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Mechanism for the chemical oxygen-induced sensitization of AgBrI microcrystals spectrally sensitized with anionic dye

In this work, the specific disperse systems are considered, which are formed in composite condense materials containing light-sensitive silver-halide microcrystals (MCs). Based on the low-temperature ($T = 77$ K) luminescent and spectroscopic properties of AgBrI MCs, a mechanism is discussed for the influence of the oxygen treatment on the MCs' spectral sensitization by an anionic dye. It is shown that, in contrast to the general view prevailing in the current literature, the effect of oxygen cannot be reduced only to decreasing the sensitivity of AgBrI MCs, and its role in the spectral sensitization of AgBrI MCs is not so unambiguous. Within the framework of the proposed mechanism, such ambiguity appears due to the fact that silver centers Ag^+ and Ag_2^+ , different in their structure, participate in the generation-recombination processes of nonequilibrium charge carriers, which interact with various aggregate forms of the dye adsorbed on the MC surface and are affected by oxygen in different ways. The results will be useful for numerous applications involving such MCs, in particular, for optimization of holographic and spectrozonal photo-materials, gas-phase sensors and in solar energy systems.

Keywords: silver-halide microcrystals, anionic-dye sensitization, low-temperature luminescence, oxygen treatment, nonequilibrium charge carriers, generation-recombination processes.

Introduction. When registering optical information, the spectral range of intrinsic sensitivity of silver-halide (AgHal) microcrystals (MCs) extends up to the wavelength $\lambda = 500$ nm [1]. Sensitization of AgHal MCs with organic dyes can change the region and value of spectral sensitivity. Remarkably, a number of dyes applied for sensitization expand the intrinsic spectral sensitivity of AgHal MCs to the long-wave region ($\lambda > 500$ nm) up to the near-infrared range, while some of them only lead to a decrease in the intrinsic sensitivity of AgHal MC. Such dyes are called sensitizer-dyes (S-dyes) and desensitizer-dyes (D-dyes), respectively.

In works [2,3], it was noted that the desensitizing effect of dyes is only manifested if the MC-carrying medium is exposed to gaseous (O_2). Considerable attention to the role of O_2 and H_2O in desensitization processes is given in works [4,5,6]. In addition, in [6] it was established that oxygen affects the intrinsic sensitivity of AgHal MC even in the absence of dye. Removal of oxygen by vacuuming leads to an increase in the intrinsic sensitivity ($\lambda < 500$ nm) of AgHal MCs, and some D-dyes, in high vacuum, become effective sensitizers [4,6].

The mechanism of the oxygen-stimulated influence on the desensitization process has not been fully elucidated, and various assumptions have been made regarding it. In interpreting our experimental data, we will adhere to the assumption made by Hamilton in [7], who explains the influence of O₂ by the fact that oxygen affects the population and release of the surface levels of AgHal MCs.

For S-dyes, the process of desensitization (decrease in sensitivity) of AgHal MCs is also poorly understood both in the spectral region of its own sensitivity and in the IR region of spectral sensitization [8,4,9]. In Refs. [10,11,12], this process of desensitization by S-dyes was defined as self-desensitization by dyes. In these works, it was also noted that oxygen and moisture actively participate in the self-desensitization process. In [12], a self-desensitization mechanism was proposed in which an oxygen anion radical should be formed as a result of the transfer of a nonequilibrium electron from the dye to oxygen; however, in our opinion, the formation of an oxygen anion radical has not received sufficient experimental confirmation.

Therefore, oxygen plays a significant role in the processes responsible for spectral sensitization, desensitization and self-desensitization of AgHal MCs by dyes, but its participation remains poorly studied and unclear to date. Accordingly, the goal of our work is to clarify the sensitization / desensitization mechanisms in dye-doped AgHal MCs in presence of oxygen, which would consistently describe both the low-temperature luminescent and spectrosensitometric properties of AgHal MCs.

Samples and research methods. The emulsion samples for the studies were synthesized using the two-stream ammonia method with the supply of one-normal (1N) solutions of AgNO₃ and KBr (3 mol % KI) at a rate of 6.0 ml/min at a temperature of 60 °C and at pAg of 8.6. The AgHal content in the finished emulsion was 0.28 gmol/l, and gelatin content was 7%. As a result, cubic AgBrI MCs of 0.2 μm in size were formed in the emulsion. After that, the Ag content in the emulsion was brought to pAg = 4.0 by introducing a solution of AgNO₃.

For spectral sensitization of AgBrI MCs, we used an anionic J-aggregating panchromatic dye – pyridine salt of 3,3'-di-γ-sulfopropyl-9-ethyl-4,5,4',5'-dibenzothia-carbocyanine-betaine, alcohol solutions of which were introduced into the finished emulsion; from now on, the term “dye” refers to this organic substance. Finally, the dye molecules (dye-M) and J-aggregates (dye-J) appear adsorbed at the surfaces of AgHal MCs thus forming the system of “AgBrI MCs with anionic dye adsorbed on their surface” (AMADAS). The dye molecules not adsorbed on the MCs surfaces were separated by centrifugation.

In our conditions, dye-induced spectral sensitization of AgBrI MCs was carried out at a concentration of 10⁻⁴ mol dye / mol AgBr. This concentration of dye was chosen so that in addition to the interaction of dye-Ms with the surface of MCs, the formation of aggregated forms of dye was ensured, which depends primarily on the interaction of the dye-Ms with each other [13, 14].

The finished emulsion samples were cast onto glass plates 9 cm wide and 12 cm long. The dried plates were exposed to light decomposed into a spectrum along the plate length in the range from 400 nm to 1100 nm in an ISP-73 high-aperture spectrograph. As a result of such exposure, latent image centers appeared in AgBrI MCs –

reduced neutral Ag centers of atomic-molecular degree of dispersion [10]. To visualize the latent image centers, a depth developer was used [15]. The depth developer reduces Ag not only in those microcrystals in which the latent image was created by illumination from the region of their intrinsic absorption ($\lambda < 500$ nm), but also from the region of absorption of the S-dye (500 – 1100 nm). Measurements of the spectral distribution of the optical density along the length of the exposed plate, which is proportional to the concentration of developed latent-image centers, was performed with an MF-4 microphotometer using the standard procedure [9].

Thus, the proposed ways of exposure and development allow us to trace the distribution of the reduced Ag centers of the atomic-molecular dispersion in AgBrI MCs depending on the illuminating light wavelength.

Measurements of the luminescence of dye-sensitized AgBrI MCs at a temperature $T = 77$ K were performed on an experimental setup that allows recording luminescence spectra in the following sequence: excitation lasts for $\sim 10^{-4}$ s, is followed by a "dark" interval of $\tau \sim 10^{-3}$ s, and only after that does luminescence recording begin for $\sim 10^{-4}$ s. Then the cycle is repeated at a frequency of 800 Hz. This approach enables recording phosphorescence and anomalously delayed fluorescence ($\tau > 10^{-3}$ s) caused by the redistribution of nonequilibrium charge carriers in the system, which is of our primary interest in this work.

Experimental results. The study of low-temperature luminescence of the dye-sensitized emulsion, not subjected to treatment in an oxygen atmosphere, showed that dye in the AMADAS structures is present both in the molecular and J-aggregated forms. In this case, the luminescence and excitation spectra are characterized by the following luminescence bands presented in Fig. 1. When AgBrI MCs are excited by light from the region of intrinsic AgHal absorption with $\lambda = 450$ nm, we observe luminescence maxima at $\lambda_{\max} \approx 565$ nm and at $\lambda_{\max} \approx 750$ nm (Fig. 1a, curve 1). When excited by light from the region of absorption of the dye-J ($\lambda = 690$ nm), the glow spectrum is characterized by an anti-Stokes luminescence band with $\lambda_{\max} \approx 565$ nm, and by a long-wave luminescence with $\lambda_{\max} \approx 790$ nm (Fig. 1a, curve 2).

In full agreement to these data is the luminescence excitation spectrum with $\lambda_{\max} \approx 565$ nm, which is characterized by two maxima at $\lambda = 450$ nm (corresponding to the absorption edge of an AgBrI MC) and at $\lambda = 690$ nm (corresponding to the absorption region of dye-J) illustrated by Fig. 1b, curve 1. The luminescence excitation spectrum at $\lambda_{\max} \approx 790$ nm is characterized by the presence of three maxima $\lambda_{\max} = 450$ nm, 600 nm and 690 nm, which are related to the absorption of AgBrI MC, dye-M and dye-J, respectively (Fig. 1b, curve 2).

Maintaining the emulsion in an oxygen atmosphere for 1 to 2 minutes results in an approximately twofold increase in the luminescence intensity I_{phos} of all luminescence bands for different excitation wavelengths, while the positions of maxima for the luminescence and luminescence excitation spectra do not change (Fig. 1c, d, e, f).

Further keeping the emulsion in an oxygen atmosphere for more than 2 minutes leads to the following changes in the luminescence intensity. The luminescence intensities I_{phos} of the bands at $\lambda_{\max} \approx 565$ nm and $\lambda_{\max} \approx 790$ nm upon excitation by light

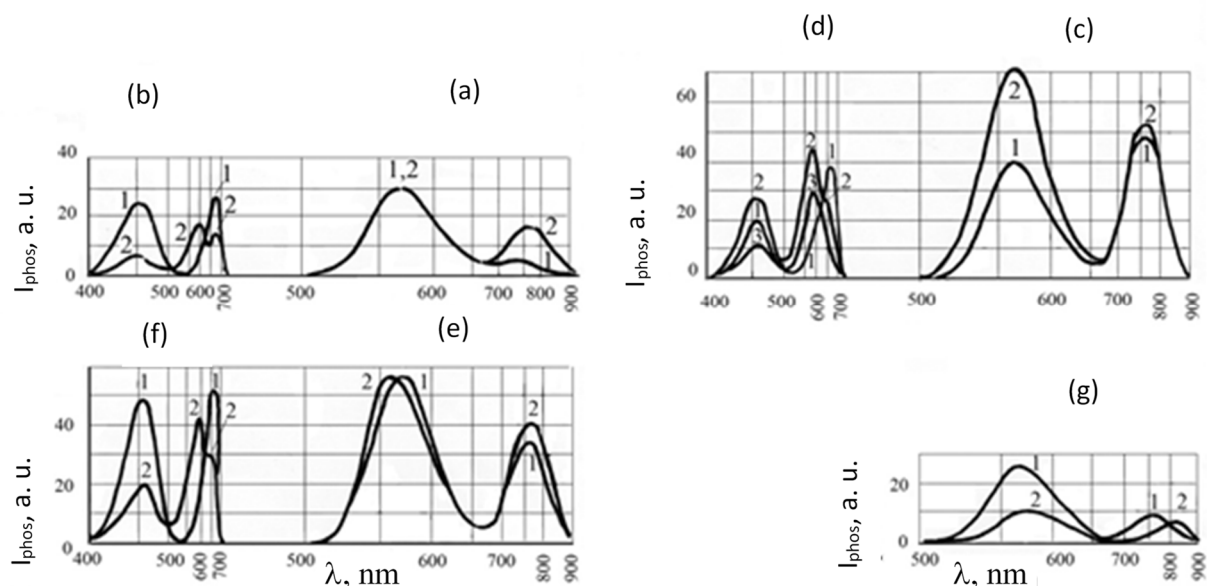


Fig. 1. Spectra of (a, c, e, g) luminescence and (b, d, f) luminescence excitation for the dye-sensitized AgBrI MCs (AMADAS) after the emulsion is maintained in oxygen atmosphere during (a, b) $t = 0$ min; (c, d) $t = 1$ min; (e, f) $t = 2$ min, and (g) $t = 4$ min.

- (a) luminescence spectra upon excitation by light with λ , nm: (1) 450; (2) 690;
 (b) excitation spectra of the luminescence bands with λ_{max} , nm: (1) 570; (2) 790;
 (c) luminescence spectra upon excitation by light with λ , nm: (1) 450; (2) 690;
 (d) excitation spectra of the luminescence bands with λ_{max} , nm: (1) 570; (2) 750; (3) 800;
 (e) luminescence spectra upon excitation by light with λ , nm: (1) 450; (2) 690;
 (f) excitation spectra of the luminescence bands with λ_{max} , nm: (1) 570; (2) 800;
 (g) luminescence spectra upon excitation by light with λ , nm: (1) 450; (2) 690.

with $\lambda = 450$ nm decrease. Moreover, upon keeping the emulsion in an oxygen atmosphere for 4 minutes, the intensities of these bands reach the level that was observed before the sample was treated in an oxygen atmosphere (Fig. 1g, curve 1). Upon excitation by light with $\lambda = 690$ nm, the anti-Stokes luminescence intensity at $\lambda_{max} \approx 565$ nm drops below the level that was observed before the sample was treated in an oxygen atmosphere, and the luminescence maximum in the long-wavelength region of the spectrum shifts from $\lambda_{max} \approx 790$ nm to $\lambda_{max} \approx 810$ nm (Fig. 1g, curve 2).

The sensitometric properties of the experimental samples are characterized by the dependence of the optical density $D - D_0$ of the developed emulsion on the illuminating light wavelength and on the time t (measured in minutes) of keeping the sample in the oxygen atmosphere, illustrated by Fig. 2. For the emulsion with $t = 0$ (no oxygen treatment), the maxima of the optical density are observed at $\lambda = 450$ nm, 600 nm and 690 nm (Fig. 2a), which correspond to the absorption region of AgBrI MC, dye-M and dye-J, respectively. The value of the optical density in the absorption region of the dye-M is maximum and 7 – 8 times exceeds that for the dye-J. Keeping the emulsion in an oxygen atmosphere for $t = 10$ min does not change the optical density in the absorption region of AgBrI MCs, which was to be expected. In the absorption region of the dye-M, the optical density decreases, and in the absorption region of the dye-J, it increases (Fig. 2b). At $t = 20$ min, the optical density in the absorption region of the dye-J reaches

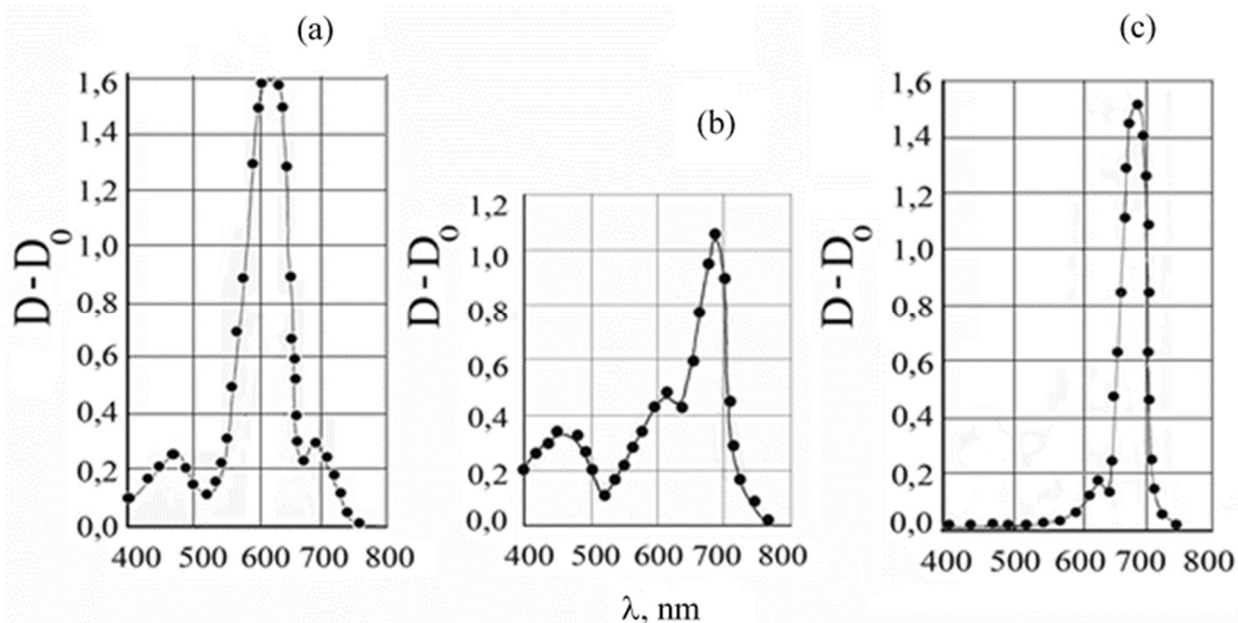


Fig. 2. Dependences of the optical density $D - D_0$ of emulsion darkening on the wavelength of the illuminating light and on the time of exposure in an atmosphere of gaseous oxygen during (a) $t = 0$ min; (b) $t = 10$ min; (c) $t = 20$ min.

the maximum for an emulsion not treated with oxygen in the absorption region of the dye-M (Fig. 2c).

Note that in sensitometric studies, the time of emulsion exposure to oxygen significantly exceeds the exposure time applied in luminescent studies. This is due to the fact that for luminescent studies it is sufficient for oxygen to affect the electronic subsystem, which responds to the effect fairly quickly. In sensitometric studies, exposure to oxygen is associated with the occurrence of topochemical reactions with the formation of Ag clusters, i.e. with changes in the ionic subsystem, which determine the process duration.

Discussion of the experimental results. The first conclusion derived from the above-presented results is that the effect of oxygen on the spectral sensitization of AgBrI MCs with anionic dye cannot be reduced, as was claimed in literature, exclusively to decrease of the MC sensitivity; in fact, the role of the oxygen treatment is more complex. When AMADAS systems are kept in a gaseous-oxygen atmosphere for up to 2 minutes, the luminescence intensity in all glow bands, really, increases; however, a decrease in the luminescence intensity in all glow bands occurs when the oxygen-exposure time exceeds 2 minutes. Differences in the effect of oxygen on the AMADAS structures are also observed in sensitometric studies. Before keeping AgBrI MCs in an atmosphere of gaseous oxygen, the highest concentration of developed Ag is observed when illuminated with light from the dye-M absorption region. The oxygen treatment of AgBrI MCs is accompanied by a decrease in the developed Ag concentration when illuminated with light from the absorption region of the dye-M, and an increase when illuminated with light from the absorption region of the dye-Js. The dependencies of the luminescent and sensitometric data on the duration of the oxygen treatment of the emulsion are shown in Fig. 3.

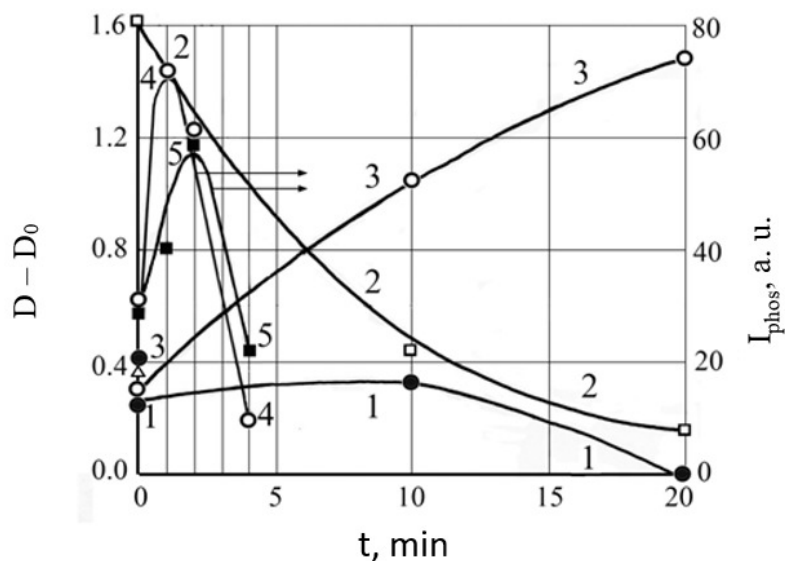


Fig. 3. Dependences of the optical density $D - D_0$ of emulsion darkening (curves 1, 2, 3) and the intensity of the glow with $\lambda_{\text{max}} \approx 565$ nm (curves 4, 5) on the time of keeping the emulsion in an atmosphere of gaseous oxygen. Wavelengths of the illuminating and exciting light are: (curves 1, 4) 450 nm, (curve 2) 590 nm, (curves 3, 5) 690 nm.

To clarify the mechanism of the influence of oxygen on the spectral sensitization of AgBrI MCs by an anionic dye (accompanied by the AMADAS formation), which enables to explain the dependences presented in Fig. 3, we employ our previously expressed assumption that the transfer of photoexcitation from AgBrI MC to the dye and from the dye to AgBrI MC occurs with the participation of Ag centers [16].

The AgBrI MCs synthesized in this work contain an excess concentration of silver ions Ag^+ compared to stoichiometry. Some of these ions Ag^+ are located in the interstitial space of the AgBrI MC crystal lattice in a mobile state. Simultaneously, a certain quantity of the ions Ag^+ are coupled with regular silver ions of the MC lattice and form thus centers of the atomic-molecular degree of dispersion Ag_2^+ .

The transfer of photoexcitation, i.e. nonequilibrium charges generated by light from the region of intrinsic absorption of AgBrI MCs to the dye-Ms and dye-Js adsorbed on their surface, as well as those generated by light from the region of absorption of the dye-J to the AgBrI MCs and dye-Ms, occurs with the participation of interstitial silver ions Ag^+ and silver centers Ag_2^+ . The process is organized as follows.

Upon excitation by light from the region of intrinsic absorption of AgBrI MC with $\lambda = 450$ nm, the centers Ag^+ and Ag_2^+ are active traps for nonequilibrium electrons, while the dye-M and paired iodine centers (I^-), located in neighboring anion sites of the crystal lattice [16], are active traps for nonequilibrium holes. The energies of electron states of these centers, together with the conduction (CB) and valence (VB) energy bands of an AgBrI MC, as well as the scheme of radiative and thermal transitions between the energy levels of our interest, are schematically shown in Fig. 4.

According to this scheme, upon excitation by light with $\lambda = 450$ nm (Fig. 4a, transition 1), the following transitions are responsible for the luminescence we observe.

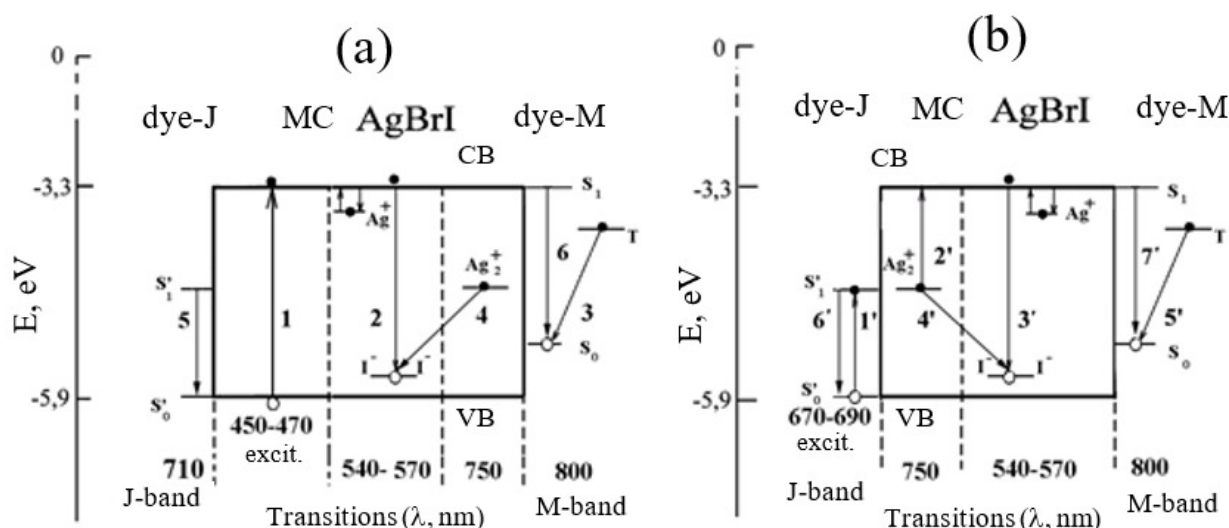


Fig. 4. Energy states of electrons and transitions between them in AMADAS systems upon excitation by light (a) with $\lambda = 450$ nm and (b) $\lambda = 690$ nm. Further explanations see in text.

Luminescence with $\lambda_{\max} \approx 565$ nm is caused by the recombination of a free electron from the CB with a hole localized at the paired iodine center (Fig. 4a, transition 2). Luminescence with $\lambda_{\max} \approx 750$ nm is caused by the recombination of an electron localized at the Ag_2^+ center with a hole localized at the paired iodine center (Fig. 4a, transition 4) [17].

When excited by light with $\lambda = 690$ nm (Fig. 4b, transition 1'), the relaxation of nonequilibrium electrons and holes occurs according to the scheme of Fig. 4b. Nonequilibrium holes are redistributed between the ground level S_0' of the dye-J and the VB of the AgBrI MC, whence they are partially captured by paired iodine centers. Electrons, excited from S_0' to the S_1' level of the dye-J, partially recombine with holes at the dye-J ground level S_0' (Fig. 4b, transition 6') and partially transfer to the Ag_2^+ centers of the MC. Electrons localized at the Ag_2^+ centers, partially recombine radiatively with holes localized at the paired iodine center, causing luminescence with $\lambda_{\max} \approx 750$ nm (Fig. 4b, transition 4'), and are partially excited by light with $\lambda = 690$ nm to the CB of AgBrI MC (Fig. 4b, transition 2'). Nonequilibrium electrons that arise in the CB as a result of two-photon excitation by light with $\lambda = 690$ nm from the S_0' level of the dye-J, partially recombine radiatively with holes localized at the paired iodine center, which causes anti-Stokes glow with $\lambda_{\max} \approx 565$ nm (Fig. 4b, transition 3'), and partially fall on the triplet level T of the dye-M, from which recombination with a hole captured by the ground level S_0 of the dye-M takes place, causing phosphorescence with $\lambda_{\max} \approx 810$ nm [18] (Fig. 4b, transition 5'). It should be noted that the phosphorescence of the dye-M ($\lambda_{\max} \approx 810$ nm), caused by the recombination of an electron at the triplet level T with a hole captured by the ground level S_0 of the dye-M, is quite clearly manifested as a maximum upon its excitation by light with $\lambda = 690$ nm after prolonged exposure of the emulsion to an atmosphere of gaseous oxygen (Fig. 1g, curve 2). When excited by light with $\lambda = 450$ nm (Fig. 4a, transition 1) and upon a short exposure of the emulsion to the gaseous oxygen atmosphere, the phosphorescence of the dye-M is not clearly visible (Figs. 1c and 1e) because it is overlapped by intense glow with λ_{\max}

≈ 750 nm, caused by the recombination of an electron localized at the Ag_2^+ center with a hole localized at the paired iodine center (Fig. 4a, transition 4).

Glow with $\lambda_{\text{max}} \approx 710$ nm, caused by recombination of the electron localized at the first excited level of the dye-J S_1' with the hole localized at the ground level S_0' (Fig. 4a, transition 5, and Fig. 4b, transition 6'), is not observed under conditions of our experiment, when phosphorescence and anomalously slow fluorescence ($\tau > 10^{-3}$ s) are recorded. Fluorescence of the dye-M with $\lambda_{\text{max}} \approx 610$ nm, caused by the transition of the electron from the first excited singlet level S_1 of the dye-M to its ground level S_0 (Fig. 4a, transition 6, and Fig. 4b, transition 7'), is also not observed under the conditions of our experiment. These glows were registered in [18], when the luminescence recording time at a temperature of $T = 77$ K was less than 10^{-3} s.

Within the framework of the proposed model, the influence of oxygen on the luminescent and sensitometric properties of the AMADAS structures can be described as follows. The dye-M adsorbed on the AgBrI MC surfaces predominantly interacts with interstitial silver ions Ag^+ , as indicated by the highest concentration of developed Ag observed when illuminated with light from the absorption region of the dye-M. This interaction does not change the role of Ag^+ in generation-recombination processes, and they remain active traps for nonequilibrium electrons. When adsorbed on the surface of AgBrI MCs, dye-Js interact predominantly with the centers Ag_2^+ , forming complexes (Ag_2^+J) on the surface of AgBrI MC, which also actively participate in generation-recombination processes upon excitation by light from both the absorption region of AgBrI MC and the dye-J.

During short-term (up to 2 minutes) oxygen exposure of AMADAS, oxygen primarily affects Ag^+ ions located near the dye-M. The presence of oxygen modifies the role of Ag^+ in generation-recombination processes, and these centers are no longer traps for nonequilibrium electrons. Accordingly, the concentration of Ag^+ traps for nonequilibrium electrons during excitation by light from both the absorption region of AgBrI MCs and the dye-Js decreases. As a consequence, this leads to an increase in the luminescence intensity of paired iodine centers in both Stokes (excitation of AgHal) and anti-Stokes (excitation of the dye-J) luminescence.

Oppositely, long-term exposure to gaseous oxygen results in oxygen interacting with Ag_2^+ to form Ag_2O molecules. This, in turn, results in the exclusion of Ag_2^+ centers from generation-recombination processes and, ultimately, leads to the observed decrease in anti-Stokes luminescence with $\lambda_{\text{max}} \approx 565$ nm and luminescence with $\lambda_{\text{max}} \approx 750$ nm (Fig. 4b, transitions 3' and 4', respectively). This assumption is consistent with the fact that, in this case, the developed Ag concentration is maximum upon excitation by light from the absorption region of the dye-J. Indeed, the electron, that has arrived from S_0' to the first excited level S_1' , now no longer moves to Ag_2^+ with subsequent excitation into the CB of the AgBrI MC (Fig. 4b transition 2'), but is fixed on the Ag_2O molecule located next to the dye-J, ensuring the growth of the developed Ag content during the depth development.

Conclusions. The first conclusion of this work is that oxygen introduced into AMADAS systems, may differently affect their luminescent and spectro-sensitometric properties depending on the oxygen concentration. At low concentrations, the lumines-

cence intensity in all emission bands of the AMADAS structures increases. With growing concentrations of introduced oxygen, the luminescence intensity significantly decreases, and the anti-Stokes emission band with $\lambda_{\max} \approx 565$ nm practically disappears. The highest concentration of developed Ag in the emulsion containing the AMADAS is observed upon illumination with light from the absorption region of the dye-J. If the emulsion does not undergo the oxygen treatment, the highest concentration of developed Ag is observed upon illumination with light from the absorption region of the dye-M.

The obtained results can be consistently explained on the base of assumption that the generation-recombination processes of nonequilibrium charge carriers in AMADAS systems involve two sorts of silver centers, Ag^+ and Ag_2^+ , which differ in their structure. On the surface of AgBrI MCs, Ag^+ predominantly interacts with the dye-M, and Ag_2^+ interacts with the dye-Js. The introduction of oxygen performs specific effects on each of these centers. Due to the oxygen action, the Ag^+ centers, being active traps for nonequilibrium electrons, are excluded from the generation-recombination processes excited by light from absorption region of both the AgBrI MCs and the dye-Js. Instead, the Ag^+ centers cooperate with the adjacent Ag_2^+ centers and form the Ag_2O molecules, thereby Ag_2^+ centers are also excluded from the generation-recombination processes. This explains the observed dependences of the luminescent and spectrosensitometric properties of AMADAS systems (Fig. 3) on the concentration of introduced oxygen.

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Механізм хімічної сенсibiliзації при обробці киснем мікрокристалів AgBrI, спектрально сенсibiliзованих аніонним барвником

Анотація

У роботі розглядаються специфічні дисперсні системи, що формуються в композитних конденсованих середовищах, які містять світлочутливі галогенісрібні мікрокристали (МК). На базі низькотемпературних ($T = 77\text{ K}$) люмінесцентних та спектросенситометричних характеристик МК AgBrI, розглядається механізм впливу кисневої обробки на спектральну сенсibiliзацію МК аніонним барвником. Показано, що вплив кисню не може зводитися, як стверджується в літературних джерелах, лише до зниження чутливості МК AgBrI, і його роль у спектральній сенсibiliзації МК AgBrI не є такою однозначною. У рамках запропонованого механізму, певна варіативність виникає через те, що срібні центри Ag^+ та Ag_2^+ , різні за своєю структурою, беруть участь у процесах генерації-рекомбінації нерівноважних носіїв заряду, які взаємодіють з різними агрегатними формами барвника, адсорбованого на поверхні МК, і по-різному зазнають впливу кисню. Результати роботи будуть корисними для численних застосувань, що використовують такі МК, зокрема для оптимізації голографічних та спектрально-зональних фотоматеріалів, газофазних сенсорів та в системах перетворення сонячної енергії.

Ключові слова: мікрокристали галогенідів срібла, сенсibiliзація аніонними барвниками, низькотемпературна люмінесценція, обробка киснем, нерівноважні носії заряду, процеси генерації-рекомбінації.