \approx 560$ nm (see curve 1 in Fig. 2a). With increasing temperature ($T > 86 \text{ K}$), the luminescence band BB1 undergoes a temperature ‘quenching’ (see curve 1 in Fig. 2c) with the activation energy $\varepsilon \approx 0.12$ eV (see insert in Fig. 2c, curve 1). The latter corresponds to the energy $\varepsilon = 0.10 \div 0.16$ eV of displacement of the interstitial silver ion Ag_i⁺ in the AgBr(I) EMCs, with the index ‘i’ indicating the interstitial location of the ion in the crystalline lattice [16].

Table 1. Spectral luminescence bands and conditions for their observation, as found at the characteristic excitation wavelength $\lambda_{\text{max}} \approx 460$ nm.

Emission-band notation	Binder	Characteristic glow wavelength λ_{max} , nm	Characteristic temperature range (at pBr = 4)	Characteristic content of Ag ⁺ ions (at $T = 77 \text{ K}$)
BB1	H ₂ O, PVA	≈ 560	$77 \text{ K} \leq T \leq 88 \text{ K}$	pBr = 4
BB2	H ₂ O, PVA	≈ 720	$86 \text{ K} \leq T \leq 95 \text{ K}$	$5 \leq \text{pBr} \leq 7$
BG1	Gel	≈ 580	$77 \text{ K} \leq T \leq 81 \text{ K}$	pBr = 4
BG2	Gel	≈ 750	$80 \text{ K} \leq T \leq 95 \text{ K}$	$4 < \text{pBr} \leq 7$

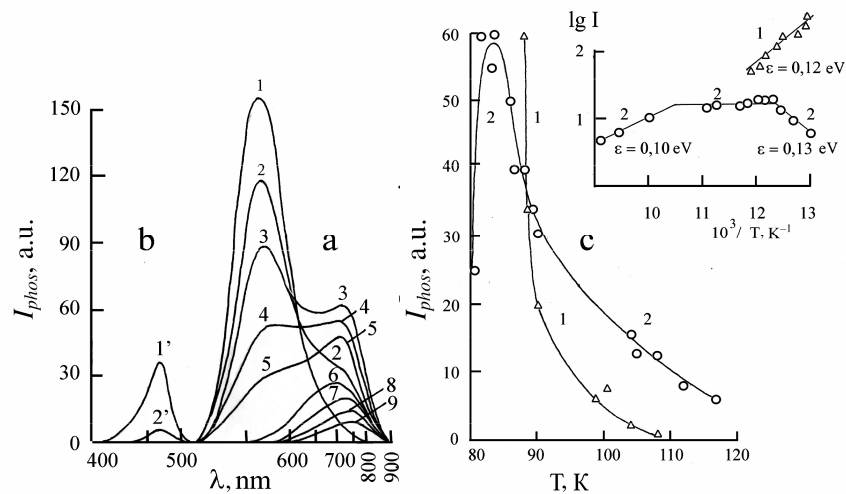


Fig. 2. (a) Luminescence spectra $I_{\text{phos}}(\lambda)$ measured for the AgBr(I) EMCs (H₂O and PVA; pBr = 4) upon excitation by $\lambda \approx 460$ nm at different temperatures T : 1 – 81 K, 2 – 86 K, 3 – 88 K, 4 – 88.5 K, 5 – 90 K, 6 – 104 K, 7 – 108 K, 8 – 112 K, and 9 – 117 K. (b) Excitation spectra of luminescence observed in the AgBr(I) EMCs in different glow bands (see Table 1): 1' – BB2 ($T = 96 \text{ K}$) and 2' – BB1 ($T = 104 \text{ K}$). (c) Temperature dependences of maximal intensities detected inside the bands BB1 (curve 1) and BB2 (curve 2). Insert shows dependence of $\lg(I_{\text{phos}})$ on the inverse temperature.

In the process of temperature ‘quenching’ of the glow band BB1, the luminescence band BB2 with $\lambda_{\text{max}} \approx 720$ nm appears (see curves 2 to 9 in Fig. 2a), of which intensity increases with increasing temperature in the region $80 \text{ K} < T < 90 \text{ K}$ but decreases at $T > 95 \text{ K}$. The increase and decrease of the BB2 luminescence intensity (see the insert in Fig. 2c, curve 2) occur with the same

thermal activation energies as those observed for the band BB1 (see the insert in Fig. 2c, curve 1).

The luminescence spectra observed for the AgBr(I) EMCs (Gel) differ in that the short-wavelength luminescence band BG1 is characterized by $\lambda_{max} \approx 580$ nm, while the long-wavelength band BG2 resulting from the temperature ‘quenching’ is observed at $\lambda_{max} \approx 750$ nm. The energy characteristics of the ‘quenching’ process are detected within the same range ($\varepsilon = 0.10 \div 0.16$ eV) as for the AgBr(I) EMCs (PVA and H₂O). For a comparison, Fig. 3 illustrates transformations of the luminescence spectra that happen in the region of temperature ‘quenching’ ($T > 90$ K) of the ‘green’ emission bands BB1 and BG1 for AgBr(I) (H₂O) and AgBr(I) (Gel).

Notably, the excitation spectra detected for the luminescence bands BB1, BG1 and BB2, BG2 are similar to each other and, regardless of the binder and the temperature, they demonstrate a single maximum located at $\lambda \approx 460$ nm (see Fig. 2b and Fig. 3b).

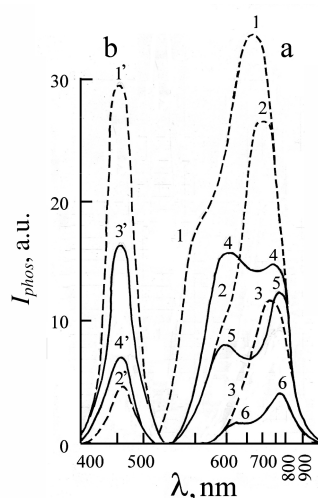


Fig. 3. (a) Luminescence spectra of AgBr(I) EMCs ($pBr = 4$) as measured for different binders: dashed curves 1, 2 and 3 correspond to H₂O and solid curves 4, 5 and 6 to Gel. The temperatures are $T = 97$ K (curves 1 and 4), 104 K (curves 2 and 5) and 112 K (curves 3 and 6). (b) Excitation spectra of luminescence in the AgBr(I) EMCs as measured for different binders: curves 1' and 2' correspond to H₂O and curves 3' and 4' to Gel. Curves 2', 3', 1' and 4' correspond respectively to the phosphorescence bands BB1, BG1, BB2 and BG2 (see Table 1). The temperatures are $T = 96$ K (curve 2'), 98 K (curve 3'), 104 K (curve 1'), and 110 K (curve 4').

For the bands BB1 and BG1 (see Table 1) observed for AgBr(I) (H₂O and PVA) and AgBr(I) (Gel; $pBr = 4$), the differences are seen both in the kinetics of luminescence intensity approaching to a stationary level and in the spectra of luminescence ‘flashes’ detected under IR irradiation. For example, the evolution of the BB1 luminescence intensity $I_{phos}(t)$ to a stationary level is monotonic for the AgBr(I) EMCs (H₂O and PVA) at 77 K (see curve k_1 in Fig. 4 and curve k_1 in Fig. 5). At the same time, the spectrum of the ‘flash’ I_{flash} observed after the excitation is turned off is characterized by the bands BB1 and BB2 under the condition of influence of the IR radiation (see Table 1 and curve 1 in Fig. 4a).

As seen from Fig. 4 (curves k_2 and k_3) and Fig. 6 (curve k_1), the evolution of the BG1 luminescence band to a stationary level is characterized by a ‘flash enhancement’ for the AgBr(I) EMCs (Gel; $pBr = 4$). Then the luminescence ‘flash’ stimulated by the IR radiation is absent in the entire spectral range under test (see curve 2 in Fig. 4a). Now let us dwell upon the AgBr(I) EMCs (Gel + PMT), where PMT implies 1-phenyl-5-mercaptotetrazole (an anti-fog additive that serves as a complexing agent for silver ions). Here the increase in the luminescence intensity inside the band BG1 up to a stationary level is monotonic, with no ‘flash enhancement’ (see curve k_4 in

Fig. 4). However, a luminescence ‘flash’ stimulated by the IR radiation is observed in this case (see curve 3 in Fig. 4a).

Remarkably, the long-wavelength bands BB2 and BG2 reveal a monotonic luminescence increase up to stationary levels in both cases of the AgBr(I) EMCs (H₂O and PVA) and the AgBr(I) EMCs (Gel; pBr = 4) (see curve k₃ in Fig. 5 and curve k₃ in Fig. 6). Notice that the bands BB2 and BG2 can appear in these systems not only due to the temperature ‘quenching’ of the ‘primary’ bands BB1 and BG1. The other reason is a changing content of silver ions in the emulsion ($4 \leq \text{pBr} \leq 7$ – see Fig. 5a and Fig. 6a), which is observed at $T = 77$ K.

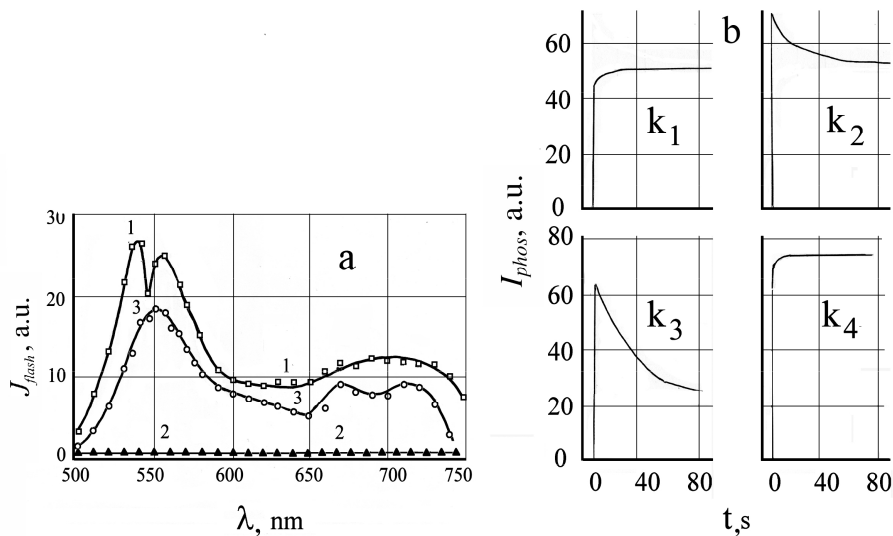


Fig. 4 (a) Spectra of luminescence ‘flashes’ stimulated by IR irradiation, as observed for the AgBr(I) EMCs at $T = 77$ K after turning off the excitation. Different curves correspond to different binders: curve 1 to H₂O and PVA, curve 2 to Gel, and curve 3 to Gel + PMT (10^{-3} mol per 1 mol of AgBr). (b) Kinetics of glow intensity $I_{\text{phos}}(t)$ observed for the AgBr(I) EMCs (pBr = 4), which correspond to different luminescence bands (see Table 1) and binders: curve k₁ – BB1 and, curve k₂ – BG1 and H₂O + Gel (5 mol %), curve k₃ – BG1 and Gel, and curve k₄ – BG1 and Gel + PMT (10^{-3} mol per 1 mol of AgBr).

Some changes are observed in the BB1-luminescence kinetics for the AgBr(I) EMCs (H₂O and PVA) with increasing pBr parameter. This kinetics is now characterized by the ‘flash enhancement’ (see curve k₂ in Fig. 5). Similar changes are found in the kinetic behaviour typical for the band BB2 (see curve k₄ in Fig. 5). It should be noted that the magnitude of the ‘flash enhancement’ is higher for the ‘green’ band BB1. This is characterized by the inequality $F(\text{BB1}) > F(\text{BB2})$ in terms of the factor F (see Eq. (3)). On the contrary, the ‘flash enhancement’ kinetics for the band BG1 in the AgBr(I) EMCs (Gel) takes place within the whole range $4 \leq \text{pBr} \leq 7$ (see curves k₁ and k₂ in Fig. 6). However, the ‘flash’ behaviour becomes more expressive with increasing content of silver ions and the numerical coefficient F increases: $F(\text{pBr} = 7) > F(\text{pBr} = 4)$.

The changes in the spectral structure of the IR-stimulated ‘flashes’ occurring in the AgBr(I) EMCs under the condition of varying content of the silver ions within the range $4 \leq \text{pBr} \leq 7$ are also noteworthy. So, the ‘flash’ spectra for the AgBr(I) EMCs (H₂O and PVA; pBr = 4) are characterized by a presence of the two bands, BB1 and BB2 (see curve 1 in Fig. 5c). The intensity I_{flash} of the BB1 ‘flash’ decreases with increasing pBr, while the corresponding intensity I_{flash} for BB2 increases (see curve 2 in Fig. 5c). Finally, only a single BB2 ‘flash’ remains at pBr = 7 (see curve 3 in Fig. 5c).

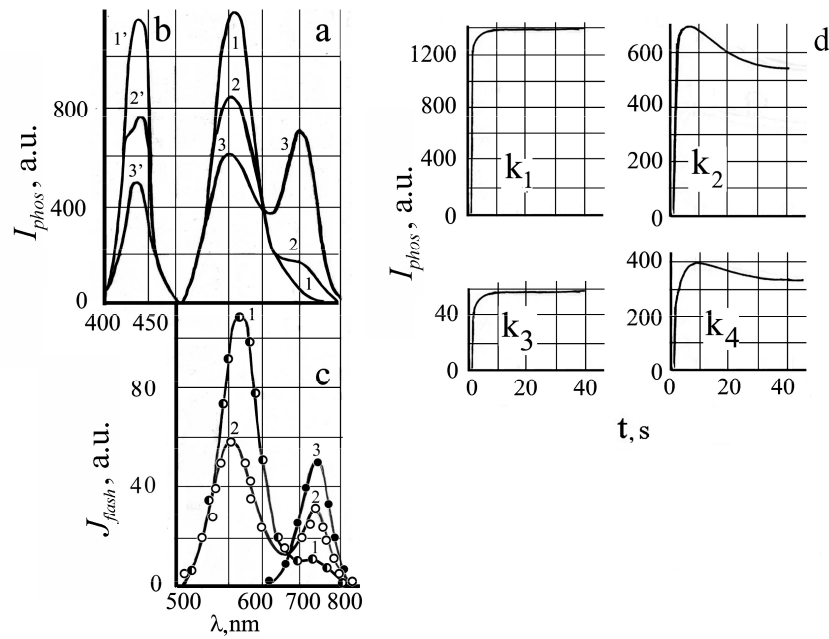


Fig. 5. (a) Luminescence spectra for the AgBr(I) EMCs (PVA) observed at pBr = 4 (curve 1), pBr = 5 (curve 2) and pBr = 7 (curve 3). The temperature is $T = 77$ K. (b) Excitation spectra observed at $T = 77$ K for the luminescence bands BB1 (curves 1' and 2') and BB2 (curve 3') at pBr = 4 (curve 1') and pBr = 7 (curves 2' and 3'). (c) Spectra of luminescence 'flashes' observed at pBr = 4 (curve 1), pBr = 5 (curve 2) and pBr = 7 (curve 3). The temperature is $T = 77$ K. (d) Kinetics of luminescence growth observed at $T = 77$ K for the bands BB1 (curves k_1 and k_2) and BB2 (curves k_3 and k_4). Curves k_1 , k_3 and k_2 , k_4 correspond respectively to pBr = 4 and pBr = 7.

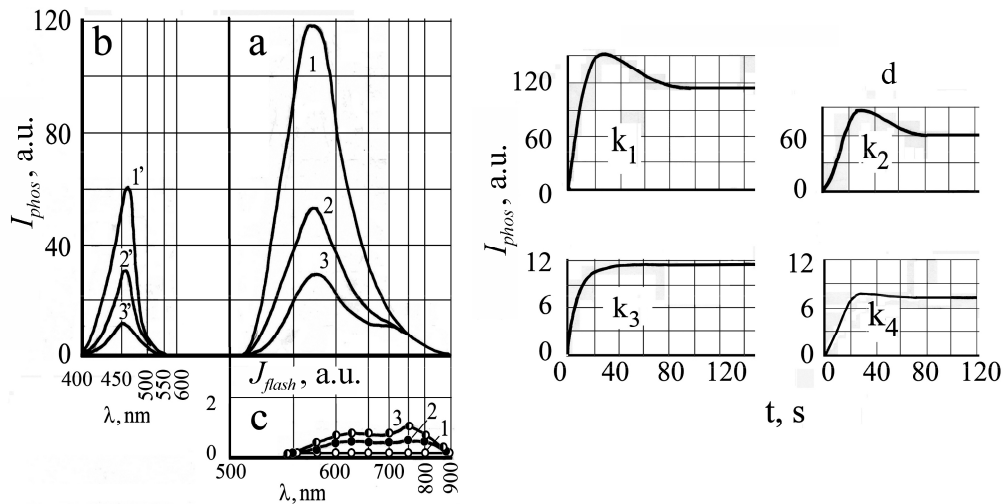


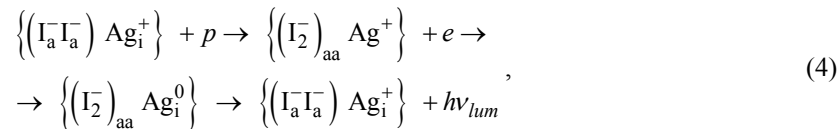
Fig. 6. (a) Luminescence spectra for the AgBr(I) EMCs (Gel) observed at pBr = 4 (curve 1), pBr = 5 (curve 2) and pBr = 7 (curve 3). The temperature is $T = 77$ K. (b) Excitation spectra observed at $T = 77$ K for the luminescence bands BG1 (curves 1' and 2') and BG2 (curve 3') at pBr = 4 (curve 1') and pBr = 7 (curves 2' and 3'). (c) Spectra of luminescence 'flashes' observed at pBr = 4 (curve 1), pBr = 5 (curve 2) and pBr = 7 (curve 3). The temperature is $T = 77$ K. (d) Kinetics of luminescence growth observed at $T = 77$ K for the bands BG1 (curves k_1 and k_2) and BG2 (curves k_3 and k_4). Curves k_1 , k_3 and k_2 , k_4 correspond respectively to pBr = 4 and pBr = 7.

There is no ‘flash’ for the AgBr(I) EMCs (Gel; pBr = 4) in the entire spectral range (see curve 1 in Fig. 6c). The ‘flash’ appears with increasing pBr and its spectrum is characterized by a presence of the two bands, BG1 and BG2 (see Table 1), of which intensities increase with increasing pBr (see curves 2 and 3 in Fig. 6c). The ratio of the BG1 and BG2 intensities reveals the same dependence on the pBr parameter as observed by us in the previous case of the BB1 and BB2 bands.

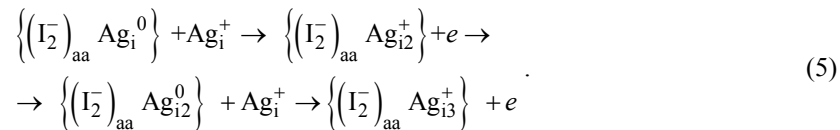
An increase in the content of silver ions up to pBr = 7 induces no change in the excitation spectra. These spectra are always characterized by a single maximum located at $\lambda \approx 460$ nm. This is valid either for the AgBr(I) EMCs (H₂O and PVA – see Fig. 5b) or for the AgBr(I) EMCs (Gel – see Fig. 6b). Moreover, the same refers to all of the luminescence bands BB1, BB2, BG1 and BG2.

4. Discussion

The centres responsible for the BB1-band luminescence in the AgBr(I) EMCs (H₂O and PVA) and its temperature transformation include a paired iodine centre ($I_a^- I_a^-$) and a closely located interstitial silver ion Ag_i^+ , which form a single donor–acceptor complex $\{(I_a^- I_a^-) Ag_i^+\}$ [3]. In view of the reaction given by Eq. (1), the origin of the ‘green’ glow can be explained by the scheme

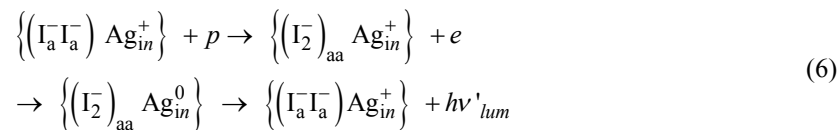


where e is the electron and hv_{lum} denotes the irradiated photon. The temperature quenching of this luminescence band is described by the series of ionic reactions:



Here $\{(I_2^-)_{aa} Ag_{in}^+\}$ denotes a cluster in which the molecular iodine centre defined by Eq. (1) is combined with several Ag ions, with $n = 2, 3, \dots$ being the number of these ions.

In our opinion, the fact that the ‘temperature quenching’ of the ‘green’ emission in the AgBr(I) EMCs is accompanied by the appearance of a new band of tunnel luminescence (BB2 for the AgBr(I) EMCs (H₂O and PVA) or BG2 for the AgBr(I) EMCs (Gel) – see Table 1) indicates that the centres responsible for the ‘green’ emission experience some structural transformation during the temperature ‘quenching’. The tunnel luminescence associated with the band BB2 located at $\lambda_{max} \approx 720$ nm can be described by the following scheme:



with hv'_{lum} being the transformed photon energy.

It is reasonable to suppose that the adsorption of gelatine molecules on the AgBr(I)-EMC surface leads to a reduction of surface electron-localization centres: interstitial silver ions Ag_i^+ (or interstitial silver molecules Ag_{i2}^+) are transformed into neutral Ag_i^0 atoms (or Ag_{i2}^0 molecules). Newly formed centres $\{Ag_{in}^0 Gel^+\}$ (with $n = 1, 2$ and Gel^+ denoting a gelatine molecule) are deeper traps for electrons; they have a smaller capture cross-section, if compared to the surface electron-localization centres $\{Ag_{in}^+\}$ ($n = 1, 2$). This manifests itself in the fact that the kinetics of the BG1

luminescence is characterized by a presence of the ‘flash enhancement’ (see curve k_3 in Fig. 4), while the luminescence ‘flash’ stimulated by the IR radiation is absent (see curve 2 in Fig. 4a). This luminescence-intensity decrease relative to its initial value (i.e., the luminescence ‘fatigue’) has earlier been studied for the AgBr(I) EMCs (Gel) at $\lambda \approx 580$ nm [14–16].

The above assumption concerning formation of the $\{\text{Ag}_{in}^0\text{Gel}^+\}$ ($n = 1, 2$) complexes is supported by the ‘flash enhancement’ observed for the AgBr(I) EMCs ($\text{H}_2\text{O} + \text{Gel}$) with additionally introduced gelatine (see curve 2 in Fig. 4a). Another confirmation can be seen in the fact that the centres $(\text{Ag}_{in}^0\text{Gel}^+)$ are not formed in the AgBr(I) EMCs (Gel + PMT) where the introduction of PMT prevents the interaction of gelatine with the surface-located interstitial silver ions. As a result, the ‘flash enhancement’ effect disappears (see curve k_4 in Fig. 4) and the luminescence ‘flash’ stimulated by the IR radiation emerges (see curve 3 in Fig. 4a).

Finally we note that, since the band BG2 (see Table 1) appears in the AgBr(I) EMCs (Gel) during the temperature ‘quenching’ of the ‘green’ emission, it would be natural to assume that the gelatine molecules interact also with the luminescence centres located on the surface, thus forming donor–acceptor complexes $\{(\text{I}_a^-\text{I}_a^-)\text{Ag}_{in}^+\text{Gel}^0\}$ ($n = 2$). The latter retain the ability for the tunnel recombination with $\lambda_{max} \approx 750$ nm, which is described by the reaction given by Eq. (6). A great energy depth and a small electron-capture cross-section for the $\{\text{Ag}_{in}^0\text{Gel}^+\}$ donor centres provide the ‘flash enhancement’ of the BG1 luminescence with $\lambda_{max} \approx 580$ nm and the absence of any ‘flash’ stimulated by the IR radiation. In its turn, this also indicates that the energy depth (counted from the conduction-band bottom) of the levels of electron localization at the centres $\{(\text{I}_a^-\text{I}_a^-)\text{Ag}_{in}^+\text{Gel}^0\}$ ($n = 1, 2$) is much greater than that of the centres $\{(\text{I}_a^-\text{I}_a^-)\text{Ag}_{in}^+\}$ ($n = 1, 2$) which are the source of the IR-stimulated ‘flash’.

The centres responsible for the tunnel recombination with $\lambda_{max} \approx 560$ nm (i.e., the band BB1) in the AgBr(I) EMCs (PVA) undergo a structural transformation not only due to the temperature ‘quenching’. At the fixed temperature $T = 77$ K, this also happens due to changes in the content of silver ions ($4 \leq \text{pBr} \leq 7$). In this case, newly formed centres retain the ability for the tunnel recombination with $\lambda_{max} \approx 720$ nm (the band BB2), which proceeds according to the scheme given by Eq. (6). In addition, just as in the case of the AgBr(I) EMCs (H_2O ; $\text{pBr} = 4$), the BB1-luminescence kinetics for the AgBr(I) EMCs (PVA; $\text{pBr} = 4$) is monotonic and we have the parameter $F = 0$ (see Eq. (3) and curve k_1 in Fig. 5). When the content of silver ions increases up to the level of $\text{pBr} = 7$, the luminescence kinetics for the BB1 and BB2 bands occurring after structural formation of the centres reveals the ‘flash enhancement’ effect (see curves k_2 and k_4 in Fig. 5). Its presence is associated with the centres of molecular-cluster dispersity Ag_{in}^+ ($n = 2, 3, \dots$).

5. Conclusions

The low-temperature luminescence phenomena in silver-halide crystals are closely related to the intrinsic and impurity defects, which determine the photosensitivity of a material and the resolution obtained at the room temperature [18]. Actually, investigations of the luminescence mechanisms and their vulnerability to various external factors offer a valuable method for studying the structure of these defects and the energy-migration processes taking place in the crystals mentioned above. A special role of the complexes that combine iodine ions and interstitial silver ions has been reliably established in the earlier works [1–3, 7, 18]. In this paper, we further develop the concepts and the ideas of Refs. [1–3, 7, 18] and apply them to the AgBr(I) EMCs where the situation is complicated due to a strong effect of the surface which acts as a ‘mega-defect’ influencing all the processes inside the microcrystals.

In particular, our experimental results lead to suggestion that the origin of the ‘green’ luminescence band BB1 in the AgBr(I) EMCs (H₂O and PVA), which is located at $\lambda_{max} \approx 560$ nm, is associated with the tunnelling mechanism and caused by recombination of the holes localized at the paired iodine centres ($I_a^- I_a^-$). Here the electrons are localized at the interstitial silver ions Ag_i^+ near the ($I_a^- I_a^-$) centres [3] rather than on the surface of the AgBr(I) EMCs. This suggestion is supported by the activation-energy value obtained by us (see the insert in Fig. 2) and by the luminescence kinetics (see Figs. 4–6), which agree well respectively with the energy and the temporal characteristics of the silver ionic subsystem [19] in the AgBr(I) EMCs. Due to IR illumination or temperature increase, the interstitial silver ions Ag_i^+ located near the paired iodine centres are able to form the centres of molecular-cluster dispersity Ag_{in}^+ ($n = 2, 3, \dots$). The electrons localized at the centres Ag_{in}^+ ($n = 2$) retain the ability for the tunnel recombination with the holes localized at the ($I_a^- I_a^-$) centres, thus producing the luminescence band BB2 with $\lambda_{max} \approx 720$ nm.

The adsorption of gelatine molecules on the AgBr(I) EMC surface leads to reduction of the surface interstitial atomic-molecular silver centres Ag_{in}^+ ($n = 1, 2$), with formation of the complexes ($Ag_{in}^0 Gel^+$) ($n = 1, 2$) that form deeper traps for electrons with a small capture cross-section. This manifests itself in a slight shift of the luminescence band BG1 (see Table 1) towards $\lambda_{max} \approx 580$ nm, as well as in a peculiar evolution of the luminescence intensity towards its stationary level. Then the kinetics is characterized by the ‘flash enhancement’ effect, i.e. the temporal behaviour of the intensity shows an initial peak after which the intensity gradually decreases to the stationary level. This is also called the ‘luminescence fatigue’ [14–16]. Moreover, the luminescence ‘flash’ stimulated by the IR radiation is absent in the entire spectral range under study. The electrons localized at the donor centres ($Ag_{in}^0 Gel^+$) ($n = 2$) retain the ability for the tunnel recombination with the holes localized at the acceptor centres ($I_a^- I_a^-$), thus inducing the luminescence band BG2 located at $\lambda_{max} \approx 750$ nm.

Note that the behaviour of the luminescence characteristics observed in the experiments is crucially determined by the EMC environment. For example, single Ag^+ ions and their aggregates in some glassy and crystalline materials produce the emission bands with the maximums located in the region 400–470 nm and the lifetimes of about 75–110 μs under the condition of photo-excitation at the wavelengths 270–470 nm [20, 21]. The difference between these data and our results is explained by the specific luminescence-centre structure discussed in Section 4 and by the influence of the EMC surface, which cannot be neglected in view of sub-micrometer sizes of the EMCs (see Fig. 1).

Our last remark concerns a ‘slow’ kinetics of the luminescence observed in Figs. 4–6, which seems to be counter-intuitive and at variance with the relaxation times 10^{-5} – 10^{-3} s typical for such phosphorescence crystals [22]. The matter is that the kinetic curves reported by us do not illustrate an ‘afterglow’ occurring sometimes after the exciting factor disappears [23] but rather show how the stationary luminescence is being established after a constant excitation factor is switched on. In this context, the kinetic curves of Figs. 4–6 are determined by the processes of formation and restructuring of the luminescence centres rather than by their radiative lifetimes. The kinetic curves presented in this paper are in good agreement with the characteristic times typical for displacements of interstitial ions, formation of clusters, diffusion of electrons and/or holes, etc., especially if we remind of our low-temperature conditions.

Our results demonstrate that the structure of the tunnel-recombination centres in the AgBr(I) EMCs suggested in this study and the transformations of this structure induced by different external factors can provide a meaningful interpretation of real experimental behaviours of the luminescence bands, including their spectral and kinetic characteristics. The interactions discussed

by us open new resources for controlling light emission and absorption properties. In particular, this can be useful while improving the AgBr(I) EMCs as materials of detectors or detecting elements for a highly sensitive and high-resolution holography, a radiography or X-ray techniques.

Additional possibilities can be associated with the processes of chemical and spectral sensitization (e.g., via admixtures of organic dyes) or applying specific atmospheric conditions to formation of the EMCs (e.g., changing oxygen concentration). The relevant studies are now in preparation and will be presented elsewhere.

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References

1. Tyurin A V and Zhukov S A, 2018. The structure of radiative tunnel recombination sites in emulsion microcrystals of AgBr(I). *Opt. Spectrosc.* **124**: 174–179.
2. Burberry M S and Marchetti A P, 1985. Low-temperature donor-acceptor recombination in silver halides. *Phys. Rev. B.* **32**: 1192–1195.
3. Kanzaki H and Sakuragi S, 1969. Optical absorption and luminescence of excitons in silver halide isoelectronic impurities. Part I. AgBr:I. *J. Phys. Soc. Japan.* **27**: 109–125.
4. Lushchik Ch B and Lushchik A Ch. Decay of Electronic Excitations with Defect Formation in Solids. Moscow: Nauka, 1989.
5. Finch C A. Polyvinyl Alcohol: Developments (2nd Edition). Wiley, 1992.
6. Belous V M, Orlovskaya N A, Akhmerov A Yu and Zenkevich I G, 1999. Photodecomposition and luminescence of silver halides. In: IS&T's PICS Conference: The 52nd Annual Conference: Final Program and Proceedings: Savannah, Georgia, April 25–28, pp. 433–437.
7. Tyurin A V, Zhukov S A and Akhmerov A Y, 2020. Influence of binder and dyes on the mechanism of tunnel luminescence of AgBr(I) microcrystals. *Opt. Spectrosc.* **128**: 1110–1117.
8. Tyurin A, Zhukov S and Bekshaev A, 2020. Interaction between the molecular and aggregated states of the photosensitive organic dyes adsorbed on the surface of AgHal microcrystals. *Proc. SPIE.* **11475**: 114751B.
9. Tyurin A, Bekshaev A and Zhukov S, 2020. Electron-hole processes determining the self-desensitization of dyes on the surface of AgHal microcrystals. *Proc. SPIE.* **11369**: 113690L.
10. Tyurin A V, Zhukov S A, Akhmerov A Y and Churashov V P, 2019. Spectral sensitization with dyes of heterophase microsystems “Nucleus – Silver Halide Shell”. In: 2019 IEEE 8th International Conference on Advanced Optoelectronics and Lasers (CAOL), pp. 143–146. doi:10.1109/CAOL46282.2019.9019425
11. James T H. The Theory of the Photographic Process. New York: Macmillan, 1977.
12. Dorokhova E N and Prokhorova G V. Problems and Questions on Analytical Chemistry. Moscow: Mir, 2001.
13. Zhukov S A. Photoinduced physicochemical processes and their sensitization in “core – silver-halide shell” microsystems. Dr. Sc. Thesis. Odesa: Odesa National University, 2018.
14. Michrina B P and Cooper W, 1974. Studies of the delayed luminescence of silver halides. I. Luminescence-time measurements of silver iodobromide emulsions. *Photon. Sci. Eng.* **18**: 512–517.
15. Latyshev A N, Bokarev V V, Voloshina T V, Kushnir M A, Raskhozhev V N and Antakanova L B, 1982. Luminescence fatigue of silver chloride crystals. *J. Appl. Spectrosc.* **37**: 1137–1141.

16. Belous V M, Akhmerov A Y, Zhukov S A and Orlovskaya N A, 2001. Influence of the products of photochemical destruction of silver halides on the kinetics of their luminescence: mechanism of the “luminescence fatigue”. J. Sci. Appl. Photogr. Cine. **46**: 19–25.
17. Muller P, 1965. Ionenleitfähigkeit von reinen und dotierten AgBr und AgCl Einkristallen. Phys. Stat. Sol. **12**: 775–794.
18. Belous V M, 1997. Review of luminescence studies of latent image formation in silver halide emulsions. J. Imag. Sci. Technol. **41**: 85–98.
19. Marchetti A P and Burberry M S, 1983. Optical and optically detect magnetic resonance studies of AgBr: Г. Phys. Rev. B. **28**: 2130–2134.
20. Meijerink A, van Heek M M E and Blasse G, 1993. Luminescence of Ag⁺ in crystalline and glassy SrB₄O₇. J. Phys. Chem. Sol. **54**: 901–906.
21. Zhao J, Yang Z, Yu C, Qiu J and Song Z, 2018. Preparation of ultra-small molecule-like Ag nano-clusters in silicate glass based on ion-exchange process: energy transfer investigation from molecule-like Ag nano-clusters to Eu³⁺ ions. Chem. Eng. J. **341**: 175–186.
22. Wiegand D A, 1959. Low-temperature luminescence and photoconductivity of AgCl. Phys. Rev. **113**: 52–62.
23. Jiang K, Wang Y, Li Z and Lin H, 2020. Afterglow of carbon dots: mechanism, strategy and applications. Mater. Chem. Front. **4**: 386–399.

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Анотація. Відомо, що тунельна люмінесценція в емульсійних мікрокристалах (ЕМК) AgBr(I) за температур $T \geq 77$ K визначається донорно-акцепторними комплексами зі специфічною структурою. Такий комплекс містить парний йодний центр, який об'єднує два сусідні вузли аніонної підґратки, і розташований поруч міжвузловий йон срібла Ag⁺. Якщо ЕМК AgBr(I) розподілені у зв'язуючій речовині, молекули якої не взаємодіють із йонами Ag⁺, то такі центри характеризуються смугою люмінесценції з характерною довжиною хвилі $\lambda_{\max} \approx 560$ нм. Зміни вмісту йонів срібла в емульсії створюють додаткову смугу люмінесценції з $\lambda_{\max} \approx 720$ нм. Якщо ЕМК AgBr(I) розподілені в желатині, то його молекули взаємодіють із кластерами йонів срібла та утворюють специфічні комплекси з характерними смугами люмінесценції, розташованими при $\lambda_{\max} \approx 580$ нм і $\lambda_{\max} \approx 750$ нм. В обох випадках можна спостерігати два типи кінетики люмінесцентного свічення, залежно від температури та концентрації Ag⁺. Це монотонне зростання інтенсивності від нуля до максимального стаціонарного рівня або швидке «посилення спалаху» з наступним поступовим спаданням до деякого нижчого значення. Примітно, що додатковий «спалах» люмінесценції, стимульований інфрачервоним випромінюванням, виявляємо щоразу, коли спостерігаємо монотонне зростання. Навпаки, в смугі люмінесценції не виникає жодного інфрачервоного свічення, якщо в цій смугі реєструємо «посилення спалаху». Усі ці результати проінтерпретовано в термінах структурних перетворень, що відбуваються з центрами тунельної рекомбінації в ЕМК AgBr(I).

Ключові слова: мікрокристали AgBr(I), низькотемпературна люмінесценція, емульсійна зв'язуюча речовина, центри тунельної рекомбінації, інфрачервоне випромінювання, кінетика люмінесценції.