

Luminescence properties of VUV single crystal scintillator based on high temperature modification of BaLu₂F₈

J. Pejchal^A, K. Fukuda^B, V. Babin^C, S. Kurosawa^A, Y. Yokota^A, M. Nikl^C, A. Yoshikawa^{A,D}

IMR, Tohoku University^A

Tokuyama Corp.^B

Institute of Physics of the Academy of Sciences of the Czech Republic^C

NICHe, Tohoku University^D

To develop new fast VUV scintillator material, Tm³⁺ and Nd³⁺-doped BaLu₂F₈ crystals (high temperature modification) were grown by modified micro-pulling-down method including quenching process. Lu-containing matrix was chosen to increase the density and modify the self-trapped exciton levels to hamper the energy transfer from the host lattice to the rare-earth 4f levels. In photoluminescence measurements, the VUV 5d-4f emission of the dopants was clearly observed together with the 4f-4f ones. However, surprisingly, in the radioluminescence measurements no 5d-4f luminescence was observed. Lowered transmittance in the VUV region does not seem to be the cause of this. Also, other luminescence processes of an intrinsic origin, such as self-trapped exciton or defect luminescence were detected.

1. Introduction

The development of new X-ray or gamma-ray radiation detection systems based on the vacuum ultraviolet (VUV) scintillators has begun in the recent past. These scintillators can be coupled with the photodetectors 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]. Recently developed micro-pixel chambers can be considered as well [3]. One of the promising candidates for the VUV scintillators can be for example the Nd-doped LaF₃ or BaY₂F₈ (BaYF). Other fluorides have been studied recently. They are for example BaF₂:Nd [4] and complex fluorides such as K₂NaLuF₆ [5]. In the latter case the Tm³⁺ luminescence center was introduced. Er³⁺ or Tm³⁺ VUV luminescence centers were studied also in LiCaAlF₆ matrix [6].

The LaF₃:Nd scintillator has been quite intensively studied in the past [1, 7, 8]. 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 [1]. Despite these favorable properties, its light yield is not so high.

The BaYF is known as a cross-luminescence scintillation material [9], it was also considered as a suitable laser host [10]. The Nd³⁺ fast VUV luminescence can be also exploited, however, its light yield also does not reach suitably high values [11] due to not so efficient energy transfer from the host to the Nd³⁺ luminescence center. Its density is a bit lower (4.97g/cm³), but still sufficient for efficient γ -ray and X-ray detection.

To improve the BaYF:Nd scintillator performance, Er co-doping was studied recently by our group [12]. Similar procedure was applied also to different complex fluorides, such as LiLuF₄ [13]. The idea was 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. It was found that the energy transfer works well but it is further complicated by a nonradiative transition from the Er³⁺ 5d levels to the 4f ones and giving rise to slow 4f-4f Er³⁺ luminescence in the UV-VIS region, which means slowing-down of the scintillator response and shifting the emission wavelength to the UV/visible range, which is not suitable for the mentioned

photodetectors. Due to a complicated level structure of the Er^{3+} (and Nd^{3+}) ion, a cross-relaxation process from the 5d state to the 4f ones can take place as well.

On the other hand, the level structure of the Tm^{3+} ion is much less complicated with respect to that of Er^{3+} and there is a large energy gap between the lowest 5d-level and the highest 4f-level [14]. Thus one may expect that the nonradiative transition to the 4f-levels is much less probable and can be even absent. Tm^{3+} was supposed to be more suitable codopant to improve the BaYF:Nd scintillator performance. It was indeed found that the energy transfer concept works well and in the photoluminescence experiments no energy transfer from the 5d to the 4f levels was observed [15]. However, after the X-ray excitation, quite significant 4f-4f luminescence peaks appeared in the UV/visible region. They were related mostly to the Tm^{3+} emission, but weak Nd^{3+} peaks were also observed. It was suggested that the enhancement of the 4f-4f luminescence is due to the energy transfer from the BaYF exciton levels to the Tm^{3+} 4f-levels [15]. The very broad exciton emission in BaYF is positioned around 300 nm and overlaps with the Tm^{3+} 4f levels. Therefore, there is a need to modify the host lattice levels to suppress such an unwanted energy transfer. First attempt to modify the BaYF host was replacing the Y ion by Yb. This increases the material density up to 7g/cm^3 , which improves its suitability for the gamma or X-ray radiation detection but narrows the band-gap around to around 160 nm due to additional charge-transfer levels [16]. The bandgap of BaYF is about 125 nm. Unfortunately, no 5d-4f emission neither from Tm^{3+} nor Nd^{3+} was observed. In the first case, the 5d-levels were buried in the lowered conduction band states and in the second case the electron-transfer quenching took place. Such a hypothesis can be well supported by a reference [18], where the Nd^{3+} 5d-state is predicted to be above the charge-transfer state of the Yb^{3+} .

Lu admixture is another possibility to modify the BaYF crystal.

Our recent study about Lu-admixed BaYF has shown relatively good overall scintillation efficiency slightly exceeding that of $\text{LaF}_3:\text{Nd}$ [19]. As the Nd concentration in the Lu-admixed BaYF was 8 times lower than for the reference $\text{LaF}_3:\text{Nd}$ scintillator, it was clear there is a room for this material optimization.

Recently, we also studied the Y-free crystal, i.e. BaLu_2F_8 (BaLuF). Such material has been of interest in the past as possible laser host or heavy scintillator [20, 21]. It is quite demanding to prepare the BaLuF due to the phase transition from orthorhombic to monoclinic structure occurring some 50°C below the melting point (945°C) and therefore the literature on this material is quite scarce and sometimes discouraging results had been obtained [21]. However, recently this material has been prepared by some of us and scintillation properties comparable to that of Lu-admixed BaYF were observed [22].

Regarding the high-temperature modification of BaLuF , interesting luminescence properties and energy transfer phenomena were found due to two inequivalent Lu sites in the matrix [20]. Therefore, such a host material would be interesting because of the possibility of enhancement of the energy transfer between rare-earth codoping ions, as was described above.

2. Experimental details

The fluoride powders of 4N purity from Stella Chemifa Co. Ltd. were used as starting materials. The stoichiometric mixture of the BaF_2 , YF_3 , LuF_3 , TmF_3 and NdF_3 powders was used. The crystals with composition of $\text{BaLu}_2\text{F}_8:\text{Tm}$ 1mol%, $\text{BaLu}_2\text{F}_8:\text{Nd}$ 1mol% , codoped $\text{BaLu}_2\text{F}_8:\text{Nd,Tm}$ 1mol% and the undoped sample were prepared. The samples will be further denoted with dopant and nominal molar percents.

Crystal growth was carried out with graphite crucible under $\text{Ar} + \text{CF}_4$ atmosphere using the modified micro-pulling-down ($\mu\text{-PD}$) method [17] with quenching process. The as grown crystals were of 2.0-2.5 mm in diameter and around 10 mm in length. 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. 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). The XRD confirmed the orthorhombic structure, with some small amount of the monoclinic low-temperature phase, though the crystals were transparent.

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. An X-ray tube operated at 60kV and 35mA with Mo 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.

As all the emission spectra were not corrected for the above mentioned experimental distortions, it is worth adding that all our conclusions based on spectral intensity comparison are not affected by this fact as we do not make intensity comparisons so far.

3. Results and discussion

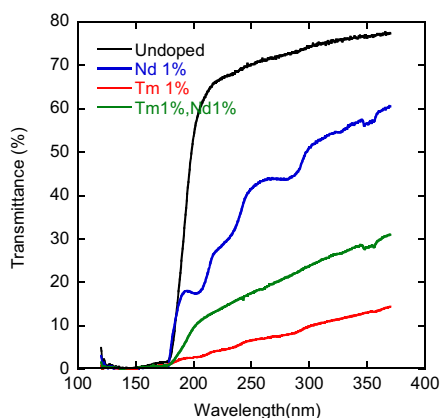


Figure 1. Transmittance spectra of all the samples in the UV/VUV region.

The transmittance spectra of all the samples are compared in the figure 1. The Tm1% sample shows the poorest values, most probably to a little reduced crystal quality. The common feature for all the curves is the sharp decrease at around 170nm. The origin of this edge is not clear, but it can be related to the presence of the monoclinic phase. The radioluminescence spectrum of the Nd1% sample is displayed in the figure 2. No apparent sign of the VUV 5d-4f emission can be seen besides the host broad band around 300nm and the 4f-4f peaks.

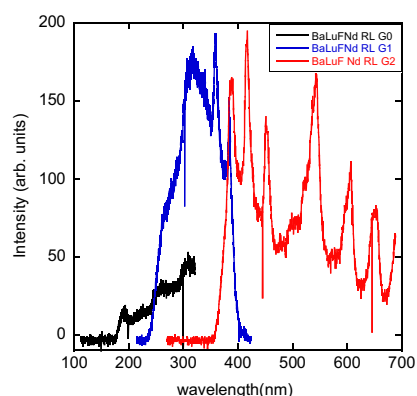


Figure 2. Radioluminescence spectrum of the Nd1% sample.

For the Tm1% sample the situation was very similar and the 4f-4f peaks were very intense.

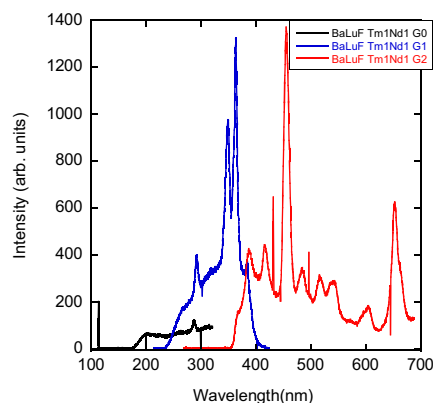


Figure 3. Radioluminescence spectrum of the Tm1%Nd1% sample.

The radioluminescence spectrum of the Tm1%Nd1% co-doped sample is displayed in the figure 3. Again, no apparent sign of the VUV 5d-4f emission of both dopants can be seen besides the host broad band around 300nm and the 4f-4f peaks, which are again more intense in case of Tm. In the case of photoluminescence, the situation is dramatically different. The photoluminescence spectrum of the Nd1% under 160nm excitation is shown in the figure 5. The Nd³⁺ 5d-4f luminescence is clearly visible (despite low transmittance in VUV/UV region) at 180, 228 and 261nm together with the 4f-4f lines. It means the 5d-4f emission is very efficiently excited. However, it seems the energy transfer from the matrix to the 5d levels under x-ray excitation is very inefficient.

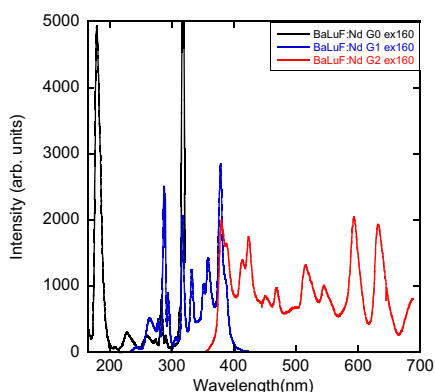


Figure 5. Radioluminescence spectrum of the Nd1% sample in the VU-visible region.

Regarding the Tm1% sample, under 157nm excitation (4f-5d Tm^{3+} absorption), the Tm^{3+} 5d-4f features were clearly observed (not shown here) but the 4f-4f ones were very weak and obscured by a broad band around 400nm. This can be related to host or defect emission, as it is excited below the band-gap. For the co-doped Nd1%Tm1% sample, under the same excitation band, 5d-4f features of both ion were observed, while those of Nd^{3+} were much more pronounced. It seems the energy transfer from Tm^{3+} to Nd^{3+} might work. A broad band around 400nm slightly overlapping with the 4f-4f features was observed, which again points to some defect luminescence.

4. Conclusions

Undoped, Tm1%, Nd1% and Tm1%Nd1% (mol) doped orthorhombic $BaLu_2F_8$ (high-temperature modification) single crystals have been successfully grown by micro-pulling down method. Some amount of monoclinic phase was detected by XRD. 5d-4f luminescence of the Tm and Nd ions was observed only in the photoluminescence measurements and were absent under X-ray excitation. Also, broad band around 400nm was observed in all the measurements and is probably related to defects, maybe connected with the unwanted monoclinic phase. It can be responsible for the absence of 5d-4f emission in radioluminescence due to competition for the excitation energy.

References

- [1] P. Schotanus, et al., IEEE T. Nucl. Sci. **36**, 132 (1989)
- [2] R. Chechik and A. Breskin, Nucl. Instrum. Meth. A **595**, 116 (2008)
- [3] A. Takada, et al., Nucl. Instrum. Meth. A **573**, 195 (2007)
- [4] T. Yanagida, et al., Radiat. Meas. **45**, 422 (2010)
- [5] N. Abe, et al., Opt. Mater. **32**, 589 (2010)
- [6] A. Yoshikawa, et al., Opt. Mater. **32**, 845 (2010)
- [7] P. Dorenbos, et al., J. Lumin. **69**, 229 (1996)
- [8] P. Dorenbos, et al., IEEE T. Nucl. Sci. **37**, 119 (1993)
- [9] P. A. Rodnyi, Radiat. Meas. **38**, 343 (2004)
- [10] A. Agnesi, et al., Opt. Express **11**, 1149 (2003)
- [11] C. W. E. van Eijk, et al., IEEE T. Nucl. Sci. **41**, 738 (1994)
- [12] J. Pejchal, et al., Radiat. Meas. **45**, 265 (2010)
- [13] J. Martincik, et al., Radiat. Meas. **45**, 403 (2010)
- [14] P. S. Pejzdel, et al., J. Solid State Chem. **178**, 448 (2005)
- [15] J. Pejchal et al., IOP Conf. Ser.: Mater. Sci. Eng. **15**, 012018 (2010).
- [16] D. N. Karimov, et al., Cryst. Reports **51**, 1009 (2006)
- [17] A. Yoshikawa, et al., J. Cryst. Growth **270**, 427 (2004)
- [18] P. Dorenbos, J. Phys. Condens. Matter **15**, 8417 (2003)
- [19] J. Pejchal et al., accepted in IEEE T. Nucl. Sci., doi: 10.1109/TNS.2012.2197418
- [20] A. A. Kaminskii et al., J. Alloys and Compounds **275–277**, 442 (1998).
- [21] J. Van't Spijker et al. J. Lumin. **85**, 11 (1999).
- [22] J. Pejchal et al., presented at ICOOPMA12 conference, accepted for publication.