

Luminescence properties of SrCl₂-Eu microcrystals embedded in NaCl host

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The formation of SrCl₂-Eu microcrystals embedded in NaCl host has been demonstrated for NaCl-SrCl₂(1 mol.%)–EuCl₃(0.02 mol.%) composition. The size of SrCl₂-Eu microcrystals is in the 1–10 μm range. The spectral and luminescence properties of NaCl-Eu(0.1 mol.%), SrCl₂-Eu(0.1 mol.%) and NaCl-SrCl₂(1 mol.%)–EuCl₃(0.02 mol.%) crystals under optical and X-ray excitation have been studied. The luminescence parameters of SrCl₂-Eu microcrystals embedded in NaCl host are revealed to be substantially similar to those of SrCl₂-Eu(0.1 mol.%) single crystal.

Для системы NaCl-SrCl₂(1 мол.%)–EuCl₃(0,02 мол.%) показана возможность образования микрокристаллов SrCl₂-Eu диспергированных в матрице NaCl. Размер микрокристаллов SrCl₂-Eu составляет 1–10 мкм. Исследованы спектрально-люминесцентные свойства кристаллов NaCl-Eu(0,1 мол.%), SrCl₂-Eu(0,1 мол.%) та NaCl-SrCl₂(1 мол.%)–EuCl₃(0,02 мол.%) при оптическом и рентгеновском возбуждении. Спектрально-люминесцентные параметры микрокристаллов SrCl₂-Eu, диспергированных в матрице NaCl, и монокристаллов SrCl₂-Eu подобны.

1. Introduction

Single crystals of MeX₂ type (Me = Ca, Sr, Ba; X = Cl, I) doped with rare-earth ions are of special interest since they are considered as materials of promise for effective scintillators [1–3]. Some of the crystals doped with europium ions show a higher light yield than the well-known CsI-Tl, NaI-Tl, CsI-Na scintillators [4]. For example, SrCl₂-Eu and SrI₂-Eu single crystals show a high light yield (above 100000 photons per MeV). Therefore, the study of the luminescence and scintillation properties of strontium halides is an actual task due to the possibility to develop the effective scintillators based thereon. However, the significant hygroscopicity of those crystals

hinders the detailed study and practical application thereof. This drawback can be eliminated by the formation of the MeX₂-Eu type microcrystals embedded in a dielectric matrix. The possibility of the Me²⁺ ion aggregation at low impurity concentrations (for Ca²⁺ and Sr²⁺ ions, about 10³ ppm) with the formation of corresponding crystalline phases in NaCl matrix have been studied in [5–8] where Eu²⁺ ions have been used as a luminescence probe to reveal the formation of the MeCl₂ type crystalline precipitates. The luminescence studies allowed us to reveal the formation of crystalline precipitates of different size and to estimate a high efficiency of Eu²⁺ ions entry therein. The study of SrCl₂-Eu²⁺ microcrystals embedded in NaCl host simplifies sig-

nificantly the preparation procedure of such hygroscopic samples. To promote the phase formation processes, we have used high concentrations of the Sr^{2+} impurity ions (1 mol.%) expecting the formation of impurity phases of several microns size. The conditions of the $\text{SrCl}_2\text{-Eu}^{2+}$ microcrystals formation embedded in NaCl host and the study of the microcrystal luminescence properties under excitation in the $4f\text{-}5d$ absorption region of Eu^{2+} ions and in the band-to-band transitions one of the NaCl matrix was the main purpose of this work.

2. Experimental

$\text{NaCl-SrCl}_2(1 \text{ mol.}\%)\text{-EuCl}_3(0.02 \text{ mol.}\%)$ ($\text{NaCl-SrCl}_2\text{-Eu}$), $\text{NaCl-Eu}(0.1 \text{ mol.}\%)$, and $\text{SrCl}_2\text{-Eu}(0.1 \text{ mol.}\%)$ crystals were grown in evacuated quartz ampoules using the previously purified salts by the Bridgman-Stockbarger technique. The as-grown $\text{NaCl-SrCl}_2\text{-Eu}$ crystals were annealed at 200°C during 100 h to activate the aggregation processes. The luminescence emission and excitation spectra and the luminescence decay kinetics of $\text{NaCl-SrCl}_2\text{-Eu}$, $\text{SrCl}_2\text{-Eu}$ and NaCl-Eu crystals were measured using the equipment of SUPERLUMI station at HASYLAB (DESY, Hamburg) [9]. A helium cryostat was used for low-temperature ($T = 10 \text{ K}$) measurements. The emission spectra were studied within the range of 350–550 nm with using Action Research Corporation (ARC) "Spectra Pro 308" 30 cm monochromator-spectrograph equipped with the Princeton Instruments CCD detector and HAMAMATSU R6358P photomultiplier. In luminescence spectra measurements, the monochromator slit spectral width of 5 nm was used. The luminescence excitation spectra were scanned with the resolution of 4 \AA within 3–12 eV by means of primary 2 m monochromator in 15° McPearson mounting and ARC monochromator as a secondary one. The X-ray luminescence spectra and decay kinetic was measured using laboratory equipment under excitation with the 2 ns X-ray (40 keV) pulses with 10–100 kHz repetition rate. The luminescence decay kinetics of Eu^{2+} centers was measured with excitation by optical quanta from flash lamp with pulse duration 1 ns and repetition rate 10–15 kHz. The luminescence decay curves in both cases were measured using the single photon counting method in the time gate of 10 μs . The crystal microstructure was studied using a scanning electron microscope (SEM JEOL JSM-T220A)

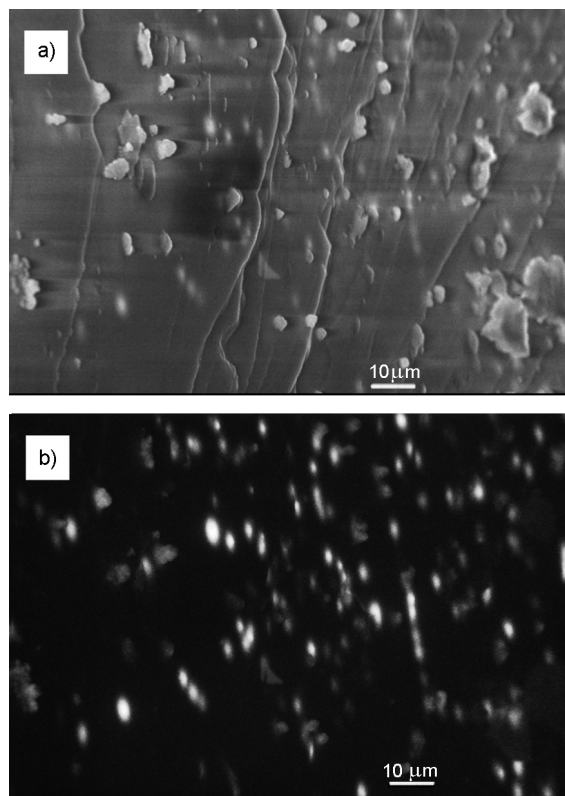


Fig. 1. Micrographs of $\text{NaCl-SrCl}_2\text{-Eu}$ freshly cleaved surface obtained by the electron beam analysis in the secondary electron mode (a) and in the cathodoluminescence mode (b) at 295 K.

with an X-ray analyzer (dispersion Si(Li) detector). Micrographs were obtained in the secondary electron and cathodoluminescence registration modes.

3. Results and discussion

The micrograph of a $\text{NaCl-SrCl}_2\text{-Eu}$ crystal freshly cleaved surface obtained by the electron beam analysis technique in secondary electron mode is presented in Fig. 1a. The crystalline aggregates of 1–10 μm size are observed in the NaCl host. These microparticles are distributed randomly and do not have any regular geometric shape. The energy dispersive spectroscopy analysis of the cleaved surface revealed that Sr^{2+} atoms are concentrated only in microinclusion areas. This could be an evidence of the SrCl_2 microcrystals formation in NaCl matrix.

Additionally, the freshly cleavage surface of $\text{NaCl-SrCl}_2\text{-Eu}$ crystals was examined in cathodoluminescence mode aiming to reveal the distribution of impurity Eu ions (Fig. 1b). As seen, the cathodoluminescence emission is located in microinclusion areas. At the same time, the emission from the NaCl matrix surface outside the microinclusion

sions is absent. Since the intrinsic luminescence of NaCl crystal is almost quenched at room temperature (RT), the main contribution in cathodoluminescence of NaCl–SrCl₂–Eu system at RT is due to the luminescence of Eu²⁺ centers. This fact serves as a proof of impurity Eu ions localization in the volume of the SrCl₂ microcrystals embedded in NaCl host.

Luminescence properties of NaCl–Eu and SrCl₂–Eu single crystals. Those were studied to clarify the nature of the luminescence in NaCl–SrCl₂–Eu system and the distribution of impurity Eu²⁺ ions between NaCl matrix and SrCl₂ microcrystals. The luminescence spectra of NaCl–Eu (a) SrCl₂–Eu (b) and NaCl–SrCl₂–EuCl₃ (c) crystals at 10 and 295 K are presented in Fig. 2. The emission band peaked at 428 nm (Fig. 2a, curves 1, 2) excited efficiently in the band-to-band transitions region of NaCl crystal (Fig. 3a) is observed in the NaCl–Eu crystal luminescence spectra at 10 K as well as at 295 K. The nature of this luminescence band was discussed in [10, 11] and attributed to the emission of Eu ions connected with single Eu²⁺–*v*_c⁻ centers or their aggregates (dimers, trimers).

The efficient excitation of the 428 nm luminescence band at *T* = 10 K and 295 K in the band-to-band transitions region of NaCl matrix (Fig. 3a) indicates that the electron excitations of NaCl matrix transfer the excitation energy to Eu²⁺ centers. In addition to the 428 nm luminescence band, the 413 nm emission band attributed to the emission of three-dimensional (3D) precipitates of EuCl₂ type in NaCl matrix [10, 11] is observed at 10 K (curve 1). The weak emission bands in the luminescence spectrum of NaCl–Eu crystal around 460, 488, and 505 nm (Fig. 2a) are observed at *T* = 295 K as well. The weak emission band around 488 nm (curve 2) is attributed to the luminescence of two-dimensional (2D) precipitates of EuCl₂ type located along the crystallographic planes {013} of NaCl [10, 11].

The luminescence spectrum of SrCl₂–Eu single crystal contains the 404 nm intense band (Fig. 2b) corresponding to the 4*f*⁶5*d* → 4*f*⁷ transitions in Eu²⁺ ion [12, 13]. The luminescence excitation spectra of the 404 nm band of SrCl₂–Eu single crystal at *T* = 8 and 295 K are presented in Fig. 3b. The excitation bands in the SrCl₂ transparency region of correspond to the 4*f*–5*d* absorption transitions (3.0–6.0 eV) of Eu²⁺ ions. The Eu²⁺ emission is weakly excited in

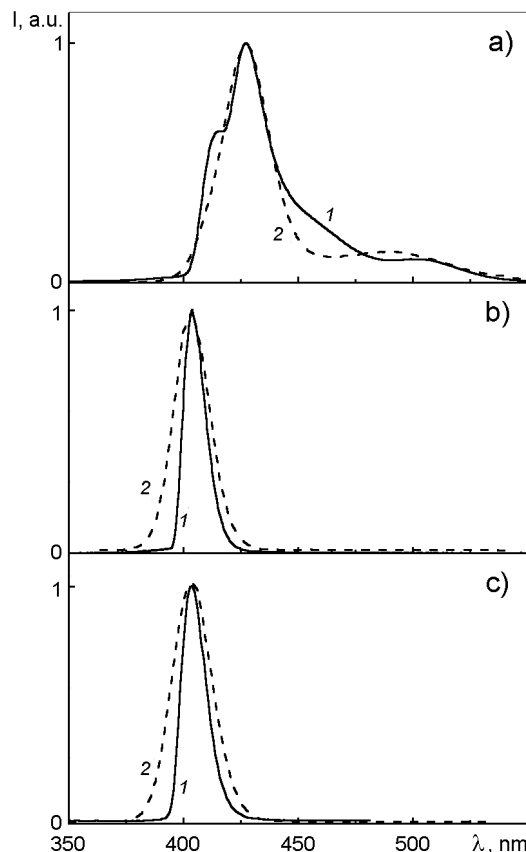


Fig. 2. Luminescence spectra of NaCl–Eu (a); SrCl₂–Eu (b) and NaCl–SrCl₂–Eu (c) crystals under excitation with $\lambda_{exc} = 333$ nm at *T* = 10 K (curve 1) and *T* = 295 K (curve 2).

the SrCl₂ fundamental absorption region. It is worth noting that the luminescence excitation bands in the 4*f*–5*d* absorption region of Eu²⁺ ions have phonon structure [14].

Luminescence properties of NaCl–SrCl₂–EuCl₃ system. The luminescence band of Eu²⁺ centers in NaCl–SrCl₂–Eu crystal is located around 404 nm. The spectral position of this band coincides with that in SrCl₂–Eu single crystal (Figs. 2c and 2b, respectively). This fact together with experimental data on the scanning electron microscopy allow us to state that in NaCl–SrCl₂(1 mol.%)–EuCl₃(0.02 mol.%) crystalline system, the SrCl₂–Eu microcrystals embedded in NaCl host are formed. At the same time, the absence of the 428 nm photoluminescence band which is typical of Eu²⁺ centers in the luminescence spectra of NaCl–Eu system, indicates that most of Eu²⁺ ions are entered the SrCl₂ microcrystals.

The Eu²⁺ center luminescence excitation spectra in NaCl–SrCl₂–Eu system in the NaCl and SrCl₂ crystal transparency region

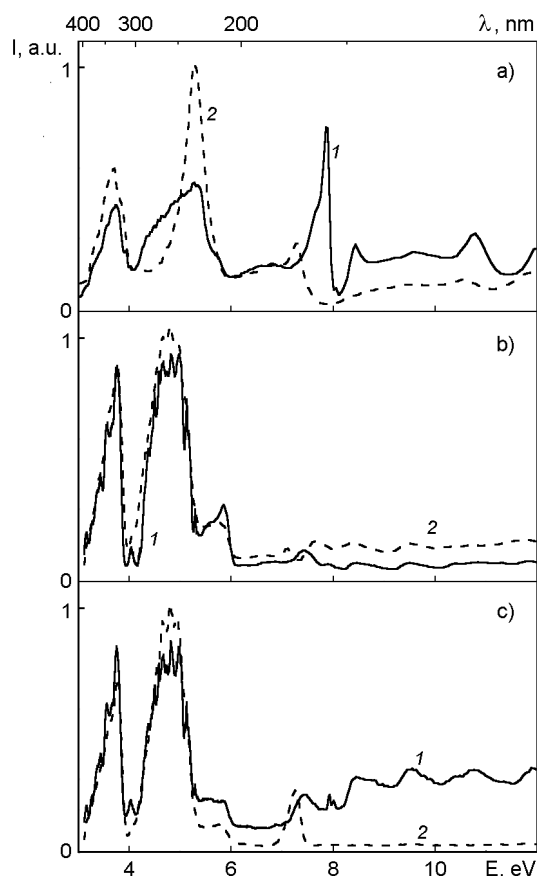


Fig. 3. Luminescence excitation spectra of impurity Eu^{2+} centers: (a) NaCl-Eu ($\lambda_{em} = 430$ nm); (b) $\text{SrCl}_2\text{-Eu}$ ($\lambda_{em} = 404$ nm) and (c) $\text{NaCl-SrCl}_2\text{-Eu}$ ($\lambda_{em} = 404$ nm) at $T = 10$ K (curve 1) and $T = 295$ K (curve 2).

contain two broad bands peaked at 3.7 and 4.8 eV (Fig. 3c) corresponding to $4f-5d$ absorption transitions in Eu^{2+} ions. These bands coincide in the spectral position and structure with excitation bands of Eu^{2+} centers in $\text{SrCl}_2\text{-Eu}$ single crystal (Fig. 3b, c). It should be noted that the electron vibrational structure of excitation bands in the case of microcrystals is identical to that in $\text{SrCl}_2\text{-Eu}$ single crystal. This means that the spectral and luminescence parameters of the $\text{SrCl}_2\text{-Eu}$ microcrystals in NaCl matrix formed during the annealing at 200°C are similar to those of the corresponding single crystal.

The Eu^{2+} ion emission in a $\text{NaCl-SrCl}_2\text{-Eu}$ crystal under excitation in the NaCl fundamental absorption region ($E_{exc} > 7.5$ eV) is observed mainly at low temperatures (Fig. 3c, curve 1). The structure of the Eu^{2+} emission band excitation spectrum in this region coincides with that of self-trapped exciton (STE) luminescence excitation band in NaCl crystal [15]. Such peculiarities of

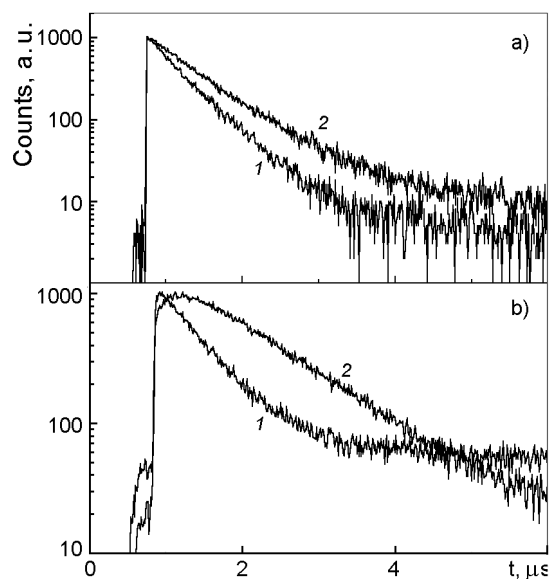


Fig. 4. Decay curves of 404 nm luminescence band in $\text{NaCl-SrCl}_2\text{-Eu}$ (curve 1) and $\text{SrCl}_2\text{-Eu}$ (curve 2) crystals under excitation with 390 nm light quanta (a) and under X-ray excitation (40 keV) (b) at $T = 295$ K.

the excitation spectrum above 7.5 eV could be explained assuming that the excitation energy is transferred only through the radiative transfer from STE to Eu^{2+} centers. The Eu^{2+} emission only comes from the re-absorption of STE emission bands (230 nm and 370 nm) of NaCl crystal, which are overlapped with the Eu^{2+} intracenter absorption bands (206–412 nm). Therefore, there is no energy transfer to emission centers through the migration of electron-hole pairs. This fact is also confirmed by the results of our preliminary energy transfer studies in micro- and nanocrystals, in particular, for CsPbCl_3 nanocrystals embedded in CsCl host and $\text{K}_2\text{LaCl}_5\text{-Ce}$ microcrystals in KCl host [16, 17].

Luminescence decay kinetics. The decay kinetics of the 404 nm emission in the $\text{SrCl}_2\text{-Eu}$ microcrystals embedded in NaCl matrix is characterized by the decay time constant of 460 ns at $T = 295$ K (Fig. 4a, curve 1). This decay time constant is shorter than that for the same luminescence band in the $\text{SrCl}_2\text{-Eu}$ single crystal (670 ns, $T = 295$ K) (Fig. 4a, curve 2). This difference in the decay time constants of Eu^{2+} center luminescence is assumed to be caused by different Eu concentration in the studied microcrystals and corresponding single crystal. It is known that with the increasing Eu^{2+} impurity center concentration, the decay time of the $\text{SrX}_2\text{-Eu}$ ($X = \text{Cl}, \text{I}$) single

crystals luminescence is significantly increased [12, 18].

Fig. 4b presents the decay kinetics of Eu center luminescence under excitation with X-ray quanta for $\text{SrCl}_2\text{-Eu}$ microcrystals (curve 1) and $\text{SrCl}_2\text{-Eu}$ single crystals (curve 2) at $T = 295$ K. The decay curves are significantly different both at the initial stage and at the decay stage of the luminescence process. In the case of single crystal, the recombination luminescence pulse intensity rises slowly enough, such a rising being almost absent for microcrystals. According to [19] the presence of slow rising stage for recombination luminescence is caused by the interaction of charge carriers with shallow traps which lifetime is less than radiative decay time of Eu center. The decay time shortening at the luminescence pulse decay stage could be caused by the smaller amounts of defects involved in the recombination process as compared to bulk crystal.

Influence of the annealing on NaCl-SrCl₂-Eu system. In the luminescence spectra of as-grown NaCl-SrCl₂-Eu crystal under X-ray excitation, only the luminescence band around 404 nm related to the Eu ions luminescence in SrCl₂-Eu microcrystals is observed (Fig. 5b, curve 1). This indicates that the majority of Eu ions is embedded in the SrCl₂ microcrystals. The close values of Sr²⁺ and Eu²⁺ ionic radii (1.32, 1.31 Å, respectively) facilitates the Eu entry in the SrCl₂ microcrystals during the crystal annealing. The efficiency of Eu²⁺ ion embedding in microcrystals is an important factor for the formation of SrCl₂-Eu microcrystals in the NaCl matrix, because the occurrence of Eu²⁺ ions in the NaCl matrix is undesirable for the development of scintillators based thereon. The latter is due to the aggregation of Eu²⁺ ions themselves in NaCl with formation of EuCl₂ precipitates [11, 10]. Numerous factors affect the formation process of the different impurity microcrystals in NaCl matrix [20]. The main factor is the long-term (above 2 days) annealing at 200–250°C. However, the long-term annealing at temperatures exceeding 400°C could result in the destruction of SrCl₂-Eu microinclusions in the NaCl matrix as it was shown in [5] for NaCl-SrCl₂-Eu samples with small concentrations of strontium (860 mol. ppm) and europium (8 mol. ppm) impurity ions. A significant decrease of the luminescence intensity attributed to Eu²⁺ centers in the SrCl₂ precipitates and the increase of the emission band intensity related

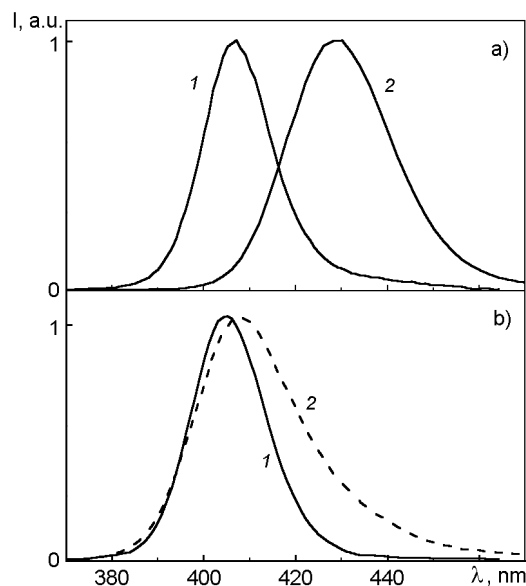


Fig. 5. X-ray excited luminescence spectra: (a) $\text{SrCl}_2\text{-Eu}$ (curve 1), NaCl-Eu (curve 2); (b) $\text{NaCl-SrCl}_2\text{-Eu}$ (curve 1) quenched from 600°C to RT (curve 2). $T = 295$ K.

to Eu^{2+} centers in the NaCl matrix was observed after annealing above 400°C [5].

We studied also the behavior of $\text{NaCl-SrCl}_2(1 \text{ mol.}\%)\text{-EuCl}_3(0.02 \text{ mol.}\%)$ crystalline system at high-temperature annealing. Our sample was annealed at 600°C during three days and quenched to RT. Immediately after quenching, the luminescence spectra were measured under X-ray excitation at RT. Such a treatment of the sample should partially destroy the SrCl₂-Eu embedded microcrystals releasing the europium ions. At the same time, the increase of europium ion concentration should take place in the NaCl matrix. Amount of SrCl₂ microcrystals and their size should be decreased as well.

In the X-ray excited luminescence spectrum of NaCl-SrCl₂-Eu quenched crystal, a shoulder around 428 nm is appeared in the long-wave branch of the 404 nm luminescence band (Fig. 5b, curve 2). The 428 nm emission band is typical of Eu^{2+} center emission in a NaCl matrix (Fig. 5a, curve 2). However, the contribution of this luminescence band responsible for Eu^{2+} luminescence in NaCl host is small at X-ray excitation. Thus, the long-term high temperature annealing at 600°C does not destroy the SrCl₂-Eu microcrystalline inclusions, whereas the SrCl₂-Eu precipitates studied in [5] are destroyed under high temperature treatment.

4. Conclusion

The possibility of SrCl₂-Eu microcrystal formation of 1–10 μm size in NaCl matrix during the long-term annealing at 200°C has been shown. The scanning electron microscopy and luminescence spectroscopy data confirm the formation of microcrystals. The luminescence characteristics of SrCl₂-Eu microcrystals embedded in NaCl matrix are shown to be similar to those of single crystal analogues. The concentration of short-lived defects in microcrystals is supposed to be significantly less than in the bulk crystal analogues. The partial destruction of SrCl₂-Eu microcrystals accompanied by the transition of some Eu²⁺ ions in NaCl host is observed at the high temperature annealing (600°C).

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Люмінесцентні властивості мікрокристалів SrCl₂-Eu, вкраплених в матриці NaCl

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Для системи NaCl-SrCl₂(1 мол.%)–EuCl₃(0,02 мол.%) показано можливість утворення мікрокристалів SrCl₂-Eu вкраплених у матрицю NaCl. Розмір мікрокристалів SrCl₂-Eu становить 1–10 мкм. Досліджено спектрально-люмінесцентні властивості кристалів NaCl-Eu(0,1 мол.%), SrCl₂-Eu(0,1 мол.%) та NaCl-SrCl₂(1 мол.%)–EuCl₃(0,02 мол.%) при оптичному і рентгенівському збудженні. Спектрально-люмінесцентні параметри мікрокристалів SrCl₂-Eu, вкраплених у матрицю NaCl, і монокристалів SrCl₂-Eu аналогічні.