Photodecomposition and Luminescence of Silver Halides

Vitaliy M. Belous, Nina A. Orlovskaya, Alexander Yu. Akhmerov,
Irina G. Zenkevich and Sergey A. Zhukov
Research Institute of Physics, Odessa State University, Odessa, Ukraine

Abstract

Photodecomposition of silver halides occurs into silver and halogen. Impurity centers appearing at this process influence on the luminescent and photographic properties of silver halide. It was shown that created under light absorption iodine, bromine and bromiodine (BrI) mole-cules determines typical luminescent bands. The same centers are able to localize electron and create addi-tional recombination channel which act on the rise kinetics of different luminescence bands (green emission in AgBrI and orange emission in AgBr), and determines the effect of "luminescence fatigue". Localized by iodine and bromiodine (BrI) molecules electrons during heating of a samples can be neutralized by movable silver ions. This effect inhibit recombination of holes with these electrons which conditions ionic mechanism of quench-ing of luminescence according to classical photolysis Gurney-Mott scheme. Influence of chemical and spectral sensitization of photographic emulsions on the effect of "luminescence fatigue" of silver halide microcrystals have been studied.

Introduction

Silver halides are distinguished by the significantly high quantum efficiency of photochemical decomposition into silver and halogen. Mechanism of the process was suggested by Gurney and Mott and consists of several stages.[1] Under light absorption by silver halide electron and hole appears in the conductive and valence bands, accordingly. Free electron created by the light is captured by some defect and gives to it negative charge. Neutralization of negative charge by movable or surface silver ion leads to the appearance of silver atom. Repeating of this two-stage process with the same defect is followed by the appearance of silver particle. But subsequently it was found out that silver centers having atom-molecular dispersity and appearing on the first stages of photolysis of silver halides are not electron traps. Therefore in order to realize two-stage electron-ionic mechanism it is necessary at the beginning to "join" silver center with movable silver ion and only then capture electron.[2]

At photochemical decomposition of silver halides simultaneously with the process of creating of silver centers it also happens accumulation and migration of holes (atoms of halogen). Atoms of halogen can amalgamate into molecules. Atoms so as molecules can discharge from the sample and in the case of microcrystals of photographical emulsions they can be localized by a surface layer of gelatin adsorbed on MC.

Some products of photochemical decomposition of silver halides can be centers of luminescence at low temperatures or influence the luminescent properties of silver halides. Therefore luminescent method can be used for the study of photochemical decomposition of silver halides.[3,4]

1. Luminescence of Some Products of Silver Halides Photochemical Decomposition

Low temperature luminescence of silver halides can be observed in the wide range of wavelengths. At this condition emission in the same spectral region can be caused by luminescent centers of different nature. Appearance of various luminescent bands depends on temperature and light frequency used for excitation. Thus for ascertaining of nature of luminescent centers it is extremely significant to study excitation spectra of luminescence and temperature dependence. Moreover it is necessary to emphasize that conclusions about centers of luminescence based on the results obtained at low temperatures (2.0 – 4.2 K) could not be spread on the case of relatively high (T=77 K) temperatures, because at 77 K luminescence in this spectral region can be determined by absolutely different centers.

In the papers[4,5] it was obtained that molecules (BrI) and I_2 appearing under light action in AgBr and AgBr(I) determine appearance of phosphorescence bands with λ_{max}=680 and 760 nm, accordingly (Fig. 1). Excitation spectrum of phosphorescence for I_2 and (BrI) has characteristic peaks with λ_{max}=600 nm in case of I_2 and with λ_{max}=520 nm in case of (BrI). Besides that mentioned phosphorescence can be excited also at the light absorption by silver halide when free electrons (e) and holes (h) appear in it. In this case phosphorescence can be described by the following scheme[4,5]:

$$I_2 + e + h \Longrightarrow (I_2)^- + h \Longrightarrow (I_2)^*$$
$$\Longrightarrow I_2 + h\nu_{phos} \, (\lambda\text{=760 nm);} \qquad (1)$$
$$(BrI) + e + h \Longrightarrow (BrI)^- + h \Longrightarrow (BrI)^*$$
$$\Longrightarrow (BrI) + h\nu_{phos} \, (\lambda\text{=680 nm),}$$
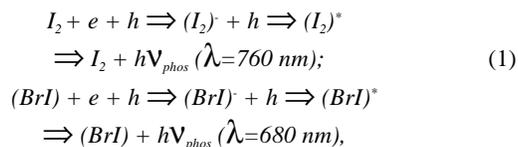
where $(I_2)^*$ and $(BrI)^*$ - excited molecular states.
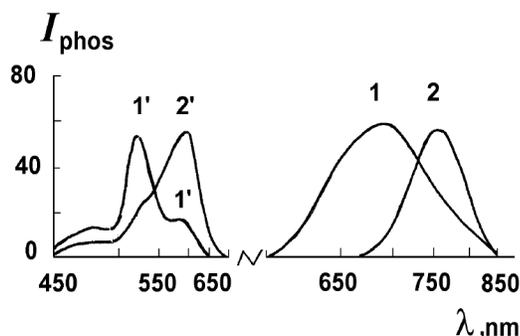
Figure 1. The phosphorescence spectra (curve 1 and 2), excitation spectra (1', 2') for AgBr emulsions (1, 1') and AgBr(I) emulsions (2, 2') with dichloride N,N'-dimethyl-4,4'-dipiridilium (heptilviologen, HV) after irradiation under ultraviolet light at 77 K during 10 min. The phosphorescence spectra are for 520 nm excitation in the case of AgBr (curve 1) and for 600 nm excitation in the case of AgBr (I) (curve 2).

Made conclusions are also confirmed by experi-mental results given below. As objects of investigation have been taken samples of chemically unsensitized AgBr and AgBr(I) emulsions with additional introduction of HV. Adsorbtion of HV on the surface of MC creates electron traps. Irradiation of samples by the ultraviolet light leads to the appearance of characteristic phosphorescence bands described above, and, moreover, as it should be expected at the presence of HV effectiveness of phosphorescence exitation sharply decreases at light absorption by silver halide (λ<460 nm), and does not significantly change at light absorption by (BrI) and I_2 molecules (bands with λ_{max}=520 and 600 nm). Phosphorescence band for iodine molecules with λ_{max}=760 nm appears not only under photochemical decomposition of AgBr(I) (sometimes this band can be observed at photochemical decomposition of AgBr because silver bromide always contains unintentional impurity of iodine), but also at adsorption of iodine molecules from gas phase on the surface of AgBr or AgBr(I).[4,5] In this connection it is interesting to pay attention on the following. In some cases under heating of AgBr monocrystals in bromine steam (T=400 C, steam pressure ~20 at) low temperature luminescence band can be observed at λ=640-650 nm. The same luminescence band (λ_{max}=640 nm) with typical excitation maximum at λ=550 nm is registered with photochemically coloured AgBr crystals (luminescence of AgBr crystals was measured at 4.2 K). Perhaps mentioned emission determined by bromine molecules (Br_2).

Mentioned above excitation bands for phosphor-escence of I_2, Br_2 and (BrI) are connected with singlet-triplet transition in these molecules (conditionally Hal_2):

$$Hal_2\,(^1\Sigma_g^+) + h\nu \Rightarrow Hal_2\,(^3\Pi(O^+_u)) \qquad (2)$$
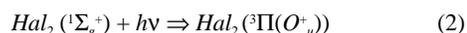
Transition of molecules from excited state $^3\Pi(O^+_u)$ into ground state can be followed either by phosphor-escence, or dissociation of a molecule into one atom in normal state ($^2P_{3/2}$) and one atom in excited state ($^2P_{1/2}$)[6]:

$$Hal_2\,(^3\,\Pi(O_u^+)) \Rightarrow Hal\,(^2P_{3/2}) + Hal\,(^2P_{1/2}) \qquad (3)$$
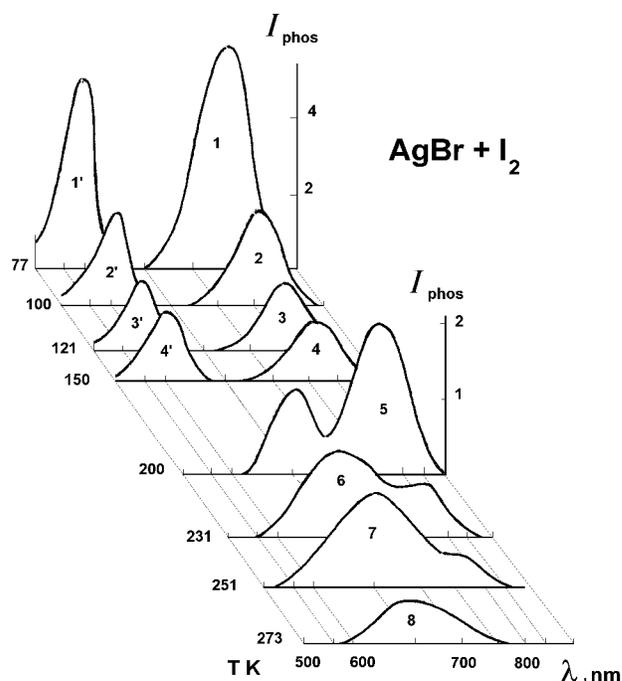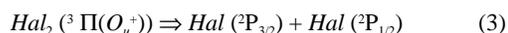
Figure 2. The phosphorescence spectra (1 through 8) and excitation spectra (1' through 4') for a layer of AgBr emulsion with adsorbed iodine molecules at different temperatures. The phosphorescence spectra are for 600 nm excitation (for all temperatures), and the excitation spectra are for monitoring wavelengths of 760 nm. Intensity values are in arbitrary units.

On Fig. 2 were shown phosphorescence spectra for the layer of silver bromide emulsion with adsorbed from gas phase iodine molecules. Monochromatic light with λ=600 nm was used for exitation. Phosphorescence of molecules is registered in the wide temperature interval. At T>150 it is observed appearance of new band with λ_{max}=640 nm. This emission is connected with a dissociation of I_2 mole-cules and appearance of excited iodine atoms according to reaction (3). Therefore iodine atoms placed on the surface of AgBr and AgBr(I) determine emission band with λ_{max}=640 nm. Note also that as it was ascertained earlier[4,5] iodine atoms placed in AgBr determine absorption bands at λ=325 (hν=3.80 eV) and λ=435 nm (hν=2.85 eV). The difference between photon energies corresponding to the two maxima of the absorbtion spectrum is 0.95 eV, which equals the energy of the spin-orbit splitting of the ground state of atomic iodine.

On Fig. 3 are shown phosphorescence spectra of (BrI) at different temperatures. Given data relate to the case when (BrI) molecules were created as a result of light exposure of AgBr emulsion microcrystals. If we use monochromatic light with λ = 520 nm for excitation of luminescence, phosphorescence of (BrI) is observed in wide temperature interval (Fig. 3). But in contrast to I_2 molecules excitation of (BrI) in mentioned temperature interval is not followed by their dissociation with appearance of emission of atoms.
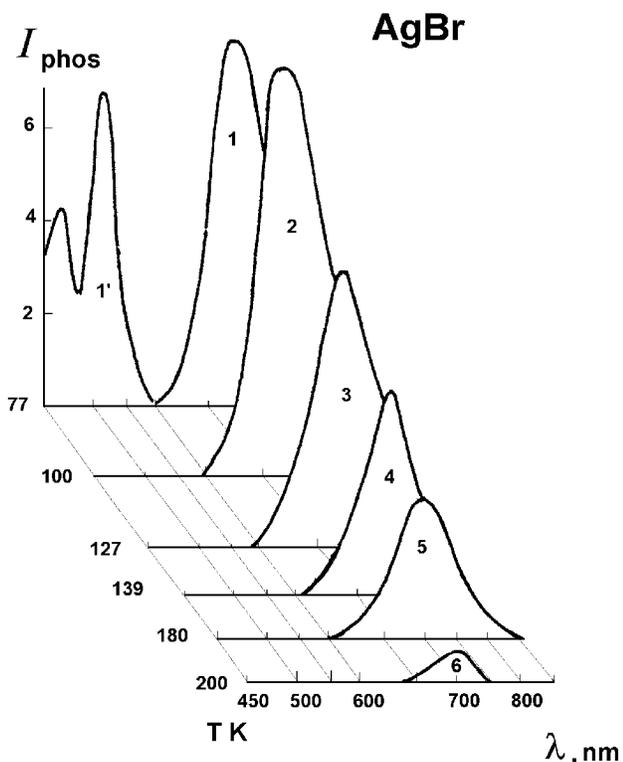
Figure 3. The phosphorescence spectra (1 through 6) and excitation spectra (1') for a layer of AgBr emulsion (after ultraviolet irradiation at 77K during 10 min) at different temperatures. The phosphorescence spectra are for 520 nm excitation (for all temperatures), and the excitation spectra are for monitoring wavelengths of 680 nm. Intensity values are in arbitrary units.
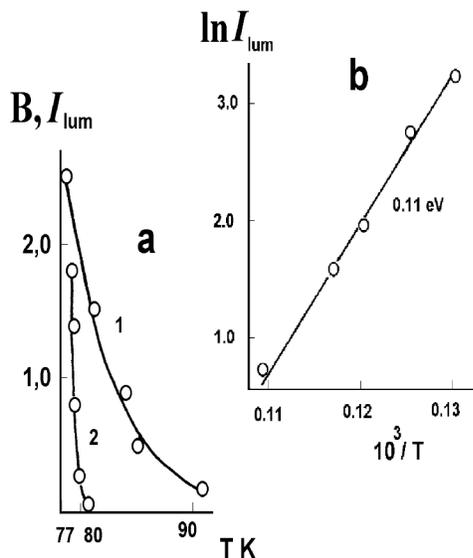
Figure 4. a) Dependence of intensity for phosphorescence band with $\lambda_{max}=760$ nm (curve 1) and value B (see text, curve 2) on temperature for a layers of AgBr(I) emulsion. Monochromatic light with $\lambda=450$ nm was used for excitation. Intensity values are in arbitrary units; b) Dependence of $\ln I_{lum}$ on $1/T$.

Under light absorption by silver halide phosphor-escence of (BrI) and I_2 originates as a result of recombination processes described by the scheme (1). In this case temperature quenching of phosphorescence can be observed at low temperatures and occurs with activation energy equal to 0.11 eV coinciding with activation energy for migration of surface and interstitial silver ion (Fig. 4).

In papers[4,5] it was shown that this quenching is connected with neutralization of localized electron by movable silver ion,—such neutralization occurs at some temperatures more earlier than a hole recombinates with this electron (ionic mechanism of temperature quenching[4,5]).

Mentioned quenching mechanism can be described by the following scheme:

$$Hal_2^- + Ag_{i,s}^+ \text{ fi } Hal_2Ag \qquad (4)$$
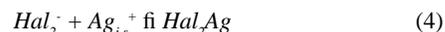
where $Ag_{i,s}^+$ - movable surface or interstitial silver ion.

Reaction (4) corresponds to Gurney and Mott classic scheme of photolysis but as distinct from given in [1] ideas in this case electron trap is halogen molecule, and not silver center.

2. Influence of the Products of Photochemical Decomposition on the Kinetics of Luminescence: Mechanism of Luminescence Fatigue

At the study of the kinetics of luminescence rise for AgBr(I) emulsion microcrystals was revealed the effect called "luminescence fatigue" (LF) (see, for example, [7,8]). This phenomenon is that under continuous excitation of luminescence by the light absorbed in silver halide occurs decrease of emission intensity until some stationary value I. For characterization of the effect it is possible to use a value of[9-11] B=$(I_0 - I)/I$, or[12] V=$(I_1 - I_2)/I_1\Delta t$, where I_0 - emission intensity at the initial moment of excitation ($I_0 > I$), I_1 and I_2 - intensities of luminescence on the stage of emission decay measured after some interval of time Δt (see Fig.5).

All earlier proposed mechanisms of LF are based on the consumption that as a result of irradiation of AgHal even at low temperature (T=77 K) happens slow creation of silver centers which are able to localize holes and create a concurrent channel for nonradiative electron recombination.[7,8,13] In this work was proposed absolutely different mechanism of LF. Indeed, under durable excitation of luminescence occurs formation of silver centers as a result of electron-ionic processes in micro-crystals. Thus one can note that spending of electrons on formation of silver centers leads to accumulation of holes in AgHal and as a result - to appearance of I_2 and (BrI) molecules which are electron traps (in the case of AgCl it can be Cl_2, Br_2, (ClBr), ClI, (BrI) or I_2 molecules because in AgCl always exists unintentional impurity of bromine and iodine (see, for example, [14])). Recombination of holes with I_2^- and (BrI)$^-$ (case of AgBr and AgBr(I)) determines appearance of new recombin-ation channel for charge carriers, that conditions decrease of emission intensity in the bands connected with other recombination channels. Given explanation can be confirmed by the following experimental results:

1. Observed under ultraviolet exitation decrease of green luminescence intensity for AgBr(I) MC correlates with increase of phosphorescence intensity for iodine molecules (band with $\lambda_{max}=760$ nm), which appears according to the scheme: $I_2^- + h \Rightarrow (I_2)^* \Rightarrow I_2 + h\nu_{phos}$ (Fig. 5).

2. Adsorption on the surface of AgBr(I) MC substances which bind silver ions (1-phenyl-5-mercaptotetrazol) or holes (semicarbazon acetone) decreases the LF effect.[12] It is conditioned by the fact that mentioned substances either depress silver centers formation and accumulation of holes in MC, or bind holes which affects formation of I_2, Br_2 or (BrI) molecules.

3. Decrease of value $B=(I_0 - I)/I_0$ at temperature (T) growth occurs in the temperature interval where it is also registered decrease of phosphorescence intensity for iodine molecules under excitation of emission by the light absorbed in silver halide (Fig. 4a, curve 2). If we take into account that in this case temperature quenching of phosphorescence is determined by ionic mechanism: $I_2^- + Ag_{i,s}^+ \Rightarrow I_2Ag$ (scheme 4) then analogous character of dependencies $B=f(T)$ and $I_{phos}=f(T)$ absolutely corresponds to the proposed mechanism.

4. If we use intermittent light pulses having duration of $\Delta\tau$ which are divided by dark intervals with duration Δt for excitation of luminescence, then the effect of LF depends on Δt value and can be observed only at the values of Δt less than some critical value of Δt_k ($\Delta t < \Delta t_k$).[12] Mentioned result can be explained by the fact that for occurrence of reaction (4) is necessary some time Δt, and if $\Delta t_k > \Delta t$ then effect LF should not be observed. Moreover, it has been ascertained that LF effect depends on the value $H=E\Delta\tau$, where E - intensity of intermittent excitation light and $\Delta\tau$ - duration of light pulse. Obviously exactly value $H=E\Delta\tau$ determines accumulation of Hal_2 molecules during radiation of AgHal emulsion microcrystals.

The effect LF for green luminescence of AgBr(I) emulsion microcrystals can be observed not only at light absorption by silver halide, but also in the case of absorption of light by some adsorbed dyes (in our experiments the effect has been registered at light absorption in the J-band of adsorbed dyes 3,3',9-triethyl-5,5'-dichlortiacarbocyaninechlorid and 3,3'-di-γ-sulfo-propyl-9-ethyl-4,5,4',5'-dibenzotiacarbocyanine betaine piridinium salt). Since wavelength of absorbed light is more than wavelength in the maximum position of luminescence band so in this case we observe the fatigue of anti-Stokes luminescence of AgBr(I). Appearance of fatigue effect for anti-Stokes luminescence clearly indicates that light absorption by adsorbed J-aggregates of the dye is followed both by appearance of electrons in the conductive band, and holes in the valence band of AgBr (see, for example, [15]).

During chemical sensitization of photographical emulsions on the surface of AgHal microcrystal appear impurity centers which are electron or hole traps. Formation of these centers affects both the accumulation of halogen molecules under excitation, and the occurrence of recombination according to scheme (1). Therefore, chemical sensitization should influence the rise kinetics of luminescence and, particularly,

the LF effect. Made conclusion is absolutely confirmed by experimental data. Particularly was obtained that on the initial stage of sulfur sensitization of AgBr(I) emulsions the value B that characterize LF effect passes through minimum. Obviously it is connected with appearance on the initial stages of sensitization not only impurity centers which are electron traps but also formation of $(Ag_2S)_n$ clusters which are hole traps[4] that decreases effectiveness of reaction (1), responsible for green luminescence fatigue.
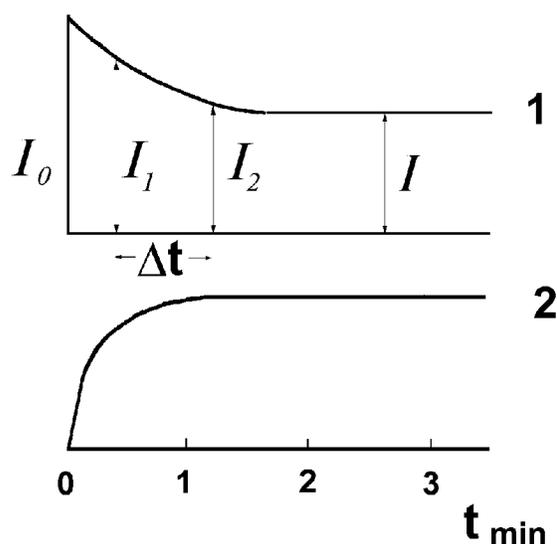
Figure 5. Rise of AgBr(I) emulsion microcrystals (cubooctahedral, d=0.24 μ) luminescence at λ=570 nm (curve 1) and λ=760 nm (curve 2). Monochromatic light with λ=450 nm was used for excitation of luminescence.

Introduction of $HAuCl_4$ solution into sulfur sensitized emulsion increase sensitivity (sulfur-plus-gold sensiti-zation), decrease value B and completely eliminate the effect of LF on the far stages of sensitization. Certainly in this case appear centers with electron capture cross-section considerably more than electron capture cross-section for I_2, Br_2 or (BrI) molecules, and therefore effectiveness of recombination process according scheme (1) sharply decreases. Obtained result is of great importance to understand the mechanism of sensitivity formation at sulfur-plus-gold sensitization in comparison with sulfur sensitization.

It is known that increase of concentration of surface silver ions in emulsion MC promotes photochemical colouring of silver halides, so decrease of pAg value leads to appearance of LF effect. The results are obtained for orange luminescence of AgBr microcrystals in polyvinyl alcohol.

Conclusion

As it follows from given experimental results photochemical decomposition of AgBr and AgBr(I) leads to the formation of impurity centers having not only silver nature but also to the appearance of I_2, Br_2 or (BrI) molecules. These molecules determine occurrence of ad-ditional luminescence bands and

influence recombination processes conditioning appearance of other luminescence bands. Formation of mentioned molecules occurs either as a result of migration of holes, or at localization of two holes on one surface center $I_s^- I_s^-$ or $Br_s^- I_s^-$:

$$I_s^- I_s^- + h \Rightarrow I_s I_s^- + h \Rightarrow I_2$$

$$Br_s^- I_s^- + h \Rightarrow Br_s^- I_s + h \Rightarrow (BrI) \tag{5}$$
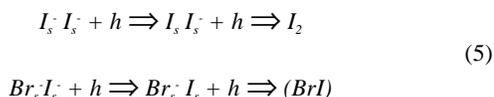
Occurrence of reactions (5) and (1) under irradiation should lead to the fatigue of both luminescence and some photoelectrical effects (particularly, photoconductivity). Besides this occurrence of reactions (5) and (1) can be one of the reasons of solarization effect.

Effect of luminescence fatigue observed not only in the case of silver halides but also for chalcogenide glass semiconductors (CGS) (see, for example, [16]). It is interesting to note that according to proposed in the paper[16] mechanism luminescence fatigue is connected with formation of new recombination centers under light action. These centers appear during transformation of some defects (so called D-centers) as a result of localization of holes by them. Given results point at the very interesting analogy of the processes determining occurrence of luminescence fatigue for silver halides and CGS.

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