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New Thermal Neutron Scintillators: $Cs_2LiYCl_6 : Ce^{3+}$ and $Cs_2LiYBr_6 : Ce^{3+}$

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***Abstract*—The thermal neutron detection properties of $Cs_2LiYCl_6 : 0.1\% Ce^{3+}$ and $Cs_2LiYBr_6 : 1\% Ce^{3+}$ single crystals are presented. The compounds show high scintillation photon yields of 70 000 and 88 200 photons emitted per absorbed thermal neutron, respectively. Events caused by primary electrons with energy below 2.9 and 3.4 MeV, respectively, can be separated from neutron-induced events by pulse-height discrimination. For $Cs_2LiYCl_6 : 0.1\% Ce^{3+}$, due to the presence of a 4-ns fast core-valence luminescence, thermal neutrons and gamma rays can also be discriminated by means of the shape of the scintillation pulse. The main part of the scintillation pulse in $Cs_2LiYCl_6 : 0.1\% Ce^{3+}$ is relatively slow, however, $Cs_2LiYBr_6 : 1\% Ce^{3+}$ has a relatively intense component with $\tau = 85$ ns decay time.**

***Index Terms*—Gamma detection, scintillators, thermal neutron detection.**

The wavelength of thermal neutrons is comparable to atomic distances in the solid state and their energy comparable with that of phonons. This makes thermal neutron scattering a powerful technique to probe condensed matter [1]. In addition, the neutron magnetic moment enables the study of the magnetic structure and dynamics. Bright neutron sources are available at for example ILL (France) and ISIS (UK), and because even more intense neutron facilities are under construction, *viz.* SNS (USA) and JSNS (Japan), there is a continuing need for efficient and fast large area neutron detectors. It is also important to discriminate thermal neutrons from gamma rays that are often present together with the neutron beam [2].

The compounds $Cs_2LiYCl_6 : Ce^{3+}$ and $Cs_2LiYBr_6 : Ce^{3+}$ contain ^6Li isotopes with 7.5% natural abundance that capture thermal neutrons and convert them into ionizing particles according to the reaction

$$^6_3Li +^1_0 n \rightarrow ^3_1 H + \alpha. \quad (1)$$

The α particle and triton share a kinetic energy of 4.78 MeV. The particles create ionization tracks, and subsequent trapping of the free charges in the luminescence center Ce^{3+} leads to a scintillation light pulse. Approximately 22%, 18%, and 60% of the captured thermal neutrons are captured by ^6Li, ^{133}Cs, and $^{35,37}Cl$ in Cs_2LiYCl_6. The numbers are 40%, 34%, and 26% for ^6Li, ^{133}Cs, and $^{79,81}Br$ in Cs_2LiYBr_6.

In this letter, we report on the scintillation response of $Cs_2LiYCl_6 : 0.1\% Ce^{3+}$ and $Cs_2LiYBr_6 : 1\% Ce^{3+}$ to γ-rays and thermal neutrons. When irradiated by ionizing radiation, $Cs_2LiYCl_6 : 0.1\% Ce^{3+}$ shows a doublet emission band at 404 and 376 nm, and $Cs_2LiYBr_6 : Ce^{3+}$ a doublet emission at 423 and 389 nm [3]. These emissions are caused by transitions from the lowest 5d excited state of Ce^{3+} to the two spin-orbit split $^2F_{7/2}$ and $^2F_{5/2}$ ground state levels.

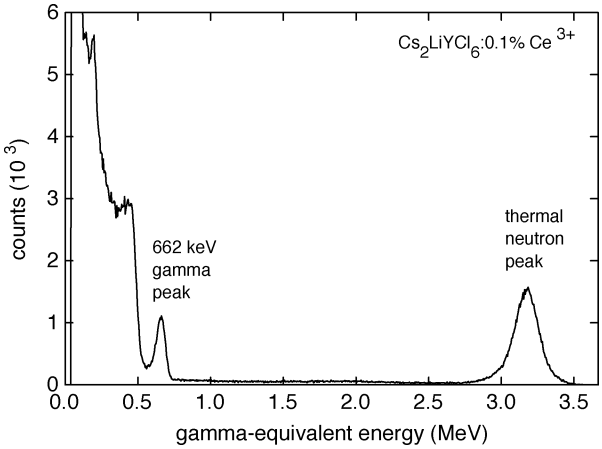

Fig. 1. The scintillation pulse-height spectrum of $Cs_2LiYCl_6 : 0.1\% Ce$ irradiated with gamma rays from a ^{137}Cs γ-source and thermal neutrons.

A fast decay time component of 65 ns was reported for $Cs_2LiYBr_6 : 1\% Ce^{3+}$. One to ten μs long components, caused by slow energy transfer to Ce^{3+} centers, were also observed in $Cs_2LiYBr_6 : 1\% Ce^{3+}$ as well as in $Cs_2LiYCl_6 : 0.1\% Ce^{3+}$ [3]. $Cs_2LiYCl_6 : Ce$ crystals exhibit 4 ns fast core-valence luminescence (CVL) under γ-ray excitation. Similar CVL was observed with gamma irradiation of $LiBaF_3$ [4], $LiBaF_3 : Ce$,Rb [5], and BaF_2 [6], however, it is absent under alpha particle or thermal neutron irradiation [7], [8]. CVL is also absent in $Cs_2LiYBr_6 : Ce^{3+}$ under gamma irradiation [3].

Cs_2LiYCl_6 and Cs_2LiYBr_6 with calculated densities of, respectively, 3.31 and 4.15 g/cm^3 were grown as single crystals by the vertical Bridgman technique [3]. They contain a natural abundance (7.5%) of ^6Li isotopes. The compounds are hygroscopic, and all experiments were performed on samples with approximate size of $3 \times 3 \times 4$ mm^3 and sealed in quartz ampoules.

For measuring gamma ray and thermal neutron scintillation pulse height spectra, the crystals, that are loosly inside a sealed quartz ampoule of 5 mm inner diameter, were mounted on a Phillips XP2020Q photomultiplier tube. Coupling fluid and Teflon tape was used to optimize light collection. The crystals were irradiated with 0.662 MeV gamma rays from a ^{137}Cs source and with thermal neutrons from the reactor at the home institute. The spectra were measured using standard techniques with 10 μs shaping, and the numbers for the absolute scintillation light yield were obtained from the single photo-electron response [9].

Fig. 1 and 2 show the results for $Cs_2LiYCl_6 : 0.1\% Ce^{3+}$ and $Cs_2LiYBr_6 : 1\% Ce^{3+}$. The 662 keV peak was used to calibrate the spectra in γ-equivalent energy. For the calibration, we assumed that the response of the scintillator is linear with gamma ray energy. Pulses from the thermal neutrons appear in the thermal neutron peak above 3 MeV γ-equivalent energy. (n, γ) reactions with caesium, chlorine, or bromine lead to the emission of γ rays. However, due to the low intensity and large escape probability from the crystals there is a small de-

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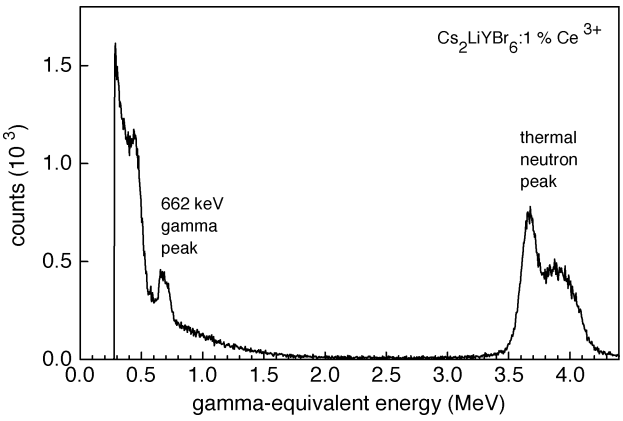

Fig. 2. The scintillation pulse-height spectrum of $Cs_2LiYBr_6 : 1\%$ Ce irradiated with gamma rays from a ^{137}Cs γ-source and thermal neutrons.

TABLE I
SCINTILLATION PROPERTIES OF $Cs_2LiYCl_6 : 0.1\%$ Ce AND $Cs_2LiYBr_6 : 1\%$ Ce UNDER γ-RAY AND THERMAL NEUTRON IRRADIATION

	^{137}Cs γ-rays		thermal neutrons		
Compound	Y (ph/MeV)	R_{662} (%)	Y (ph/n)	F_γ	R_n (%)
Cs_2LiYCl_6 0.1%Ce^{3+}	21600	8.0	70000	0.66	5.5
Cs_2LiYBr_6 1% Ce^{3+}	23600	7.0	85800	0.76	4.5
	24700	8.5	88200	0.75	9.0

tection probability and related photo-peaks do not appear in the pulse height spectra of Fig. 1 and 2. One does observe a continuum background extending up to 2.7 MeV in Fig. 1 and up to 2 MeV in Fig. 2 that can be attributed to the β decay of ^{38}Cl and ^{80}Br isotopes with half life times of $\tau_{0.5} = 37$ and 18 min, respectively. Possibly also compton scattered gamma rays contribute to these parts of the spectra.

The scintillation photon yield Y obtained with gamma rays, expressed as the number of photons emitted per MeV absorbed gamma ray energy (ph/MeV), and the yield per thermal neutron (ph/n) are compiled in Table I. $Cs_2LiYBr_6 : 1\%\ Ce^{3+}$ shows larger pulse heights and photon yields than $Cs_2LiYCl_6 : 0.1\%\ Ce^{3+}$ both for gamma rays and thermal neutrons. The peak resolution R_{662} defined as the width (FWHM) over the peak position of the 662 keV gamma peak and R_n of the neutron peak are compiled in Table I. $Cs_2LiYCl_6 : 0.1\%\ Ce^{3+}$ shows 662 keV and neutron peaks with resolution of 8% and 5.5%. The 0.662 MeV peak and the neutron peak in the spectrum for $Cs_2LiYBr_6 : 1\%\ Ce^{3+}$ are clearly composed of two sub-peaks. We could not find any electronic origin for the double peak and we conclude that it must be an intrinsic property of the crystal. Apparently one part of the crystal produces more photons than another part. The two rows in Table I give the numbers for both subpeaks.

For $Cs_2LiYCl_6 : 0.1\%\ Ce^{3+}$, the thermal neutron peak appears at $\approx$4.6 times higher energy than the 662 keV gamma peak. It corresponds with 70 000 ph/n. For $Cs_2LiYBr_6 : 1\%\ Ce^{3+}$ the thermal neutron peak is situated at $\approx$5.5 times higher energy than the 0.662 MeV gamma peak. It corresponds with even higher photon yield of 88 200 ph/n.

We define the γ-equivalent factor F_γ as

$$F_\gamma = \frac{E_\gamma(4.78)}{4.78} \tag{2}$$

where $E_\gamma(4.78)$ is the γ-equivalent energy of the neutron peak when 4.78 MeV energy is deposited in the scintillator. F_γ for $Cs_2LiYBr_6 : 1\%\ Ce^{3+}$ is higher than for $Cs_2LiYCl_6 : 0.1\%\ Ce^{3+}$,

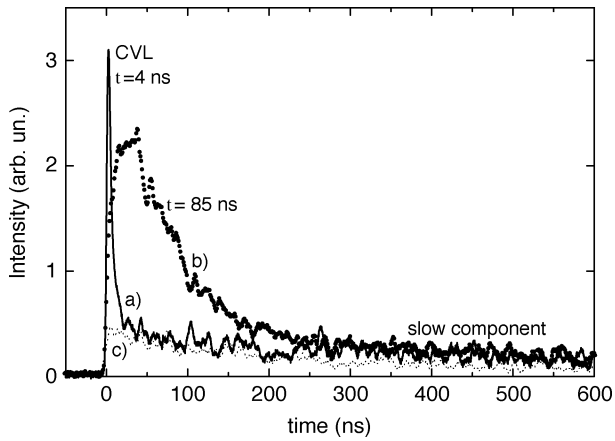

Fig. 3. 662 keV gamma ray excited scintillation pulse from (a) $Cs_2LiYCl_6 : 0.1\%$ Ce solid curve. (b) $Cs_2LiYBr_6 : 1\%$ Ce dotted curve. (c) The neutron excited pulse in $Cs_2LiYCl_6 : 0.1\%$ Ce.

see Table I. Thermal neutrons from reaction (1) can be distinguished from γ-rays by placing a threshold in the pulse height spectrum. For example, placing the threshold at $4.78 \times (F_\gamma - R_n) = 2.9$ or 3.4 MeV for, respectively, $Cs_2LiYCl_6 : 0.1\%\ Ce^{3+}$ and $Cs_2LiYBr_6 : 1\%\ Ce^{3+}$ one still accepts more than 98% of the neutron events while minimizing acceptance of gamma events.

Fig. 3 shows individual scintillation pulses measured with a digital oscilloscope in single shot mode. The scintillation pulse from $Cs_2LiYCl_6 : 0.1\%\ Ce^{3+}$ when irradiated by γ-rays from a ^{137}Cs source shows very clearly the 4 ns fast CVL component on top of a nonexponential decaying component. The CVL represents $\approx$8% of the total signal emitted in the first 1600 ns. The CVL is completely absent with thermal neutron excitation whereas the other component remains the same. Hence, excellent pulse shape discrimination is possible based on the presence of CVL with γ excitation and on its absence with thermal neutron excitation.

The scintillation pulse of $Cs_2LiYBr_6 : 1\%\ Ce^{3+}$ shows an 85 ns decay component representing $\approx$39% of the total signal plus a slower 2.5 μs component. CVL is not observed. The pulse shape remains the same when the compound is irradiated with γ-rays only. Therefore no pulse shape discrimination is possible for $Cs_2LiYBr_6 : 1\%\ Ce^{3+}$. However, pulse height discrimination is possible at a relatively high counting rate thanks to the fast component. The rise time in the scintillation pulse and the presence of more than one decay time component indicates that different processes are involved in the excitation of Ce^{3+} [3]. One may expect that the light output and decay time may change with the Ce^{3+} concentration, and the optimal concentration needs still to be found.

These first results demonstrate that the new scintillators are good thermal neutron detectors with an emission that matches the maximum sensitivity of bi-alkali photomultiplier tubes. The yields of 70 000 and 88 200 ph/n are significantly higher than the 51 000 ph/n for the well known $^6LiI : Eu^{2+}$ scintillator [10]. Only a mixture of ^6LiF with $ZnS : Ag^+$ has a higher neutron light yield of 160 000 ph/n [10]. Another advantage is the high F_γ factors of 0.66 and 0.76 for $Cs_2LiYCl_6 : 0.1\%\ Ce^{3+}$ and $Cs_2LiYBr_6 : 1\%\ Ce^{3+}$. Values of 0.31, 0.45, and 0.86 were reported for ^{6}Li-glass, LiF-ZnS:Ag, and $^6LiI : Eu$. A disadvantage is the relatively low Li concentration in Cs_2LiYX_6. The absorption lengths of 0.18 nm neutrons in 100% ^{6}Li-enriched crystals is calculated to be 3.2 mm and 3.7 mm for respectively $Cs_2LiYCl_6 : 0.1\%\ Ce^{3+}$ and $Cs_2LiYBr_6 : 1\%\ Ce^{3+}$, and relatively thick layers are needed for efficient detection. For these enriched materials, respectively, 78% and 90% of the absorbed neutrons react with ^{6}Li. The materials have the cubic elpasolite structure

and probably ceramic techniques can be used to produce layers with good optical transmission.

Fast count rates can be obtained with $Cs_2LiYBr_6 : 1\% Ce^{3+}$ because of the fast thermal neutron scintillation pulse with 85 ns decay time. It makes $Cs_2LiYBr_6 : 1\% Ce^{3+}$ very competitive to Ce^{3+} doped ^{6}Li-glass with $\tau = 75$ ns and 6000 ph/n [11], to $^6LiI : Eu^{2+}$ with $\tau = 1.2\ \mu s$ [12], and to $LiF - ZnS : Ag^+$ with $\tau \approx 1\ \mu s$ [13]. When better quality crystals are synthesized, we anticipate that the neutron peak resolution may reach 4.5% which is much better than the 13–22% for the best available commercial ^{6}Li glass (NE 902) and the 10% for $^6LiI : Eu$ [11]. $Cs_2LiYCl_6 : 0.1\% Ce^{3+}$ has a slightly poorer ph/n yield and F_γ than $Cs_2LiYBr_6 : 1\% Ce^{3+}$, and its response is also slower. However, pulse shape discrimination between neutrons and γ-rays is possible due to the presence of CVL under gamma ray excitation.

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