Scintillation response of Lu$_3$Al$_5$O$_{12}$:Pr$^{3+}$ single crystal scintillators

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A B S T R A C T
In this paper, we present the scintillation responses of Pr$^{3+}$-doped Lu$_3$Al$_5$O$_{12}$ single crystals grown by the Czochralski method with different Pr$^{3+}$ concentration of 0.19, 0.31, and 0.43 mol% in the crystal. The light yield and energy resolution were measured using photomultiplier tube (XP5200B PMT) readout. High light yield of 15'900 photons per MeV and an energy resolution of 6.5% for 662 keV γ-rays ($^{137}$Cs source) were obtained with the LuAG:Pr (0.19%) crystal. The variation of light yield and energy resolution with praseodymium concentration was also observed. The light yield non-proportionality and energy resolution versus γ-ray energy were measured and the intrinsic resolution was calculated after correcting the measured energy resolution for PMT statistics. Very good proportionality of the light yield was found within 5% over the energy range from 1274.5 keV down to 32 keV. The estimated photoefficiency for LuAG:Pr in the pulse height spectra of 320 and 662 keV γ-rays was also determined and compared with the ratio of the cross-sections for the photoelectric effect to the total one calculated using WinXCom program.

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1. Introduction

Research and development of new scintillating materials is mainly triggered by the growing needs of modern medical imaging as well as of nuclear and high-energy physics research. A number of Ce$^{3+}$-doped oxides based scintillators have been intensively studied. Gd$_2$SiO$_4$:Ce (GSO:Ce) [1], Lu$_2$SiO$_5$:Ce (LSO:Ce) [2], (Lu,Y)$_2$SiO$_5$:Ce (LYSO:Ce) [3,4], Lu$_3$Si$_2$O$_7$:Ce (LPS:Ce) [5], Lu$_2$Al$_5$O$_{12}$:Ce (LAP:Ce) [6,7], Lu$_3$Al$_5$O$_{12}$:Ce (LuAG:Ce) [8], and Lu$_3$Al$_5$O$_{12}$:Ce (LuYAP:Ce) [9]. These scintillators exhibit desirable properties for gamma-ray detection: high stopping power, high light output and fast scintillation decay.

Pr$^{3+}$-doped Lu$_3$Al$_5$O$_{12}$ (LuAG:Pr) single crystal was recently reported as a new, even faster and efficient scintillator [10–12]. LuAG:Pr exhibits high stopping power, fast decay time of 20 ns, and high light yield of almost 300% of Bi$_4$Ge$_3$O$_{12}$ (BGO) [11]. LuAG:Pr grown by Czochralski method exhibits very good energy resolution of 4.6–5.2% observed at 662 keV gamma rays [13,14]. The density of LuAG is of about 6.67 g/cm$^3$ and its effective atomic number is of about 59. These properties make LuAG:Pr a very promising scintillator for a number of applications. It was found that the light yield of LuAG:Pr increases with Pr concentration from 0.1 to 0.22 mol%, peaks at about 0.22–0.24 mol%, and then decreases [11,15]. The decrease of the light yield with increasing Pr concentration from 1.5 to 10 mol% was also reported [16].

In the present work, we have performed characterization of the scintillation responses of LuAG:Pr crystals grown by the Czochralski method with Pr concentration of 0.19, 0.31, and 0.43 mol%. This investigation involved measurements of light output, energy resolution, and non-proportionality of light yield. The estimated photoefficiency for LuAG:Pr in the pulse height spectra of 320 and 662 keV gamma rays was also determined and compared with the ratio of the cross-sections for the photoelectric effect to the total one obtained from WinXCom program.

2. Experimental

Single crystals of LuAG:Pr were produced by CRYTUR Ltd. in Czech Republic. The crystals were grown using Czochralski method with different Pr concentration of 0.19, 0.31, and 0.43 mol% in the crystal which was determined by the X-ray fluorescence method. The crystals were grown using high purity 5 N raw Lu$_2$O$_3$, Al$_2$O$_3$ powders and 4 N Pr$_6$O$_{11}$ powder was used for doping [17]. They were grown within the same growth batch so that their optical and structural quality should be comparable. Plates of 7 × 7 × 1 mm$^3$ were cut and polished for all measurements.

Photonelectron yield and energy resolution were measured with a Photonis XP5200B photomultiplier tube (PMT) having a high blue photocathode sensitivity of 12.5 mA/mm$^2$. In order to maximize
light collection, the samples were optically coupled by silicone grease to the PMT and covered with several layers of white Teflon (PTFE) tape in a configuration of a reflective umbrella. The signal from the PMT anode was passed to a Canberra 2005 preamplifier and then to a Tenelec TC243 spectroscopy amplifier. The measurements were carried out with 4 μs shaping time constant in the amplifier. The PC-based multichannel analyzer (MCA), Tukan 8 k, was used to record pulse height spectra. Gaussian functions were fitted to the full energy peak, using procedures in the MCA, to determine their position and energy resolution. It included also the analysis of complex double peaks, characteristic of KX-rays and those exhibiting an escape peak.

The photoelectron yield, expressed as a number of photoelectrons released from the PMT photocathode per MeV (phe/MeV) of γ-energy deposited in the crystal, was determined by means of a single photoelectron method [18,19]. In this method the number of photoelectrons is measured by comparing the position of a full energy peak of γ-rays detected in the crystals with that of the single photoelectron peak from the PMT photocathode.

The measurements of light yield non-proportionality and energy resolution were carried out for a series of Xγ-rays emitted by different radioactive sources (241Am, 137Ba, 51Cr, 133Cs, 59Co, and 22Na) in the energy range from 32.1 to 1274.5 keV. All the measurements were carried out at room temperature (RT).

3. Results and discussion

3.1. Energy spectra and photoelectron yield

Fig. 1 presents the pulse height spectra of γ-rays from 137Cs (662 keV) and 51Cr (320 keV) sources as measured with LuAG:Pr (0.19%) crystal at 4 μs shaping time constant. Good energy resolution of 6.5% for 662 keV peak is obtained. Worse energy resolution for a studied LuAG:Pr than that reported in Refs. [13,14] could be associated with its lower photoelectron yield obtained in this measurement, see below. Good energy resolution of 9.8% for 320 keV peak from a 51Cr source is also observed, where the Lu KX-rays escape peak is well separated from the photopeak.

In the measurements with the XP5200B PMT, the studied LuAG:Pr (0.19%) sample showed a photoelectron yield of $3660 \pm 200$ phe/MeV as measured at 662 keV γ-rays. Note a significantly lower photoelectron yield from the studied LuAG:Pr (0.19%) crystal, by about 20–40%, compared to that quoted in Refs. [13,14] for the crystals with higher concentration of about 0.23 mol% Pr.

The photoelectron yield of 3660 ± 200 phe/MeV measured for LuAG-Pr (0.19%) corresponds to a light yield of 15,000 ± 1600 ph/MeV, assuming 23% effective quantum efficiency of PMT for Pr$^{3+}$ 5d → 4f emission (300–440 nm, peaks at 310 and 370 nm).

We also studied variations in light output of LuAG:Pr crystals as a function of the Pr concentration. Crystals with Pr concentration of 0.19, 0.31, and 0.43 mol% were investigated. An example of pulse height spectra of 320 keV γ-rays from a 51Cr source as measured...
with different Pr concentrations are shown in Fig. 2. As seen in the figure, the light output of LuAG:Pr samples decreases when the Pr concentration increases from 0.19% to 0.43%, indicating the concentration quenching of the Pr$^{3+}$ in the LuAG host. This fact, together with the results in Refs. [14–16], agrees with the conclusions of Ogino et al. [11] that the light yield of LuAG:Pr first increases with concentration, peaks at about 0.22–0.24% Pr, and decreases. Table 1 summarizes the values of photoelectron yield and energy resolution (at 662 keV) for the studied crystals coupled to the XPS2008 PMT. Very poor energy resolution for LuAG:Pr (0.31%) sample can be attributed to its lower quality, which should be seen in a much higher contribution from its intrinsic resolution, see below.

The energy resolution ($\Delta E/E$) of a full energy peak measured with a scintillator coupled to a photomultiplier can be written as [20]

$$
\Delta E/E = (\delta_{ae})^2 + (\delta_{t})^2 + (\delta_{st})^2
$$

(1)

where $\delta_{ae}$ is the intrinsic resolution of the crystal, $\delta_{t}$ is the transfer resolution and $\delta_{st}$ is the statistical contribution of PMT to the resolution.

The statistical uncertainty of the signal from the PMT can be described as

$$
\delta_{st} = 2.355 \times \frac{1}{N^{1/2}} \times (1 + \epsilon)^{1/2}
$$

(2)

where $N$ is the number of the photoelectrons and $\epsilon$ is the variance of the electron multiplier gain, equal to 0.1 for an XPS2008 PMT.

The intrinsic resolution of a crystal is mainly associated with the non-proportional response of the scintillator [20,21] and many effects such as inhomogeneities in the scintillator which can cause local variations in the scintillation light output and non-uniform reflectivity of the reflecting cover of the crystal.

Overall energy resolution and PMT resolution can be determined experimentally. If $\delta_{t}$ is negligible, intrinsic resolution $\delta_{ae}$ of a crystal can be written as follows

$$
(\delta_{ae})^2 = (\Delta E/E)^2 - (\delta_{st})^2
$$

(3)

Fig. 3 presents the overall energy resolution as a function of $\gamma$-ray energy, measured for the studied LuAG:Pr crystals. Direct comparison of the intrinsic resolution for all studied crystals is shown in Fig. 4. Both LuAG:Pr (0.19%) and LuAG:Pr (0.43%) samples exhibit comparable intrinsic resolution $\delta_{ae}$ over whole energy range from 32 to 1274.5 keV. The intrinsic resolution at high energies is almost a factor of two poorer for LuAG:Pr (0.31%) sample, which seems to follow a poor overall energy resolution, see Fig. 3. An analysis of the 662 keV energy resolution for LuAG:Pr crystals is presented in Table 2. The poor energy resolution of LuAG:Pr (0.31%) crystal is mainly due to a large contribution of intrinsic resolution $\delta_{ae}$ which reflects to a lower quality of this sample. Despite of crystal preparation in the same batch, such a fluctuation could be attributed to an inhomogeneity of dopant and/or some defects in this crystal arising due to accidental fluctuation of the growth parameters (temperature, atmosphere) resulting, e.g. in local structural distortions.

### Table 1

<table>
<thead>
<tr>
<th>Pr concentration (mol%)</th>
<th>Photoelectron yield (phot/eV)</th>
<th>Light yield (phot/hz)</th>
<th>Energy resolution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.19</td>
<td>3640 ± 200</td>
<td>15,000 ± 1500</td>
<td>6.9 ± 0.2</td>
</tr>
<tr>
<td>0.31</td>
<td>3460 ± 200</td>
<td>15,000 ± 1500</td>
<td>11.9 ± 0.3</td>
</tr>
<tr>
<td>0.43</td>
<td>3340 ± 200</td>
<td>14,500 ± 1500</td>
<td>6.3 ± 0.2</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Pr concentration (mol %)</th>
<th>$N$ (electrons)</th>
<th>Energy resolution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.19</td>
<td>2420</td>
<td>6.5, 5.6, 4.1</td>
</tr>
<tr>
<td>0.31</td>
<td>2280</td>
<td>11.9, 5.2, 10.7</td>
</tr>
<tr>
<td>0.43</td>
<td>2210</td>
<td>6.4, 5.3, 3.6</td>
</tr>
</tbody>
</table>

### 3.2. Non-proportionality of light yield

Non-proportionality of light yield is defined as the ratio of light yield measured at specific $\gamma$-ray energies relative to the light yield at the 662 keV $\gamma$-peak. The data presented in Fig. 5 exhibit a high proportional scintillation response of all LuAG:Pr crystals. Over the energy range from 1274.5 keV down to 32 keV, the non-proportionality in its light yield is about 5%. The behavior obtained in these measurements for small LuAG:Pr samples ($7 \times 7 \times 10^{-2}$ mm$^3$) is about the same (decrease less than 6% down to 32 keV) as the ones measured for larger samples $10 \times 10 \times 5$ mm$^3$[13] and $10 \times 10 \times 10$ mm$^3$[14]. These results demonstrate that the non-proportionality response of LuAG:Pr crystal is not strongly affected by the crystal size and praseodymium concentration. The high proportionality of its light yield is one of the main reasons (in conjunction with its high light yield) behind a good energy resolution for LuAG:Pr scintillator.
3.3. Photofraction

The photofraction is defined here as the ratio of counts under the photopeak (including X-ray escape peak) to the total counts of the spectrum as measured at a specific γ-ray energy. The photofraction for LuAG:Pr at 320 and 662 keV γ-peaks is presented in Table 3. For a comparison, the ratio of the cross-sections for the photoelectric effect to the total one calculated using WinXCom program [22] is also given. The estimated photofractions of LuAG:Pr at both energies are in good agreement with the cross-section ratios (σ-ratios) obtained from WinXCom program.

4. Conclusion

In this work, we have investigated the scintillation responses of LuAG:Pr crystals grown by the Czochralski method. The LuAG:Pr sample doped with praseodymium concentration of 0.19 mol% has high light yield of about 15.900 ph/MeV as measured with 4 μs shaping time constant. It exhibits very good proportionality of light yield, down to 32 keV, which results in a good energy resolution. Moreover, inhomogeneity of dopant and some defects in crystals could affect the energy resolution, and the crystalline quality of these samples could be further improved.

This fact and together with a considerably high detection efficiency for γ-rays (~p20%) will make it the scintillator of choice for γ-ray spectrometry and medical imaging. A high speed of fast component (~20 ns) in the scintillation pulse [17] and high light yield also assure the capability of LuAG:Pr crystal for high counting rate measurements and fast timing applications.

Acknowledgements

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