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## Spectral-Kinetic Study of LaCl<sub>3</sub>:Ce Crystals

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### Abstract

Luminescent spectral-kinetic parameters of LaCl<sub>3</sub>:Ce crystals with different activator concentration are studied under both optical and pulse X-ray excitation. The mechanism of Ce<sup>3+</sup> centre luminescence at high-energy excitation is discussed. Possible schemes for the Ce<sup>3+</sup> ion excitation process are suggested.

**Keywords:** luminescence, decay kinetics, hot carriers, V<sub>k</sub>-center, self-trapped exciton (STE)

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### Introduction

Ce<sup>3+</sup>-ions are known to be effective activators for the fast inorganic scintillators with high light output. Luminescent characteristics of LaCl<sub>3</sub>:Ce crystals with 0.05 and 0.5 mol.% activator concentrations have been studied in [1,2]. In particular, the luminescence excitation spectra of LaCl<sub>3</sub>:0.05 mol.% Ce in 4–20 eV energy region have been studied and the energy structure of the 5d-level of Ce<sup>3+</sup>-ion in the C<sub>3h</sub>-symmetry field of the matrix has been established [2].

In this paper the influence of Ce<sup>3+</sup> activator concentration (in the range of 0.05–1.0 mol.%) on the ratio of fast and slow components of low-temperature (10 K) emission and excitation spectra for LaCl<sub>3</sub>:Ce crystals are studied in the case of both the activator and the exciton luminescence. Mechanisms of Ce<sup>3+</sup>-centre luminescence under high-energy excitation are

discussed. On the basis of analyses of the luminescence decay time, the emission and the excitation spectra, the possible schemes for the Ce<sup>3+</sup>-ion excitation process are suggested.

### Experiment

LaCl<sub>3</sub>:Ce single crystals were grown from the melt by the Bridgman-Stockbarger technique in quartz ampoules from the raw material purified of oxygen impurities, using the method described in [2].

The experiments were performed at SUPERLUMI station of HASYLAB (DESY, Hamburg) under synchrotron radiation excitation in the energy region of 4–16 eV and at the Ivan Franko National University of Lviv under the excitation with a laboratory pulse X-ray source.

The luminescence emission and excitation spectra under the excitation with synchrotron radiation were measured by using the time-

resolved luminescence spectroscopy technique. Fast components of the luminescence decay were measured in 5 ns time window just after the synchrotron excitation pulse. Slow components were registered in 80 ns time window with 100 ns delay after the excitation pulse.

The luminescence spectra under the X-ray excitation were measured in integral mode as a total signal recorded by a photomultiplier.

### Luminescence excitation spectra

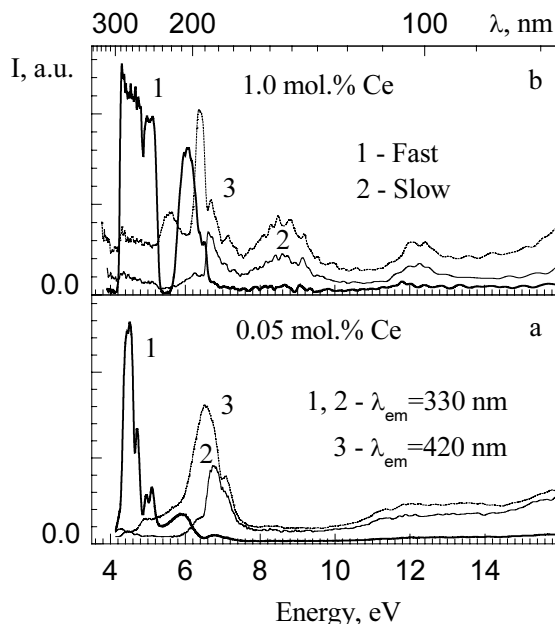
Luminescence excitation spectra of LaCl<sub>3</sub>:Ce crystals for different activator concentrations of Ce<sup>3+</sup>-centers are presented in Fig. 1. For LaCl<sub>3</sub>:0.05 mol.% Ce crystals, the intrinsic emission with a dominating long-time emission component is mainly excited in the wide band peaking at 6.5 eV (Fig. 1a, curve 3). This band is ascribed to absorption of self-trapped excitons (STE) in LaCl<sub>3</sub> and it shifts towards 6.4 eV with increasing activator concentration up to 1.0 mol.% Ce (Fig. 1b, curve 3).

The main maxima in the excitation spectra of the fast component of the Ce-emission are peaked at 4.46; 4.55; 4.73; 4.94 and 5.10 eV for

LaCl<sub>3</sub>:0.05 mol.% crystal. The corresponding maxima are considered as responsible for the 4f-5d transitions in Ce<sup>3+</sup> ions. Besides these maxima, the excitation spectrum of the fast emission in LaCl<sub>3</sub>:Ce crystal also contains the two rather wide and weaker bands in the spectral regions of 5.5-6.5 eV and 6.5-7.0 eV. The maximum of the first band for LaCl<sub>3</sub>:0.05 mol.% Ce crystal is situated at 5.9 eV (Fig. 1a, curve 1). The increase in cerium concentration leads to the shift of this maximum into high-energy spectral region up to 6.05 eV for LaCl<sub>3</sub>:1.0 mol.% Ce crystal. The quantum efficiency of this luminescence excitation band increases sharply and becomes comparable with the main bands of the impurity excitation.

The 5.9 eV band in LaCl<sub>3</sub>:Ce with low cerium concentration, in which the fast decay component of impurity luminescence is efficiently excited, lies far from the vicinity of f-d transitions in Ce<sup>3+</sup> ions. Therefore, this band can rather be attributed to STE perturbed by Ce<sup>3+</sup> ions. Such excitons perturbed by impurity are well-known, for example, in CsCl-Tl crystals [3]. Contrary to the perturbed exciton in CsCl-Tl crystals, the perturbed exciton in LaCl<sub>3</sub>:1.0 mol.% Ce does not possess the intrinsic emission band. It recombines non-radiatively with Ce-centers.

The band in the luminescence excitation spectrum of LaCl<sub>3</sub>:1.0 mol.% Ce crystals peaked at 6.05 eV is responsible for absorption of such near-activator excitons. The appearance of this band is accompanied by characteristic changes in the shape of the STE luminescence excitation band. The characteristic deep at 6.05 eV appears at the low-energy side of this band (Fig. 1b, curve 3). The excitation spectrum of the long-time component of Ce luminescence (Fig. 1b, curve 2) reflects a transfer of the matrix excitation energy to the activator emission centre due to electron-hole recombination processes that lead to an increase of the cerium emission duration.



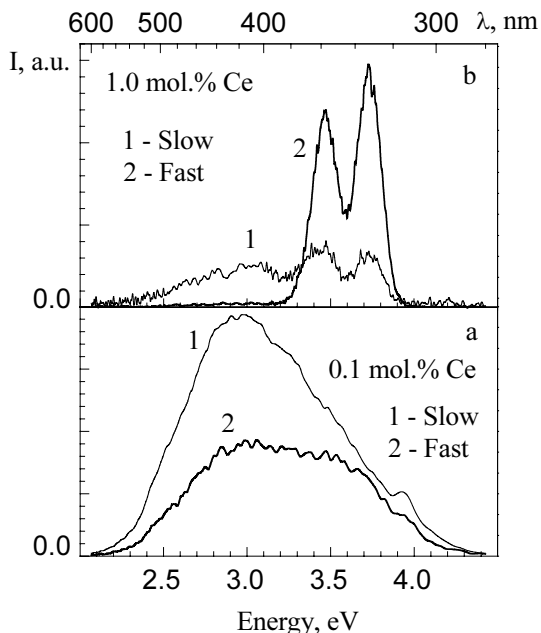
**Fig. 1.** Luminescence excitation spectra of the activator (curves 1 and 2) and the exciton (3) emission in LaCl<sub>3</sub>:Ce.

### Emission spectra

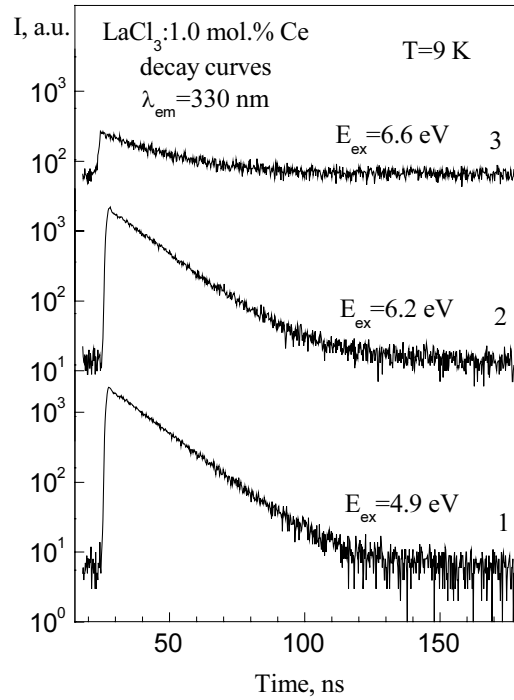
The low-temperature ( $T=8\text{ K}$ ) luminescence spectra of  $\text{LaCl}_3:\text{Ce}$  crystals under excitation in the energy range specific for the formation of near-activator exciton ( $E=6.2\text{ eV}$ ) reveal essential concentration dependence (Fig. 2). Thus, the long-time STE emission responsible for wide band peaking at  $2.95\text{ eV}$  dominates in the case of  $\text{LaCl}_3:0.1\text{ mol.}\% \text{ Ce}$  crystals (Fig. 2 a). At the same time, the bands of fast cerium luminescence peaking at  $3.72$  and  $3.47\text{ eV}$  (Fig. 2 b, curve 2) considerably prevail in  $\text{LaCl}_3:1.0\text{ mol.}\% \text{ Ce}$  crystal. The total contribution of the long-time emission component in this crystal is considerably weaker.

### Decay kinetics

Direct optical excitation of the impurity centre ( $E_{\text{exc}}=4.9\text{ eV}$ ,  $E_{\text{em}}=3.44\text{ eV}$ ) leads to exponential decay with the time constant  $\tau=14.6\text{ ns}$  which is characteristic for  $5d-4f$  transitions of  $\text{Ce}^{3+}$  centre (Fig. 3, curve 1). After irradiation in the range of near-activator exciton, the exponential component of the excited  $\text{Ce}^{3+}$  centres with the



**Fig. 2.** Luminescence spectra of  $\text{LaCl}_3:\text{Ce}$  under the excitation in the energy region of formation of the near-activator exciton ( $E_{\text{exc}}=6.2\text{ eV}$ ,  $T=8\text{ K}$ ).



**Fig. 3.** Decay time curves in the regions of inter-activator excitation (1), near-activator energy region excitation (2) and band-to-band transitions (3) for  $\text{LaCl}_3:1.0\text{ mol.}\% \text{ Ce}$ .

decay constant  $\tau=14.6\text{ ns}$  also remains dominating (Fig. 3, curve 2).

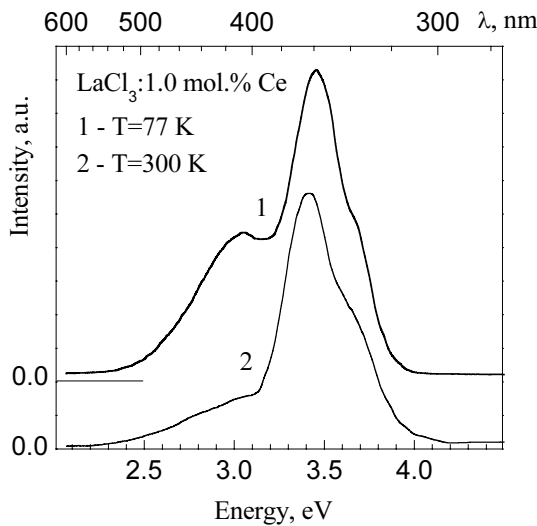
The emission relaxation processes become qualitatively different under excitation in the region of band-to-band transitions ( $E_{\text{exc}}=6.6\text{ eV}$ ). The corresponding luminescence decay curve (Fig. 3, curve 3) becomes hyperbolic, thus evidencing a recombination nature of the luminescence. Hence, the analysis of the luminescence decay curves confirms the conclusion drawn earlier on the basis of spectral measurements: the fast luminescence component in  $\text{LaCl}_3:1.0\text{ mol.}\% \text{ Ce}$  crystal is dominating under excitation in the region close to the fundamental absorption edge. This conclusion is also confirmed by the existence of near-activator excitons in these crystals.

### Luminescence of $\text{LaCl}_3-\text{Ce}$ crystals under X-ray excitation

The investigations of the luminescence emission spectra and the decay kinetics under X-ray excitation were carried out for  $\text{LaCl}_3:\text{Ce}$  crystals

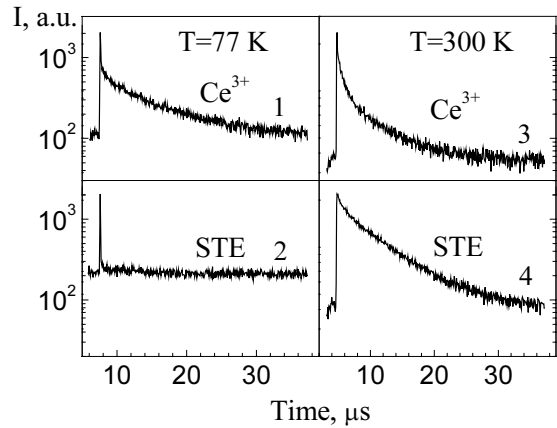
in order to clarify the mechanisms for excitation of  $\text{Ce}^{3+}$  centre in this compound.

The luminescence spectra under the X-ray excitation (or X-ray luminescence spectra) for both liquid-nitrogen (LNT) and room (RT) temperatures contain the band of Ce-emission with the maxima near 3.5 eV and the wide STE emission band at 3.05 eV (Fig. 4). As the temperature increases, the intensity of STE emission decreases essentially. At the same time, the intensity of Ce-emission exhibits higher temperature stability and enhances slightly while the temperature increases from LNT up to RT.



**Fig. 4.** Emission spectra under the X-ray excitation of  $\text{LaCl}_3: 1.0 \text{ mol.}\% \text{ Ce}$ .

The kinetics of the X-ray luminescence decay for the Ce-emission manifests the components with the time constants of  $0.02\sim 100 \mu\text{s}$  (Fig. 5, curves 1 and 3, and Fig. 6, curve 1). The decay time measured in the spectral range of the STE emission ( $E_{\text{em}}=3.0 \text{ eV}$ ) at LNT has a long ( $\sim 100 \mu\text{s}$ ) component recorded as intensive background and a rather short component with the time constant of 8 ns (Fig. 5, curve 2; Fig. 6, curve 2). Clarification of the nature of the 8 ns-decay component needs additional studies since it is absent under the excitation in the energy range of band-to-band transitions (for example, at 10 eV). The decay

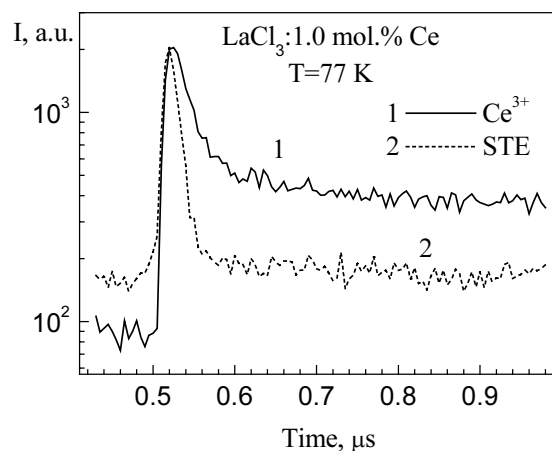


**Fig. 5.** STE and Ce-emission decay curves for  $\text{LaCl}_3:1.0 \text{ mol.}\% \text{ Ce}$  at different temperatures.

time constants of the long-time components for both the Ce and the STE emissions become less when the temperature increases (Fig. 5, curves 3 and 4, respectively).

The analysis of the X-ray luminescence spectra and the corresponding decay curves allows to reveal a number of mechanisms for the excitation of  $\text{Ce}^{3+}$  centre.

The separated charge carriers are created in the crystal under the X-ray radiation excitation. A part of the electrons and holes recombines with the  $\text{Ce}^{3+}$  centres just after their creation, resulting in the Ce-emission component with the decay time of 20 ns (Fig. 6, curve 1). This time constant is close to that characteristic for the Ce-emission under the optical excitation within



**Fig. 6.** STE and Ce emission decay curves for  $\text{LaCl}_3:1.0 \text{ mol.}\% \text{ Ce}$  at 77 K.

the 4f-5d absorption region of the Ce centres.

The other fraction of charge carriers undergoes a localization. In particular, there is a possibility for creation of a  $V_k$ -centre [1] that can recombine with the  $Ce^{3+}$  centre which, in its turn, has a previously captured electron ( $Ce^{3+} + e^- = Ce^{2+}$ ). Capturing of an electron by a localized hole ( $V_k$ -centre) is also probable and it leads to the creation of STE. The excitation of  $Ce^{3+}$  ions through its recombination with the  $V_k$ -centres results in a long hyperbolic component of Ce-emission decay (Fig. 5, curves 1, 3). Indeed, on the time stage of the luminescence decay occurring at 50 ns after a maximum of luminescence intensity, the decay curve of Ce-emission is non-exponential. It can be roughly approximated by exponential dependence with the decay constant of 8  $\mu s$  at 77 K (Fig. 5, curve 1).

The kinetics of the Ce-emission decay at 77 K includes a long-time component (Fig. 5, curve 1), which is observed as an intensive background. Ce-emission can reveal such a long decay time due to re-absorption of the STE-emission quanta by Ce-centres. The necessary conditions for such a re-absorption are overlapping of the STE-emission band with the absorption bands of  $Ce^{3+}$  centres. Taking into account the fact that the overlapping of the STE-emission and the absorption bands of Ce is rather small for  $LaCl_3:Ce$ , the presence of the long decay component characteristic for the STE emission in the kinetics of Ce-emission decay could be partially explained by the overlapping of the STE- and Ce-emission bands in the spectral region where the decay kinetics for the luminescence of  $Ce^{3+}$ -centres is registered.

Another mechanism for the excitation of  $Ce^{3+}$  centre is associated with thermally activated STE migration process [1]. As is well known, the STE migration is caused by delocalization of its hole component, implying a temporal dissociation of STE into  $V_k$ -centre and  $e^-$ , a diffusion of the  $V_k$ -centre, and a recombination of the transferred  $V_k$ -centre with  $e^-$  resulting in

creation of the STE. On the stage of diffusion, the STE or its hole component interact with  $Ce^{3+}$ -centre, resulting in the increase of Ce-emission intensity. Due to the transfer of the STE energy to  $Ce^{3+}$ -centres, the decay time of the STE emission becomes shorter, being characterized by the value of  $\sim 6 \mu s$  at 300 K (Fig. 5, curve 4), the intensity of the STE emission decreases and the intensity of the Ce emission increases.

Such temperature changes in the intensity of Ce-emission have been clearly observed in the case of  $LaCl_3:0.57 \text{ mol.}\% \text{ Ce}$  [1]. At higher cerium concentration (the concentration of 1 mol.% for the  $Ce^{3+}$  ions), the thermally stimulated increase in the Ce-emission intensity is inessential in comparison with its total intensity.

The mobility of free  $V_k$ -centres increases at higher temperatures, leading to a decrease of the probability for their recombination with Ce-centres. This manifests itself in "shortening" the kinetics for Ce-emission decay from 8  $\mu s$  at 77 K down to 0.8  $\mu s$  at 300 K (Fig. 5, curves 1 and 3, respectively). The contribution of the 0.8  $\mu s$ -component to the total intensity of the Ce emission amounts to 55% at 300 K.

Besides, the long component (6  $\mu s$ ) is also observed at 300 K for the Ce-emission decay (Fig. 5, curve 3), with the 40%-contribution to the total intensity. The value of the decay time constant (6  $\mu s$ ) for the Ce emission coincides with that of the STE emission at 300 K. Thus, the presence of the 6  $\mu s$ -component in the kinetics of Ce-emission decay at 300 K can be explained by (i) the overlapping of the STE- and Ce-emission bands in the spectral region of registration of decay kinetics for the luminescence of  $Ce^{3+}$ -centres, or by (ii) re-absorption of the STE-emission quanta by  $Ce^{3+}$  centres. The  $Ce^{3+}$  centres excited by hot carriers give the contribution of 5% into the total Ce-emission output, emitting with the decay constant of 20 ns.

## Conclusions

Keeping in mind the above results of studies of the luminescence in LaCl<sub>3</sub>-Ce, the following mechanisms for the excitation of Ce<sup>3+</sup> centres can be pointed out:

- i) direct optical excitation ( $E_{exc} = 4\div 5.5 \text{ eV}$ );
- ii) energy transfer from near-activator exciton ( $E_{exc}=5.6\div 6.4 \text{ eV}$ );
- iii) re-absorption of the STE emission by Ce<sup>3+</sup> centres ( $E_{exc}>6.0 \text{ eV}$ );
- iv) recombination with the hot carriers ( $E_{exc}>6.5 \text{ eV}$ );
- v) recombination with the V<sub>k</sub>-centres ( $E_{exc}>6.5 \text{ eV}$ );
- vi) thermally activated diffusion of the STE to Ce<sup>3+</sup>-centres ( $E_{exc}>6.0 \text{ eV}$ );

The two latter mechanisms make a major contribution into the luminescence intensity under high-energy excitation.

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