Luminescence mechanism in doubly Gd,Nd-codoped fluoride crystals for VUV scintillators

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Abstract

The Nd-doped, Gd-doped and doubly Nd,Gd-codoped BaLu_{1.2}Y_{0.8}F₈ (BaLuYF) and LuF₃ single crystals were grown by micro-pulling-down method. Their photoluminescence, radioluminescence and alpha-ray-excited pulse-height spectra were studied in the vacuum-ultra-violet (VUV) region to confirm their possible application as fast VUV scintillators. Complementary photoluminescence measurements in the ultra-violet/ visible spectral region were performed as well. The possibility of scintillation performance improvement by Gd codoping was tested. The overall scintillation efficiency of BaLuYF:Nd1% was comparable to that of the LaF₃:Nd8% reference sample and only slight improvement was observed after Gd1% codoping. The positive effect of Gd codoping was confirmed for higher dopant concentrations. This was explained by an energy transfer from the high-energy Gd³⁺ 4f ²G(0)_{7/2} level to the Nd³⁺ 5d state. On the other hand, pulse –height spectra showed degradation of the light yield under alpha-ray excitation, which was explained by introduction of slow components due to Gd codoping. On the other hand, no positive effect of Gd codoping was found for the overall scintillation efficiency of Nd-doped LuF₃, despite the same energy transfer process was confirmed. Slight improvement of the light yield under alpha-ray excitation was confirmed.

Keywords: barium-lutetium-yttrium fluoride, lutetium fluoride; scintillator; VUV luminescence

1. Introduction

Scintillators materials find their application in radiation detectors in several fields, such as medical imaging, security scanning, nuclear physics or astronomy. Requirement of very fast response with a scintillation decay time of several nanoseconds in some of the applications (nuclear physics applications or high-frame-rate imaging) triggered the search for new material systems. The Nd³⁺ -

doped wide-band-gap fluorides emitting in the vacuum-ultra-violet (VUV) region were considered as the candidate materials [1-3]. Since the decay time of the rare earth 5d-4f emission is proportional to the emission wavelength as $\tau \sim \lambda^3$ [7], the Nd^{3+} 5d-4f VUV emission has the decay time of several nanoseconds. Other rare-earth luminescence ions emitting at even shorter wavelengths, such as Tm^{3+} or Er^{3+} , can be considered as well [4]. When coupled to the contemporary fast VUV photodetectors such as gas electron multiplier (GEM) with micro-pixel chamber or a photomultiplier (PMT) with CsI-coated photocathode [5,6], fast position-sensitive detection system can be obtained.

The first studied VUV scintillator was the Nd-doped LaF_3 [1-3] with the Nd^{3+} 5d-4f luminescence at 175nm and fast decay time of 6-9 ns. It was proved that its scintillation performance is high enough for imaging with multiwire chamber [1] and its suitability for imaging applications were confirmed also in the recent study employing GEM and micro-pixel chamber [8]. In our research we choose this material as a reference.

Another material was Nd-doped BaY_2F_8 studied also by some of us [10]. The Nd^{3+} 5d-4f emission is shifted to longer wavelengths at 186 nm and therefore its decay time is prolonged to some 15 ns. Admixture of Lu into the BaY_2F_8 matrix and concentration optimization led to new material $\text{BaLu}_{1.2}\text{Y}_{0.8}\text{F}_8$ (BaLuYF). The overall scintillation efficiency of the Nd-doped BaLuYF was as high as that of $\text{LaF}_3\text{:Nd}$ [12], also partially due to increased density resulting from the Lu admixture.

Very favorable scintillation properties in the group of the VUV-emitting fluorides were found for Nd-doped LuF_3 , such as very high overall scintillation efficiency exceeding several times that of $\text{LaF}_3\text{:Nd}$ [14], emission peaking at around 180 nm, the scintillation response with a leading decay time of 8 ns, high density of 8.3g/cm^3 resulting in high stopping power for gamma-ray detection and so on. The scintillation properties were reported also for the high-quality Czochralski-grown single crystal [15].

Attempts to improve the scintillation efficiency by codoping of other VUV-emitting rare earth ions such as Er^{3+} or Tm^{3+} were also performed by some of us. In most of the fluoride matrices the 5d-4f emission spectrum of Er^{3+} or Tm^{3+} overlaps with the excitation spectrum of Nd^{3+} and energy transfer is therefore possible. The energy transfer from Er^{3+} to Nd^{3+} was successfully proved in the Er^{3+} co-doped $\text{BaY}_2\text{F}_8\text{:Nd}$ [11]. Slight improvement of the overall scintillation efficiency by the energy transfer from the Tm^{3+} codoping ions was observed also in the $\text{BaY}_2\text{F}_8\text{:Nd}$ [17], $\text{BaLu}_2\text{F}_8\text{:Nd}$ [13] and $\text{BaLuYF}\text{:Nd}$ [12] single crystals.

Recently, improvement of scintillation properties by Gd^{3+} codoping was observed for the $\text{LiLuF}_4\text{:Nd}$ VUV scintillator [18]. However, no detailed explanation about this phenomenon was given and it was only noted that there the energy transfer the highest Nd^{3+} 5d state is improved in the presence of Gd^{3+} . At the same time, the energy transfer from the Nd^{3+} 5d-states to the Gd^{3+} 4f-ones was proved. Possible energy transfer from the Gd^{3+} 4f-levels towards the Nd^{3+} 4f-levels was suggested. It can be interesting to test the improvement of the scintillation efficiency of the other Nd-doped fluoride-based VUV scintillation materials by Gd-codoping.

The aims of this work are to study the luminescence and scintillation properties of the doubly Gd,Nd-

doped BaLuYF and LuF₃ VUV scintillators and investigate the possibility of improvement of their performance by Gd codoping and sketch the possible luminescence mechanism.

2. Experimental

Fluoride powders of 4N purity from Stella Chemifa Co. Ltd. were used as starting materials. To grow the BaLuYF crystals, the mixture of the BaF₂, LuF₃, YF₃, NdF₃ and/or GdF₃ powders was used. The samples with following dopants and concentrations (molar percents) were prepared: Nd1%, Gd1%, Nd5%, Gd5%, and doubly doped Gd1%Nd1%, Gd5%Nd5% and Gd20%Nd5%. The dopants substituted for the Lu³⁺ ion.

Crystal growth was carried out with graphite crucible under Ar + CF₄ (9:1) atmosphere using the micro-pulling-down (μ -PD) furnace with vacuum-tight systems tailored for fluoride growth, for details see [16]. The undoped BaY₂F₈ was used as the seed crystal. The crystal melts congruently at around 950°C. The crystal was pulled out at a pulling speed of 0.1 mm/min. The as-grown crystals were 2 mm in diameter and 50mm in length.

To grow the LuF₃ crystals, the mixture of LuF₃ and NdF₃ and/or GdF₃ was used. The samples with the following composition were grown: Nd1%, Gd1%, Nd5%, and doubly doped Gd1%Nd1% and Gd5%Nd5%.

The crystals were grown with the same micro-pulling-down setup as described above.

43mol% LiF was added to each charge to diminish the melting point of the mixture below the phase transition temperature. The phase transition occurs some 250°C below the melting point which is around 1160°C. The as grown crystals were of 2.0-2.5 mm in diameter and 5-10 mm in length. The surface of the crystals was a bit rough and opaque, but the crystals were transparent inside.

The as-grown BaLuYF and LuF₃ crystals were cut along the growth axis and polished with 0.3 μ m diamond paste. Obtained plates with the dimension of 2.0x5.0-10.0x1.0 mm³ were used for optical experiments.

To identify the phase, powder X-ray diffraction analysis (XRD) was carried out in the 2θ range from 20° to 80° using the RIGAKU diffractometer (RINT2000).

Transmittance, photoluminescence and radioluminescence (RL) emission spectra were obtained at the Spectrofluorometer (Bunko-keiki Co. Ltd.) using VUV sensitive CCD (Andor) and D₂ steady-state lamp as an excitation source. An X-ray tube operated at 50 kV and 20 mA with Cu anode has been used for the X-ray excitation. Measurements were not corrected for experimental distortions, which include the CCD sensitivity and monochromator throughput that are spectrally dependent. Such correction has not been made as no calibrated VUV emission source is available so far to enable precise correction curve measurement. The experimental distortions can influence the spectra in a way that mutual intensities of particular peaks can be different in our spectra and in reality. However, mutual comparisons of the intensities are possible due to flat spectral sensitivity of the CCD in the 170-180 nm region. The sample dimensions and experiment geometry was kept strictly the same, so

that the peak intensities at the same wavelengths are mutually comparable in an absolute way for different samples, except for the Nd-doped one due to its smaller size. The metallic mask enabled light collection from the same area of each sample. To compare the radioluminescence (RL) intensity, RL of high quality $\text{LaF}_3\text{Nd}8\%$ standard sample was measured.

The measurements of the photoluminescence excitation spectra in the VUV emission region were performed using synchrotron radiation at SUPERLUMI station of the DORIS positron storage ring in HASYLAB, DESY, Hamburg [19]. The spectra were corrected for detector sensitivity and monochromator throughput using correction curve obtained from measurement of excitation spectrum of sodium salicylate for its 400 nm emission peak. Due to technical issues it was impossible so far to measure the decay kinetics in VUV region which would help to better clarify the energy transfer and luminescence processes at high excitation energies. Such experiments are planned for the future.

Complementary measurements in the ultra-violet/visible (UV/VIS) region were performed with custom-made Horiba 5000M series spectrofluorometer under Xe-lamp excitation. The true decay times were extracted by a deconvolution procedure with instrumental response using SpectraSolve software (Ames Photonics Inc.).

To measure the light output, the crystal samples were excited with alpha rays from a ^{241}Am (5.5 MeV) source. The scintillation photons were detected by a photomultiplier (PMT, R8778, Hamamatsu), and then the signal from the PMT was amplified, shaped with a shaping time of 500 ns (572A, ORTEC), and read out with a multi-channel analyzer (Pocket MCA 8000A, AMPTEK). After obtaining the pulse height spectra, the channel positions of the full absorption peak was estimated. Similarly as for X-ray-excited RL spectra, the $\text{LaF}_3\text{Nd}8\%$ was measured as a reference. The alpha-ray source was used as the small size of the crystals grown by the micro-pulling-down method did not allow measurements under gamma-ray excitation.

3. Results and discussion

3.1. BaLuYF crystals

Transparent and crack-free Nd-doped, Gd-doped, and doubly Gd,Nd BaLuYF crystals were successfully grown (not shown here). The XRD analysis confirmed the monoclinic structure (space group C2/m) similar to that of BaY_2F_8 , but with slightly smaller lattice constant due to smaller ionic radii of Lu^{3+} when compared to that of Y^{3+} .

Also the transparent and crack-free Nd-doped, Gd-doped, and doubly Gd,Nd-doped LuF_3 crystals were successfully grown (not shown here). Just the size of the Nd1% sample was quite small (around 3 mm in length) due to crystal growth difficulties caused probably by more significant difference between Lu^{3+} and Nd^{3+} cation radii. The XRD analysis confirmed the low-temperature orthorhombic LuF_3 phase and the diffraction peaks corresponded to the 32-0612 JCPDS chart.

The comparison of the radioluminescence spectra in the VUV/UV region under X-ray excitation for

the Gd1%, Nd1% and Gd1%Nd1% BaLuYF single crystals is shown in the figure 1 together with the spectrum for the LaF₃:Nd8% reference crystal with optimized Nd concentration. For both the Nd-containing BaLuYF samples, the Nd³⁺ emission related to the transition from the 5d-state to the ⁴I multiplet is situated around 185 nm. Transitions from the 5d-state to the higher ⁴F or ⁴G multiplets can be observed at 235 and 270 nm, respectively. The same can be observed for the LaF₃:Nd reference but the peaks are shifted towards shorter wavelengths due to decreased crystal field in the LaF₃ matrix. The intensity of the Nd³⁺ 5d-4f emission peak at 185 nm for the BaLuYF:Nd1% is lower than that for the LaF₃:Nd reference. On the other hand, the BaLuYF:Gd1%Nd1% sample slightly outperforms the reference scintillator, which can be a sign of a positive effect of Gd codoping on the overall scintillation efficiency in the VUV region. For the BaLuYF:Gd1% sample, obviously, only the intense 4f-4f Gd³⁺ lines can be observed at 250, 275 and 311 nm. The can be ascribed to the ⁶D_{9/2}→⁸S_{7/2}, ⁶I_{9/2}(⁶I_{7/2})→⁸S_{7/2} and ⁶P_{7/2}→⁸S_{7/2} transitions, respectively. The same transitions are observed also in the doubly-doped BaLuYF:Gd1%Nd1%, but their intensities are significantly lower than those in the Nd-free BaLuYF:Gd1% sample. Thus, there can be a mechanism preventing the excitation energy from being transferred towards the Gd³⁺ 4f-levels, or there can be a process withdrawing the energy from the Gd³⁺ 4f-levels.

It is worth noticing that the Nd³⁺ concentration in the LaF₃:Nd reference is 8 times higher when compared to the above discussed BaLuYF samples. So, there is a question how is the influence of the dopants concentration on the overall scintillation efficiency of the BaLuYF scintillation material. The comparison of the radioluminescence spectra for the Nd5%, Gd5%Nd5% and Gd20%Nd5% samples is shown in the figure 2 together with the radioluminescence spectrum for the LaF₃:Nd8% reference. The spectrum for the BaLuYF:Nd5% sample shows that the increase of the Nd concentration does not bring significant improvement of the overall scintillation efficiency, though some slight increase in the Nd³⁺ 5d-4f emission intensity can be observed. However, addition of 5% of Gd leads to significant increase of the Nd³⁺ 5d-4f emission peak at 185 nm. The BaLuYF:Gd5%Nd5% outperforms the Nd5% sample and the LaF₃:Nd8% by a about a factor of 2. This is an apparent proof that Gd³⁺ codoping improves the scintillation efficiency for higher dopant concentration. It will be shown later that there is an energy transfer mechanism from the Gd³⁺ 4f levels to the Nd³⁺ 5d ones, as was suggested in [18]. Further increase of the Gd concentration to 20% decreases the the intensity of the Nd³⁺ 185 nm peak, most probably due to increased energy migration over the Gd³⁺ ions and consequent concentration quenching. This idea is also supported by the fact that the intensities of the Gd³⁺ 4f-4f lines almost do not increase in the BaLuYF:Gd20%Nd5% with respect to the Gd5%Nd5% sample. The decrease of the Nd³⁺ 5d-4f emission intensity in the presence of large amount of Gd can be also explained by an increased probability of an energy back-transfer from the Nd³⁺ 5d-levels to the Gd³⁺ 4f ones, which was also concluded in [18].

Let us focus on clarification of the energy transfer from the Gd³⁺ ions to the Nd³⁺ ones. As described in the introduction, in the Er³⁺ and Nd³⁺ -doped crystals, the 5d-4f Er³⁺ emission in the VUV region

overlaps with the Nd^{3+} 4f-5d absorption making the energy transfer possible. There is a question what is the mechanism of the energy transfer and if there is such a suitable emission in the VUV region for the Gd^{3+} ion. Such an emission was indeed observed for the first time. Figure 3 shows the emission spectrum for the BaLuYF:Gd5% sample under 120 nm excitation, which corresponds to the band-to-band transition. Such an excitation simulates the very last stage of the scintillation process, when the electron-hole pair is transferred to the dopant, in this case the Gd^{3+} ion. The spectrum is quite noisy due to lower intensity of the deuterium excitation lamp at 120 nm, but two peaks can be still clearly observed at 157 nm and 147 nm. The 157 nm peak is a scattered stray light always observed in our apparatus, however, the sharp line at 147 nm is a real luminescence that was ascribed to the Gd^{3+} $^2\text{G}(0)_{7/2} \rightarrow ^8\text{S}_{7/2}$ transition and has never been reported before. Taking into account the Gd^{3+} complicated level structure at high energies [20], one can suggest that there should be an inevitable energy leak from the $^2\text{G}(0)_{7/2}$ to the lower lying $^2\text{Q}_{23/2}$ level separated by some 520 cm^{-1} gap and this would lead to quenching of the radiative transition from the $^2\text{G}(0)_{7/2}$ level. On the other hand, the total orbital and angular momentum quantum numbers of the $^2\text{Q}_{23/2}$ level are unusually high and the transition from the $^2\text{G}(0)_{7/2}$ can be strongly forbidden enabling the radiative transition from the $^2\text{G}(0)_{7/2}$ state to the $^8\text{S}_{7/2}$ ground state (or other higher-lying states) responsible for the 147 nm emission [21].

Figure 4 shows the excitation spectrum of the 185 nm Nd^{3+} 5d-4f emission measured with Superlumi station at DESY. The three broad peaks at 135, 157 and 178 nm are due to transitions from the $^4\text{I}_{9/2}$ ground state to the splitted 5d levels. The vertical line denotes the 147 nm wavelength, which is still located at the long-wavelength shoulder of the 135 nm excitation. This makes the overlap of the Nd^{3+} excitation spectrum with the Gd^{3+} $^2\text{G}(0)_{7/2} \rightarrow ^8\text{S}_{7/2}$ radiative transition possible and satisfies the necessary condition for an energy transfer from the Gd^{3+} ion to the Nd^{3+} one.

Thus, we can conclude that the Gd^{3+} $^2\text{G}(0)_{7/2} \rightarrow ^8\text{S}_{7/2}$ transition can really take place and can improve the energy transfer towards the Nd^{3+} ion, which leads to the increase of the BaLuYF:Nd overall scintillation efficiency. Moreover, this process probably causes the decrease of the Gd^{3+} 4f-4f emission intensity observed in the figure 1 in the spectrum for the BaLuYF:Gd1%,Nd1% sample. Significant part of the excitation energy from the Gd^{3+} ion is transferred to the Nd^{3+} ion before the Gd^{3+} 4f-4f luminescence can take place. On the other hand, energy transfer from the Gd^{3+} 4f-level might introduce a slow component in the scintillation decay process. There is a question what is the decay time of the transition from the Gd^{3+} $^2\text{G}(0)_{7/2}$ level, which might be also affected both by still possible nonradiative transition to the $^2\text{Q}_{23/2}$ level or by the energy transfer to the Nd^{3+} itself. As mentioned above, the decay kinetics measurement in the VUV region is planned for the future to verify these processes. Measurement of the pulse-height spectra using VUV-sensitive PMT might bring certain insight to the scintillation process in the VUV region. Comparison of the pulse-height spectra for the Nd1%, Nd5%, Gd1%Nd1% and Gd5%Nd5% BaLuYF samples together with the $\text{LaF}_3\text{:Nd8\%}$ reference sample is shown in the figure 5. Unlike for the X-ray-excited RL spectra, all the samples perform significantly worse than the $\text{LaF}_3\text{:Nd}$ reference, whose peak is the only one well resolved

from the background. From the studied samples, the Nd5% sample seems to have the highest light yield which overcomes the Gd5%Nd5% sample. Considering the 500 ns shaping time, these results could suggest that Gd codoping introduces slow components and most of the light is emitted beyond the 500 ns time gate.

One has also take into account that under gamma-ray the material might have different response and performance due to its much higher penetrability and smaller ionization density.

As stated for the BaLuYF:Gd20%Nd5% above and in [18], there can be an energy back-transfer from the Nd^{3+} levels to the Gd^{3+} ones, which can consist in overlapping of the other Nd^{3+} 5d or 4f levels with the Gd^{3+} 4f ones. The comparison of the Nd^{3+} 5d-4f photoluminescence emission spectrum under 147 nm excitation for the BaLuYF:Nd1% sample with the transmittance spectrum for the BaLuYF:Gd20% crystal is displayed in the figure 6. There is an apparent overlap of the Nd^{3+} 5d- $^4\text{G}_J$ transition with the Gd^{3+} $^8\text{S}_{7/2} \rightarrow ^6\text{I}_{7/2}, ^6\text{I}_{9/2}$ absorption transitions around 270 nm. This can be the main pathway of the energy back-transfer to the Gd^{3+} ions. Moreover, weaker Gd^{3+} transitions at 200 and 195 nm attributed to $^8\text{S}_{7/2} \rightarrow ^6\text{G}_{9/2}, ^6\text{G}_{13/2}$, respectively, overlap with the leading Nd^{3+} 5d- $^4\text{I}_J$ broad-band centered at 185 nm. This pathway can also contribute to the energy back-transfer.

Reference [18] suggests an energy transfer from the lowest Gd^{3+} $^6\text{P}_{7/2}$ level to the Nd^{3+} $^2\text{L}_{17/2}$ one in the LiLuF₄ host. To test this hypothesis, we have measured photoluminescence decay kinetics of the Gd^{3+} $^6\text{P}_{7/2} \rightarrow ^8\text{S}_{7/2}$ transition at 311 nm under 306 nm direct excitation for the Gd1% sample (figure 7a), Nd^{3+} emission at 360 nm corresponding to the $^4\text{D}_{3/2} \rightarrow ^4\text{I}_{9/2}$ transition under 275 nm excitation (ascribed to the Nd^{3+} $^4\text{I}_{9/2} \rightarrow ^2\text{H}_{11/2}$ transition [22]) for the Nd1%-only sample (figure 7b) and the same Nd^{3+} emission at 360 nm under 275 nm excitation for the Nd, Gd sample (figure 7c). It is worth noting the 275 nm excitation also matches the Gd^{3+} $^8\text{S}_{7/2} \rightarrow ^6\text{I}_{7/2}$ transition and the $^6\text{I}_{7/2}$ level can be also populated from the Nd^{3+} 5d- $^4\text{G}_J$ transition under high-energy excitation as shown above. In the Nd^{3+} decay process under 275 nm excitation, the electron nonradiatively deexcites from the $^2\text{H}_{11/2}$ level to the $^4\text{D}_{3/2}$ one from which the luminescence takes place. The decay time of the Gd^{3+} 311 nm emission for the Gd-doped sample in the figure 7a is around 7.5 ms while that of the 360 nm Nd^{3+} emission for the Nd-doped sample in the figure 7b is around 2 ms. The decay curve of the Nd^{3+} 360 nm under 275 nm excitation for the Gd,Nd-doped sample clearly shows both 2 ms and slower 6.7 ms component and proofs the energy transfer from the Gd^{3+} ion to the Nd^{3+} one. Acceleration of this slow component is most probably the consequence of the energy transfer itself, which works as another energy-loss channel. Some part of the Nd^{3+} ions are still excited directly as the Nd^{3+} 2 ms component is still present. When the Gd,Nd sample was excited under 306 nm, very similar result was obtained, which means that the Nd^{3+} ion is excited probably to the $^2\text{H}_{9/2}$ level from which again nonradiatively deexcites to the $^4\text{D}_{3/2}$ one and 360 nm luminescence takes place. The slow component in the Nd^{3+} decay is a proof that its $^2\text{L}_{17/2}$ level is populated from the Gd^{3+} $^6\text{P}_{7/2}$ one. Nonradiative transition from the $^2\text{L}_{17/2}$ level to the $^4\text{D}_{3/2}$ one takes place. The the transition to the ground state yields the 360 nm emission. Decay kinetics of the 390 nm and 418 nm Nd^{3+} emissions were tested under excitation into

$\text{Gd}^{3+} {}^6\text{P}$ multiplet, but the decay curves became more complicated. Further analysis, which is out of the scope of this article, needs to be done to clarify such processes. No schematic of the above described processes is given and the reader is referred to the figure 7 in [22] and related appendix. The scintillation mechanism in the doubly-doped $\text{BaLuYF}:\text{Gd},\text{Nd}$ scintillation crystal is summarized in the schematics shown in the figure 8. The energy transfer processes related to the UV/VIS emitting 4f levels are omitted for simplicity. Thermalized electron-hole pairs can be captured directly on the Nd^{3+} luminescence center giving rise to the 5d-4f Nd^{3+} luminescence. Under direct photoluminescence excitation into the Nd^{3+} 4f-5d bands of the $\text{BaLuYF}:\text{Nd}1\%$ sample the Nd^{3+} 4f-4f emission intensities are very small, so we can consider the nonradiative energy leak from the 5d-levels to the 4f ones to be insignificant. A bit more intense Nd^{3+} 4f-4f peaks were observed under X-ray excitation, which would mean that they can be populated not only via the leak from the 5d-levels, but also from the excited host levels. The thermalized electron-hole pair can be captured also on the Gd^{3+} codoping ion, which can further de-excite via the 4f-4f luminescence or the energy can be transferred from the ${}^2\text{G}(0)_{7/2}$ level towards Nd^{3+} 5d one. At the same time, when a transition from the Nd^{3+} 5d level to the highest ${}^4\text{G}_J$ multiplet takes place, the energy can be transferred to the $\text{Gd}^{3+} {}^6\text{I}_{7/2}$ level. The thermalized electron-hole pairs do not need to be necessarily captured only at the doping ions but can be captured also at the host levels giving rise for example to the above-mentioned increase of the Nd^{3+} 4f-4f luminescence intensity. The luminescence related to the host levels of undoped BaLuYF single crystal was reported for example in [12]. The host levels can be also involved in various quenching processes competing with the energy transfer towards the doping ions. These processes were also omitted for simplicity in the schematic in the figure 8.

3.2. LuF_3 crystals

The radioluminescence spectra under X-ray excitation for the $\text{Gd}1\%$, $\text{Nd}1\%$ and $\text{Gd}1\%\text{Nd}1\%$ LuF_3 single crystals are compared in the figure 9 together with the spectrum for the $\text{LaF}_3:\text{Nd}8\%$ reference crystal. Again, the Nd^{3+} 5d-4f emission bands can be observed, but they are shifted towards shorter wavelengths due to weaker crystal field in LuF_3 matrix. The leading Nd^{3+} 5d- ${}^4\text{I}_J$ transition is situated at around 175 nm. The Gd^{3+} 4f-4f bands are observed as well. In this case the most striking difference with respect to BaLuYF is that both Nd-containing samples significantly outperform the reference scintillator showing almost 8 times higher overall scintillation efficiency in the VUV region. This confirms observations reported in [15]. However, the intensity of the Nd^{3+} 5d-4f emission is slightly lower for the doubly-doped $\text{Gd}1\%\text{Nd}1\%$ sample. Further increase of dopant concentration leads to degradation of scintillation efficiency. The intensity of the leading Nd^{3+} emission at 175 nm decreases for the $\text{LuF}_3:\text{Nd}5\%$ crystal almost 3 times when compared to the $\text{LuF}_3:\text{Nd}1\%$ one, most probably due to concentration quenching. The leading Nd^{3+} emission for the $\text{LuF}_3:\text{Gd}5\%\text{Nd}5\%$ reaches the same value as that for the $\text{LaF}_3:\text{Nd}8\%$ reference crystal (not shown here). We can conclude that the Gd codoping does not bring any positive effects on the $\text{LuF}_3:\text{Nd}$ overall scintillation efficiency. Despite this

fact the energy transfer from the Gd^{3+} luminescence center towards the Nd^{3+} one can still work. The unusual luminescence ascribed to the $\text{Gd}^{3+} {}^2\text{G}(0)_{7/2} \rightarrow {}^8\text{S}_{7/2}$ transition at 147 nm can be also observed in the LuF_3 sample under 120 nm (band-to-band) excitation (figure 10), similarly as for the Gd-doped BaLuYF one. The overlap of this emission with the excitation spectrum of the Nd^{3+} 5d-4f VUV luminescence is also confirmed in the figure 11, where the vertical line indicates the 147 nm wavelength. Concerning other back-transfer processes from Nd^{3+} to Gd^{3+} , the overlap of the Nd^{3+} 5d- ${}^4\text{G}_J$ transition with the $\text{Gd}^{3+} {}^8\text{S}_{7/2} \rightarrow {}^6\text{I}_{7/2}, {}^6\text{I}_{9/2}$ absorption transitions already does not occur due to shift of the Nd^{3+} emission spectrum towards shorter wavelengths, which can be seen from the comparison of the photoluminescence emission spectrum under 149 nm excitation for $\text{LuF}_3:\text{Nd}1\%$ and transmittance spectrum for the $\text{LuF}_3:\text{Gd}5\%\text{Nd}5\%$ (figure 12). In this case, there is an absorption line in the Gd-containing sample around 185 nm tentatively ascribed to the $\text{Gd}^{3+} {}^8\text{S}_{7/2} \rightarrow {}^6\text{F}_{9/2}$ transition which overlaps with the Nd^{3+} 5d- ${}^4\text{I}_J$ transition. This can be the pathway of energy back-transfer from Nd^{3+} to Gd^{3+} . It is also worth noting that the $\text{Gd}^{3+} {}^6\text{P}_{7/2} \rightarrow {}^8\text{S}_{7/2}$ emission at 311 nm was observed under 156 nm excitation into the Nd^{3+} 4f-5d band in the $\text{LuF}_3:\text{Gd}1\%\text{Nd}1\%$ crystal (not shown here). This also confirms that some back-transfer process takes place.

The comparison of the alpha-ray-excited pulse-height spectra for the $\text{LuF}_3:\text{Nd}1\%$ and $\text{LuF}_3:\text{Gd}1\%\text{Nd}1\%$ crystals is compared in the figure 13. Due to the high high yield of the LuF_3 crystals, the number of channels and the amplifier gain were chosen to be different from the measurements in the figure 5, that is why the position of the peak for the reference crystal is at different channel number. Interestingly, we can see not only that both of them significantly outperform the $\text{LaF}_3:\text{Nd}8\%$ reference, but the Gd-codoped sample performs slightly better than the Nd-only doped counterpart. This suggests that for low dopant concentrations around 1% Gd^{3+} codoping improves the energy transfer towards Nd^{3+} centers and is fast enough not to introduce significant amounts of slow components. Further studies of time-resolved measurements are necessary to clarify this process and explain the discrepancy between the pulse-height spectra and X-ray excited RL. As already stated, one must keep in mind different penetration depth and ionization density of alpha particles and high-energy photons.

Enhancement of Nd^{3+} 4f-4f lines in the UV-visible region was observed in the presence of Gd in photoluminescence measurements (not shown here). This may also point to an energy transfer from Gd^{3+} 4f levels towards Nd^{3+} 4f ones, as suggested in [18] for LiLuF_4 host and shown above for the BaLuYF crystals. Similar photoluminescence simple study to test the energy transfer between Nd^{3+} and Gd^{3+} 4f energy levels emitting in UV region was performed. Again, the decay kinetic of the Gd^{3+} 311 nm emission under 306 nm excitation was performed for the $\text{LuF}_3:\text{Gd}1\%$ sample yielding slightly longer decay time of 7.8 ms. The decay time of the 360 nm emission for the Nd^{3+} emission under 275 nm and 306 nm excitations for the Nd-doped sample only was again around 2 ms (not shown here). On the other hand, when the Nd^{3+} 360 nm emission decay kinetics was measured for the doubly doped $\text{LuF}_3:\text{Gd}1\%\text{Nd}1\%$ sample under excitation at 306 nm into $\text{Gd}^{3+} {}^6\text{P}$ multiplet or at 275 nm into $\text{Gd}^{3+} {}^6\text{I}$

multiplet, a curve with around 7 ms decay time was obtained (figure 14). The value is again close to that of Gd^{3+} , even if the Nd^{3+} emission is monitored. The slight decay acceleration with respect to the Gd^{3+} emission is again caused by the energy transfer itself. Unlike for the Gd,Nd doubly-doped BaLuYF sample (figure 7c), no component close to Nd^{3+} emission is observed. The fast 670 ns component spreads over only some 8 channels and its physical meaning is doubtful. Further research is necessary to clarify these observations.

4. Conclusions

The Gd-doped, Nd-doped and doubly Gd,Nd-codoped $BaLu_{1.2}Y_{0.8}F_8$ and LuF_3 VUV scintillation crystals were successfully grown by micro-pulling-down method. Positive effect of Gd-codoping on overall scintillation efficiency in the VUV region was confirmed for the Nd-doped $BaLu_{1.2}Y_{0.8}F_8$ crystals. This effect is due to an energy transfer from the Gd^{3+} to Nd^{3+} ions. . On the other hand, the light yield under alpha-ray excitation was significantly degraded probably due to introduction of slow components in scintillation decay process by Gd codoping. An unwanted back-transfer from Nd^{3+} to Gd^{3+} ions was confirmed as well. Similar phenomena were observed also for the LuF_3 scintillation crystals, however, no improvement in the overall scintillation efficiency in the VUV region was confirmed, though it was confirmed for the alpha-ray excited light yield. Further research involving time-resolved spectroscopy in VUV region is necessary to clarify these complicated processes.

In both $BaLu_{1.2}Y_{0.8}F_8$ and LuF_3 Gd-only-doped crystals an unusual Gd^{3+} 4f-4f luminescence at 147 nm was observed for the first time and was ascribed to the $^2G(0)_{7/2} \rightarrow ^8S_{7/2}$ transition. This luminescence transition is most probably involved in the energy transfer from the Gd^{3+} to the Nd^{3+} ions in both materials.

5. Acknowledgments

This work is partially supported by

- (i) Japan Society for the Promotion of Science (JSPS)
- (ii) Development of Systems and Technology for Advanced Measurement and Analysis (SENTAN), Japan Science and Technology Agency (JST),
- (iii) Adaptable and Seamless Technology Transfer Program through Target-driven R&D (A-STEP), JST,
- (iv) Health Labour Sciences Research Grant, The Ministry of Health Labour and Welfare,
- (v) The New Energy and Industrial Technology Development Organization (NEDO),
- (vi) Supporting Industry program, Ministry of Economy, Trade and Industry (METI)
- (vii) the Association for the Progress of New Chemical Technology
- (viii) Czech MEYS KONTAKT LH14266 and
- (ix) DESY II-20100033 project

In addition, we would like to thank following persons for their support: Mr. Yoshihiro Nakamura of Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, and Mr. Hisakazu Nagato, Mr. Hiroshi Uemura, Ms. Keiko Toguchi, Ms. Megumi Sasaki, Ms. Yuka Takeda and Ms. Kuniko Kawaguchi of IMR, Tohoku University. Dr. Aleksei Kotlov of Hasylab, DESY is also acknowledged for technical help with measurements at Superlumi station.

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Figure1

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