

Effect of pBr on Luminescence and Photographic Characteristics of AgBr Microcrystals

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Abstract

Low temperature (from 9K to 90K) photoluminescence of AgBr microcrystals has been studied at different excitation levels. AgBr microcrystals were made by double-jet precipitation at $pBr = 3.2$ (cubes) or $pBr = 0.8$ (octahedrons). Luminescence spectra of cubic and octahedral microcrystals differ from each other. This difference is explained by the fact that during the synthesis of octahedral microcrystals ($pBr = 0.8$) the polyhalogenoargentate complex anions (PHACA) are being formed in the reaction mixture and adsorbed on microcrystal surface, which result in the appearance of new bands in the luminescence spectra. The possibility of participation of adsorbed PHACA in various processes taking place during reduction and sulfur sensitization of octahedrons is discussed. The presence of adsorbed complexes on the octahedral surface inhibits lateral diffusion of Ag_2S molecules that are formed in the course of sulfur sensitization. Because of that, rather big ($d > 20\text{\AA}$) $(Ag_2S)_pAg^+$ or $(Ag_2S)_q$ ($q > p$) clusters that act as electron traps at room temperature are not formed. We conclude that sensitivity centers formed in the course of sulfur sensitization are different in cubic and octahedral microcrystals.

Introduction

Synthesis of AgBr microcrystals (MC) was carried out by the double-jet precipitation at a constant pBr. MC habitus depends on pBr [1, 2]. At small pBr ($pBr < 3.0$) octahedral MC are formed, at higher pBr cubic MC are created. The effect of pBr on MC morphologies is due to formation of different polybromoargentate complex anions ($AgBr_2^-$, $AgBr_3^{2-}$ or $AgBr_4^{3-}$) in the reaction mixture at small pBr. Adsorption of these complexes on MC changes the crystal face growth rate, and consequently, MC of a certain habitus are evolved [1, 2]. If reaction mixture contains I^- the formation of $AgBr_m I_n^{(m+n-1)-}$ ($m, n \geq 1$) is also possible.

The effect of MC morphologies on kinetics of sulfur and reduction sensitization of photographic emulsions was discussed in numerous papers (see, e.g. [3, 4]), and the influence of pBr on luminescence spectra of AgBr(I) emulsions was described in [5]. In the present paper we continue to study the pBr effect on luminescence characteristics of MC and the process of chemical sensitization.

Experimental

Photoluminescence (PL) spectra of octahedral and cubic MC of $0.24\mu m$ in size (samples A and B) are shown in Figs. 1A and 1B. Such MCs were made by the double-jet precipitation and separated from gelatin by centrifugation. The conditions of MC synthesis were: pH 6.5, $T = 55^\circ C$, $pBr = 3.2$ (cubic MC), and $pBr = 0.8$ (octahedral MC). In the PL spectra of both sample A and B

at $T < 50K$ we observed a band with $\lambda_{max} = 497nm$. This band was associated with an iodine-bound exciton and described in

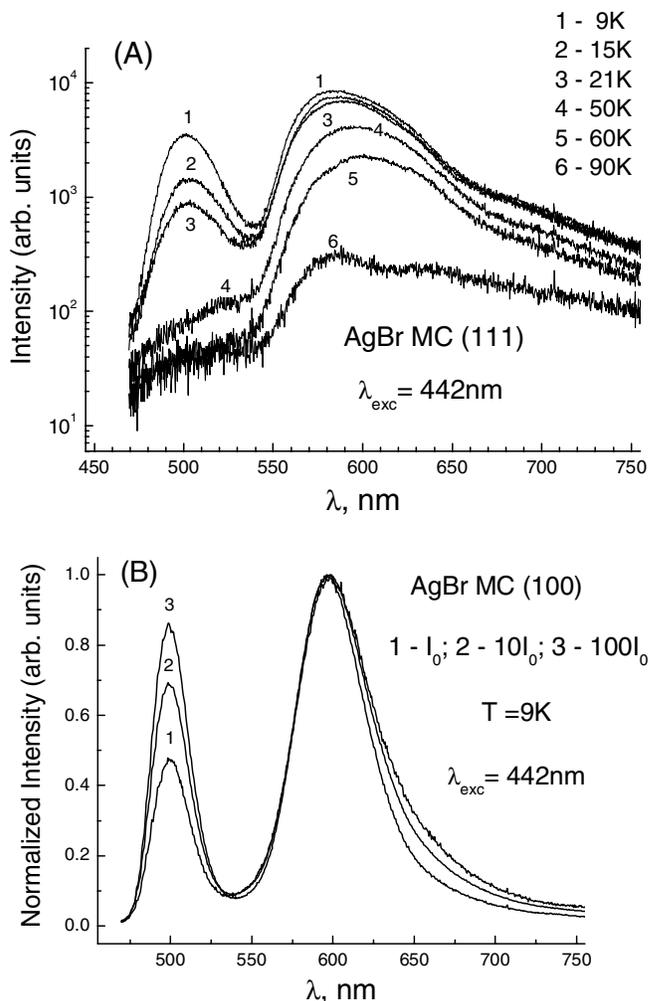


Figure 1 Photoluminescence Spectra of octahedral (A) and cubic (B) AgBr MC (at different excitation intensities)

several papers. On the other hand, PL of MC at $\lambda > 540nm$ depends on pBr in the course of synthesis. In the case of cubic MC ($pBr = 3.2$) there is only one band with $\lambda_{max} = 600nm$ ($T = 9K$), whereas in the case of octahedral MC ($pBr = 0.8$) PL in the range $\lambda > 540nm$ consists of several overlapping bands (Figs. 1A and 1B). Obviously, this difference is related to conditions during MC synthesis. At $pBr = 0.8$ and $T = 55^\circ C$, when octahedral or tabular MC are formed, there are different polyhalogenoargentate complex anions (PHACA) in the reaction mixture, such as $AgBr_2^-$,

AgBr_3^{2-} , AgBr_4^{3-} , AgBrI , $\text{AgBr}_2\text{I}^{2-}$. Not only high concentration of bromine ions, but also inefficient mixing can create their high local concentration [6] that facilitates the formation of PHACA. These complexes may be adsorbed on the surface of already formed octahedral MC consisting of (111) AgBr lattice faces.

It is well known that the (111) face represents alternate succession of Ag^+ and Br^- layers. The distance between layers is 3.536\AA . In the excess of Br^- ions in the reaction mixture the surface layer of MC consists of Br^- where single ions or islets of Ag^+ ions are located. Negatively charged PHACA can be adsorbed on these Ag^+ islets (this is shown for AgBr_2^- in Fig.2). In this case

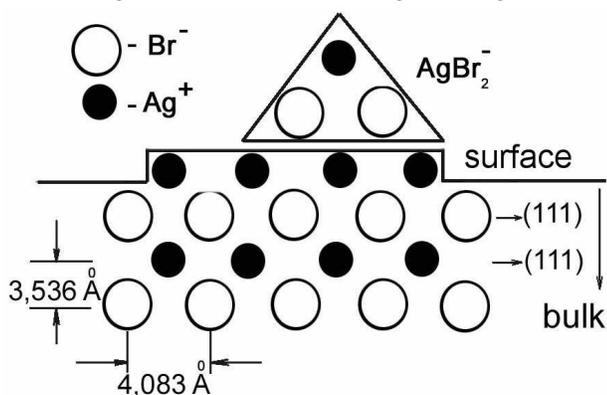


Figure 2 Schematic Diagram of AgBr_2^- complex adsorption on silver islet (shown as a step)

negative charge of Br^- or I^- is partially compensated for by Ag^+ ions. Configuration of this complex (Ag^+ ion is located above adsorbed Br^- ions) closely resembles arrangement where Ag^+ is located near negative surface step in cubic AgBr MC. Such a step is termed negative kink (-K) in [7]. According to quantum mechanical calculations [7], Ag^+ ion near -K or negative double kink (-DK) produces energy level for an electron below AgBr conduction band (ionization potential of Ag atom near -K is 3.72eV , and 4.01eV near -DK which is greater than AgBr conduction band (3.6eV)). These results are in good agreement with those obtained in Ref. 8, where it was shown that the silver ion located above two Br^- ions on the (111) face of AgBr MC is able to capture an electron.

Considering the above, it can be assumed that adsorbed PHACA, whose negative charge is partially compensated for by surface silver ions, can create electron traps. Then, it is possible that the adsorbed complexes can participate in reactions during MC synthesis and chemical sensitization of an emulsion. In turn, these interactions could alter 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 above or beside a silver ion of (111) face thereby creating Ag_2^+ . It is plausible that such an event could also result from attraction between localized electron and interstitial silver ion. An electron in antibonding orbital could lead to the former process, whereas an electron in a bonding orbital could result in the latter process. A molecular Ag_2^+ ion is a deep electron trap, after capturing an electron from a reducing agent it becomes Ag_2 . Such molecules

can stay by the remaining negatively charged fragment (NCF) of the adsorbed complex ($(\text{Br}^- \text{Br}^-)_{\text{ads}}$ in the case of AgBr_2^- complex), or migrate from it and aggregate to form a silver cluster (e.g., see Ref. 9). Transformation of the complexes can also take place in the course of sulfur sensitization due to interaction of Ag^+ ion from complex with sulfur sensitizer.

The mentioned NCF are efficient hole traps. Thus, simultaneous presence of adsorbed complexes and NCF on octahedral surface brings about creation of a whole system of

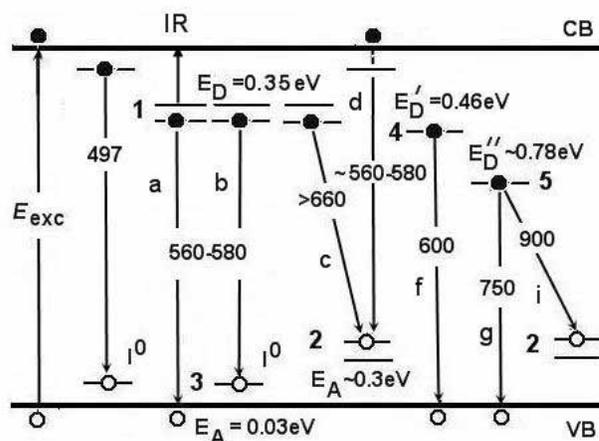


Figure 3 The energy level scheme of some of the centers of AgBr MC (111): 1 - $(\text{PHACA})_{\text{ads}}e$; 2 - $(\text{NCF})_{\text{ads}}h$; 3 - I^0 ; 4 - $+\text{DK}(\text{Ag}_2\text{S})_2e$; 5 - $+\text{DK}(\text{Ag}_2\text{S})_2\text{Ag}_n e$ ($n = 1$ or 2). Here, e and h are electron and hole localized on shown centers. The energy levels are shown relatively to the AgBr conduction (CB) and valence (VB) bands. Arrows indicate photoluminescence (PL) transitions with numbers, given in nm, specifying λ_{max} of the corresponding PL band.

electron and hole energy levels. Participation of these localized charge carriers in various recombination processes explains several overlapping bands observed in PL spectra of octahedral AgBr MC at $\lambda > 540\text{nm}$ (Figs.1A and 3).

It has been shown previously (e.g., see Ref. 10) that if AgBr or AgBr(I) PL occurs as a result of recombination of a localized electron and a valence band hole (Lambe-Klick mechanism) or by donor-acceptor mechanism, then illumination of a sample by infra-red (IR) light brings about quenching without PL flash. The reason for this is liberation of electrons from localization levels (Fig.3, transition IR). The PL at $\lambda = 560 - 580\text{ nm}$ results from transitions a and b (Fig. 3) because in the case of octahedral AgBr MC optical quenching without PL flash is observed. As well known, I^- ion in the AgBr lattice point produces a hole localization level with $E_A = 0.03\text{ eV}$ [11]. Thus, at $T < 50\text{K}$ emission of octahedrons in the $570\text{-}580\text{ nm}$ range can result from recombination of an electron localized by the adsorbed complex with I^0 (localization level depth is denoted E_D). At $T > 50\text{K}$ PL arises according to Lambe-Klick mechanism (Fig.3, transition a).

The radiation energy E_0 of such a donor-acceptor pair transition (Fig. 3, transition b, PL band with $\lambda_{\text{max}} = 580\text{ nm}$, $E_{\text{max}} = 2.14\text{eV}$) is described by $E_g - (E_D + E_A)$ where E_g is AgBr forbidden gap ($E_g = 2.69\text{eV}$, $T = 9\text{K}$) and in the assumption that the Coulomb interaction is negligible because of the large distance between the donor and the acceptor. 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 electron-phonon coupling in solids and in AgBr, in particular, during radiative recombination that also accounts for broad PL bands. The Huang-Rhys factor [12], S_0 is considered a measure of electron-phonon coupling. 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 iodine ion in AgBr $S_0 = 9.64$ [11] (interaction with longitudinal optical (LO) phonons having energy $h\nu_{LO} = 0.017\text{eV}$). At large S_0 ($S_0 \gg 1$) PL band has Gaussian shape, $S_0 = p$, where p is the number of phonons in electron-phonon coupling. In case of observed broad PL bands the energy difference $E = E_0 - E_{\max}$ can be evaluated by $S_0 h\nu_{LO}$, i.e. for $S_0 \approx 10$ $E \approx 0.17\text{eV}$. This correction should be taken into account when determining pure electron transition energy, E_0 . Knowing $E_0 = 2.31\text{eV}$ and $E_A = 0.03\text{eV}$ one can determine $E_D = 0.35\text{eV}$ (see Fig. 3). At room temperature dwelling time of an electron in a trap with a depth of $\sim 0.35\text{eV}$ before thermal release into AgBr conduction band is longer than neutralization time (τ) of the trapped electron by a mobile silver ion ($\tau \approx 10^{-6}\text{s}$). This fact can explain one of the possible mechanisms of PHACA transformation with Ag_2^+ formation.

Transformation of adsorbed complexes into NCF is manifested by new PL bands described by transitions c and d in Fig.3. Infra-red light-induced PL flash should be observed in PL band described by transition d (the Schoen-Klasens model). Since adsorbed complexes are transformed in the course of chemical sensitization, then prolonged sensitization facilitates accumulation of NCF. In this case we anticipate appearance of new PL bands where PL flash can be stimulated by infra-red light. This conclusion is in excellent agreement with the experiment. As an example, spectra of AgBr(I) MC (3 mole% AgI) are shown in Fig. 4. The PL spectrum of AgBr(I) MC at 77K (Fig. 4, curve 1) in the range of $\lambda = 500 - 800$ nm consists of overlapping bands, in the band with $\lambda_{\max} = 700$ nm PL flash can be induced by infra-red light (Fig. 4, curve 2). The reason for the absence of the flash in the range $\lambda = 500 - 650$ nm is not the fact that deep electron traps are not present (there is a flash in the band with $\lambda_{\max} = 700$ nm), rather it is associated with the mechanism of PL in the indicated spectral range.

Since during synthesis of AgBr(I) MC there are complexes $\text{AgBr}_m \text{I}_n^{(m+n-1)-}$ ($m = 1, 2; n = 1, 2$) and $\text{AgI}_m^{(m-1)-}$ ($m = 2, 3, 4$) in the reaction mixture, it can be assumed that transition of an electron localized by these adsorbed complexes to AgBr valence band hole (type a transition, Fig. 3) accounts for the emission at $\lambda = 500 - 650$ nm (Fig. 4, curve 1). Under illumination by infra-red light the electron is released from a recombination level, and the PL is quenched. On the other hand if such an emulsion undergoes sulfur or sulfur-gold sensitization, then after a certain time when fog density, $D_0 = 0.2$, we observe an intense PL flash at $\lambda_{\max} = 580\text{nm}$. This band results from NCF after adsorbed complexes are transformed by sulfur sensitization. The PL flash indicates that emission in the new band at $\lambda_{\max} = 580\text{nm}$ occurs by Schoen-Klasens model (Fig. 3, transition d, $E_A \approx 0.3\text{eV}$).

Participation of the surface localization levels for electrons and holes with the depth of 0.3eV in the photographic processes was discussed in Ref. 13.

It was shown [10] that in the excitation spectrum of the

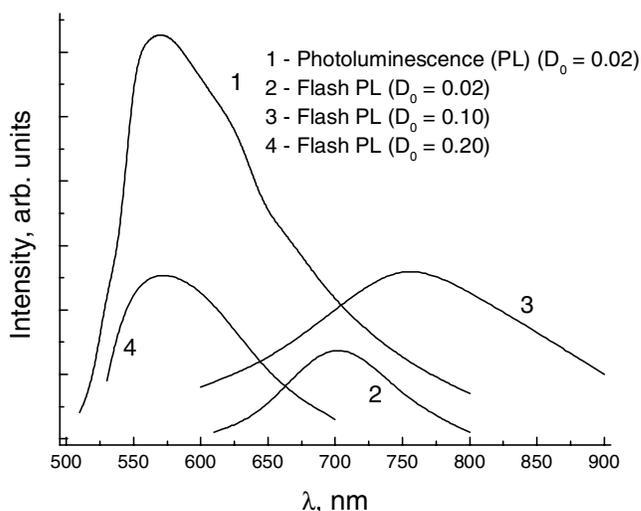


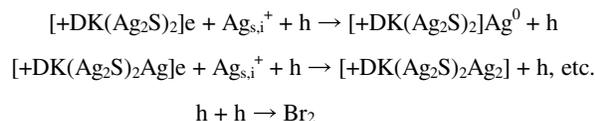
Figure 4 Photoluminescence Spectrum and Spectra of PL Flash of sulfur sensitized AgBr(I) MC

orange emission of emulsion MC there are bands with $\lambda_{\max} = 470$ and 490 nm. It is possible that these bands are associated with the absorption of light by negatively charged fragments of polyhalogenoargentate complex anions.

Synthesis of cubic MC takes place at $p\text{Br} > 3.0$, at these $p\text{Br}$ levels PHACA are not formed, and only one band at $\lambda_{\max} = 600$ nm is observed (Fig. 1B). Since this band is observed only if MC synthesis is carried out in the presence of gelatin [14], it implies that this band is a result of interaction of gelatin with AgBr. It is known that there are sulfur-containing impurities in gelatin. Interaction of these impurities with AgBr results in formation of Ag_2S molecules on MC surface that could form $(\text{Ag}_2\text{S})_2$ dimers, $(\text{Ag}_2\text{S})_3$ trimers, and $(\text{Ag}_2\text{S})_n$ clusters. Located near positively charged double kink (+DK), dimers $(\text{Ag}_2\text{S})_2$ create an electron trap with $E_D' \approx 0.41 - 0.46\text{eV}$ [15]. Taking into account the fact that the IR irradiation quenches the orange emission without PL flash, and that the increase in the excitation intensity (I_0) by two orders of magnitude (Fig. 1B) does not shift spectral position of the emission band peak (such a spectral shift is characteristic of the donor-acceptor pair PL), it can be assumed that the band with $\lambda_{\max} = 600$ nm results from recombination between an electron localized by $[\text{+DK}(\text{Ag}_2\text{S})_2]$ -center and a valence band hole (Fig. 3 transition f). For the band with $\lambda_{\max} = 600$ nm ($E_{\max} = 2.07\text{eV}$) $E_0 = E_{\max} + 0.17\text{eV} = 2.24\text{eV}$, thus the depth of the electron localization level (E_D') is 0.46eV ($E_g = 2.70\text{eV}$), that agrees very well with theoretical value [15]. Octahedral MC also have emission band with $\lambda_{\max} = 600$ nm, but it is masked by intense emission resulting from adsorbed PHACA. The complexes adsorbed on the surface of octahedrons inhibit migration and aggregation of Ag_2S molecules formed in the course of sulfur sensitization. In the case of cubic MC Ag_2S molecules merge to form rather big $(\text{Ag}_2\text{S})_p\text{Ag}^+$ or $(\text{Ag}_2\text{S})_q$ ($q > p, d > 20\text{\AA}$) clusters that can localize electrons at room temperature [10, 16, 17] and act as photographic sensitivity centers. In emulsions with octahedral MC sulfur sensitization results in formation of rather small $(\text{Ag}_2\text{S})_n$

clusters ($n \geq 4$, $d < 20 \text{ \AA}$ [18], $(\text{Ag}_2\text{S})_n$ clusters are hole traps [10]), and $[\text{+DK}(\text{Ag}_2\text{S})_2]$ -centers act as photographic sensitivity centers [15].

Temperature quenching of the PL band with $\lambda_{\text{max}} = 600 \text{ nm}$ occurs by ionic mechanism with the activation energy $\varepsilon = 0.11 \text{ eV}$ that corresponds to the translational energy of the interstitial or the surface silver ion (see, e.g. Ref. 10). In this case a localized electron first interacts with such an ion, $(\text{Ag}_{s,i}^+)$ and then - with the hole (h):



There also appears a new PL band with $\lambda_{\text{max}} = 750 \text{ nm}$ ($E_{\text{max}} = 1.65 \text{ eV}$) [10] (Fig. 3 transition g), which can be quenched by the IR light without 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 an AgBr valence band hole. Given $E_{\text{max}} = 1.65 \text{ eV}$, $E_0 = E_{\text{max}} + 0.17 \text{ eV}$ and $E_g = 2.6 \text{ eV}$ ($T = 80 \text{ K}$), the depth of the electron trap (E_D'') in this case is $E_D'' = 2.6 - 1.82 = 0.78 \text{ eV}$ (see Fig. 3).

$[\text{+DK}(\text{Ag}_2\text{S})_2]\text{Ag}^0$ - and $[\text{+DK}(\text{Ag}_2\text{S})_2\text{Ag}_2]$ -centers are formed during sulfur sensitization of octahedrons (besides $(\text{Ag}_2\text{S})_n$ clusters that are hole traps [10]) due to reducing properties of gelatin. In addition, at later stages of octahedral MC sensitization the concentration of NCF of adsorbed complexes increases (see above). Recombination between the 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 and the hole localized by NCF ($E_D'' = 0.78 \text{ eV}$, $E_A = 0.30 \text{ eV}$, Fig. 3, transition i) accounts for the PL band with $\lambda_{\text{max}} = 900\text{-}920 \text{ nm}$ that was observed experimentally [19].

Conclusions

Our results indicate that the PHACA adsorbed on MC surface play an important role in the PL of the AgBr octahedral MCs. These complexes can be transformed in two cases: (i) after the capture an electron from a reducer and (ii) after the interaction of Ag^+ , within the complex, with a sulfur sensitizer. The negatively charged fragments formed after such a transformation are efficient hole traps. It is plausible that these fragments act as so called R-centers (see, e.g. Ref. 20) in octahedral MC. The presence of the adsorbed complexes on MC surface inhibits lateral diffusion of the Ag_2S molecules created in the course of sulfur sensitization. Hence, in the case of octahedral MC, $(\text{Ag}_2\text{S})_2$ -dimers situated near a positively charged double kink, $[\text{+DK}(\text{Ag}_2\text{S})_2]$, [15] can serve as sensitivity centers (the increase in the luminescence intensity at 600 nm during sulfur sensitization is described in Ref. 21). Since conditions of cubic MC synthesis are such that the adsorbed PHACA are not formed, lateral diffusion of Ag_2S molecules created in the course of sulfur sensitization is not hindered, and they merge to form $(\text{Ag}_2\text{S})_p\text{Ag}^+$ or $(\text{Ag}_2\text{S})_q$ ($q > p$, $d > 20 \text{ \AA}$) clusters that are electron traps [10, 16, 17] and act as sensitivity centers. In this case the PL band with $\lambda_{\text{max}} = 900 \text{ nm}$ is due to the $(\text{Ag}_2\text{S})_p$ clusters [10]. Hence, there is no "universal" model for a sensitivity center – different emulsion types can have different impurity centers acting as sensitivity centers.

NCF formed after transformation of adsorbed complexes can play an important role in spectral sensitization of photographic emulsions via participation in reductive processes of photoexcited molecules or aggregates of some dyes or in regeneration of ionized dye molecules or their aggregates.

References

- [1] E. Klein, E. Moisar, *Bensenges Phys. Chem.*, 67, 349, 949 (1963).
- [2] C.R. Berry, D.S. Skillman, a) *Phot. Sci. Eng.*, 6, 159, (1962); 8, 65 (1964); b) *J. Photogr. Sci.*, 16, 137 (1968).
- [3] E. Moisar, *J. Photogr. Sci.*, 16, 102 (1968); *Phot. Sci. Eng.*, 25, 45 (1981).
- [4] S.S. Collier, *Phot. Sci. Eng.*, 23, 113 (1979) and references therein.
- [5] V.M. Belous, V.I. Tolstobrov, V.P. Churachov, V.V. Suvorin, *Zh. Nauch. Prikl. Foto i Kinematografii*, 22, 390 (1977).
- [6] C.R. Berry, *Phot. Sci. Eng.*, 18, 4 (1974).
- [7] R.C. Baetzold, *J. Imaging Sci. Technol.*, 43, 30 (1999).
- [8] P. Gutta, R. Hoffman, *Proceeding ICIS*, 2002, Tokio, p.214
- [9] T. Tasaka, M. Murofushi, T. Tani, *J. Imag. Sci. Technol.*, 47, 463 (2003).
- [10] V.M. Belous, *J. Imaging Sci. Technol.*, 41, 85 (1997).
- [11] W. Czaja, A. Baldereschi, *Bericht der Frühjahrstagung der Schweizerischen Physikalischen Gesellschaft*, 50, 606 (1977).
- [12] K. Huang, and A. Rhys, *Proc. Roy. Soc.*, A204, 406 (1950).
- [13] V.M. Belous, *J. Imaging Sci. Technol.*, 43, 1 (1999).
- [14] V.M. Belous, *Advanc. Imaging Sci. (Russian)*, 25, 5 (1989).
- [15] R.C. Baetzold, *J. Imaging Sci. Technol.*, 45, 247 (2001).
- [16] V.P. Oleshko, R.H. Gijbel, V.M. Belous, W.A. Jacob, M.V. Alfimov, *ICIS Proceedings*, Antwerp, p. 275 (1998).
- [17] S.H. Ehrlich, *J. Imag. Sci. Technol.*, 37, 73 (1993).
- [18] H. Mifune, M. Mizuno, Y. Toyama, T. Shiozawa, J. Okuda, *J. Imaging Sci. Technol.*, 46, 262 (2002).
- [19] H. Kanzaki, Y. Tadakuma, *J. Phys. Chem. Solids*, 58, 221 (1997).
- [20] T. Tani, *J. Imaging Sci. Technol.*, 48, 278 (2004).
- [21] V.M. Belous, L.P. Melnichuk, K.V. Chibisov, *Dokl. AN SSSR*, 172, 1357 (1967); 175, 349 (1967); 182, 862 (1968); 193, 1087 (1970).

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The Effect of Iodide on Silver Centers Formation in AgBr (111) and AgBrI (111) Microcrystals

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Abstract

One of the major factors determining the AgBr microcrystal photosensitivity is impurity of iodine ions. Increasing photosensitivity, impurity of iodine ions effect on crystallization kinetics, size and shape of forming crystals. These aspects of iodide effect on the AgBr microcrystal surface have been studied rather well. At the same time the correlation of photosensitivity and other characteristics of photographic properties of emulsion with the way of the iodide distribution in AgBrI mixed microcrystals are not scrutinized. This paper shows the research of AgBr and AgBrI microcrystal surface with iodide concentration (0.25 – 3 mol. %) by the electron-microscope method and the properties of silver center formation on the primitive microcrystal surface and after the maturation stage.

Introduction

Silver halide photography has a long and favorable history and is a striking example of using scientific progress in technology. In spite of progress of digital aids of data logging, the systems of logging based on silver halides (AgHal) still dominate in medicine, geodesy and space observation, as these systems have good image quality and sensitive potential. As a rule, because of these advantages photomaterials based on AgHal found new areas of application. Modern fast emulsions consist of silver halide mixtures (mostly silver bromide and silver iodide). Last time various combinations of halide composition (not only concentrations of co-crystallizing halides, but topography of their distribution and ways of combination) become one of the effective factors of photographic process management in all stages. Iodide ion plays a significant role in making latent image. One effect of iodide ions to influence emulsion sensitivity is light energy absorption increase. The other effect of iodide ions is connected with latent image creation effectiveness [1]. Kasado revealed when iodide content increased, the concentration of interstitial silver ions increased too. Bert, Takada and Peng deduced when iodide content changed from 1 to 4 mol. %, ionic conduction of AgBrI microcrystals rose slowly. As iodide content increased from 4 to 12 mol. %, as ionic conduction rose linearly. If iodide content continued growing, ionic conduction didn't rise.

When iodide content is 6 – 10 mol. %, a large number of interstitial silver ions compete in capturing photoelectron, therefore a lot of pre- and sub-centers are formed, causing latent image creation effectiveness decrease. When iodide content is more than 10 mol. %, concentration of interstitial silver ions rises while light energy absorption increases, rising amount of photoelectrons so that latent image creation effectiveness increases slightly.

The conclusions of the papers aimed at examining the photographic systems of data logging showed that researchers focused close attention to a common problem of increasing

photoprocess effectiveness. However, in spite of practical progress many questions have to be discussed. Moreover, a number of questions concerning materials based on silver halides have been investigated a little.

This paper aims to investigate the surface of AgBr (111) and AgBrI (111) microcrystals and peculiarity of silver center formation on the surface of AgBrI microcrystals by the electron – microscope method.

Experimental Technique

To solve experimental problems we synthesized AgBr emulsive microcrystals of octahedral habitus of 0.7 μm by the controlled double jet crystallization method. The obtained emulsion was processed in KI solution (converting) under iodide concentration 0.25 – 3 mol. % during 15 min. under 52°C. Then we selected a sample for the electron-microscope analysis. The rest has been subjected to chemical maturation by the spontaneous sensitization procedure (without intake of any photographically active agents) for 3 hours. To make electron-microscope analysis we released the microcrystals from gelatine by the way of enzyme split in protease aqueous solution under pH = 10. The residue obtained under hydrolyzation was centrifuged, deposited on the object-plate and dried. We divided the samples into some groups and examined:

1. distribution of concentration centers by the delayed development method before and after the maturation of AgBrI microcrystals;
2. distribution of concentration centers by the photographic decoration before and after the maturation of AgBrI microcrystals.

Then we made coal replicas which were detached by us from the object – plate by the hydrofluoric acid etch. After that we washed out the replica with distilled water several times. Further we dissolved AgBrI microcrystals in 15 % sodium thiosulfate solution. We caught and deposited the washed out replica on the object – net. We viewed the replicas with the help of the electron microscope.

The Obtained Results and Discussion

We observed a large amount of fine – dyspersated silver particles of 6 – 20 nm on the surface of primitive AgBr microcrystals when using diluted 1:100 developer. The particles were distributed freely all along the surface without any clusters; the concentration of silver particles was up to $1.4 \times 10^{10} \text{ cm}^{-2}$. We could see particles of various sizes on the surface of the developed AgBrI microcrystals. Those particles started growing nearby peaks and edges of the microcrystals. The concentration of silver particles was 10^{10} cm^{-2} . When using diluted 1:100 developer we could see increase in the number of particles and their size on the

surface of the exposed AgBrI microcrystals (in comparison with the developed but not preliminary exposed AgBr (111) microcrystals). At the same time particles on the faces of AgBrI microcrystals were distributed evenly all along the surface with a small setback from the edges of the microcrystals. The concentration of silver particles was up to $1.9 \times 10^{10} \text{ cm}^{-2}$ (Table 1).

Table 1. The number of Ag particles 10^{10} cm^{-2} revealed on the surface of microcrystals depending on the iodide concentration and particle maturation time under development and exposition

Maturation time	Iodide concentration, mol. %						
	0	0,25	0,75	1,0	1,5	2,0	3,0
Primitive	1,9	1,2	1,4	2,5	2,5	4,1	3,4
1 hour	3,1	2,8	2,6	2,8	-	-	-
2 hour	3,7	2,6	2,5	2,5	-	-	-
3 hour	3,5	2,3	2,7	2,4	2,4	2,6	3,1

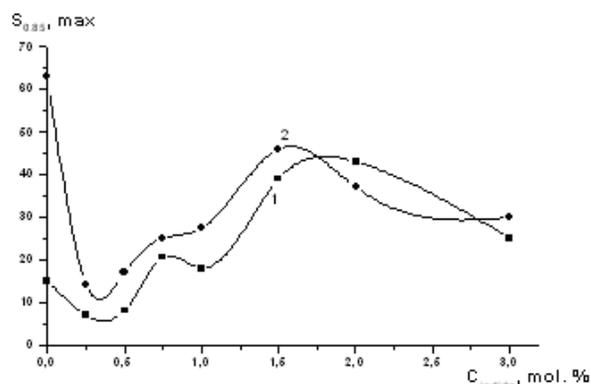
To reveal active zones on the surface of AgBr and AgBrI microcrystals after maturation we developed them in diluted 1:100 developer. Finally, we could see fine – dyspersed round-shaped silver particles of 9 – 20 nm, distributed all along the surface of microcrystals. The concentration of silver particles was from $2.1 \times 10^{10} \text{ cm}^{-2}$ to $2.8 \times 10^{10} \text{ cm}^{-2}$ (Table 2) depending on maturation time.

Table 2. The number of Ag particles 10^{10} cm^{-2} revealed on the surface of microcrystals depending on the iodide concentration and particle maturation time under development

Maturation time	Iodide concentration, mol. %						
	0	0,25	0,75	1,0	1,5	2,0	3,0
Primitive	1,4	-	-	1,0	-	-	-
1 hour	2,1	2,0	1,2	1,3	-	-	-
2 hour	2,5	1,5	1,4	1,6	-	-	-
3 hour	2,5	2,2	1,6	0,6	1,1	1,0	1,0

After AgBrI microcrystals had been developed we could see silver particles distributed stochastically on the surface of the microcrystals. The size of silver particles was 9 – 27 nm. The concentration of silver particles changed from $1.5 \times 10^{10} \text{ cm}^{-2}$ to $2.2 \times 10^{10} \text{ cm}^{-2}$ (Table 2) depending on maturation time and iodine concentration in the initial emulsion. When using diluted 1:100 developer we could observe increase in the number of particles and their size on the surface of the exposed AgBrI microcrystals (in comparison with the developed but not preliminary exposed AgBr (111) and AgBrI (111) microcrystals). At the same time silver particles were distributed rather evenly all along the surface of AgBr microcrystals. The concentration of silver particles changed from $3.0 \times 10^{10} \text{ cm}^{-2}$ to $3.7 \times 10^{10} \text{ cm}^{-2}$ (Table 1) depending on maturation time. On the surface of AgBrI microcrystals silver particles were distributed stochastically, varying in their size from 9 nm (in the center of the microcrystals) to 22 nm (on the edges of the microcrystals). The concentration of silver particles changed from $2.4 \times 10^{10} \text{ cm}^{-2}$ to $3.2 \times 10^{10} \text{ cm}^{-2}$ (Table 1) depending on maturation time. When the samples were exposed, we could make conclusion that as soon as we increased iodide concentration in the initial emulsion, silver particles began growing. The maximum number of silver particles could be seen at the maximum iodide concentration (2 %). The number of silver particles didn't change

and was approximately $2.5 \times 10^{10} \text{ cm}^{-2}$ at the surface of microcrystals selected at their different maturation stages. The results obtained in this work were comparable with sensitometric data. When we put AgBr microcrystals in KI solution, we might observe photosensitivity fall at small iodine concentration. If to continue increasing KI concentration in the solution, photosensitivity rose. A small rise in photosensitivity could be seen at iodide concentration 2 mol. %, but as soon as we increased iodide concentration in the emulsion, photosensitivity fell (Figure 1).



—■— Primitive emulsions
—●— Spontaneous-sensitive emulsions

Figure 1. Dependence of photosensitivity level from iodide concentration for primitive and spontaneous-sensitive emulsive AgBr microcrystals ($d = 0.7 \mu\text{m}$) put in KI solution.

We might see the same trend in our experimental data (Table 1). It should be noted that fog level decreased in comparison with pure AgBr emulsion all over the range of iodide concentration. Decrease of maximum photosensitivity under increase of iodine concentration above 2 % might be connected with etching iodide effect on AgBr microcrystals. It was well known that etching occurred mostly on defective zones of the microcrystal and it caused photosensitivity fall. Iodide admixture addition also facilitated photosensitivity rise at spontaneous sensitization stage (Figure 1, table 1).

Therefore, we may conclude that iodine ions make considerable impact on the rise of crystal lattice defects. Iodide addition increases concentration of interstitial silver ions which rise concentration of silver ion holes. It means that photoelectrons are captured easily and photosensitivity decreases.

The Main Results and Conclusions

1. We examined the surface of AgBr (111) and AgBrI (111) microcrystals with iodine content from 0.25 to 3 mol. %, and peculiarity of silver center formation on the surface of primitive microcrystals and after their maturation stage by the electron – microscope method.
2. The surface of primitive AgBr (111) and AgBrI (111) microcrystals has approximately 10^{10} cm^{-2} concentration centers, where silver particles can be formed under photolysis and development.

3. Concentration of silver particle growth centers on the surface of microcrystals coincides with the number of special zones connected with Br_s^- ions in kinks of sites. It enables examine Br_s^- defects as centers of silver concentration.

References

- [1] Z. Hau, "The Investigation of Preparation and Properties of Nucleus – Shell Emulsions" J. of Imag. Sci., 5, 155 (1990).

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