

On the nature of photoinduced absorption in photochromic $(\text{AgCl})_x(\text{CuCl})_{1-x}$ films

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Absorption spectrum of photochromic $(\text{AgCl})_x(\text{CuCl})_{1-x}$ films has been studied. The intense band of induced absorption in visible region has been established to be a superposition of two bands, namely, that of absorption by silver colloid particles shaped as ellipsoids or chains of spherical particles and absorption band of Cu^{2+} ions in AgCl.

Исследован спектр поглощения фотохромных пленок $(\text{AgCl})_x(\text{CuCl})_{1-x}$. Установлено, что интенсивная полоса наведенного поглощения в видимом диапазоне представляет собой суперпозицию двух полос: полосы поглощения коллоидных частиц серебра эллипсоидальной формы или цепочек из сферических частиц сферической формы и полосы поглощения ионов Cu^{2+} в AgCl.

In spite of numerous studies of photochromic silver halide glasses (PSHG), the nature of photoinduced absorption therein remains still unclear. So in [1], it is assumed that under irradiation, Cu^0 centers are formed in CuHal along with colloid Ag particles in AgHal, those centers being responsible for longer-wavelength absorption bands in PSHG. In [2], the longer-wavelength position of the induced absorption band in PSHG as compared to the calculated one is believed to be associated with formation of Ag shells around a glass nucleus (shell model). According to [3, 4], the induced absorption band in PSHG corresponds to tiny Ag particles of anisotropic shape. Studies of colored photochromic PSHG using EPR and absorption spectroscopy [5] have shown that the formed Cu^{2+} ions are responsible for the non-selective absorption amounting about 50 % of the total induced absorption.

$(\text{AgCl})_x(\text{CuCl})_{1-x}$ photochromic films are convenient modeling objects to study the photochromic effect in the PSHG active

component, since the glass matrix influence at various stages of the coloration and discoloration process is eliminated in this case. In this work, studied are the spectra of $(\text{AgCl})_x(\text{CuCl})_{1-x}$ photochromic films ($x = 0.7$) with the purpose of investigating the nature of the induced absorption therein.

The samples were prepared by evaporation of AgCl and CuCl powder mixtures of a predetermined composition onto quartz substrates heated up to 100°C . Such preparation method provides the mixed biphasic films [6] as is evidenced by their absorption spectra and electron diffraction patterns. The absorption spectra of such films contain exciton bands peculiar to AgCl and CuCl. As it has been shown in [6], it is the biphasic character of thin $(\text{AgCl})_x(\text{CuCl})_{1-x}$ films, i.e., a heterojunction at the AgCl/CuCl grain interface, that is an necessary condition of photochromism thereof. The thin films of $\text{Ag}_x\text{Cu}_{1-x}\text{Cl}$ solid solutions showing a structure similar to those under study and formed by evaporation of the powder mixture onto a cold (20°C) substrate show no

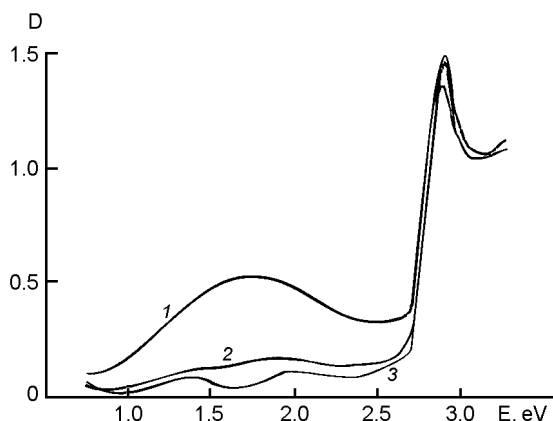


Fig. 1. Absorption spectra of a thin $(\text{AgCl})_{0.7}(\text{CuCl})_{0.3}$ film irradiated by non-filtered mercury lamp radiation, exposure $H = 0.36 \text{ J/cm}^2$ (1), after spontaneous discoloration (2), and prior to irradiation (3).

coloration even under mercury lamp UV irradiation at high exposures [6].

At the same time, a pronounced photochromic effect is observed in the biphasic films. Under UV lamp irradiation, a broad absorption band appears peaked at about 2.3 eV (Fig. 1). It is supposed to answer to the absorption of colloidal Ag and of Cu^{2+} ions in AgCl. The presence of colloidal Ag in the irradiated films is evidenced by chemical analysis: iodination of the colored films results in a narrow exciton band at 2.94 eV that answers to AgI (Fig. 2). As the temperature decreases, this band becomes more narrow and sharp, thus confirming its excitonic origin (Fig. 2, inset). The induced absorption, however, is not removed completely by iodination (Fig. 2). The remaining absorption band position is close to that of Cu^{2+} ions in AgCl. According to [7], two absorption bands peaked at 2.37 and 3.24 eV are observed in the $\text{AgCl}:\text{Cu}^{2+}$ spectrum. The second band is close in position to the excitonic one in CuCl (3.3 eV), thus causing an increased absorption in this spectral region in the irradiated $(\text{AgCl})_x(\text{CuCl})_{1-x}$ films (Figs. 1, 2). The presence of Cu^{2+} ions in PSHG is confirmed by EPR data [3, 5] and agrees well with the photochromic process mechanism in PSHG and photochromic $(\text{AgCl})_x(\text{CuCl})_{1-x}$ films proposed in [6, 8, 9].

The physical model of photochromic process in AgCl–CuCl films is based on the excitonic photoexcitation mechanism and the presence of a heterojunction between AgCl and CuCl grains. A specific feature of that junction is the presence of a potential

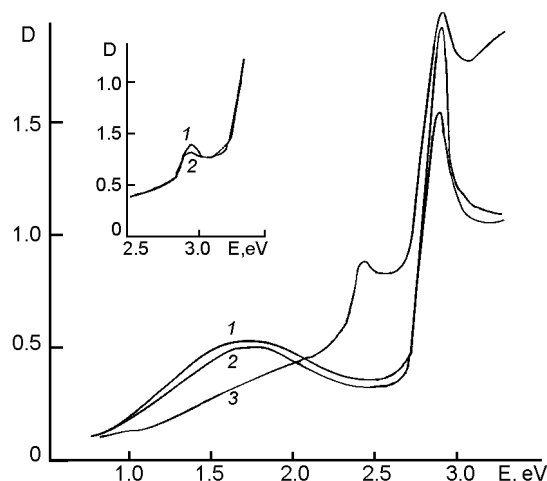


Fig. 2. Absorption spectra of a thin $(\text{AgCl})_{0.7}(\text{CuCl})_{0.3}$ film repeatedly irradiated at $H = 1.2 \text{ J/cm}^2$ (1), $H = 0.6 \text{ J/cm}^2$ (2), and after iodination (3). Inset: excitonic absorption band of AgI at 90 K (1) and 290 K (2).

barrier for electrons in CuCl and for holes in AgCl [6]. The film coloration is favored by discrimination of the current carriers and localization thereof. The initial electronic stage of the coloration is defined by the excitation of excitons in CuCl, the thermal decomposition thereof into electrons and holes followed by the tunneling of electrons across the barrier at the CuCl/AgCl interface and capturing by the traps in AgCl. The electrons localized in AgCl give rise to local electric fields and attract the interstitial Ag^+ ions. The Ag^+ ions capturing the electrons are reduced to neutral Ag atoms that, in turn, act as electron traps, thus resulting in the end in formation of colloidal particles. The localization of electrons on the neutral particles results in the negative charge accumulation in the AgCl layer and formation of an internal electric field directed normally to the CuCl/AgCl interface and favoring the transfer of Cu^{2+} ions from CuCl to AgCl. A similar photochromic process mechanism is observed in thin $\text{CuHal}-\text{CdHal}_2$ films ($\text{Hal} = \text{Cl}, \text{Br}, \text{I}$) [10, 11].

It follows from the experimental data and the photochromic effect model proposed in [6], the presence of a heterojunction between CuCl and AgCl grains is a necessary condition of photochromism in $(\text{AgCl})_x(\text{CuCl})_{1-x}$. The mechanism proposed in [1, 12] for the formation of Cu^0 color centers in the light-sensitive CuHal nanocrystals and Ag^0 ones in AgHal nanocrystals distributed in the PSHG glass matrix is erroneous in our opinion. It seems that in

PSHG, as well as in our films, the photochromic effect occurs in $(\text{AgCl})_x(\text{CuCl})_{1-x}$ nanocrystals distributed in the glass matrix. Under irradiation, colloidal silver is released at the CuCl–AgCl grain interface, as in $(\text{AgCl})_x(\text{CuCl})_{1-x}$ thin films. No colloidal copper was revealed in the irradiated $(\text{AgCl})_x(\text{CuCl})_{1-x}$ films. Iodination of the colored films results only in excitonic AgI band (2.94 eV) appearance in the absorption spectrum while there is no excitonic absorption of CuI (3.06 eV) (see Fig. 2).

The maximum position for the colloidal Ag in AgCl can be calculated using the formula for smallest spherical colloidal particles:

$$\omega_m = \frac{\omega_p}{\sqrt{(\varepsilon_m + 2\varepsilon)}}, \quad (1)$$

where $\omega_p = 1.3 \cdot 10^{16} \text{ s}^{-1}$ is the Ag plasma frequency; $\varepsilon_n = 4.1$, the dielectric constant due to interband transitions in metallic Ag; $\varepsilon = n^2 = 4.3$, the dielectric constant of the medium surrounding the grain. The so calculated value $\lambda_m = 515 \text{ nm}$ is much lower than the experimental value. The long-wavelength shift of the colloidal band is explained in the frame of Mie theory by increasing size of the colloidal particle. It follows from the calculations that the presence of Ag particles up to 60 nm size is to be assumed to explain the induced absorption in the PSHG. This is not confirmed by electron microscopy [13]. At the same time, according to calculations presented in [4], the absorption spectra of PSHG are approximated well by the absorption of ellipsoidal Ag particles. It is just the calculated absorption spectrum for a system of elongated ellipsoidal Ag particles of about 1 nm size in AgCl that is most similar to the experimental one observed in the PSHG and $(\text{AgCl})_x(\text{CuCl})_{1-x}$ photochromic films [4]. In the photochromic $(\text{AgCl})_x(\text{CuCl})_{1-x}$ films, anisotropic structures in the form of chains consisting of spherical silver particles [14]. The intensity of the calculated spectrum is substantially lower as compared to the induced absorption in PSHG observed in ex-

periments [15]. To approximate the experimental spectrum, the authors [15] have taken into account also the absorption spectrum of Cu^{2+} ions in AgCl. As is mentioned above, the direct experiment using iodination of the irradiated $(\text{AgCl})_x(\text{CuCl})_{1-x}$ films confirms that the induced absorption therein is contributed by Cu^{2+} ions in AgCl.

As the exposure increases, the induced absorption band in thin $(\text{AgCl})_x(\text{CuCl})_{1-x}$ films becomes shifted towards longer wavelengths (Fig. 2), thus evidencing the size increase of the colloidal Ag particles.

Thus, the the induced absorption band in photochromic $(\text{AgCl})_x(\text{CuCl})_{1-x}$ films is defined by absorption of Cu^{2+} ions and fine ellipsoidal Ag grains or chains consisting of spherical silver grains, the size thereof being increasing with the radiation exposure.

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**Про природу фотоіндукованого поглинання
у фотохромних плівках $(\text{AgCl})_x(\text{CuCl})_{1-x}$**

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Досліджено спектр поглинання фотохромних плівок $(\text{AgCl})_x(\text{CuCl})_{1-x}$. Установлено, що інтенсивна смуга наведеного поглинання у видимому діапазоні являє собою суперпозицію двох смуг: смуги поглинання колоїдних часток срібла еліпсоїдальної форми або ланцюжків зі сферичних часток сферичної форми і смуги поглинання іонів Cu^{2+} у AgCl .