Luminescence of Cu$^+$ and Cu$^{2+}$ ions in CsBr crystals

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Cupper ions in the different charge states usually create the set of strongly localized states in the ionic compounds [1] that, in principle, may be used for development of the storage phosphors and materials for thermoluminescent (TL) dosimetry [2]. The luminescence of Cu$^+$ and Cu$^{2+}$ ions in CsBr crystals was studied in our previous papers [2, 4] by the traditional spectroscopic methods. In this work, we continue investigation of nature of the luminescent centers created by the cupper dopant in CsBr host using the synchrotron radiation (SR) excitation.

The CsBr:Cu and CsBr:CuBr$_2$ crystals with dominant valence state Cu$^+$ and Cu$^{2+}$, respectively [2, 4], were chosen for investigation. Crystals were grown by Bridgman-Stockbarger method from the CsBr salt of 5N purity and doped by adding the metallic Cu and CuBr$_2$ bromide in concentration of 0.5 mole %, respectively. The luminescence of these crystals was investigated at 10 and 300 K at the Superlumi station (HASYLAB, DESY) under excitation by SR with an energy of 3.7-25 eV. The emission and excitation spectra were measured in the limits of SR pulse with a repetition time of 200 ns and duration of 0.127 ns. The decay kinetics of luminescence was measure in the time range 0-200 ns.

The emission spectrum of the CsBr:Cu crystal under excitation at 5.29 eV in the range of low-energy absorption band related to partly-allowed $^1A_{1g} \rightarrow ^1T_{2g}$ transition of Cu$^+$ ions presents the complex emission band in visible rage as a superposition of the two sub-bands peaked at 2.62 and 2.235 eV (Fig.1a, curve 1). The dominant high-energy emission band corresponds to the $^1T_{2g} \rightarrow ^1A_{1g}$ radiation transitions in the presence of the $^1T_{1g}$ metastable level of Cu$^+$ ions [5]. In work [2] we noted that as opposed to the typical one-component character of Cu$^+$ emission [6], the luminescence spectrum of Cu$^+$ ions in CsBr:Cu crystal under $^1A_{1g} \rightarrow ^1T_{2g}$ band excitation consists also of second low-energy emission band peaked at 2.235 eV. The possible reasons for the existence of two band of Cu$^+$ emission are as follows: (i) the on- and off-centre configurations of the relaxed excited state of Cu$^+$ ions [7] with different prevailing mechanism of excitation; (ii) the formation of the dimer or other complex Cu$^+$ centers.

The excitation spectra of two emission bands of Cu$^+$ ions in CsBr:Cu crystal are shown in Fig.2a. The excitation spectrum of high-energy band consists of two bands in the CsBr transparency range peaked at 4.47 and 5.45 eV related to the $^1A_{1g} \rightarrow ^1T_{2g}$ transition of Cu$^+$ ions. In the exciton range this spectrum contains the band peaked at 5.83 eV corresponding to the energy of formation of excitons bound with Cu$^+$ ions. The shape of excitation spectrum of low-energy band of Cu$^+$ luminescence significantly changes in comparison with the same spectra for the high-energy band (Fig.2a, curve 2). Specifically, the emission in this band weakly excited in the fundamental absorption range but effectively excited in the wide band peaked approximately at 4.47 eV which strongly overlapped with the low-energy absorption band of Cu$^+$ ions. Most probably, this excitation band corresponds to the charge transfer transition (CTT) between the bottom of valence band formed by the Br$^-$ states and ground state of Cu$^+$ or Cu$^{2+}$ ions.

Fig.1. Emission spectra (normalized) of CsBr:Cu and CsBr:CuBr$_2$ crystals at 300 K under excitation by SR in the range of Cu$^+$ and Cu$^{2+}$ ions absorption bands at 5.29 (1a) and 4.09 eV (1b), exciton range at 6.04 (2a) and 5.98 eV (2b) and interband transition range at 6.88 (3a) and 6.765 eV (3b), respectively.

The emission spectrum of the CsBr:Cu crystal under excitation at 5.29 eV in the range of low-energy absorption band related to partly-allowed $^1A_{1g} \rightarrow ^1T_{2g}$ transition of Cu$^+$ ions presents the complex emission band in visible rage as a superposition of the two sub-bands peaked at 2.62 and 2.235 eV (Fig.1a, curve 1). The dominant high-energy emission band corresponds to the $^1T_{2g} \rightarrow ^1A_{1g}$ radiation transitions in the presence of the $^1T_{1g}$ metastable level of Cu$^+$ ions [5]. In work [2] we noted that as opposed to the typical one-component character of Cu$^+$ emission [6], the luminescence spectrum of Cu$^+$ ions in CsBr:Cu crystal under $^1A_{1g} \rightarrow ^1T_{2g}$ band excitation consists also of second low-energy emission band peaked at 2.235 eV. The possible reasons for the existence of two band of Cu$^+$ emission are as follows: (i) the on- and off-centre configurations of the relaxed excited state of Cu$^+$ ions [7] with different prevailing mechanism of excitation; (ii) the formation of the dimer or other complex Cu$^+$ centers.

The excitation spectra of two emission bands of Cu$^+$ ions in CsBr:Cu crystal are shown in Fig.2a. The excitation spectrum of high-energy band consists of two bands in the CsBr transparency range peaked at 4.47 and 5.45 eV related to the $^1A_{1g} \rightarrow ^1T_{2g}$ transition of Cu$^+$ ions. In the exciton range this spectrum contains the band peaked at 5.83 eV corresponding to the energy of formation of excitons bound with Cu$^+$ ions. The shape of excitation spectrum of low-energy band of Cu$^+$ luminescence significantly changes in comparison with the same spectra for the high-energy band (Fig.2a, curve 2). Specifically, the emission in this band weakly excited in the fundamental absorption range but effectively excited in the wide band peaked approximately at 4.47 eV which strongly overlapped with the low-energy absorption band of Cu$^+$ ions. Most probably, this excitation band corresponds to the charge transfer transition (CTT) between the bottom of valence band formed by the Br$^-$ states and ground state of Cu$^+$ or Cu$^{2+}$ ions.
The emission spectrum of CsBr:Cu crystal under excitation at 6.04 and 6.88 eV (Fig.1a, curve 1 and 2, respectively) presents the dominant band peaked at 3.01 eV corresponding to emission of excitons localized around Cu\(^{2+}\) ions. This emission band is excited mainly in the exciton range (5.5-6.2 eV) (Fig.2, curve 3) what confirms their exciton origin. The maxima of excitation bands peaked at 6.0 and 6.66 eV in the exciton and fundamental absorption ranges, respectively, correspond to the energies of creation of such excitons.

The luminescence spectrum of CsBr:CuBr\(_2\) crystal under excitation with an energy of 4.09 eV in strong absorption band of this crystal consists of the dominant emission band of Cu\(^{2+}\) ions peaked at 2.49 eV with low-intensity bump in the low-energy side (Fig.1b, curve 1). The excitation spectrum of the Cu\(^{2+}\) luminescence (Fig.2b, curve 1) in CsBr transparency range consists of the intensive band peaked at 4.09 eV which coincides with the above mentioned strong absorption band. Most probably, this band (Fig.2, curve 1) is related to the formation of Cu\(^{2+}\) state via CTT from the ground state of Cu\(^{2+}\) ions to conductive band with following recombination luminescence of Cu\(^{2+}\) ions. The intensive bands at 6.65 and 6.9 eV in the fundamental absorption range are related to excitation of Cu\(^{2+}\) emission via e/h recombination. The dominant bands peaked at 6.0 eV in the exciton range corresponds to energy of formation of excitons bound with the Cu\(^{2+}\) ions. Besides the emission band of Cu\(^{2+}\) ions, under excitation of the CsBr:CuBr\(_2\) crystal in the exciton range at 5.98 eV we also observed two emission bands of Cu\(^{2+}\) ions peaked at 2.71 and 2.55 eV (Fig.1b, curve 2). The low intensive band at 4.66 and 5.76 eV, most probably, is related just to the excitation band of Cu\(^{2+}\) ions (Fig.2b, curve 1). The luminescence spectrum of CsBr\(_2\) crystal under excitation at 6.765 eV in the fundamental absorption range presents the wide emission band peaked at 2.86 eV (Fig.1b, curve 3). Probably, this band is complex superposition of the emission of Cu\(^{+}\) and Cu\(^{2+}\) ions and the luminescence of excitons localized around Cu\(^{2+}\) and partly Cu\(^{+}\) ions. The excitation spectrum of the low-energy side of this complex band registered at 3.26 eV (Fig.2b, curve 2) besides the set of high-intensive band in the fundamental absorption range consist also the low-intensive band peaked at 6.05 eV corresponding to the energy of creation of excitons localized around Cu\(^{2+}\) ions.

The existence of the emission bands of different origin (intrinsic radiative transition of Cu\(^{+}\) ions in off- and on-centre configurations, recombination luminescence of Cu\(^{2+}\) ions as well luminescence excitons localized around Cu\(^{+}\) and Cu\(^{2+}\) ions) reflect the complicated character of formation of the luminescence centers in CsBr crystals due to copper doping which can participate in the storage or TL processes in such phosphors.

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Fig.2. Excitation spectra of CsBr:Cu and CsBr:CuBr\(_2\) crystals luminescence at 300 K in the range of Cu\(^{+}\) ions emission at 2.69 (1a) and 2.06 eV (2a), Cu\(^{2+}\) ions emission at 2.25 eV (1b) and localized exciton emission at 3.13 (3a) (at 10 K) and 3.26 eV (2b).