

# Reduction Sensitization of AgBr Emulsions: Photoluminescence Studies

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## Abstract

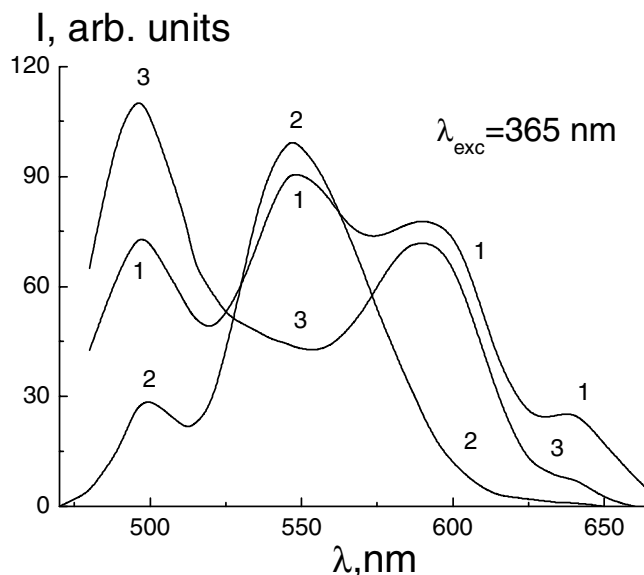
Photoluminescence (PL) spectra and photoluminescence excitation (PLE) spectra ( $\lambda \geq 240\text{nm}$ ,  $T \geq 4.2\text{K}$ ) of reduction sensitized cubic and octahedral AgBr emulsions have been studied. PLE spectra consist of several maxima, which correspond both to the excitonic absorption in AgBr and to various impurity centers formed in the course of reduction sensitization. The analysis of the both PL and PLE spectra with account for a strong electron-phonon coupling in AgBr, allowed us to construct the system of the energy levels of the impurity centers and determine the corresponding electron and hole binding energies. Specifically, it was established that  $\text{Ag}_2$  molecule, which is located near positively charged microcrystal surface defect, is the 0.36eV electron trap.

## Introduction

It has been shown in Refs. 1-3 that during reduction sensitization of AgBr(I) emulsions, prepared by the single-jet method, results in the increases of sensitivity at the initial stages of sensitization and the intensity of the emulsion microcrystals (MC) photoluminescence (PL) band with  $\lambda_{\text{max}} = 640\text{-}650\text{nm}$ . This suggests that the impurity centers created during reduction sensitization play a double role: they facilitate the room temperature sensitivity increase as well as determine the orange-red emission ( $\lambda_{\text{max}} = 640\text{-}650\text{nm}$ ) at low temperatures ( $T = 77\text{K}$ ).

The PL measurements performed at  $T = 4.2\text{K}$  of AgBr emulsions, obtained by the double-jet method, allowed to determine [4] that reduction sensitization not only increases the intensity of the 640nm band but also leads to an appearance of a new band with  $\lambda_{\text{max}} = 550\text{nm}$  and an increase of the emission intensity in the spectral range of 580-590nm (Fig. 1, curve 1). In the photoluminescence excitation (PLE) spectrum of the 550nm band there are several maximums: at 254nm (4.82eV), 283nm (4.38eV) and 442nm (2.8eV) (Fig. 2, curve 1) [4], whereas the excitation spectrum of the 590 band has maximums at 254nm (4.88eV), 279nm (4.44eV), 325nm (3.81eV) and 430nm (2.88eV) (Fig. 2, curves 2, 3) [3]. It is important to note that the maximum at  $\lambda = 442\text{nm}$  is also observed in the PLE spectrum of the 640nm PL band (Fig. 2, curve 4). The two narrow PLE maximums at 257nm (254nm) and 283nm (279nm) are owing to the creation of the anion exciton in the  $\Gamma^-$ -point of the AgBr Brillouin zone. This doublet structure of the AgBr excitonic absorption is due to the spin-orbit splitting of the valence band in the  $\Gamma^-$  point (transition  $\Gamma_8^- \rightarrow \Gamma_6^+$ ) [5], which is very close to energy of the spin-orbit splitting of a free bromine atom (0.44eV).

It has been shown in Refs. 6, 7 that if  $\text{SnO}_2$  is used as sensitizing agent for AgBr emulsion the PL ( $T = 6\text{K}$ ) consists of



**Figure 1** Photoluminescence (PL) Spectra ( $T = 4.2\text{K}$ ) AgBr emulsions after reduction sensitization (curve 1) and after treatment in  $\text{AgNO}_3$  solution (curve 3). For comparison PL of AgBr(I) emulsions (curve 2) is also shown.

the 550nm and 640nm bands, which have a characteristic PLE maximum at  $\lambda = 442\text{nm}$ . At the same time reduction sensitization leads to an increase in the intensity of the 590nm emission (PLE maximum at  $\lambda = 430\text{nm}$ ). Both results are consistent with those obtained in Refs. 3 and 4. The PL and PLE spectra presented in Refs. 6 and 7 are observed only from the reduction sensitized tabular or octahedral AgBr MCs that were synthesized in the reaction medium ( $\text{pAg} = 10.0$ , temperature of the synthesis is between  $55^\circ\text{C}$  and  $70^\circ\text{C}$ ) with relatively high concentration of  $\text{Br}^-$  ions. However, in the case of cubic MCs, which were synthesized at  $\text{pAg} = 7.0$ , the reduction sensitization does not lead to described in Refs. 6, 7 photoluminescence or excitation spectra, but rather accompanied by the appearance of a single band with  $\lambda_{\text{max}} = 570\text{nm}$  [6a]. The PLE spectrum of the 570nm band (spectral region with  $\lambda > 400\text{nm}$ ) does not have any characteristic maximums and its long wavelength edge coincides with the long wavelength edge of the absorption spectrum of AgBr [6a].

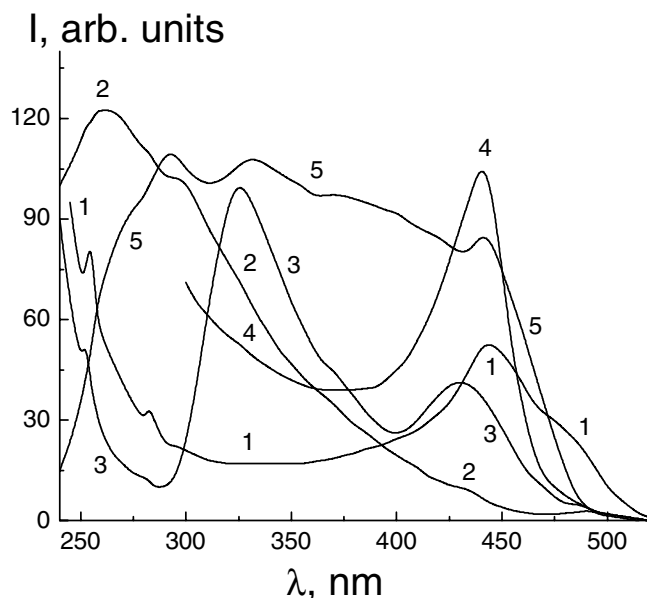
It has been concluded in Refs. 6, 7 that the 550nm band is due to a singlet-singlet transition (lifetime  $< 10\text{ns}$ ), whereas the 640nm band is due to a triplet-singlet transition, within an excited  $\text{Ag}_2$  center that appears as a result of reduction sensitization and

that is located next to a positively charged surface defect ("positive kink"). The 590nm band has been assigned to the donor-acceptor pair (DAP), radiative transition, in which an  $\text{Ag}_2^+$  center is an acceptor [6, 7]. Furthermore, the authors of Refs. 6 and 7 believe that the nature of luminescent centers in the reduction sensitized AgBr MC as well as the mechanism of the luminescence are supported by the results they obtained from optically detected magnetic resonance (ODMR).

In this paper we present results that show that the process of reduction sensitization of AgBr emulsions is different for the emulsions with cubic and octahedral MCs. These results lead to the model for the luminescent centers and related luminescence mechanisms that are different from those proposed in Refs. 6, 7.

## Experimental

It has been noted in Ref. 3 that 550nm PL band ( $T = 4.2\text{K}$ ) with characteristic excitation maximum at 442nm, which appear in AgBr MC after their reduction sensitization, is also observed from non-sensitized AgBr(I) MC. In Fig. 1 (curve 2) we show, as an example, the PL spectrum ( $T = 4.2\text{K}$ ) of AgBr(I) emulsion (3mole% AgI) with octahedral MC [8], whereas its PLE spectrum is shown in Fig. 2 (curve 5) [9]. The excitation spectra of the green emission of AgBr(I) shows the following maximums:  $\lambda =$



**Figure 2** Photoluminescence Excitation (PLE) Spectra at 4.2K of AgBr emulsion (the monitoring wavelengths are 550nm (curve 1), 590nm (curves 2, 3) and 640nm (curve 4)) before (curve 2) and after (curve 1, 3, 4) reduction sensitization. Curve 5 is PLE of AgBr(I) emulsion, the monitoring wavelength is 550nm.

290nm (4.28eV, excitonic absorption),  $\lambda = 330\text{nm}$  (3.75eV), and  $\lambda = 442\text{nm}$  (2.80eV). The 550nm PL band from AgBr(I) MC is determined by the presence in the MCs of pair iodine centers (two nearest neighbor iodine ions ( $\text{I}^{\cdot\cdot}$ ) [10]). The existence of the 330nm and 442nm PLE maximums is entirely consistent with this center's luminescence model. These maximums are due to the light absorption by iodine ion (transitions  $5p^6 \rightarrow 5p^6(^2P_{1/2})6s$  and  $5p^6 \rightarrow 5p^6(^2P_{3/2})6s$ ). Moreover, as expected, the energy difference

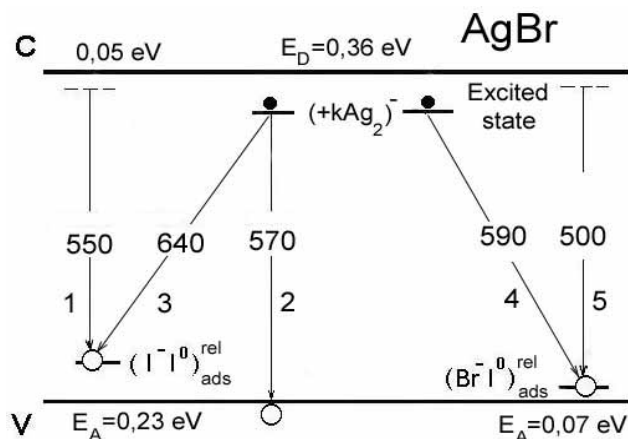
between these excitation maximums is 0.95eV, which coincides with the energy of the spin-orbit splitting of the iodine atom ground state. Since the energy that corresponds to the maximums in the excitation spectrum is larger than the AgBr bandgap, the excited iodine ion ionizes, and the created free electron recombines with the "relaxed" ( $\text{I}^{\cdot\cdot}$ )<sup>rel</sup>-center, resulting in the 550nm luminescence.

The appearance of pair iodine centers during reduction sensitization of AgBr emulsions can be explained as follows. The 550nm PL appears after reduction sensitization of AgBr emulsions only when MC's synthesis is carried out under very high concentration of  $\text{Br}^-$  ions (pBr between 1.0 and 0.5;  $T = 55^\circ\text{C} - 70^\circ\text{C}$ ). Under such conditions a number of polyhalogenoargentate complex anions appear in the reaction medium [11]. KBr and NaBr solutions (used for MC synthesis) always contain some iodine impurities; thus, depending on the chemical purity of KBr and NaBr, the reaction medium can contain not only  $\text{AgBr}_2^-$  and  $\text{AgBr}_3^{2-}$ , but also  $\text{AgBrI}^-$ ,  $\text{AgBr}_2\text{I}^-$ ,  $\text{AgBrI}_2^{2-}$ , and  $\text{AgI}_2^-$  [11]. Minute amounts of  $\text{AgI}_2^-$  can be created if the iodine concentration is  $\sim 10^{-6}$  mole/l at  $25^\circ\text{C}$  and  $\sim 10^{-4}$  mole/l at  $250^\circ\text{C}$  and  $70^\circ\text{C}$ , for the synthesis temperature between  $55^\circ\text{C}$  and  $70^\circ\text{C}$ , the  $\text{AgI}_2^-$  centers are created if the concentration of iodide ions is about  $3 \times 10^{-6}$  mole/l. Such a concentration of iodine ions can be easily achieved in KBr and NaBr solutions at pBr between 1.0 and 0.5. In this case a  $\text{AgI}_2^-$  complex is being formed even during synthesis of nominally pure AgBr MCs. These conclusions are based on the average values for the concentration of  $\text{Br}^-$  and  $\text{I}^-$  in the solution. Moreover, because of ineffective mixing, it is possible that the local concentrations of  $\text{Br}^-$  and  $\text{I}^-$  ions are substantially higher than the average values [14]. This results in the increased formation efficiency not only for  $\text{AgI}_2^-$  but also for such complexes as  $\text{AgBrI}^-$ ,  $\text{AgBr}_2\text{I}^-$ ,  $\text{AgBrI}_2^{2-}$ , and  $\text{AgI}_3^{2-}$ . It must be noted that a decrease in the synthesis temperature will further enhance formation of these complexes.

The  $\text{AgI}_2^-$  complexes (as well as the other) can adsorb on the surface of the tabular and octahedral AgBr MCs. It is well known that the surface of the tabular and octahedral AgBr MCs consists of  $\text{Br}^-$  ions, which are partially covered by silver ions or silver ions islets. A polyhalogenoargentate complex (e.g.  $\text{AgI}_2^-$ ) can attach to these islets via its negatively charged halogen ions. In this case, the silver ion of the complex will be right above the adsorbed halogen anions. As the negative charge of the complex is partially compensated by the positive charge of  $\text{Ag}^+$ , the adsorbed complex behaves as an electron trap. (We note, for comparison, that according to the calculations [15] a silver ion, which is located near a negative kink side or a negative double kink side in cubic AgBr MCs, creates an electron capture level within AgBr. These results are in good agreement with those obtained in Ref. 16, where it was shown that a silver ion located above two  $\text{Br}^-$  ions on the (111) face of an AgBr MC is able to capture an electron). After the electron (supplied by the reduction agent) is trapped by the complex, the complex can fragment via one of the following mechanisms:

- The silver ion (or atom) belonging to the complex shifts to the adjacent site that is above or next to the silver ion of the MC, resulting in the formation of  $\text{Ag}_2^+$ ;
- The captured by the complex electron attracts either a surface or an interstitial silver ion, with the same result of  $\text{Ag}_2^+$ .

Since  $\text{Ag}_2^+$  is a deep electron trap, the formation of  $\text{Ag}_2$  molecule, in the presence of the reduction agent, is highly probable (we note that the  $\text{Ag}_2$  molecules can migrate over the MC surface and form  $\text{Ag}_n$  clusters). After the fragmentation, the MC surface will contain an adsorbed  $\text{I}^{\cdot-}$  pair ( $(\text{I}^{\cdot-})_{\text{ads}}$ ), which is a very efficient hole trap. The appearance, as a result of reduction sensitization, of  $(\text{I}^{\cdot-})_{\text{ads}}$  on the surface of the tabular or octahedral AgBr MC is the cause of the 550nm PL, similarly to that observed in AgBr(I) MCs. This PL is due to radiative recombination between an electron from the AgBr conduction band and the hole



**Figure 3** Schematic diagram of the energy levels of different impurity centers in the reduction sensitized tabular or octahedral AgBr MC. The energy levels are shown relatively to the AgBr conduction (C) and valence (V) bands at  $T = 4.2\text{K}$ . Arrows indicate photoluminescence (PL) transitions with the numbers, given in nm, specifying  $\lambda_{\text{max}}$  of the corresponding PL band.

localized at pair iodide centers ( $(\text{I}^{\cdot-})_{\text{ads}}$ ) (Fig. 3, transition 1). This PL can be excited either by a direct absorption by the  $\text{I}^{\cdot-}$  ion (in  $(\text{I}^{\cdot-})_{\text{ads}}$ ) (the 442nm PLE maximum, Fig. 2, curve 1) or by absorption in AgBr [4, 6, 7].

If during the synthesis of AgBr MC the concentration of  $\text{Br}^-$  ions is kept low ( $p_{\text{Ag}} = 7.0$ ), then the cubic AgBr MCs are produced, and polyhalogenoargentate complexes are not formed. Therefore, reduction sensitization helps in formation of silver centers, and, firstly, of  $\text{Ag}_2$  molecules. The low temperature ( $T = 6\text{K}$ ) PL from cubic AgBr MCs consists of only one band with  $\lambda_{\text{max}} = 570\text{nm}$  [6a]. Since  $\text{Ag}_2$ -centers, located near positive kink site (+k) of the cubic AgBr MC, create localization levels for electrons [15], the 570nm PL is due to the recombination between a hole from the AgBr valence band and the electron localized at a neutral  $(+\text{kAg}_2)^{\cdot-}$  center (Fig. 3, transition 2). With the increase in temperature to 77K the  $\lambda_{\text{max}}$  of this band shifts to the 590-600nm due to the reduction in the AgBr band gap. Under the infra-red (IR) irradiation of AgBr MC, the intensity of the 570nm PL (Fig. 3, transition 2) decreases due to the release of the  $(+\text{kAg}_2)^{\cdot-}$ -center localized electron into the AgBr conduction band, in good agreement with the proposed here mechanism.

To establish the binding energies of electrons ( $E_D$ ) and holes ( $E_A$ ) shown in Fig. 3, we first determine the energy ( $E_0$ ) of zero-phonon ("pure" electronic) recombinations responsible for the PL bands with  $\lambda_{\text{max}} = 550\text{nm}$  ( $E_{\text{max}} = 2.25\text{eV}$ ), 570nm (2.17eV), 590nm (2.10eV), and 640nm (1.94eV). For this, we note that the

full width at half maximum (FWHM) of the PL bands in crystalline solids is mostly determined by the strengths of electron-phonon interaction and the Huang-Rhys constant ( $S_0$ ) [17] is often taken as its measure. If the interaction of the carriers with the lattice is weak ( $S_0 \ll 1$ ), the radiative transition occurs without significant contribution from the lattice vibrations. In the opposite case ( $S_0 \gg 1$ ) the PL develops into a Gaussian symmetric band, and the energy difference  $E = E_0 - E_{\text{max}}$  can be estimated as  $S_0 \hbar \omega_{\text{LO}}$ , where  $\hbar \omega_{\text{LO}}$  is the energy of the LO-phonon (for AgBr,  $\hbar \omega_{\text{LO}} = 0.017\text{eV}$ ). Since the FWHM of the AgBr MC PL is quite large, it can be assumed that  $S_0 \geq 10$ , and thus, we take that  $E_0 \approx E_{\text{max}} + 0.17\text{eV}$ . For the 570nm band, this gives  $E_0 = 2.34\text{eV}$ . Thus, the difference  $E_D = E_g - E_0$  gives the estimate for the energy of the electron localization at  $(+\text{kAg}_2)^{\cdot-}$ -centers, which for the AgBr ( $E_g = 2.70\text{eV}$ , at 4.2K) gives the value of  $E_D = 0.36\text{eV}$ . This value is lower than that predicted from the theory (0.68eV) [15].

As discussed earlier, the 550nm PL band from AgBr MCs, which appear after reduction sensitization is due to the recombination between an electron from the AgBr conduction band and a  $(\text{I}^{\cdot-})_{\text{ads}}^{\text{rel}}$ -center. This emission is thermally quenched ( $T < 80\text{K}$ ) with the activation energy of  $\Delta E \sim 0.05\text{eV}$ . Apparently, this recombination occurs through the excited state of the  $(\text{I}^{\cdot-})_{\text{ads}}^{\text{rel}}$ -center, which has the energy of  $\sim 0.05\text{eV}$  below the bottom of the AgBr conduction band; thus, the temperature quenching of this PL takes place via thermal excitation of the electron from the excited level into the AgBr conduction band. Then, knowing  $E_0$  (2.42eV) and  $\Delta E$  ( $\sim 0.05\text{eV}$ ) for the 550nm emission, we estimate that the ionization energy of an  $(\text{I}^{\cdot-})_{\text{ads}}^{\text{rel}}$  acceptor center is  $E_A = 0.23\text{eV}$ . When  $\text{I}^{\cdot-}$  from the  $(\text{I}^{\cdot-})_{\text{ads}}$  absorbs light (PLE maximums at  $\lambda = 330\text{nm}$  and  $442\text{nm}$ ) leads to the ionization of iodine. The resulting free electron can either recombine with an  $(\text{I}^{\cdot-})_{\text{ads}}^{\text{rel}}$ -center or get localized at a  $(+\text{kAg}_2)^{\cdot-}$ -center. Then, the recombination between the electron localized at  $(+\text{kAg}_2)^{\cdot-}$ -center ( $E_D = 0.36\text{eV}$ ) and the hole localized at an  $(\text{I}^{\cdot-})_{\text{ads}}^{\text{rel}}$ -center ( $E_A = 0.23\text{eV}$ ) gives rise to the PL with  $\lambda_{\text{max}} = 640\text{nm}$  (Fig. 3, transition 3;  $E_{\text{max}} = E_g - E_D - E_A - 0.17\text{eV}$ ; it is also assumed that the distance between the donor and acceptor centers is very large). The proposed recombination schemes are in good agreement with experimentally observed PLE spectra (Fig. 2, curves 1 and 4) and the different life times for the 550nm and 640nm PL bands [6,7].

The proposed here causes for the appearance of the 550nm and 640nm bands are, thus, in stark disagreement with those given in Refs. 6 and 7.

Our conclusions are further supported by the fact that treatment of AgBr emulsion layers in  $\text{AgNO}_3$  solution (which causes an appearance of silver centers on the surface of MCs) does not promote emergence of the 550nm band (Fig. 1, curve 3).

Reduction sensitization of AgBr MCs leads to substantial increase in the intensity of the 590nm PL band ( $E_{\text{max}} = 2.10\text{eV}$ ,  $E_0 = 2.27\text{eV}$ ), whose PL spectrum has two maximums at 325nm (3.81eV) and 430nm (2.88eV) (Fig. 2, curve 3) [3]. The energy difference between these maximums is 0.93eV; this corresponds to the energy of the spin-orbit splitting in the iodine atom, which suggests that the 590nm PL is due to an excited iodide ion located on the surface of AgBr MCs (transitions  $5p^6 \rightarrow 5p^6(^2P_{1/2})6s$  and  $5p^6 \rightarrow 5p^6(^2P_{3/2})6s$ ). We therefore propose that this ion belongs to the  $(\text{BrI})_{\text{ads}}^{\cdot-}$ -center located on the MC surface. This center

appears as a result of transformation of the adsorbed  $(\text{AgBrI})_{\text{ads}}^-$  complexes at reduction sensitization.

Therefore, the 590nm emission occurs via the following mechanism. Having absorbed the light (the PLE maximums at  $\lambda = 325\text{nm}$  and  $430\text{nm}$ ), the iodine ion is ionized by releasing the electron into the AgBr conduction band, resulting in the formation of a  $(\text{BrI}^0)_{\text{ads}}^{\text{rel}}$ -center. This electron is, then, trapped by a  $[\text{+kAg}_2]$ -center ( $E_D = 0.36\text{eV}$ ), and the 590nm PL appear as the DAP recombination, where  $[\text{+kAg}_2]$  is the donor and  $(\text{BrI}^0)_{\text{ads}}^{\text{rel}}$  is the acceptor ( $E_A = 0.07\text{eV}$ ;  $E_A = E_G - E_D - E_{\text{max}} - 0.17\text{eV}$ ;  $E_G = 2.70\text{eV}$ ) (Fig. 3, transition 4). This model is in agreement with the ODMR results obtained in Refs. 6, 7, if the acceptor g-factor ( $g = 1.99$ ) is associated with the  $(\text{BrI}^0)_{\text{ads}}^{\text{rel}}$ -center. For comparison, we note that  $g = 1.99$  is close to the g-factor value of  $V_k$ -centers ( $\text{Hal}_2^-$  - centers) in alkali-halide crystals.

The surface localized exciton  $[(\text{BrI}^0)_{\text{ads}}^{\text{rel}}e]$  is formed upon recombination between the conduction band electron and the  $(\text{BrI}^0)_{\text{ads}}^{\text{rel}}$ -center. It is also well known that bulk  $\text{I}_v^-$  ions create an acceptor level ( $\text{I}_v^0$ ) with  $E_A = 0.03\text{eV}$  [18] and that the iodine-localized exciton ( $\text{I}_v^0e$ ) is responsible for the 497nm PL ( $E_{\text{max}} = 2.50\text{eV}$ ) (see e.g., Ref. 18). Since the  $(\text{BrI}^0)_{\text{ads}}^{\text{rel}}$ -center energy level of is above that of  $\text{I}_v^0$  (by  $0.04\text{eV}$ ), we suggest that the surface localized exciton  $[(\text{BrI}^0)_{\text{ads}}^{\text{rel}}e]$  is responsible for the emission with  $E_{\text{max}} = 2.46\text{eV}$  ( $\lambda_{\text{max}} = 500\text{nm}$ , Fig. 3, transition 5).

If synthesis of AgBr MCs is done under low pBr ( $1.0 - 0.5$ ), the medium will contain not only, considered above, complexes of  $\text{AgBrI}$  and  $\text{AgI}_2^-$ , but also complexes of  $\text{AgBr}_2^-$ ,  $\text{AgBr}_3^{2-}$ ,  $\text{AgBr}_2\text{I}^{2-}$ , and  $\text{AgBrI}_2^{2-}$ . These complexes can adsorb on the surface of the octahedral MCs. During reduction sensitization, these complexes convert into  $(\text{BrBr})_{\text{ads}}^-$ ,  $(\text{BrBrBr})_{\text{ads}}^-$ ,  $(\text{BrBrI})_{\text{ads}}^-$ , and  $(\text{BrII})_{\text{ads}}^-$  centers. After these centers capture a hole, they transform in the corresponding centers in the relaxed state:  $(\text{BrBr}^0)_{\text{ads}}^{\text{rel}}$ ,  $(\text{BrBr}^0)_{\text{ads}}^{\text{rel}}$ ,  $(\text{BrBrI}^0)_{\text{ads}}^{\text{rel}}$ , and  $(\text{BrII}^0)_{\text{ads}}^{\text{rel}}$ .

Using data from 4.2K PL, we concluded that the emission bands with  $\lambda_{\text{max}} = 520\text{nm}$ ,  $540\text{nm}$ , and  $565\text{nm}$  are due to recombination of a conduction band electron with  $(\text{BrBrBr}^0)_{\text{ads}}^{\text{rel}}$ ,  $(\text{BrBrI}^0)_{\text{ads}}^{\text{rel}}$ , and  $(\text{BrII}^0)_{\text{ads}}^{\text{rel}}$ , respectively. The further investigation of the PLE spectra of these PL bands resulted in the conclusions that PLE maximums at  $455\text{-}460\text{nm}$ ,  $470\text{nm}$ , and  $490\text{nm}$  are due to light absorption by the  $\text{I}^-$ -ion from  $(\text{BrII})_{\text{ads}}^-$ , by the  $\text{Br}^-$ -ion from  $(\text{BrBrBr})_{\text{ads}}^-$  and by the  $\text{I}^-$ -ion from  $(\text{BrBrI})_{\text{ads}}^-$ , respectively. We note that a role of the surface  $\text{Br}^-$  and  $\text{I}^-$  ions in the appearance of the  $470\text{nm}$  and  $490\text{nm}$  maximums in the PLE spectra of AgBr MC has been previously reported in Ref. 19.

## Conclusions

The results of this paper are in good agreement with those of photographic and photoelectric measurements on reduction sensitized octahedral AgBr emulsions [20, 21]. It was concluded [21] that the increase of sensitivity during initial stages of reduction sensitization is due to creation of hole trap centers (so-called R-centers). According to our model, this takes place when polyhalogenoargentate complex anions transform into the corresponding "negatively charged fragments" (e.g.  $(\text{BrBrBr})_{\text{ads}}^-$ ,  $(\text{BrI})_{\text{ads}}^-$ , etc.). In the case of the low-pAg sensitization "negatively charged fragments" do not form. Instead, the silver centers that are electron traps are created [20]. The sensitivity increase under high-pH sensitization is determined by several

thermally stimulated reactions [22]:



which results in an appearance of the electron capture silver centers.

Finally, we would like to comment on magnetic properties of silver centers in AgBr emulsions. Light illumination of AgBr MCs results not only in formation of silver centers (particles) but also in an appearance of halide molecules such as  $\text{Br}_2$ ,  $\text{BrI}$ , and  $\text{I}_2$ . These molecules are efficient electron traps [19]. Thus, by capturing either photoelectrons or the electrons provided by the developer, these molecules become  $\text{Br}_2^-$ ,  $(\text{BrI})^-$ , and  $\text{I}_2^-$  anions, which in turn can adsorb on the silver centers. As these anions are paramagnetic the formation of the silver center and an adsorbed anion possesses paramagnetic properties. In contrast, at reduction sensitization, only silver centers appear; thus, no paramagnetic properties can be observed. The difference in the magnetic behavior of the silver centers obtained via reduction sensitized and light illumination has been reported in Ref. 23. We note that the explanation given in Ref. 23 differs from that presented here.

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## Author Biography

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