Luminescence of Eu^{2+}-doped Microcrystals Embedded in the NaBr matrix

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Single crystals of MeX_2 type (Me=Ca, Sr, Ba; X=Cl, Br, I) doped by europium ions are of special interest due to the presence of high light yield [1–3], which exceeds the one of well-known scintillators such as CsI-Tl, CsI-Na, NaI-Tl [4]. This gives the perspective of the creation of novel efficient scintillator materials on their base. However, significant hygroscopicity and low symmetry of crystal lattice of these crystals prevents their detailed study and application. The use of MeX_2-Eu as microcrystals embedded in the insulator matrix (i.e. formation of the systems of "microcrystal-in-crystal" type) stable to atmosphere influences could be a solution to this problem.

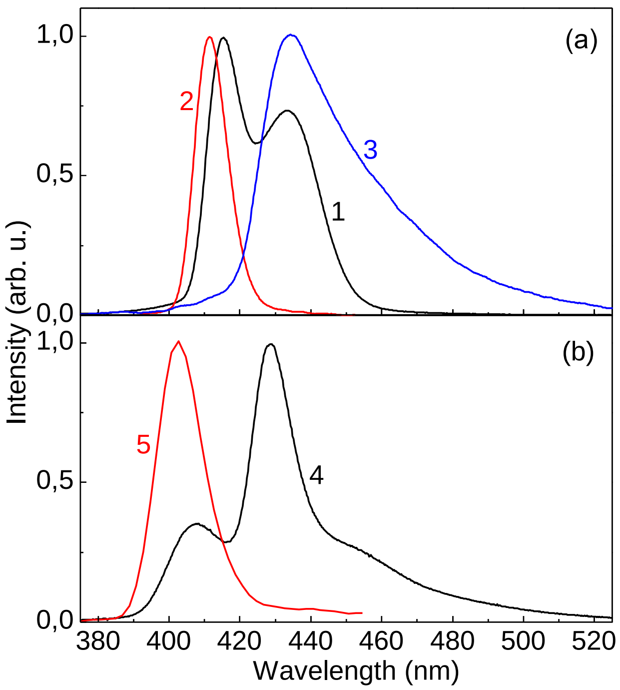

Figure 1: (a) emission spectra of NaBr-$SrBr_2$-Eu (curve 1), $SrBr_2$-Eu (curve 2) and NaBr-Eu (curve 3); (b) emission spectra of NaBr-$BaBr_2$-Eu (curve 4), $BaBr_2$-Eu (curve 5) upon the 300 nm excitation. T = 8 K.

The efficient formation of $MeCl_2$-Eu microcrystals with size of 1–10 µm embedded in the NaCl matrix [5] was revealed studying the possibility of Me^{2+} (Me=Sr, Ba) ions aggregation in this matrix. Since scintillation properties of MeX_2-Eu type crystals are enhanced in the Cl→Br→I series, the bromide and iodide crystalline systems are of great interest. The goal of this work is the study of the possibility of the formation of Eu^{2+}-ions doped $MeBr_2$ (Me=Sr, Ba) microcrystals embedded in the NaBr matrix.

NaBr-$MeBr_2$(1 mol. %)-$EuBr_3$(0.02 mol. %), $MeBr_2$-Eu(0.1 mol. %) (Me=Sr, Ba) and NaBr-Eu(0.1 mol.%) crystals were grown in evacuated quartz ampoules using the Bridgman–Stockbarger technique. The as-grown NaBr-$MeBr_2$-Eu crystals were annealed at 200 ºC during 100 h for an activation of aggregating processes. Time-resolved luminescent spectroscopy studies were performed at T = 9–300 K using the facility of SUPERLUMI station at HASYLAB.

The luminescence spectrum of the NaBr-$SrBr_2$-Eu crystalline system consists of two bands peaked at 415 and 433 nm (Fig. 1 a, curve 1). The presence of the intensive 415 nm emission band which are close by the spectral position to the emission band of europium ions in the $SrBr_2$ matrix (Fig. 1 a, curve 2) indicates the formation of impurity $SrBr_2$ aggregates doped by Eu^{2+} ions. Similar to the case of NaCl-$SrCl_2$-Eu [5], it could be assumed that the size of these aggregates is within 1–10 µm range. The presence of the 433 nm emission band coinciding by spectral position with the europium luminescence in NaBr (curve 3) indicates that the certain part of the europium ions remains in the NaBr matrix.

In case of the NaBr-$BaBr_2$-Eu crystalline system, the emission bands peaked at 407, 428 nm and 455 nm are observed (Fig. 1 b, curve 4). The 428 nm emission band is the dominant one corresponding to the europium ions luminescence in the NaBr matrix (Fig. 1 a, curve 3). It indicates that the major part of impurity ions remains in the NaBr matrix and only tiny quantity enters to the $BaBr_2$ microcrystals. The formation of $BaBr_2$-Eu microcrystals is confirmed by the appearance of the 407 nm emission band typical to europium luminescence in $BaBr_2$ (curve 5).

The mechanisms of entering of europium ions in the NaBr matrix were studied in [6]. There, it was revealed the aggregation processes of europium ions resulting in the formation of the $EuBr_2$. The emission maximum of such precipitates is at 450 nm [6]. The luminescence band located at 460 nm was registered by us for the NaBr-Eu single crystal (Fig. 1 a, curve 3). We assume that the formation of the $EuBr_2$ precipitates for the NaBr-$BaBr_2$-Eu crystalline system takes place, since the 455 nm emission band inherent for $EuBr_2$ precipitates is observed in the luminescence spectrum of this system (Fig. 1 b, curve 4). The possibility of the formation of such precipitates in the NaBr-$BaBr_2$-Eu system is caused by significant number of europium ions which remains in the NaBr matrix due to inefficient formation of $BaBr_2$-Eu microcrystals.

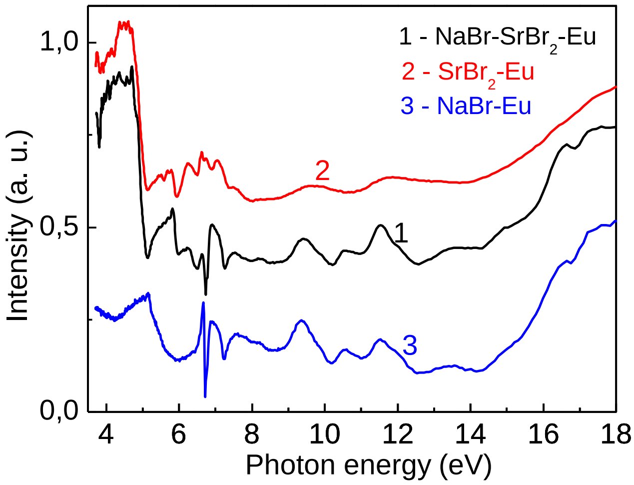

Figure 2: Luminescence excitation spectra of europium luminescence in the $SrBr_2$-Eu microcrystals embedded in the NaBr matrix (curve 1) and the $SrBr_2$-Eu single crystal (curve 2) and the NaBr-Eu single crystals (curve 3), T = 8 K.

Thus, strontium ions is more perspective impurity comparing to barium ions for the obtaining "microcrystal-in-crystal" type crystalline systems due to more efficient formation of the $SrBr_2$-Eu microcrystals in the NaBr matrix.

The excitation spectrum of europium luminescence band in NaBr-Eu (λ_{em} = 440 nm) reveals the range of intracenter 4f→5d absorption of europium ions at $h\nu < 6$ eV, as well as the range connected with energy transfer from the matrix to europium. One can distinguish processes involving excitons (area $h\nu > 6$ eV) and the region of multiplication of electronic excitations due to inelastic electron-electron scattering with a threshold at $h\nu \sim 14$ eV. The excitation spectrum of microphase $SrBr_2$-Eu embedded in NaBr in range of NaBr matrix transparency coincides with the excitation spectrum of a single crystal $SrBr_2$-Eu (Fig. 2, curves 1 and 2). It additionally confirms the incorporation of europium ions in $SrBr_2$. However, the excitation spectrum of $SrBr_2$-Eu microphase is similar with that for NaBr-Eu (Fig. 2, curve 3). This indicates the energy transfer from the matrix to the NaBr microcrystals. The possible mechanism of this transfer is radiative due to reabsorption of self-trapped exciton emission of the NaBr matrix (Fig. 2).

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