Scintillation properties of LaBr$_3$:Ce$^{3+}$ crystals: fast, efficient and high-energy-resolution scintillators

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Abstract

The scintillation properties of LaBr$_3$ doped with different Ce concentrations, studied by means of optical, X-ray, and $\gamma$-ray excitation are presented. Under optical and $\gamma$-ray excitation, Ce$^{3+}$ emission is observed peaking at 356 and 387 nm. For pure LaBr$_3$ and LaBr$_3$ doped with 0.5%, 2%, 4% and 10% Ce$^{3+}$ we measured a light yield of $17\times10^3$, $61\times10^3$, $48\times10^3$, $48\times10^3$ and $45\times10^3$ photons per MeV (ph/MeV) of absorbed $\gamma$-ray energy, respectively. The scintillation decay curve of LaBr$_3$:Ce$^{3+}$ can be described by a single exponential decay function with a decay time of $30\pm5$ ns. It represents over 90% of the total light yield. An energy resolution (FWHM over peak position) for the 662 keV full energy peak of, respectively, 2.9 ± 0.1, 3.8 ± 0.4, 3.5 ± 0.4 and 3.9 ± 0.4 was observed for LaBr$_3$:0.5%, 2%, 4% and 10% Ce$^{3+}$. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the search for the “ideal scintillator” most efforts have been directed towards the oxide materials. Certainly, attractive oxide scintillators have been developed, some with a high density, others with a relatively large light output, and many have found widespread utilization in medical and high-energy physics applications. Nonetheless, renewed interest in scintillators based on halides, particularly chlorides and bromides has resulted in the discovery of new inorganic scintillators like K$_2$LaCl$_5$:Ce$^{3+}$ [1,2] and RbGd$_2$Br$_7$:Ce$^{3+}$ [3,4]. Both show a high light yield in combination with a fast decay and excellent energy resolution. Undoubtedly, these materials are very attractive in selected applications were demands of energy resolution and timing dominate over density and attenuation length. In the family of the rare earth trihalides (LnX$_3$:Ce$^{3+}$ with Ln = La, Gd, Lu; X = Cl, Br) a substantial amount of research has been carried out in the last few years. Starting with LaF$_3$ [5,6] and CeF$_3$ [7,8], it was eventually shown that LaCl$_3$:Ce [9–11] unites several good qualities in an inorganic scintillator should posses: a high light yield, a fast decay, good timing properties and an excellent energy resolution. However, to achieve these properties a relatively high Ce concentration...
was needed and the contribution of the short decay component to the total light yield was never to exceed 69% [10,11].

In this paper an analogue to the LaCl$_3$:Ce$^{3+}$ scintillator is described, Ce doped LaBr$_3$. It is shown that LaBr$_3$:Ce$^{3+}$ has even better scintillator properties than LaCl$_3$:Ce$^{3+}$ and already at low Ce concentrations a fast luminescence decay is observed, representing over 90% of the total light yield.

2. Results

Crystals of pure LaBr$_3$, LaBr$_3$:0.5%, 2%, 4% and 10% Ce$^{3+}$ were prepared according to the ammonium halide method [12,13]. Crystals were grown by the Bridgman technique. LaBr$_3$ crystallizes in the UCl$_3$ type structure space group $P6_3/m$ [14]. The calculated density is 5.29 g/cm$^3$. Details on experimental techniques can be found in Ref. [9].

The X-ray excited optical luminescence spectra of some of these crystals at room temperature are shown in Fig. 1. Each spectrum has been corrected for the transmission of the system and normalized in such a way that the integral over all wavelengths is equal to the absolute light yield in photons per MeV as found from pulse height spectra recorded with a shaping time of 10 $\mu$s. For pure LaBr$_3$, the X-ray excited optical luminescence spectrum at 100 K (see inset) consists of two broad bands with maxima located near 340 and 430 nm, respectively. Both bands are attributed to self-trapped exciton (STE) luminescence. However, at elevated temperatures the band near 340 nm has completely disappeared and the maximum of the 430 nm band shifts to shorter wavelengths (higher energy). For other bromides [3,4,9,15] and pure LaCl$_3$ [9,11] similar bands have been observed and were readily assigned to STE emission. The X-ray excited optical luminescence spectra of the cerium doped LaBr$_3$ crystals at room temperature are dominated by a broad emission band located between 325 and 425 nm. It is attributed to Ce$^{3+}$ luminescence. In contrast to LaCl$_3$:Ce$^{3+}$ [11], no residual STE emission is present. However, for LaBr$_3$:10% Ce$^{3+}$ we did observe an additional luminescence band near 275 nm. This band was not present in the room temperature X-ray excited optical luminescence spectrum of pure LaBr$_3$ showing only STE luminescence near 450 nm. Probably, the luminescence band near 275 nm is due to impurity...
(Ce$^{3+}$) trapped STE luminescence or some other defect related to Ce$^{3+}$. Note that when the Ce concentration is increased, the intensity of the Ce$^{3+}$ emission band decreases.

The total light yield as function of temperature for pure LaBr$_3$ and LaBr$_3$:0.5% Ce$^{3+}$ is shown in Fig. 2. From 100 to 400 K the total light yield of both pure LaBr$_3$ and LaBr$_3$:0.5% Ce$^{3+}$ decreases with temperature. For LaBr$_3$ doped with 2%, 4% and 10% Ce$^{3+}$ a similar correlation between total light yield and temperature is observed. Note that the light yield at 100 K for both pure LaBr$_3$ and LaBr$_3$:0.5% Ce$^{3+}$ is the same, 67000±3000 photons/MeV.

Light yields derived from pulse height spectra under $^{137}$Cs 662 keV $\gamma$-ray excitation, expressed in photons per MeV (ph/MeV) are compiled in Table 1.

The pulse height spectrum of LaBr$_3$:0.5% Ce$^{3+}$ [16] is shown in Fig. 3. In many cases, the photopeak is accompanied by a shoulder at lower energy, due to the escape of characteristic K$_{a}$, K$_{b}$ X-rays of lanthanum. Pure LaBr$_3$ has the lowest light output with 17,000±2000 ph/MeV, obtained with a shaping time of 10 $\mu$s (see Table 1). For LaBr$_3$ doped with different Ce concentrations, light yields in the order of 45,000–61,000 ph/MeV of absorbed $\gamma$-ray energy were measured. Energy resolutions $R$ (FWHM over peak position) for the 662 keV full energy peak are between 2.9% and 3.9%. These energy resolutions are the best for inorganic scintillator detectors ever-reported in literature [10,11,16]. In contrast to cerium doped LaCl$_3$, the LaBr$_3$ crystals doped with 2%, 4% or 10% Ce$^{3+}$ show considerable afterglow when exposed to ambient light. However, it seemed to dwindle within the hour. For LaBr$_3$:0.5% Ce$^{3+}$ we did not observe any afterglow component.

Scintillation decay time spectra of pure LaBr$_3$ and LaBr$_3$:0.5% Ce$^{3+}$ [16] at room temperature under $^{137}$Cs $\gamma$-ray excitation are shown in Fig. 4.

![Fig. 2. Temperature dependence of the total light yield for pure LaBr$_3$ and LaBr$_3$:0.5% Ce$^{3+}$. Vertical bars give errors. The errors for LaBr$_3$:0.5% Ce$^{3+}$ are of the size of the triangles.](image1)

![Fig. 3. Pulse height spectrum of LaBr$_3$:0.5% Ce$^{3+}$ under $^{137}$Cs $\gamma$-ray excitation, recorded with a shaping time of 10 $\mu$s. The inset shows part of the spectrum on a linear scale.](image2)

### Table 1

<table>
<thead>
<tr>
<th>Host</th>
<th>[Ce$^{3+}$] (%)</th>
<th>Photon yield (10$^3$ ph/MeV)</th>
<th>Energy resolution $R$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaBr$_3$</td>
<td>—</td>
<td>17±2</td>
<td>14±2</td>
</tr>
<tr>
<td>LaBr$_3$ 0.5</td>
<td>—</td>
<td>61±5</td>
<td>2.9±0.1</td>
</tr>
<tr>
<td>LaBr$_3$ 2</td>
<td>48±5</td>
<td>48±5</td>
<td>3.8±0.4</td>
</tr>
<tr>
<td>LaBr$_3$ 4</td>
<td>48±5</td>
<td>48±5</td>
<td>3.5±0.4</td>
</tr>
<tr>
<td>LaBr$_3$ 10</td>
<td>45±5</td>
<td>45±5</td>
<td>3.9±0.4</td>
</tr>
</tbody>
</table>
The scintillation decay curves have been normalized such that the time integral equals the absolute light yield as found from pulse height spectra recorded with a shaping time of 10 μs. At first sight, the decay curves are not single exponential and are probably composed of several decay components; e.g. a relatively short decay component due to Ce3+ luminescence and a relatively long decay component due to energy transfer to Ce3+ centers by STE diffusion. Nevertheless, looking at the shape of the decay curves of LaBr3:0.5%, 2%, 4% and 10% Ce3+ it is clear that the contribution of this long decay component to the total light yield is relatively small. Thus, for practical purposes a simple exponential decay function was used to analyze these curves. To correct for deviations at time scales up to 200 μs an additional error in the decay time was taken into account. In contrast to pure LaCl3 [9,11], pure LaBr3 seems to have both a relatively long decay component and a short decay component. The latter is probably due to some trace of Ce3+. The relatively long decay component of about 300 ns is most likely due to (quenched) STE luminescence. For LaBr3:Ce3+ the decay time of the short decay component is 30 ± 5 ns, representing over 90% of the total light yield.

3. Discussion and conclusions

Although LaCl3 and LaBr3 are closely related with respect to crystal structure and other physical properties, doping these matrices with trivalent cerium results in two distinct scintillators. LaBr3:Ce3+, which scintillates fast and very efficiently already at low Ce concentrations and LaCl3:Ce3+ which, contrarily needs a relatively high Ce concentration to obtain 60% intensity with a decay component of 25 ns [10,11]. Another difference is the presence of STEs at room temperature in LaCl3:Ce3+; they appear to be absent in LaBr3:Ce3+. Nevertheless, assuming that STEs do play an important role in the scintillation mechanism of LaBr3:Ce3+, the diffusion rate of the STEs ought to be much higher than the diffusion rate of STEs in LaCl3:Ce3+ to account for both the efficient scintillation of LaBr3:Ce3+ at low Ce concentrations and the absence of STE luminescence at room temperature. However, if STE diffusion is the predominant mechanism in LaBr3:Ce3+, the scintillation pulse should display a risetime depending on the speed of STE diffusion. The risetime of the scintillation pulse of LaBr3:0.5% Ce3+ seems to confirm this hypothesis. Another possibility is direct capture of electron–hole pairs on Ce3+. In this case, the decay time profile is characteristic of the lifetime of the excited state of Ce3+ only. Then, an increase in Ce concentration would also mean an increase in the relative contribution of this decay component to the total light yield. However, already for LaBr3:0.5% Ce3+ the short decay time component represents over 90% of the total light yield. Thus, increasing the Ce concentration would hardly have any effect on the decay time profile of LaBr3:Ce3+. To give a more definitive judgement, experiments like electron-paramagnetic resonance (EPR) and temperature-dependent decay time measurements have to be performed.

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References