Luminescence of BaCl$_2$-Eu microcrystals embedded in NaCl matrix

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Recently interest to the BaX$_2$ and SrX$_2$ (Cl, Br, I) single crystals doped with Eu$^{2+}$ ions as scintillation materials is renewed. It is known that BaCl$_2$, BaBr$_2$, BaI$_2$ single crystals doped with rare-earth Eu$^{2+}$ and Ce$^{3+}$ ions possess the high light yield upon the excitation by γ-quanta. The light yield for barium halides activated with europium is in the range of 16000–32000 ph/MeV [1, 2]. Therefore the barium halides can be the promising matrices for effective scintillation materials. However, mentioned crystals possess a high hygroscopicity. Last circumstance is a hindrance to its detailed study and applications. The synthesis of BaCl$_2$-Eu microcrystals embedded in NaCl crystalline matrix and characterization of its luminescence properties especially in the range of band-to-band transitions was the aim of this work. Such approach considerably simplifies the samples preparation procedure and allows to avoid the hygroscopicity.

In this work the results of spectral-luminescent and luminescent-kinetic studies of NaCl-Eu and NaCl-BaCl$_2$-Eu crystals at room temperature are reported. The NaCl-BaCl$_2$(1 mol.%)-EuCl$_3$(0.02 mol.%) and NaCl-EuCl$_3$(0.02 mol.%) crystalline systems were grown in sealed quartz ampoules using Stockbarger growth technique. The obtained NaCl-BaCl$_2$-Eu crystals underwent the annealing at 150-200°C during 100 hours with the purpose to facilitate the thermal-activated migration of ions resulted in the formation of BaCl$_2$ microcrystals embedded in NaCl host.

The emission spectra of NaCl-Eu and NaCl-BaCl$_2$-Eu crystals upon optical and X-ray excitation are presented in Fig. 1. In the emission spectrum of NaCl-Eu crystals the luminescence band peaked at 430 nm is observed (Fig. 1 a, curve 1). The spectral position of this band is characteristic for the emission of impurity europium ions in NaCl crystal. In the emission spectrum of NaCl-BaCl$_2$-Eu crystal the band with maximum at 400 nm (Fig. 1 a, curve 2) dominates. The spectral position of this band coincides with that for the emission band of impurity Eu$^{2+}$-centers of BaCl$_2$-Eu crystal [2]. From this fact we can conclude that the temperature annealing of NaCl-BaCl$_2$(1 mol.%)-EuCl$_3$(0.02 mol.%) crystalline system resulted in the creation of BaCl$_2$-Eu microcrystals embedded in the NaCl matrix. In the emission spectrum of NaCl-BaCl$_2$-Eu crystal the band peaked at 430 nm which are characteristic for NaCl-Eu crystal appears as the long-wave shoulder. It means that the significant quantity of europium ions enters into the BaCl$_2$ microcrystals. In the same time the part of europium ions are present as the single luminescence centers in the NaCl matrix. The similarity of luminescence excitation spectra for the emission band with $\lambda_{\text{max}}$=430 nm for NaCl-BaCl$_2$-Eu and NaCl-Eu crystals (Fig. 2 a, curve 1 and Fig. 2 b, respectively) also confirms this conclusion. The dips in the excitation spectra of NaCl-BaCl$_2$-Eu and NaCl-Eu crystals at 7.8 eV correspond to the excitonic reflection peak of NaCl crystal. The considerable increase of the excitation efficiency of mentioned emission bands at the energies $E_{\text{exc}} > 16$ eV most probably is caused by photon multiplication processes. It is necessary to note that the emission of BaCl$_2$ microphase is effectively excited in the region of the band-to-band transition of NaCl matrix.

The structure of X-ray excited emission spectra of NaCl-BaCl$_2$-Eu crystal (Fig. 1 b, curve 2) is the same as upon the light excitation, but in this case the 430 nm emission band of europium centers in NaCl crystals (Fig. 1 b, curve 1) has considerably greater intensity.
The obtained results of spectral-luminescence measurements of NaCl-BaCl$_2$-Eu and NaCl-Eu crystals allow us to conclude that the activated BaCl$_2$-Eu microcrystals are formed in NaCl matrix as a result of the annealing.

![Emission spectra](image1)

Figure 1: Emission spectra of NaCl-Eu (curves 1) and NaCl-BaCl$_2$-Eu crystals (curves 2) upon the light excitation with $\lambda_{exc}$=172 nm (a) and X-ray excitation (b) at $T$=295 K.

![Luminescence excitation spectra](image2)

Figure 2: Luminescence excitation spectra of NaCl-BaCl$_2$-Eu (frame (a), curves: 1 - $\lambda_{em}$=430 nm, 2 - $\lambda_{em}$=400 nm) and NaCl-Eu (frame (b), $\lambda_{em}$=430 nm) crystals at 295 K.

References