## University of Latvia Department of Physics and Mathematics

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## Luminescence processes in Er<sup>3+</sup> doped NaLaF<sub>4</sub>

Summary of the Doctoral Thesis

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### Abstract

This Thesis is dedicated to the spectroscopic studies of  $Er^{3+}$  doped NaLaF<sub>4</sub>, which is a promising material for obtaining up-conversion luminescence. During the process of up-conversion, the photons with lower energy (usually – infrared radiation) are converted to the photons with higher energy (visible and ultraviolet radiation).

In the NaLaF<sub>4</sub>:Er<sup>3+</sup> luminescence spectrum, Er<sup>3+</sup> characteristic luminescence bands with a dominant green luminescence band ( ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ , 540 nm) can be observed. As Er<sup>3+</sup> concentration increases (0.1 – 10 mol%), concentration quenching is observed for the green luminescence band, which is associated with interaction processes between Er<sup>3+</sup>.

The studies of luminescence spectra and kinetics show that up-conversion luminescence is excited by two processes: excited state absorption and energy transfer. The contribution of these processes to the excitation of green up-conversion luminescence depends on the excitation wavelength.

Analysis of the measured luminescence spectra and luminescence decay kinetics at different excitation wavelengths (482 - 490 nm) at low temperatures (15 K) confirm that  $Er^{3+}$  can incorporate into several non-equivalent sites in crystal structure of NaLaF<sub>4</sub>. It is shown that energy transfer occurs between  $Er^{3+}$  located in non-equivalent sites. Up-conversion luminescence spectrum is a superposition of  $Er^{3+}$  luminescence spectra appearing as  $Er^{3+}$  occupies different positions at the crystalline structure of NaLaF<sub>4</sub>.

Spectroscopic data obtained at different temperatures (15 - 300 K) allow to conclude that apart from  ${}^{4}S_{3/2}$  state, an adjacent  ${}^{2}H_{11/2}$  state is also involved in  $\mathrm{Er}^{3+}$  interaction processes leading to the concentration quenching for the green luminescence.

**Keywords:** luminescence, up-conversion luminescence, NaLaF<sub>4</sub>, kinetics of luminescence spectra, site-selective spectroscopy.

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## 1 Introduction

### 1.1 Motivation

For many years much attention has been paid for studies of up-conversion processes involving transformation of lower energy photons (longer wavelength) into the higher energy photons (shorter wavelength). It is possible to obtain up-conversion luminescence in the case of gradually absorbing and accumulating the energy of excitation source photons. In 1959, Bloembergen suggested a hypothesis that the infrared radiation could be detected by means of consecutive absorption of several photons in a single ion [1]. Some years later, in 1966, Auzel had observed the up-conversion luminescence for the first time, and had associated this process with excitation energy transfer between 2 activator ions [2]. Up-conversion luminescence can be used in several practical applications, e.g., in solid-state lasers [3], temperature sensors [4], white light simulation [5], to improve the efficiency of solar cells [6], in biologic markers [7], photodynamic therapy [8], amplification of the signal in optical fibres [9], as well as in other applications.

Up-conversion luminescence can be observed in different kinds of materials containing dopant ions – activator ions. The main prerequisite for these activator ions is several equidistant real energy levels. The most rare-earth elements comply with this prerequisite as their energy level scheme comprises several discreet energy levels divided by equal energy gaps. With aforementioned requirements complies also  $Er^{3+}$  which is a promising rareearth element for doping a material in order to observe up-conversion luminescence [10, 11, 12]. Depending on the choice of a matrix material,  $Er^{3+}$  concentration, and other factors, it is possible to obtain intensive green [13], red [14] or yellow luminescence [15] using infrared radiation as an excitation source.

Application of luminescent materials is related to the efficiency of luminescence. Efficiency of up-conversion luminescence depends on several factors, e.g., material phonon energy, appropriate crystal structure with a possibility for an activator ion to incorporate into, and optimal concentration of activator ions. Depending on the mode of application, various materials are required, e.g., transparent crystals or glasses, powder-like materials or nanoparticles. The efficiency of the up-conversion luminescence changes in different materials. Hence, each application requires the most suitable material, for example, a good transparency and intensive up-conversion luminescence or nanosize grains with a specific luminescence wavelength.

One of the conditions affecting the efficiency of luminescence is matrix phonon energy. The probability for nonradiative transition - a process associated with the losses of excitation energy, namely, lower luminescence

efficiency, is lower in the materials with lower phonon energy [16]. Iodide, bromide, and chloride compounds (LaI<sub>3</sub>, LaBr<sub>3</sub>, LaCl<sub>3</sub>) are considered to be promising materials in this sense [17] owing to their low phonon energy. The practical application for these materials is hindered by their hygroscopic features though; that is why it is not possible to use them unshielded. This is the reason why fluoride compounds are considered to be **promising materials for the practical applications of up-conversion luminescence** [18]. These materials also feature low phonon energy, as well as higher endurance towards the environmental factors.

Apart from various materials containing rare-earth-doped fluoride (LaF<sub>3</sub>, CaF<sub>2</sub>, YF<sub>3</sub>, SrF<sub>2</sub>, LiYF<sub>4</sub>, etc.), hexagonal NaLnF<sub>4</sub> (Ln=Y, La-Lu) have also been mentioned in the literature as promising materials for successful obtaining of up-conversion luminescence. At present, NaYF<sub>4</sub> doped with different types of rare-earth elements is considered to be one of the most promising materials. Not only low phonon energy of the material explains high efficiency of up-conversion luminescence, but also the structure of the crystal lattice, which is favourable for incorporation of rare-earth elements into the non-equivalent sites in the crystal lattice [19 – 25].

NaLaF<sub>4</sub> also belongs to the same crystal structure as NaLnF<sub>4</sub>. Compared with the other representatives of the NaLnF<sub>4</sub> family featuring both hexagonal and cubic crystal structure, only hexagonal structure has been observed for the NaLaF<sub>4</sub>. The experiments performed at the Optical Spectroscopy Laboratory, Institute of Solid State Physics, University of Latvia (ISSP UL) revealed that NaLaF<sub>4</sub> effective phonon energy is ~290 cm<sup>-1</sup> [26], which is lower than that in NaYF<sub>4</sub> (~360 cm<sup>-1</sup>) [25]. Lower phonon effective energy indicates that nonradiative transitions could be supressed more effectively than in NaYF<sub>4</sub>; that is why the efficiency of up-conversion luminescence in rare-earth-doped NaLaF<sub>4</sub> is expected to be better that in NaYF<sub>4</sub>.

The first studies related to the spectroscopic features of NaLaF<sub>4</sub> had been already performed in 1972, when Kano et al had investigated spectroscopic features of  $Er^{3+}$  and  $Yb^{3+}$  doped NaLaF<sub>4</sub> [27]. Up to now, a very few investigations associated with methods of synthesis of doped NaLaF<sub>4</sub> and its spectroscopic features had been performed [26, 28 – 31].

These investigations have revealed that in  $Er^{3+}$  doped NaLaF<sub>4</sub>, green up-conversion luminescence has been observed. The increase in  $Er^{3+}$  concentration changes the ratio between the intensities of green and red up-conversion luminescence bands. Besides, concentration quenching is observed for the green luminescence band ( ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ ), that is, increased  $Er^{3+}$  concentration leads to faster decrease of population at the excited state  ${}^{4}S_{3/2}$ . Up to now, no investigations of mechanisms of concentration quenching in NaLaF4: $Er^{3+}$  have been performed.

Structural analysis shows that crystal lattice structure of NaLnF<sub>4</sub> belongs to  $P\overline{6}$  group [19, 32 – 34]. This crystal structure contains 3 different cation sites, where a rare-earth element as an activator ion is expected to be incorporated. Various experimental efforts confirmed that a rare-earth element can be incorporated in 3 non-equivalent sites in NaLnF<sub>4</sub> crystal structure, e.g.,  $\beta$ -NaEuF<sub>4</sub> [33], NaYF<sub>4</sub>:Pr<sup>3+</sup> [35]. Although it has also been observed that the number of corresponding sites for a rare-earth element to be able to incorporate may differ from 3, e.g., in the case of NaGdF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3</sup> [19], only 2 sites have been found, but in the case of NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup>, 7 different Er<sup>3+</sup> green luminescence spectra ( ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ ) have been observed [20]. No studies associated with the determining of non-equivalent sites and the effect of different surroundings of crystalline field on spectroscopic properties of activator ion of NaLaF4:Er<sup>3+</sup> have been conducted up to now.

## 1.2 The goal and the tasks of the Doctoral Thesis

The main goal of this Doctoral Thesis is to perform an extended research and comprehend the luminescence processes in  $Er^{3+}$  doped NaLaF<sub>4</sub>. The following tasks have been set to achieve this goal:

- Synthesis of Er<sup>3+</sup> doped NaLaF<sub>4</sub> with different concentrations;
- Exploring the effect of Er<sup>3+</sup> concentration on luminescence properties of NaLaF<sub>4</sub>:Er<sup>3+</sup>;
- Exploring the influence of possible different surroundings (sites) of Er<sup>3+</sup> in NaLaF<sub>4</sub> on luminescence.

## **1.3** Novelty of the work

The studies performed within this work will allow to comprehend:

- the effect of Er<sup>3+</sup> concentration on spectroscopic properties of NaLaF<sub>4</sub>;
- The impact of possible non-equivalent  $Er^{3+}$  sites on spectroscopic properties of NaLaF<sub>4</sub>: $Er^{3+}$ .

## 1.4 Author's contributions

The synthesis of the samples has been performed by the Author together with MSc. Guna Doke. Luminescence spectra, excitation spectra, luminescence kinetics at different temperatures have been obtained by the Author unassisted. The analysis of all the experimental data, interpretation of the results, and preparing the publications is Author's own work entirely, with the consultations with the scientific advisors: Dr. habil. phys. Māris Spriņģis and Dr. phys. Anatolijs Šarakovskis.

X-ray diffraction measurements of the synthesised samples have been performed by Dr. phys. Līga Grīnberga; SEM measurements of the synthesised samples have been performed by BSc. Guna Krieķe.

## 2 Fundamentals

## 2.1 Mutual interaction of activator ions

Concentration of activator ions in material significantly affects spectroscopic properties of the material, e.g., luminescence spectrum, luminescence kinetics, and luminescence efficiency. Depending on the concentration of activator ions, changes of the aforementioned values are related to the mutual interaction of these ions.

In the case of evenly distributed activator ions within the volume of the material and at low concentration, the mutual distance between the activator ions is large (several mm). Therewith, the probability of activator ions to "feel" the presence of each other is low, and each activator ion is considered to be an individual luminescence centre.

As the concentration of activator ions increases or another type of activator ions is introduced, the mutual distance between them decreases. Decreased mutual distance increases the probability for them to "feel" each other's presence, and to interact mutually. The effect of this interaction on the position of energy levels may be negligible (and often indistinguishable), but mutual interaction is sufficient to transfer excitation energy from one activator ion to another. Therefore, energy transfer between activator ions may change the spectroscopic properties of the material, including luminescence spectra and luminescence kinetics. Examining the luminescence kinetics makes it possible to determine the type of the interaction between the activator ions.

#### 2.1.1 Direct relaxation, donor-acceptor interaction

One of the types of interaction between the activator ions is direct relaxation manifesting itself as a donor-acceptor interaction. In the case of this interaction, the excited donor transfers the excitation energy to the acceptor, and this energy cannot return to the donor.

It is possible to describe the donor's luminescence kinetics in the approximation of dipole-dipole interaction using Förster's and Dexter's [36, 37] assumptions on multipole-multipole interaction between the donor and acceptor:

$$\phi(t) = \phi(0)e^{-\left(w_0 t + \frac{4}{3}\pi^2 R_0^3 n_a(w_0 t)^{\frac{1}{2}}\right)}$$
(2.1)

where  $w_0$  is transition probability of donor's excited state,  $n_a$  is the concentration of acceptor ions,  $R_0$  is a critical donor-acceptor distance when the probability of energy transfer is equal to the transition probability of donor's excited state  $w_0$ . Expression (2.1) allows to conclude that the curve of luminescence kinetics will not have a simple exponential nature.

In a material having a single type of activator ions, these ions may act both as donor and acceptor. In this case, mutual interaction between activator ions manifests itself as a cross-relaxation process.

#### 2.1.2 Fast migration

If the donors' mutual distances are short, excitation energy may migrate among the donors untill there is a possibility for donor-acceptor interaction to occur, or untill the donor emits excitation energy in a form of a photon. In this case, donor's luminescence kinetics can be described by the following exponential expression [38]:

$$\phi(t) = \phi(0)e^{-(w_0 + w_D)t}$$
(2.2)

where  $w_D$  is migration probability among the donors, which depends linearly on the concentration of the donors [39, 40].

#### 2.1.3 Migration-limited relaxation

The situation looks more complex in the case if the both aforementioned processes – direct relaxation and fast migration – may occur at equal probability. Under the assumption that excitation energy between donors can propagate in the manner of diffusion, and donor-acceptor interaction occurs in the approximation of dipole-dipole interaction, Yokota and Tanimoto have obtained an analytical expression [41], which can be used efficiently to describe the donor's luminescence kinetics in the case or migration-limited relaxation in different materials [42 - 44]:

$$\phi(t) = \phi(0)e^{-w_0 t}e^{-\frac{4}{3}\pi^2 R_0^3 n_a(w_0 t)^{\frac{1}{2}} \left(\frac{1+10.87x+15.50x^2}{1+8.743x}\right)^{\frac{3}{4}}}$$
(2.3)

where  $x = DC^{-\frac{1}{3}}t^{\frac{2}{3}}$ , D – diffusion coefficients featuring donor-donor interaction, and C – coefficient featuring donor-acceptor interaction in dipole-dipole approximation. Expression (2.3) allows to conclude that that donor's luminescence kinetics does not have a simple exponential feature.

#### 2.2 Up-conversion luminescence



**Fig. 2.1.** Energy relaxation mechanisms with corresponding curves of luminescence kinetics: a) excited state absorption, b) energy transfer process

*Figure 2.1* shows 2 main mechanisms to excite up-conversion luminescence. *Figure 2.1 a* shows excited state absorption, when a consecutive absorption of two (or several) photons of excitation radiation occurs in one ion. In this case, the curve of up-conversion luminescence kinetics coincides with curve of luminescence measured under the direct excitation – Stokes luminescence.

Figure 2.1 b shows the process of energy transfer. Absorbing photons of excitation radiation, activator ions are excited to the first excited state (E1). With certain probability, an activator ion (J1) returning to the ground state will not emit energy in the form of luminescence photon, but will transfer the energy to the adjacent activator ion (J2) exciting it to the state of higher energy (E2). In the case of energy transfer, the curve of luminescence kinetics will show the increase in the intensity at the end of excitation radiation.

Experimentally, more complicated up-conversion luminescence kinetics consisting of the both abovementioned energy relaxation mechanisms are observed.

## 2.3 NaLaF<sub>4</sub>

One of the crucial aspects to be able to observe luminescence with higher efficiency is choosing a material with low phonon energy. Low phonon energy of the material decreases the probability of nonradiative transition, which increases the efficiency of luminescence. In the case of up-conversion luminescence, when luminescence excitation occurs through several excited states, it is important that the number of excited ions is not decreased by other processes, including nonradiative transition.

NaLaF<sub>4</sub> is a promising material which allows obtaining up-conversion luminescence as this material features low phonon energy  $\sim 290 \text{ cm}^{-1}$  [26].

According to its crystal structure, NaLaF<sub>4</sub>, as the other representatives of NaLnF<sub>4</sub> family, belongs to  $P\overline{6}$  group (*Fig. 2.2*) [19, 32 – 34]. In this structure, La<sup>3+</sup> supersedes site 1*a* (Wyckoff name) with C<sub>3h</sub> symmetry. Site 1*f*, which is also of C<sub>3h</sub> symmetry, is shared between La<sup>3+</sup> and Na<sup>+</sup> ( $\frac{1}{2}$  of the site is occupied by La<sup>3+</sup>, and  $\frac{1}{2}$  – by Na<sup>+</sup>). Half of the site 2*h* (C<sub>3</sub> symmetry) in the structure is occupied by Na<sup>+</sup>, and the other half – by Na vacancy (V<sub>Na</sub>). Fluorine ions F1 and F2 occupy 2 non-equivalent sites: 3*j* and 3*k* having C<sub>8</sub> symmetry [45].



Fig. 2.2. Structure of NaLaF<sub>4</sub> depicted as Na<sub>1.5</sub>La<sub>1.5</sub>V<sub>Na</sub>F<sub>6</sub> crystal in  $P\overline{6}$  group [45]

In the representatives of NaLnF<sub>4</sub> family, three cation sites: 1a, 1f and 2h has been mentioned as the most suitable position in the crystal lattice for rareearth elements to get incorporated [33, 35]. It is expected that this can also be attributed to NaLaF<sub>4</sub> as a representative of NaLnF<sub>4</sub> family. Clearly, the possibility that a rare-earth element gets incorporated into the interstitial space cannot be excluded.

## 3 Experimental methods

## **3.1** Synthesis of the sample

The method of synthesis of  $NaLaF_4:Er^{3+}$  comprises of mixing of raw material and heating it in the particularly designed furnace in fluorine atmosphere.

#### **3.2** Structural analysis

To determine the structure of the sample, X-ray diffraction analysis has been used. X'Pert Pro MPD diffractometer has been used for the X-ray diffraction measurements. The diffractometer is equipped with copper anode ( $\lambda_{XRD}$ = 0.154056 nm). Operational voltage is 40 kV, and current 30 mA. Accuracy of the diffractometer is 0.07<sup>0</sup>.

## **3.3 Morphology analysis**

For morphology analysis of the sample, Zeiss EVO50 XVP scanning electron microscope has been used (15 kV, 100 pA).

#### **3.4** Luminescence measurements

To excite both traditional and up-conversion luminescence, tunable (210 - 2300 nm, using optical parametric oscillator) pulsed NT342/3UV EKSPLA laser (pulse length ~ 5 ns, repetition frequency 10 Hz) has been used. To detect luminescence, DU-401 BV CCD ANDOR camera and iCCD ANDOR camera iSTAR DH734 18mm connected to ANDOR SR-303i-B monochromator/spectrometer has been used. To detect infrared spectrum, ANDOR iDus 1.7µm InGaAs CCD (DU490A-1.7) camera connected to the same spectrometer has been used. For low temperature measurements, the sample has been placed into closed cycle He cryostat DE202N, Advanced Research Systems. To control the temperature of the sample, LakeShore 325 temperature controller  $(accuracy \pm 1 \text{ K})$  has been used.

To record luminescence excitation spectra, the described experimental setup has been used. Luminescence spectra have been obtained and recorded by changing the wavelength of the excitation laser (in the interval 210 - 710 nm with a step of 0.1 nm; in the interval 710 - 2300 nm with a step of 0.3 nm). Obtained luminescence spectra at different wavelengths have been processed by the programme written in LabView environment by the Author.

Luminescence kinetics have been experimentally obtained by means of two methods: using photoelectron multiplier (PEM) and iCCD camera.

Photoelectron multiplier  $\Phi \Im Y$ -115 connected to the output slit of ANDOR SR-303i-B in the monochromator regime has been used to record luminescence kinetics. The signal from PEM has been recorded by Tektronix oscilloscope TDS 684A. Total system resolution is better than 10 ns.

The second method used to record luminescence spectra kinetics, is the use of iCCD camera allowing to record several luminescence spectra at different time values after the laser pulse. Using consecutive time delays one after another, it is possible to record luminescence spectra during the whole luminescence process. It is possible to derive luminescence kinetics from these luminescence spectra obtained at different moments of time. Obtained data massive has been processed by the programme written in LabView environment by the Author.

## 4 Results and analysis

# 4.1 Composition and structure of the synthesised samples

As a result of the described method of synthesis, white polycrystalline powder of  $NaLaF_4$  doped with  $Er^{3+}$  in different concentrations (0.1 – 10 mol%) has been obtained.

SEM data analysis demonstrates that samples consist of polycrystalline grains comprising  $NaLaF_4$  crystallites grown together. Grains are of equal size, which is of order of several microns.

## 4.2 Influence of concentration of Er<sup>3+</sup> on Stokes luminescence of NaLaF<sub>4</sub>:Er<sup>3+</sup>



Fig. 4.1. Luminescence spectrum of NaLaF<sub>4</sub> doped with 0.2 and 10 mol% Er<sup>3+</sup> excited at 489 nm

After excitation NaLaF<sub>4</sub> doped with different  $Er^{3+}$  concentrations with 489 nm ( ${}^{4}F_{7/2}$  state), it is possible to observe luminescence bands characteristic to  $Er^{3+}$  in visible and infrared spectral regions (*Fig. 4.1*). All experimental measurements described in this (4.2) and the next (4.3) chapter have been conducted at room temperature. After changing the wavelength of excitation radiation in a small spectral range (470 – 495 nm), no changes in the luminescence spectra have been observed.

In the samples with different  $Er^{3+}$  concentrations in NaLaF<sub>4</sub> matrix, changes in the interrelations between intensities of luminescence bands have been observed (*Fig. 4.1*).



**Fig. 4.2.** Dependence of luminescence bands intensity on  $Er^{3+}$  concentration (double log scale). Blue line indicates luminescence intensity, which is expected to be proportional to activator ion concentration if no mutual interaction of activator ions occurs

*Figure 4.2* compares the intensities of green (540 nm), red (660 nm), and infrared (980 nm) luminescence bands for different  $Er^{3+}$  concentrations.

Increase in the intensity of red luminescence band is linearly proportional to  $Er^{3+}$  concentration similar to the case if no mutual interaction between activator ions occurs [46].

The intensity of green luminescence band reaches its maximum when  $\mathrm{Er}^{3+}$  concentration is ~2 mol%. At higher  $\mathrm{Er}^{3+}$  concentrations, the intensity of the luminescence decrease.

For the infrared band (980 nm), a rapid increase in the luminescence intensity is observed. It is more rapid than expected (blue line in the *Fig. 4.2*).

Decrease of the intensity of green luminescence after increasing  $Er^{3+}$  concentration can be associated with the concentration quenching [16] when energy transfer leads to cross-relaxation between erbium ions, resulting in decreasing of the number of ions in excited  ${}^{4}S_{3/2}$  state and in increasing of the numbers of ions at excited  ${}^{4}I_{11/2}$  state (*Fig. 4.3*) [47].

At the chosen diapason of  $\text{Er}^{3+}$  concentrations, the curves of red luminescence kinetics have not changed, and they feature simple exponential form (*Fig. 4.4 a*), which gives evidence that for this luminescence band, concentration quenching is not observed.



**Fig. 4.3.** Possible cross-relaxation processes in Er<sup>3+</sup>: arrow with thick line – radiation transition (luminescence), arrow with dashed line – process of energy transfer, arrow with dotted line – nonradiative transition



**Fig. 4.4.** Luminescence kinetics (semilog scale) of  ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$  (a) and  ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$  (b) optical transitions at different  $Er^{3+}$  concentrations. Wavelengths of excitation radiation are (a) 650 nm and (b) 520 nm

Curves of the green luminescence kinetics are shown in *Fig. 4.4 b*. For the green luminescence band, changes in curves of luminescence kinetics are observed for the samples with different  $\text{Er}^{3+}$  concentrations, which is an evidence of mutual interaction between activator ions. From the expressions (2.1), (2.2), and (2.3), the experimental curves of luminescence kinetics can be best described by the expression (2.3). This suggests the occurrence of both energy migration and direct relaxation – cross-relaxation.

#### 4.2.1 Conclusions

- The luminescence spectrum for NaLaF<sub>4</sub> doped with different Er<sup>3+</sup> concentration reveals characteristic Er<sup>3+</sup> luminescence bands in the green, red and infrared spectral regions;
- No concentration quenching was observed for the red luminescence (660 nm) in the chosen  $\text{Er}^{3+}$  concentration range (0.2 10 mol%);
- In the chosen  $Er^{3+}$  concentration range (0.2 10 mol%) considerable quenching of the green luminescence (540 nm) occurs. This quenching is attributed to a cross-relaxation and energy migration process.

## 4.3 Up-conversion luminescence of NaLaF<sub>4</sub>:Er<sup>3+</sup>

In up-conversion luminescence spectrum of NaLaF<sub>4</sub>: $Er^{3+}$  excited at 980 nm, the characteristic  $Er^{3+}$  luminescence bands like those at direct excitation are observed (*Fig. 4.1*).



**Fig. 4.5.** Green up-conversion luminescence kinetics (540 nm) of NaLaF<sub>4</sub>:Er<sup>3+</sup> (2 mol%) excited at different wavelengths

Under excitation with different excitation wavelengths (966 – 982 nm), no changes in green up-conversion luminescence spectra have been observed, but the changes in the curves of the green up-conversion luminescence kinetics have been observed (*Fig. 4.5*). The ratio of excited state absorption and energy transfer changes with the change of excitation wavelength (*Fig. 4.6*). At shorter

excitation wavelengths, excited state absorption is a dominant process, whereas at longer ones, energy transfer process dominates.



**Fig. 4.6.** Excited state absorption and energy transfer processes in Er<sup>3+</sup> energy level scheme, after excitation at 980 nm



Fig. 4.7. Energy level scheme: a) excited state absorption occurs, b) excited state absorption does not occur as excitation energy is not enough, c) energy transfer is possible

Due to the electric field existing in the crystal structures,  $Er^{3+}$  energy levels are split into a number of sublevels – Stark components, and form a relative small zone (*Fig. 4.7*). In addition, energy differences between *E1-E0* ( ${}^{4}I_{15/2} - {}^{4}I_{11/2}$ ) and *E2-E1* ( ${}^{4}I_{11/2} - {}^{4}F_{7/2}$ ) do not coincide, and are not equal.

For an excitation with shorter wavelength (966 nm), photon energy is sufficient ( $\Delta E_1$  Fig. 4.7 a) to overcome the energy difference E1-E0 and E2-E1 (Fig. 4.7). In this case, excited state absorption is observed.

For an excitation with longer wavelength (978 nm), photon energy ( $\Delta E_2$  *Fig. 4.7 b*) is sufficient to overcome the energy difference *E1-E0* (*Fig. 4.7 b*), but not sufficient to overcome the second energy difference *E2-E1*, (*Fig. 4.7 b*). In this case, excited state absorption cannot be observed.

The lacking amount of energy to overcome the second energy difference E2-E1 is possible to obtain from the crystal lattice of the matrix (thermal energy). When ion state E1 is excited, the population of Stark sublevels conforms to Boltzmann distribution, namely, at higher temperature the probability for an ion to appear at the higher energies of the excited state E1 is greater.

In this case, when ion returns from the higher Stark levels of the state *E1* to the ground state *E0* lower Stark levels, it transfers to the adjacent  $\text{Er}^{3+}$  an energy higher than the one of the excitation photon ( $\Delta E_3 > \Delta E_2$ ), which is sufficient to overcome the energy difference *E2-E1* (*Fig.* 4.7 *c*).

#### 4.3.1 Conclusions

- NaLaF<sub>4</sub>:Er<sup>3+</sup> up-conversion luminescence spectra reveals characteristic Er<sup>3+</sup> luminescence bands in the ultraviolet, visible and infrared spectral regions with dominant green luminescence band (540 nm);
- Green (540 nm) up-conversion luminescence is excited via excited state absorption and energy transfer processes;
- When excitation wavelength is increased energy transfer become dominant mechanism to excite green up-conversion luminescence.

## 4.4 Luminescence spectra of NaLaF<sub>4</sub>:Er<sup>3+</sup> and luminescence decay kinetics at low temperatures (15 K)

#### 4.4.1 Stokes luminescence

Changes in wavelengths of excitation radiation lead to the significant changes in green luminescence spectra of NaLaF<sub>4</sub>: $Er^{3+}$  (2 mol%). *Figure 4.8* shows the excitation spectra ( ${}^{4}F_{7/2}$  state) of green luminescence.

There are evident narrow, well-resolved components of Stark levels in the green luminescence (542.3 nm) excitation spectrum (*Fig. 4.8*, left graph). In addition to narrow Stark components, a wide band can also be observed to the shorter wavelengths of excitation radiation (about 478 nm). Such wide band in the excitation spectrum to the shorter wavelengths from the narrow Stark components can also be observed in the cases when green luminescence is excited through  ${}^{4}F_{3/2,5/2}$ ,  ${}^{2}H_{11/2}$ ,  ${}^{4}S_{3/2}$ . The occurrence of the wide excitation band is associated with adjacent phonon side bands [48, 49]. In the case of NaLaF<sub>4</sub>, wide band is located at about 300 cm<sup>-1</sup> to the shorter wavelengths from the Stark components, which is in good agreement with phonon energy of NaLaF<sub>4</sub> matrix ~ 290 cm<sup>-1</sup>.

When luminescence has been excited at wavelength corresponding to the wide band in the excitation spectrum, no changes in green luminescence spectrum have been observed. When luminescence has been excited at different wavelength corresponding to Stark sublevels, significant changes in the green luminescence spectrum have been observed. These especially sensitive changes in the green luminescence spectrum depending on the wavelength of excitation radiation suggest that  $\mathrm{Er}^{3+}$  is located at different sites in the crystal structure of NaLaF<sub>4</sub>.



**Fig. 4.8.** Luminescence and its excitation spectra for NaLaF<sub>4</sub> doped with 2 mol%  $Er^{3+}$  measured at 15 K. Excitation is performed in  ${}^{4}F_{7/2}$  state and luminescence has been observed in  ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$  transition

#### Table 4.1.

Spectroscopic characteristic values for  $\mathrm{Er}^{3+}$  occupying different positions in NaLaF4 crystal lattice

Site	Er(1)	Er(2)	Er(3)
Wavelength of the excitation radiation, nm	482.8	484.8	485.2
Luminescence wavelength, nm	544.4	545.5	539.9

The analysis of the green luminescence spectra excited at different wavelengths (481 - 495 nm) allowed to select 3 distinct green luminescence spectra. The number of the obtained spectra allows concluding that  $\text{Er}^{3+}$  may be located at three non-equivalent sites in the NaLaF<sub>4</sub> crystal lattice. To be completely sure about that, additional analysis of green luminescence spectra has been performed. To simplify, each of the obtained green luminescence spectra will be denoted as Er(1), Er(2) and Er(3). Characteristic (explicitly different)

wavelengths of the excitation radiation and luminescence wavelengths for explicitly different Stark subbands are shown in *Table 4.1*.



**Fig. 4.9.** Green luminescence kinetics of NaLaF<sub>4</sub>:Er<sup>3+</sup> (2 mol%) excited at different wavelengths corresponding to different positions of Er<sup>3+</sup>. The spectra have been recorded at 15 K

In green luminescence spectra Er(1), Er(2) and Er(3) at different luminescence wavelengths, various luminescence kinetics have been observed (*Fig. 4.9*). When erbium ion has been excited at a specific position, e.g., Er(1), the luminescence kinetics of the same position (Er(1)) was exponential. This suggest that cross-relaxation process does not occur at low temperatures.

When  $Er^{3+}$  has been excited at one position, e.g., Er(1), there is an increase in luminescence kinetics of the other position, e.g., Er(2). The occurrence of the increased part is an evidence of the process of energy transfer (energy migration) happening between  $Er^{3+}$  at different positions of the crystal structure of NaLaF<sub>4</sub>.

Decay kinetics of green luminescence spectra (*Fig.* 4.9) show that 3 unique green luminescence spectra which could characterise  $\text{Er}^{3+}$  in different NaLaF<sub>4</sub> crystalline sites are slightly influenced though by the rest of  $\text{Er}^{3+}$ 

luminescence spectra. In order to obtain more unique  $\text{Er}^{3+}$  luminescence spectra, it is necessary to record them at the moment when the energy transfer is low, that is, at the beginning of the luminescence kinetics right after the end of excitation laser pulse. Luminescence spectra recorded in this manner can be observed in *Fig. 4.10*.



**Fig. 4.10.** 3 dominant NaLaF<sub>4</sub>:Er<sup>3+</sup> (2 mol%) green luminescence spectra obtained at the beginning of the luminescence kinetics excited at different wavelengths. The spectra have been recorded at 15 K

Using superposition of the 3 unique luminescence spectra obtained at the beginning of the luminescence kinetics (*Fig. 4.10*), it is possible to describe all experimentally obtained luminescence spectra of NaLaF<sub>4</sub>: $Er^{3+}$  (2 mol%), which intensity at different wavelength of excitation radiation (470 – 495 nm) is not less than 5% of maximal observed luminescence intensity. This result shows that experimentally observed luminescence spectra are the superposition of at least 3 different luminescence spectra corresponding to erbium ion at 3 different crystalline regions.

Assigning one of three unique luminescence spectra to erbium ion occupying a specific cation site in NaLaF<sub>4</sub> crystal lattice is rather complicated. Comparing luminescence spectra of samples with different  $Er^{3+}$  concentrations (0.1 mol% and 2 mol%) allows to conclude that  $Er^{3+}$  distribution among non-equivalent sites in NaLaF<sub>4</sub> crystal matrix is uniform as interrelations between the intensities of three unique luminescence spectra for the samples with mentioned  $Er^{3+}$ concentrations are the same.



**Fig. 4.11.** Kinetics of green luminescence spectra of NaLaF<sub>4</sub>:Er<sup>3+</sup> (2 mol%) excited at 972 nm. Recorded at 15 K. On the left – up-conversion luminescence kinetics for 544.4 nm (Er(1)) and 545.5 nm (Er(2)) luminescence bands

In the case of up-conversion luminescence, the change of the wavelength of the excitation radiation (960 - 980 nm) did not result in significant changes in green up-conversion luminescence spectrum, and the shape of the spectrum coincided with luminescence spectrum obtained after excitation at wavelengths (470 - 480 nm) corresponding to the broad band in the excitation spectrum (*Fig. 4.8*, graph on the left). This is an evidence to the fact that the green up conversion luminescence spectrum is also a superposition of Er(1), Er(2) and Er(3) spectra.

At different wavelengths of the excitation radiation (960 - 980 nm), the same character of change in the mechanisms of excitation as at the room temperature has been observed, that is, at shorter wavelength of the excitation radiation, excited state absorption dominated, and at the longer ones – energy transfer was a dominant process.

Under the excitation of green up-conversion luminescence spectra at 972 nm, different luminescence wavelengths corresponding to Er(1) or Er(2) has different luminescence kinetics (*Fig. 4.11*). It proves that at 972 nm up-conversion luminescence Er(1) is excited by means of energy transfer, and Er(2) – by excited state absorption.

#### 4.4.3 Conclusions

- NaLaF<sub>4</sub>:Er<sup>3+</sup> low-temperature (15 K) excitation spectra reveals sharp peaks corresponding to the electronic transitions between the ground and excited state;
- Broad band appearance in the excitation spectra is attributed to Er<sup>3+</sup>-lattice phonons interaction;
- Green luminescence spectra including green up-conversion luminescence spectra could be reproduced using superposition of three distinct luminescence spectra;
- Er<sup>3+</sup> are incorporated into three non-equivalent positions in NaLaF<sub>4</sub> crystalline structure;
- All Er<sup>3+</sup> positioned at non-equivalent sites are involved in up-conversion process.

## 4.5 Luminescence spectra of NaLaF<sub>4</sub>:Er<sup>3+</sup> and luminescence decay kinetics at different temperatures (15 – 300 K)

## 4.5.1 Changes in the green luminescence spectra and decay kinetics

At low temperature (15 K), 3 unique luminescence spectra have been explicitly observed, although no changes in the green luminescence spectra at room temperature have been observed when the wavelengths of excitation radiation have been changed. *Figure 4.12* show the dependence of the green luminescence spectra on the temperature of the sample under excitation of erbium ions (2 mol%) occupying different positions in NaLaF<sub>4</sub> crystal lattice (Er(1), Er(2), Er(3)). As demonstrated, increasing temperature of the sample leads to the overlapping of the unique Er(1), Er(2) and Er(3) luminescence spectra.

Luminescence excitation spectra show that increasing temperature of the sample leads to overlapping of luminescence excitation bands of different erbium ions (*Fig. 4.13*). Thus, it may be concluded that one wavelength of excitation radiation may excite different  $\text{Er}^{3+}$ .



**Fig. 4.12.** Temperature dependences of green luminescence spectra of NaLaF<sub>4</sub>: $Er^{3+}$  (2 mol%) exciting  $Er^{3+}$  at different positions (Er(1), Er(2) and Er(3))



**Fig. 4.13.** Luminescence excitation spectra of different erbium ions in NaLaF<sub>4</sub>:Er<sup>3+</sup> (2 mol%) recorded at different temperatures. Excitation spectra are normalised

The measurements of luminescence kinetics also approve the suggested overlapping of different  $Er^{3+}$  luminescence excitation bands. The analysis of temperature dependencies of luminescence kinetics (*Fig. 4.14*) shows that the decrease of the rising part in the luminescence kinetics curves is an evidence that numbers of excited  ${}^{4}S_{3/2}$  among the different  $Er^{3+}$  has been equalized. That means that the excitation at the wavelengths of the excitation radiation characteristic to Er(2), Er(1) is also excited. This corresponds to the observed experimental results on overlapping of different  $Er^{3+}$  luminescence excitation bands (*Fig. 4.13*).



Fig. 4.14. Green luminescence kinetics of NaLaF<sub>4</sub>: $Er^{3+}$  (2 mol%) at 544.4 nm (Er(1)) and 545.5 nm (Er(2)) under excitation at 484.8 nm (Er(2)) at different temperatures

## 4.5.2 Analysis of the green luminescence kinetics

Analysis of the dependence of green luminescence kinetics on the temperature of the sample shows that in the case of energy transfer (e.g., Er(2)  $\rightarrow$  Er(1)), luminescence kinetics becomes more rapid as the temperature increases (*Fig. 4.15 a*). Examining of the excited luminescence kinetics of one type of Er<sup>3+</sup> (e.g., Er(2), *Fig. 4.15 b*) demonstrates that in the range of 15 – 150 K, luminescence kinetics does not change its shape; however, in the range of 150 – 300 K, luminescence kinetics quenching becomes more rapid. In addition,

luminescence kinetics appeared to be of non-exponential nature. Shortening of the luminescence kinetics, or more rapid quenching, means more rapid decrease of the number of ions at the excited  ${}^{4}S_{3/2}$  state.



Fig. 4.15. Green luminescence kinetics of NaLaF<sub>4</sub>: $Er^{3+}$  (2 mol%) at a) 544.4 nm and b) 545.5 nm under excitation at 484.8 nm (Er(2)) at different temperatures



**Fig. 4.16.** Green luminescence spectra (520 nm) of NaLaF<sub>4</sub>:Er<sup>3+</sup> (2 mol%) excited at 484.8 nm (Er(2)) at different temperatures

As the temperature of the sample varies, the changes in luminescence spectrum at 525 nm (*Fig. 4.16*) can be observed. At low temperatures (15 – 100 K), this spectral region shows no luminescence. Temperature rise to 150 K leads to the appearance of the luminescence band at 525 nm, transition  ${}^{2}\text{H}_{11/2} \rightarrow {}^{4}\text{I}_{15/2}$ . Temperature rise (150 – 300 K) leads to the increased intensity of this luminescence band. The appearance of a luminescence band at 525 nm at 150 K and the increase of the luminescence band intensity are in a good

agreement with the changes in the number of ions at the excited  ${}^{4}S_{3/2}$  state (curve of luminescence kinetics in *Fig. 4.15 b*), when more rapid quenching of luminescence kinetic occurs above 150 K. Excited states  ${}^{2}H_{11/2}$  and  ${}^{4}S_{3/2}$  are thermally connected, which means that  ${}^{2}H_{11/2}$  state is thermally excited by the  ${}^{4}S_{3/2}$  state [50].

The shortening of experimentally obtained luminescence kinetics (*Fig. 4.15 b*) could be attributed to the different lifetime of the excited states  ${}^{4}S_{3/2}$  and  ${}^{2}H_{11/2}$ , namely, the lifetime of the excited  ${}^{2}H_{11/2}$  state is shorter. The present experimental equipment does not allow measure luminescence kinetics experimentally and determine the lifetime of the excited  ${}^{2}H_{11/2}$  state. The assumption that the lifetimes of these excited states are different can be ascertained in a different way. Similar changes in green luminescence kinetics (transition  ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ ) with the variation of the sample temperature must be also observed for the samples with different  $\mathrm{Er}^{3+}$  concentration.



**Fig. 4.17.** Green luminescence kinetics of NaLaF<sub>4</sub>:Er<sup>3+</sup> (0.1 mol%) at a) 545.5 nm and b) 544.4nm excited at 484.8 nm (Er(2)) at different temperatures

Recording the luminescence kinetics for the sample with lower  $Er^{3+}$  concentration (0.1 mol%) did not demonstrate significant changes in the curves of green luminescence kinetics ( ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ ) (*Fig. 4.17*). This allows concluding that more rapid change of the number of ions at the excited  ${}^{4}S_{3/2}$  state for the sample with  $Er^{3+}$  concentration of 2 mol% is caused not by the different lifetimes of excited states  ${}^{4}S_{3/2}$  and  ${}^{2}H_{11/2}$ , but by some other process that leads to the decrease of the number of ions at the excited  ${}^{4}S_{3/2}$  state.

The chapter on the dependence on the concentration shows that the changes in the curves of green luminescence (540 nm) kinetics are associated to the processes of energy migration and cross-relaxation. As a result of cross-

relaxation process, the number of ions at the excited  ${}^{4}S_{3/2}$  state decreases, and the number of ions at the excited  ${}^{4}I_{11/2}$  state increases.

*Figure 4.18* shows the temperature dependencies of the infrared spectra recorded for the samples with different  $Er^{3+}$  concentrations (0.1 mol% and 2 mol%) under the excitation at 484.8 nm (at Er(2) position). All obtained luminescence spectra are normalised to the intensity of luminescence band at 840 nm appearing at the transition from  ${}^{4}S_{3/2}$  to the first excited state  ${}^{4}I_{13/2}$ . Luminescence bands at 840 nm and 540 nm occur at the same excited state; that is why the changes in the intensities of any of these luminescence bands will characterise the changes in the number of ions at the excited  ${}^{4}S_{3/2}$  state. This normalisation of the luminescence spectra allows demonstrating of more illustrative mutual comparison of the ratios of the intensities of 840 nm and 980 nm bands.



**Fig. 4.18.** Luminescence spectra in infrared spectral region excited at 484.8 nm (Er(2)) at different temperatures, NaLaF<sub>4</sub> with different  $Er^{3+}$  concentrations

At low concentrations of  $\text{Er}^{3+}$  (*Fig. 4.18 a*), it is evident that the changes in the intensity of 980 nm luminescence band are relatively small as the temperature of the sample increases. As the temperature changes, the changes in the infrared radiation spectrum of the sample with higher  $\text{Er}^{3+}$  concentration (2 mol%) are much more pronounced (*Fig. 4.18 b*). In the temperature interval of 15 – 100 K, the intensity of 980 nm luminescence band remains unchanged. As the temperature rises to 150 K the intensity of 980 nm luminescence band increase. At higher temperatures (200 – 300 K), the intensity of 980 nm luminescence band increases more rapidly. That means that the number of ions at the excited  ${}^{4}\text{I}_{11/2}$  state increases with the increase of temperature.

As several spectroscopic values begin to change when the temperature of 150 K has been reached, it is possible to conclude that  ${}^{2}H_{11/2}$  state (*Fig. 4.16*) is

also involved in cross-relaxation processes, which leads to decrease of the number of ions at the excited  ${}^{4}S_{3/2}$  state (*Fig. 4.15 b*) and the increase of the number of ions at the excited  ${}^{4}I_{11/2}$  state (*Fig. 4.18 b*). In the suggested cross-relaxation processes (*Fig. 4.3*), excited states  ${}^{4}S_{3/2}$  and  ${}^{2}H_{11/2}$  must be considered together. Excited  ${}^{2}H_{11/2}$  state (*Fig. 4.19*) makes the larger contribution into the processes.



**Fig. 4.19.** Supplemented scheme of the process of cross-relaxation in Er<sup>3+</sup> involving also the excited <sup>2</sup>H<sub>11/2</sub> state: arrow with thick line – radiation transition (luminescence), arrow with dashed line – process of energy transfer, arrow with dotted curve – nonradiative transition

#### 4.5.3 Conclusions

- At room temperature Er<sup>3+</sup> green luminescence spectra is superposition of luminescence spectra origin from different Er<sup>3+</sup> (Er(1), Er(2), Er(3));
- In energy transfer (energy migration and cross-relaxation) processes between  $Er^{3+}$  not only  ${}^{4}S_{3/2}$  state but also  ${}^{2}H_{11/2}$  state is involved.

## 5 Theses

- Er<sup>3+</sup> incorporates into 3 non-equivalent sites in NaLaF<sub>4</sub> matrix. As a result, green luminescence spectrum is a superposition of three different luminescence spectra. Energy migration occurs between Er<sup>3+</sup> incorporated into the non-equivalent sites in NaLaF<sub>4</sub> matrix.
- Excitation mechanism of intensive  $Er^{3+}$  doped NaLaF<sub>4</sub> green up-conversion luminescence band depends on photon energy of the excitation source: excited state absorption dominates at higher excitation photon energy; in turn, at lower photon energies, energy transfer is dominant.
- Concentration quenching of the green luminescence, which is distinctly observable at higher than 2 mol% of Er<sup>3+</sup>, is mainly associated with the energy migration between Er<sup>3+</sup> resulting in cross-relaxation.

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## 8 Participation in conferences

#### 8.1 International conferences:

- 12th Russia/CIS/Baltic/Japan Symposium on Ferroelectricity and 9th International conference on Functional Materials and Nanotechnologies – RCBJSF-2014-FM&NT, Riga, Latvia, 2014
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- 17th International Conference on Luminescence and Optical Spectroscopy of Condensed Matter (ICL2014)
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- CFI Zinātniskā konference, 2014, Rīga J. Grūbe, G. Doķe, A. Šarakovskis, M. Spriņģis, DAŽĀDU KRISTĀLISKĀ REŽĢA VIETU IETEKME UZ Er<sup>3+</sup> LUMINISCENCI NaLaF4 MATRICĀ, LU CFI 30. zinātniskās konferences tēzes, 2014, 9. lpp
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I have been indicated as a co-author in more than 10 presentations.

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