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Radiation Measurements

journal homepage: www.elsevier.com/locate/radmeas Doubly doped BaY₂F₈:Er,Nd VUV scintillatorJan Pejchal^{a,b,*}, Martin Nikl^b, Kentaro Fukuda^c, Noriaki Kawaguchi^c, Takayuki Yanagida^a, Yuui Yokota^a, Akira Yoshikawa^{a,d}, Vladimir Babin^e^a Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan^b Institute of Physics AS CR, Cukrovarnicka 10, 16253 Prague, Czech Republic^c Tokuyama Corporation, Shibuya 3-chome, Shibuya-ku, Tokyo 150-8383, Japan^d New Industry Creation Hatchery Center (NICHe), Tohoku University, 6-6-10 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan^e Sincrotrone Trieste S.C.p.A., Basovizza-Trieste 34012, Italy

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ABSTRACT

Doubly doped BaY₂F₈:Er,Nd scintillation crystals were grown by modified micro-pulling-down method. The Er co-doping was chosen to enhance the energy transfer from the host lattice to the Nd³⁺ luminescence center via the 5d-levels of Er³⁺, which can be enabled by the overlap of Er³⁺ 5d-4f emission spectrum with the Nd³⁺ 4f-5d absorption. The energy transfer was clearly evidenced in the BaY₂F₈:Er,Nd. The processes are complicated by energy migration to killer centres and/or cross-relaxation processes. The luminescence and energy transfer mechanism are discussed.

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1. 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 (Schotanus et al., 1989; Chechik and Breskin, 2008). One of the promising candidates for the VUV scintillators can be for example the Nd-doped LaF₃ or BaY₂F₈ (BaYF).

The LaF₃:Nd scintillator has been quite intensively studied in the past (Schotanus et al., 1989; Dorenbos et al., 1996; Dorenbos et al., 1993). The 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 Nd³⁺ ion (Schotanus et al., 1989).

The BaYF is known as a cross-luminescent scintillation material (Rodnyi, 2004), it was also considered as a suitable laser host (Agnesi et al., 2003). The Nd³⁺ fast VUV luminescence can be also exploited,

however, its light yield does not reach suitably high values (van Eijk et al., 1994) due to inefficient energy transfer from the host to the Nd³⁺ luminescence center. Its density is a bit lower (4.97 g/cm³), but still sufficient for efficient γ -ray and X-ray detection.

One of the ways of improving the scintillation properties can be the Er co-doping. The idea is to enhance the energy transfer to the Nd³⁺ ions via the Er³⁺ excited levels, as the Er³⁺ 5d-4f emission spectrum overlaps with the Nd³⁺ 4f-5d absorption band, see Fig. 1.

2. Experimental details

The fluoride powders of 4 N purity from Stella Chemifa Co. Ltd. were used as starting materials. For BaYF the stoichiometric mixture of the BaF₂, YF₃, ErF₃ and NdF₃ powders was used. The crystals of the formula BaY_{2-x-y}Er_yNd_xF₈ with composition of $y = 0.01, 0.1, 0.3$ and 1 both for $y = 0.01$ and 0.05 were prepared. The samples will be further denoted in nominal molar percents.

Crystal growth was carried out with graphite crucible under Ar + CF₄ atmosphere using the micro-pulling-down (μ -PD) furnace with vacuum-tight systems tailored for fluoride growth, for details see (Yoshikawa et al., 2004).

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).

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Fig. 1. Scheme of the expected energy transfer in the Nd,Er doubly doped scintillator.

The chemical composition was analyzed by electron probe micro-analysis (EPMA) using an electron probe focused to 10 μm spot with JEOL JXA-8621MX analyzer.

Emission spectra were obtained at the Spectrofluorometer (Bunko-keiki Co. Ltd.) using VUV sensitive PMT (R374, Hamamatsu) and D₂ steady-state lamp as an excitation source. Measurements were not corrected for experimental distortions.

The decay time and some emission spectra measurements in the VUV emission region were performed using SUPERLUMI station of the DORIS positron storage ring in HASLAB, DESY, Hamburg (Zimmerer, 2007).

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.

3. Results and discussion

3.1. Crystal growth

The as grown crystals were of 2.0–2.5 mm in diameter and around 40–70 mm in length. Neither visible inclusions nor cracks were observed. The surface of the BaYF crystals was a bit rough and opaque, but the crystals were transparent inside. In this case no segregation was observed and both dopants were well incorporated into the lattice. The XRD confirmed the monoclinic BaYF structure.

The crystals were cut along the growth axis and polished with 0.3 μm 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.

Fig. 2. The emission spectrum of the BaYF:Er 10% sample under 147 nm excitation. The excitation spectrum for the 185 nm emission of the Er-free BaYF:Nd 1% sample is also included to demonstrate the possibility of energy transfer.

Fig. 3. Emission spectrum of the BaYF:Er1%Nd1% sample under 140 nm excitation.

3.2. Luminescence characteristics

The emission spectrum of the BaYF:Er 10% sample under 147 nm excitation is shown in the Fig. 2. Two 5d-4f luminescence transitions to the Er^{3+} ground state are observed. The fast luminescence originating from the spin-allowed low spin (LS) state and slow one from the spin-forbidden high spin (HS) state (Wegh and Meijerink, 1999) are peaking at 161 and 169 nm, respectively. The excitation spectrum for the 185 nm Nd^{3+} emission of the Er-free BaYF:Nd 1% sample is also included. The overlap of the Er^{3+} emission and Nd^{3+} excitation spectra is apparent. The necessary condition for energy transfer from the Er^{3+} ion to the Nd^{3+} one is well fulfilled.

It is important to emphasize the presence of slow component in the fast LS peak and fast component in the slow HS one in BaYF:Er 10%, Fig. 2. This might be due to some interaction or coupling of these two levels in Er^{3+} . However, it can be simply an instrumental effect, since the decay curve of the fast LS peak covers both the fast and slow measurement time windows. The same is obviously valid for the long HS peak-related decay curve.

It is also worth mentioning that Er^{3+} 4f-4f emission features were observed above 300 nm, which is a consequence of the energy leak to the 4f Er^{3+} levels.

The emission spectrum of the doubly doped BaYF:Er1%Nd1% sample under 140 nm (Er^{3+} 4f-5d band) excitation is shown in the Fig. 3. The Nd^{3+} 5d-4f emission dominates in the spectrum at

Fig. 4. The photoluminescence decay curve for the BaYF:Er1%Nd1% 185 nm emission under 147 nm excitation. The equation of the fitted function is included.

Fig. 5. Radioluminescence spectra of various BaYF:Er,Nd samples.

185 nm, while the Er^{3+} 5d–4f luminescence at 161 and 169 nm is very weak. This implies that the Er^{3+} emission is significantly reabsorbed by the Nd^{3+} ion, as can be expected from the overlap of the Nd^{3+} excitation and Er^{3+} emission spectra shown in Fig. 2. This can be a proof for the expected energy transfer. However, it is important to keep in mind that the excitation spectra of both ions significantly overlap (Pejchal, unpublished), so there can be also a competition between these ions for the excitation energy and the Nd^{3+} luminescence can be also excited directly. Moreover, Er^{3+} 4f–4f features were again observed above 300 nm, and then some energy is also transferred to the 4f-levels within the Er^{3+} ions. To obtain further proof of the energy transfer, the photoluminescence (PL) decay curves have been measured (Fig. 4). The curve has been fitted with two-exponential function. In the initial part the curve is characterized by an exponential with negative amplitude, which is a consequence of (most probably non-radiative) energy transfer from Er^{3+} to the Nd^{3+} . The rest of the curve is governed by the decay time around 30 ns, which is 2 times longer than Nd^{3+} emission in Er-free BaYF crystals (van Eijk et al. 1994). This discrepancy has not been explained yet. It is connected most probably to the prolongation of the decay time of the Er^{3+} LS-peak-related emission observed in the BaYF:Er10% sample (Pejchal, unpublished). Then the curve continues in the background level (Fig. 4), which is, however, about 6 times higher than the true instrumental background. It means that some component, much longer than the measurement time window, is present. It can be related to the (most probably radiative) energy transfer from the Er^{3+} spin-forbidden HS level to the Nd^{3+} .

The radioluminescence spectra in the VUV/UV range under X-ray excitation are shown in Fig. 5. The BaYF:Er10% sample shows a clear Er^{3+} HS 5d–4f luminescence peak at 169 nm. The LS 5d–4f

luminescence peak at 161 nm is much less intense. This can be an instrumental effect, as the spectra were not corrected for the spectral sensitivity of the detection part (the spectrum in the Fig. 2 was measured with different apparatus). Nd^{3+} codoping suppresses the Er^{3+} emission and the Nd^{3+} emission appears; this is most significant in the BaYF:Er1%Nd1% sample where the concentrations of both doping ions are equal. The energy transfer from Er^{3+} to Nd^{3+} is apparent again. Further increase of Er^{3+} concentration leads to Nd^{3+} luminescence intensity decrease and slight increase of the Er^{3+} emission. The former is caused by the energy migration over the Er-sublattice towards some killer centres. This fact implies that the Er^{3+} concentration must be low enough to hamper this undesired energy migration (it might be also probably some cross-relaxation process drawing energy off the Nd^{3+} luminescence center). The optimal Er^{3+} and Nd^{3+} concentrations should be found. The Er^{3+} emission intensity increases with increasing Er^{3+} concentration because the Nd^{3+} ion concentration is not sufficient to draw the energy off the Er-sublattice and radiative recombination takes place also on the Er^{3+} ions.

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