Luminescence Mechanism in Doubly Doped $\text{LaF}_3\text{:Er,Nd}$ VUV Scintillator

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Abstract—Doubly doped $\text{LaF}_3\text{:Er,Nd}$ scintillation crystals were grown by modified micropulling-down method. The Er codoping was chosen to enhance the energy transfer from the host lattice to the Nd^{3+} luminescence center via the 5d-levels of Er^{3+} , which can be enabled by the overlap of Er^{3+} 5d-4f emission spectrum with the Nd^{3+} 4f-5d absorption. However, no relevant energy transfer was found by photo- and radioluminescence spectra measurements. The reasons of no significant positive effect of Er codoping are discussed.

Index Terms—Codoping, energy transfer, luminescence, rare-earth fluorides, scintillators.

I. INTRODUCTION

THE development of new radiation detection systems based on the vacuum ultraviolet (VUV) scintillators has been started recently. These scintillators can be coupled with the detectors filled with photosensitive gases such as tetrakis dimethylamine ethylene (TMAE) or triethylamine (TEA) or to the other VUV-sensitive detectors, for example a photomultiplier with CsI photocathode [1], [2]. One of the promising candidates for the VUV scintillator is the Nd-doped LaF_3 .

The $\text{LaF}_3\text{:Nd}$ VUV emission around 175 nm with a very short decay time of several nanoseconds is due to the spin- and parity-allowed 5d-4f dipole transition of the Nd^{3+} ion [1]. This way very fast radiation detector systems can be developed. Another advantage of this material is its high density 5.94 g/cm³ which makes it suitable for γ -ray and X-ray detection. However, the scintillator light output is affected by inefficient energy

Fig. 1. Scheme of the expected energy transfer in the doubly doped $\text{LaF}_3\text{:Nd,Er}$ scintillator.

transfer from the host lattice to the Nd^{3+} luminescence center, which can be excited only either by primary electrons released after high energy photon absorption or a direct consecutive capture of an electron-hole pair from the conduction and valence bands [3], [4]. The way to increase light output by increasing the Nd^{3+} concentration has a limit in the 5d-4f luminescence concentration quenching, which occurs above the 5 mol% of Nd [3]. Therefore, other concepts of improving the material performance should be searched for. One way can be the Er co-doping. The idea is to enhance the energy transfer to the Nd^{3+} ions via the Er^{3+} excited levels, as the Er^{3+} 5d-4f emission spectrum overlaps with the Nd^{3+} 4f-5d absorption band, see Fig. 1.

II. EXPERIMENTAL DETAILS

Stoichiometric mixture of LaF_3 , ErF_3 and NdF_3 powders of 4N purity (Stella Chemifa Co., Ltd.) was used to prepare the starting charge. Nominally, ErF_3 and/or NdF_3 were added in the LaF_3 host with the formula of $\text{La}_{1-x-y}\text{Er}_y\text{Nd}_x\text{F}_3$, where $y = 0.02$ and $x = 0, 0.01, 0.02, 0.05$.

Crystal growth was carried with graphite crucible under $\text{Ar} + \text{CF}_4$ atmosphere using the micropulling-down (μ -PD) furnace with vacuum-tight systems tailored for fluoride growth [5]. Iridium wire was used as the seed for the crystal growth. The growth rate was 0.1 mm/min. Following typical baking procedure for fluorides the chamber was evacuated to 10^{-4} Torr and the crucible was heated to about 600 °C for 150 min in order to remove the sources of possible oxygen impurities, such as moisture. After the baking procedure, the chamber was filled with Ar (99.999%) and high-purity CF_4 (99.999%) in the proportion 9: 1 and the crucible was heated up to the powder melting temperature.

To identify the phase, powder X-ray diffraction analysis was carried out in the 2θ range from 20° to 80° using the RIGAKU diffractometer (RINT2000). Measurements were performed in air at room temperature (RT) and the X-ray source was $\text{CuK}\alpha$,

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Fig. 2. $\text{La}_{0.96}\text{Er}_{0.02}\text{Nd}_{0.02}\text{F}_3$ crystal. The blob at the final part of the crystal is composed mostly of ErF_3 -rich phase due to Er segregation.

the accelerating voltage and tube current were 40 kV and 40 mA, respectively.

The chemical composition was analyzed by electron probe microanalysis (EPMA) using JEOL JXA-8621MX analyzer with an electron probe focused to a $10\ \mu\text{m}$ spot.

Emission spectra were obtained at the spectrofluorometer (Bunko-Keiki Co., Ltd.) using VUV sensitive PMT (R374, Hamamatsu) and D_2 steady-state lamp as an excitation source. All the spectroscopic measurements in VUV region were performed under N_2 atmosphere. Measurements were not corrected for experimental distortions.

The decay time measurements in the VUV emission region were performed using SUPERLUMI station of the DORIS positron storage ring in HASLAB, DESY, Hamburg [6].

The resulting decay curves were decomposed into the sum of exponentials $I(t) = \sum A_i \exp[-t/\tau_i] + c$ (where c is a constant standing for the background) using deconvolution procedure with the SpectraSolve software from Ames Photonics, Inc.

All the measurements were performed at room temperature.

III. RESULTS AND DISCUSSION

A. Crystal Growth

The as grown crystals were of 2.0-2.5 mm in diameter and around 40 mm in length. Neither visible inclusions nor cracks were observed. The as grown crystal looks transparent, with smooth surface (Fig. 2). At the end of each crystal there was a nontransparent blob composed of ErF_3 rich phase. This points to a significant Er segregation, which resulted in lowered Er concentration in the crystals. The crystals were cut along the growth axis and polished with $0.3\ \mu\text{m}$ diamond paste. Obtained plates with the dimension of $2.0 \times 7.0 \times 1.0\ \text{mm}^3$ were used for the optical experiments.

From the result of powder X-ray diffraction analysis, single phase with hexagonal crystal system, space group of $\text{P}\bar{3}1\text{c}$ was confirmed for all the samples in the regular crystal growth. The ErF_3 impurity phase was confirmed in the blob at the final part of the grown crystal.

The EPMA analysis has shown lowered Er concentration in the crystal around 0.6 mol%.

B. Photo- and Radioluminescence Measurements

The comparison of photoluminescence spectra of the $\text{La}_{0.98-x}\text{Er}_{0.02}\text{Nd}_x\text{F}_3$ single crystals for $x = 0.01, 0.02, 0.05$

Fig. 3. Comparison of photoluminescence spectra of the $\text{La}_{0.98-x}\text{Er}_{0.02}\text{Nd}_x\text{F}_3$ single crystals for $x = 0.01, 0.02, 0.05$ under 160 nm excitation.

under 160 nm excitation (corresponding to the excitation from the Nd^{3+} ground ^4I multiplet to the 5d state) is shown in Fig. 3. The Nd^{3+} 5d - 4f luminescence peaks are clearly observed in the VUV/UV region at 173, 216, and 245 nm. They can be ascribed to the transitions from the 5d level to the ground ^4I , ^4F and ^4G multiplets, respectively, [7]. The shapeless feature between 300 and 500 nm might correspond to the host exciton (defect)-related emission together with the weak Nd^{3+} luminescence. The two peaks at 521 and 544 nm can be ascribed to the Er^{3+} impurity $^2\text{P}_{3/2} - ^4\text{I}_{9/2}$ and $^4\text{S}_{3/2} - ^4\text{I}_{15/2}$ 4f - 4f transitions.

To verify energy transfer from the Er^{3+} sublattice to Nd^{3+} ions emission spectra under the excitation in the Er^{3+} 4f - 5d absorption band were measured. The Nd^{3+} luminescence features are expected, if the mentioned energy transfer works efficiently. An example of such a spectrum is displayed in the Fig. 4 for the $\text{La}_{0.97}\text{Er}_{0.02}\text{Nd}_{0.01}\text{F}_3$ single crystal under 140 nm excitation (Er^{3+} 4f - 5d absorption band). The Nd^{3+} 5d - 4f luminescence is indeed observed in the VUV region. However, also the slow Er^{3+} 4f - 4f luminescence peaks are present in the spectral region 350-600 nm. This shows that the expected energy transfer is not so efficient and that there is a significant energy leak from the Er^{3+} 5d -level to the 4f -ones resulting in the observed 4f - 4f luminescence. In fact the excitation spectra of the 5d - 4f VUV luminescence of both Er^{3+} and Nd^{3+} overlap noticeably [8], which means that both ions are excited by the 140 nm wavelength and the observed spectra are a mixture of directly excited Er^{3+} and Nd^{3+} centers with possible contribution and modification due to the mentioned energy transfer.

Fig. 5 displays the photoluminescence spectrum of the Nd-free $\text{La}_{0.98}\text{Er}_{0.02}\text{F}_3$ single crystal sample under 140 nm excitation (the Er^{3+} 4f - 5d absorption band). The mentioned nonradiative energy leak from the 5d level to the 4f -ones is apparent. It is also necessary to remind that the spectra were not corrected for experimental distortions. However, taking

Fig. 4. Photoluminescence spectrum of the $\text{La}_{0.97}\text{Er}_{0.02}\text{Nd}_{0.01}\text{F}_3$ single crystal under 140 nm excitation.

Fig. 5. Photoluminescence spectrum of the Nd-free sample $\text{La}_{0.98}\text{Er}_{0.02}\text{F}_3$ single crystal under 140 nm excitation. The 4f-4f luminescence features are ascribed.

into account the sensitivity of the detector, this fact would not change the conclusions significantly. To prevent such energy leak, another codopant can be suggested instead of Er^{3+} , for example Tm^{3+} , which does not have any 4f-levels in the VUV/UV region [9]. However, it has been shown recently that some energy leak to the Tm^{3+} 4f-levels also takes place in the LaF_3 host [10] so that a kind of more complex cross-relaxation processes might explain such a situation especially when aggregation of rare earth dopant can be expected.

However, the energy transfer from the Er^{3+} sublattice to the Nd^{3+} ions does work up to some extent, as the Er^{3+} 5d-4f VUV emission peak at 160 nm (see Fig. 5) is not observed in the Fig. 4 and one can assume that this luminescence/energy has been at least partially transferred to the Nd^{3+} ions. The energy transfer can be diminished by the already mentioned lower Er concentration. The Er^{3+} and Nd^{3+} cannot reach sufficiently

Fig. 6. Comparison of the photoluminescence decay curves of the $\text{La}_{0.97}\text{Er}_{0.02}\text{Nd}_{0.01}\text{F}_3$ single crystal under excitation into the Er^{3+} band (solid curve, $\lambda_{\text{ex}} = 145$ nm) and directly into the Nd^{3+} (dashed curve, $\lambda_{\text{ex}} = 160$ nm). The corresponding equations describing the fitted curves are: $I = 12818\exp[-t/8 \text{ ns}] + 131\exp[-t/32 \text{ ns}] + 22.58$ for 145 nm excitation and $I = 14401\exp[-t/8.4 \text{ ns}] + 1877.7\exp[-t/4.1 \text{ ns}] + 13.74$ for 160 nm excitation.

small average distance and due to the distance (r) dependence $\sim 1/r^6$ of the energy transfer rate this concept cannot work efficiently. Decay time measurements provide another insight in the energy transfer mechanism. Preliminary measurements (see Fig. 6) have shown some minor slowdown of the decay and increase of the background level under excitation in the Er^{3+} 4f-5d band (145 nm) with respect to the direct excitation into the Nd^{3+} . This “background” constant difference (almost factor of 2) points to the presence of the components considerably slower with respect to the measurement time window. Apart from the above discussed nonradiative energy transfer there can be also just a radiative one from the Er^{3+} ion to the Nd^{3+} one via the emission and absorption of the VUV 5d-4f luminescence photon. This idea is supported by the following facts: 1) The Er^{3+} concentration is low; 2) The occurrence of a very slow component in the luminescence decay of the Nd^{3+} 5d-4f emission can correspond to the slow spin-forbidden emission of the Er^{3+} 5d-4f high spin transition [11].

Fig. 7 shows the comparison of radioluminescence spectra of the $\text{La}_{0.98-x}\text{Er}_{0.02}\text{Nd}_x\text{F}_3$ single crystals for $x = 0.01, 0.02, 0.05$ under X-ray excitation. Very low intensity of the Nd^{3+} 5d-4f VUV luminescence is apparent. Besides the Er^{3+} VUV features in the UV/VIS region, very strong Nd^{3+} 4f-4f lines are observed. They correspond to the transition from the $^4D_{3/2}$ to the 4I multiplet. The former level can be populated via the self-trapped exciton [3], see also Fig. 3, which is well overlapped with the mentioned emission lines within 320-420 nm.

IV. CONCLUSION

$\text{La}_{0.98-x}\text{Er}_{0.02}\text{Nd}_x\text{F}_3$ single crystals for $x = 0.01, 0.02, 0.05$ were grown by micropulling-down method. Er segregation has been observed and resulted in lower concentration of Er in the crystal. The searched energy transfer from the Er^{3+} to Nd^{3+}

Fig. 7. Comparison of radioluminescence spectra of the $\text{La}_{0.98-x}\text{Er}_{0.02}\text{Nd}_x\text{F}_3$ single crystals for $x = 0.01, 0.02, 0.05$ under X-ray excitation.

ions does not work efficiently, which is also confirmed by preliminary decay time measurements. Apart from low achievable Er concentration, this concept is negatively influenced by an energy leak from the Er^{3+} 5d level to the 4f ones which might be caused by the Er ion aggregation in LaF_3 host and cross-relaxation processes in such clusters can occur as a consequence. Replacing Er^{3+} with Tm^{3+} does not offer good solution [10], neither due to the same reason. Energy transfer from the host to 5d Er^{3+} and Nd^{3+} states is also troubled by an efficient creation of the self-trapped exciton (STE) which transfers energy directly to the Nd^{3+} 4f-levels. Another host material must be searched for

the suggested energy transfer concept. It should have weak tendency to create STE and should incorporate easily large amount of Er^{3+} or Tm^{3+} ions.

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