SOME LUMINESCENT PROPERTIES OF ADDITIVELY COLORED KBr·Ag CRYSTALS

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The luminescent characteristics of additively colored KBr·Ag crystals are investigated. In particular, the decay of the phosphorescence, the flash of emission due to IR light in relation to the silver concentration, and the temperature quenching of the steady luminescence are discussed. It is shown that the investigated crystals have a complex system of shallow and deep traps. The thermal activation energy for nonradiative transitions in the B centers is found. It is concluded that the luminescence is produced by an electron-recombination mechanism.

There has been a whole series of investigations dealing with silver-activated alkali-halide crystals (AHC). These investigations have been conducted mainly on uncolored and x-irradiated specimens, however. There have been relatively few such investigations on additively colored crystals and they relate mainly to KCl·Ag [1-8]. KBr·Ag crystals have not yet been adequately investigated [9, 10, 11]. In view of this the aim of the present work was to investigate the luminescent properties of additively colored KBr·Ag crystals and to compare our results with the data obtained for other silver-activated phosphors.

We investigated KBr·Ag crystals grown by the Kyropoulos method from "specially pure" material. The activating additive, in the form of AgBr salt, was added in concentrations of 0.05, 0.1, and 0.2 mole % to the mixture before melting. The crystals were additively colored by exposure to metallic potassium vapor at 620-640°C for 4 h followed by quenching in water. Crystals treated in this way were uniformly colored throughout their volume. For the spectral measurements we split off plates 0.17-0.4 mm thick. The absorption spectra in the wavelength range 220-1000 nm were measured on a SF-4 spectrophotometer. To investigate the luminescent properties we constructed an apparatus which could be used for work at room and nitrogen temperatures. The B-center emission spectra were measured in the range 400-500 nm with UM-2 monochromators and a FÉU-18A photomultiplier. The excitation source was a SVD-250 mercury lamp used in conjunction with a UFS-2 filter. From the data of the colored-glass catalog and our measurements a UFS-2 filter 3 mm thick has a low transmission factor in the IR region (3% at 720 nm). In this way we practically excluded the effect of IR light on the specimens during excitation, since preliminary investigations showed that IR light of such low intensity had no detectable effect on the crystals. The emission spectra were not corrected for the photomultiplier response, since they were measured on specimens of the same type for comparison in relation to the experimental conditions, and the changes in the photomultiplier response in the particular region introduced the same distortions into all the spectra. The excitation spectrum was determined with yellow lumogen by the method described in [12]. The excitation source was a VSFU-3 hydrogen lamp, whose light was decomposed by a quartz monochromator. The integral luminescence intensity was measured with a FÉU-18A photomultiplier.

Figure 1A shows the absorption spectra of additively colored KBr·Ag crystals with different activator concentrations. An increase in silver content prevented the formation of F centers and their very simple clusters (Fig. 1A, curve 2). This can be attributed to the greater ionization energy of silver atoms in comparison with that of potassium atoms (εAg = 7.54 eV, εK = 4.34 eV). The internal layers of KBr + 0.2 mole % AgBr crystals in some cases contained mainly B centers and centers responsible for bands with maxima at 342 and 440-450 nm (Fig. 1A, curve 3). The first of these was more distinct after the B band had been bleached at 100°C. The nature of this first band is still obscure. Various suggestions have...
been made regarding the nature of the band at 440-450 nm. Toporets [9, 10] attributes this band to silver colloids on the basis of temperature behavior and Savost'yanova's calculations. Etzel and Schulman [11] attribute the band with the maximum in this region in x-irradiated KBr · Ag crystals to E centers. We should mention that these centers in our specimens were thermally stable up to destruction of the crystal.

The shape of the B band (λ_{max} = 302 nm) indicates its complexity (Fig. 1B). As was shown in [1], the B band in KC1 · Ag consists of two components — B_I and B_{III}, which can be resolved only at 80°K after bleaching of the B band at 408°K. We can conclude from our data that the ratio of bands B_I and B_{III} in KBr · Ag is different from that in KC1 · Ag. In KBr · Ag these bands are of comparable intensity before bleaching.

According to our measurements, the excitation spectrum of additively colored KBr · Ag crystals coincides with the B band. This indicates that the only luminescent centers are the B centers. As distinct from KC1 · Ag crystals, additively colored KBr · Ag has an intense and prolonged afterglow. The intensity of the steady luminescence depends on the silver concentration. The fluorescence and phosphorescence spectra coincide and consist of a symmetric band with a maximum at 453 nm, which agrees with the data of [11] for x-irradiated KBr · Ag crystals. The intensity and duration of the phosphorescence depend on the concentration of B centers. Crystals with silver concentrations of 0.2 and 0.1 mole % emit a fairly intense phosphorescence, which decays in 2 to 10 min at room temperature. The shape of the decay curve is complex. Initially (1-2 sec) there is an exponential portion, whose length depends on the intensity of the exciting light if the excitation time is constant. At low excitation intensities the decay is hyperbolic from the start. The hyperbolic index α lies in the range 0.4-1 for different specimens. Such small values of α indicate that in KBr · Ag crystals the probability of second capture is much higher than the probability of recombination [13]. The presence of phosphorescence at 80°K indicates that such crystals have not only deep, but also shallow, traps. In these conditions, however, the intensity and duration of the phosphorescence have much smaller values than at room temperature. In crystals with a relatively low concentration of B centers (the concentration was determined from the value of the absorption coefficient at the maximum of the B band) there was either no phosphorescence at all at room temperature or it was of very low intensity and decay in 20-25 sec. At 80°K, however, the same crystals exhibited a relatively intense phosphorescence with a decay time of 2-4 min. We can conclude from these facts that the phosphorescence at room and nitrogen temperatures is due to different systems of traps. A similar conclusion is indicated by the fact that if the crystal is excited at 300°K, and then cooled rapidly to 80°K as soon as excitation ceases, no phosphorescence is observed.

KBr · Ag crystals emit a flash when irradiated with infrared light during excitation and on removal of the infrared light. The spectral composition of the flash is the same as that of the steady luminescence produced by IR light with wavelength in the range 600-1700 nm. All these facts confirm the electron-recombination mechanism of the luminescence in KBr · Ag crystals. An investigation of the flash of the steady luminescence showed that its intensity depended on the exciting light intensity and the temperature. At...