

On Differences in Photoluminescent and Photographic Characteristics of AgBr (100) and AgBr (111) Microcrystals I: Unsensitized and Reduction Sensitized Emulsions

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Abstract. A study has been carried out on photoluminescence (PL) and photoluminescence excitation (PLE) of unsensitized and reduction sensitized cubic and octahedral AgBr emulsions. It has been determined that the PL spectra of cubic and octahedral microcrystals differ. This difference is explained by the formation of polyhalogenoargentate complex anions (PHACA) during the synthesis of octahedral microcrystals. These PHACA adsorb on the microcrystal surface, resulting in appearance of PL bands which are not observed for cubic microcrystals. PHACA can be transformed, after capturing an electron from a reducing agent, into negatively charged fragments, which are efficient hole traps. It is found that AgI_2^- and AgBrI^- complexes, which can be formed during the synthesis of nominally pure AgBr octahedral microcrystals, play an important role in reduction sensitization. The PLE spectra of the 550 and 590 nm PL bands, which appear upon reduction sensitization of octahedral AgBr microcrystals, have maxima at 3.75 and 2.80 eV for the 550 nm band and 3.81 and 2.88 eV for the 590 nm band. The energy difference between these PLE maxima corresponds to the energy of the spin-orbit splitting in the iodine atom ground state. This leads to the conclusion that the negatively charged fragments responsible for the 550 and 590 nm PL bands contain iodide ions. Finally, our results show that the AgBr emulsion PL consists not only of microcrystal PL but also of the emission due to impurity centers formed in gelatin during synthesis of AgBr microcrystals. © 2007 Society for Imaging Science and Technology.

[DOI: 10.2352/J.ImagingSci.Technol.(2007)51:6(530)]

INTRODUCTION

Recent developments in digital photography have resulted in a substantial decrease in the use and applications of silver halide photographic materials. However, in our opinion, this tendency does not have to be accompanied by a decrease in the research into physical and chemical processes taking place during the formation of photographic sensitivity of AgBr microcrystals. Chemical sensitization of AgBr microcrystals and latent image formation are determined by the creation and evolution of impurity centers of various

dimensions—from molecules to relatively small clusters to nanocrystals (quantum dots). The formation mechanism of quantum size centers is one of the most exciting problems in current materials science. Thus, the results obtained in scientific photography could be of high interest for other areas of nanotechnology.

The synthesis of AgBr microcrystals is usually carried out via the double-jet precipitation at a constant pBr. Microcrystal morphology depends on pBr.^{1–5} At small pBr (pBr < 3.0) octahedral microcrystals are formed, whereas higher pBr results in cubic microcrystals. This effect of pBr on microcrystal morphologies is due to different polyhalogenoargentate complex anions (PHACA), which are formed only at low pBr. Adsorption of these complexes on microcrystals changes the crystal face growth rate and, consequently, microcrystals of a certain habit are evolved.^{1–5}

The morphology of AgBr microcrystals controls the properties and evolution of impurity centers that appear during chemical sensitization. For instance, it has been established^{6,7} that at the initial stages of reduction sensitization of octahedral AgBr microcrystals impurity centers appear which are hole traps (so-called R-centers),^{8,9} whereas reduction sensitization of cubic AgBr microcrystals results in the appearance of impurity centers, which are electron traps (so-called P-centers).^{8,9} It has been proposed^{10–12} that the hole trapping centers (R-centers) are silver dimers (Ag_2) located at a neutral site and the electron trap centers (P-centers) are the silver dimers located at a positively charged kink site (+K) on the AgBr surface. At the same time, Belous¹³ has proposed that extra surface Br_5^- and I_5^- anions that appear as a result of reduction sensitization of AgBr microcrystals (after silver center formation) play a part in the formation of the R-center (it must be remembered that I^- anions are always present in AgBr as an adventitious impurity). Thus, until now there has been no common explanation for either the formation mechanism of impurity centers during chemical sensitization or the role of these centers on photographic sensitivity.

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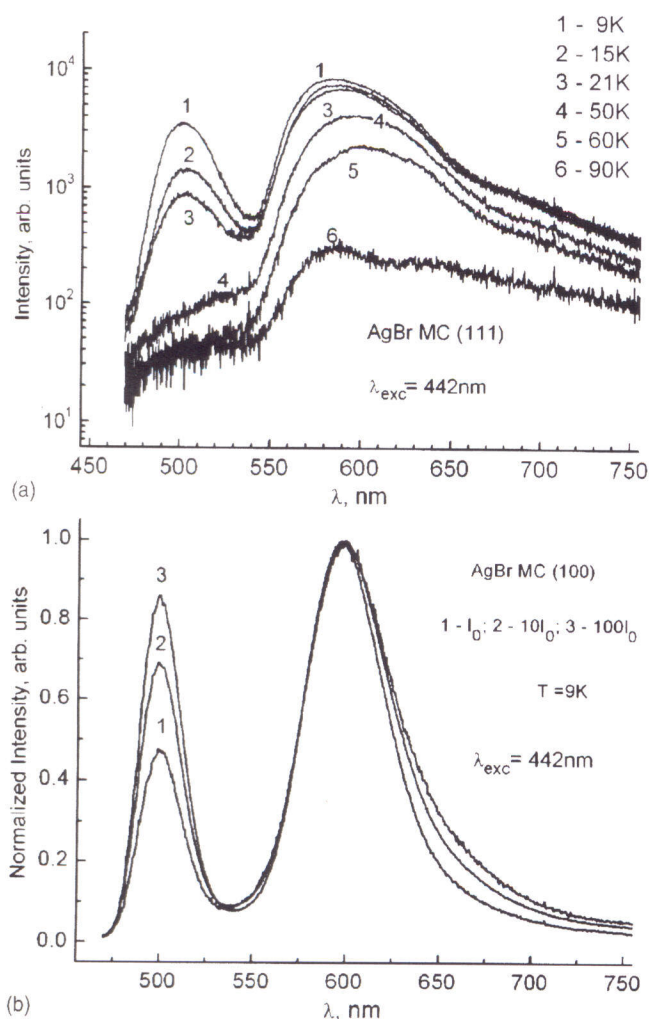


Figure 1. Photoluminescence spectra of octahedral (a) and cubic (b) AgBr microcrystals at different temperatures and excitation intensities (I_0).

Certain impurity centers appearing on chemical sensitization of photographic emulsions have been shown¹³⁻¹⁵ to induce new PL bands of emulsion microcrystals at low temperature. Therefore, the nature and functions of these impurity centers have been investigated by the luminescence spectroscopy method.¹³⁻¹⁵ It has been shown¹⁵⁻¹⁷ that during reduction sensitization of AgBr(I) emulsions, prepared by a single-jet method, both light sensitivity and the intensity of the emulsion microcrystal PL band with $\lambda_{\max} = 640-650$ nm increase at the initial stages of sensitization. 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 red emission ($\lambda_{\max} = 640-650$ nm) at low temperature ($T = 77$ K).

The PL measurements¹⁸ performed at $T = 4.2$ K on AgBr emulsions, obtained by the double-jet method, show that reduction sensitization not only increases the intensity of the 640 nm band but also leads to an appearance of a new PL band with $\lambda_{\max} = 550$ nm and an increase of the emission intensity in the spectral range of 580-590 nm.¹⁹ In the PLE spectrum of the 550 nm PL band there are several maxima:

at 257 nm (4.82 eV), 283 nm (4.38 eV) and 442 nm (2.80 eV),¹⁸ whereas the excitation spectrum of the 590 nm band has maxima at 254 nm (4.88 eV), 279 nm (4.44 eV), 325 nm (3.81 eV) and 430 nm (2.88 eV).¹⁶ It is important to note that the maximum at 442 nm is also observed in the PLE spectrum of the 640 nm PL band.

It has been shown²⁰⁻²² that if SnO₂ is used as the reduction sensitizing agent for AgBr emulsion the PL ($T = 6$ K) consists of the 550 and 640 nm bands, which have a characteristic PLE maximum at 442 nm. At the same time, reduction sensitization leads to an increase in the intensity of the 590 nm emission (PLE maximum at $\lambda = 430$ nm). Both results are consistent with those obtained in Refs. 16 and 18. The PL and PLE spectra presented in Refs. 20-22 are observed only from the reduction sensitized tabular or octahedral AgBr microcrystals that were synthesized in the reaction medium ($pAg = 10.0$, temperature of synthesis between 55°C and 70°C) with a relatively high concentration of Br⁻ ions. However, in the case of cubic microcrystals, which were synthesized at $pAg = 7.0$, the reduction sensitization leads to a single emission band with maximum at 570 nm.²⁰ The PLE spectrum of the 570 nm band (spectral region $\lambda > 400$ nm) does not have any characteristic maxima and its long wavelength edge coincides with the long wavelength edge of the absorption spectrum of AgBr.²⁰

It has been concluded²⁰⁻²² that the 550 nm band is due to a singlet-singlet transition (lifetime < 10 ns), whereas the 640 nm band is due to a triplet-singlet transition, within an excited Ag₂ center that appears as a result of reduction sensitization and is located next to a positive kink site on the microcrystal surface. The 590 nm band has been assigned to the donor-acceptor pair (DAP) radiative transition, in which an Ag₂⁺ center is an acceptor. Furthermore, these authors believe that the nature of luminescent centers in the reduction sensitized AgBr microcrystals as well as the mechanism of the luminescence is supported by the results they obtained from optically detected magnetic resonance (ODMR).

On the other hand, it has been noted¹⁶ that the 550 nm PL band ($T = 4.2$ K, characteristic excitation maximum at 442 nm), which appears in AgBr microcrystals after their reduction sensitization, is also observed from unsensitized AgBr(I) microcrystals. Thus, it was concluded¹⁶ that iodide ions take part in the emergence of this 550 nm PL band.

Therefore, there exist several points of view on the nature of the 550 nm PL band of reduction sensitized AgBr (111) microcrystals. The present work provides evidence that the 550 nm PL band is due to an adsorbed I⁻ pair $[(I^-)_{\text{ads}}]$, which appears as a result of transformation of the AgI₂⁻ complex upon reduction sensitization of octahedral AgBr microcrystals. Such AgI₂⁻ complexes always form during synthesis of nominally pure octahedral AgBr microcrystals due to adventitious iodide impurities. Furthermore, we show that other PHACA adsorbed on the surface of the octahedral microcrystals also play a key role in luminescent and photographic properties of octahedral AgBr emulsions. Moreover, since PHACA are not formed in cubic emulsions, AgBr (100) and AgBr (111) microcrystals must have differ-

ent photographically active impurity centers formed on their surfaces during reduction sensitization and, thus, exhibit very different luminescent as well as photographic characteristics. An important conclusion of our work is that the origin of photoluminescent and photographic properties obtained from studies of cubic microcrystals cannot be extended to octahedral and tabular microcrystals and vice versa.

EXPERIMENTAL

AgBr microcrystals were studied via temperature and intensity dependent PL as well as PLE. For excitation we used either a dual wavelength (325 nm or 442 nm) HeCd laser, a Xenon lamp coupled with a monochromator, or a nitrogen pulsed laser (337 nm, 4 ns pulse width, 20 Hz repetition rate). The 4.2 K measurements were performed with the use of a MPF-4 spectrofluorometer; the samples resided within liquid helium in an in-house-made cryostat. For low temperature other measurement samples were cooled in a closed cycle refrigerating system with the lowest temperature of 9 K. In this case, the PL was dispersed through a $\frac{3}{4}$ meter monochromator and directed onto a GaAs photomultiplier tube connected to a SR400 photon counter (5 ns pulse-pair resolution; 0.4 s gate and 0.2 s dwell time).

The microcrystals (average size is 0.24 μm) were synthesized in aqueous gelatin solution (5%) via a double-jet precipitation under the following conditions: pH 6.5, $T=55^\circ\text{C}$, $p\text{Br}=0.8$ (octahedral microcrystals, Sample A) and $p\text{Br}=3.2$ (cubic microcrystals, Sample B).

PHOTOLUMINESCENCE OF UNSENSITIZED AgBr MICROCRYSTALS

Role of Polychalogenoargentate Complex Anions in Luminescent and Photographic Characteristics of AgBr (111) Microcrystals

The PL spectra of octahedral and cubic microcrystals (Samples A and B) are shown in Figures 1(a) and 1(b). Such microcrystals were separated from gelatin by centrifugation. In the PL spectra of both samples A and B at $T < 50$ K we observed a band with $\lambda_{\text{max}} = 497$ nm. This band was associated with an iodide-bound exciton and described in several papers.²³⁻²⁶ On the other hand, PL of microcrystals at $\lambda > 540$ nm depends on $p\text{Br}$ in the course of synthesis. In the case of cubic microcrystals ($p\text{Br}=3.2$) there is only one band with $\lambda_{\text{max}}=600$ nm ($T=9$ K), whereas in the case of octahedral microcrystals ($p\text{Br}=0.8$) PL in the range $\lambda > 540$ nm consists of several overlapping bands [Figs. 1(a) and 1(b)]. Obviously, this difference is related to conditions during microcrystal synthesis. At $p\text{Br}=0.8$ and $T=55^\circ\text{C}$, when octahedral or tabular microcrystals are formed, there are different PHACA in the reaction mixture, such as AgBr_2^- , AgBr_3^{2-} , AgBr_4^{3-} , AgBrI^- , $\text{AgBr}_2\text{I}^{2-}$, AgI_2 , and AgI_3^{2-} (see Ref. 27; iodide ions are present in the reaction mixture as uncontrolled impurities). Not only a high concentration of bromide ions, but also inefficient mixing can create high local halide concentration²⁸ that facilitates the formation of PHACA. These complexes may be adsorbed on the surface

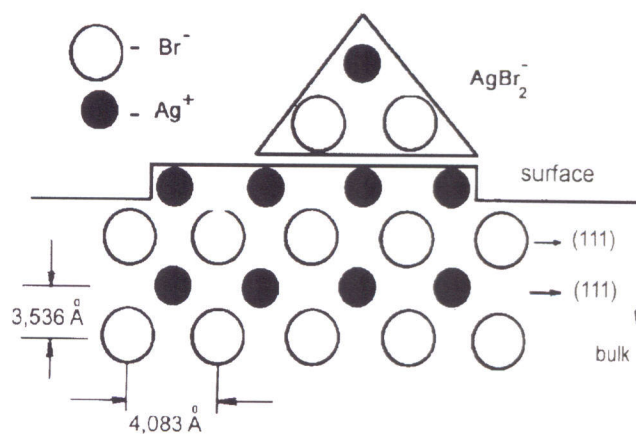


Figure 2. Schematic diagram of AgBr₂⁻ complex adsorbed on a silver islet (shown as a step).

of already formed octahedral microcrystals consisting of (111) AgBr lattice faces.

An ideal (111) surface of AgBr consists of alternate succession of Ag⁺ and Br⁻ layers with hexagonal symmetry. The distance between layers is 3.536 Å. In excess of Br⁻ ions in the reaction mixture, the microcrystal surface layer consists of Br⁻ with different size islets of Ag⁺ ions formed on this surface. (See also Ref. 29 and discussion therein of the Hamilton and Brady model.³⁰) Negatively charged PHACA can be adsorbed on such Ag⁺ islets, as shown for AgBr₂⁻ in Figure 2. In this case the negative charge of Br⁻ or I⁻ is partially compensated for by Ag⁺ ions. Configuration of this complex (Ag⁺ ion located above adsorbed Br⁻ ions) closely resembles the arrangement in which an Ag⁺ ion is located above two Br⁻ ions on the (111) face of AgBr microcrystal. This Ag⁺ ion is able to capture an electron.³¹

Given the above considerations, it can be assumed that adsorbed PHACA, whose negative charge is partially compensated for by surface silver ions, can create electron traps. Accordingly, it is possible that the adsorbed complexes can participate in reactions during microcrystal synthesis and chemical sensitization of an emulsion. In turn, these reactions could alter the complexes themselves. For example, as a result of some reducing process (either due to the reducing ability of gelatin or reduction sensitization), after an electron is localized by an adsorbed complex a silver ion or atom could be displaced from the complex into a neighboring position beside a silver ion on the (111) face, thereby creating Ag₂⁺. It is plausible that such an event could also result from the attraction between localized electron and interstitial silver ion. An electron in an antibonding orbital of the complex could lead to the former process, whereas an electron in a bonding orbital could result in the latter process. A molecular Ag₂⁺ ion is a deep electron trap; after capturing an electron from a reducing agent it becomes Ag₂. Such molecules can stay by the remaining negatively charged fragments (NCFs) of the adsorbed complex (in the case of AgBr₂⁻ complex it is (Br⁻Br⁻)_{ads}), or migrate from it and aggregate to form a silver cluster (e.g., see Ref. 32).

These negatively charged fragments are efficient hole traps. Thus, the simultaneous presence of adsorbed com-

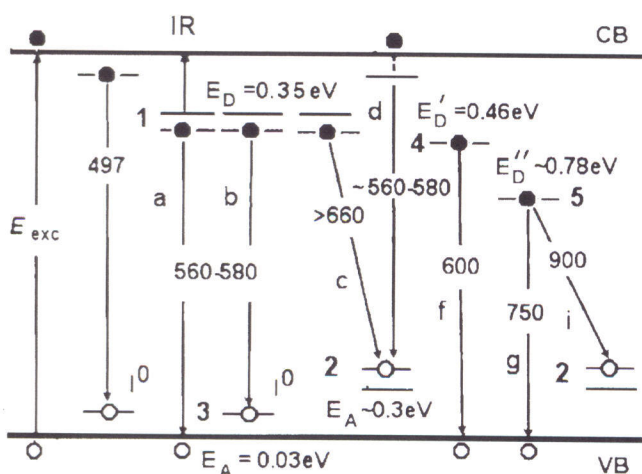


Figure 3. The energy levels scheme of some of the centers of AgBr(111) microcrystals: 1-[PHACA]_{ads}e; 2-[NCF]h; 3-I⁰; 4-[+DK(Ag₂S)₂]e; 5-[+DK(Ag₂S)₂Ag_n]e (n=1 or 2). Here, e and h are electron and hole localized on shown centers. The energy levels are shown relative to the AgBr conduction (CB) and valence (VB) bands. Arrows indicate emission transitions with numbers, given in nm, specifying λ_{\max} of a corresponding PL band.

plexes and negatively charged fragments on an octahedral surface brings about creation of a whole system of electron and hole trapping energy levels. Participation of these localized charge carriers in various recombination processes explains several overlapping bands observed in PL spectra of octahedral AgBr microcrystals at $\lambda > 540$ nm [Fig. 1(a)].

It has been shown previously¹³ that if AgBr or AgBr(1) PL occurs as a result of recombination of a localized electron and a valence band hole (the Lambe-Klick mechanism) or by the DAP mechanism, then illumination of a sample by infrared (IR) light leads to PL quenching without a PL flash. The reason for this is release of electrons from localization levels (Figure 3, transition IR). The PL at $\lambda = 560-580$ nm results from transitions a and b shown in Fig. 3 because in the case of octahedral AgBr microcrystals optical quenching without PL flash is observed. It is well known, I⁻ ion in an AgBr lattice position produces a hole localization level with $E_A = 0.03$ eV²⁵; thus, at $T < 50$ K emission from octahedra in the 560–580 nm range can result from recombination of an electron localized by the adsorbed complex with I⁰ (Fig. 3, transition b; electron localization level depth is denoted by E_D). At $T > 50$ K PL arises according to the Lambe-Klick mechanism (Fig. 3, transition a).

The radiation energy E_0 (the zero-phonon transition) of such a DAP recombination (Fig. 3, transition b, PL band with $\lambda_{\max} = 580$ nm, $E_{\max} = 2.14$ eV) is described by $E_g - (E_D + E_A)$ where E_g is the AgBr band gap energy ($E_g = 2.69$ eV, $T = 9$ K) and in the assumption that the Coulomb interaction is negligible because of the large distance between donors and acceptors. The value of $h\nu_{\text{lum}} = E_0$ is not the same as the photon energy (E_{\max}) corresponding to the PL peak. The reason is the electron-phonon coupling in solids and in AgBr, in particular. This interaction is also responsible for broad PL bands. The measure of the electron-phonon coupling is a so-called Huang-Rhys factor, S_0 .³³ If interaction of an electron with the lattice is weak, S_0 is small

(when transition takes place without contribution of lattice vibrations $S_0 = 0$). When radiation results from an exciton localized on iodide ion in AgBr, $S_0 = 9.64$ (Refs. 23 and 34) (interaction with longitudinal optical (LO) phonons having energy $\hbar\omega_{\text{LO}} = 0.017$ eV). For $S_0 \gg 1$, PL bands have the Gaussian shape with peak energy, $E_{\max} = E_0 - S_0\hbar\omega_{\text{LO}}$; in this case $S_0 = p$, where p is the most probable number of phonons involved in the transition. For broad bands observed in the AgBr PL, we take $S_0 \approx 10$. Therefore, $E_0 = E_{\max} + 0.17$ eV. This correction should be taken into account when determining the pure electron (zero-phonon) transition energy E_0 .

For the 580 nm PL band, $E_0 = 2.31$ eV. Thus, $E_A = 0.03$ eV, which leads to $E_D = 0.35$ eV (see Fig. 3). At room temperature electron trap lifetime (trap depth ~ 0.35 eV) is longer than the time, τ , required for a mobile silver ion to neutralize this electron ($\tau \approx 10^{-6}$ s). This fact can explain one of the possible mechanisms of PHACA transformation with Ag₂⁺ formation.

The electrons localized at various adsorbed PHACA ([PHACA]_{ads}e-centers) can recombine not only with I⁰ and the AgBr valence band holes, but also with holes localized at negatively charged fragments ([NCF]h-centers). If we assume that the binding energy of the hole at a certain negatively charged fragment is $E_A \approx 0.3$ eV (see also next section), then the radiative recombination within {[PHACA]_{ads}e-[NCF]h} pairs can explain the appearance of the PL bands in the spectral range with $\lambda > 660$ nm (Fig. 3, transition c). In addition, the AgBr conduction band electron can recombine with [NCF]h via an excited level (see also next section), which causes appearance of the PL bands with $\lambda_{\max} \approx 550-590$ nm (Fig. 3, transition d).

Synthesis of cubic microcrystals takes place at $p\text{Br} > 3.0$. At these $p\text{Br}$ levels PHACA are not formed, and only two PL bands with maxima at 497 and 600 nm are observed [Fig. 1(b)]. Since the emission band with $\lambda_{\max} = 600$ nm is observed only if microcrystal synthesis is carried out in the presence of gelatin (see also Ref. 16), this band is a result of interaction of gelatin with AgBr. It is known that there are sulfur-containing impurities in gelatin. The interaction of gelatin sulfur-containing impurities with AgBr leads to formation of surface Ag₂S molecules, which can migrate over the microcrystal surface and aggregate into dimers, trimers, and larger clusters.^{35,36}

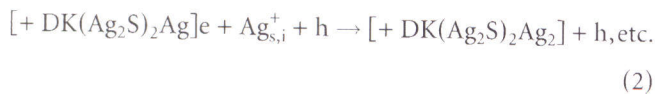
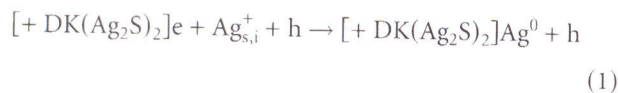
In order to determine the mechanism of appearance of the 600 nm PL band we note the following:

- The change of the excitation intensity by a factor 100 does not lead to a spectral shift of this PL band [Fig. 1(b), curves 1–3]; this corresponds to the case when emission is due to the recombination between a conduction band electron and a localized hole (transition 1) or due to the recombination between a valence band hole and a localized electron (transition 2).
- Irradiation of the sample by IR light results in quenching of the orange-red emission without PL flash. In the case of AgBr this is characteristic of tran-

sition 2 (see, e.g., Ref. 13; the IR light releases the electron from the recombination level).

Since Ag_2S molecules adsorbed on the AgBr surface do not create localization levels for electrons,³⁷ it is reasonable to assume that the PL band with $\lambda_{\text{max}}=600$ nm is due to the recombination between a hole from the AgBr valence band and the electron localized at a $[\text{+DK}(\text{Ag}_2\text{S})_2]$ -center³⁷ (here $[\text{+DK}(\text{Ag}_2\text{S})_2]$ center is a $(\text{Ag}_2\text{S})_2$ dimer, which is located next to a double positive kink site (+DK) in AgBr³⁷). The 600 nm PL band has a very large full-width-at-half-maximum (FWHM), which suggests a strong electron-phonon coupling. In this case the energy of zero-phonon transition (E_0) can be estimated from the short wavelength edge of the band. For this band, it corresponds to $\lambda \approx 550\text{--}555$ nm (i.e., $E_0 \approx 2.24$ eV). The same value for E_0 is obtained with the use of the Hung–Rhys theory.³³ Furthermore, since the valence band hole recombines with a $[\text{+DK}(\text{Ag}_2\text{S})_2]e$ -center, which has the formal charge $-\frac{1}{2}$ upon electron (e) trapping,³⁸ the recombination takes place without the hole's initially occupying an excited level (Fig. 3, transition f). Thus, using the values of the AgBr band gap ($E_g=2.7$ eV, $T=4.2$ K) and $E_0=2.24$ eV we estimate that a $[\text{+DK}(\text{Ag}_2\text{S})_2]$ creates a localization level for an electron with the depth $E'_D=0.46$ eV. This value is in good agreement with that given in Ref. 37, based on computer calculations. Octahedral microcrystals also have an emission band with $\lambda_{\text{max}}=600$ nm, but it is masked by intense emission resulting from adsorbed PHACA.

Temperature quenching ($T>77$ K) of the 600 nm PL band occurs via neutralization of a trapped electron by a mobile interstitial or surface silver ion (Ag_{is}^+); the activation energy of the quenching is $\varepsilon=0.11$ eV, which corresponds to the Ag_{is}^+ translational energy (see, e.g. Ref. 13). The ionic quenching mechanism can be described by the following reactions (here h denotes a hole):



The centers that appear as results of reactions (1) or (2) determine a new PL band with $\lambda_{\text{max}}=750$ nm ($E_{\text{max}}=1.65$ eV)¹³ (Fig. 3, transition g), which can be quenched by the IR light without the PL flash. It suggests that such an emission results from recombination of an electron localized by a $[\text{+DK}(\text{Ag}_2\text{S})_2\text{Ag}^0]$ - or a $[\text{+DK}(\text{Ag}_2\text{S})_2\text{Ag}_2]$ -center with a hole from the AgBr valence band. Given $E_{\text{max}}=1.65$ eV, we get $E_0=E_{\text{max}}+0.17$ eV and the depth of the electron trap $E'_D=2.6-1.82=0.78$ eV ($E_g=2.6$ eV at $T=80$ K; see Fig. 3). Reactions (1) and (2) correspond to the process of latent image formation of unsensitized AgBr emulsions.

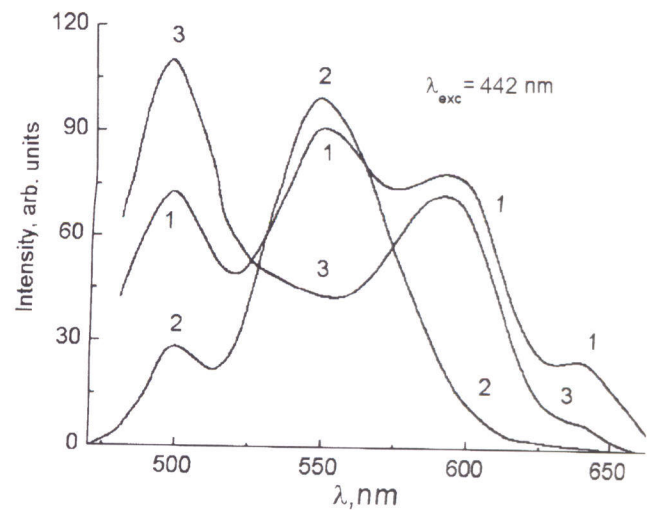


Figure 4. Photoluminescence spectra ($T=4.2$ K) of AgBr emulsions after reduction sensitization (curve 1) and Sample C (curve 3). For comparison PL of AgBr(I) emulsions is also shown (curve 2).

The $[\text{+DK}(\text{Ag}_2\text{S})_2\text{Ag}_m]$ -centers ($m=1$ or 2) can appear in octahedral microcrystals owing to the reduction function of gelatin. In the presence of the negatively charged fragments, this can result in the DAP PL with $\lambda_{\text{max}}=900$ nm (Fig. 3, transition i). A 900 nm PL band was observed from sheet AgBr microcrystals.³⁹

DISTINCTIONS IN PHOTOLUMINESCENCE AND PHOTOGRAPHIC PROPERTIES OF REDUCTION SENSITIZED CUBIC AND OCTAHEDRAL AgBr EMULSIONS

The results presented in the previous sections lead to conclusions that the adsorbed PHACA exist on the surface of octahedral AgBr microcrystals and that these $[\text{PHACA}]_{\text{ads}}$ are electron traps. Upon electron capture, the $[\text{PHACA}]_{\text{ads}}$ can transform into negatively charged fragments. Next, we present results that detail an important role of PHACAs in the reduction sensitization of photographic emulsions.

As discussed in the introduction, reduction sensitization of AgBr emulsions, obtained by the double-jet method, leads to an appearance of a new PL band with $\lambda_{\text{max}}=550$ nm and an increase of the emission intensity in the spectral range of 580–590 nm (Figure 4, curve 1).^{18,19} In the PLE spectrum of the 550 nm band there are several maxima: at 257 nm (4.82 eV), 283 nm (4.38 eV) and 442 nm (2.8 eV) (Figure 5, curve 1),¹⁸ whereas the excitation spectrum of the 590 nm band has maxima at 254 nm (4.88 eV), 279 nm (4.44 eV), 325 nm (3.81 eV) and 430 nm (2.88 eV) (Figure 5, curves 2, 3).¹⁶ It is important to note that the maximum at 442 nm is also observed in the PLE spectrum of the 640 nm PL band (Fig. 5, curve 4). The two narrow PLE maxima at 257 nm (254 nm) and 283 nm (279 nm) are owing to the creation of the anion exciton in the Γ -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 Γ -point (transition $\Gamma_8^- \rightarrow \Gamma_6^+$ and $\Gamma_6^- \rightarrow \Gamma_6^+$),⁴⁰ which is very close to energy of the spin-orbit splitting of the free bromine atom ground state (0.44 eV). Since the energy of anion exciton (Γ^- -exciton) is larger than the energy of the

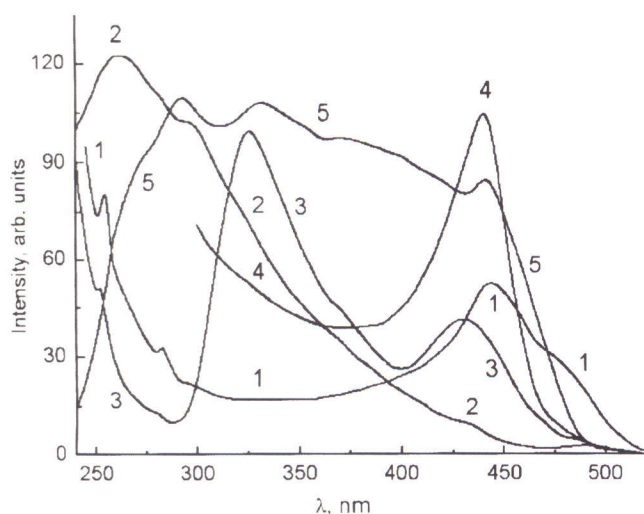


Figure 5. Photoluminescence excitation spectra ($T=4.2$ K) of AgBr emulsion for the monitoring wavelengths of 550 nm (curve 1), 590 nm (curves 2, 3) and 640 nm (curve 4) before (curves 1, 3, 4) reduction sensitization. Curve 5 is PLE spectrum of AgBr(I) emulsion for the monitoring wavelength of 550 nm.

indirect band gap in AgBr, this exciton auto-ionizes into free electron and hole,^{41,42} which further participate in recombination processes.

It has been noted¹⁶ that the 550 nm PL band ($T=4.2$ K), with characteristic excitation maximum at 442 nm, that appears in AgBr microcrystals after their reduction sensitization, is also observed from unsensitized AgBr(I) microcrystals. In Fig. 4 (curve 2) we show, as an example, the PL spectrum ($T=4.2$ K) of AgBr(I) emulsion (3 mol % AgI) with octahedral microcrystals,⁴³ whereas its PLE spectrum is shown in Fig. 5 (curve 5).⁴⁴ The excitation spectra of the green emission of AgBr(I) shows the following maxima: $\lambda=290$ nm (4.28 eV, excitonic absorption), $\lambda=330$ nm (3.75 eV), and $\lambda=442$ nm (2.80 eV). The 550 nm PL band from AgBr(I) microcrystals is determined by the presence of pair iodide centers (two nearest neighbor iodide ions $(I^-)^{45}$) in the microcrystals. The existence of the 330 and 442 nm PLE maxima is completely consistent with this center's luminescence model. These maxima are due to the light absorption by iodide ion: transitions $5p^6 \rightarrow 5p^5(^2P_{1/2})6s$ and $5p^6 \rightarrow 5p^5(^2P_{3/2})6s$. Moreover, as expected, the energy difference between these excitation maxima is 0.95 eV, which coincides with the energy of the spin-orbit splitting of the iodine atom ground state. Since the energy that corresponds to the maxima in the excitation spectrum is larger than the AgBr bandgap, the excited iodide ion ionizes, and the resulting free electron recombines with the "relaxed" $(I^-)^{rel}$ -center, resulting in the 550 nm luminescence.

The appearance of pair iodide centers during reduction sensitization of AgBr emulsions can be explained as follows. The 550 nm PL band appears after reduction sensitization of AgBr emulsions only when microcrystal synthesis is carried out under a high concentration of Br^- ions. Under such conditions, a number of PHACAs appear in the reaction medium.²⁷ KBr and NaBr solutions (used for microcrystal

synthesis) always contain some iodide impurities;⁴⁶ thus, depending on the chemical purity of KBr and NaBr, the reaction medium can contain not only $AgBr_2^-$ and $AgBr_3^{2-}$, but also $AgBrI^-$, $AgBr_2I^{2-}$, $AgBrI_2^{2-}$, AgI_2^- , and AgI_3^{2-} . Minute amounts of AgI_2^- can be created if the iodide concentration is about 10^{-6} M at 25°C and 10^{-4} M at 250°C.^{47,48} Thus, for the synthesis temperatures between 55°C and 70°C, the AgI_2^- centers are created if the concentration of iodide ions is about 3×10^{-6} M. Such a concentration of iodide ions can be easily achieved in KBr and NaBr solutions at pBr between 1.5 and 0.5. In this case an AgI_2^- complex is being formed even during synthesis of nominally pure AgBr microcrystals. These conclusions are based on the average values for the concentration of Br^- and I^- in the solution. Moreover, because of ineffective mixing, it is possible that the local concentrations of Br^- and I^- ions are substantially higher than the average values.²⁸ This results in the formation of not only AgI_2^- but also such complexes as $AgBrI^-$, $AgBr_2I^{2-}$, $AgBrI_2^{2-}$, and AgI_3^{2-} . It must be noted that a decrease in the synthesis temperature will further enhance the formation of these complexes.

The AgI_2^- complexes (as well as the other) can adsorb on the surface of the tabular and octahedral AgBr microcrystals. It is well known that the surface of the tabular and octahedral AgBr microcrystals consists of Br^- ions, which are partially covered by silver ion islets of different sizes. A PHACA (e.g. 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 Ag^+ , the adsorbed complex behaves as an electron trap (see above). After the electron (supplied by the reduction agent) is trapped by the complex, the complex can fragment into Ag_2 and NCF (in this case NCF is an adsorbed I^-I^- pair $[(I^-)_{ads}]$ (see above). For comparison, we note that in the Bridgeman-grown AgBr monocrystals the iodine pair centers appear at iodine concentrations higher than $8.2 \times 10^{18} \text{ cm}^{-3}$,⁴⁹ whereas in reduction sensitized AgBr emulsion microcrystals these centers can be formed at substantially lower iodine concentrations.

The Ag_2 molecules can migrate over the microcrystal surface and form Ag_n clusters. After the fragmentation, the microcrystal surface will contain isolated $(I^-)_{ads}$, which are very efficient hole traps. Comparing photoluminescence from reduction sensitized AgBr and unsensitized AgBr(I) microcrystals, we propose that the appearance of $(I^-)_{ads}$ on the surface of the tabular or octahedral AgBr microcrystals after reduction sensitization is the cause of the 550 nm PL. This PL is due to radiative recombination between an electron from the AgBr conduction band and the hole localized at pair iodide centers $[(I^-)_{ads}^{rel}]$ (Figure 6, transition 1). This PL can be excited either by a direct absorption by the I^- ion in $(I^-)_{ads}$ (the 330 and 442 nm PLE maxima, Fig. 5, curve 1) or by absorption in AgBr.

If during the synthesis of AgBr microcrystals the concentration of Br^- ions is kept low (pAg=7.0), i.e., PHACAs are not formed, the cubic AgBr microcrystals are produced.

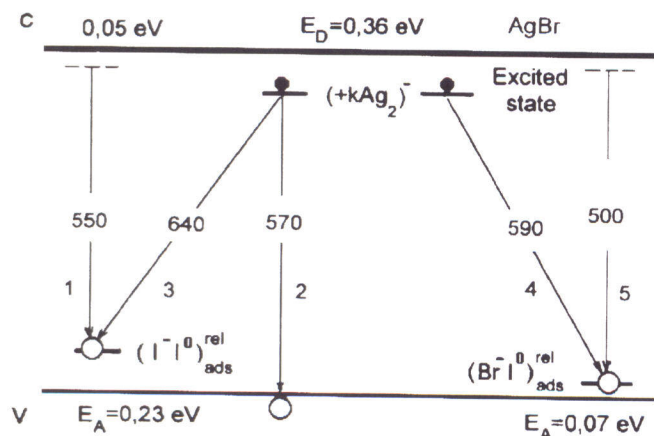


Figure 6. Schematic diagram of the energy levels of different impurity centers in the reduction sensitized tabular or octahedral AgBr microcrystals. The energy levels are shown relatively to the AgBr conduction (C) and valence (V) bands at $T=4.2$ K. Arrows indicate emission transitions with the numbers, given in nm, specifying λ_{\max} of the corresponding PL band.

Therefore, reduction sensitization facilitates the formation of silver centers, and, first of all, of Ag_2 molecules. The low temperature ($T=6$ K) PL from cubic AgBr microcrystals consists of only one band with $\lambda_{\max}=570$ nm.²⁰ Since Ag_2 -centers, located near (+K) of the cubic AgBr microcrystals, create localization levels for electrons,^{50,51} the 570 nm PL is due to the recombination between a hole from the AgBr valence band and the electron localized at a $(+\text{KAg}_2)^-$ center (Fig. 6, transition 2). With the increase in temperature to 77 K the λ_{\max} of this band shifts to the 590–600 nm due to the reduction in the AgBr band gap. Under IR irradiation of AgBr microcrystals, the intensity of the 570 nm PL (Fig. 6, transition 2) decreases due to the release of the $(+\text{KAg}_2)^-$ -center localized electron into the AgBr conduction band. This is in good agreement with the proposed mechanism of the 570 nm PL band.

To establish E_D and E_A shown in Fig. 6, we first determine E_0 for the PL bands with $\lambda_{\max}=550$ nm (2.25 eV), 570 nm (2.17 eV), 590 nm (2.10 eV), and 640 nm (1.94 eV). It has been determined earlier that for broad AgBr PL bands, $E_0=E_{\max}+0.17$ eV. For the 570 nm band, this gives $E_0=2.34$ eV and $E_D=0.36$ eV ($E_D=E_g-E_0$, $E_g=2.70$ eV, at 4.2 K). We note that this value of E_D is in good agreement with 0.32 eV predicted by theory for the $(+\text{KAg}_2)^-$ center.⁵¹

As discussed earlier, the 550 nm PL band from AgBr microcrystals, which appear after reduction sensitization, is due to the recombination between an electron from the AgBr conduction band and a $(\text{I}^- \text{I}^0)_{\text{ads}}^{\text{rel}}$ -center. This emission is thermally quenched ($T < 80$ K) with the activation energy of $\Delta E \sim 0.05$ eV. Apparently, this recombination occurs through the excited state of the $(\text{I}^- \text{I}^0)_{\text{ads}}^{\text{rel}}$ -center (Fig. 6, transition 1), which has the energy of ~ 0.05 eV below the bottom of the AgBr conduction band; thus, the temperature quenching of this PL takes place via thermal release of the electron from the excited level into the AgBr conduction band. Then, knowing E_0 (2.42 eV) and ΔE (~ 0.05 eV) for the 550 nm emission, we estimate that the binding energy of

an $(\text{I}^- \text{I}^0)_{\text{ads}}^{\text{rel}}$ acceptor center is $E_A=0.23$ eV. When I^- from the $(\text{I}^- \text{I}^0)_{\text{ads}}^{\text{rel}}$ absorbs light (PLE maxima at $\lambda=330$ and 442 nm) it again leads to ionization of iodide anion. The resulting free electron can either recombine with an $(\text{I}^- \text{I}^0)_{\text{ads}}^{\text{rel}}$ -center or become trapped at a $(+\text{KAg}_2)^-$ -center. Then, the recombination between the electron localized at $(+\text{KAg}_2)^-$ -center ($E_D=0.36$ eV) and the hole localized at an $(\text{I}^- \text{I}^0)_{\text{ads}}^{\text{rel}}$ -center ($E_A=0.23$ eV) gives rise to the PL with $\lambda_{\max}=640$ nm (Fig. 6, transition 3; $E_{\max}=E_g-E_D-E_A-0.17$ eV). It is also assumed in this model 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. 5, curves 1 and 4) and the different lifetimes of the 550 and 640 nm PL bands.^{20–22} Thus, the mechanisms proposed here for the appearance of the 550 and 640 nm bands are in stark disagreement with those given in Refs. 20–22.

Our conclusions are further supported by the fact that the bathing of unsensitized AgBr emulsion¹⁹ layers in 0.1 M AgNO_3 solution at 20°C (Sample C), which causes appearance of silver centers on the surface of the microcrystals, does not promote emergence of the 550 nm band (Fig. 4, curve 3).

Reduction sensitization of AgBr microcrystals leads to substantial increase in the intensity of the 590 nm PL band ($E_{\max}=2.10$ eV, $E_0=2.27$ eV), whose PLE spectrum has two maxima at 325 nm (3.81 eV) and 430 nm (2.88 eV) (Fig. 5, curve 3).¹⁶ The energy difference between these maxima is 0.93 eV; this corresponds to the energy of the spin-orbit splitting in the iodine atom ground state, which suggests that these maxima are due to an excited iodide ion located on the surface of AgBr microcrystals: transitions $5p^6 \rightarrow 5p^5(^2P_{1/2})6s$ and $5p^6 \rightarrow 5p^5(^2P_{3/2})6s$. We therefore propose that this ion belongs to the $(\text{Br}^- \text{I}^0)_{\text{ads}}^{\text{rel}}$ -center located on the microcrystal surface. This center appears as a result of the transformation of the adsorbed $(\text{AgBrI})_{\text{ads}}^-$ complexes on reduction sensitization. Therefore, the 590 nm emission occurs via the following mechanism. Having absorbed the light (the PLE maxima at 325 nm and 430 nm), the iodide ion is ionized by releasing the electron into the AgBr conduction band, resulting in the formation of a $(\text{Br}^- \text{I}^0)_{\text{ads}}^{\text{rel}}$ -center. This electron is then trapped by a $[\text{KAg}_2]^-$ -center ($E_D=0.36$ eV), and the 590 nm PL appear as a pair recombination, where $[\text{KAg}_2]^-$ is the donor and $(\text{Br}^- \text{I}^0)_{\text{ads}}^{\text{rel}}$ is the acceptor ($E_A=0.07$ eV; $E_A=E_g-E_D-E_{\max}-0.17$ eV; $E_g=2.70$ eV) (Fig. 6, transition 4). This model is in agreement with the ODMR results obtained in Refs. 20–22 if the acceptor g-factor ($g=1.99$) is associated with the $(\text{Br}^- \text{I}^0)_{\text{ads}}^{\text{rel}}$ -center. For comparison, we note that $g=1.99$ is close to the g-factor value of homonuclear or heteronuclear V_k^- or V_F^- -centers (Hal_2^- -centers) in alkali-halide crystals.^{52–54} It should be noted that the $g=1.99$ resonance (the $(\text{Br}^- \text{I}^0)_{\text{ads}}^{\text{rel}}$ -center) is not observed on reduction sensitized cubic microcrystals obtained at $\text{pAg}=7.0$.²⁰

The surface localized exciton $[(\text{Br}^- \text{I}^0)_{\text{ads}}^{\text{rel}} e]$ is formed upon recombination between the conduction band electron and the $(\text{Br}^- \text{I}^0)_{\text{ads}}^{\text{rel}}$ -center. It is also well known that bulk I_2^-

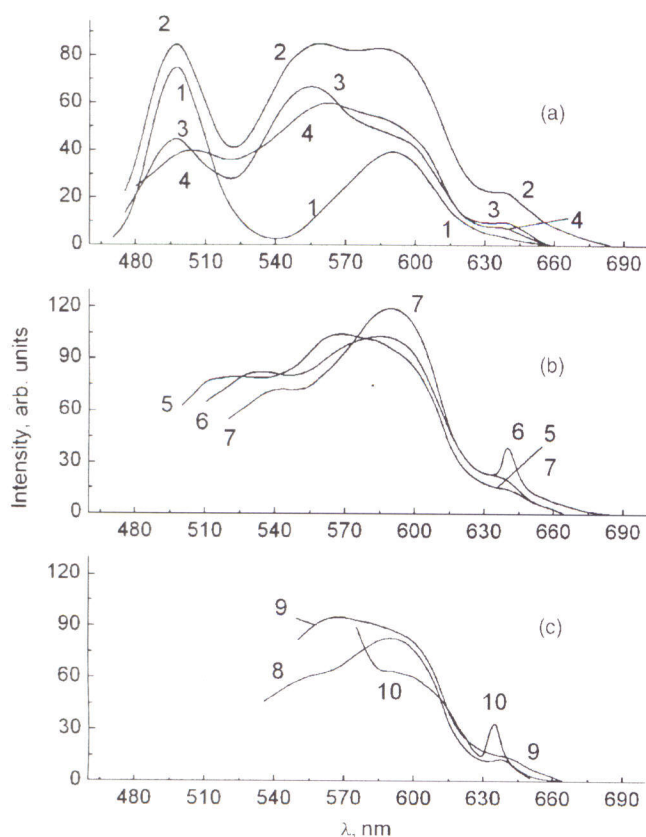


Figure 7. Photoluminescence ($T=4.2$ K) spectra of reduction sensitized AgBr octahedral emulsion. The PL was excited by monochromatic light (wavelengths are in nm): (a) 1–365, 2–440, 3–450, and 4–460; (b) 5–470, 6–480, 7–490; and (c) 8–500, 9–510, 10–530.

ions create an acceptor level (I_V^0) with $E_A=0.03$ eV^{25,34} and that the iodide-localized exciton (I_V^0e) is responsible for the 497 nm PL ($E_{\max}=2.50$ eV) (see e.g., Ref. 23–26 and 34). Since the $(Br^-I^0)_{\text{ads}}^{\text{rel}}$ -center energy level of is above that of I_V^0 (by 0.04 eV), we suggest that the surface localized exciton $[(Br^-I^0)_{\text{ads}}^{\text{rel}}e]$ is responsible for the emission with $E_{\max}=2.46$ eV ($\lambda_{\max}=500$ nm; Fig. 6, transition 5).

If synthesis of AgBr microcrystals is done under low pBr (1.5–0.5), the medium will contain not only, considered above, complexes of $AgBrI^-$ and AgI_2^- , but also complexes of $AgBr_2^-$, $AgBr_3^{2-}$, $AgBr_2I^{2-}$, $AgBrI_2^{2-}$, and AgI_3^{2-} . These complexes can adsorb on the surface of the octahedral microcrystals. During reduction sensitization, these complexes convert into $(Br^-Br^-)_{\text{ads}}$, $(Br^-Br^-Br^-)_{\text{ads}}$, $(Br^-Br^-I^-)_{\text{ads}}$, $(Br^-I^-I^-)_{\text{ads}}$, and $(I^-I^-I^-)_{\text{ads}}$ centers. After these centers capture a hole, they transform in the corresponding centers in the relaxed state: $(Br^-Br^-)_{\text{ads}}^{\text{rel}}$, $(Br^-Br^-Br^-)_{\text{ads}}^{\text{rel}}$, $(Br^-Br^-I^-)_{\text{ads}}^{\text{rel}}$, $(Br^-I^-I^-)_{\text{ads}}^{\text{rel}}$, and $(I^-I^-I^-)_{\text{ads}}^{\text{rel}}$. These centers can capture a conduction electron and form various localized surface excitons: $[(Br^-Br^-)_{\text{ads}}^{\text{rel}}e]$, $[(Br^-Br^-Br^-)_{\text{ads}}^{\text{rel}}e]$, $[(Br^-Br^-I^-)_{\text{ads}}^{\text{rel}}e]$, $[(Br^-I^-I^-)_{\text{ads}}^{\text{rel}}e]$, and $[(I^-I^-I^-)_{\text{ads}}^{\text{rel}}e]$. Such an assumption is in good agreement with the PL results ($T=4.2$ K) from reduction sensitized octahedral AgBr emulsions (conditions of synthesis and R -sensitization are the same as described in Ref. 19, except with pBr=0.8) when the PL is excited using monochromatic light ($\Delta\lambda=1.5$ nm) as shown in Figure 7. It

turns out that changing the excitation wavelength (λ_{exc}) leads to the appearance of different PL bands (Fig. 7). We suggest that the PL bands with $\lambda_{\max}=520$, 540, and 565 nm are due to the radiative recombination of $[(Br^-Br^-Br^-)_{\text{ads}}^{\text{rel}}e]$, $[(Br^-Br^-I^-)_{\text{ads}}^{\text{rel}}e]$, and $[(Br^-I^-I^-)_{\text{ads}}^{\text{rel}}e]$ excitons, respectively. Therefore, it must be concluded that light with $\lambda=455$ –460 nm is absorbed by the I^- -ion from $(Br^-I^-I^-)_{\text{ads}}$, whereas the light with $\lambda=470$ and 490 nm is absorbed by the Br^- -ion from $(Br^-Br^-Br^-)_{\text{ads}}$ and by the I^- -ion from $(Br^-Br^-I^-)_{\text{ads}}$, respectively (Fig. 7).

If the PL is excited with $\lambda=490$ nm, in addition to appearance of the 540 nm PL band, one observes a substantial increase in the intensity of the orange-red emission with $\lambda_{\max}=590$ nm (Fig. 7). Thus, the PL in the orange-red spectral region is not only due to the radiative recombination in the $([+KAg_2]^- - (Br^-I^0)_{\text{ads}}^{\text{rel}})$ pairs (Fig. 6), but also due to other impurity centers. The intensity of the orange-red PL ($\lambda_{\max}=580$ –595 nm) increases with increasing concentration of iodide ions in AgBr emulsion microcrystals and strongly depends on the rate of iodide addition.^{25,55–58} The microscopic nature of the impurity centers is discussed in Refs. 56, 58, and 59. It is also possible that the 590 nm luminescence band is determined by radiative recombination in $[(I^-I^-I^-)_{\text{ads}}^{\text{rel}}e]$ exciton; light with $\lambda_{\max}=490$ nm is absorbed by one of the I^- ions in $[(I^-I^-I^-)_{\text{ads}}]$.

A role of the surface Br^- and I^- ions in the appearance of the 470 and 490 nm maxima in the PLE of the orange-red emission of AgBr microcrystals has been previously reported in Ref. 13. These maxima can be observed also at reduction sensitization of AgBr (100) microcrystals obtained at pAg=8.6.^{13,60} Apparently, the synthesis conditions we chose and sensitization lead to the formation of $(Br^-Br^-Br^-)_{\text{ads}}$ and $(Br^-Br^-I^-)_{\text{ads}}$ centers, which, as previously noted are responsible for the previously described excitation bands. At $T \geq 77$ K, the hole is thermally released from both $(Br^-Br^-Br^-)_{\text{ads}}^{\text{rel}}$ - and $(Br^-Br^-I^-)_{\text{ads}}^{\text{rel}}$ -centers into the AgBr valence band, where these holes can participate in processes that lead to the appearance of various emission bands. Moreover, it should be noted that on reduction sensitization of AgBr (100) microcrystals positive kink site (+K) converts into negative kink site (–K) after formation of Ag^0 (see e.g. Ref. 50). The Br^- and I^- that form (–K) can also absorb light in the region $\lambda > 460$ nm (see e.g., Ref. 61).

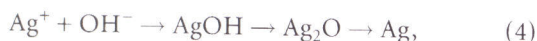
The mechanism proposed above for the PL bands with $\lambda_{\max}=520$, 540, 550, and 565 nm implies that if Ag_2 molecules are located next to an NCF, these molecules cannot capture the NCF localized holes. Therefore, these Ag_2 molecules cannot play a part in “two electron sensitization,” which is a process of electron generation in the microcrystal after Ag_2 captures a hole, followed by thermal decomposition of $Ag_2^+ \rightarrow Ag^+ + Ag^+ + e^-$, i.e., the so-called “Low mechanism”).

Photoluminescence of the emulsion layers excited with monochromatic light with $\lambda=480$ nm (2.58 eV) exhibits an additional band with $\lambda_{\max}=640$ nm, whereas excitation with $\lambda=530$ nm (2.34 eV) results in an additional band with $\lambda_{\max}=635$ nm (Fig. 7, curves 6 and 10). These bands do not

arise owing to reduction sensitization, but rather appear owing to sulfur containing impurities that are always present in gelatin. According to numerical calculations reported by Baetzold,³⁷ the energy of singlet-singlet (S_0 - S) and singlet-triplet (S_0 - T) transitions in a free Ag_2S molecule are 2.57 eV and 2.10 eV, respectively, whereas in Ag_4S_2 dimers they are 2.33 eV and 2.00 eV, respectively. These molecules and dimers can be formed during the synthesis of AgHal microcrystals as a result of interaction between Ag^+ and the sulfur impurities in gelatin. Therefore, we propose that the 640 and 635 nm PL bands are due to the $T \rightarrow S_0$ transition in the excited Ag_2S molecules and Ag_4S_2 dimers dispersed in the gelatin solution, respectively.

The results of PL studies on reduction sensitized octahedral AgBr emulsions are in good agreement with results of photographic and photoelectric measurements.^{7,12} It was concluded there that the increase of sensitivity during initial stages of reduction sensitization is due to the creation of hole trap centers (R-centers). According to our model, this takes place when adsorbed PHACA transform into the corresponding negatively charged fragments. Therefore, we argue that in the case of AgBr (111) the R-centers are negatively charged fragments, which can localize holes at room temperature.

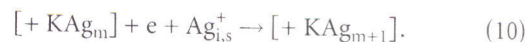
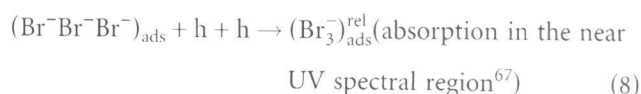
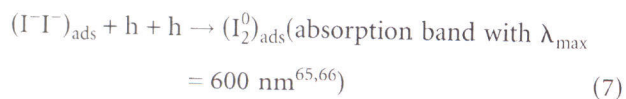
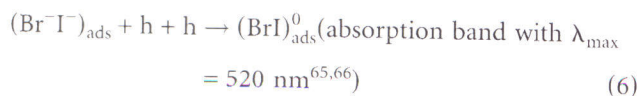
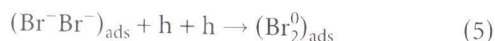
In the case of the low pAg sensitization, negatively charged fragments do not form. Instead, only the silver centers that are electron traps are created.⁷ The sensitivity increase under high pH sensitization⁷ is determined by several thermally stimulated reactions,⁶² e.g.,



which result in an appearance of the silver centers that are the electron traps⁷ (the transformations of AgOH into Ag_2O and Ag_2O into Ag occur with the activation energies of 4.6 ± 0.4 kcal/mole and 10.5 ± 0.4 kcal/mole, respectively).⁶²

The Br^- and I^- anions that make up negatively charged fragments determine the AgBr microcrystal PLE bands in the spectral region between 430 nm and 500 nm. It is important to note that absorption of reduction sensitized (early stages) AgBr microcrystals is observed in the same spectral region.^{11,29,63,64} Thus, the absorption spectra reported in Refs. 11, 29, 63, and 64 could describe not only absorption by Ag_2 species but also by Br^- and/or I^- that constitute negatively charged fragments and/or (-K).

Upon illumination of AgBr microcrystals by light with $\lambda < 460$ nm, the following transformations of NCFs (some NCFs are R-centers) and P-centers take place:



$(BrI)_{ads}^0$ and $(I_2)_{ads}^0$ are excellent electron traps.^{13,65,66} These molecules, formed during illumination of AgBr microcrystals, are responsible for the "fatigue effect" observed for some PL bands of emulsion microcrystals.^{65,66} Moreover, the result^{9,68} that the gold latensification renders developable only P-centers but not R-centers also supports our model for the R-center.

The studies of photoelectrical properties of emulsion AgBr microcrystals have allowed to establish that adding iodide ions to the microcrystals leads to the creation of hole traps, whose thermal trap depths are 0.029, ~ 0.090 , and 0.2–0.3 eV.⁶⁹ These are in agreement with the analysis of the PL properties of AgBr microcrystals discussed above. Indeed, I_V^- creates a 0.03 eV hole trap, whereas $(Br^-I^-)_{ads}$ and $(I^-I^-)_{ads}$ create hole traps with depths of 0.07 and 0.23 eV, respectively (Fig. 6).

The energy levels of the highest occupied molecular orbitals (HOMO) of R-centers are higher by 0.31 eV than the top of the AgBr valence band.¹¹ According to the model of the R-center proposed in this work, 0.31 eV determines the maximum value for the HOMO of negatively charged fragments.

The negatively charged fragments formed after the transformation of adsorbed complexes can play an important role in the spectral sensitization of photographic emulsions via participation in reductive processes of photoexcited molecules or aggregates of some dyes or in the regeneration of ionized dye molecules or their aggregates (see also Ref. 60).

Finally, we would like to comment on magnetic properties of silver nanoparticles in AgBr emulsions. Illumination of AgBr microcrystals results not only in the formation of silver nanoparticles but also in the appearance of halide molecules such as Br_2 , BrI , and I_2 [see reactions (3), (5)–(7)]. These molecules are efficient electron traps.^{13,65,66} Thus, by capturing either photoelectrons or the electrons provided by the developer, these molecules become Br_2^- , $(BrI)^-$, and I_2^- anions (Hal_2^- centers), which in turn can adsorb on the silver nanoparticles (perhaps molecular anions Hal_2^- reside within thin layer of the gelatin adsorbed on the silver nanoparticles). Since these molecular anions are paramagnetic, silver nanoparticles with an adsorbed molecular anion possess paramagnetic properties. In contrast, with reduction sensitization, only silver clusters and nanoparticles appear and no paramagnetic properties (or very weak signals compared with the previous case) are expected. Such differences in the magnetic properties were reported by Tani,⁷⁰ who showed that the magnetic susceptibility was three orders of magnitude smaller in the case of reduction sensitization

compared to one when the impurity centers are formed by light. Moreover, there is a difference in the shapes of the ESP signals, which is symmetric in for Hal_2^- centers and asymmetric for silver centers.⁷⁰ The explanation given here differs from that of Ref. 70.

CONCLUSIONS

Our results indicate that the PHACAs adsorbed on the microcrystal surface play an important role in the PL of the AgBr octahedral microcrystals. These complexes can be transformed after capturing an electron from a reducing agent into negatively charged fragments, which are efficient hole traps. Some of these fragments act as so-called R-centers in octahedral microcrystals. AgI_2^- and AgBrI^- complexes are formed during synthesis of AgBr octahedral microcrystals due to residual iodide ion impurities in KBr or NaBr. Upon reduction sensitization of nominally pure octahedral AgBr microcrystals, these complexes fragment with the formation of $(\text{I}^-)_{\text{ads}}$ and $(\text{Br}^-)_{\text{ads}}$ centers, which are responsible for the 550 and 590 nm PL bands, respectively. The PLE spectra of the 550 and 590 nm PL bands have maxima at 3.75 and 2.80 eV, and 3.81 and 2.88 eV, respectively. The energy difference between these PL excitation maxima corresponds to the energy of the spin-orbit splitting in the iodine atom ground state (transitions $5p^6 \rightarrow 5p^5(^2P_{1/2})6s$ and $5p^6 \rightarrow 5p^5(^2P_{3/2})6s$). This leads to the conclusion that the negatively charged fragments responsible for the 550 and 590 nm PL bands contain iodide ions. Finally, our results show that the AgBr emulsion PL consists not only of microcrystal PL but also of the emission due impurity centers formed in gelatin during synthesis of AgBr microcrystals.

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