A preliminary assessment of Lu₂Y₂Al₂O₉:Pr (LuYAM:Pr) as a potential scintillator

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Highlights

- LuYAM:Pr crystals have been grown by the μPD method.
- Radio-, photo-, and thermoluminescence of LuYAM:Pr have been studied.
- At RT fast d-f luminescence of Pr³⁺ ions has not been detected.

Abstract

Lu₂Y₂Al₂O₉:Pr crystals have been grown by the micro-pulling-down method and their basic luminescence properties have been examined in order to estimate their utility for scintillator applications. The performed studies comprise the measurements of radioluminescence spectra as a function of temperature, photoluminescence emission and excitation spectra, and low temperature thermoluminescence glow curves. A comparison of the present results with those obtained recently for Y₄Al₂O₉:Pr indicates that in spite of a higher density Lu₂Y₂Al₂O₉:Pr is a much less promising material, which is mainly due to the absence of the fast Pr³⁺ d-f emission.

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1. Introduction

In our previous paper (Drozdowski et al., 2015) we have shown that among praseodymium activated materials, besides the quite well-known RE₃Al₅O₁₂ garnets (Nikl et al., 2013; Nikl and Yoshikawa, 2015) and REAlO₃ perovskites (Nikl et al., 2010; Nikl and Yoshikawa, 2015), the third group of compounds belonging to the RE₂O₃-Al₂O₃ system (Schneider et al., 1961), namely the RE₂Al₂O₆ monoclincs, should also be considered in the quest for new scintillators. The examined representative of this group, Y₄Al₂O₆:0.1%Pr (YAM:0.1%Pr), has been found to produce fast (~24 ns), yet not efficient (~2000 ph/MeV) scintillation, clearly leaving some room for improvement.

In the recent years a lot of attention has been focused on multicomponent materials, basically grown in a spirit of a so-called bandgap engineering (Fasoli et al., 2011), intended to give some control on the locations of trapping levels within the bandgap and, following a well-thought-out selection of composition, to elevate the scintillation yield. Mixed (Lu₀.₇₅Y₀.₂₅)₃Al₅O₁₂:Pr (Lu₀.₇₅Y₀.₂₅AG:Pr) crystals provide a nice example of a compromise between the increase of light output (by up to 70%) and the decrease of density (by 0.5 g/cm³) compared to Lu₃Al₅O₁₂:Pr (Lu₃AG:Pr). Interestingly, there is no benefit after a further reduction.

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of the Lu-to-Y ratio (i.e. moving towards YAG:Pr), since both the density and the light yield go down (Drozdowski et al., 2014, 2016). If a similar tendency occurred in the yttrium/lutetium monoclinic family, mixed (Lu1−x Yx)2Al2O9:Pr (LuYAM:Pr) crystals would offer both a higher density and a better scintillator performance than YAM:Pr.

In this paper we present a first assessment of LuYAM:Pr, carried out with a Lu2Y2Al2O9:0.1%Pr crystal. Such a composition increases the density from 4.5 g/cm³ (YAM:Pr) to 6.1 g/cm³, whilst the praseodymium concentration of 0.1 at% ensures a compatibility with the previous research (Drozdowski et al., 2015). Our studies comprise the measurements of radioluminescence (RL) and photoluminescence (PL) spectra as a function of temperature, as well as low temperature thermoluminescence (ITTL) glow curves.

2. Materials and experiment

The crystalline fiber of Lu2Y2Al2O9:0.1%Pr (Fig. 1) was grown at the Institute of Electronic Materials Technology (ITME) in Warsaw by the micro-pulling-down (µPD) method. The melt was prepared from the following high purity oxides: Y2O3, Lu2O3, Pr6O11 (99.999%), and Al2O3 (99.99%). The components were mixed in stoichiometric ratios. The growth process was conducted in an iridium crucible under nitrogen atmosphere, at a pulling rate of 0.1 mm/min. The investigated samples were 3–4 mm long rods with a diameter of 2.5 mm. Although Lu2Y2Al2O9:Pr is only an individual representative of the whole family of mixed LuYAM:Pr (i.e. (Lu1−x Yx)2Al2O9:Pr) crystals, for simplicity in Sections 3 and 4 we will refer to it as to LuYAM:Pr.

To verify the structural state of the as-grown fibers, powder X-ray diffraction (XRD) experiments were performed. The XRD data were collected with a Siemens D500 diffractometer. The intensity of the diffraction peaks was recorded in the range of 2θ = 10°–80° with a step of 0.02° and an integration time of 10 s per step. The peak positions observed for LuYAM:Pr (Fig. 2) are well matched with the reference data of Liddell et al. (1998), which confirms that we deal with a monoclinic structure.

A standard set-up constructed out of an Inel generator with a Cu-anode X-ray tube, an ARC SP-500i monochromator, a Hamamatsu R928 photomultiplier tube (PMT), and an APD Cryogenics closed-cycle helium cooler with a Lake Shore 330 temperature controller, was used to record RL spectra and ITTL glow curves between 10 and 350 K. The consecutive RL measurements were started at 350 K and terminated at 10 K to avoid any thermal contribution of the ambient temperature to the RL yield. Prior to the ITTL runs, the samples were exposed for 10 min to X-rays at 10 K. For PL spectroscopy studies, a typical facility consisting of a Princeton Instruments X5424 xenon lamp, two ARC monochromators (SP-2300i for excitation and SP-150 for emission), and a Hamamatsu 1P28 PMT, was employed.

3. Results and discussion

3.1. Radioluminescence

Contrary to room temperature (RT) 137Cs pulse height spectra recorded with Lu2Y2Al2O9:0.1%Pr (not shown), which display no resolvable photopeak at any shaping time, preventing from even a rough estimation of light yield and energy resolution, X-ray induced emission spectra demonstrate a clear response of the crystal to the incident ionizing radiation. At any temperature between 10 and 350 K (Fig. 3a and b) they are yet dominated by the intraconfigurational Pr3+ 4f6 → 4f2 (f-f) luminescence above 480 nm, with only some weak contribution from shorter wavelength bands, strongly decreasing towards RT. This is confirmed by Fig. 3c, in which the integrals of the spectra, both total (190–900 nm) and divided into two ranges (190–480 and 481–900 nm), are depicted as a function of temperature. In this respect, LuYAM:Pr provides an opposition to YAM:Pr, in case of which the bands below 480 nm prevail in RL from 10 K up till RT (Drozdowski et al., 2015). These bands, that have been attributed to both the host emission and the interconfigurational Pr3+ 4f5d → 4f2 (d-f) transitions in YAM:Pr, are almost absent in LuYAM:Pr, at least at RT and above. Unfortunately, such a feature makes LuYAM:Pr a poor scintillator and accounts for the lack of the photopeak in the RT pulse height spectra. Actually, the contribution from the bands located between 260 and 480 nm becomes significant below, say, 200 K. The thermally-dependent variations of their shapes and intensities suggests a multicomponent nature, possibly with some input from the d-f luminescence of the Pr3+ ions occupying different crystallographic sites (Ching and Xu, 1999). The maximum total RL yield is achieved at about 150 K, nevertheless its decrease towards 10 K is almost negligible.

3.2. Photoluminescence

RT excitation spectra of the prominent f-f lines in LuYAM:Pr, 3P0 → 1H4 (485 nm), 3P0 → 1H6 and 1D2 → 1H4 (both 610 nm), are presented in Fig. 4a. The distinct bands between 430 and 480 nm indicate that the aforesaid emissions are excited via the 3P0,1,2 and 1H4, multiplets of the 4f6 configuration (the second component of the 610 nm luminescence also via the 1D2 multiplet). However, in both spectra some weaker bands peaking at 236, 253, 265, and 290 nm appear. Supposedly they are related to the 4f5d configuration. A RT emission spectrum of LuYAM:Pr, measured at a 265 nm excitation...
(expected to produce some $d$-$f$ luminescence), is dominated, likewise in RL, by the Pr$^{3+}$ $f$-$f$ lines, mostly originating from the $^3P_{00}$ level and terminating at the $^3H_{4M}$, $^3H_{6M}$, and $^3F_{2M}$ levels (strong lines within 485–513 nm and 610–674 nm in Fig. 4b), as well as at the $^3H_{5M}$, $^3F_{3M}$, and $^3F_{4M}$ ones (weaker features within 540–575 nm and 713–771 nm in Fig. 4b). Besides, there is a less pronounced, ascending structure between 400 and 480 nm, albeit it is hard to attribute it to the Pr$^{3+}$ $d$-$f$ transitions, which should cover the whole area from near UV to blue (310–470 nm; see the violet arrows in Fig. 4b).

To explain the complete absence of the Pr$^{3+}$ $d$-$f$ luminescence at RT under either ionizing or optical excitation we refer to a simple configuration-coordinate diagram in Fig. 5. The diagram has been built for LuYAM:Pr considering the Born-Oppenheimer approximation and the Franck-Condon principle. Our calculations have utilized a free-ion part of the Hamiltonian as proposed by Carnall et al. (1989) and a crystal-field part following Göriller-Walrand and Binnemans (1996), with all necessary parameters taken after Rabinovitch et al. (2004). The energy values have been determined in a linear approximation (a Taylor expansion at equilibrium), with a presumption of the same curvature for all the parabolas (Henderson and Imbush, 1989). Finally, for the 4f$^5d$ parabola a Stokes shift value of 3150 cm$^{-1}$ has been deduced from our PL experiments, while a maximum phonon energy of 813 cm$^{-1}$ has been assumed after Kaczkan et al. (2014). Now let us suppose that following the 265 nm excitation the system relaxes to the lowest 4f$^5d$ level, from which the $d$-$f$ emission should occur as indicated by the violet arrows in Fig. 4b. However, the lowest 4f$^5d$ parabola intersects with several 4f$^2$ parabolas very close to its minimum. Therefore a strong tendency of the system to relax nonradiatively to the 4f$^2$ states results in a complete quenching of the $d$-$f$ luminescence. Such a tendency must be much weaker in YAM:Pr, in which
3.3. Low temperature thermoluminescence

the &d emission is observed, thus the lowest 4f5d level should lie higher in YAM:Pr compared to LuYAM:Pr. We note that a similar situation takes place amidst perovskites (e.g. YAP:Ce vs. LuAP:Ce; Palczewski, 2016), but an opposite one is met for garnets (YAG:Ce vs. LuAG:Ce; YAG:Pr vs. LuAG:Pr; Ivanovskikh et al., 2012). Although with respect to some structural parameters of the RE2O3·Al2O3 system (Ching and Xu, 1999), monoclinics seem to be in fact closer to perovskites than garnets, this issue clearly deserves a further attention.

3.3. Low temperature thermoluminescence

Fig. 6. A simple configuration-coordinate diagram for LuYAM:Pr.

Fig. 6 compares a long TL glow curve of Lu2Y2Al2O9·0.1%Pr with a curve of Y2Al2O3·0.1%Pr (Drozdowski et al., 2015) recorded under the same experimental conditions. There are more differences than similarities: although both curves are the most intensive between, say, 80 and 240 K, that of LuYAM:Pr consists of less but much broader peaks in this range. Moreover, the TL signal of YAM:Pr vanishes above 320 K (unless there are traps peaking above 350 K), while in case of LuYAM:Pr it increases towards 350 K. Such a feature could indicate that traps are generally deeper in LuYAM:Pr than in YAM:Pr, which agrees with the previous predictions and observations for (Lu,Y)AG:Pr (Dorenbos, 2013; Drozdowski et al., 2014, 2016). Likewise in LuAG:Pr and other materials displaying extraordinarily broad glow peaks, a complex structure of the peaks detected in long TL of LuYAM:Pr (with a probable contribution from quasi-continuous trap distributions) is expected (Brylew et al., 2014), hence there is no point in deconvoluting them into single peaks obeying one of the simple TL models (e.g. that of Randall and Wilkens, 1945). Taking into account the unfavorable role of traps in host-to-ion energy transfer processes, LuYAM:Pr seems to be a slightly better material than YAM:Pr. Simply the value of the “TL/(TL + ssRL)” ratio, interpretable as the fraction of the total excitation energy delivered by the incident radiation that has been accumulated in traps (Drozdowski et al., 2005), is lower for LuYAM:Pr (11%) than for YAM:Pr (16%), nevertheless the disparity is not large.

4. Conclusions

According to the presented data, the first impression on Lu2Y2Al2O9·Pr is rather inauspicious. It is quite straightforward that such benefits as the higher density and the decreased role of charge traps in the energy transfer cannot compensate for the lack of the Pr3+/d-f emission (at least at RT), which has been expected to provide a fast and efficient scintillation in LuYAM:Pr. However, there is a crumb of hope that the current results are biased by the far from ideal growth process, yet insufficiently developed for this particular compound. To verify this option, similar studies on LuYAM:Ce vs. YAM:Ce will be undertaken soon. New series of LuYAM:Pr crystals, differing by the Pr3+/ concentration and/or the Lu-to-Y ratio, are also under consideration.

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