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SYNTHESIS AND UP-CONVERSION LUMINESCENCE OF ERBIUM DOPED LANTHANUM CONTAINING FLUORIDE STRUCTURES

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Abstract

Up-conversion (UC) process involves conversion of low-energy light photons into higher-energy light photons. This is being achieved by a “ladder” type stepwise excitation of a luminescent ion through sequential absorption of lower-energy photons followed by the emission of the accumulated energy in a form of luminescence. In this case the luminescence light has shorter wavelength (higher photon energy) than any of the absorbed photon.

In the present work the main focus is set on erbium doped $NaLaF_4$ crystalline material and erbium doped transparent oxyfluoride glass ceramics containing LaF_3 nanocrystallites.

Structure, photoluminescence and UC luminescence of $NaLaF_4:Er^{3+}$ are studied by means of x-ray diffraction (XRD), stationary and time-resolved spectroscopy methods. It will be shown that the increase of Er^{3+} concentration in $NaLaF_4:Er^{3+}$ causes the formation of $Na(LaEr)F_4$ complex compound responsible for the shortening of the lifetime of Er^{3+} UC luminescence. The quenching of the UC luminescence in $NaLaF_4:Er^{3+}$ annealed at different temperatures is due to Er^{3+}-oxygen related defects. Additionally, a novel synthesis route of $NaLaF_4:Er^{3+}$ will be shown allowing to synthesize the material without using hazardous hydrofluoric acid.

Oxyfluoride silicate glass ceramics containing $LaF_3:Er^{3+}$ is synthesized by thermal treatment of the precursor glass and UC properties of the material are studied at room temperature and 50 K. It will be shown that the dominance of either excited-state-absorption (ESA) or energy-transfer (ET) mechanisms of the UC luminescence mechanisms in oxyfluoride glass ceramics containing $LaF_3:Er^{3+}$ nanocrystals is temperature dependent. A dominance criterion of either of the two mechanisms of the UC luminescence in the crystalline phase of the glass ceramics will be provided.

1. Introduction

1.1. Topicality and motivation for the research

UC process involves conversion of low-energy light photons into higher-energy light photons. This is being achieved by a “ladder” type stepwise excitation of a luminescent ion through sequential absorption of lower-energy photons followed by the emission of the accumulated energy in a form of luminescence. In this case the luminescence light has shorter wavelength (higher photon energy) than any of the absorbed photon. This type of luminescence has attracted interest of scientists since it was first recognized and treated by Auzel in 1966 [1]. Possible applications of the UC luminescence involve but are not limited to visualization of infrared radiation [2], reading of x-ray reusable memory plates [3], 3-D display technology [4], white light simulation [5], temperature sensors [6], active medium for UC lasers [7], biological markers [8], optical fiber amplifiers [9], enhancing the efficiency of solar cells [10] and others.

In principle any ion which has several discrete energy levels (transition metals, lanthanides, actinides) might be used in UC processes [11], when incorporated in, for example, a solid state material. RE (RE) ions and particularly Er^{3+} ion is the most recognized and often used for UC purposes. It is for a series of nearly equidistant energy levels of Er^{3+}, which make it perfectly suited for UC excitation and thus desirable as an activator in many different hosts.

Depending on a particular application different classes of the host matrixes must be used. For example, if the material is expected to be used as an active medium for a laser, than it must be of high optical durability and heat resistance, while fine granularity rather than the durability is of great importance if the material is used as a luminescent display. In any case, **materials characterized by high efficiency of the UC luminescence are persistently searched for.**

Low-phonon energy media, which can be doped with RE ions, are attractive hosts for UC purposes, because they enable emissions from RE ion energy levels that would quenched by multi-phonon relaxations in high-phonon energy materials [12]. Shalav et al. [10] has shown that heavy halides of lanthanum (LaI_3, $LaBr_3$, $LaCl_3$) are featured by high efficiency of the UC luminescence. The high efficiency can be explained by the reduced rate of non-radiative transitions in the materials due to small phonon energy of the hosts and also by the possibility of effective doping of the materials due to the affinity of La^{3+} to any other trivalent RE activators. However, extremely high sensitivity of the heavy halides towards moisture diminishes their chances to become widely used in various applications.

Fluorides, belonging to the class of halides, are characterized by much lower hygroscopicity compared to their heavier counterparts still possessing a small phonon energy required for an efficient UC process. These facts make the **RE doped La^{3+} containing fluorides attractive media for UC purposes.**

UC luminescence was studied in many RE doped heavy fluorides (LaF_3 [13], GdF_3 [14], YF_3 [15], BaF_2 [16], CaF_2 [17], $BaYF_5$ [18], SrF_2 [19], PbF_2 [20], $NaGdF_4$ [21] and others). RE doped $NaYF_4$ is one of the most prospective and extensively studied materials among the efficient UC luminophors [11, 22-25]. At room temperature (RT) two types of stable lattice structures are reported for $NaYF_4$: cubic and hexagonal [26, 27]; the efficiency of the UC luminescence in the hexagonal phase is about 10 times higher than that reported for the cubic [22]. The high efficiency of the UC process in the hexagonal $NaYF_4$ is explained partly because of the small effective phonon energy of the medium (~360 cm^{-1} [11]) and partly by the multisite nature of $NaYF_4$ crystalline lattice, meaning that RE ions can occupy various non-equivalent states in the crystalline lattice [28, 29], thus enhancing the efficiency of the UC process.

Compared to $NaYF_4$ UC properties of RE doped $NaLaF_4$ up to now have not been extensively studied. $NaLaF_4$ doped with Er^{3+} and Yb^{3+} was first examined as an UC host in 1972 [26], however **no** further studies of the UC luminescence in RE doped $NaLaF_4$ have followed. The similarity in chemical composition of $NaLaF_4$ and $NaYF_4$ ($Y^{3+} \leftrightarrow La^{3+}$) as well as their isostructure ($NaLaF_4$ has a hexagonal lattice structure [30]) predict **RE doped $NaLaF_4$ to be an efficient UC host.** Moreover, the existence of exclusively hexagonal structure of $NaLaF_4$ suggests easier synthesis routine of the material while the existence of both the cubic and hexagonal crystalline structures of $NaYF_4$ stable at room temperature sometimes makes the synthesis of the purely hexagonal $NaYF_4$ rather problematic [10, 31]. The above mentioned considerations make **the synthesis of RE doped $NaLaF_4$ and the studies of the UC processes in the material important and prospective for future development of new effective UC media.**

RE doped fluorides in powder form are prospective materials to be used as efficient UC luminophors, for example, in luminescent displays. However some applications require synthesis of large size **transparent** media with efficient UC properties. Rather high temperatures and special (oxygen-free) atmosphere conditions required for the synthesis of large size and highly durable bulk fluoride crystals make the production of the materials a challenging task. Additionally, limited fusion-spliceability of the bulk fluorides to conventional telecommunication fibres diminishes chances for the materials to be used in photonics applications.

The synthesis of large size RE doped glasses, for example silicate glasses, is much easier; the synthesis usually occurs at lower temperature and therefore the synthesis procedure is cost-effective and energy-efficient. Finally, the affinity of the silicate glass to the optical fibres opens up the possibility for the material to be used in the field of telecommunication and optical signal processing.

Despite much easier synthesis routine, RE doped silicate glasses suffer from increased probability of non-radiative transitions within luminescent RE ions related to rather high phonon energies of the matrix. As a result the efficiency of the UC luminescence observed in RE doped silicate glasses is usually small.

Transparent oxyfluoride glass ceramics, having RE doped fluoride nanocrystals embedded in a silicate matrix, provides both the high efficiency of the UC process (the efficient UC luminescence occurs in the fluoride nanocrystals) and excellent chemical, mechanical and durability properties of the silicate glass [12].

Conventional synthesis of an oxyfluoride glass ceramics [12] involves annealing of the initially properly composed precursor oxyfluoride glass at certain temperature corresponding to the crystallization of the glass. The heat treatment of the glass triggers the formation of RE doped fluoride nanocrystals.

Different oxyfluoride ceramics systems have been synthesized with PbF_2 [32- 34], CaF_2 [35-38], BaF_2 [39-41] crystallites doped with various RE dopants since the first oxyfluoride glass ceramics was reported [42]. A group of Wang have succeeded in the preparation of an oxyfluoride silicate ceramics, which contains Er^{3+} doped LaF_3 nanocrystals. Various properties of this system related to the synthesis of the material and UC processes have been thoroughly studied at room temperature [43-45]. At present, no results on the studies of the UC luminescence performed at low temperatures in this system have been published. **The detailed studies of the UC luminescence in oxyfluoride glass ceramics at low temperatures might be of great importance to understand the true nature of the UC processes occurring in the material that are otherwise impossible to observe at higher temperatures.**

1.2. Main goals and tasks of the work

The main focus in this work is set on two representatives of the most prospective classes of UC hosts: erbium doped $NaLaF_4$ crystalline material and erbium doped transparent oxyfluoride glass ceramics containing LaF_3 nanocrystallites.

The goal of the present work is **to study the UC luminescence in Er^{3+} doped $NaLaF_4$ crystalline material** and **to study the UC luminescence in Er^{3+} doped oxyfluoride glass ceramics at different temperatures.** To achieve the goal the following tasks were set:

- synthesize Er^{3+} doped $NaLaF_4$,
- develop a novel synthesis method for $NaLaF_4$:Er^{3+},
- study the structure of $NaLaF_4$:Er^{3+} and the influence of the structure on the UC luminescence properties of the material at different Er^{3+} doping levels,
- study oxygen impact on the UC properties of $NaLaF_4$:Er^{3+},
- synthesize Er^{3+} doped oxyfluoride glass and glass ceramics with LaF_3 nanocrystallites,
- study the UC luminescence properties of the oxyfluoride glass and glass ceramics at different temperatures.

1.3. Novelty of this work

Experimental investigations performed in this work allowed to:

- develop a novel synthesis technique of $NaLaF_4$:Er^{3+} material without using a hydrofluoric acid,
- identify the impact of oxygen related defects on the UC luminescence of $NaLaF_4$:Er^{3+},
- establish regularities leading to the dominance of either ESA or ET mechanisms of the UC luminescence in Er^{3+} doped oxyfluoride glass ceramics at different temperatures.

1.4. Author contribution

Synthesis of all the samples mentioned in this work, measurements of UC and photoluminescence spectra, excitation spectra and luminescence kinetics, differential thermal analysis, x-ray diffraction patterns as well as the analysis of the obtained results have been performed solely by the author.

Raman spectrum of $NaLaF_4$ material was measured by *Dr. phys*. Georgijs Čikvaidze, infrared absorption spectra of $NaLaF_4$ materials were measured by *Dr. habil. phys.* Larisa Grigorjeva.

2. Physical background

2.1. Synthesis and up-conversion luminescence in rare-earth doped NaLaF$_4$

The first report on NaLaF$_4$ doped with Er^{3+} and Yb^{3+} has appeared in 1972 [26]. Various works related to NaF-LaF$_3$ phase diagram [46-48], optical phonon modes in Raman polarized spectra of the bulk NaLaF$_4$ [30] and thermostimulated luminescence of different RE ions in polycrystalline NaLaF$_4$ [49] are virtually the only information known about the material.

From x-ray diffraction measurements the lattice structure for most of Na(RE)F$_4$ is proposed to be hexagonal [48, 50]. Thoroughly the structure of NaLaF$_4$ was studied by the polarized Raman spectra measurements [30]. In this work it is claimed that the $C_{3h}(P\overline{6})$ *gagarinite* structure is the correct one for NaLaF$_4$ crystal. The authors describe NaLaF$_4$ as Na$_{1.5}$La$_{1.5}$V$_{Na}$F$_6$, where V$_{Na}$ represents vacant Na sites (**Fig. 2.1**).

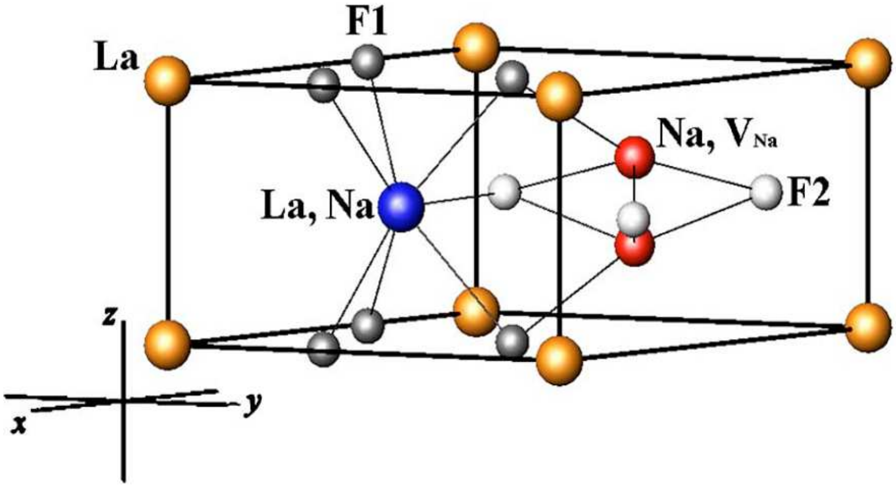

Fig. 2.1: The structure of NaLaF$_4$ [30].

The studies on RE doped NaYF$_4$, which has the same hexagonal structure as NaLaF$_4$, revealed that RE activators may occupy two or three non-equivalent sites in the crystalline structure, substituting for Y^{3+} and Na^{+}. The isostructure of NaLaF$_4$ to NaYF$_4$ supposes that the RE activators might substitute for La^{3+} and Na^{+}.

The conventional Czochralski technique has been reported for the synthesis of bulk undoped $NaLaF_4$ single crystals. $NaLaF_4$ has an incongruent melt point which means that $NaLaF_4$ can be grown directly only from non-stoichiometric melt, containing excess of NaF [30]. Due to nonstoichiometric melt, only small single crystals sized as few cm^3 can be grown at very low pulling speeds (0.1 mm/h).

Two other synthesis methods of polycrystalline RE doped $NaLaF_4$ material have been reported [26, 49].

In [26] it was shown that the powder samples can be synthesized by firing the mixture of Na_2SiF_6 and $La_{1-x}RE_xF_3$. The latter was precipitated by hydrofluoric acid HF from an aqueous nitrate or chloride solution of the proper RE composition. During the synthesis at around $600^{O}C$ temperature Na_2SiF_6 decomposes to produce NaF and SiF_4 gas. The reaction between NaF and $La_{1-x}RE_xF_3$ yields $NaLa_{1-x}F_4:RE_x$. UC luminescence in Yb^{3+}, Er^{3+} doped $NaLaF_4$ synthesized by this method is mentioned in the same work [26], however no further studies of the UC properties of RE doped $NaLaF_4$ have followed.

In [49] it was shown that RE doped $NaLaF_4$ can be prepared from La oxide and other RE oxides, considered to be used as dopants in the final material, Na_2CO_3 and aqueous 47% HBr and 40% HF solutions of acids. The mixture of the respective RE oxides is dissolved in HBr and the fluorides REF_3 are precipitated with HF. The liquid is evaporated and HF is added again. The appropriate amount of Na_2CO_3 is dissolved in water and slowly added to the mixture. The product is dried, and the addition of HF and drying are repeated. Then the solid is transferred into a glassy carbon boat and heated to 550 °C in a HF/Ar gas stream for 20 h. In this step, the reaction toward hexagonal $NaLa_{1-x}F_4:RE_x$ takes place. The powder is ground up in mortar and heated to 590 °C in an Ar gas stream for another 20 h. Finally, the product is washed with water and then dried at 100 °C. The final product – $NaLaF_4$ doped with various RE ions – was thoroughly studied by Krumpel et al. [49] to obtain the energetic positions of RE dopant levels in the band gap of $NaLaF_4$ but no additional information on UC properties of the material have followed.

In the both synthesis methods [26, 49] highly poisonous hydrofluoric acid HF is used. The high corrosivity of the acid towards many materials including glass makes the synthesis of the $NaLaF_4$ rather complicated.

Both lack of the detailed information on UC luminescence in RE doped $NaLaF_4$ and its complicated synthesis led to **the studies of the UC processes in Er^{3+} doped $NaLaF_4$ and elaboration of new synthesis technique of Er^{3+} doped $NaLaF_4$ presented in this work.**

2.2. *Synthesis and up-conversion luminescence in rare-earth doped oxyfluoride glass ceramics*

Transparent low-phonon energy hosts are desirable media for UC applications. Oxyfluoride glass ceramics, having RE doped fluoride nanocrystals embedded in a silicate matrix, provides both the high efficiency of the UC process (the efficient UC luminescence occurs in the fluoride nanocrystals) and excellent chemical, mechanical and durability properties of the silicate glass [12]. Comparison of three main types of RE doped hosts is given in **Table 2.1**.

After the first synthesis of the oxyfluoride glass ceramics by Wang and Ohwaki in 1993 [42] different oxyfluoride ceramics systems have been synthesized with PbF_2 [32], CaF_2 [36], BaF_2 [39], $BaYF_5$ [51], $NaYF_4$ [52] crystallites doped with various RE dopants. In 1998, Dejneka [12] reported that LaF_3 is one of the most suitable fluoride hosts for RE ions in oxyfluoride glass ceramics because it has a great solid solubility of RE ions and is characterized by low phonon energy.

Table 2.1: Physicochemical properties of different hosts prospective in UC applications.

Crystalline phase *(Heavy fluorides)*	Oxide glass *(SiO_2 or GeO_2 base)*	Oxyfluoride glass ceramics *(SiO_2 with LaF_3)*
Complex synthesis	Easy synthesis	Easy synthesis
Costly	Cheap	Cheap
Hard to obtain large sized materials of good optical grade	Easy to obtain large sized materials of good optical grade	Easy to obtain large sized materials of good optical grade
NOT fusion-spliceable to conventional optical fiber	Fusion-spliceable to conventional optical fiber	Fusion-spliceable to conventional optical fiber
High efficiency of UC process	Low efficiency of UC process	High efficiency of UC process

A group of Wang have succeeded in the preparation of SiO_2 based glass ceramics with Er^{3+} doped LaF_3 nanocrystals. Various properties of this system related to the synthesis and UC processes have been thoroughly studied [43-45]. According to their research first of all an oxyfluoride glass with the composition 41.2 SiO_2 – 29.4 Al_2O_3 – 17.6 Na_2CO_3 – 11.8 LaF_3 – 1.0 ErF_3 has to be melted. The melting occurs in a covered Pt crucible at 1350^OC. Afterwards the precursor glass is thermally treated at a glass crystallization temperature to yield transparent glass ceramics. The structural composition (XRD and transmission electron microscopy measurements) of the glass ceramics revealed that the thermal treatment of the glass triggers the formation of LaF_3 nanocrystallites.

During the thermal treatment Er^{3+} ions initially present in the glass phase partly incorporate into the LaF_3 nanocrystallites greatly improving the efficiency of the UC luminescence. It was argued that considerably lower phonon energy of LaF_3 crystalline phase (~350 cm^{-1} [12]) compared to the precursor silicate glass (~1100 cm^{-1} [12]) is responsible for the boost of the efficiency of the UC luminescence observed in the glass ceramics.

Considerably less attention has been paid to the studies of the time-resolved UC luminescence in oxyfluoride glass ceramics containing LaF_3:Er^{3+} and no information on the UC luminescence and its temporal characteristics measured at low temperatures for this system could be found.

A considerable dearth of the information on UC processes in Er^{3+} doped oxyfluoride glass ceramics at low temperature led to **the studies of the UC processes at low temperatures in Er^{3+} doped oxyfluoride glass ceramics with LaF_3 nanocrystallites presented in this work.**

3. Experimental methods

3.1. *Synthesis*

For the synthesis of the samples in air atmosphere a temperature controlled furnace Carbolite HTF 18/8 was used. The heating elements of the oven are $MoSi_2$, allowing to achieve temperature as high as 1800^{O}C.

The annealing of $NaLaF_4$ in fluorine flow was performed in a special apparatus made of nickel, which withstands fluorine atmosphere at elevated temperature. For the fluorination a mixture of 10% F_2 90% He was used.

3.2. *Differential thermal analysis*

In the present work the differential thermal analysis (DTA) was used to identify the crystallization temperature of the oxyfluoride silicate glass related to the appearance of LaF_3 crystalline phase in the glass matrix. The DTA measurements were performed using Shimadzu DTG-60 apparatus.

3.3. *Structure investigations*

For the XRD measurements x-ray diffractometer X'Pert Pro MPD was used. The diffractometer was equipped with an x-ray tube (anode material – Cu, wavelength 0.154056 nm) operating at 40 kV and 30 mA. The crystallite size determination was performed using the software provided with the diffractometer.

3.4. *Infrared absorption and Raman spectra measurements*

Infrared absorption spectra were measured using FTIR spectrometer Bruker Equinox 55 (resolution <0.5 cm^{-1}). Raman measurements were performed using SPEX-RAMALOG Laser Raman Spectrometer system (resolution <0.15 cm^{-1}) equipped with laser MLL-671 nm–300mW from CNI laser.

3.5. *Luminescence measurements*

UC and photoluminescence of all the samples were excited either in CW regime by a temperature-power controlled IR laser diode system λ_{em}=975 nm (power up to 1W)

(Thorlabs) or in pulsed regime by a wavelength tunable (optical parametric oscillator) pulsed laser from Ekspla NT342/3UV. Laser pulse duration was 5 ns. The spectra have not been corrected for the spectral sensitivity of the equipment. For low temperature measurements closed cycle He cryostat ARSCRYO was used. Temperature of the sample was controlled by a temperature controller LakeShore 325 with a precision ±1 K.

For the measurements of the luminescence spectra a CCD camera Andor DU-401-BV attached to Andor SR-303i-B monochromator/spectrometer was used. For power dependence measurements of the UC luminescence neutral density filters were used in the excitation channel to attenuate the excitation power while the intensity of the UC luminescence was detected by CCD camera. The excitation power was monitored by Thorlabs PDA55 amplified Si photodetector.

For the excitation spectra measurements the same tunable laser, monochromator/spectrometer and CCD camera were used. The measurement technique involved the measurement of the luminescence spectra at different excitation wavelengths and processing of the measured data by author’s developed software (LabVIEW) to yield the excitation spectra measured for a fixed luminescence position. The spectra have not been corrected for the spectral sensitivity of the equipment.

Luminescence kinetics was measured by a photomultiplier tube ФЭУ-115 attached to Andor SR-303i-B monochromator/spectrometer and detected by Tektronix TDS 684A oscilloscope. The overall temporal resolution of the system was less than 10 ns.

4. Summary

4.1. Erbium doped $NaLaF_4$

Synthesis

1) Erbium doped polycrystalline $NaLaF_4$ material was synthesized from 65NaF – $35LaF_3$ – $xErF_3$ (x = 0.05, 0.1, 0.5, 1, 2, 4, 5, 7 and 10 mol %), 65NaF – $10LaF_3$ – $25ErF_3$ melt (in mol %).
2) Novel synthesis procedure of $NaLaF_4:Er^{3+}$ without using hydrofluoric acid has been developed. $NaLaF_4:Er^{3+}$ (Er^{3+} concentration 0.5 mol%) was prepared from La_2O_3, Er_2O_3, NaF and hydrochloric acid. For the synthesis of the material the RE oxides were dissolved in hydrochloric acid yielding $LaCl_3$ and $ErCl_3$:

   $La_2O_3 + 6HCl \rightarrow 2LaCl_3 + 3H_2O$

   $Er_2O_3 + 6HCl \rightarrow 2ErCl_3 + 3H_2O$

   After evaporation of the liquid the chlorides were dissolved in deionized water while in separate beaker a water solution of sodium fluoride was prepared. The addition of NaF solution to the dissolved chlorides led to the precipitation of LaF_3 and ErF_3:

   $LaCl_3 + 3NaF \rightarrow LaF_3 + 3NaCl$

   $ErCl_3 + 3NaF \rightarrow ErF_3 + 3NaCl$

   The precipitate was washed several times with deionized water to remove NaCl species. Later, additional amount of NaF was added to the precipitate and the solution was evaporated to dryness. The following synthesis procedure involved heat treatment of the synthesized powders at different temperatures from 400 °C to 650 °C for 15h in air. The structure analysis of the $NaLaF_4:Er^{3+}$ materials has shown that optimal synthesis temperature of the material is 650 °C.

Structure and UC properties

3) The XRD patterns measured for $NaLaF_4$ material at different doping levels of ErF_3 showed considerable lattice distortion of $NaLaF_4$ and the formation of a complex $Na(LaEr)F_4$ compound when Er^{3+} content was increased (**Fig 4.1)**.

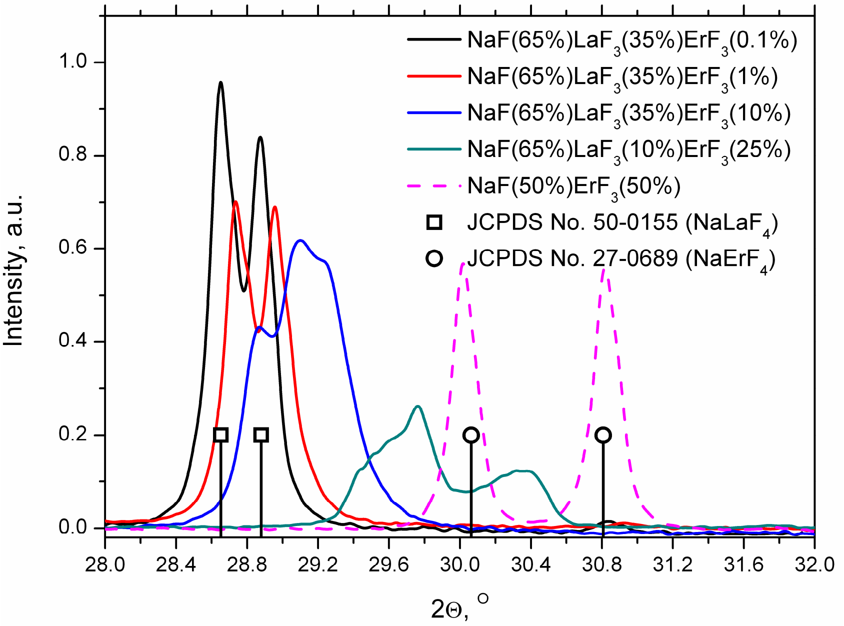

Fig. 4.1: XRD pattern of $NaLaF_4:Er^{3+}$ material for samples with different LaF_3 and ErF_3 contents.

4) The effective phonon energy of $NaLaF_4$ derived from Raman measurements for the undoped material was estimated E_{ph}~290 cm^{-1} (**Fig. 4.2**).
5) The UC luminescence spectra measured for $NaLaF_4:Er^{3+}$ under excitation at 975 nm revealed the characteristic luminescence bands in the violet ($^2H_{9/2} \rightarrow {}^4I_{15/2}$), green ($^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$) and red ($^4F_{9/2} \rightarrow {}^4I_{15/2}$) spectral regions (**Fig. 4.3**).

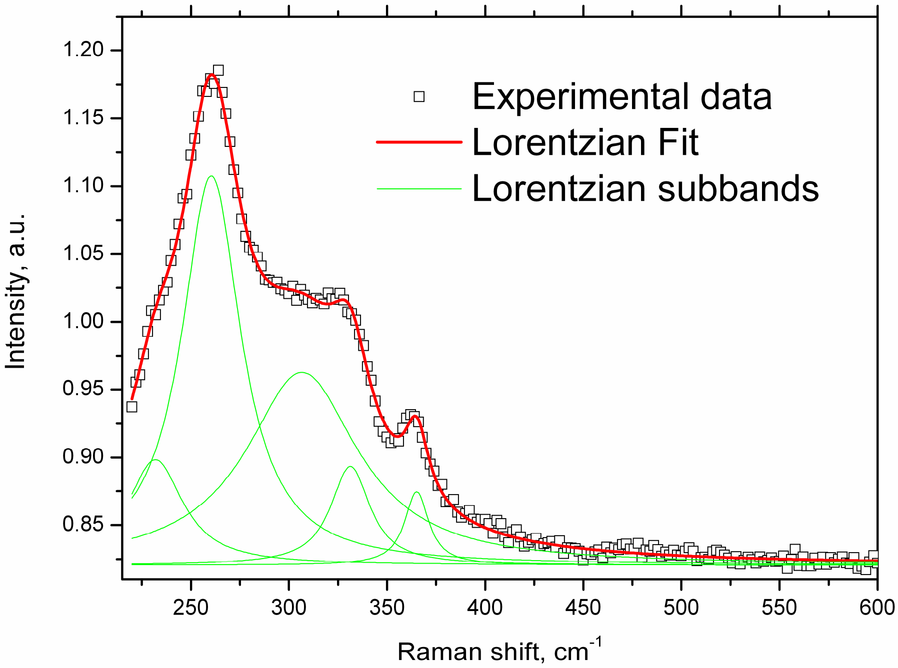

Fig. 4.2: Raman spectrum of undoped $NaLaF_4$ sample.

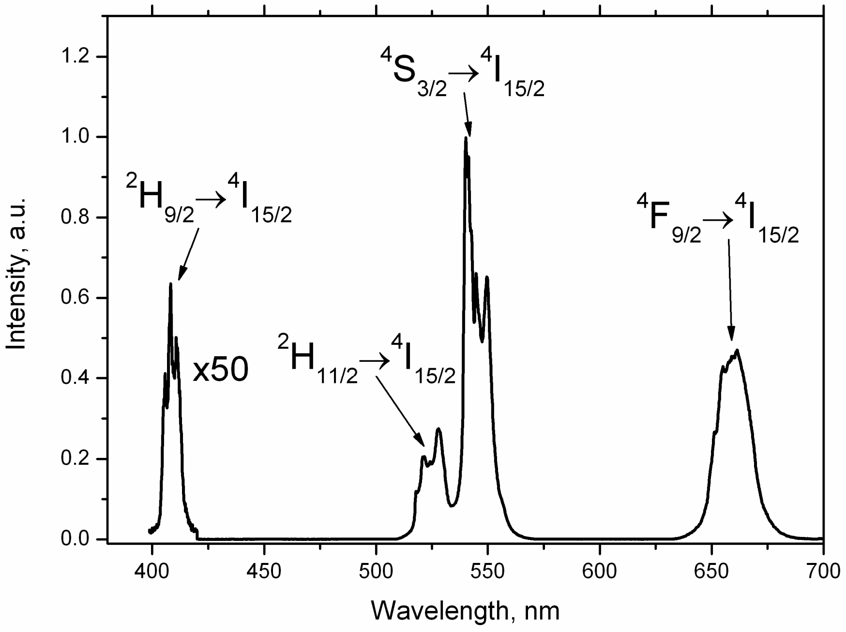

Fig. 4.3: Stationary UC luminescence spectrum of 2% Er^{3+} doped $NaLaF_4$ excited at 975 nm measured at room temperature.

6) The luminescence decay curves originating from $^4S_{3/2}$ and $^4F_{9/2}$ levels of Er^{3+} ions in $NaLaF_4$ crystalline structure were measured and the lifetimes of the corresponding levels were determined. It was found that both the “green” and “red” luminescence decay kinetics are composed of two components: fast and slow (**Table 4.1**). The fast component is attributable to strongly distorted $Na(LaEr)F_4$ phase, while the slow component is related to $NaLaF_4:Er^{3+}$.

Table 4.1: Lifetimes (in μs) of the main optical transitions in Er^{3+} doped $NaLaF_4$ samples at different doping levels and $NaErF_4$, measured under direct excitation at room temperature.

		0.05 %	0.1 %	0.5 %	1 %	2 %	4 %	10 %	$NaErF_4$
$^4S_{3/2}\downarrow{}^4I_{15/2}$	fast	50	40	35	30	25	20	7	0.275
	slow	510	490	470	410	350	240	80	
$^4F_{9/2}\downarrow{}^4I_{15/2}$	fast	110	100	90	85	70	60	30	5
	slow	530	520	510	480	450	390	230	

7) It was found that pure ET mechanisms are responsible for the “red” and “violet” UC luminescence, while a combination of ESA and ET mechanisms is involved in the creation of the “green” UC luminescence (**Fig. 4.4**).

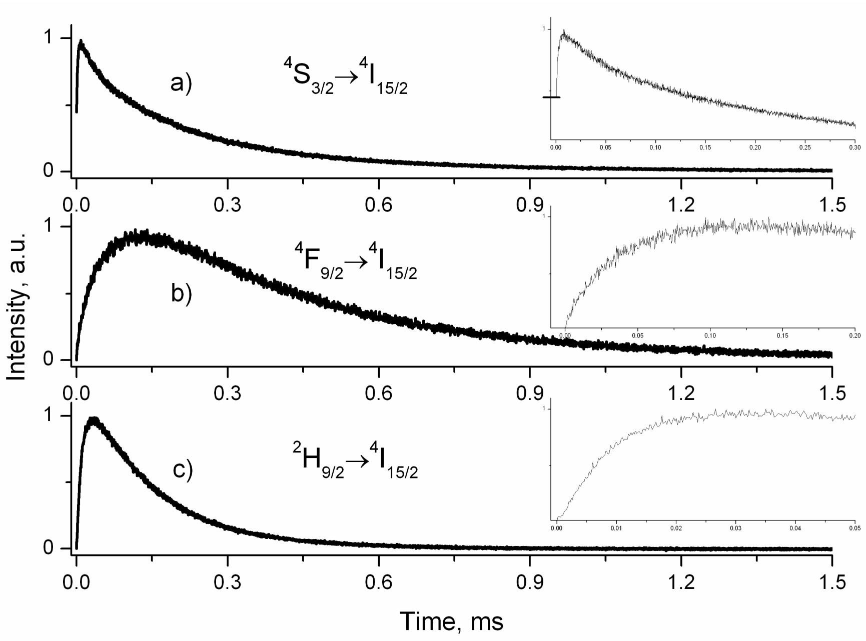

Fig. 4.4: Decay profiles for (a) $^4S_{3/2}$ → $^4I_{15/2}$, (b) $^4F_{9/2}$ → $^4I_{15/2}$, (c) $^2H_{9/2}$ → $^4I_{15/2}$ optical transitions in $NaLaF_4$:Er^{3+}(0.5mol%) excited at 980 nm measured at room temperature.

8) Mechanisms involved in the UC processes of Er^{3+} in $NaLaF_4$ were determined (**Fig. 4.5**). It was found that the appearance of the green luminescence band at 540 nm is a result of an ESA_1 process i.e. sequential two photon absorption process: $^4I_{15/2}$ + hν → $^4I_{11/2}$ +hν → $^4F_{7/2}$. Afterwards the relaxation to $^2H_{11/2}$ and $^4S_{3/2}$ populates the emitting levels for the green luminescence. Another route to populate the $^4S_{3/2}$ level is by ET_1 process: ($^4I_{11/2}$, $^4I_{11/2}$) → ($^4I_{15/2}$, $^4F_{7/2}$) (ET_1).

   The appearance of the red luminescence at 660 nm might be caused by a cross-relaxation (CR) and subsequent ET_2 process, for example, ($^4S_{3/2}$, $^4I_{15/2}$) → ($^4I_{9/2}$, $^4I_{13/2}$) (CR) and later ($^4I_{13/2}$, $^4I_{11/2}$) → ($^4I_{15/2}$, $^4F_{9/2}$) (ET_2).

   The appearance of the violet band could be explained by a CR and subsequent ET_3 process ($^4S_{3/2}$, $^4I_{15/2}$) → ($^4I_{9/2}$, $^4I_{13/2}$) (CR) and later ($^4S_{3/2}$, $^4I_{13/2}$) → ($^2H_{9/2}$, $^4I_{15/2}$) (ET_3).

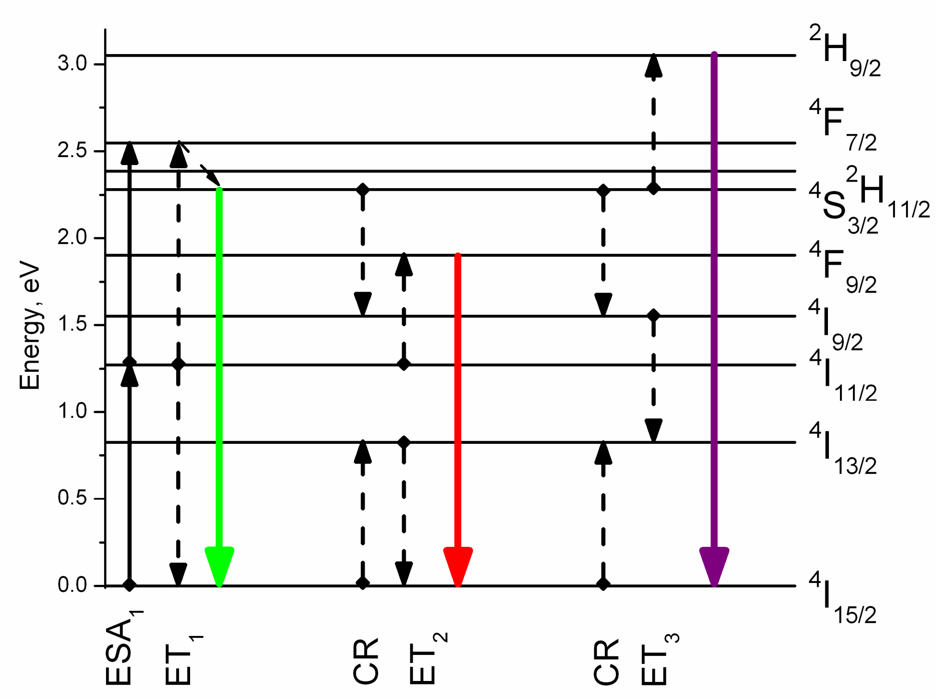

Fig. 4.5 Schematic energy level diagram and the main radiative transitions in Er^{3+} ion. Full and dashed arrows are radiative and non-radiative transitions, respectively.

9) For the samples synthesized at the temperatures up to 500 °C by the novel method the UC luminescence is quenched mostly by OH^- groups.
10) The concentration of OH^- groups present in the material at the first stage of the synthesis is decreasing as the annealing temperature grows (**Fig. 4.6**).
11) The increase of the synthesis temperature above 500 °C promotes the creation of other Er^{3+}-oxygen defects in the material, responsible for the quenching of the UC luminescence.
12) The post-treatment of $NaLaF_4$:Er^{3+} in a fluorine atmosphere at 500 °C helps to remove the oxygen impurities from the material thus increasing the efficiency of the UC luminescence (**Fig. 4.7**).

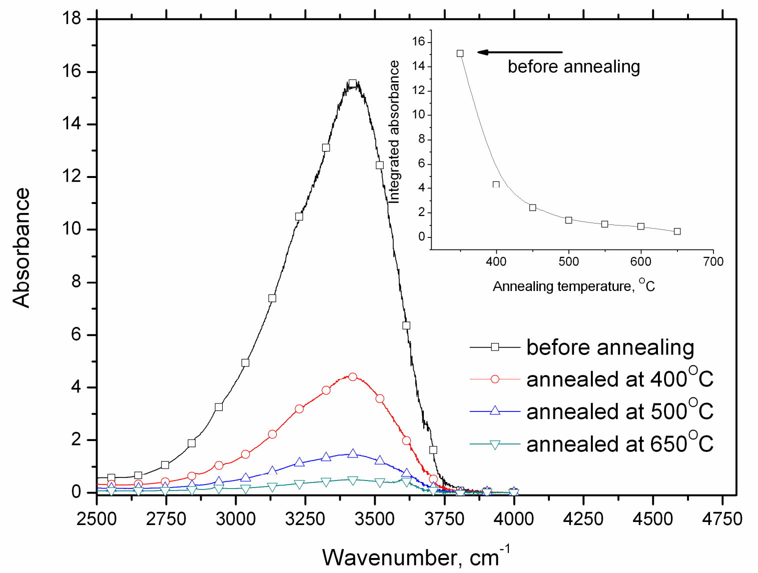

Fig. 4.6: Absorption spectra measured for the samples annealed at different temperatures. The band at 3400 cm^{-1} is described as OH$^-$ absorption. Inset: integrated absorbance for the samples annealed at different temperatures.

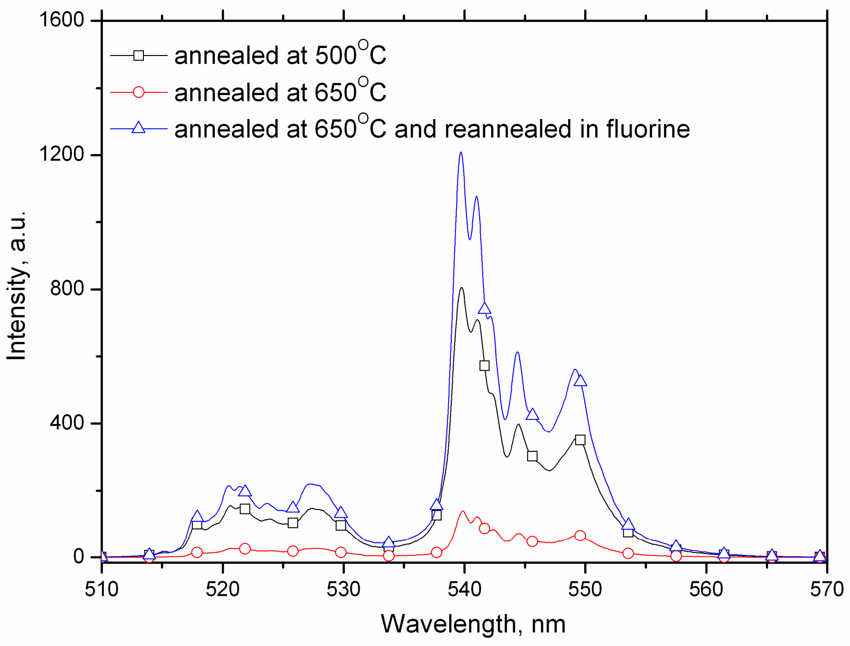

Fig. 4.7: "Green" UC luminescence excited at 975 nm measured for the sample annealed at different temperatures.

4.2. Erbium doped oxyfluoride glass ceramics

Synthesis

1) Oxyfluoride silicate glass and transparent glass ceramics containing LaF_3 crystallites has been synthesized. For the synthesis of the glass the following chemical composition was used $40SiO_2–25Al_2O_3–19Na_2CO_3–3NaF–9LaF_3–0.5ErF_3$. The batch of the raw materials (~10g) was melted in a covered corundum crucible for 1 h at 1450 °C in air atmosphere followed by the casting of the liquid between two preheated stainless steel plates. The glass ceramics was prepared by heating of the precursor glass at its crystallization temperature obtained from DTA measurements (**Fig. 4.8**)

Structure and UC properties

2) During the synthesis the activator ions partially incorporate in the crystalline phase and $LaF_3:Er^{3+}$ is formed.
3) The UC luminescence spectra, the excitation spectra and the decay kinetics of the "green" luminescence band of Er^{3+} were measured for the GC sample at 50 K and RT (**Fig. 4.9, 4.10, 4.11, 4.12**).

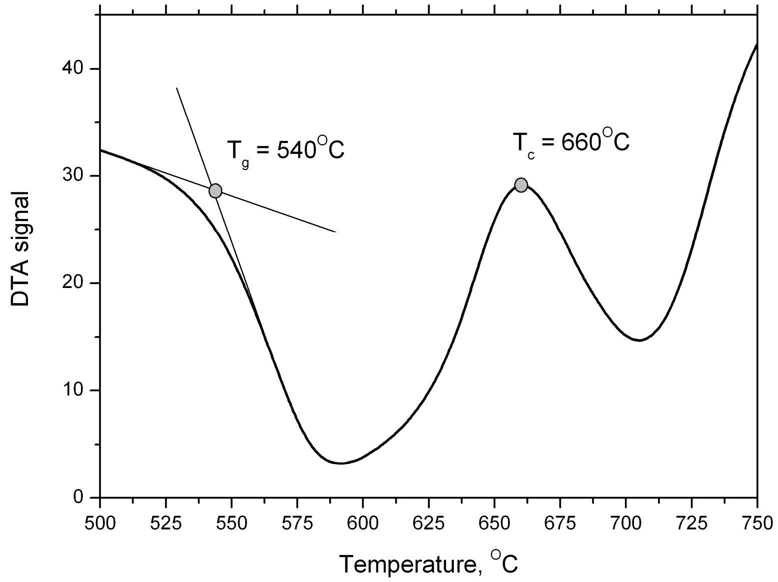

Fig. 4.8: DTA curve of the precursor glass. T_g – glass transition temperature, T_c – crystallization temperature.

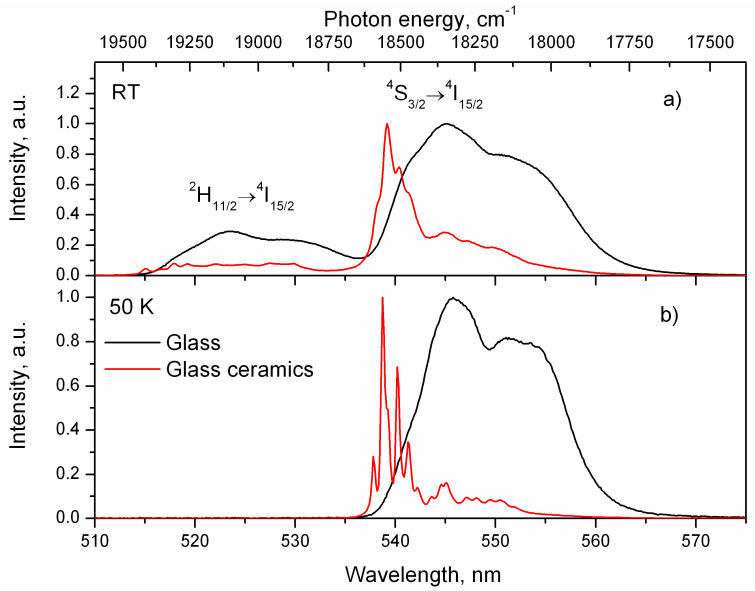

Fig. 4.9: UC luminescence spectra of the G (black line) and GC (red line) samples measured at a) RT and b) 50 K under 970 nm excitation.

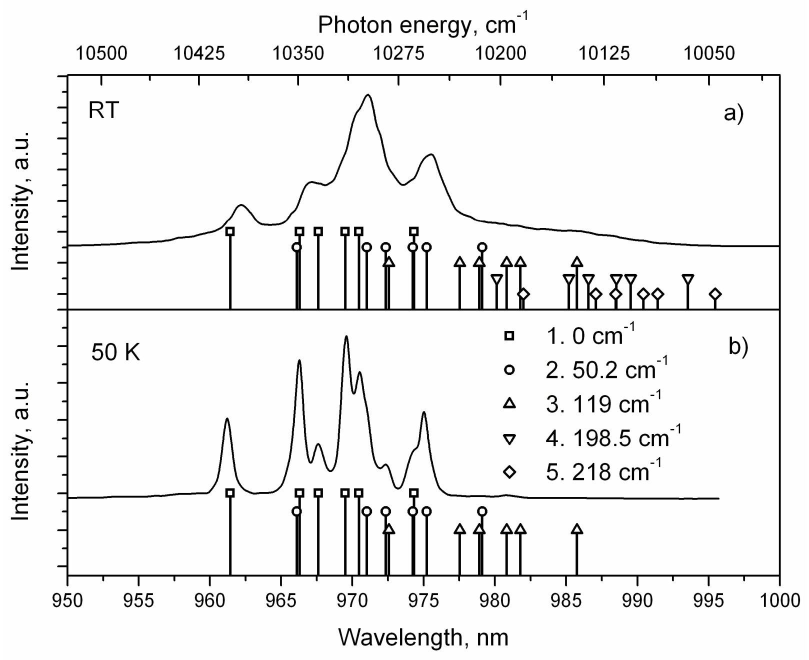

Fig. 4.10: Excitation spectra of the UC luminescence at 539 nm measured for the GC sample at a) RT and b) 50 K. Vertical bars under the plots correspond to the transitions from different Stark sublevels of the ground state $^4I_{15/2}$ (energetic positions of the sublevels are given in the legend) to the Stark sublevels of the $^4I_{11/2}$ [53].

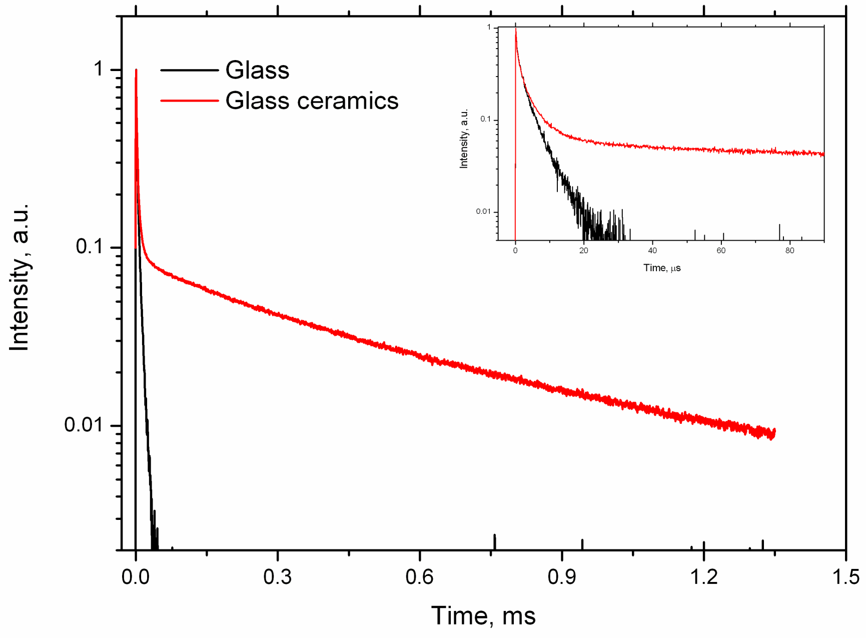

Fig. 4.11. Decay kinetics of the UC luminescence for the G (black line) and GC (red line) samples under 970 nm excitation measured at RT. Inset: magnified initial part of the decay kinetics. Luminescence position set to 539 nm.

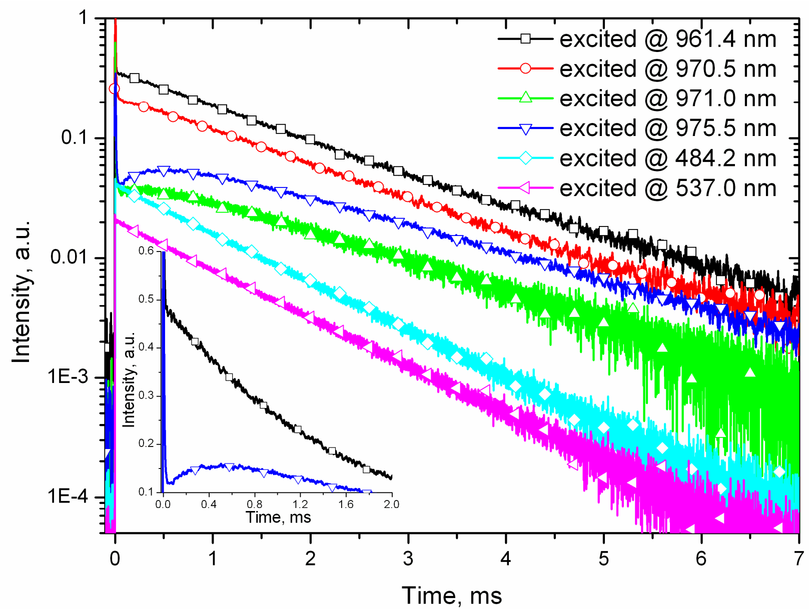

Fig. 4.12: Decay kinetics of the UC and traditional luminescence for the GC sample under various excitation wavelengths measured at 50 K. Inset: magnified initial part of the decay kinetics. Luminescence position set to 539 nm.

4) From the analysis of the kinetics of the UC luminescence it is concluded that at RT the dominant mechanism of the UC luminescence in the GC sample is ESA (**Fig. 4.11**), while at 50 K – the ET mechanism prevails (**Fig. 4.12**).
5) The ESA mechanism of the UC luminescence is still active at 50 K for the excitation energies, at which the energetic off-resonance between the GSA and ESA is less than 6 cm^{-1} (**Fig. 4.13**)

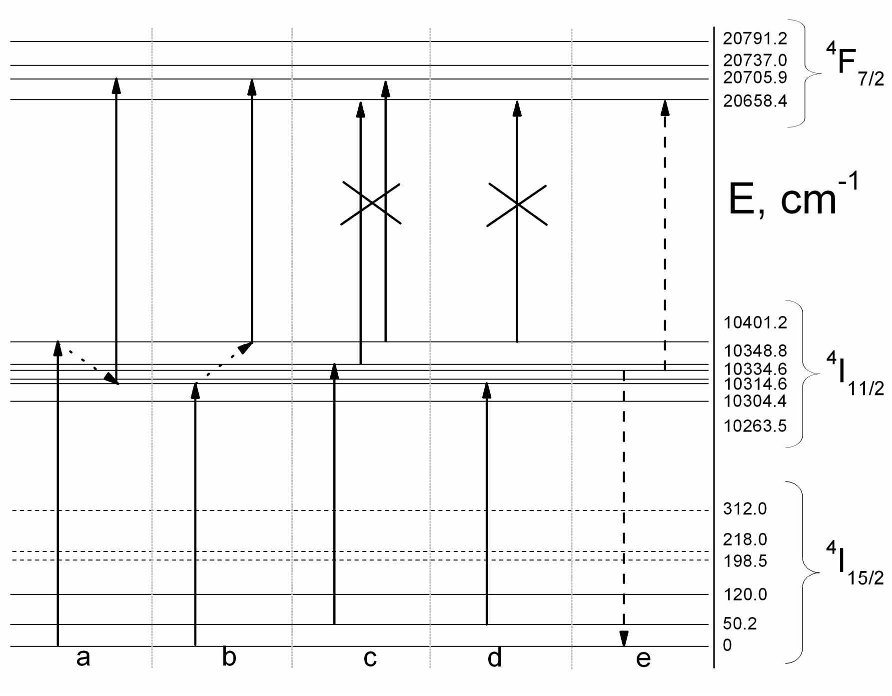

Fig. 4.13: Energy level scheme of Er^{3+} ion in LaF$_3$ [53] and possible mechanisms of the UC luminescence in the crystalline phase of the GC sample at 50 K. (a) and (b) – ESA is possible, (c) and (d) – ESA is impossible, (e) – ETU.

5. Thesis

- Novel synthesis method of $NaLaF_4:Er^{3+}$ has been developed allowing to synthesize the material without using a hydrofluoric acid.

- Luminescence properties of $NaLaF_4:Er^{3+}$ depend on the synthesis conditions:
    - The increase of Er^{3+} concentration in $NaLaF_4:Er^{3+}$ causes the formation of $Na(LaEr)F_4$ complex compound responsible for the shortening of the lifetime of Er^{3+} luminescence.
    - The quenching of the up-conversion luminescence in $NaLaF_4:Er^{3+}$ depends on the annealing temperature: below 500 °C the up-conversion luminescence is quenched by OH^- related defects, but above 500 °C – the quenching is due to other oxygen related defects.
    - The post-treatment of $NaLaF_4:Er^{3+}$ in a fluorine atmosphere at 500 °C reduces the content of oxygen impurities in the material and significantly diminishes the quenching effect of the up-conversion luminescence.

- The dominance of either excited-state-absorption or energy-transfer mechanisms of the up-conversion luminescence in oxyfluoride glass ceramics containing $LaF_3:Er^{3+}$ nanocrystals is temperature dependent.

- A criterion, which entails the dominance of energy-transfer over excited-state-absorption mechanism of the up-conversion luminescence in the crystalline phase of the glass ceramics at 50 K, is the energy mismatch of more than 6 cm^{-1} between ground-state-absorption and excited-state-absorption.

6. Outlook

In this work two prospective materials for UC purposes, namely $NaLaF_4:Er^{3+}$ and oxyfluoride glass ceramics containing $LaF_3:Er^{3+}$ were investigated.

It was concluded that the increase of Er^{3+} concentration in $NaLaF_4:Er^{3+}$ causes the formation of $Na(LaEr)F_4$ complex compound responsible for the shortening of the lifetime of Er^{3+} UC luminescence, while the quenching of the UC luminescence in $NaLaF_4:Er^{3+}$ synthesized at different temperatures is explained by Er^{3+}-oxygen related defects.

From application point of view the existence of oxygen defects in fluorides is undesirable because they act as “killers” of the UC luminescence due to their involvement in the enhanced non-radiative de-excitation of RE ions leading to the decrease of the UC efficiency. From scientific point of view the existence of such defects in $NaLaF_4:RE^{3+}$ raises a series of challenging questions to be answered: what is the structure of these defects? What is the mechanism of their formation? What is the mechanism of the energy transfer from RE^{3+} to the oxygen defect? Once these questions are answered, possible applications like, for example, fluorine sensors may follow.

Another material investigated in this work is the transparent oxyfluoride silicate glass ceramics containing $LaF_3:Er^{3+}$. It was synthesized by thermal treatment of the precursor glass and UC properties of the material were studied at RT and 50 K. It was shown that the dominance of either ESA or ET mechanisms of the UC luminescence in oxyfluoride glass ceramics containing $LaF_3:Er^{3+}$ nanocrystals is temperature dependent. A dominance criterion of either of the two mechanisms of the UC luminescence in the crystalline phase of the glass ceramics was provided, however, some general unanswered questions related to the glass ceramics still remain.

Although the glass ceramics provides an interesting model, where two different phases (glass and crystalline) coexist, the studies of the UC luminescence in such systems reported in the literature are strictly targeted on either of the two phases: the glass or the crystallites. But is there any energy transfer between the two phases and if it can be observed, what are the mechanisms of such energy transfer?

On the other hand, the efficiency of the UC luminescence in oxyfluoride glass ceramics is defined by the efficiency of the UC process in the fluoride component of the ceramics. At the present, the most efficient fluoride host for the UC purposes is considered to be $NaYF_4$ mainly due to its low phonon energy. Soon after the excellent UC properties of crystalline RE^{3+} doped $NaYF_4$ were reported, a number of works, in which oxyfluoride glass ceramics with $NaYF_4$ nanocrystallites, appeared.

In the present work the Raman spectrum measured for $NaLaF_4$ showed that the phonon energy of the latter is lower than that reported for $NaYF_4$, suggesting that the efficiency of the UC luminescence in $NaLaF_4:RE^{3+}$ might be comparable or even better than that of $NaYF_4:RE^{3+}$ matrix. This raises another challenging task – to obtain oxyfluoride glass ceramics with $NaLaF_4:RE^{3+}$ nanocrystals.

The raised questions are the subjects of further investigations that will be continued after the defending of the present thesis.

7. References

[1] F. Auzel, *Compteur quantique par transfert d'énergie entre deux ions de terres rares*, Comptes Rendus l'Académie Des Sci. (Paris) **262**, 1016 (1966).

[2] Y. Wang, J. Ohwaki, *High efficiency infrared to visible upconversion of* Er^{3+} *in* $BaCl_2$, Journal of Applied Physics **74**, 2 (1993), p. 1272 – 1278.

[3] J. M. Breteau, J. L. Ayral, F. Micheron, F. Auzel, *Medical x-ray imaging in infrared to visible upconverting materials*, Journal of Applied Physics **67**, 2 (1990), p. 1102 – 110.

[4] E. Downing, L. Hesselink, J. Ralston, R. Macfarlane, *A Three-Color, Solid-State, Three-Dimensional Display*, Science **273**, 5279 (1996), p. 1185 – 1189.

[5] J. E. C. Silva, G. F. de Sa, P. A. Santa-Cruz, *White light simulation by up-conversion in fluoride glass host*, Journal of Alloys and Compounds **344**, 1–2, (2002), p. 260 – 263.

[6] C. Li, B. Dong, S. Li, C. Song, Er^{3+}–Yb^{3+} *co-doped silicate glass for optical temperature sensor*, Chemical Physics Letters **443**, 426 (2007), p. 426 – 429.

[7] L. F. Johnson, H. J. Guggenheim, *Infrared-Pumped Visible Laser*, Applied Physics Letters **19**, 2, (1971**)**, p. 44 – 47.

[8] H. J. M. A. A. Zijlmans, J. Bonnet, J. Burton, K. Kardos, T. Vail, R. S. S. Niedbala, H.J. Tanke, *Detection of Cell and Tissue Surface Antigens Using Up-Converting Phosphors: A New Reporter Technology*, Analytical Biochemistry **267**, 1 (1999) p. 30 – 36.

[9] B.N. Samson, P.A. Tick, N.F. Borrelli, *Efficient neodymium-doped glass-ceramic fiber laser and amplifier*, Optics Letters **26**, 3 (2001), p. 145 – 147.

[10] A. Shalav, B.S. Richards, M.A. Green, *Luminescent layers for enhanced silicon solar cell performance: Up-conversion*, Solar Energy Materials and Solar Cells **91**, 9 (2007), p. 829 – 842.

[11] J.F. Suyver, J. Grimm, M.K. van Veen, D. Biner, K.W. Krämer, H.U. Güdel, *Upconversion spectroscopy and properties of* $NaYF_4$ *doped with* Er^{3+}, Tm^{3+} *and/or* Yb^{3+}, Journal of Luminescence **117**, 1 (2006), p. 1 – 12.

[12] M. Dejneka, *Transparent oxyfluoride glass ceramics*, MRS Bulletin 23, 11 (1998), p. 56 – 62.

[13] Jisen Zhang, W. Qin, D. Zhaoa, Degejihu, J. Zhang, Y. Wang, C. Cao, *Spectral variations and energy transfer processes on both* Er^{3+} *ion concentration and excitation densities in* Yb^{3+}–Er^{3+} *codoped* LaF_3 *materials*, Journal of Luminescence **122-123** (2007), p. 506 – 508.

[14] Rayko Simura, A. Jouini, K. Kamada, A. Yoshikawa, K. Aoki, Y. Guyot, G. Boulon, T. Fukuda, *Growth and characterization of* Pr^{3+}*-doped* $Gd_{1-x}Yb_xF_3$ *fluoride single crystal for visible up-conversion luminescence applications*, Journal of Crystal Growth **291**, 1 (2006), p. 309 – 313.

[15] C. Cao, W. Qin, J. Zhang, Y. Wang, P. Zhu, G. Wang, G. Wei, L. Wang, L. Jin, *Enhanced ultraviolet up-conversion emissions of* Tm^{3+}/Yb^{3+} *codoped* YF_3 *nanocrystals*, Journal of Fluorine Chemistry 129, 3 (2008), p. 204 – 209.

[16] M. Bouffard, J. P. Jouart, M.-F. Joubert, *Red-to-blue up-conversion spectroscopy of* Tm^{3+} *in* SrF_2, CaF_2, BaF_2 *and* CdF_2, Optical Materials **14**, 1 (2000), p. 73 – 79.

[17] C. Cao, W. Qin, J. Zhang, Y. Wang, G. Wang, G. Wei, P. Zhu, L. Wang, L. Jin, *Up-conversion white light of* $Tm^{3+}/Er^{3+}/Yb^{3+}$ *tri-doped* CaF_2 *phosphors*, Optics Communications **281**, 6 (2008), p. 1716 – 1719.

[18] X.P. Chen, Q.Y. Zhang, C.H. Yang, D.D. Chen, C. Zhao, *Comparative investigation on structure and luminescence properties of fluoride phosphors codoped with* Er^{3+}/Yb^{3+}, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy **74**, 2 (2009), p. 441 – 445.

[19] S. A. Pollack, D. B. Chang, *Ion-pair upconversion pumped laser emission in* Er^{3+} *ions in YAG, YLF,* SrF_2*, and* CaF_2 *crystals*, Journal of Applied Physics **64**, 6 (1988), p. 2885 – 2893.

[20] J. Zhang, Z. Duan, D. He, S. Dai, L. Zhang, L. Hu, *Intense blue up-conversion luminescence in* Tm^{3+}/Yb^{3+} *codoped oxyfluoride glass–ceramics containing* β-PbF_2 *nanocrystals*, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy **62**, 4-5 (2005), p. 831 – 834.

[21] J.F. Suyver, A. Aebischer, D. Biner, P. Gerner, J. Grimm, S. Heer, K.W. Krämer, C. Reinhard, H.U. Güdel, *Novel materials doped with trivalent lanthanides and transition metal ions showing near-infrared to visible photon upconversion*, Optical Materials **27**, 6 (2005), p. 1111 – 1130.

[22] K.W. Kramer, D. Biner, G. Frei, H. U. Gudel, M. P. Hehlen, S. R. Luthi, *Hexagonal Sodium Yttrium Fluoride Based Green and Blue Emitting Upconversion Phosphors*, Chemistry of Materials **16**, 7 (2004), p. 1244 – 1251.

[23] J. Shan, Y. Ju, *Controlled synthesis of lanthanide-doped* $NaYF_4$ *upconversion nanocrystals via ligand induced crystal phase transition and silica coating*, Applied Physics Letters **91**, 12 (2007), p. 123103 – 123105.

[24] G. Wang, W. Qin, L. Wang, G. Wei, P. Zhu, R. Kim, *Intense ultraviolet upconversion luminescence from hexagonal* $NaYF_4{:}Yb^{3+}/Tm^{3+}$ *microcrystals*, Optics Express **16**, 16 (2008), p. 11907 – 11914.

[25] S. Heer, K, Kompe, H. U. Gudel, M. Haase, *Highly efficient multicolour upconversion emission in transparent colloids of lanthanide doped* $NaYF_4$ *nanocrystals*, Advanced Materials **16**, 23-24 (2004), p. 2102 – 2105.

[26] T. Kano, H. Yamamato, Y. Otomo, $NaLnF_4{:}Yb^{3+}$, Er^{3+} *(Ln:Y, Gd, La): efficient green-emitting infrared-excited phosphors*, Journal of Electrochemical Society: Solid State Science and Technology **119**, 11 (1972), p. 1561 – 1564.

[27] Z. Wang, F. Tao, L. Yao, W. Cai, X. Li, *Selected synthesis of cubic and hexagonal* $NaYF_4$ *crystals via a complex-assisted hydrothermal route*, Journal of Crystal Growth **290**, 1 (2006), p. 296 – 300.

[28] N. Martin, P. Boutinaud, M. Malinowski, R. Mahiou, J. C. Cousseins, *Optical spectra and analysis of* Pr^{3+} *in* β-$NaYF_4$, Journal of Alloys and Compounds **275-277** (1998), p. 304 – 306.

[29] A. Grzechnik, P. Bouvier, M. Mezouar, M. D. Mathews, A. K. Tyagi, J. Kohler, Hexagonal $Na_{1.5}Y_{1.5}F_6$ at High Pressures, Journal of Solid State Chemistry 165 (2002), p. 159 – 164.

[30] M. M. Lage, F. M. Matinaga, J.-Y. Gesland, R. L. Moreira, *Optical phonon modes and crystal structure of* $NaLaF_4$ *single crystals*, Journal of applied Physics 99 (2006), p. 053510 – 053517.

[31] G. S. Yi, G. M. Chow, *Synthesis of hexagonal-phase* $NaYF_4{:}Yb,Er$ *and* $NaYF_4{:}Yb,Tm$ *nanocrystals with efficient up-conversion fluorescence*, Advanced Functional Materials **16** (2006), p. 2324 – 2329.

[32] S.F. León-Luis, J. Abreu-Afonso, J. Pena-Martinez, J. Mendez-Ramos, A.C. Yanes, J. del-Castillo, V.D. Rodriguez, *Up-conversion and colour tuneability in*

Yb^{3+}–Er^{3+}–Tm^{3+} co-doped transparent nano-glass-ceramics, Journal of Alloys and Compounds **479**, 1-2 (2009), p. 557 – 560.

[33] F. C. Guinhos, P. C. Nobrega, P. A. Santa-Cruz, *Compositional dependence of up-conversion process in Tm^{3+}–Yb^{3+} codoped oxyfluoride glasses and glass-ceramics*, Journal of Alloys and Compounds **323-324** (2001), p. 358 – 361.

[34] J. Mendez-Ramos, V.K. Tikhomirov, b, V.D. Rodriguez, D. Furniss, *Infrared tuneable up-conversion phosphor based on Er^{3+}-doped nano-glass–ceramics*, Journal of Alloys and Compounds **440**, 1-2 (2007), p. 328 – 332.

[35] D. Chen, Y. Wang, E. Ma, Y. Yu, F. Liu, *Partition, luminescence and energy transfer of Er^{3+}/Yb^{3+} ions in oxyfluoride glass ceramic containing CaF_2 nano-crystals*, Optical Materials **27**, 12 (2007), p. 1693 – 1699.

[36] D. Chen, Y. Wang, Y. Yu, E. Ma, F. Bao, Z. Hu, Y. Cheng, *Influences of Er^{3+} content on structure and upconversion emission of oxyfluoride glass ceramics containing CaF_2 nanocrystals*, Materials Chemistry and Physics **95** (2006), p. 264–269.

[37] Y. Kishi, S. Tanabe, *Infrared-to-visible upconversion of RE doped glass ceramics containing CaF_2 crystals*, Journal of Alloys and Compounds **408-412** (2006), p. 842 – 844.

[38] Z. Hu, Y. Wang, E. Ma, D. Chen, F. Bao, *Microstructures and upconversion luminescence of Er^{3+} doped and Er^{3+}/Yb^{3+} co-doped oxyfluoride glass ceramics*, Materials Chemistry and Physics **101** (2007), p. 234 – 237.

[39] X. Qiao, X. Fan, M. Wang, X. Zhang, *Spectroscopic properties of Er^{3+}–Yb^{3+} co-doped glass ceramics containing BaF_2 nanocrystals*, Journal of Non-Crystalline Solids **354** (2008), p. 3273 – 3277.

[40] D. Chen, Y. Wang, Y. Yu, E. Ma, L. Zhou, Microstructure and luminescence of transparent glass ceramic containing Er^{3+}:BaF_2 nano-crystals, Journal of Solid State Chemistry **179** (2006), p. 532 – 537.

[41] Y. Yu, D. Chen, Y. Wang, F. Liu, E. Ma, *A new transparent oxyfluoride glass ceramic with improved luminescence*, Journal of Non-Crystalline Solids **353** (2007), p. 405 – 409.

[42] Y. Wang, J. Ohwaki, *New transparent vitroceramics codoped with Er^{3+} and Yb^{3+} for efficient frequency upconversion*, Applied Physics Letters **63**, 24 (1993), p. 3268 – 3270.

[43] E. Ma, Z. Hu, Y. Wang, F. Bao, *Influence of structural evolution on fluorescence properties of transparent glass ceramics containing LaF_3 nanocrystals*, Journal of Luminescence **118** (2006), p. 131 – 138.

[44] Z. Hu, E. Ma, Y. Wang, D. Chen, *Fluorescence property investigations on Er^{3+}-doped oxyfluoride glass ceramics containing LaF_3 nanocrystals*, Materials Chemistry and Physics **100** (2006), p. 308 – 312.

[45] Z. Hu, Y. Wang, F. Bao, W. Luo, *Crystallization behavior and microstructure investigations on LaF_3 containing oxyfluoride glass ceramics*, Journal of Non-Crystalline Solids **351** (2005), p. 722 – 728.

[46] F. Abdoun, M. Gaune-Escard, G. Hatem, Calorimetric and thermal analysis investigations of the MF-LaF_3 Mixtures (M = Alkali Metal), Journal of Phase Equilibria 18, 1 (1997), p. 6 – 20.

[47] R.E. Thoma, H. Insley, and G.M. Hebert, The sodium fluoride-lanthanide trifluoride systems, Inorganic Chemistry **5**, 7 (1966), p. 1222 – 1229.

[48] P. Fedorov, I. I. Buchinskaya, O. S. Bondareva, A. A. Bystrova, L. L. Vistin, D. A. Ershov, S. P. Ivanov, V. A. Stasyuk, and B. P. Sobolev, *Phase Diagrams of the NaF-*RF_3 *(R = La, Ce, Pr, Nd, Sm) Systems*, Russian Journal of Inorganic Chemistry **45**, 6 (2000), p. 949 – 953.

[49] A. H. Krumpel, E. van der Kolk, D. Zeelenberg, A. J. J. Bos, K. W. Krämer, P. Dorenbos, *Lanthanide 4f-level location in lanthanide doped and cerium-lanthanide codoped* $NaLaF_4$ *by photo- and thermoluminescence,* Journal of Applied Physics 104 (2008), p. 073505 – 073515.

[50] J. H. Burns, Crystal structure of hexagonal sodium neodymium fluoride and related compounds, Inorganic Chemistry 4, 6 (1965), p. 881 – 886.

[51] F. Liu, Y. Wang, D. Chen, Y. Yu, E. Ma, L. Zhou, P. Huang, *Upconversion emission of a novel glass ceramic containing* Er^{3+}*:* $BaYF_5$ *nano-crystals*, Materials Letters **61**, 28 (2007), p. 5022 – 5025.

[52] F. Liua, E. Ma, D. Chen, Y. Wang, Y. Yua, P. Huang, *Infrared luminescence of transparent glass ceramic containing* Er^{3+}*:*$NaYF_4$ *nanocrystals*, Journal of Alloys and Compounds 467, 1-2 (2009), p. 317 – 321.

[53] W. F. Krupke, and J. B. Gruber, *Absorption and fluorescence spectra of* Er^{3+} $(4f^{11})$ *in* LaF_3, Journal of Chemical Physics **39**, 4 (1963), p. 1024 – 1030.

8. List of publications

1. A. Sarakovskis, L. Dimitrocenko, A. Misnevs, U. Rogulis, M. Springis, *Up-conversion process in erbium doped lithium fluoride bulk crystal, lithium borate glass and glass ceramics*, Journal of Physics: Conference Series **93** (2007) p. 012041 – 012047.

2. J. Grube, A. Sarakovskis, L. Dimitrocenko, M. Springis, Temperature Effects in *Up-Conversion Processes of Erbium - Ytterbium Doped Oxyfluoride Silicate Glass*, Latvian Journal of Physics and Technical Sciences 45, 6 (2008), p. 47 – 54.

3. A. Sarakovskis, J. Grube, G. Doke, M. Springis, *Excited state absorption and energy-transfer mechanisms of up-conversion luminescence in* Er^{3+}*-doped oxyfluoride glass ceramics at different temperatures*, Journal of Luminescence, **130**, 5 (2010), p. 805 - 811. ***{SCI}***

4. A. Sarakovskis, J. Grube, A. Mishnev, M. Springis, *Up-conversion processes in* $NaLaF_4:Er^{3+}$, Optical Materials **31**, 10 (2009), p. 1517 – 1524. ***{SCI}***

5. A. Sarakovskis, J. Grube, G. Doke, and M. Springis, *Selective excitation of up-conversion luminescence by* Yb^{3+}*-*Er^{3+} *energy transfer in glass and crystalline phase of oxyfluoride glass ceramics*, Optical Materials, accepted for the publication. ***{SCI}***

9. List of conference abstracts

1. A. Sarakovskis, L. Dimitrocenko, A. Petruhins, J. Grube, I. Tale, U. Rogulis, M. Springis, *Up-conversion luminescence of* Er^{3+} *in LiF crystals*, 23rd Scientific Conference in Institute of Solid State Physics, Riga, Latvia, February 13 – 15, 2007.

2. A. Sarakovskis, L. Dimitrocenko, A. Misnevs, U. Rogulis, M. Springis, *Up-conversion process in erbium doped lithium fluoride bulk crystal, lithium borate oxyfluoride glass and glass ceramics,* International Baltic Sea Region conference Functional Materials and Nanotechnologies, Riga, Latvia, April 2 – 4, 2007.

3. A. Sarakovskis, L. Dimitrocenko, A. Petruhins, J. Grube, A. Misnevs, U. Rogulis, M. Springis, *Multiphoton processes in RE doped oxyfluoride glasses*, Developments in Optics and Communications, Riga, Latvia, April 27 – 29, 2007.

4. A. Sarakovskis, L. Dimitrocenko, J. Grube, M. Springis, *Spectral and time-resolved studies of up-conversion luminescence in glass ceramics containing* $NaYF_4$*:Er nanocrystals*, 24th Scientific Conference in Institute of Solid State Physics, Riga, Latvia, February 20 – 22, 2008.

5. A. Sarakovskis, J. Grube, L. Dimitrocenko, M. Springis, *Time-resolved spectroscopy of up-conversion processes in Er doped* $NaYF_4$ *silicate glass ceramics*, International Baltic Sea Region conference Functional Materials and Nanotechnologies, Riga, Latvia, April 1 – 4, 2008.

6. A. Sarakovskis, J. Grube, L. Dimitrocenko, S. Fomins, M. Springis, *Up-conversion luminescence studies on* Er^{3+}, Yb^{3+} *and* Tm^{3+} *doped oxyfluoride glass and glass ceramics*, The 6th International Conference on Advanced Optical Materials and Devices, Riga, Latvia, August 24 – 27, 2008.

7. A. Sarakovskis, J. Grube, A. Misnovs, G. Doke, M. Springis, *Energy transfer in* Er^{3+} *and* Yb^{3+} *doped silicate glass and glass ceramics,* 25th Scientific Conference in Institute of Solid State Physics, Riga, Latvia, February 11 – 13, 2009.

8. A. Sarakovskis, J. Grube, M. Springis, *Synthesis and up-conversion luminescence properties of* $NaLaF_4:Er^{3+}$, International conference Functional Materials and Nanotechnologies, Riga, Latvia, March 31 – April 4, 2009.

9. A. Sarakovskis, J. Grube, G. Doke, M. Springis, *Synthesis and up-conversion luminescence properties of* $NaLaF_4:Er^{3+}$, Developments in Optics and Communications, Riga, Latvia, April 24 - 26, 2009.

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