**Scintillation Properties of Ce⁢⁺⁺⁻⁻ and Pr⁢³⁺⁺⁻⁻-Doped LuAG, YAG and Mixed LuₓY₁−ₓAG Garnet Crystals**

Jiri A. Mares, Martin Nikl, Alena Beiterova, Petr Horodysky, Karel Blazek, Karel Bartos, and Carmelo D’Ambrosio

**Abstract**—We summarize the latest R&D state-of-art of Ce⁢⁺⁺⁻⁻ and Pr⁢³⁺⁺⁻⁻-doped mixed (LuₓY₁−ₓ)₃Al₅O₁₂ (LuYAG) garnet scintillator crystals and compare their properties with those of Lu₃Al₅O₁₂ (LuAG) and Y₃Al₅O₁₂ (YAG) single crystal analogues. Light yield, energy resolution and proportionality were studied under radioisotope excitation within 8–1300 keV energy range. The highest light yield of about 27000 ph/MeV is obtained in the newest prepared Ce⁢⁺⁺⁻⁻-doped LuAG crystals while up to 17000 ph/MeV was measured in the Pr⁢³⁺⁺⁻⁻-doped ones. On the contrary, the energy resolution and proportionality are noticeably better in the Pr⁢³⁺⁺⁻⁻-doped crystals. Mixed Ce⁢⁺⁺⁻⁻⁻⁻ or Pr⁢³⁺⁺⁻⁻-doped LuₓY₁−ₓAG (x = 0.9 – 1) crystals show comparable light yield and energy resolution compared to those doped pure LuAG, but the content of slow components in scintillation pulses lower.

**Index Terms**—Ce⁢⁺⁺⁻⁻ and Pr⁢³⁺⁺⁻⁻ doping, energy resolution, light yield, LuAG, proportionality, scintillation, YAG and LuₓY₁−ₓAG garnet crystals.

**I. INTRODUCTION**

Single crystals of the Ce⁢⁺⁺⁻⁻-doped complex oxides, namely the garnet, silicate or perovskite structures are intensively studied in last two decades [1]–[9]. These scintillating crystals are used in various scintillating detectors and medical imaging modalities (PET, PEM, CT) using X- or γ-rays. Ce⁢⁺⁺⁻⁻ emission centres in these complex oxide hosts are characterized by (i) broad 5d₁ → 4f emission peaking in the near UV-visible spectral ranges mainly and (ii) fast decays in the range of tens of nanoseconds. After few earlier studies [10] in the last decade the Pr⁢³⁺⁺⁻⁻-doped hosts became of renewed interest due to “faster-than-cerium” decay characteristics based on the same 5d₁ → 4f emission transitions in UV spectral region [11]–[15]. The Pr⁢³⁺⁺⁻⁻-doped aluminum garnets, Y₃Al₅O₁₂ (YAG) [11] and Lu₃Al₅O₁₂ (LuAG) [16], prepared by the Czochralski method in bulk single crystal form have been reported. The latter single crystal characterized by 5d₁ → 4f emission peaking at ~310 nm, short decay time values of about 20 ns and thermal quenching onset high above room temperature (500 K) became of considerable interest.

Besides important medical imaging applications of the bulk Pr⁢³⁺⁺⁻⁻ or Ce⁢⁺⁺⁻⁻-doped aluminum garnets, perovskites or silicates there are other modern applications in the field of 2-D imaging with spatial resolution down to µm scale where thin plates or liquid phase epitaxy grown films are used [17]–[19]. LuAG:Prₚ pixel array is used in Positron Emission Mamography [15].

Lu-based aluminum garnets (LuAG), silicates (LSO) or aluminum perovskites (LuAP) are characterized by favourable properties as high Zₑff, high density but their drawbacks are a presence of slow decay components or even afterglow [20]–[23]. The Y-based aluminum garnets (YAG), silicates (YSO) or aluminum perovskites (YAP) have lower Zₑff and medium density but show much lower content of slow decay components or afterglow [22], [24]. That is why the mixed (LuₓY₁−ₓ)AG, (LuₓY₁−ₓ)SO or (LuₓY₁−ₓ)AP hosts have become of interest and their practical importance and intrinsic advantages were demonstrated mainly in the case of orthosilicates [20], [21]. To our best knowledge, no such study has been reported so far in the case of aluminum garnets.

The aim of this paper is to present scintillation response and properties (Nₚħₑₑ, photoelectron and L.Y. yields, energy resolution and proportionality) of recently prepared Ce⁢⁺⁺⁻⁻ and Pr⁢³⁺⁺⁻⁻-doped pure LuAG and YAG crystals and to compare their properties with those of the mixed LuₓY₁−ₓAG (for x between 0.9–1) crystals. Also detailed time development of scintillation response will be studied in the range of 0.5–10 µs time scale.

**II. EXPERIMENTAL**

Scintillation response studies were carried out using a Hybrid Photomultiplier (HPMT). Different X- or γ-ray lines are used in the energy range 8–1300 keV [22], [25], [26]. Pulse height spectra were measured using setup with HPMT DEP PP0470 and by spectroscopic amplifier ORTEC 672 with six shaping times from 0.5 to 10 µs and accuracy of this setup is ±5% [22], [26]. An example of one spectrum from the measured pulse height spectra is presented in Fig. 1. Because an escape peak
Fig. 1. Pulse height spectrum of $^{22}Na$ 511 keV energy line of LuAG:Pr (as grown crystal, thickness 1 mm) measured with 1 $\mu$s shaping time.

is observed in Lu containing compounds we evaluated energy resolution carefully from only a photopeak of the used X- or $\gamma$-ray energy lines. Decomposition of part of the pulse height spectrum of 511 keV energy line (the photopeak and the escape peak) is displayed in Fig. 2. In some measurements of pulse height spectra it was not possible to separate clearly the escape and the photopeak as is seen in Fig. 2. In this case the energy resolution was evaluated from the whole observed photopic band. Halfwidths (FWHM’s) of photopeak bands were evaluated from using Maestro or KaleidaGraph programs [26].

L.Y.(E)’s were calculated from $N_{ph,es}$ yields using integral quantum efficiency of the used HPMT and wavelengths of emission spectra of crystals investigated [25]–[27]. The used HPMT PP0470 photomultiplier has the highest quantum efficiency ~25% in the UV spectral range 200–400 nm where $Pr^{3+}$ narrow emission spectra in (Lu,Y)AG crystals are lying. Broad $Ce^{3+}$ emission spectra in garnets are observed in the visible spectral range 450–600 nm where quantum efficiency of HPMT decreases from 20 to 7% [26]. Calculated integral quantum efficiencies are ~9 for LuAG:Ce and YAG:Ce while ~3.97 both for LuAG:Pr and YAG:Pr. Time dependences (in the time range 0.5–10 $\mu$s) of L.Y.’s were approximated using method described by Prusa et al. in [28].

The $Ce^{3+}$- or $Pr^{3+}$-doped LuAG, YAG or Lu$_x$Y$_{1-x}$AG (x = 0.9 – 1) single crystals were grown by the Czochralski method1. Measurements were carried out with thin samples (thickness from 0.79 mm up to 2.35 mm) to eliminate reabsorption effect due to limited Stokes shift of $Ce^{3+}$ or $Pr^{3+}$ emission centers [29]. Samples were either regular plates of 7 x 7 mm or slices of 8 or 10 mm in diameter. Ce concentrations in measured samples were between 0.2–0.3% while those of Pr were ~0.2%. Either LuAG:Ce, YAG:Ce and YAG:Pr reference samples (indicated by ref in Tables I and II and in figures) were also measured and their scintillation properties were compared with the new prepared LuAG:Ce pixels and Ce- and Pr-doped mixed Lu$_x$Y$_{1-x}$AG (x = 0.9 – 1). Pr-doped Lu$_x$Y$_{1-x}$AG 2c and 3b samples (see Tables I. and II.) were prepared from the same as-grown crystal (from the beginning or final part of the crystal bulb, respectively). In order to obtain the highest $N_{ph,ls}$ photoelectron yield of $Ce^{3+}$-doped pure or mixed (Lu,Y)AG crystals we used teflon tape for wrapping ($Ce^{3+}$ emission is peaking in the visible region). Because $Pr^{3+}$ emission of pure or mixed (Lu,Y)AG garnets is in the UV range ($\lambda_{eck}$ ~ 310 nm) we tested different wrapping materials and the highest reflectivity for the UV scintillation was obtained using BaSO$_4$. This cover was also used for LuAG:Pr pixels in PEM equipment by Yoshikawa et al. [15].

III. RESULTS AND DISCUSSIONS

A. $Ce^{3+}$ and $Pr^{3+}$-Doped LuAG, YAG and Lu$_x$Y$_{1-x}$AG Crystals: $N_{ph,es}$ Photoelectron and L.Y. Yields and Energy Resolutions

$N_{ph,es}$ photoelectron or L.Y. yields per MeV and energy resolutions (FWHM) of fast (at 1 $\mu$s shaping time) and fast&slow (at the longest shaping time 10 $\mu$s) decay curve components of $Ce^{3+}$- and $Pr^{3+}$-doped garnets under study are summarized in Table I. Detailed shaping time L.Y. progress of the studied $Ce^{3+}$- and $Pr^{3+}$-doped (pure or mixed) garnets are displayed in Figs. 3 and 4, respectively (in Figs. 3 and 4 LuYAG means mixed Lu$_x$Y$_{1-x}$AG where x = 0.9 – 1). From Table I we can clearly observe that the highest L.Y.’s (at the longest shaping time 10 $\mu$s) exhibit LuAG:Ce crystals—almost up to 27000 ph/MeV. L.Y.’s of mixed Lu$_x$Y$_{1-x}$AG : Ce (x = 0.9 – 1) crystals can reach up to 23500 ph/MeV and YAG:Ce around 21000 ph/MeV. $Pr^{3+}$-doped garnet crystals exhibit only small difference between L.Y.’s of LuAG:Pr and Lu$_x$Y$_{1-x}$AG : Pr crystals: ~17000 ph/MeV against 16500 ph/MeV, respectively. The lowest L.Y. exhibits YAG:Pr sample ~11300 ph/MeV.

From these measurements we observed that L.Y. of $Ce^{3+}$-doped LuAG or YAG is about 40–30% higher than that of the same $Pr^{3+}$-doped crystals. This difference can be caused either by a fact that (i) $Ce^{3+}$-doped crystals were intensively developed more than 12 years including various thermal treatment after growth [5] while (ii) $Pr^{3+}$-doped ones are studied ~6 years [12]. The highest L.Y. was observed on LuAG:Ce pixel which was prepared from one of the newest grown crystals. We studied two mixed LuYAG:Pr 2c and 3b samples (see Table I) which were from the same crystal bulb.1

1Crystals were prepared by the Company Crytur Ltd., Palackeho 175, 511 01 Turnov, Czech Republic
TABLE I
PHOTOELECTRON AND L.Y. LIGHT YIELDS, AND FWHM (EVALUATED FROM ONLY PHOTOPEAK OF 662 keV ENERGY WITHOUT THE ESCAPE PEAK) AT 1 µs AND 10 µs SHAPING TIMES OF Ce³⁺- AND Pr³⁺-doped LuAG, Lu₁₋ₓYₓAG (x = 0.9 − 1) AND YAG CRYSTALS. (NO POS MEANS THAT IT WAS NOT POSSIBLE TO OBSERVE AND FIT ONLY PHOTOPEAK AND FWHM VALUES IN BRACKETS ARE THOSE VALUES WHERE ESCAPE PEAK COULD NOT BE SEPARATED)

<table>
<thead>
<tr>
<th>Crystal</th>
<th>d [mm]</th>
<th>N_{phots} (1 µs) phels/MeV</th>
<th>L.Y. (1 µs) phels/MeV</th>
<th>FWHM at 1 µs in % at 662 keV</th>
<th>N_{phots} (10 µs) phels/MeV</th>
<th>L.Y. (10 µs) phels/MeV</th>
<th>FWHM at 10 µs in % at 662 keV</th>
</tr>
</thead>
<tbody>
<tr>
<td>LuAG:Ce ref</td>
<td>2.05</td>
<td>1549</td>
<td>1394</td>
<td>5.8 (9)</td>
<td>2284</td>
<td>20556</td>
<td>5.6 (7.6)</td>
</tr>
<tr>
<td>LuAG:Ce pixel</td>
<td>2</td>
<td>2448</td>
<td>18000</td>
<td>5.5 (7.3)</td>
<td>3627</td>
<td>26669</td>
<td>3.2 (6.1)</td>
</tr>
<tr>
<td>Lu₁₋ₓYₓAG:Ce:Ce annealed</td>
<td>0.79</td>
<td>2093</td>
<td>18837</td>
<td>7.7 (8.9)</td>
<td>2607</td>
<td>23463</td>
<td>2.9 (4.7)</td>
</tr>
<tr>
<td>YAG:Ce ref</td>
<td>2.34</td>
<td>2320</td>
<td>20880</td>
<td>no pos (5.4)</td>
<td>2310</td>
<td>20790</td>
<td>no pos (7.0)</td>
</tr>
<tr>
<td>LuAG:Pr</td>
<td>0.99</td>
<td>3002</td>
<td>11918</td>
<td>no pos (6.3)</td>
<td>4281</td>
<td>16996</td>
<td>2.1 (5.0)</td>
</tr>
<tr>
<td>Lu₁₋ₓYₓAG:Pr - 2c</td>
<td>1.37</td>
<td>3594</td>
<td>14268</td>
<td>3.4 (9.6)</td>
<td>3776</td>
<td>14991</td>
<td>3.0 (4.7)</td>
</tr>
<tr>
<td>Lu₁₋ₓYₓAG:Pr - 3b</td>
<td>1.39</td>
<td>3801</td>
<td>15090</td>
<td>no pos (7.3)</td>
<td>4137</td>
<td>16424</td>
<td>no pos (3.2)</td>
</tr>
<tr>
<td>YAG:Pr ref</td>
<td>1</td>
<td>2728</td>
<td>10830</td>
<td>no pos (5.5)</td>
<td>2855</td>
<td>11334</td>
<td>no pos (3.4)</td>
</tr>
</tbody>
</table>

TABLE II
PROPERTIES OF Ce³⁺- AND Pr³⁺-dOPED LuAG, Lu₁₋ₓYₓAG (x = 0.9 − 1) AND YAG CRYSTALS EVALUATED FROM LIGHT YIELD TIME DEPENDENCE IN THE TIME RANGE 0.5–10 µs. DIFF IS DIFFERENCE IN % BETWEEN N_{phots} YIELD AT 10 µs AND 0.5 µs, K_{rel} IS THE RELATIVE INTENSITY OF FAST SCINTILLATION FRACTION AND t_{slow} THE DECAY TIME OF SLOW COMPONENTS (DETAILS SEE [28], [30])

<table>
<thead>
<tr>
<th>Sample</th>
<th>d [mm]</th>
<th>DIFF (%) (0.5–10 µs)</th>
<th>K_{rel} [%]</th>
<th>t_{slow} [µs]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LuAG:Ce ref</td>
<td>2.05</td>
<td>82</td>
<td>42.9</td>
<td>1.64</td>
</tr>
<tr>
<td>LuAG:Ce pixel</td>
<td>2</td>
<td>59</td>
<td>55.3</td>
<td>3.7</td>
</tr>
<tr>
<td>Lu₁₋ₓYₓAG:Ce:Ce annealed</td>
<td>0.79</td>
<td>45</td>
<td>56.6</td>
<td>1.5</td>
</tr>
<tr>
<td>YAG:Ce ref</td>
<td>2.35</td>
<td>15</td>
<td>25.9</td>
<td>0.3</td>
</tr>
<tr>
<td>LuAG:Pr</td>
<td>0.99</td>
<td>60</td>
<td>54.8</td>
<td>2.8</td>
</tr>
<tr>
<td>Lu₁₋ₓYₓAG:Pr - 2c</td>
<td>1.37</td>
<td>21.7</td>
<td>77.1</td>
<td>1.5</td>
</tr>
<tr>
<td>Lu₁₋ₓYₓAG:Pr - 3b</td>
<td>1.39</td>
<td>24.7</td>
<td>79.3</td>
<td>3.6</td>
</tr>
<tr>
<td>YAG:Pr ref</td>
<td>1</td>
<td>−10</td>
<td>−90.6</td>
<td>−2.8</td>
</tr>
</tbody>
</table>

Fig. 4. L.Y.’s of Pr³⁺-doped LuAG, YAG and Lu₁₋ₓYₓAG (x = 0.9 − 1) crystals measured in the shaping time range 0.5–10 µs (exponential fits were carried out and displayed).

The increase of L.Y. both for Ce³⁺- and Pr³⁺-doped garnets should be influenced by thermal treatment after growth.¹

The energy resolution as a function of X- or γ-ray energy are presented in Table I and Fig. 5(a) and 5(b). From the data in Fig. 5(a) and Table I the FWHM values are in the range of 5.5–10% for Ce³⁺-doped LuAG and Lu₁₋ₓYₓAG crystals while those of Pr³⁺-doped ones are between 5.5–7.7% (measured with fast shaping time 1 µs). Due to L.Y. increase with shaping time both on Lu pure or mixed garnets, the FWHM values are better when measured at 10 µs shaping time (see Table I and Fig. 5(b)). For Ce³⁺-doped samples the FWHM values are in the range 3–7% while for Pr³⁺-doped ones are between 2.1–5%. Generally, energy resolutions (FWHM) of Pr³⁺-doped LuAG, Lu₁₋ₓYₓAG (x = 0.9 − 1) and YAG garnets are better than those of Ce³⁺-doped ones. This is also presented in Figs. 5(a) and 5(b) where FWHM of different samples are displayed in the energy range 10–1300 keV. Some of evaluated FWHM values of 2–3% must be taken with caution as they were only observed at a few measured samples and decomposition of superponed
Fig. 5. (a) Energy resolution (FWHM) of different Ce3+- and Pr3+-doped LuAG, YAG and Lu1-xYx:AG (x = 0.9 – 1) crystals as a function of energy at 1 µs shaping time. (b) Energy resolution (FWHM) of different Ce3+- and Pr3+-doped LuAG, YAG and Lu1-xYx:AG (x = 0.9 – 1) crystals as a function of energy at 10 µs shaping time.

The decomposition was performed e.g., for 22Na 511 keV energy line (into bands of the photopeak and the escape peak, see Fig. 2) but on some samples this decomposition was not possible (see Table I, e.g., samples YAG:Pr ref and LuAG:Pr and Lu1-xYx:AG : Pr – 3b). Evaluation of FWHM for various energy lines from pulse height spectra was performed using Maestro program including check of results obtained for all measured samples.

B. Time Behaviour of L.Y.

L.Y.’s (in ph/MeV) were measured and evaluated in the energy range ~10–1300 keV for 6 shaping time in the time rage 0.5–10 µs. Results of measurements are presented in Figs. 3 and 4 for Ce3+- or Pr3+-doped samples, respectively. The observed

dependences were fitted using method described by Prusa et al. in [28]. We used exponential function fits for L.Y. (tsh) at tsh shaping time starting from the shortest 0.5 µs shaping time

so 

L.Y. (tsh) \sim \exp(-m_3 t_{sh})

where \(m_1, m_2\) and \(m_3\) are parameters (see [28], [30]). Fitted curves are displayed in Figs. 3 and 4. Physical parameters as \(K_{f/e} \approx 1 - \pi/m_2/m_1\) (the relative intensity of the fast decay component) and \(\tau_{slow} \approx 1/m_3\) (decay time of the slow decay component) were evaluated and are summarized in Table II. From Table II and Figs. 3 and 4 we can conclude that there is substantial difference between L.Y.’s measured at fast (0.5 or 1 µs) and fast/slow (up to 10 µs) shaping times (DIFF in Table II). With Ce3+- or Pr3+-doped LuAG garnets DIFF values are between ~60–80% while YAG garnets exhibit DIFF values only between 10–15% (see Table II). Mixed Ce3+- or Pr3+-doped Lu1-xYx:AG (x = 0.9 – 1) crystals exhibit lower DIFF values between 20–45% than those observed with pure LuAG crystals but this differences are lower for Pr3+-doped mixed crystals where are only between 20–25%. The lowest DIFF values exhibit YAG:Ce and YAG:Pr crystals (only between 10–15%) but fits of these samples exhibit R-square fitting values ~0.2 and 0.76, respectively while R-square values of fits for other samples from Table II are between 0.80–0.98.

Last column of Table II shows evaluated values of \(\tau_{slow}\) decay components which are lying between 1.5–3.7 µs for Ce3+- or Pr3+-doped LuAG and YAG crystals while the mixed Lu1-xYx:AG crystals exhibit \(\tau_{slow}\) around 1.5 µs (with an exception for one of Lu1-xYx:AG :Pr 3b mixed crystal where \(\tau_{slow}\) is 3.6 µs). Especially, Pr3+-doped mixed Lu1-xYx:AG crystals are characterized by high portion of fast decay component around 78% while other Ce3+-doped pure or mixed LuAG garnets have lower portion of the fast decay component (around 55%, see Table II).

C. Proportionality of \(N_{ph(eV)}(E)\) Photoelectron Response

Progress of proportionality of L.Y.(E) yields (responses) of Ce3+- and Pr3+-doped LuAG, YAG and Lu1-xYx:AG crystals are presented in Figs. 6 and 7 (again for measurements in the energy range 8–1300 keV). Fitting of the observed proportionality data is not easy (we have around 10 points in the energy range 10–1300 keV) and we decided to use the smooth function to fit these dependences. Ce3+-doped garnets exhibit R-square values ~0.94–0.96 while those of Pr3+-doped exhibit worse R-square values among 0.73–0.89. For Pr3+-doped garnets we observed good proportionality in the energy range 80–1300 keV (between 85 to 100%) but below 80 keV proportionality is worse and at 10 keV is only between 60–70%. Pr3+-doped LuAG, YAG and mixed Lu1-xYx:AG crystals show excellent proportionality between 70–1300 keV (90–105%) but below 70 keV proportionality decreases up to 80% at 10 keV energy. Generally, Pr3+-doped garnets exhibit better proportionality compared with Ce3+-doped ones.

Interestingly, we notice the unexpected relation between the light yield, energy resolution and proportionality between the group of Ce3+- and Pr3+-doped garnet crystal samples. The latter group shows in average better energy resolution and proportionality despite of lower light yield. An intense ongoing
show a positive influence on the content of slower components in the scintillation response. Despite of lower light yield in the Pr$^{3+}$-doped materials, distinctly better energy resolution and better proportionality was found in comparison with the Ce$^{3+}$-doped ones. Such finding points to importance of the emission center ability to capture migrating carriers and to the way how it can interact with the exciton state of the host. This result may provide further hints to the ongoing nonproportionality studies in scintillators. This R&D study showed that in Ce$^{3+}$- and Pr$^{3+}$-doped LuAG and Lu$_x$Y$_{1-x}$AG crystals the Lu escape peak can influence the energy resolutions of the crystals studied.

Now, detailed studies of an influence of Lu escape peak on scintillation properties of (Lu,$Y$)AG are necessary including detailed evaluation of FWHM of the photopeak and the escape peak. These studies are in progress, now.

IV. CONCLUSIONS

Light yield, energy resolution and proportionality were evaluated under radioisotope excitation within 8–1300 keV energy range for the group of Ce$^{3+}$- and Pr$^{3+}$-doped aluminum garnet crystals with the aim to compare the yttrium admixed Lu$_x$Y$_{1-x}$Al$_5$O$_{12}$ (up to 10%) and pure lutetium garnet hosts. Now, the influence of yttrium admixture appears unimportant for the values of light yield and energy resolutions, while it does not have a positive influence on the content of slower components in the scintillation response. Despite of lower light yield in the Pr$^{3+}$-doped materials, distinctly better energy resolution and better proportionality was found in comparison with the Ce$^{3+}$-doped ones. Such finding points to importance of the emission center ability to capture migrating carriers and to the way how it can interact with the exciton state of the host. This result may provide further hints to the ongoing nonproportionality studies in scintillators. This R&D study showed that in Ce$^{3+}$- and Pr$^{3+}$-doped LuAG and Lu$_x$Y$_{1-x}$AG crystals the Lu escape peak can influence the energy resolutions of the crystals studied.

Now, detailed studies of an influence of Lu escape peak on scintillation properties of (Lu,$Y$)AG are necessary including detailed evaluation of FWHM of the photopeak and the escape peak. These studies are in progress, now.

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