Optical and Scintillation properties of Cs$_2$LiYCl$_6$:Ce$^{3+}$ and Cs$_2$LiYCl$_6$:Pr$^{3+}$ Crystals

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Abstract—In this paper we report on the optical and scintillation properties of Cs$_2$LiYCl$_6$:Ce$^{3+}$ and Cs$_2$LiYCl$_6$:Pr$^{3+}$ crystals. Crystals of Cs$_2$LiYCl$_6$ doped with different Ce$^{3+}$ and Pr$^{3+}$ concentrations were grown and studied under optical, X-ray, gamma ray, and thermal neutron excitation. These scintillators exhibit core-valence and self-trapped exciton luminescence in addition to fast emission from Ce$^{3+}$ and Pr$^{3+}$. Efficient thermal neutron detection was observed for both scintillators. The position of the neutron peak in its pulse height spectrum was found at about 5 times the channel number of the position of the gamma peak.

I. INTRODUCTION

SCINTILLATORS for gamma ray and thermal neutron detection have the ability to efficiently detect and discriminate between gamma rays and low energy neutrons, either by the difference in light output, time response, emission spectra or a combination of the three. To detect thermal neutrons efficiently, the scintillator material should contain an isotope with high neutron-capture cross-section, such as $^6$Li or $^{10}$B. Interaction of thermal neutrons with $^6$Li or $^{10}$B yields high energy reaction products that in turn deposit their energy in the scintillator.

Recently, a new thermal neutron scintillator has been discovered, Cs$_2$LiYCl$_6$:Ce$^{3+}$, that shows a reasonable light output under gamma ray excitation and has good neutron/gamma discrimination properties [1-3]. In this paper we present results on two thermal neutron scintillators, Cs$_2$LiYCl$_6$:Ce$^{3+}$ and Cs$_2$LiYCl$_6$:Pr$^{3+}$. We report on the crystal growth of these materials and explore their properties under optical, X-ray, gamma ray and neutron excitation. X-ray excited optical luminescence, optical excitation and emission spectra, pulse height spectra and scintillation decay time spectra are presented.

II. EXPERIMENTAL

Large single crystals of Cs$_2$LiYCl$_6$:0.2% Ce$^{3+}$ (Ø 10 mm x 5 mm), Cs$_2$LiYCl$_6$:0.5% Ce$^{3+}$ (Ø 10 mm x 12 mm) and Cs$_2$LiYCl$_6$:0.2% Pr$^{3+}$ (Ø 10 mm x 13 mm) were grown by the Bridgman technique in vertical silica ampoules under vacuum.

Starting materials were CsCl (99.98%), LiCl (99.995%), YCl$_3$ (99.9%), CeCl$_3$ (99.9%) and PrCl$_3$ (99.99%) from Aldrich. Cs$_2$LiYCl$_6$ has a cubic elpasolite structure with space group Fm$ar{3}$m (no. 225). The calculated density is 3.31 g/cm$^3$. The crystals are slightly hygroscopic and are kept in mineral oil to prevent hydration of the surface.

X-ray excited optical luminescence spectra were recorded with a Philips X-ray tube having a Cu anode operated at 30 kV and 20 mA. Optical excitation and emission spectra were recorded with a McPherson 932 deuterium discharge lamp. In both cases, light was dispersed through a McPherson 234/302 monochromator equipped with a holographic grating (1200 grooves/mm) and detected with a Hamamatsu R2059 photomultiplier tube (PMT).

Pulse-height spectra were recorded with a Hamamatsu R2059 PMT. The signal output of the PMT was connected to a Canberra 2005 preamplifier and a Canberra 2020 spectroscopic amplifier. The crystals were optically coupled onto the window of the PMT using Bicron BC-630 optical grease. To minimize losses in light yield, the crystals were wrapped in several layers of 0.1-mm UV reflecting Teflon tape. Nitrogen was flushed around the crystal to prevent hydration of the surface during measurement. Light yields expressed in photoelectrons per megaelectronvolt (MeV) of absorbed $\gamma$-ray energy (phe/MeV), were determined by comparing the peak position of the 662 keV full energy peak in the pulse height spectra with the position of the peak in the spectrum of single photoelectrons. The absolute light yield, expressed in photons per MeV of absorbed $\gamma$-ray energy (ph/MeV), was determined from the detection efficiency of the PMT. The detection efficiency was assumed to be 24% and 21% for Cs$_2$LiYCl$_6$:Ce$^{3+}$ and Cs$_2$LiYCl$_6$:Pr$^{3+}$, respectively. Pulse height spectra under thermal neutron excitation were recorded using a $^{252}$Cf source. The source was placed in a cylindrical polyethylene enclosure of 6 cm thickness. The enclosure moderated a large fraction of the neutrons to thermal energies. A few millimeters thick aluminum plate and a 5 cm thick lead brick were present between the enclosure and the scintillator to reduce gamma and X-ray interactions in the crystal.

Scintillation decay time spectra were recorded using a $^{137}$Cs source and a Tektronix TDS 220 oscilloscope connected to the output of the PMT.
III. RESULTS AND DISCUSSION

The X-ray excited optical luminescence spectra of Cs$_2$LiYCl$_6$:0.2% Pr$^{3+}$ and Cs$_2$LiYCl$_6$:0.5% Ce$^{3+}$ are shown in Fig. 1. The spectrum of Cs$_2$LiYCl$_6$:0.5% Ce$^{3+}$ (dotted trace) consists of a broad emission band located between 350 and 450 nm. It is due to Ce$^{3+}$ $5d \rightarrow 4f$ emission. Transitions from the lowest $5d$ excited state to the $^2F_{5/2}$ and $^2F_{7/2}$ states of the $4f^1$ configuration are found at 373 nm and 411 nm, respectively. The weak band around 315 nm is attributed to self-trapped exciton (STE) emission [1-3]. For several other chloride elpasolites [4] similar bands were observed in this spectral range and were ascribed to Ce$^{3+}$ and STE emission.

For Cs$_2$LiYCl$_6$:0.2% Pr$^{3+}$ (solid trace), the X-ray excited optical luminescence spectrum is dominated by a broad structured emission band. A large part of this band, between 300 and 400 nm, is due to STE emission. However, core-valence (CV) luminescence [5] may also be present. The short wavelength side of the spectrum is ascribed to Pr$^{3+}$ emission. The two peaks at 264 and 279 nm are assigned to transitions from the lowest $5d$/$4f$ excited state to the $^2H_1$ ground state of Pr$^{3+}$. The doublet peaking at 489 nm and 499 nm is assigned to Pr$^{3+}$ $4f \rightarrow 4f$ transitions. Furthermore, several impurities are present. The sharp line at 314 nm is attributed to the Gd$^{3+}$ $^4S_3/2 \rightarrow ^4S_{1/2}$ transition, whereas the long wavelength side of the broad emission band, between 350 and 340 nm, is probably due to Ce$^{3+}$ $5d \rightarrow 4f$ emission.

Figure 2 presents both the excitation and emission spectrum of Cs$_2$LiYCl$_6$:0.2% Pr$^{3+}$ at room temperature. Excitation spectra at 130 K and room temperature emission spectra of Cs$_2$LiYCl$_6$:Ce$^{3+}$ can be found in [2]. The excitation spectrum of Cs$_2$LiYCl$_6$:0.2% Pr$^{3+}$ (a) consists of a broad structured band peaking at 190 nm and 230 nm. We assign this band to Pr$^{3+}$ $4f \rightarrow 4f/5d$ transitions. Similar spectra were obtained for Cs$_2$NaYCl$_6$:Pr$^{3+}$ by Laroche et al. [6].

Empirically, the energetic position of the lowest $4f/5d$ excited state of Pr$^{3+}$-doped materials can be estimated from the energetic position of the lowest $5d$ excited state of Ce$^{3+}$ in the same material [7,8]. In general, the following relation holds:

$$E[Pr^{3+}, 4f/5d] = E[Ce^{3+}, 5d] + 12240 \text{ cm}^{-1} \pm 750 \text{ cm}^{-1},$$

where $E$ is the energy of the lowest level of the $4f/5d$ and $5d$ configuration of Pr$^{3+}$ and Ce$^{3+}$, respectively. If we assume that the lowest $5d$ excited state of Ce$^{3+}$ is located at 340 nm [2] then the lowest $4f/5d$ excited state of Pr$^{3+}$ will be found at 240 ± 4 nm. This value is in reasonable agreement with the maximum at 230 nm in the excitation spectrum of Cs$_2$LiYCl$_6$:0.2% Pr$^{3+}$. The assignment of the band at 265 nm in the absorption spectrum of Cs$_2$NaYCl$_6$:Pr$^{3+}$ [6] is probably incorrect. It is due to an impurity and not due to Pr$^{3+}$ excitation. Furthermore, excitation of Cs$_2$LiYCl$_6$:0.2% Pr$^{3+}$ at 230 nm (b) yields three intense emission bands peaking at 266, 280, and 303 nm, corresponding to the different transitions from the lowest $4f/5d$ excited state to the $^2H_4$, $^2H_6$, and $^4I_6$ manifolds, respectively, of the ground state of Pr$^{3+}$. Transitions from the lowest $4f/5d$ excited state of Pr$^{3+}$ to the $^2F_1$ levels may contribute to the long wavelength side of the 303 nm peak. The weak band at 350 nm is ascribed to $4f/5d \rightarrow 1G_4$ transitions. When Cs$_2$LiYCl$_6$:0.2% Pr$^{3+}$ is excited at 200 nm, its optical emission spectrum closely resembles its X-ray excited optical luminescence spectrum (compare inset with Fig. 1). We assume that the similarity arises from band-to-band excitation. Apparently, energy transfer from the host to Pr$^{3+}$ centers is rather inefficient and host excitation mainly yields STE emission. This was also observed for Cs$_2$LiYCl$_6$:Ce$^{3+}$ [2].

Light yields derived from pulse height spectra under $^{137}$Cs 662 keV $\gamma$-ray and thermal neutron excitation for Cs$_2$LiYCl$_6$:0.5% Ce$^{3+}$ and Cs$_2$LiYCl$_6$:0.2% Pr$^{3+}$ are compiled in Table 1. All light yields of Table 1 are obtained with crystals in mineral oil, contained in teflon-wrapped quartz tubes.
Pulse height spectra of Cs$_2$LiYCl$_6$:0.5% Ce$^{3+}$ and Cs$_2$LiYCl$_6$:0.2% Pr$^{3+}$ under $^{137}$Cs 662 keV $\gamma$-ray and thermal neutron excitation are shown in Fig. 3 and 4, respectively. The highest light yield of 21000 ± 2000 ph/MeV was obtained for Cs$_2$LiYCl$_6$:0.5% Ce$^{3+}$ with a shaping time of 4 µs (see Table I).

Energy resolutions $R$ (full-width at half-maximum over peak position) for the 662 keV full energy peak are 8%, 6%, and 15%, for Cs$_2$LiYCl$_6$:0.2% Ce$^{3+}$, Cs$_2$LiYCl$_6$:0.5% Ce$^{3+}$, and Cs$_2$LiYCl$_6$:0.2% Pr$^{3+}$, respectively. These energy resolutions are comparable to those reported in literature [1,3], but were obtained with much larger single crystals.

Figures 5 and 6 show the scintillation decay time spectra of Cs$_2$LiYCl$_6$:0.2% Ce$^{3+}$ and Cs$_2$LiYCl$_6$:0.2% Pr$^{3+}$ under gamma ray excitation show a short decay component of about 1 ns which is attributed to CV luminescence. The decay component with a decay time of about 35 ns in the spectrum of Cs$_2$LiYCl$_6$:0.2% Ce$^{3+}$ is ascribed to Ce$^{3+}$ emission (see inset of Fig. 5). Furthermore, the decay component with a decay time of about 2 µs is due to STE emission. In contrast, the scintillation decay profile of Cs$_2$LiYCl$_6$:Ce$^{3+}$ and Cs$_2$LiYCl$_6$:Pr$^{3+}$ under thermal neutron excitation does not show the fast decay component due to CV luminescence, see curve (b).

<table>
<thead>
<tr>
<th>Scintillator</th>
<th>Light Yield $\gamma$ (ph/MeV)</th>
<th>Resolution $R$ (%) at 662 keV n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs$_2$LiYCl$_6$:0.2% Ce$^{3+}$</td>
<td>12000</td>
<td>8</td>
</tr>
<tr>
<td>Cs$_2$LiYCl$_6$:0.5% Ce$^{3+}$</td>
<td>21000</td>
<td>6</td>
</tr>
<tr>
<td>Cs$_2$LiYCl$_6$:0.2% Pr$^{3+}$</td>
<td>10000</td>
<td>15</td>
</tr>
</tbody>
</table>

Fig. 3 Pulse height spectra of Cs$_2$LiYCl$_6$:0.5% Ce$^{3+}$ under (a) $^{137}$Cs 662 keV $\gamma$-ray excitation and (b) thermal neutron excitation.

Fig. 4 Pulse height spectra of Cs$_2$LiYCl$_6$:0.2% Pr$^{3+}$ under (a) $^{137}$Cs 662 keV $\gamma$-ray excitation and (b) thermal neutron excitation.
Under thermal neutron excitation, the decay profiles exhibit a rise time of the order of 100 ns and a decay time characteristic of STE luminescence. We could not distinguish a decay component due to \(\text{Ce}^{3+}\) or \(\text{Pr}^{3+}\) emission. The absence of a fast component upon neutron interaction allows effective n/\(\gamma\) discrimination on the basis of pulse shape analysis.

**IV. CONCLUSION**

If we compare the scintillation properties of \(\text{Cs}_2\text{LiYCl}_6:\text{Ce}^{3+}\) and \(\text{Cs}_2\text{LiYCl}_6:\text{Pr}^{3+}\) with those of other thermal neutron scintillators, \(\text{Cs}_2\text{LiYCl}_6:\text{Ce}^{3+}\) and \(\text{Cs}_2\text{LiYCl}_6:\text{Pr}^{3+}\) show a fast response, have good n/\(\gamma\) discrimination and are relatively easy to grow as large single crystals. For applications where a combination of these properties is required, both \(\text{Cs}_2\text{LiYCl}_6:\text{Ce}^{3+}\) and \(\text{Cs}_2\text{LiYCl}_6:\text{Pr}^{3+}\) will be an excellent choice.

**V. REFERENCES**

[1] C.M. Combes, P. Dorenbos, C.W.E. van Eijk, K.W. Krämer, H.U. Güdel, "Optical and scintillation properties of pure and Ce\(^{3+}\) -doped \(\text{Cs}_2\text{LiYCl}_6\) and \(\text{Li}_3\text{YCl}_6:\text{Ce}^{3+}\) crystals," *J. Lum.*, vol. 82, pp. 299-305, 1999.


