

33000 photons per MeV from mixed $(\text{Lu}_{0.75}\text{Y}_{0.25})_3\text{Al}_5\text{O}_{12}:\text{Pr}$ scintillator crystals

Winicjusz Drozdowski,^{1,*} Kamil Brylew,¹ Andrzej J. Wojtowicz,¹ Jarosław Kisielewski,² Marek Świrkowicz,² Tadeusz Łukasiewicz,² Johan T.M. de Haas,³ and Pieter Dorenbos³

¹*Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Toruń, Poland*

²*Institute of Electronic Materials Technology (ITME), Wolczynska 133, 01-919 Warsaw, Poland*

³*Luminescence Materials Research Group, Faculty of Applied Sciences, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands*

*wind@fizyka.umk.pl

Abstract: $(\text{Lu}_x\text{Y}_{1-x})_3\text{Al}_5\text{O}_{12}:\text{Pr}$ ($x = 0.25, 0.50, 0.75$) crystals have been grown by the Czochralski method and their scintillation properties have been examined. Compared to the well-respected LuAG:Pr scintillator, which has so extensively been studied in the recent years, the new mixed LuYAG:Pr crystals display markedly higher light yields, regardless of the value of x . In particular, $(\text{Lu}_{0.75}\text{Y}_{0.25})_3\text{Al}_5\text{O}_{12}:0.2\%\text{Pr}$ characterized by a yield of 33000 ph/MeV, an energy resolution of 4.4% (at 662 keV), and a density of 6.2 g/cm³, seems to be an ideal candidate to supercede $\text{Lu}_3\text{Al}_5\text{O}_{12}:0.2\%\text{Pr}$ (19000 ph/MeV, 4.6%, 6.7 g/cm³) in various applications. The observed enhancement of light output following the partial substitution of lutetium by yttrium is most probably related to some specific differences in distributions of shallow traps in particular materials.

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OCIS codes: (160.5690) Rare-earth-doped materials; (250.0040) Detectors; (260.2160) Energy transfer; (290.5930) Scintillation

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1. Introduction

Praseodymium activated lutetium aluminum garnet, $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Pr}$ (LuAG:Pr), one of the most notable materials introduced to the market in the 21st century, was first pointed out as a promising heavy and fast scintillator in 2005 by Nikl *et al.* [1]. With a density of 6.7 g/cm^3 , an exquisite energy resolution of 4.6% (at 662 keV), and a fast decay constant of 20 ns, it quickly attracted a lot of attention and was considered and/or implemented into diverse applications, mostly in the field of medical diagnostics [2, 3]. Among a few weaker points of LuAG:Pr there was its scintillation light yield which, not exceeding 20000 ph/MeV, rather failed to measure up to present-day standards and expectations. Efforts were made to increase this value by thermal annealing of crystals in various atmospheres, but the accomplished magnitude of improvement ($\leq 17\%$) was still relatively low [4, 5].

Since the overall scintillation properties of LuAG:Pr were clearly better than those of its isostructural counterpart $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Pr}$ (YAG:Pr), little attention was called to mixed $(\text{Lu}_x\text{Y}_{1-x})_3\text{Al}_5\text{O}_{12}:\text{Pr}$ (LuYAG:Pr) crystals. Mares *et al.* [6] studied a series of Czochralski-grown $(\text{Lu}_x\text{Y}_{1-x})_3\text{Al}_5\text{O}_{12}:0.2\%\text{Pr}$ crystals with $0.9 \leq x < 1$ and observed light outputs between 15000 and 16500 ph/MeV. More promising results were reported by Kamada *et al.* [7] for μPD -grown $\text{Lu}_2\text{YAl}_5\text{O}_{12}:1\%\text{Pr}$ samples, displaying yields up to 24500 ph/MeV. In this paper we prove that the " LuYAG:Pr direction" is correct, present the already achieved scale of the scintillation yield increase, and tentatively explain the mechanism responsible for the enhancement.

2. Materials and experiment

The crystals of $(\text{Lu}_x\text{Y}_{1-x})_3\text{Al}_5\text{O}_{12}:\text{Pr}$ ($x = 0.25, 0.50, 0.75$) were grown at ITME, Warsaw, by the Czochralski method using the Cyberstar Oxypuller 05-03 equipment with an inductive Hüttinger generator. The thermal system consisted of a $\varnothing 50 \times 50 \text{ mm}^3$ iridium crucible embedded in a Zircar zirconia grog, a $\varnothing 60 \times 80 \text{ mm}^3$ passive iridium afterheater placed around the crucible top on the grog, and alumina heat shields around the afterheater. The growth processes were performed in pure nitrogen atmospheres with a pulling rate of 1.0–1.5 mm/h, a rotation rate of 15–20 rpm, and a post-growth cooling time of at least 24 h. In this way optically high-quality single crystals with diameters up to 1 inch and about 2 inch long were obtained. The reference crystals of LuAG:Pr were grown by the Czochralski method at Furukawa Co. Ltd. as described in detail by Ogino *et al.* [8] for the purposes of our previous studies [4, 5, 9]. The basic properties of the LuAG:Pr and LuYAG:Pr crystals used in the current research are listed in Table 1.

Table 1. The basic properties of the studied crystals

Host	Activator and concentration ^a	Density (g/cm ³) ^b	Grown at
Lu ₃ Al ₅ O ₁₂	Pr ³⁺ , 0.23 at%	6.7	Furukawa
(Lu _{0.75} Y _{0.25}) ₃ Al ₅ O ₁₂	Pr ³⁺ , 0.16 at%	6.2	ITME
(Lu _{0.5} Y _{0.5}) ₃ Al ₅ O ₁₂	Pr ³⁺ , 0.17 at%	5.7	ITME
(Lu _{0.25} Y _{0.75}) ₃ Al ₅ O ₁₂	Pr ³⁺ , 0.23 at%	5.2	ITME

^aReal values of praseodymium concentration in the LuYAG:Pr crystals were determined by means of the inductively coupled plasma optical emission spectrometry (ICP-OES).
^bReal values of density of the LuYAG:Pr crystals were measured by the pycnometer method.

Pulse height spectra necessary to determine the values of scintillation yield and energy resolution were collected at room temperature (RT) under ¹³⁷Cs 662 keV gamma excitation. The pulsed output signal from a Hamamatsu R2059 photomultiplier (PMT) was processed by a Canberra 2005 integrating preamplifier, a Canberra 2022 spectroscopy amplifier, and a multichannel analyzer. Based on the photopeak positions, the numbers of photoelectrons released from the photocathode per 1 MeV of energy deposited in the crystal were calculated. Subsequently, the values of scintillation yield were estimated following the approach of de Haas and Dorenbos [10]. Representative samples of LuAG:Pr and LuYAG:Pr were also tested with an “enhanced” setup [11] equipped with a Hamamatsu R1791 PMT, which was more dedicated to gamma spectroscopy than R2059. The shaping time was equal to 2 μs at the “standard” setup and 3 μs at the “enhanced” one. Although the yields determined with both PMTs were fully compatible, better energy resolutions were observed with R1791.

We note that in case of all studied materials we had at our disposal at least three polished samples of each size specified in Table 2. Moreover, for a better accuracy of the data, pulse height spectra of each “cube” (6 × 6 × 6 mm³ or 5 × 5 × 5 mm³) were recorded 3 times (i.e. using 3 different sides of the cube to stick it to the PMT window with Viscasil). Similarly, pulse height spectra of each “cuboid” or “plate” (2.7, 1.6 or 1 mm high) were taken twice (i.e. from both sides of the largest surface). In this way for each series of samples we obtained no less than 9 or 6 values of photoelectron yield and energy resolution (for the “cubes” or the other shapes, respectively). Since the spreads within such sets were lower than an arbitrary level of 5% mostly approved as uncertainty of yield determination, for clarity of the paper in Table 2 we present the highest observed yields and lowest resolutions.

Temperature-dependent pulse height spectra were measured with a setup described in detail by Bizarri *et al.* [12]. The crystals were kept in clean vacuum inside a Janis cryostat and excited by a ¹³⁷Cs source. A 3 μs shaping time constant of the spectroscopy amplifier was selected.

A typical setup consisting of an Inel X-ray generator, an ARC SP-150 monochromator, a Hamamatsu R928 PMT, and an APD Cryogenics closed-cycle helium cooler with a Lake Shore 330 temperature controller, was employed to record low temperature thermoluminescence (ltTL). Prior to the ltTL runs the samples were exposed to X-rays for 10 min at 10 K. The glow curves were taken between 10 and 300 K at a heating rate of 0.14 K/s.

3. Results and discussion

Representative pulse height spectra of LuAG:Pr and LuYAG:Pr are depicted in Fig. 1. The values of scintillation yield and energy resolution of all the studied crystals, derived from their spectra, are summarized in Table 2. The prominent sample, (Lu_{0.75}Y_{0.25})₃Al₅O₁₂:Pr, displays a remarkably high yield of 33000 ph/MeV, accompanied with an energy resolution of 4.4% (at 662 keV). Considering that besides a somewhat lower density (6.2 g/cm³ vs. 6.7 g/cm³) the other luminescence and scintillation properties of (Lu_{0.75}Y_{0.25})₃Al₅O₁₂:Pr are roughly the same as those of LuAG:Pr [7, 13], a significant step forward in the field of modern oxide scintillators can easily be noticed. The two remaining mixed crystals, (Lu_{0.5}Y_{0.5})₃Al₅O₁₂:Pr and (Lu_{0.25}Y_{0.75})₃Al₅O₁₂:Pr, are also better than LuAG:Pr, but not to such an extent as (Lu_{0.75}Y_{0.25})₃Al₅O₁₂:Pr. Evidently the content of

lutetium at the level of $x = 0.75$ is close to an optimal choice, providing a distinct increase of light yield ($\sim 70\%$) at an expense of a bit lower density.

On the way to explain our motivation to grow and investigate the $(\text{Lu}_x\text{Y}_{1-x})_3\text{Al}_5\text{O}_{12}:\text{Pr}$ crystals and to get across the reported enhancement of yield in LuYAG:Pr compared to LuAG:Pr we remind that the precedent studies on the light output of LuAG:Pr used to indicate some room for improvement. In particular, it was noticed that at 450 K the yield of LuAG:Pr was higher by about 40% than at RT [9]. This feature, reflected by a characteristic $Y = Y(T)$ curve presented in Fig. 2 (Y – yield, T – temperature), was soon attributed to the existence of shallow electron traps and their contribution to the energy transfer from the LuAG host to the Pr^{3+} ions, resulting in the temperature-dependent yield deterioration [14]. It became clear that if only the aforesaid curve could be shifted to the left by about 100-150 K, the RT scintillation yield of LuAG:Pr would be increased to the maximum value available for this material. However, a proper idea to achieve this goal was missing.

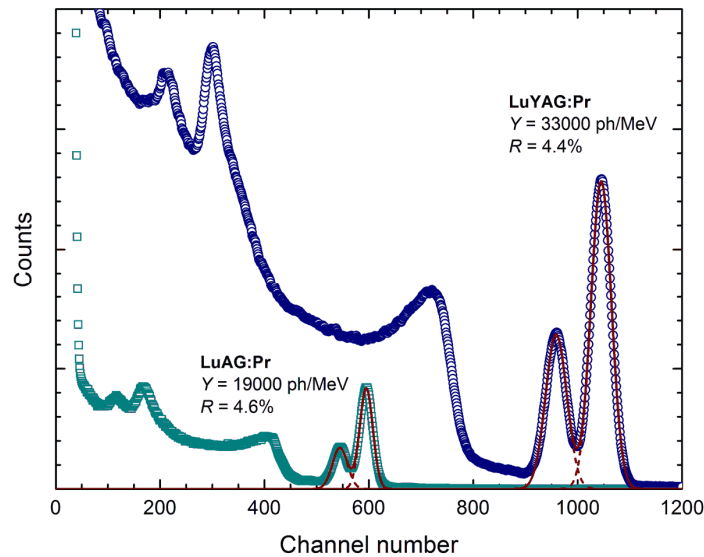


Fig. 1. ^{137}Cs pulse height spectra of $(\text{Lu}_{0.75}\text{Y}_{0.25})_3\text{Al}_5\text{O}_{12}:\text{Pr}$ and $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Pr}$.

Our current concept is based on an observation that generally traps present in LuAG:Pr crystals are deeper than in isostructural YAG:Pr ones [15, 16]. We anticipated that in mixed LuYAG:Pr crystals the traps corresponding to those responsible for the decreased RT yield in LuAG:Pr would be shallower. According to the model of Wojtowicz *et al.* [17] this would shift the $Y = Y(T)$ curve toward lower temperatures and the light output of the mixed crystals at RT would not be affected by traps any more, reaching a maximum value. Despite an obvious simplification (frequency factors also play a role), the overall idea proves correct and seems to provide the expected outcome.

Figure 2 compares the thermal dependences of the scintillation yield, derived from pulse height measurements on two selected samples: LuAG:0.23%Pr ($Y = 18500$ ph/MeV) and $(\text{Lu}_{0.75}\text{Y}_{0.25})_3\text{Al}_5\text{O}_{12}:\text{Pr}$ ($Y = 32300$ ph/MeV). It is apparent that the anticipated lower-temperature shift of the $Y = Y(T)$ curve of LuYAG:Pr indeed takes place. Contrary to LuAG:Pr, the yield of LuYAG:Pr at RT is very close to the maximum, which explains, at least in part, the observed improvement.

Figure 3 shows a typical ItTL glow curve of $(\text{Lu}_{0.75}\text{Y}_{0.25})_3\text{Al}_5\text{O}_{12}:\text{Pr}$ drawn in parallel to a curve of LuAG:Pr. Although both curves need a thorough analysis, it can be roughly deduced from the peak positions and shapes that the traps in LuYAG:Pr are in fact somewhat shallower than those in LuAG:Pr. This feature is most probably responsible for the above mentioned shift of the $Y = Y(T)$ curve to lower temperatures and thereby accounts for the higher yield in LuYAG:Pr than in LuAG:Pr.

Table 2. The RT values of photoelectron yield and energy resolution (at 662 keV) of the examined samples

Material	Size (mm ³)	Yield (ph/MeV) ^a	Resolution (%) ^{a,b}
Lu ₃ Al ₅ O ₁₂ :Pr	6 × 6 × 6	16700	4.8, 6.1
	6 × 6 × 1	19000	4.6, 5.9
(Lu _{0.75} Y _{0.25}) ₃ Al ₅ O ₁₂ :Pr	5 × 5 × 5	27000	5.3
	5 × 5 × 2.7	30500	4.6, 5.5
	5 × 5 × 1.6	32500	6.0
	5 × 5 × 1	33000	4.4, 6.0
(Lu _{0.5} Y _{0.5}) ₃ Al ₅ O ₁₂ :Pr	5 × 5 × 5	21800	5.9
	5 × 5 × 2.7	26100	6.3
	5 × 5 × 1.6	26600	6.4
(Lu _{0.25} Y _{0.75}) ₃ Al ₅ O ₁₂ :Pr	5 × 5 × 5	20600	6.1
	5 × 5 × 2.7	22700	7.1
	5 × 5 × 1.6	24200	7.6

^aThe uncertainties of yield and resolution determination are below 5%.

^bIf two values are given, the first one corresponds to the “enhanced” setup (R1791 PMT), while the other, as well as each single value, to the “standard” one (R2059 PMT).

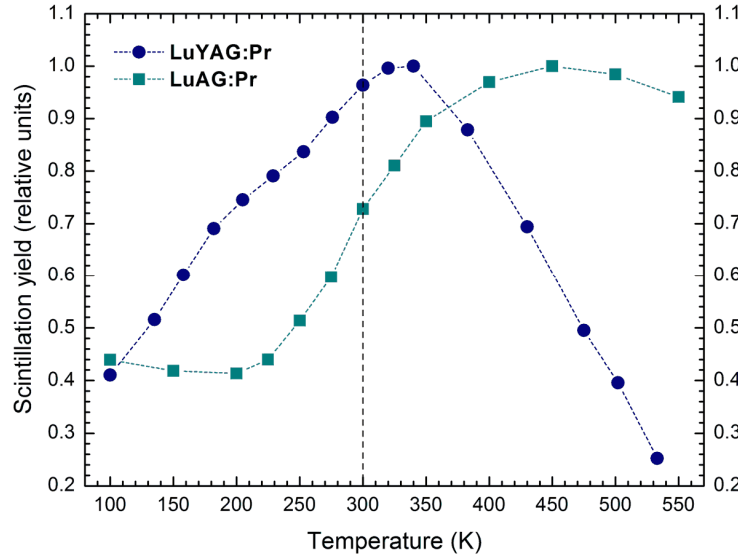


Fig. 2. Scintillation yields of (Lu_{0.75}Y_{0.25})₃Al₅O₁₂:Pr and Lu₃Al₅O₁₂:Pr (normalized to unity at their maxima) as functions of temperature.

We remark that the observations and conclusions based on Figs. 2 and 3 are fully consistent with the recent predictions of Dorenbos [18], according to which the replacement of lutetium with yttrium would lower the bottom of the conduction band, but should not affect the distribution of traps itself. Therefore the corresponding traps should be indeed shallower in LuYAG:Pr than in LuAG:Pr. Furthermore, the energy difference between the Pr³⁺ 5*d* levels and the bottom of the conduction band should be reduced in LuYAG:Pr compared to LuAG:Pr, leading to a lower thermal quenching energy barrier. Actually the Pr³⁺ luminescence in (Lu_{0.75}Y_{0.25})₃Al₅O₁₂:Pr is significantly quenched already above 350 K unlike in LuAG:Pr (Fig. 2). Most probably in case of (Lu_{0.5}Y_{0.5})₃Al₅O₁₂:Pr and (Lu_{0.25}Y_{0.75})₃Al₅O₁₂:Pr the quenching starts at even lower temperatures, which would explain the drop of the RT yield with increasing yttrium-to-lutetium ratio.

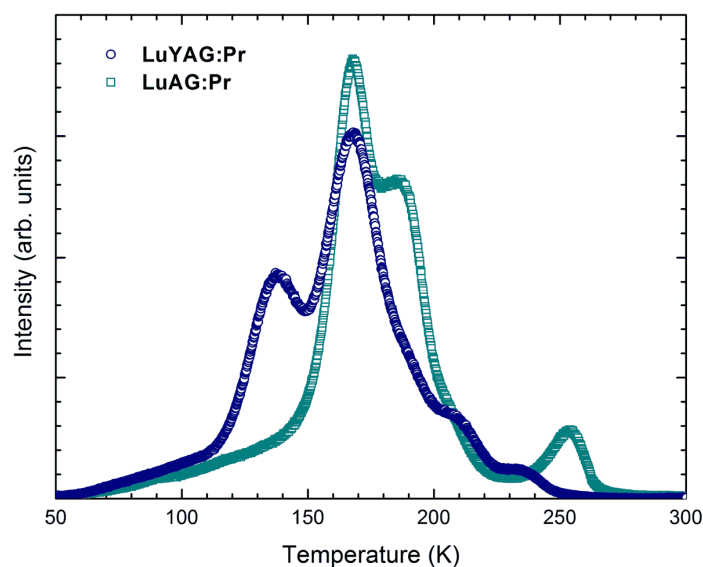


Fig. 3. Glow curves of $(\text{Lu}_{0.75}\text{Y}_{0.25})_3\text{Al}_5\text{O}_{12}:\text{Pr}$ and $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Pr}$, recorded at a heating rate of 0.14 K/s following a 10 min X-ray irradiation.

4. Conclusions

Of the investigated mixed LuYAG:Pr crystals the $(\text{Lu}_{0.75}\text{Y}_{0.25})_3\text{Al}_5\text{O}_{12}:\text{Pr}$ one turns out to be the best choice for a scintillator that could possibly replace LuAG:Pr in these applications, in which an increased light output (~ 33000 ph/MeV instead of ~ 20000 ph/MeV) would be a real benefit, whereas a bit lower density (6.2 g/cm^3 instead of 6.7 g/cm^3) would not matter so much. The aim of this paper is to report the acquired knowledge on the real potential of the LuYAG:Pr crystals and the related mechanism of the scintillation yield enhancement as against LuAG:Pr. Nevertheless, the grown $(\text{Lu}_x\text{Y}_{1-x})_3\text{Al}_5\text{O}_{12}:\text{Pr}$ crystals clearly require further studies. In particular, measurements of radioluminescence as a function of temperature, low and high temperature thermoluminescence, and scintillation time profiles are more than desired. These experiments are currently being carried on and the results with a detailed quantitative analysis will be published elsewhere.

Acknowledgments

This research has been financed from the funds of the Polish National Science Centre granted on the basis of Decision no. DEC-2012/05/B/ST5/00324. Thermoluminescence measurements have been performed at the National Laboratory for Quantum Technologies (NLTK) supported by the EU from the European Regional Development Fund.