LUMINESCENCE OF MIXED CRYSTALS OF SILVER HALIDES AT HIGH EXCITATION DENSITIES

L. G. Grigor'eva, D. K. Millers, and E. A. Kotomin

UDC 535.37:535.343

Silver salts are of interest both because of their applications in photography and because fiber light guides for the IR range are prepared from mixed crystals of silver halides [1, 2]. In the first case, the materials must have a high photosensitivity, while in the second case, on the contrary, the main problem is to obtain radiation-resistant transparent crystals and fibers. In order to control these properties it is necessary to understand the mechanism by which primary defects form and the processes of their recombination, aggregation, and accumulation. In silver halides these fundamental problems have still not been clarified. In the present paper, employ the luminescence method to investigate a series of solid solutions $AgBr_{1-x}Cl_x$ ($0 < x < 1$).

There is now no doubt that the cationic sublattice plays the decisive role in the formation of defects in silver halides. Investigation of the short-lived induced absorption in silver halides [3, 4] suggests that the primary pair of radiation defects is $Ag^{2+}V_C^-$ and Ag_i^0($Ag^{2+}V_C^-$ is a hole localized on a cationic vacancy and Ag_i^0 is an interstitial silver atom). The fundamental difference between electronic processes in AgCl and AgBr lies in the fact that in AgCl holes are self-localized in the form $[Ag^{2+}Cl_6]^{4-}$, while in AgBr the conditions for self-localization of electronic excitations are not satisfied [5].

In the solid solutions which we investigated there occurs a unique situation in which self-localized and free electronic excitations coexist. In AgBr at high excitation densities electronic excitations (excitons) condense in the form of excitonic molecules (EMs) and electron–hole liquid [6]. Decay of the excitonic molecules is accompanied by luminescence; in the present work we investigated luminescence of EMs in mixed crystals of silver halides excited with a pulsed beam of accelerated electrons.

Photoluminescence in the region 2.5-2.6 eV is well-known in AgCl [3]. The luminescence occurs by a recombination mechanism; the complicated decay kinetics is not described either by a monomolecular or bimolecular law. Similar luminescence has also been observed in $AgBr_{0.75}Cl_{0.25}$ crystals [4]. In the present work we measured the rate of decay of this luminescence for a number of mixed crystals in a wide range of times and we constructed a theoretical kinetic model of the luminescence decay based on a diffusion-controlled process.

Samples and Method of Investigation. The samples for the investigations were synthesized at a pilot plant of State Scientific Research and Planning Institute of the Rare Metals Industry. The content of cationic impurities was equal to 10^{-4}-10^{-5} mass %. The ratio of the halogen concentrations (x) in the mixed crystals was checked according to the position of the fundamental absorption edge, measured at 100 K. The luminescence was investigated at temperatures of 80-300 K.

The luminescence at high excitation densities was investigated with an electron accelerator with the following parameters: electron energy 270 keV; excitation density 15 MW/cm^2; excitation pulse width 10 nsec; system time resolution 30 nsec. The spectra were recorded every 30 nsec after the accelerator was turned on. The signal from the photomultiplier was recorded on an S8-7A storage oscillograph. When the luminescence of the excitonic molecules was investigated, the spectral resolution in the region of the spectrum near 2.5 eV was equal to 0.0025 eV.

The rate of decay of the luminescence was recorded after the samples were excited with 3.67 eV photons (region of interband transitions). The excitation source was a LGI-21 laser and the excitation pulse width was equal to ~8 nsec. This apparatus makes it possible to

Institute of Solid State Physics of the Latvian University, Riga. Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 55, No. 5, pp. 826-831, November, 1991.

 0021-9037/91/5505-1140$12.50 © 1992 Plenum Publishing Corporation

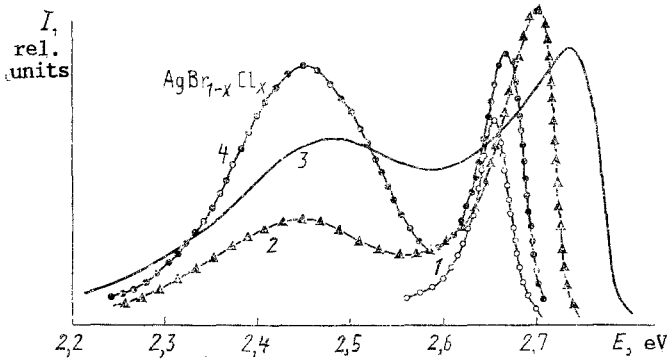

Fig. 1. Luminescence spectra measured every nsec after excitation with the electron-beam pulse. x = 0 (1), 0.15 (2), 0.3 (3), and 0.003 (4).

cover the time range from 255 nsec up to several milliseconds with variable time resolution from 1 nsec to 5 msec.

Luminescence Spectra Measured after Excitation of the Samples with a Pulsed Electron Beam. The formation of excitonic molecules (biexcitons) accompanying excitation with a laser pulse at temperatures below 4.5 K was investigated in detail for pure AgBr samples [6, 7]. The presence of impurity results in localization of electronic excitations on it, and at low excitation densities this impurity luminescence predominates. For example, in AgBr with residual iodine impurity the luminescence at 2.5 eV with lifetime 18 μsec (1.9 K) is associated with radiative recombination of an exciton on iodine [7]. Increasing the excitation density makes it possible to study condensation of characteristic electronic excitations (excitonic molecules and electron—hole liquid) under the condition that the concentration of impurity is much lower than that of the electronic excitations created. The lifetimes of the free excitons and excitonic molecules are significantly shorter than those of the excitons bound on the impurity, and for this reason we used time-resolved spectral methods to investigate the luminescence.

Excitation of pure AgBr crystals with a high-density pulsed electron beam was conducted in [8] and it was established that the luminescence with a maximum at 2.655 eV at 77 K is related with the luminescence of excitonic molecules. Figure 1 shows the luminescence spectra of the solid solutions $AgBr_{1-x}Cl_x$; the spectra were measured every 30 nsec after the electron accelerator was turned on. We found that the luminescence spectrum of the AgBr crystal is qualitatively the same as the spectrum presented in [8]; this gives us a basis for attributing the observed luminescence to radiative recombination of excitonic molecules. At the same time, the low-energy part is more pronounced in the measured spectrum; this could be due to the higher concentration of excitonic molecules, created in our case. This can be explained by the higher excitation density employed in the present investigation. The luminescence spectra of mixed crystals shown in Fig. 1, in contrast to pure AgBr, contain, aside from a narrow high-energy luminescence band, a wide emission band in the region 2.3-2.6 eV. Emission in this spectral region is observed for x > 0 and it can be similar to that observed in silver chloride, i.e., it is governed by recombination of self-localized excitons. Luminescence was not observed in this spectral region in pure silver bromide excited with an electron beam.

As the chlorine concentration in AgBr increases the position of the maximum of luminescence of excitonic molecules is displaced into the high-energy region. The half-width of the luminescence peak increases in the process, primarily owing to an increase in the contribution of the low-energy side. On the high-energy side the luminescence peak could be distorted by the superposition of the fundamental absorption edge of the samples. As x increases from 0.03 to 0.3 the band maximum shifts monotonically and the band is broadened monotonically. This shows that the environment of an excitonic molecule affects the position of its energy levels; it is also possible that the binding energy of the excitonic molecule changes. As x increases a new band does not appear in the lower energy region of the spectrum, indicating localization of excitonic molecules on chlorine ions, as observed for AgBr—I [7]. Experiments must be performed at a lower temperature in order to completely resolve this question.

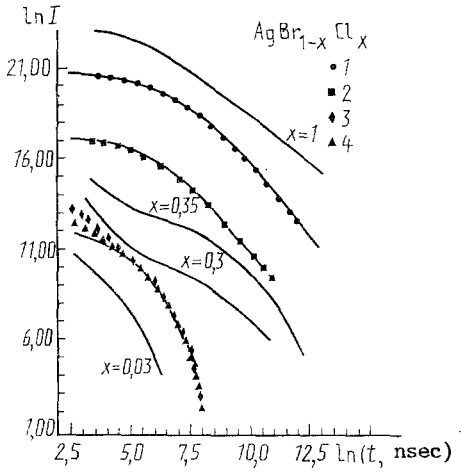

Fig. 2. Rate of decay of luminescence in the spectral region 2.4-2.5 eV. The solid lines represent the measurements and the dots represent the calculations performed with the following parameters: T = 100 K; $D_0 = 3.5 \cdot 10^{11}$ Å$^2 \cdot$sec^{-1}; R_0 = 0.1 nm; $\alpha \lesssim 0.05$ eV/Å^3; E_a = 0.105 (1), 0.0975 (2) and 0.06 eV (3, 4); ℓ_1 = 0.2498 (50%) (1-3) and 0.6286 nm (50%) (4); ℓ_2 = 0.4783 (50%) (1-3) and 0.7495 nm (50%) (4); x = 0.75 (1), 0.5 (2), 0.15 (3, 4).

It was not possible to establish the law of decay of luminescence of excitonic molecules because the resolution (≥ 30 nsec) of the measuring system was too low.

The luminescence in the spectral region 2.3-2.6 eV, manifested in the luminescence spectrum for x > 0, is associated with localization of excitons on chlorine ions.

The rate of decay of luminescence in the region 2.3-2.6 eV was recorded with the samples excited with nitrogen laser radiation. Figure 2 shows the results for crystals having different composition. The following scheme is proposed: The last stage of the observed luminescence is the excitonic stage, and the exciton is created in a diffusion-controlled process, i.e.,

$$Ag^{2+}V_c^- + Ag_i^0 \rightarrow (Ag^+V_c^-)^* + Ag_i^+ \rightarrow Ag^+ + Ag^+ + h\nu, \tag{1}$$

where $Ag^{2+}V_c$ is a hole localized at a cationic vacancy (investigations of the short-lived absorption confirmed the existence of such holes [4]); Ag_i^0 and Ag_i^+ is an interstitial ion respectively; $(Ag_i^+V_c^-)^*$ is an exciton localized at a cationic vacancy; and Ag^+ is a silver ion at a regular site of the crystal lattice.

Theory of the Rate of Decay of Luminescence. The standard theory of diffusion-controlled reactions between defects, which is based on the model of a random distribution of defects of two types, leads to the following dependence of the decay of the intensity I of recombinational luminescence:

$$I \sim \frac{dC_A}{dt} = \frac{dC_B}{dt} = -KC_A C_B, \tag{2}$$

where the reaction rate is

$$K = 4\pi D R_0 \left(1 + \frac{R_0}{\sqrt{\pi D t}}\right), \tag{3}$$

R_0 is the recombination radius, D is the mutual diffusion coefficient, $D = D_0 \exp(-E_a/kT)$, D_0 is the rate factor, and E_a is the diffusion activation energy.

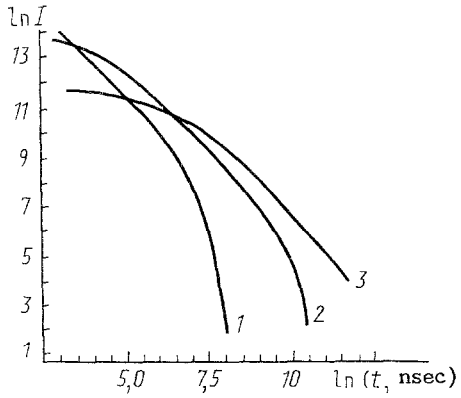

Fig. 3. Theoretical decay curves for activation energies E_a = 0.06 (1), 0.0825 (2), and 0.105 eV (3); T = 100 K; D_0 = $3.5 \cdot 10^{11}$ Å$^2 \cdot$sec^{-1}; $\alpha \lesssim 0.05$ eV/Å^3; R_0 = 0.1 nm; ℓ_1 = 0.2498 nm; ℓ_2 = 0.4783 nm.

It follows from Eq. (3) that after a transitional period ($t \gg R_0^2/D$) and for equal concentrations of defects ($C_A = C_B = C$) the concentrations and intensity decay according to a a hyperbolic law $C \sim t^{-1}$ and $I \sim t^{-2}$, respectively. For this reason, in the coordinates log C(I)—log t the time dependence should be a straight line, the tangent of whose slope angle is equal to −1 and −2.

Figure 2 clearly shows that the experimental time dependence, measured in a quite wide time interval, is almost everywhere nonlinear. Although for the composition $AgBr_{0.97}Cl_{0.03}$ at long times a region of linear decay of intensity can be separated, the tangent of the slope angle is found to be equal to −3. The observed time dependences most likely indicate significant spatial correlation of the defects. Thus, from an investigation of alkali-halide crystals [10] it is well known that the primary Frenkel' defects are spatially strongly correlated (the average distance in such a so-called genetic pair is much shorter than the distance between the pairs).

We now examine the kinetics of correlated recombination taking into account the elastic interaction of defects (which, as is well known [11, 12], strongly affects the recombinational kinetics in alkali-halide crystals) [13].

We shall study the following model. A pair of complementary Frenkel' defects separated by a distance ℓ is created by radiation. In a AgCl crystal close pairs $Ag^{2+}V_C^- - Ag_i^0$ can be separated by the following distances: 0.250, 0.478, 0.628, and 0.749 nm, which we shall enumerate as 1-4 neighbors in the crystal lattice.

One of the defects (Ag_i^0) migrates with the diffusion coefficient $D = D_0 \exp(-E_a/kT)$ and recombines with $Ag^{2+}V_C^-$, leading to excitonic luminescence according to the reaction (1). Their annihilation is stimulated by an elastic interaction.

The kinetics of this process is described by an equation for the pair density Y of finding defects of different types separated by a distance r [14]:

$$\frac{\partial Y(r,\ t)}{\partial t} = D\left(\Delta Y + \frac{1}{kT}\nabla\left(Y\nabla\varphi(r)\right)\right), \tag{4}$$

where $\Delta = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}$ is the Laplacian and $\phi(r) = \alpha/r^3$ is the elastic interaction potential. The boundary and initial conditions have the form

$$Y(r \leqslant R_0,\ t) = 0,\ Y(r,\ 0) = \sum_i \frac{\delta(r - l_i)}{4\pi l_i^2}. \tag{5}$$

The fraction of defects recombining up to the moment t is equal to the particle flux through the recombination sphere

$$S(t) = \frac{C}{C_0} = \int_0^t 4\pi R_0^2 D dt' \left.\frac{\partial Y}{\partial r'}\right|_{r=R_0}, \tag{6}$$

where C is the concentration of defects and C_0 is the initial concentration.

After substituting Y = y/r Eq. (4) assumes the form

$$\frac{\partial y}{\partial t} = D\left[y'' - \frac{3gy'}{r^4} + \frac{9gy}{r^5}\right], \tag{7}$$

where g = a/kT and characterizes the strength of the elastic interaction.

Results. As one can see from Eqs. (4)-(7), the rate of decay of the luminescence intensity is determined by the following parameters: R_0, D_0, E_0, a, ℓ_1 (the collection of initial distances in the genetic pairs). The initial values of these parameters were taken from calculations for analogous primary Frenkel' defects – F and H centers in alkali-halide crystals, after which they were varied over a wide range of values in order to determine how each parameter affects the rate of decay.

Figure 3 shows the effect of a change in the activation energy of the diffusion of Ag_i^0. It is obvious that doubling of E_a is accompanied by a sharp increase of the luminescence decay time. This effect cannot be achieved by any variation of the distribution of defects over distances. Figure 2 shows the results of adjustment of the parameters of the theoretical calculation for three different compositions. One can see that changing the initial distribution from one or two neighbors (in equal concentration) to three or four neighbors affects only the initial stage of decay of luminescence. The main conclusion is that in order to describe the sharp decrease of the rate of decay of luminescence the quantity E_a must vary linearly with the composition in the range from 0.06 ($AgBr_{0.97}Cl_{0.03}$) to 0.105 eV (pure AgCl). (We note that in [14] the theoretical estimate 0.07 eV was obtained for the migration energy of Ag^0 along the AgBr surface.) The corresponding quantity for an H center in KBr is equal to 0.09 eV, i.e., it is of the same order of magnitude.

The obtained elastic interaction parameter ($a \leq 0.05$ eV/Å^3) is almost two orders of magnitude smaller than the corresponding values for the F, H pair in KBr [14]. This evidently reflects the significant difference between the interstitial halide atom, forming an $(X_2^-)_a$ molecule at an anionic site of the lattice and strongly deforming the surrounding lattice, and Ag_i^0, freely entering the void between anions along the spatial diagonal.

Thus we investigated by the luminescence method impurity localization of excitons and radiative annihilation of excitonic molecules and excitonic molecules localized on a homological anion at high excitation densities in mixed crystals of silver halides. Theoretical modeling of the rate of decay of luminescence near 2.5 eV indicates that the recombination of complementary genetic pairs of defects is controlled by diffusion.

LITERATURE CITED

1. H. T. James, The Theory of Photographic Processes, New York (1977).
2. V. G. Artyshenko, L. N. Butvina, V. V. Voitsekhovsky, et al., in: Proc. Soc. Photo-Opt. Instrum. Eng., 618, 103 (1986).
3. H. Kanzaki and S. Sakuragi, Photogr. Sci. Eng., 17, No. 1, 69-77 (1973).
4. L. G. Grigor'eva, D. K. Millers, E. A. Kotomin, et al., Opt. Spektrosk., 67, No. 3, 608-612 (1989).
5. H. Yashioka and M. Yamaga, J. Phys. Soc. Jpn., 54, No. 2, 841-845 (1985).
6. T. Baba and T. Masumi, J. Phys. Soc. Jpn., 56, No. 7, 2549-2564 (1987).
7. Th. Kleinefeld and W. von der Osten, Phys. Status Solidi B, 125, 293-303 (1984).
8. T. É. Kekhva, in: Abstracts of Reports, 7th All-Union Conference on Radiation Physics and Chemistry of Inorganic Materials, Part 1, Riga (1989), pp. 312-313.
9. T. R. Waite, Phys. Rev., 57, No. 5, 463-470 (1957).
10. Ch. B. Lushchik and A. Ch. Lushchik, Decay of Electronic Excitations with Formation of Defects in Solids [in Russian], Moscow (1989).