



Synchrotron radiation studies on luminescence of Eu^{2+} -doped LaCl_3 microcrystals embedded in a NaCl matrix

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ABSTRACT

$\text{LaCl}_3:\text{Eu}^{2+}$ microcrystals dispersed in the NaCl matrix have been obtained in the $\text{NaCl-L aCl}_3(1 \text{ mol.}\%)-\text{EuCl}_3(0.1 \text{ mol.}\%)$ crystalline system. The low-temperature luminescent properties of these microcrystals have been studied upon the VUV and UV excitation by the synchrotron radiation. The spectroscopic parameters as well as decay time constants of Eu^{2+} -doped LaCl_3 host have been established. The excitation mechanism of divalent europium centers through energy transfer and reabsorption is discussed.

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1. Introduction

The divalent europium ions Eu^{2+} are widespread activators for inorganic luminescent materials [1–11]. In recent years, Eu^{2+} was considered as a promising dopant for scintillator applications due to a high light yield of doped single crystals [12,13]. In this paper, we studied the luminescent properties of Eu^{2+} -doped LaCl_3 microcrystals embedded in the NaCl matrix.

The LaCl_3 single crystal is a well-known scintillation material which belongs to the hexagonal UCl_3 -type structure with the point symmetry C_{3h} at the lanthanide site. It possesses excellent optical transparency and low phonon frequencies [14]. La-containing cerium-doped single crystals with this structure type show outstanding scintillation properties such as light yield, energy resolution, etc. [15,16]. However, it is difficult to grow and study such single crystals due to their considerable hygroscopicity. Therefore, we have performed experiments on LaCl_3 microcrystals embedded into a stable host (NaCl). The feasibility of the formation of Ce^{3+} -doped LaCl_3 microcrystals embedded in the NaCl host has already

been shown [17]. The spectroscopic characteristics of the $\text{LaCl}_3:\text{Ce}$ microcrystals was found to be substantially similar with those of the LaCl_3 single crystal.

2. Experiment

A single crystal of the $\text{NaCl-L aCl}_3(1 \text{ mol.}\%)-\text{EuCl}_3(0.1 \text{ mol.}\%)$ composition was grown in evacuated quartz ampoule from NaCl, LaCl_3 and CeCl_3 by the Bridgman–Stockbarger technique using a moving vertical ampoule and a static furnace with one hot zone. The LaCl_3 (99.9% purity), EuCl_3 (99.5% purity) and NaCl (99.99% purity) raw materials were commercially obtained from the *Manufacture of rare metals compounds* (Russia). The as-grown $\text{NaCl-L aCl}_3-\text{Eu}$ crystal was annealed at 600 K during 48 h, aiming to activate aggregation processes.

Note that NaCl crystal belongs to the class of wide band-gap materials and its experimental band gap and first exciton peak were reported to be at 8.75 and 7.96 eV, respectively [18,19]. Thus, in this paper we use the synchrotron radiation, which due to its broad and continuous spectrum is a very useful tool for the investigation of optical and luminescence properties of wide band-gap materials [20–27] that are dominated by UV and VUV excitation. In particular, in the case of NaCl crystal, excitonic and electron–

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hole processes as well as the processes of multiplication of anion and cation electronic excitations have been studied in details in [28,29].

Luminescence emission and excitation spectra were measured upon the excitation by the synchrotron radiation from DORIS III storage ring (DESY, Hamburg) using the facility of SUPERLUMI station at HASYLAB [30]. The measurements were carried out at $T = 10$ K. Emission spectra with the resolution of 0.5 nm were studied within 300–750 nm range using ARC “Spectra Pro 308” 0.3 m monochromator–spectrograph equipped with the CCD detector and HAMAMATSU R6358P photomultiplier tube (PMT). Luminescence excitation spectra scanned within 3.7–22 eV range were measured by the primary 2 m monochromator in 15° McPherson.

The measurements of the luminescence excitation spectra within 3–6 eV were performed by the laboratory MDR-2 monochromator. All luminescence excitation spectra have been corrected using the excitation spectrum of Na-salicylate as a reference.

The luminescence decay kinetics of Eu^{2+} centers was measured upon the excitation by optical quanta from the laboratory flash lamp with the pulse duration of 1 ns and the repetition rate of 10–15 kHz. Luminescence decay curves were measured utilizing the single photon counting technique in the time gate of 10 μs .

3. Results and discussion

3.1. Origin of Eu^{2+} in the NaCl– LaCl_3 crystalline system

Europium ions could enter LaCl_3 in the tripositive as well as dipositive state [31,32]. In the case of Eu^{3+} , the narrow bands within 520–630 nm corresponding to the intraconfigurational f – f transitions are observed [33]. This occurs in a Cl_2 atmosphere during the crystal growth. Vacuum or a H_2 atmosphere insures the reaction $\text{EuCl}_3 \rightarrow \text{EuCl}_2 + 0.5\text{Cl}_2$ which occurs at high temperatures thus resulting in the $\text{LaCl}_3:\text{Eu}^{2+}$ single crystal. The stable state of Eu^{2+} ions in this crystal is achieved by the presence of a large concentration of anion vacancies not associated with electrons [31]. The intensive broadband emission is observed in the blue region of a spectral range originating from interconfigurational $5d$ – $4f$ transition in Eu^{2+} ions. However, the spectroscopic data of LaCl_3 activated by divalent europium are incomplete and inconsistent (e.g. the position of the emission maximum is determined as 410 nm [31] and 420 nm [32]). In our case, the absence of chlorine atmosphere is not the crucial condition for insuring the divalent state of europium, due to a large amount of NaCl in the ampoule. As well-known, europium ions enter NaCl strictly in the divalent state [34]. Thus, we suppose that during the growth and subsequent annealing of the NaCl– LaCl_3 (1 mol.%)– EuCl_3 (0.1 mol.%) crystalline system, europium ions enter the LaCl_3 microcrystals also as Eu^{2+} .

3.2. Luminescence

The luminescence spectra of the NaCl– LaCl_3 –Eu and NaCl:Eu $^{2+}$ crystals upon the excitation in the absorption energy range of europium ions is shown in Fig. 1. In the case of the NaCl– LaCl_3 –Eu crystal, the intensive broad emission band is observed in the range of 385–440 nm peaking at 410 nm (3.02 eV), which corresponds to the $4f^65d \rightarrow 4f^7$ transitions of Eu^{2+} in LaCl_3 (Fig. 1a). The small shoulder at about 3.35 eV is probably due to some Eu^{2+} aggregates in LaCl_3 . The luminescence spectrum of NaCl:Eu $^{2+}$ reveals the complex structure with the main maximum at 428 nm that can be decomposed into four emission bands: 2.45 eV (505 nm), 2.8 eV (442 nm), 2.9 eV (428 nm) and 3.0 eV (413 nm). Accordingly to [1,30,35], all these emission bands correspond to the Eu^{2+} centers in a different crystalline environment. In particular, the 428 nm emission band is attributed to the luminescence of

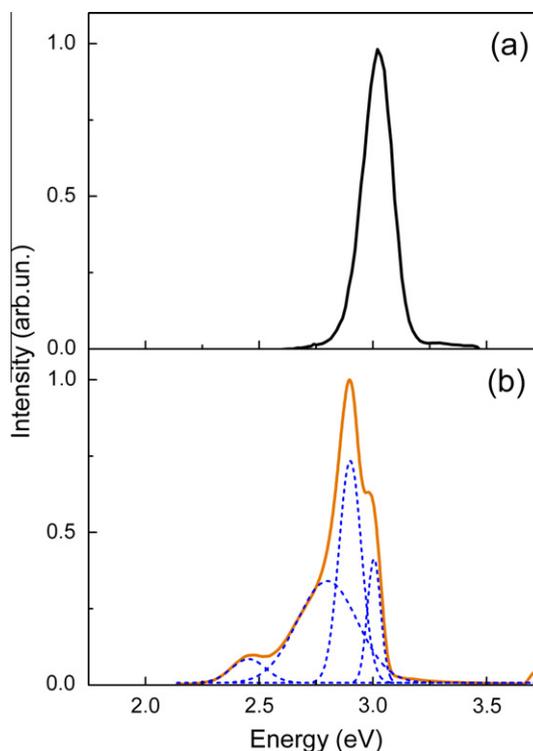


Fig. 1. Luminescence spectra of: (a) NaCl– LaCl_3 (1 mol.%)– EuCl_3 (0.1 mol.%) crystal upon the 301 nm excitation and (b) NaCl– EuCl_3 (0.01 mol.%) crystal upon the 275 nm excitation decomposed into four components. $T = 10$ K.

the Eu^{2+} – v_c^- single centers or their aggregates incorporated in NaCl. The origin of the 413 nm luminescence band is connected with the emission of three dimensional (3D) precipitates of EuCl_2 –type in the NaCl matrix [34]. Thus, the absence of these emission bands in the luminescence spectrum of the NaCl– LaCl_3 –Eu crystal (Fig. 1a) indicates that the majority of europium ions enter the LaCl_3 microcrystals.

Upon the excitation within the LaCl_3 fundamental absorption range (excitation quanta of 6.72 eV), the additional broad emission band peaking at 2.88 eV (430 nm) is observed in the luminescence spectrum of the NaCl– LaCl_3 –Eu crystal (Fig. 2b). The spectral position and shape of this emission band coincides with that inherent to intrinsic luminescence of LaCl_3 originating from the radiative recombination of self-trapped excitons (STE) [36]. In this spectrum the intensive Eu^{2+} luminescence band is also present. It means that the excitation energy efficiently transfers from STE in LaCl_3 to Eu^{2+} ions.

Upon the excitation in the NaCl fundamental absorption range (excitation quanta of 7.74 eV), the two emission bands corresponding to the Eu^{2+} luminescence in LaCl_3 and the STE luminescence of LaCl_3 are also observed within the 1.65–4.12 eV (300–750 nm) spectral range (Fig. 2c). This indicates the efficient energy transfer from the STE emission of the NaCl crystal to Eu^{2+} ions with a possible involvement of STE in LaCl_3 . More detailed information concerning the energy transfer mechanisms in our system can be obtained from the analysis of the excitation spectra of the Eu^{2+} emission.

3.3. Excitation mechanisms of Eu^{2+} centers

A comparison of the luminescence excitation spectra of the NaCl– LaCl_3 –Eu and NaCl:Eu crystals (Fig. 3) serves as an additional proof of the Eu^{2+} ions emission in the LaCl_3 microcrystals. The Eu^{2+} luminescence excitation spectrum of the NaCl– LaCl_3 –Eu system in

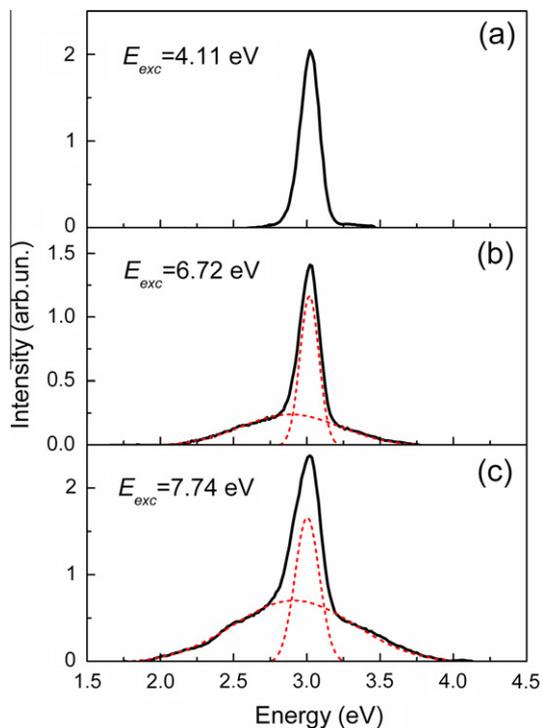


Fig. 2. Luminescence spectra of the NaCl–LaCl₃(1 mol.%)–EuCl₃(0.1 mol.%) crystal upon the: (a) 301 nm (4.11 eV) excitation, (b) 184 nm (6.72 eV) excitation decomposed on two components and (c) 160 nm (7.74 eV) excitation decomposed also into two components. $T = 10$ K.

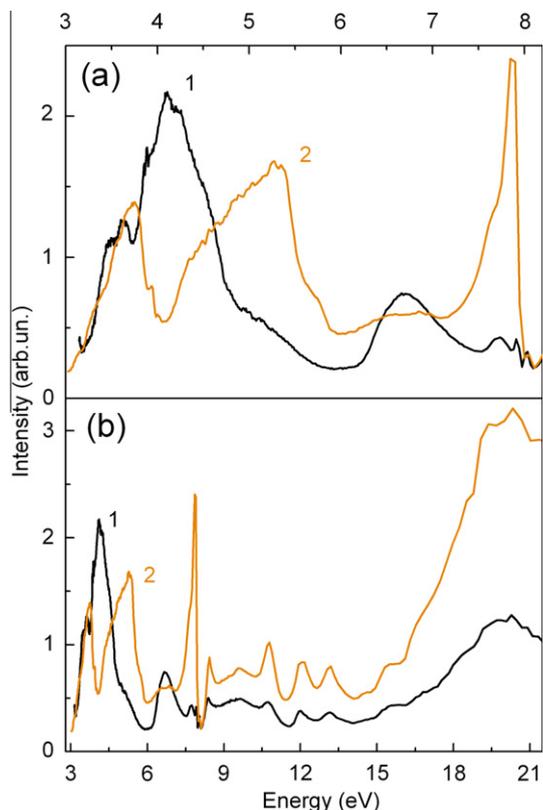


Fig. 3. Luminescence excitation spectra of Eu²⁺ single centers in the NaCl–LaCl₃(1 mol.%)–EuCl₃(0.1 mol.%) crystal ($\lambda_{em} = 405$ nm, curve 1) and the NaCl–EuCl₃(0.01 mol.%) crystal ($\lambda_{em} = 428$ nm, curve 2) within (a) Eu²⁺ ions and LaCl₃ absorption range, (b) the whole measured range. $T = 10$ K.

the transparency region of NaCl and LaCl₃ contain two bands with maxima around 3.5 and 4.18 eV (Fig. 3a, curve 1) corresponding to the $4f^7 \rightarrow 4f^65d$ absorption transitions within Eu²⁺ ions in the LaCl₃ crystal. The band positions differ from those inherent to the Eu²⁺– v_c^- single centers in NaCl (Fig. 3a, curve 2) which were estimated ~ 3.7 and 5.25 eV, respectively.

The high-energy band is the transition from the $4f^7$ ($^8S_{7/2}$) ground state to the e_g component of the $4f^65d$ configuration, while the low-energy band is the transition from the ground state to the t_{2g} component. The presence of the e_g band in the excitation spectrum points out on the nonradiative relaxation from the e_g level to the t_{2g} , from which the luminescence arises. The energy separation between these levels is caused by the crystal field splitting of the 5d orbitals. In the case of the NaCl–LaCl₃–Eu crystal, a very small crystal field splitting has been estimated to be ~ 5485 cm⁻¹. This fact is conformable to the obtained result for the Ce³⁺-doped LaCl₃ single crystal where splitting was estimated as low as 5600 cm⁻¹ [14]. In the case of the NaCl:Eu crystal, the splitting is about 12,660 cm⁻¹ that is in a good agreement with the result obtained in [34].

Some theoretical predictions concerning the position of the emission maximum and the luminescence excitation maximum of Eu²⁺ ions in LaCl₃ could be made employing the empirical relations [37]: $E_{df}(Eu^{2+}) = 0.64E_{df}(Ce^{3+}) + 0.53$ (eV) and $\Delta S(Eu^{2+}) = 0.61\Delta S(Ce^{3+})$, where E_{df} is the energy position of the emission maximum and ΔS is the Stokes shift.

Thus, the emission of Eu²⁺ in LaCl₃ is expected at 428 nm which is in good agreement with data in Fig. 2 (within the 4% error). Such an error for the Eu²⁺ emission in LaBr₃ was about 4.9% [38]. Using the Stokes shift of 0.72 eV found for Ce³⁺ [14], the anticipated first $4f^7 \rightarrow 4f^65d$ transition in Eu²⁺ is at 3.33 eV. As can be observed in Fig. 3a, the experimental value is of 3.5 eV. Thus, the obtained results again are in a reasonable agreement with experiment, with the error of 4.8%. All the calculated and experimental data concerning to luminescent parameters are collected in Table 1.

The excitation spectrum of the Eu²⁺ luminescence in NaCl–LaCl₃–Eu (Fig. 3a, curve 1) shows also the intensive excitation band at 6.7 eV in the range of the fundamental absorption of the LaCl₃ microcrystalline matrix (6.2–7.5 eV). It points out on the efficient energy transfer from STE of LaCl₃ to Eu²⁺ ions.

In the fundamental absorption range of NaCl (7.5–22 eV), the excitation spectrum of the Eu²⁺ emission of NaCl–LaCl₃–Eu (Fig. 3b, curve 1) shows several maxima and significant intensity increase above 16 eV. Such a structure correlates well with that of the STE excitation band in the NaCl crystal [39]. As it was shown for LaCl₃:Ce microcrystals embedded in NaCl [17], there is no energy transfer from electron–hole pairs and V_k -centers of NaCl to emission centers through the hole migration. Therefore, the excitation of the Eu²⁺ emission in the range of the NaCl host absorption could arise by the two next reasons: (i) the overlapping of π -component (3.4 eV) of STE emission of NaCl with the Eu²⁺ intra-center absorption in the 3.3–4.7 eV range; (ii) the overlapping of σ -component (5.5 eV) of STE emission of NaCl with the STE absorption band of LaCl₃ (4.8–7.3 eV) with subsequent energy transfer to Eu²⁺ ions.

3.4. Decay kinetics of the Eu²⁺ emission in LaCl₃

The decay kinetics of the Eu²⁺ emission band at 410 nm upon the excitation with 4 eV quanta of the NaCl–LaCl₃–Eu crystal reveals the single-exponential profile with the decay time constant of 254 ns which does not depend on temperature changes (Fig. 4). This decay time constant should be close to those inherent to the Eu²⁺ emission of the LaCl₃ single crystal, as it was shown for the Ce³⁺-doped LaCl₃ microcrystals. It is worth noting that the decay time could vary with the concentration of Eu²⁺ centers. In par-

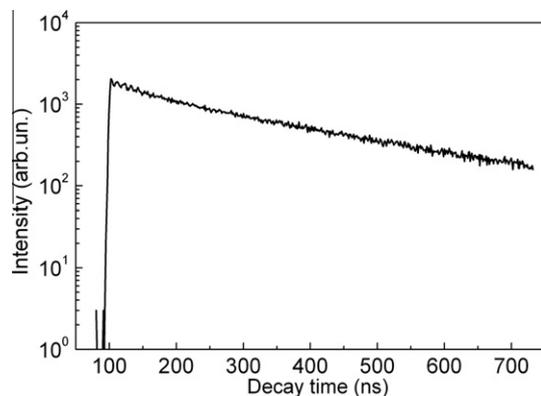


Fig. 4. Decay kinetics of the Eu^{2+} luminescence of the $\text{NaCl-LaCl}_3(1 \text{ mol.}\%)-\text{EuCl}_3(0.1 \text{ mol.}\%)$ crystal at room temperature.

Table 1

Luminescent parameters of the $5d-4f$ emission of Ce^{3+} and Eu^{2+} -doped LaCl_3 .

Ion	E_{df} , eV	$\Gamma(10 \text{ K})$, eV	E_{fd} , eV	ΔS , eV	Crystal field splitting, cm^{-1}
Ce^{3+}	3.43	0.2	4.43, 4.52,	0.72	5600
	(360 nm),	0.18	4.71, 4.96,		
	3.69		5.10		
(335 nm)					
Eu^{2+}	3.02	0.15	3.5	0.44	5485
	(410 nm)		4.18		

ticular, the decay time of the Eu^{2+} luminescence of the $\text{SrI}_2:\text{Eu}$ single crystals is significantly increased with the concentration increasing of europium single centers [40].

4. Conclusions

The low-temperature Eu^{2+} luminescence spectrum contains the intensive band peaking at 410 nm (3.02 eV) with half-width of 0.15 eV corresponding to the $4f^65d \rightarrow 4f^7$ transitions of Eu^{2+} ion in the LaCl_3 host upon the excitation in the absorption range of europium ions.

The Eu^{2+} luminescence excitation spectrum of the $\text{NaCl-LaCl}_3-\text{Eu}$ crystalline system reveals efficient excitation in the range of:

- i) intra-center absorption of Eu^{2+} ion with a maxima at 3.6 and 4.1 eV;
- ii) fundamental absorption of LaCl_3 peaked at 6.7 eV that indicates the efficient energy transfer from STE of LaCl_3 to Eu^{2+} ions;
- iii) fundamental absorption of NaCl . Here, the excitation of Eu^{2+} emission is the result of the overlapping of π -component of STE emission of NaCl with the Eu^{2+} intra-center absorption and the overlapping of σ -component of STE emission of NaCl with the STE absorption band of LaCl_3 with subsequent energy transfer to Eu^{2+} ions.

Crystal field splitting has been estimated for Eu^{2+} in LaCl_3 to be about 5485 cm^{-1} , which is in a reasonable agreement with the result (5600 cm^{-1}) for Ce^{3+} -doped LaCl_3 single crystal.

The decay kinetics reveals the single-exponential profile with the temperature independent decay time constant of about 254 ns.

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