Fundamental study of inorganic–organic hybrid scintillator using Pr:Lu₃Al₅O₁₂ and plastic scintillator
1. Introduction

Scintillator materials combined with photo detectors are used to detect high energy photons and particles, e.g., in X-ray computed tomography (CT), positron emission tomography (PET) and other medical imaging techniques, high energy and nuclear physics detectors, etc. In most of these applications, scintillators that possess properties such as high stopping power, high light yield, short decay time, and very good energy resolution should be used. Moreover, it is important to match emission wavelength of a scintillator with the maximum of spectral sensitivity of the coupled photo-detector to optimize the light output. In the past decades, great effort was made to develop more efficient and fast scintillators to detect ionizing radiation.

Recently, single crystal Lu$_3$Al$_5$O$_{12}$:Pr (Pr:LuAG) has attracted attention because of its interesting properties such as Pr$^{3+}$ 5d–4f emission at 310 nm wavelength, non-hygrosopic nature, high density (6.7 g/cm$^3$), high light output (around 20000 photons/MeV), very short decay time (20 ns), and good energy resolution (4.8% at 662 keV for a 10 × 10 × 10 mm Pr:LuAG sample).\(^{1-18}\) Table I shows a comparison of Pr:LuAG and popular cerium-activated scintillators such as Ce:Lu$_2$SiO$_5$ (Ce:LSO),\(^{19-21}\) (Lu,Y)AlO$_3$ (LuAP),\(^{21-24}\) and Ce:LaBr$_3$.\(^{24-27}\) Owing to this excellent properties, Pr:LuAG scintillator is attracting attention for $\gamma$-ray detectors for oil well logging and has potential applications in high-energy physics and medical field such as PET. In order to apply Pr:LuAG to $\gamma$-ray detection applications, we are making efforts to establish mass production of Pr:LuAG single crystals. As a result of our effort, 2-in.-diameter Pr:LuAG have been commercially available now.\(^{7,11}\) However, as shown in Fig. 1, the position of its scintillation emission spectrum peaking around 311 nm does not match well the spectral sensitivity of the general photodetectors such as photomultiplier tube (PMT).

Organic scintillators (plastics, liquids) on the contrary are composed of aromatic hydrocarbons. Plastic scintillators are non-fluid solutions consisting of fluorescent organic compounds dissolved in a solidified polymer matrix. Organic scintillators are made of low $Z$-elements and have a low density. Therefore, the main interaction mechanism is Compton scattering. The photoelectric effect is dominant only at low energies (typically below 20 keV). Because of the low density, more volume (thickness) is required to obtain reasonable detection efficiency. However, the relatively low cost of plastic scintillators more than compensates for this when large area detectors are required. The low intrinsic scintillation efficiency of organic scintillators results in rather weak pulses for X-ray/$\gamma$-ray energies below 100 keV. Standard plastic scintillators, such as BC-400 series (Saint-

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**Table I. Comparison between Pr:LuAG and popular cerium-activated scintillators.**

<table>
<thead>
<tr>
<th></th>
<th>Pr:LuAG</th>
<th>LSO:Ce</th>
<th>LuYAP:Ce</th>
<th>LaBr$_3$:Ce</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light output (photons/MeV)</td>
<td>20000</td>
<td>38000</td>
<td>&lt;20000</td>
<td>70000</td>
</tr>
<tr>
<td>Energy resolution at 662 keV (%)</td>
<td>4.6</td>
<td>8</td>
<td>6.8</td>
<td>3</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>6.73</td>
<td>7.4</td>
<td>6.1–8</td>
<td>5.1</td>
</tr>
<tr>
<td>Effective Z</td>
<td>62.9</td>
<td>66</td>
<td>40–63</td>
<td>47</td>
</tr>
<tr>
<td>Emission wavelength (nm)</td>
<td>310</td>
<td>420</td>
<td>360</td>
<td>380</td>
</tr>
<tr>
<td>Decay time (ns)</td>
<td>~20</td>
<td>40</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>

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**Fig. 1.** Quantum efficiency of PMT (Hamamatsu R9800) and emission spectrum of Pr:LuAG.
Gobain\cite{28,29} have a light output which is about a factor of 2–4 lower than that of LYSO. Therefore, the main use of plastic scintillators for gamma detection is for gamma energies below 100 keV.

In this study, we have investigate the effect of covering the Pr:LuAG with plastic scintillators to shift the luminescence wavelength towards the region of higher spectral sensitivity of PMT.

2. Methods

2.1 Sample preparations

Pr:LuAG single crystals were grown using Czochralski (CZ) method\cite{6,11} with an RF heating system in Furukawa. Pr concentration is 0.25 at.\% (with respect to Lu). Crystal growth was carried out with the rotation rate of 8–12 rpm and growth rate was 1.0 mm/h. An automatic control system was used to control the crystal diameter. Crystals of approximately 100 mm in diameter and 100 mm long were grown from an Ir crucible. An Ar atmosphere was used to prevent Ir crucible from oxidization. The seed crystals were [100] oriented Pr:LuAG crystal. At the end of crystal growth process, the crystal was pulled above the melt and gradually cooled down to room temperature. Sample pieces were cut and polished into with 10 × 10 × 10 mm$^3$ size.

The plastic scintillator used in this system is an organic scintillator made of poly(vinyl toluene) base doped with aromatic additives to increase its scintillation efficiency. These plastic scintillators are available commercially in different nomenclature depending on the wavelength of the emission desired. In this study, a colorless transparent plastic scintillator nominated as BC-499 (Saint-Gobain), which have excitation peak at around 300 nm and emission peak at 430 nm with fast decay time of 2.1 ns, was selected as the candidate for the effective wavelength shifter of Pr:LuAG. As shown in Fig. 2, Pr:LuAG single crystal was coupled with BC499 thin film and five plane of the cubic crystal were covered with Teflon tape. One plane, which is faced towards the window of PMT (Hamamatsu R9800).

2.2 Optical, luminescence, and radiation response measurements

Absorption and photoluminescence spectra were obtained by a spectrophotometer (Hitachi U-4000) and fluorescence spectrophotometer (Hitachi F-4500), respectively. Radioluminescence spectra were obtained by a spectrofluorometer SR163 (ANDOR) using an X-ray tube (operated at 40 kV and 20 mA, Cu cathode).

To determine light yield, the energy spectra were collected under 662 keV $\gamma$-ray excitation ($^{137}$Cs source) using an amplifier with a shaping time of 0.5 $\mu$s, the PMT and a multichannel analyzer in the pulse height mode. Once the photo-absorption peak was detected, double Gaussian function was applied to fit the peak. In such analysis, the light yield and energy resolution were compared each other.

The decay time was also measured by using pico second pulse X-ray equipped streak camera system which was our original instrument.\cite{30} The measured wavelength was set to be 420 nm for WLS applied Pr:LuAGs and 315 nm for Pr:LuAG, respectively. The averaged energy of emitted X-rays was 20 keV and the timing resolution was around 80 ps.

Fig. 2. (Color online) The geometry of the light output measurements.

(a)

(b)

Fig. 3. (a) Excitation and emission spectra of BC499 and (b) radioluminescence spectra of the hybrid scintillator and Pr:LuAG itself.

3. Result and discussion

3.1 Luminescence measurements

Emission spectrum of BC-499 was measured at 310 nm excitation by Hitachi F-2700. As shown in Fig. 3(a), emission peaks at 384 and 434 nm were observed. These emission peaks suit to sensitive wavelength of the PMT. Fluorescence spectrophotometer. Excitation spectra were also measured at 384 and 434 nm. E excitation peaks of BC-499 are well matched with the Pr:LuAG emission peak at 310 nm. Radioluminescence spectrum of hybrid scintillator
using Pr:LuAG and BC-499 was measured with a spectrofluorometer 199S (Edinburgh Instrument) using an X-ray tube (operated at 35 kV and 16 mA, Mo cathode). As shown in Fig. 3(b), emission wavelength of the hybrid scintillator successfully shifted to around 430 nm.

3.2 Light output measurements
Gamma ray response of Pr:LuAG coated with BC-499 on a face and all faces of the 10 mm cubic sample were measured under 137Cs excitation at room temperature. Obtained energy spectra were shown in Fig. 4. Light output of one face and all faces coated hybrid scintillator were 118 and 130%, respectively, higher than that of Pr:LuAG itself. Energy resolutions of Pr:LuAG itself, one face and all faces coated hybrid scintillator were 12.4, 10.1, and 10.3%, respectively. Shifting of Pr:LuAG emission towards the region of higher sensitivity of the used PMT by BC-499 could be an effective solution to improve light output and energy resolution.

3.3 Decay curve measurement
Let us suppose that all the photons from inorganic scintillator will reach to organic scintillator. We consider the case as a classical donor–accept radiative energy transfer, where the donors and acceptors are the Pr3+ and plastic scintillator emission centers, respectively. (N: excited state number at t = 0.) Decay curve of emission from Pr:LuAG due to Pr3+ 4f–5d transition was written as1-11)

\[
\frac{dN_i}{dt} = -\frac{1}{\tau_i} N_i \Leftrightarrow N_i(t) = N \exp\left(-\frac{t}{\tau_i}\right). \tag{1}
\]

\(N_0\) stands for the number of excited states in organic scintillator, Here, \(\tau_0\) is its decay time and \(\alpha\) defines as ratio of absorbed photons by organic scintillator generated from inorganic scintillator. \(\tau_i\) is decay time of inorganic scintillator. \(\varepsilon_i\) is luminescent efficiency:

\[
\frac{dN_0}{dt} = \alpha \frac{\varepsilon_i N_i}{\tau_i} \exp\left(-\frac{t}{\tau_i}\right) - \frac{1}{\tau_0} N_0. \tag{2}
\]

If the initial condition is \(N_0(t = 0) = 0\),

\[
N_0(t) = \alpha \frac{\varepsilon_i N_0}{\tau_i} \left[\exp\left(-\frac{t}{\tau_i}\right) - \exp\left(-\frac{t}{\tau_0}\right)\right]. \tag{3}
\]

When wavelength shifter works ideally, \(\alpha = 1\) and

\[
S_{\text{shifted}}(t) = \alpha_0 \frac{\varepsilon_i N_0}{\tau_i - \tau_0} \left[\exp\left(-\frac{t}{\tau_i}\right) - \exp\left(-\frac{t}{\tau_0}\right)\right]. \tag{4}
\]

Decay curves of the hybrid scintillator coated with BC-499 on all faces of the Pr:LuAG. Pr:LuAG itself and the hybrid scintillator were obtained at the range between 405 and 435 nm under the X-ray excitation. Experimentally obtained decay curves and simulated one using the above equation are shown in Fig. 5 with decay curve of the Pr:LuAG itself at the range between 300 and 460 nm. Decay time of Pr:LuAG and the BC-499 itself are \(\tau = 18.7\) and \(\tau_0 = 2.1\), respectively. These obtained decay time are used for the simulation. It is found that the simulated decay curve well reproduced the experimentally observed curve.

4. Conclusion
It is concluded that the hybrid scintillator realized with the Pr:LuAG scintillator covered by BC-499 can improve the scintillation performance when using the PMT. Emission wavelength of the hybrid scintillator successfully shifted to around 430 nm in which PMT have better quantum efficiency than that of 310 nm. In the case of the hybrid scintillator, light output was increased up to 130% compared to Pr:LuAG itself. Decay curve of the Pr:LuAG sample coupled with the WLS was also measured and successfully modeled.

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\[\text{Fig. 4. (Color online) Energy spectra of Pr:LuAG itself and hybrid scintillators.}\]

\[\text{Fig. 5. Decay curves of Pr:LuAG itself and hybrid scintillator.}\]
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