

Formation and luminescent properties of MeBr₂-Eu (Me=Sr, Ba) microcrystals dispersed in NaBr matrix

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The formation of europium doped MeBr₂ microcrystals (Me=Sr, Ba) embedded in NaBr matrix is revealed in NaBr-MeBr₂-Eu crystalline system. The spectral-luminescent properties of embedded MeBr₂-Eu microcrystals are studied upon the synchrotron radiation excitation. The mechanisms of luminescence excitation of europium centers in NaBr-MeBr₂-Eu crystalline system and features of Me²⁺ and Eu²⁺ impurity ions aggregation processes in NaBr matrix are discussed.

В кристаллической системе NaBr-MeBr₂-Eu обнаружено образование активированных ионами европия микрокристаллов MeBr₂ (Me = Sr, Ba). Исследованы спектрально-люминесцентные свойства диспергированных микрокристаллов MeBr₂-Eu при возбуждении синхротронным излучением. Обсуждаются механизмы возбуждения люминесценции центров европия в кристаллической системе NaBr-MeBr₂-Eu и особенности агрегатирования примесных ионов Me²⁺ и Eu²⁺ в матрице NaBr.

Формування і люмінесцентні властивості мікрокристалів MeBr₂-Eu (Me = Sr, Ba), диспергованих у матриці NaBr. А.С.Пушак, В.В.Вістовський, А.Котлов, З.А.Хапко, О.П.Васьків, О.В.Гектін, А.С.Волошиновський.

У кристалічній системі NaBr-MeBr₂-Eu виявлено утворення активованих іонами Європію мікрокристалів MeBr₂ (Me = Sr, Ba), диспергованих у матриці NaBr. Досліджено спектрально-люмінесцентні властивості вкраплених мікрокристалів MeBr₂-Eu за умови збудження синхротронним випромінюванням. Обговорюються механізми збудження люмінесценції центрів Європію у кристалічній системі NaBr-MeBr₂-Eu та особливості агрегування домішкових іонів Me²⁺ і Eu²⁺ у матриці NaBr.

1. Introduction

Bulk MeX₂ (Me = Ca, Sr, Ba; X = Cl, Br, I) crystals activated by lanthanide ions attract attention as possible new high-performance scintillators due to their high

light yield [1–5]. Especially high light yield observed for europium doped CaI₂ and SrI₂ crystals. The estimated light yield for these systems is more than 10⁵ photons/MeV, which is significantly greater comparing with one for well known scintillators such

as CsI–Tl, CsI–Na and NaI–Tl [6]. However, the strong hygroscopicity and the low symmetry of the crystals prevent their careful research and practical application. Usage of MeX₂–Eu compounds in a form of microcrystals dispersed in the dielectric matrix, i.e. creation of "microcrystal in crystal" systems to prevent an influence of atmospheric moisture can be a way to solve the hygroscopicity problem. It is convenient to use alkali-halide crystals as dielectric matrixes for the formation of dispersed MeX₂–Eu microcrystals. To form such the "microcrystal in crystal" type system the MeX₂ impurity (Me = Ca, Sr, Ba; X = Cl, Br, I) is added in the AX matrix (A = Na, K) and after crystal growth the system is annealed at 150–200°C during several days to promote an aggregation processes of the impurity ions. In result of the temperature treatment the impurity ions form embedded micro- or nanocrystals [7]. For formation of the lanthanide doped microcrystals the LnX₃ salt (Ln = Eu, Ce) is also added in appropriate concentration relatively main impurity Me²⁺. The study of a possibility of the Me²⁺ (Me = Sr, Ba) impurity ions aggregation in NaCl matrix has revealed an effective formation of 1–10 μm size MeCl₂–Eu microcrystals dispersed in the matrix of NaCl [8, 9]. Also the aggregation processes has been revealed for La³⁺ ions in the NaX (X = Cl, Br) matrixes, where the embedded LaX₃ microcrystals has been observed [10–12]. Chemical composition of the microcrystals not always corresponds to an activator composition. For example, when KCl crystal is activated by LaCl₃ the formation of K₂LaCl₅ microcrystals in KCl matrix was observed [13].

Since an improvement of the MeX₂–Eu crystals scintillation properties is observed in Cl → Br → I halogen series [14–16], first of all the bromide and iodide compounds are of practical interest. The aim of this work was to determine the possibility of the europium doped MeBr₂ (Me = Sr, Ba) microcrystals formation in NaBr matrix. As it is known from previous studies of the formation of microcrystals dispersed in NaX (X = Cl, Br, I) matrix the sodium ions do not create the compounds with the ions of alkaline-earth elements [8–12]. Thus, it is convenient to use NaBr crystal for the formation of embedded MeBr₂ (Me = Sr, Ba) microcrystals.

2. Experimental

NaBr–MeBr₂ (1 mol.%)–EuBr₃ (0.02 mol.%) (Me = Sr, Ba), NaBr–Eu (0.1 mol.%) and

MeBr₂–Eu (0.1 mol.%) crystals were grown in evacuated quartz ampoules by the Bridgman-Stockbarger technique using a moving vertical ampoule and a static furnace with one hot zone. As-grown NaBr–MeBr₂–Eu crystals were annealed at 200°C during 100 h for an activation of impurity ion aggregation.

Measurements of the emission and luminescence excitation spectra of NaBr–MeBr₂–Eu, MeBr₂–Eu and NaBr–Eu crystals were performed using the facility of SUPERLUMI station at HASYLAB (DESY, Hamburg) [17]. A cryostat with flowing helium was used to carry out the low-temperature ($T = 10$ K) measurements. Emission spectra were studied within 300–800 nm range with a spectral resolution of 1 nm using Action Research Corporation (ARC) "Spectra Pro 308" 30 cm monochromator-spectrograph equipped with the Princeton Instruments CCD detector and HAMAMATSU R6358P photomultiplier. The luminescence excitation spectra were scanned with the resolution of 4 Å within 4–18 eV by means of primary 2 m monochromator in 15° McPearson mounting and ARC monochromator as a secondary one. The luminescence excitation spectra were corrected on the intensity of synchrotron radiation.

3. Results and discussion

The luminescence spectrum of NaBr–SrBr₂–Eu crystal system consists of two bands with maxima at 415 and 433 nm (Fig. 1, curve 1). Since the spectral position of 415 nm band is close to the position of the europium emission band in SrBr₂ matrix (curve 2), this band can be ascribed to the emission of europium ions in SrBr₂ microcrystals dispersed in NaBr matrix. It is assumed that the size of embedded microcrystals is close to one in similar NaCl–MeCl₂–Eu (Me = Sr, Ba) crystalline systems [8, 9]. For these systems, the size of inclusions identified by electron microscopy is of 1–10 μm range.

The presence of 433 nm band corresponding to emission of europium ions in NaBr matrix (Fig. 1, curve 3) in the luminescence spectrum of the crystalline system of NaBr–SrBr₂–Eu (Fig. 1, curve 1) indicates that the part of europium ions remains in NaBr matrix. This fact indicates that the formation of SrBr₂–Eu microcrystals in the matrix of NaBr is less effective in comparison with the formation of MeCl₂–Eu (Me = Sr, Ba) microcrystals in NaCl matrix [8, 9]. In the

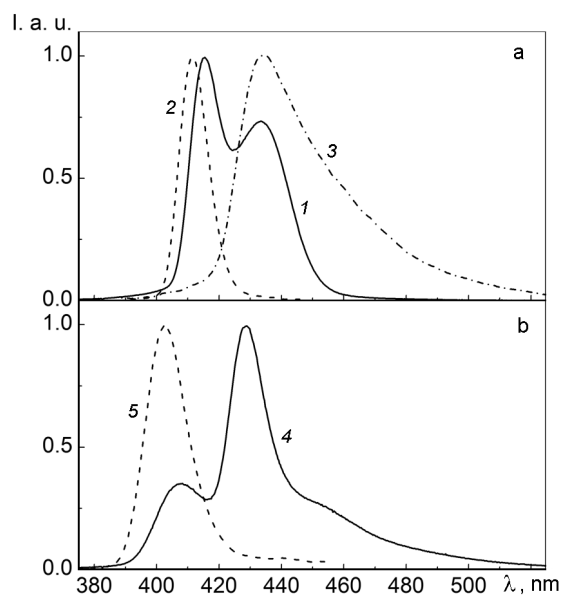


Fig. 1. Luminescence spectra of NaBr-SrBr₂-Eu (curve 1), SrBr₂-Eu (curve 2), NaBr-Eu (curve 3), NaBr-BaBr₂-Eu (curve 4) and BaBr₂-Eu (curve 5) crystals at $\lambda_{exc} = 300$ nm, $T = 10$ K.

case of chloride NaCl-MeCl₂-Eu systems the europium ions in NaCl matrix are almost absent, because there is no emission peaked at 428 nm inherent for europium ions in NaCl matrix (Fig. 2, curve 3). Lower efficiency of bromide SrBr₂-Eu microcrystals formation may be caused by the reduction of impurity strontium ions mobility in the NaBr in comparison with NaCl matrix. The larger ion radius of Br increases the packing density of cells in the NaBr as compared with NaCl matrix leading to the decrease of the strontium ions mobility in the NaBr matrix.

A slight difference between the position of the luminescence bands maxima of europium centers in SrBr₂-Eu microcrystals and SrBr₂-Eu single crystal (415 and 411 nm, Fig. 1, curves 1 and 2, respectively) can be explained by the presence of the following size effects. In NaBr-SrBr₂-Eu system SrBr₂ microcrystals of different size is created and SrBr₂ phases of small size (precipitates) also are present in NaBr matrix [18]. The lattice parameters of SrBr₂ precipitates can differ from that for the microcrystals, consequently impurity europium ions in the precipitates may possess the different luminescence properties. The same situation occurs when europium ions are located on the surface of SrBr₂ microcrystals. The emission band of Eu²⁺ ions located in SrBr₂ precipitates or on the surface of SrBr₂ microcrystals

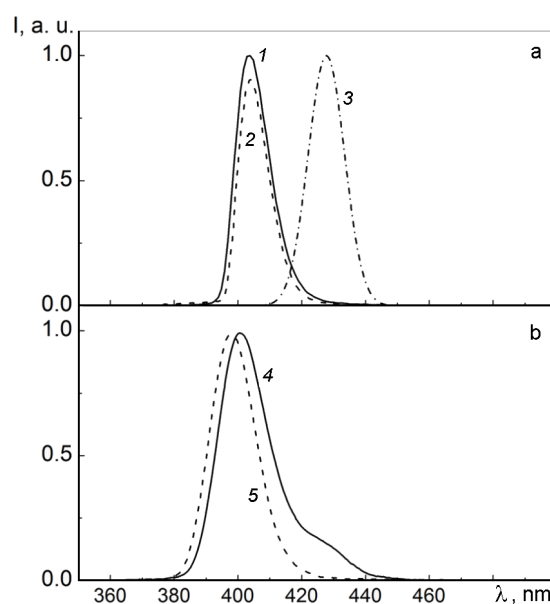


Fig. 2. Luminescence spectra of NaCl-SrCl₂-Eu ($\lambda_{exc} = 265$ nm curve 1), SrCl₂-Eu ($\lambda_{exc} = 280$ nm curve 2), NaCl-Eu ($\lambda_{exc} = 330$ nm curve 3), NaCl-BaCl₂-Eu ($\lambda_{exc} = 280$ nm curve 4) and BaCl₂-Eu ($\lambda_{exc} = 330$ nm curve 5) crystals at $T = 10$ K.

tals can correspond to the band observed at 415 nm. This position is intermediate between the emission band of europium centers in SrBr₂ (411 nm) and NaBr (433 nm). The shift of the europium emission band also can be caused by the influence of the matrix hydrostatic pressure on the microcrystals. As it was shown in [19] for BaBr₂-Eu single crystal under external hydrostatic pressure in the range of 0–27.4 GPa the maximum of the europium emission band is linearly shifted to longwave size from 404 to 580 nm. The matrix hydrostatic pressure also can influence on the position of the exciton levels as it was shown for CsPbCl₃ nanocrystals dispersed in CsCl matrix [20].

In the luminescence spectra of NaBr-BaBr₂-Eu crystalline system (Fig. 1b, curve 4) an emission band at 428 nm corresponding to the luminescence of Eu²⁺ ions located in NaBr matrix is considerably more intensive comparing with the band of Eu²⁺ ions located in BaBr₂ microcrystals (407 nm). The low efficiency of BaBr₂ microcrystals formation in NaBr-BaBr₂-Eu system can be reason for this. In the case of NaBr-BaBr₂-Eu system the efficiency of microcrystals formation is lower comparing with NaBr-SrBr₂-Eu because the ionic radius of Ba²⁺ (1.38 Å) is greater than that of Sr²⁺ (1.12 Å) and con-

sequently the barium ion mobility in NaBr matrix is lower comparing with that for the strontium ions.

Besides the mentioned bands at 407 and 428 nm the emission band peaked at 455 nm is observed in the luminescence spectrum of NaBr–BaBr₂–Eu system (Fig. 1b, curve 4). Presumably, this band corresponds to the emission of EuBr₂ type precipitates formed in NaBr matrix. The aggregation of europium ions in NaBr matrix was studied in [21]. The emission band of EuBr₂ precipitates in NaBr matrix was revealed at 450 nm. The EuBr₂ precipitates formation in NaBr–BaBr₂–Eu crystalline system is possible because the high quantity of europium ions remains in NaBr matrix.

In the transparency range of NaBr matrix (3.5–6 eV) the structure of excitation spectrum of NaBr–SrBr₂–Eu for the luminescence band peaked at 415 nm is similar to one for 411 nm band of SrBr₂–Eu crystal (Fig. 3, curves 2 and 3, respectively). This further confirms the ascribing of 415 nm band to emission of europium ions in SrBr₂–Eu microcrystals dispersed in NaBr matrix. In the fundamental absorption range of NaBr matrix ($h\nu_{exc} > E_g$) the structure of the europium luminescence excitation spectrum of SrBr₂–Eu microcrystals (curve 2) is similar to the structure of that for europium centers located in NaBr matrix (curve 1). This indicates that an energy transfer from NaBr matrix to embedded SrBr₂–Eu microcrystal takes place. Presumably, the mechanism of this energy transfer is radiative: the impurity europium ions located in SrBr₂–Eu microcrystals reabsorb the intrinsic emission of NaBr matrix due to overlapping of self-trapped exciton band of NaBr (4.6 eV) with the Eu²⁺ intracenter absorption range. The radiative mechanism of the energy transfer from the matrix to embedded micro- or nanocrystals also was revealed for a range of other micro- or nanocomposites, namely: NaCl–MeCl₂–Eu [8, 9], NaX–LaX₃–Ce [10, 11], NaCl–LaCl₃–Eu [12], KCl–K₂LaCl₅–Ce [13, 22], CsBr–CsSnBr₃ [23] and CsCl–CsPbCl₃ [7].

4. Conclusions

The processes of Me²⁺ (Me = Sr, Ba) impurity ions aggregation resulting in the formation of dispersed MeBr₂–Eu microcrystals in NaBr matrix are less efficient than in the case of chloride NaCl–MeCl₂–Eu systems. Low mobility of the impurity Me²⁺ ions due to higher packing density of NaBr matrix

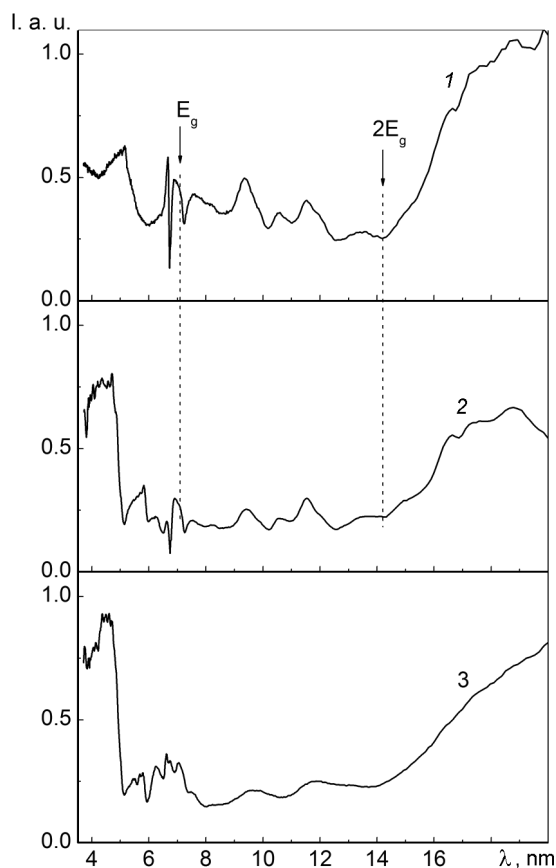


Fig. 3. Luminescence excitation spectra of NaBr–Eu ($\lambda_{em} = 433$ nm, curve 1), NaBr–SrBr₂–Eu ($\lambda_{em} = 415$ nm, curve 2) and SrBr₂–Eu crystal ($\lambda_{em} = 411$ nm, curve 3) at $T = 10$ K.

cells can be possible reason for this. The formation of embedded microcrystals in NaBr–SrBr₂–Eu is more effective than in NaBr–BaBr₂–Eu crystalline system. Spectral-luminescent properties of the embedded MeBr₂–Eu microcrystals are similar to ones of their bulk analogues. The main mechanisms of luminescence excitation of europium ions located in the microcrystals are $4f \rightarrow 5d$ absorption transitions and the reabsorption of the STE emission of NaBr matrix.

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