IMPACT OF Er^{3+} CONCENTRATION ON LUMINESCENCE IN NaLaF_4

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In this work, NaLaF_4 doped with Er^{3+} of different concentrations was synthesized. The luminescence spectrum for $\text{NaLaF}_4:\text{Er}^{3+}$ (0.2 mol%) at 489 nm excitation reveals characteristic Er^{3+} luminescence bands in the green (540 nm), red (660 nm) and infrared (980 nm) spectral regions. The green luminescence band originated from the $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transition is the most intensive one in the luminescence spectrum. As the concentration of the activator is increasing, the intensity of all luminescence bands changes significantly. The super-linear increase of the infrared luminescence intensity with increasing Er^{3+} concentration as well as the quenching of green luminescence at the concentrations exceeding 2 mol% can be attributed to the cross-relaxation process between the activator ions.

Keywords: *erbium; luminescence; cross-relaxation.*

1. INTRODUCTION

For several decades, the attention of scientists has been attracted to up-conversion (UC) processes related to absorption of several light photons (usually infrared (IR)) followed by emission of light in the visible or even ultraviolet spectral regions [1]. The UC effect could be used in different areas like solid state lasers [2], temperature sensors [3], multicolor and white light simulation [4, 5], improvement of the efficiency of solar cells [6] and others.

Although UC luminescence is observable in materials doped with various transition metal and rare-earth (RE) ions, the most useful systems are materials doped with Er^{3+} , Tm^{3+} , Yb^{3+} , for example, crystals, glasses, ceramics or nanostructures [7-9]. Since the excitation of the UC luminescence in RE ions has a ladder nature (sequential absorption of excitation photons), non-radiative transitions from the intermediate energy levels are playing essential role in the efficiency of the whole process. To suppress the non-radiative losses and obtain higher quantum efficiency of the UC luminescence the host materials with low phonon energy are to be used. For this purpose, different binary and complex fluorides, including CaF_2 [10], BaF_2 [11], LaF_3 [12], BaYF_5 [13], LiYF_4 [14], NaYF_4 [15] doped with various optically active RE ions have been employed.

Up to now, NaYF₄ doped with Yb³⁺, Er³⁺ and Tm³⁺ has been considered as one of the most efficient materials for infrared radiation (at ~1µm) transformation into visible (blue, green and red) luminescence bands with possible applications including – and certainly not limited to – visualization of infrared radiation [16] and biomedical applications [17]. As a result of the increased interest towards this material, many papers related to different synthesis methods of RE doped NaYF₄ and characterization of its spectroscopic properties have been published recently [15, 18-21].

Recent studies have shown that the efficiency of the UC luminescence in NaLaF₄:RE could be comparable to that of NaYF₄:RE [22-24]. However, up to now only few papers have reported some of the basic spectroscopic properties of NaLaF₄ doped with Er³⁺ [22, 25-28].

The aim of the current work is to study the behaviour of the “green” photoluminescence (⁴S_{3/2}→⁴I_{15/2}) in NaLaF₄:Er³⁺ at direct excitation. We will qualitatively explain the luminescence quenching that was experimentally observed as variations in the intensity and decay kinetics of the luminescence in NaLaF₄ at different Er³⁺ concentrations. The obtained results might be useful for future studies of the UC processes in NaLaF₄:Er³⁺ and similar materials.

2. EXPERIMENTAL

In this work, Er³⁺ doped NaLaF₄ with different activator concentrations (0.2, 1, 2, 4, 10 mol%) was synthesized using the wet chemistry method. La₂O₃, Er₂O₃ were dissolved in hydrochloric acid yielding LaCl₃ and ErCl₃. After evaporation of liquid the chlorides were dissolved in deionised water, while in a separate beaker the water solution of NaF was prepared. Addition of this solution to the dissolved chlorides led to the LaF₃ and ErF₃ precipitation. The precipitate was washed several times with deionised water. Later, some amount of NaF was added to the precipitate and the solution was evaporated to dryness. Subsequently, the powder was annealed in He₂/F₂ gas flow at 600°C for 6h to obtain polycrystalline (powder) NaLaF₄:Er³⁺ material. Afterwards the powder was pressed to obtain tablets.

The structure of samples was checked by X-ray diffraction (XRD) analysis (*XPert Pro MPD*, Cu anode, operating at 40kV 30mA). Photoluminescence in the sample was excited by a pulsed solid-state laser NT342/3UV (pulse duration ~ 4ns) from *Ekspla* (wavelength tunable from 210 nm to 2300 nm). The spot size of 20mJ laser beam on the sample was controlled by diaphragm and was in the order of 8 mm². The luminescence decay kinetics was measured by an Andor SR-303i-B monochromator/spectrometer coupled to a photomultiplier tube (time resolution better than 10ns) and a Tektronix TDS 684A digital oscilloscope. The same spectrometer coupled to a CCD camera (Andor DU-401-BV) was used for studying the luminescence spectra.

Special care was taken at placing the sample tablets in the sample holder to achieve equal measurement conditions for all the samples. All measurements were performed at room temperature.

3. RESULTS AND DISCUSSION

Sample characterization using XRD for NaLaF₄ doped with different amount of Er³⁺ is shown in Fig. 1.

Fig. 1. XRD patterns measured for NaLaF₄:Er³⁺ (0.2 and 10 mol %).

For small Er³⁺ ion concentrations mainly NaLaF₄ diffraction peaks are observed. Some traces of NaF crystalline phase are also visible. When Er³⁺ concentration is increased, the peaks corresponding to NaLaF₄ crystalline phase are shifted to higher angles (Fig. 1, inset), which could be explained by the difference in La³⁺ and Er³⁺ ionic radii. The radius of Er³⁺ (88 pm) is smaller than that of La³⁺ (106 pm), which means that the incorporation of activator ions in NaLaF₄ crystalline lattice would lead to a decrease in the lattice parameter of the latter, and the corresponding positions of XRD peaks would shift to higher degrees [22], which is observed experimentally (see Fig. 1, inset).

The luminescence spectrum for NaLaF₄:Er³⁺ (0.2mol%) at 489nm excitation reveals characteristic Er³⁺ luminescence bands in the green, red and IR spectral regions (Fig. 2), while the green band at about 540nm is dominating.

Fig. 2. Luminescence spectra for NaLaF₄:Er³⁺ (0.2 and 10 mol%) excitation at 489nm. Spectra are normalized to the maximum intensity value.

As the concentration of the activator is increased, the luminescence band positions and shapes do not vary. However, variations of the luminescence intensity are observed for the green ($^4S_{3/2} \rightarrow ^4I_{15/2}$), red ($^4F_{9/2} \rightarrow ^4I_{15/2}$) and IR ($^4I_{11/2} \rightarrow ^4I_{15/2}$) bands. The dependence of the intensities on the Er^{3+} concentration is shown in Fig. 3. In order to show this more clearly, the luminescence band intensities are normalized to 1 for the lowest Er^{3+} concentration.

Fig. 3. Dependence of the intensity for some luminescence bands on Er^{3+} concentration in log-log scale. Dashed line represents luminescence intensity which should be proportional to the activator ion concentration.

It could be seen that the intensity of the red luminescence band is proportional to the activator concentration. Such behaviour is expected in the case of non-interacting activator ions when the increase in the number of activator ions is solely responsible for the luminescence intensity increase (dashed line in Fig. 3) [29]. The dependence of the green luminescence band intensity on the concentration is somewhat different: at lower Er^{3+} concentration the intensity increases but to a lesser degree as compared with the red luminescence band. The luminescence intensity reaches maximum at ~ 2 mol% of Er^{3+} concentration, and at higher Er^{3+} concentrations the luminescence intensity decreases. At the same time, the intensity of the 980 nm IR luminescence band excited at 520nm has a super-linear dependence on the concentration (the intensity increases ~ 160 times while Er^{3+} concentration increases 50 times).

The decrease in the luminescence intensity at higher activator concentrations is usually attributed to the concentration quenching [30] when the rates of non-radiative transitions (migration, cross-relaxation, etc.) between the activator ions increase. The super-linear increase in intensity of the 980 nm luminescence ($^4I_{11/2} \rightarrow ^4I_{15/2}$) at higher activator concentrations could signify an involvement of some energy transfer mechanism responsible for the population of the $^4I_{11/2}$ level. This problem has been addressed in various works (e.g. [31]); in [32] several cross-relaxation (CR) processes in which $^4S_{3/2}$ and $^4I_{11/2}$ levels are involved were proposed.

Fig. 4. Possible cross-relaxation processes in Er^{3+} : solid bold arrows – excitation and luminescence, dashed arrows – energy transfer process, and dotted arrows – non-radiative transition.

Some of possible CR processes ($^4\text{S}_{3/2}; ^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}; ^4\text{I}_{9/2}$) and ($^4\text{S}_{3/2}; ^4\text{I}_{15/2} \rightarrow ^4\text{I}_{9/2}; ^4\text{I}_{13/2}$) shown in Fig. 4 seem to be most probable in our case. In the first case, the energy from $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{13/2}$ transition is transferred to the neighboring Er^{3+} and electron from $^4\text{I}_{15/2}$ (ground state) is excited to $^4\text{I}_{9/2}$. In the second case, the electron from $^4\text{S}_{3/2}$ relaxes to $^4\text{I}_{9/2}$ and the energy is transferred to other Er^{3+} where electron from $^4\text{I}_{15/2}$ is excited to $^4\text{I}_{9/2}$. In both these CR processes the initial state is $^4\text{S}_{3/2}$ and the final states are $^4\text{I}_{13/2}; ^4\text{I}_{9/2}$. After reaching the $^4\text{I}_{9/2}$ energy level, Er^{3+} in nonradiative way relaxes to the $^4\text{I}_{11/2}$ energy level, and the IR luminescence at 980 nm is observed. Obviously, in the mentioned CR processes the intensity of the green luminescence band would decrease due to depopulation of $^4\text{S}_{3/2}$ energy level, while the intensity of the 980 nm band would increase as shown in Fig. 3.

This assumption about CR processes is confirmed by the luminescence decay kinetics: in Fig. 5 the kinetics of red and green luminescence bands measured under direct excitation are shown for NaLaF_4 with different Er^{3+} concentration.

Fig. 5. Decay profiles (log scale) for the $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ (a) and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ (b) optical transition in NaLaF_4 at different Er^{3+} concentrations; excitation at 650nm (a) and 520nm (b).

For the given Er^{3+} concentration range the red luminescence decay kinetics (Fig. 5a) maintains the same profile and has a simple exponential nature. This indicates that there are no energy transfer processes (concentration quenching) which depopulated $^4\text{F}_{9/2}$ energy level under direct excitation.

The situation is somewhat different for the green luminescence decay kinetics shown in Fig. 5b. For smaller Er^{3+} concentration this kinetics has a simple exponent nature. As Er^{3+} concentration is increased, the decay kinetics of green luminescence becomes faster, and its nature is no longer simple exponential.

Fig. 6. Effective lifetime for the red and green luminescence decay kinetics under direct excitation.

Such luminescence decay kinetics is characterized with effective lifetime τ_{eff} [33]:

$$\tau_{eff} = \frac{\int t \cdot I(t) dt}{\int I(t) dt},$$

where $I(t)$ is the luminescence intensity at time moment t . Figure 6 shows comparison of effective lifetime obtained for the green and red luminescence decay kinetics. For the red luminescence band the effective lifetime only slightly varies over the given Er^{3+} concentration range. In the green luminescence band a small decrease in the effective lifetime is observed for the sample with low Er^{3+} concentration (0.2 - 1 mol%). At higher Er^{3+} concentrations a considerable decrease in the effective lifetime is observed. The decrease in the lifetime and the non-exponential nature of the green luminescence decay kinetics correlates well with the intensity change of the green and IR bands (Fig.3) and support the previous assumption about the concentration quenching of green band due to CR processes.

4. CONCLUSIONS

The conclusions drawn from the results of measuring the photoluminescence spectra and luminescence decay kinetics of NaLaF_4 doped with Er ions in different concentration are as follows.

1. The maximum intensity of the green luminescence band is for Er^{3+} concentration of 2 mol%.

2. At higher Er^{3+} concentrations considerable quenching of the green luminescence occurs. This quenching is attributed to a cross-relaxation process which depopulates the $^4\text{S}_{3/2}$ energy level and populates the $^4\text{I}_{11/2}$ energy level.

3. No concentration quenching was observed for the red luminescence.

The obtained results will be useful for further studies of the up-conversion mechanisms in $\text{NaLaF}_4\text{:Er}^{3+}$ and similar materials.

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KONCENTRĀCIJAS IETEKME UZ Er^{3+} LUMINISCENCI NaLaF₄ MATRICĀ

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Kopsavilkums

Darbā pētīta Er^{3+} fotoluminiscences atkarība no Er^{3+} koncentrācijas NaLaF₄ matricā. Pieaugot Er^{3+} koncentrācijai līdz 2mol% luminiscences intensitātes raksturīgajām Er^{3+} joslām zaļā (540nm), sarkanā (660nm) un infrasarkanajā (980 nm) spektra apgabalā pieaug. Pie Er^{3+} koncentrācijas virs 2mol% novērojama izteikta zaļās luminiscences koncentrācijas dzēšana un virslineārs infrasarkanās luminiscences joslas pieaugums, kas saistīts ar kross-relaksācijas procesiem starp aktivatora joniem.

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