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Photoluminescence of mixed $\text{AgCl}_{0.45}\text{Br}_{0.55}$ crystals

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Abstract. The steady-state photoluminescence (PL) of mixed AgCl–AgBr crystals was studied. Absorption and emission spectra as well as excitation spectra and temperature-dependences of the main emission bands were measured. For comparison, the same properties of nominally pure AgCl and AgBr were investigated. A 515 nm emission band in the mixed $\text{AgCl}_{0.45}\text{Br}_{0.55}$ crystals is apparently identical to the emission band of pure AgCl crystals at the same wavelength and is attributed to an intrinsic self-trapped-exciton (STE) recombination process. This assumption is supported by the measured temperature-dependence and excitation spectrum of this band in both crystals. The 515 nm emission becomes dominant in PL of the mixed $\text{AgCl}_{0.45}\text{Br}_{0.55}$ crystal only after annealing in N_2 atmosphere to 300 °C, while PL of pristine mixed crystals is dominated by a 565 nm emission band, attributed to iodide impurity ions, which are apparently present even in the highly pure starting material. This is supported by PL measurements of samples annealed in an I_2 atmosphere. Our results also indicate that the nominally pure AgBr crystals contain iodide ion impurities. Thermal treatment of the mixed AgCl–AgBr crystal in a Br_2 atmosphere did not influence the PL bands at 515 and 565 nm, but caused strong increase in intensity of a 750 nm emission band. This 750 nm band also appeared in nominally pure AgBr crystals, and might be due to bromine interstitials.

1. Introduction

Optical properties of silver halides have been intensively studied during the last three decades and results reviewed by various authors [1–3]. Some previous luminescence measurements were carried out near liquid He temperature, others at liquid N_2 temperature and higher temperatures [4–8]. The main luminescence band of pure AgCl crystals at about 515 nm has generally been attributed to an intrinsic process of radiative decay of self-trapped excitons (STE) [9]. The temperature-dependence of this emission band in AgCl has also been measured by various authors and it was found to be stable at relatively high temperatures, up to 120 K [4–8, 10]. No STE emission appears in pure AgBr crystals [3]. The main low-temperature emission bands in AgBr at 495 and 520 nm have been attributed to an exciton bound to an isolated iodide ion or to iodide ion pairs [11]. These conclusions have recently been supported by resonant light scattering [12] and ODMR measurements, at temperatures as low as 2 K [3, 13]. These measurements also enabled detection of a fine structure in the absorption and emission near the zero phonon line. The emission band at 495 nm in AgBr is

stable at low temperatures only and decays above about 40 K [14, 15].

Studies of optical properties of silver halides are of importance due to the various applications of these materials. In addition to well-known applications in photographic materials, silver halides are also used for optical fibres, in particular in the middle-infrared region. Mixed $\text{AgCl}_{0.45}\text{Br}_{0.55}$ crystals were found to be very useful for IR optical fibres due to their mechanical and optical properties [16]. It appears, however, that these properties are strongly influenced by the quality of the starting materials and by mechanical and thermal treatments.

In the present work, luminescence properties of high-quality $\text{AgCl}_x\text{Br}_{1-x}$ ($x = 0.45$) single crystals were studied. Emission and excitation spectra as well as optical absorption were measured. For comparison, the same measurements were carried out with nominally pure AgCl and AgBr crystals. In the course of this work the effects of thermal pre-treatment in various gaseous atmospheres on optical absorption and photoluminescence were also investigated.

2. Experimental procedures

For most of our experiments mixed $\text{AgCl}_x\text{Br}_{1-x}$ ($x \approx 0.45$) crystals were used. The mixed as well as the pure single crystals were grown in the optical fibre laboratory at Tel Aviv University by the Bridgman–Stockbarger method [16]. Samples of 1 cm^2 cross section and about 3 mm thickness were kept in a vacuum cryostat. The absorption measurements were taken with a Cary-17 spectrophotometer. Photoluminescence was excited with a 150 W high-pressure xenon lamp and a Jarrell Ash 0.25 m double monochromator. The incident photon flux in the spectral region $250\text{--}600 \text{ nm}$ was measured with a pyroelectric radiometer. The emission spectra were measured with a 0.5 m Bausch and Lomb grating monochromator, equipped with a fast scanning stepping motor and controlled by an electronic device. The reciprocal linear dispersion of the monochromator was 3.3 nm mm^{-1} and the slit width was normally 0.5 mm . The spectra were recorded with a thermoelectrically cooled EMI-9558-QB photomultiplier (S20-response). Appropriate optical filters were applied in order to exclude stray light and second-order effects. Further experimental details were given elsewhere [17].

Thermal treatments of the samples were performed in N_2 , Br_2 and I_2 atmospheres. For annealing in bromine or iodine atmospheres the samples were kept for 2 h at saturated vapour pressure at 300°C under a dry nitrogen stream and then slowly recooled to room temperature (RT).

3. Experimental Results

In the course of the present study the photoluminescence of the different samples was excited with various wavelengths in the visible and UV region. The PL emission spectra of pristine $\text{AgCl}_{0.45}\text{Br}_{0.55}$ crystals showed, when excited with a 430 nm light at liquid N_2 temperature (LNT), a main emission band at 565 nm and a weaker band centred at 750 nm . This is shown by curve (a) of figure 1. Annealing of the sample to about 300°C in a dry nitrogen atmosphere and slow recooling to RT caused notable changes in PL emission. The emission spectra of a sample after such thermal treatment are given by curves (b) and (c) of figure 1 for excitation wavelengths 430 and 320 nm respectively. It can be seen that, after thermal treatment in a N_2 atmosphere, a strong 515 nm emission appeared, while the 565 nm band markedly decreased. A wavelength of 320 nm was most efficient for excitation of the 515 nm band. The 750 nm band remained almost unchanged.

Excitation spectra of the main PL emission bands were measured in the spectral range $250\text{--}650 \text{ nm}$ and results are given in figure 2. The absorption near the edge of this mixed crystal is shown by curve (d) of figure 2.

The 515 nm emission, which appears in the PL after thermal treatment, has a broad excitation maximum around 320 nm while the other emission bands

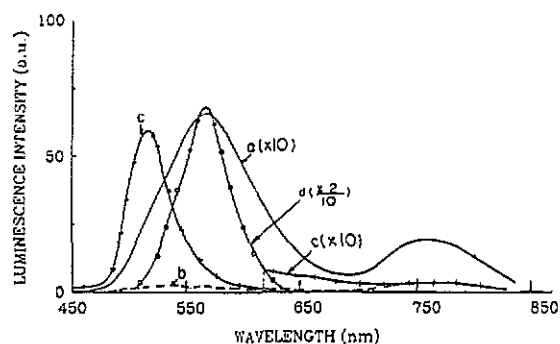


Figure 1. Photoluminescence emission spectra of $\text{AgCl}_{0.45}\text{Br}_{0.55}$ crystal: (a) before thermal treatment ($\lambda_{\text{exc}} = 430 \text{ nm}$); (b) after thermal treatment in N_2 atmosphere ($\lambda_{\text{exc}} = 430 \text{ nm}$); (c) after thermal treatment in N_2 atmosphere ($\lambda_{\text{exc}} = 320 \text{ nm}$) and (d) after additional annealing in I_2 atmosphere ($\lambda_{\text{exc}} = 430 \text{ nm}$).

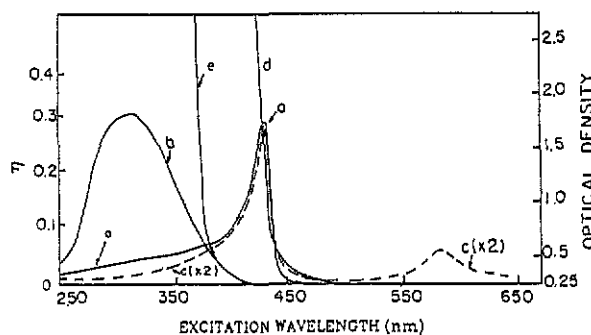


Figure 2. Excitation spectra of $\text{AgCl}_{0.45}\text{Br}_{0.55}$: (a) before thermal treatment, $\lambda_{\text{lum}} = 565 \text{ nm}$; (b) after N_2 thermal treatment, $\lambda_{\text{lum}} = 515 \text{ nm}$; (c) before and after N_2 thermal treatment, $\lambda_{\text{lum}} = 750 \text{ nm}$; (d) absorption near the edge of $\text{AgCl}_{0.45}\text{Br}_{0.55}$; (e) absorption near the edge of AgCl crystals.

show a main excitation maximum at about 430 nm , which coincides with the long-wavelength tail of the fundamental absorption. The 750 nm emission has a second excitation maximum at 580 nm .

Temperature dependences of the various PL emission bands were measured during cooling and during heating between 80 and 300 K and showed different behaviours; results are given in figure 3. The 565 nm emission shows a steep decay between 80 and 120 K and disappears above 120 K , while the 515 nm emission decreases slowly in the 80 to 200 K range. The 750 nm emission remains steady even at somewhat higher temperatures.

Some of the samples were heated gradually to 300°C in a dry nitrogen atmosphere and the changes in the luminescence properties were measured at steps of 25°C . A gradual change in the luminescence was observed by gradual heating up to about 250°C . Above 250°C these properties remained almost unchanged. After thermal treatment in dry nitrogen atmosphere some of the specimens were heated in a Br_2 atmosphere to 300°C and then re-cooled to RT.

The emission spectra of this crystal after thermal treatment in Br_2 atmosphere are shown in figure 4. A comparison with results given in figure 1 shows the appearance of a main broad PL emission band centred at about 600 nm , which may be an envelope

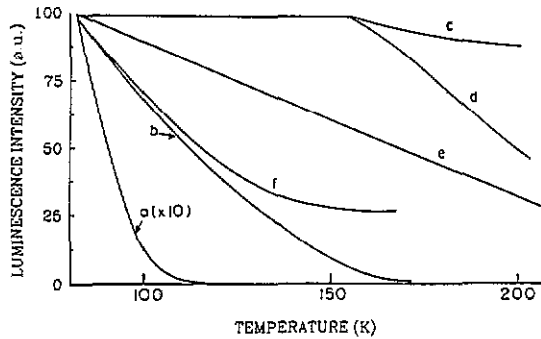


Figure 3. Temperature-dependences of the main luminescence bands in $\text{AgCl}_{0.45}\text{Br}_{0.55}$: (a) before thermal treatment ($\lambda_{\text{lum}} = 565$ nm, $\lambda_{\text{exc}} = 430$ nm); (b) after N_2 thermal treatment ($\lambda_{\text{lum}} = 515$ nm, $\lambda_{\text{exc}} = 320$ nm) and of AgBr; (c) before thermal treatment ($\lambda_{\text{lum}} = 510$ nm, $\lambda_{\text{exc}} = 450$ nm); (d) before and after N_2 thermal treatment ($\lambda_{\text{lum}} = 750$ nm, $\lambda_{\text{exc}} = 450$ nm); (e) after N_2 thermal treatment ($\lambda_{\text{lum}} = 595$ nm, $\lambda_{\text{exc}} = 330$ nm); (f) before thermal treatment ($\lambda_{\text{lum}} = 640$ nm, $\lambda_{\text{exc}} = 330$ nm).

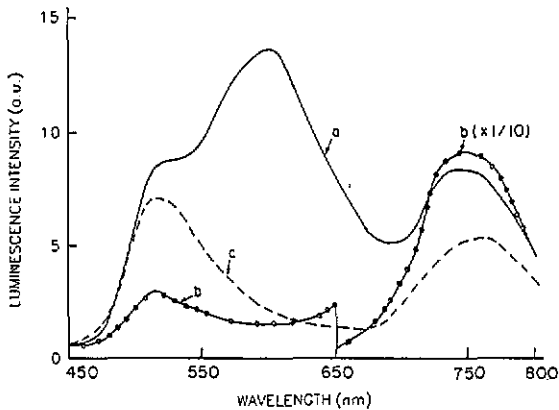


Figure 4. Photoluminescence emission spectra of $\text{AgCl}_{0.45}\text{Br}_{0.55}$ crystals after thermal treatments in N_2 and subsequently in Br_2 atmosphere excited by (a) $\lambda_{\text{exc}} = 320$ nm ($T = 80$ K), (b) $\lambda_{\text{exc}} = 430$ nm and (c) $\lambda_{\text{exc}} = 320$ nm ($T \geq 110$ K).

covering more than one emission band. When excited at 320 nm, the 515 nm emission appears now as a shoulder of the strong and broad 600 nm emission, but by excitation with 430 nm light it becomes the main emission band in the green spectral region. The intensity of the broad red emission band near 750 nm markedly increased after thermal treatment in Br_2 atmosphere and becomes dominant when excited at 430 nm. This 750 nm emission remained stable up to about 180 K and markedly decayed by excitation at higher temperatures. It may be noted, that the 600 nm band decays above 100 K (figure 4, curve (c)).

Other samples of mixed crystals, which had previously been annealed in an N_2 atmosphere, were heated to 300°C in iodine atmosphere and then slowly re-cooled to RT. The PL emission spectra recorded after this additional thermal treatment in I_2 atmosphere are given by curve (d) of figure 1. Comparison with results recorded for the same sample before and after thermal treatment in N_2 atmosphere (figure 1, curves (a)–(c)) shows that the main PL emission band at 565 nm with excitation maximum at 430 nm, which appeared in the

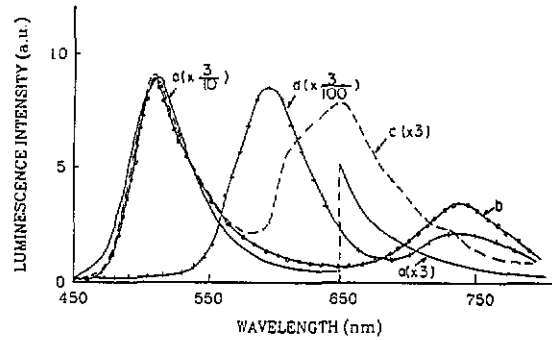


Figure 5. Photoluminescence emission spectra: (a) of AgCl ($\lambda_{\text{exc}} = 320$ nm) and AgBr crystals; (b) before thermal treatment ($\lambda_{\text{exc}} = 450$ nm); (c) before thermal treatment ($\lambda_{\text{exc}} = 330$ nm); (d) after N_2 thermal treatment ($\lambda_{\text{exc}} = 330$ nm).

pristine crystal and disappeared after thermal treatment in N_2 atmosphere, recovered after additional treatment in I_2 atmosphere. The 515 nm band, which appeared in the PL only after treatment in N_2 atmosphere, disappeared after additional I_2 treatment. The emission spectrum after the thermal treatment in I_2 atmosphere becomes similar to that of the pristine crystal except for an increase in the emission intensity of the 565 nm band.

In order to learn more about the nature of the luminescence bands of this mixed crystal, the luminescence of nominally pure AgCl and AgBr crystals was also investigated. These measurements were performed before and after thermal treatment and results are compared with those obtained for the mixed crystals.

In figure 5 (curve (a)) the PL emission spectrum of an untreated AgCl crystal, excited at LNT by UV light of 320 nm, is given. The temperature-dependence of the main emission band at 515 nm was found to be identical to that observed for the 515 nm emission in the mixed crystal (see curve (b) of figure 3). Thermal treatment in dry nitrogen atmosphere did not influence the PL of the AgCl crystal, which already has an emission spectrum similar to that of the mixed crystal after N_2 annealing.

The PL of nominally pure pristine AgBr crystals showed at LNT a main emission band at 510 nm and a weaker band at 750 nm (figure 5, curve (b)). The 510 nm emission could be excited by 400 nm as well as by 330 nm light, while the excitation maxima for the 750 nm emission are at 450 and 580 nm. The UV irradiation at 330 nm also caused excitation of an additional band at 650 nm with a shoulder at about 596 nm (figure 5, curve (c)). This 595 nm band became dominant after thermal treatment in N_2 atmosphere, while the strong 510 and 650 nm bands disappeared (figure 5, curve (d)). The different temperature dependences of the various AgBr emission bands are given in figure 3, curves (c)–(f).

Excitation spectra of nominally pure AgBr crystal are shown in figure 6. The excitation spectrum of the 515 nm emission band in AgCl was measured and appears to be identical with that for the mixed crystal shown in figure 2, curve (b). The absorbance of these crystals near the absorption edge are given by curve (e) of figure 6 and by curve (e) of figure 2 respectively.

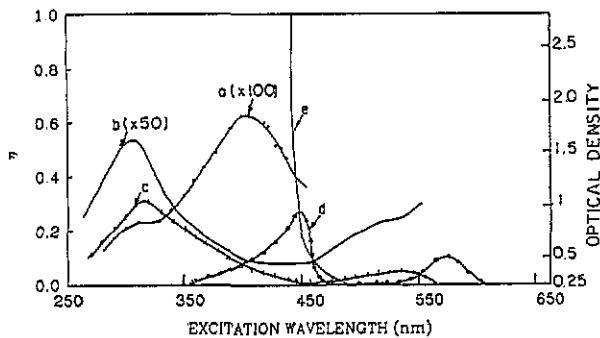


Figure 6. Excitation spectra of AgBr crystal: (a) before thermal treatment, ($\lambda_{lum} = 510$ nm); (b) before thermal treatment ($\lambda_{lum} = 640$ nm); (c) after N_2 thermal treatment ($\lambda_{lum} = 595$ nm); (d) before and after thermal treatment ($\lambda_{lum} = 750$ nm); (e) absorption of AgBr.

4. Discussion

Comparison of experimental results obtained for mixed $AgCl_{0.45}Br_{0.55}$ crystals with those obtained for nominally pure and pristine AgCl and AgBr crystals showed a shift of the absorption edge from about 370 nm in pure AgCl to about 426 nm in the mixed crystal and 447 nm in pure AgBr. The excitation maxima of the various emission bands in all examined crystals appeared in two different spectral regions of photon energies, one corresponding to a band-to-band transition, and the other to long-wavelength tails of the fundamental absorption of the various crystals. The 750 nm band, which appeared in both AgBr and $AgCl_{0.45}Br_{0.55}$ but not AgCl crystals, had excitation maxima at 450 and 430 nm respectively, which correspond to the long-wavelength tail of the fundamental absorption of these two crystals. Annealing of the mixed $AgCl_{0.45}Br_{0.55}$ crystal in N_2 and I_2 atmospheres did not affect the 750 nm emission band, but this luminescence was strongly enhanced by annealing in Br_2 atmosphere. In AgBr crystals this emission band has previously been attributed to various models [18]. The fact that this band is strongly enhanced by bromine diffusion into the crystal, might possibly be due to the formation of bromine interstitials. Our results indicate that the 750 nm emission bands in $AgCl_{0.45}Br_{0.55}$ and in AgBr crystals are due to analogous processes. This is also supported by the measurements of the temperature dependences, which showed an identical behaviour for both crystals.

The main 515 nm PL emission band in AgCl is excited by photons corresponding to photon energies of interband transition and no emission could be excited in this crystal by lower photon energies. Our results have shown, that a 515 nm emission band is dominant in PL of the mixed crystal after annealing in N_2 atmosphere. This emission band shows the same excitation spectrum and the same temperature-dependence as in the pure AgCl crystal. The 515 nm emission band in pure AgCl has previously been ascribed to a radiative decay of a STE [9]. Our results indicate that the 515 nm band in the mixed crystal is due to the same processes as in the pure AgCl crystal. This agrees with the fact, that only free excitons but no STE exist in pure AgBr [1, 3], and that

the free exciton emission decays in this crystal at about 40 K, far below the temperature of our measurements [14, 15]. In AgCl this emission is not affected by thermal treatment. The relative intensity of this band of the mixed crystal was, however, found to depend on thermal pre-treatment. In the PL of the untreated mixed crystal the 515 nm emission was relatively weak compared with the main 565 nm band, but became dominant after annealing in N_2 atmosphere. The intensity of this band was not affected by subsequent annealing in Br_2 atmosphere, but decreased again after annealing in I_2 atmosphere, which caused a strong increase in intensity of the 565 nm band. The 565 nm band is apparently due to iodide ions, which diffused into the crystal during annealing in I_2 atmosphere. The fact that the 565 nm band also appeared in our pristine $AgCl_{0.45}Br_{0.55}$ samples may perhaps be due to some casual iodide impurities in these crystals. The observed decrease in the intensity of this band after annealing in N_2 atmosphere is not yet well understood; this decrease may possibly be due to out-diffusion of iodide impurities.

Recent investigations in our laboratory have shown that the purity of silver halide crystals is of great importance when using these crystals as starting materials for infrared optical fibres and that optical properties of these fibres, such as the decrease in the threshold of laser-induced breakdown, may be affected by pre-treatment of the materials [19]. The results of the present investigation may, therefore, provide relevant information regarding the properties of mixed silver halide crystals and regarding the appropriate treatment to influence optimally the optical properties of the samples. This appears to be of importance when preparing optical fibres from these mixed crystals.

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