Luminescence and scintillation properties of rare-earth-doped LuF₃ scintillation crystals

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ABSTRACT

The Nd-doped and Er-doped LuF₃ single crystals were grown by the micro-pulling-down method to study their scintillation properties in the vacuum-ultraviolet (VUV) region. The doubly Nd–Er codoped single crystal was grown to study possibility of scintillation performance improvement by energy transfer from Er³⁺ to Nd³⁺ ions. The LiF flux was to avoid phase transition below melting temperature. The 1%Nd-doped sample showed the highest overall scintillation efficiency under X-ray excitation which was 7 times as high as that of the LaF₃:Nd 8% standard. The leading Nd³⁺ 5d–4f emission was situated at 176 nm, while the Er³⁺ 5d–4f emission for Er-doped samples was observed at 163 nm, which better matches the sensitivity of some VUV-sensitive photodetectors. The optimum Er concentration was determined to be around 1–3 mol%. No Er³⁺ 5d–4f emission was observed for the doubly Er,Nd-codoped sample due to energy transfer from the Er³⁺ to Nd³⁺ ions. Slight improvement of the light yield was observed in the doubly-doped sample with respect to the Nd-only doped one.

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1. Introduction

Scintillators work as convertors of the energy of an ionizing radiation into visible or ultraviolet light and therefore they find their application in radiation detectors in many fields, such as medical imaging, security scanning, nuclear physics or astronomy. The nuclear physics applications or high-frame-rate imaging require scintillation materials with very fast response. The vacuum ultra-violet (VUV) scintillators can be one solution. They have been investigated since about two decades ago [1] and they are based on wide band-gap fluorides doped with Nd³⁺ ion. They employ the fast short-wavelength 5d–4f luminescence of the Nd³⁺ ion which is characterized by a decay time of several nanoseconds [1–3]. Other rare-earth luminescence ions emitting at even shorter wavelengths, such as Tm³⁺ or Er³⁺, can be considered as well [4]. The advantage of the shorter emission wavelength consists in better matching with the spectral sensitivity of contemporary VUV photodetectors such as gas electron multiplier (GEM) with micro-pixel chamber or a photomultiplier (PMT) with CsI-coated photocathode [5,6]. As the lifetime of the 5d–4f emission is proportional to the

square of the emission wavelength [7], even shorter response can be expected for the materials doped with Tm³⁺ or Er³⁺. However, the f-shell of these elements contains more than 7 electrons (i.e. it is more than half-filled) which results in existence of the spin allowed high-spin (HS) and spin forbidden low spin (LS) transitions [4]. The lifetime of the latter ones are in the order of microseconds [4], which is a demerit of these ions considering the VUV scintillator applications.

The first studied VUV scintillator was the Nd-doped LaF₃ [1–3]. The Nd³⁺ 5d–4f luminescence is situated at 175 nm and has fast decay time of 6 ns. Its overall scintillation efficiency is high enough for imaging with multiwire chamber [1] and the imaging capabilities of this material were confirmed also in the recent study employing GEM and micro-pixel chamber [8]. In our research we choose this material as a reference.

We have made an attempt to improve the scintillation properties of LaF₃:Nd by Er³⁺ codoping [9]. It was found that the emission spectrum of Er³⁺ overlaps with the excitation one of Nd³⁺ in the VUV region. Therefore, energy transfer from the Er³⁺ 5d-levels toward the Nd³⁺ 5d ones was expected. It was supposed that introduction of such a transfer stage may lead to improvement of the energy transfer from the host matrix to the Nd³⁺ luminescence centers. The energy transfer from the Er³⁺ ions to the Nd³⁺ ones

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was finally proved but no improvement of scintillation efficiency was reliably confirmed.

Another candidate was Nd-doped BaY_2F_8 , which was studied also by some of us [10]. The Nd^{3+} emission is shifted to longer wavelengths at 186 nm and therefore its decay time is prolonged to some 15 ns. We also tried to improve this material by Er^{3+} codoping following the above described idea. Again, the energy transfer from Er^{3+} to Nd^{3+} was proved. On the other hand, the Er^{3+} 4f-levels were populated also via the host levels under X-ray excitation which resulted in strong slow 4f–4f emission. Partial admixture of Lu into the BaY_2F_8 host matrix led to improvement of the scintillation efficiency which was as high as that of $\text{LaF}_3:\text{Nd}$ [12]. Similar scintillation efficiency was also observed for the Nd-doped monoclinic BaLu_2F_8 analogue [13] in the VUV region. However, in both cases, the population of the 4f-levels of the doping ions via the host levels was significant and another matrix needed to be searched for.

Very favorable properties, such as very high overall scintillation efficiency exceeding several times that of $\text{LaF}_3:\text{Nd}$, were found for the Nd-doped LuF_3 heavy fluoride [14]. The Nd^{3+} emission was peaking at around 180 nm and the scintillation response was characterized by a leading decay time as fast as 8 ns. Its high density of 8.3 g/cm^3 resulting in high stopping power is also an advantage for gamma-ray detection. The scintillation properties were reported for the high-quality Czochralski-grown single crystal [15]. The Er^{3+} and Tm^{3+} dopants were tested as well [14]. Despite the relatively low overall scintillation efficiency, the 5d–4f emission of Er^{3+} and Tm^{3+} was shifted to shorter wavelengths around 160 nm, where for example the PMT with CsI-coated photocathode is several times more sensitive than at 180 nm [6].

The aims of this work are to develop Nd-doped, Er-doped and doubly Er,Nd-codoped LuF_3 VUV scintillation crystals and study their luminescence and scintillation properties and also confirm energy transfer from Er^{3+} to Nd^{3+} ions in the doubly doped sample and possible scintillation efficiency improvement. Another aim is to find the optimal Er concentration in the Er-doped samples.

2. Experimental

Fluoride powders of 4N purity from Stella Chemifa Co. Ltd. were used as starting materials. The mixture of the LuF_3 , NdF_3 and/or ErF_3 powders was used. The undoped sample and the samples with following dopants and concentrations (molar percents) were prepared: Nd 1%, Er 1%, Er 3%, Er 5%, Er 10% and doubly doped $\text{Er}1\%\text{Nd}1\%$. The samples will be further denoted by dopant and nominal molar percents.

Crystal growth was carried out with graphite crucible under $\text{Ar} + \text{CF}_4$ (9:1) atmosphere using the micro-pulling-down (μ -PD) furnace with vacuum-tight systems tailored for fluoride growth, for details see [16]. 43 mol% 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 melting and growth process was monitored by CCD camera. 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. They were cut along the growth axis and polished with 0.3 μm diamond paste. Obtained plates with the dimension of $2.0 \times 5.0 \times 1.0 \text{ mm}^3$ 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 PMT (R374, Hamamatsu) and D_2

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 PMT 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. 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. To compare the RL intensity, RL of high quality $\text{LaF}_3:\text{Nd}8\%$ standard sample was measured.

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 (model 113, ORTEC), shaped (572A, ORTEC) with a shaping time of 500 ns, and read out with a multi-channel analyzer (8000A, AMPTEK). After obtaining the pulse height spectra, the channel positions of the full absorption peak was estimated. Again, the $\text{LaF}_3:\text{Nd}8\%$ was measured as a reference.

3. Results and discussion

The transparent LuF_3 crystals doped with Nd1%, Er1%, 3%, 5%, 10% together with the undoped and doubly doped $\text{Er}1\%\text{Nd}1\%$ LuF_3 crystals were successfully grown by the micro-pulling-down method (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 transmittance spectra for the undoped, Er1%, Nd1% and doubly doped $\text{Er}1\%\text{Nd}1\%$ in the VUV/UV region are shown in Fig. 1. Most of the samples are quite transparent in this region. The transmittance of the Nd1% sample was decreased probably due to sample size. The transmittance drop at 155 nm for Er-doped sample is due to the Er^{3+} 4f–5d transition, while that at 170 nm for the Nd-containing samples is due to the Nd^{3+} 4f–5d transition. In

Fig. 1. Transmittance spectra in the VUV/UV region for the undoped, Er1%, Nd1% and $\text{Er}1\%\text{Nd}1\%$ LuF_3 crystals.

the spectra of the Er-containing samples, the sharp peaks related to Er^{3+} 4f–4f transitions can be clearly observed. The most intense one at 255 nm was ascribed to the $^4\text{I}_{15/2}$ – $^2\text{I}_{7/2}$ transition.

The transmittance spectra for the samples with different Er concentrations were measured as well (not shown here). All of them are very similar to that for the Er1% sample, but the magnitude of the Er^{3+} 4f–4f absorption peaks increases with increasing Er^{3+} concentration. Moreover, systematic improvement of transmittance with increasing Er^{3+} concentration was clearly noticed between 160 and 230 nm. No explanation has been found so far for this phenomenon.

To estimate the overall scintillation efficiency of the samples, the X-ray-excited radioluminescence spectra in the VUV/UV region were measured for the Er1%, Nd1% and Er1%Nd1% samples. They are compared together with the spectrum for the $\text{LaF}_3\text{:Nd8\%}$ in Fig. 2. The overall scintillation efficiency of $\text{LuF}_3\text{:Er1\%}$ is roughly 640% of that for the $\text{LaF}_3\text{:Nd8\%}$ reference scintillator. It is worth reminding that imaging capability was confirmed for the LaF_3 reference scintillator by other research teams [1,6]. The dominant emission wavelength at 163 nm was ascribed to the Er^{3+} 5d–4f HS transition. Weak fast low-spin LS emission was also observed at 155 nm. The efficiency of the $\text{LuF}_3\text{:Er1\%Nd1\%}$ is even slightly higher – 720% and the dominant emission wavelength at 176 nm is due to the Nd^{3+} 5d–4f emission. It is necessary to note that the Er^{3+} 5d–4f HS band is completely absent (in the spectrum for the Er,Nd doped sample), which is due to the energy transfer from Er^{3+} to Nd^{3+} . The overall scintillation efficiency of $\text{LuF}_3\text{:Nd1\%}$ is the highest, despite the small sample size and decreased transmittance (Fig. 1), but not as high as observed for the high-quality Czochralski-grown $\text{LuF}_3\text{:Nd}$ crystal observed in [15]. It might be that there is also a competition between the Er^{3+} and Nd^{3+} ions for excitation energy in the doubly doped sample, which can be the reason for slight decrease of its overall scintillation efficiency.

Fig. 3 compares the radioluminescence spectra of the samples with different Er concentrations. The samples with 1% and 3% Er have the highest overall scintillation efficiency, while with increasing Er concentration the efficiency decreases due to concentration quenching. The optimal Er concentration can be therefore between 1% and 3%.

To investigate further the scintillation and luminescence mechanism, the radioluminescence spectra in the UV–visible region under X-ray excitation were measured for the Er1%, Nd1% and doubly doped Er1%Nd1% samples (Fig. 4). In this region, numerous

Fig. 2. X-ray-excited radioluminescence spectra in the VUV/UV region for the, Er1%, Nd1% and Er1%Nd1% LuF_3 crystals compared together with the $\text{LaF}_3\text{:Nd8\%}$ reference scintillator.

Fig. 3. X-ray-excited radioluminescence spectra in the VUV/UV region for the, Er1%, Er3% and Er5% and Er10% LuF_3 crystals.

4f–4f peaks can be observed in all the spectra. The 4f–4f emission was negligible for Nd1% sample. For the Er1%Nd1% sample the Er^{3+} 4f–4f intensities considerably decreased with respect to the Er-only doped sample. It seems that the energy transfer from Er^{3+} to Nd^{3+} is competitive to the energy leak from Er^{3+} 5d level to the 4f ones [4]. The same was observed also in complementary photoluminescence measurements, when the same spectra were taken under 138 nm excitation, which corresponds both to the 4f–5d excitation of Er^{3+} (not shown here). While strong 4f–4f emission was observed for the Er1% sample under 4f–5d excitation, this emission was considerably weaker for the doubly doped Er1%Nd1% sample. On the other hand in the scintillation process under X-ray excitation also a simple competition between Er^{3+} and Nd^{3+} for excitation energy can take place as a parallel process.

The luminescence mechanism in the Er1%Nd1% doubly doped sample can be described by the schematic depicted in Fig. 5. The thermalized electrons and holes can recombine directly on Nd^{3+} giving rise to the fast Nd^{3+} 5d–4f emission. Or, they can be captured by the Er^{3+} ion. Here the excitation energy can migrate to the Nd^{3+} (as described by the green dashed arrows) or, it can leak from the Er^{3+} 5d-level to the $^2\text{F}_{5/2}$ f-level (as described by the small red arrow) giving rise to the 4f–4f emission. These two processes are in competition. It is necessary to add that the f-levels can be

Fig. 4. X-ray-excited radioluminescence spectra in the UV–visible region for the, Er1%, Nd1% and Er1%Nd1% LuF_3 crystals.

Fig. 5. The schematic of the luminescence mechanism in doubly doped LuF₃:Er1%Nd1% crystal.

Fig. 7. The pulse height spectra for the Er1%, Er3%, Er5% and Er10% LuF₃ crystals.

also populated via the excitonic levels of the LuF₃ host. Obviously, the Er³⁺ 5d state should consist of two close-lying levels, the high spin one and the low spin one at slightly higher energy. This was omitted for simplicity.

To determine the scintillation light yield, the pulse height spectra were also measured for the samples using the ²⁴¹Am 5.5 MeV alpha-ray source and a photomultiplier with CsI-coated photocathode (Fig. 6). It is worth pointing out that all the LuF₃ crystals outperform the LaF₃:Nd8% reference crystal. The light yield for Er1%-doped sample was considerably lowered probably due to slow HS component of Er³⁺ 5d–4f emission with a decay time of microsecond order, which was too long for the 500 ns shaping time. The Er1%Nd1% doubly-doped sample shows the highest light yield, despite its overall scintillation efficiency was inferior to that of the Nd-doped sample. Further research is necessary to clarify these results. One can also keep in mind that the charge carrier density for alpha ray excitation is completely different when compared to that for gamma-ray or X-ray excitation. Therefore, the samples are excited in different way when measuring the X-ray-excited radioluminescence spectra and alpha-ray-excited light yield. The alpha-ray excitation was chosen due to small sample size, which decreases the probability to capture gamma-ray photon. However, it is worth mentioning that some small signal could be observed in the light yield experiment upon gamma-ray excitation from ¹³⁷Cs source, but it was hard to determine position of the full absorption peak. No signal was observed for the LaF₃:Nd8%, which again confirms the high efficiency of the LuF₃-based scintillators.

Fig. 7 compares the pulse height spectra for the LuF₃ samples with different Er concentration. All the crystals again outperform

the LaF₃:Nd8% reference. The Er3% sample showed the highest light yield among the Er-doped samples, even though its overall efficiency was the same as for the Er1% sample. The light yield of the other samples with higher Er concentration is most probably degraded by the concentration quenching.

4. Conclusions

The Nd-doped, Er-doped and Nd,Er doubly doped LuF₃ single crystals were grown by micro-pulling-down method. The LuF₃:Er1% showed good scintillation efficiency (6 times of that of LaF₃:Nd8% reference scintillator) and suitable position of the emission spectra in the sensitivity region of the CsI-photocathode. Er³⁺ 5d–4f high-spin transition is dominant at 163 nm, but due to presence slow component of microsecond order, its light yield was lowered for the 500 ns shaping time.

From the results on samples with different Er concentration, the optimal Er concentration is between 1 and 3 mol%. Systematic increase of transmittance in the VUV region was observed with increasing Er concentration.

The overall scintillation efficiency of LuF₃:Er1%Nd1% crystal exceeded that of LaF₃:Nd8% about 7 times and the Nd³⁺ 5d–4f emission is dominant in VUV region at 176 nm. Energy transfer seems to work from Er³⁺ to Nd³⁺ ion as the Er³⁺ 5d–4f emission is not observed under X-ray excitation. Er-codoping does not seem to improve the overall scintillation efficiency, but increased the light yield.

The overall scintillation efficiency of LuF₃:Nd1% was the highest, despite small sample size and degraded transmittance.

5. Uncited reference

[11].

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Fig. 6. The pulse height spectra for the Er1%, Nd1% and Er1%Nd1% LuF₃ crystals compared together with that of the LaF₃:Nd8% reference scintillator.

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