Scintillating properties of $LiYSiO_4$:Ce*

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Abstract: $LiYSiO_4$:Ce is a promising scintillator and some of its properties have been reported in previous papers. In this paper, samples doped with different concentrations of Ce are prepared and studied. First, the relative light yields of the samples are measured as 28.1%–37.1% compared with a standard anthracene crystal being irradiated by α particles and as ∼27.2% compared with NaI being irradiated by X-rays. Second, the effects of sample thicknesses on light yields are presented. Finally the timing behaviors of samples with different doped concentrations being irradiated with alpha particles and X-rays are discussed. The result shows that $LiYSiO_4$:Ce is a kind of fast scintillator (∼ 30 ns) with a moderate light yield that can be used for neutron detection.

Key words: $LiYSiO_4$:Ce, Ce^{3+}, neutron scintillator, light yield, decay time

PACS: 29.40.Mc, 29.40.Wk, 29.30.Lw **DOI:** 10.1088/1674-1137/35/12/010

1 Introduction

With spallation neutron sources being constructed and under development, intense pulsed-neutron beams will be produced and large area position-sensitive detectors (∼ 10 m^2) will be needed with a response time of ⩽100 ns [1]. Because of a ^{3}He supply shortage, there has been great interest in various neutron detection technologies especially the neutron scintillator.

A good neutron scintillator should have a large absorption probability, suitable color of scintillation light, high light yield, short decay time, γ ray insensitivity and low afterglow, etc.

A neutron scintillator, especially for thermal neutron detection, can be based on ^{6}Li, ^{10}B and ^{155,157}Gd (the ^{6}Li version is the most promising). Though the scintillator based on ^{155,157}Gd has a large cross section in neutron detection, the useful energy deposition is often around 80 keV for a thin neutron convertor and the 8 MeV γ ray generated may escape easily from the detectors. This is particularly true of neutron imaging detectors. In addition, Gd itself is sensitive to γ rays, thus it minimizes the signal-to-noise ratio. For a scintillator based on ^{6}Li, the reaction energy of 4.8 MeV is shared between the ^{4}He and ^{3}H with a range of the order of 10 μm. For charged particles such as ^{4}He, ^{3}H and ^{7}Li, generally the lighter particle gives rise to more light output than the heavier particle in the scintillator. Since a scintillator based on ^{10}B generates the heavier particle of ^{7}Li and releases less energy than that of a scintillator based on ^{6}Li in neutron detection, in principle ^{10}B is less favorable than ^{6}Li in neutron scintillator applications.

ZnS:Ag/LiF and Li glass are two kinds of widely used neutron scintillator. ZnS:Ag/LiF is characteristic with a high light output and long decay time (∼1 μs) [1], while lithium glass has a quick response ability but a low light output (∼6000 photons per neutron) [1].

$LiYSiO_4$ doped with a rare-earth element was first reported by Blasse et al. [2]. The decay time of

Received 14 March 2011, Revised 3 May 2011
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$LiYSiO_4$:Ce was measured as 38 ns when excited by ^{60}Co, and the light yield was measured around 10000 photons per neutron [3]. The decay time of $LiYSiO_4$:Ce in another paper [4] was 30 ns by using synchrotron radiation at 302 nm, and the emission spectrum was characteristic with the emission band of Ce^{3+} 5d-4f transitions with a maximum at 400 nm, which matches well with most of the PMTs or APDs. Furthermore, unlike the ZnS/LiF, the $LiYSiO_4$:Ce has no afterglow.

In fact, energy spectra of radiative particles incident on $LiYSiO_4$:Ce have not been reported in previous papers, so one cannot acquire the energy resolution and the light output specifically. In a previous paper, some properties of $LiYSiO_4$ with different rare-earth elements were studied [5]. In this paper, $LiYSiO_4$ samples doped with different concentrations of rare-earth element Ce are prepared. Further measurements are done on relative light yield and timing behavior using α particles and X-rays to exite samples.

2 Experimental setup

The $LiYSiO_4$:Ce^{3+} samples are prepared with three concentrations of Ce^{3+} dopants corresponding to 1 at%, 2 at% and 5 at%, and here at% represents the molar concentration. There are three thicknesses, 0.5 mm, 1 mm and 1.5 mm, for each concentration. The chemical reaction equations for the preparations are shown below:

$$0.99Li_2CO_3+0.99Y_2O_3+2SiO_2+0.02CeO_2 \rightarrow 2Ce_{0.01}(LiY)_{0.99}SiO_4+CO_2\uparrow$$

$$0.98Li_2CO_3+0.98Y_2O_3+2SiO_2+0.04CeO_2 \rightarrow 2Ce_{0.02}(LiY)_{0.98}SiO_4+CO_2\uparrow$$

$$0.95Li_2CO_3+0.95Y_2O_3+2SiO_2+0.1CeO_2 \rightarrow 2Ce_{0.05}(LiY)_{0.95}SiO_4+CO_2\uparrow$$

In the process, the highly pure materials of Y_2O_3, SiO_2, Li_2CO_3 and CeO_2 are mixed in an atmosphere of O_2 at a temperature of 1000 °C to get the polycrystalline material. Then the polycrystalline material powder is put into a vacuum system to make seed crystals and a polycrystalline rod, both of which should be cooled to reach room temperature within three hours after firing at 1100 ℃ for 5 hours. Two reference scintillators, anthracene and NaI crystals, are also prepared. According to the reference scintillators, the diameter and height of NaI are both 5 cm, while the height and diameter of anthracene are 2 cm and 5 cm respectively.

In the test, the samples and the reference scintillators are greased with silicon oil to couple with PMT (XP2020) and irradiated with α particles and X-rays. The single photoelectron (SPE) of the PMT is 13 channels (0.25pC/channel) at a high voltage of 2000 V. In the test, the signals are attenuated if they are beyond the dynamic range of the QADC (Lecroy 2249 w).

In the experiment, ^{239}Pu and ^{241}Am are used. The α particles are generated by ^{239}Pu, and they have three kinds of energies, most of which are around 5.2 MeV. The X-rays are generated by ^{241}Am, α emissions from which are shielded to get clear X-rays. The tyvek films are employed for the packages in order to collect as much as possible of the scintillation light.

All the tests are done at room temperature, and Fig. 1 shows the test setup. The scintillator generates scintillating light when it is irradiated by ^{239}Pu or ^{241}Am, and the light is received by the PMT. Via a Fan-In-Fan-Out module (FIFO, Lecroy 428F), three channels of output signals are obtained from the PMT. The signal of the first channel is sent to the oscilloscope (Lecroy wavepro 7100) to record the signal pulse shapes with the sampling frequency at 20GHz. This step is intended to measure the timing behavior of the samples. The second channel signal is sent into the QADC as a gate after a discriminator. The last channel signal is sent into the QADC to measure the distribution of pulse height spectra. The input gate of the QADC is 580 ns in the NaI measurement, and in the other measurements, the input gates are all 200 ns. The signals are attenuated for 0.5 mm thick samples being irradiated with ^{239}Pu. This step is to measure the energy spectra by which the relative light yield can be studied.

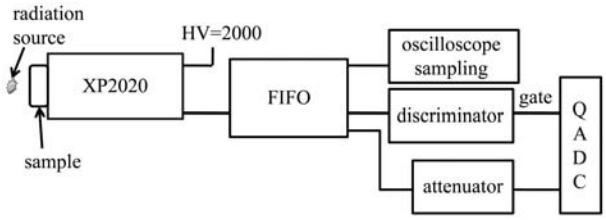

Fig. 1. The test setup of light yield and decay time.

3 Results and discussion

3.1 Light yield

The light yield is an important factor for a scintillator in defining imaging capabilities. In the test of light yields of 0.5 mm thick samples excited by α particles, the signals from the PMT are attenuated by 5 db, and the attenuation contributions are corrected in dealing with the data analysis processes.

Figure 2(a) shows the energy spectra of the reference anthracene and the three 0.5 mm thick prepared samples. In the spectra, the transitions from the $5d$ state to the ground state of $^2f_{5/2}$ and $^2f_{7/2}$ cannot be resolved. In Fig. 2(a), the photo-peak positions are derived by fitting around the spectra peaks using Landau and Gaussian functions for the anthracene and the samples respectively. The background position is centered at the channel around No. 70, so its contribution should be subtracted from the relative light yield calculation.

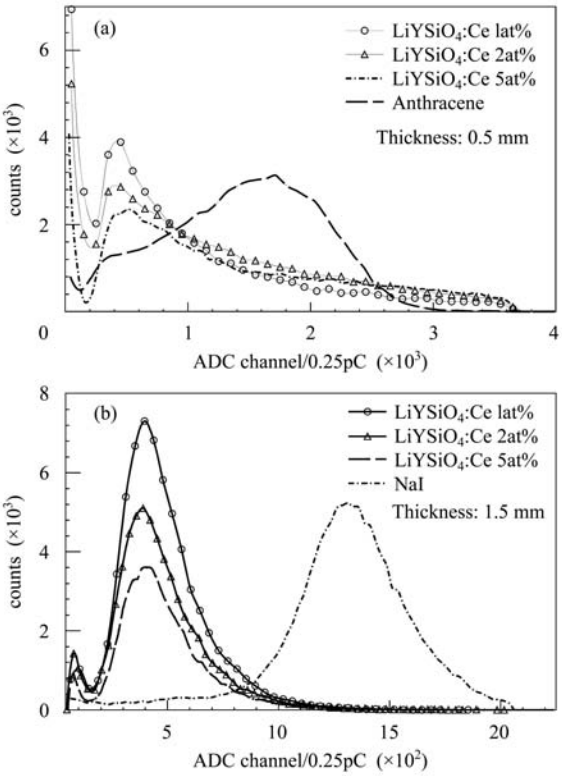

Fig. 2. The pulse height spectra of samples with the reference scintillator irradiated by ^{239}Pu in (a) and ^{241}Am in (b).

The photo-peak positions and their corresponding relative light yields are depicted in Table 1, in which the pedestal of the test system has been subtracted from the values of the photo-peak positions. As the standard, the light yield of anthracene at the photo-peak is supposed to be 100, then the light yields of the samples at the photo-peaks are calculated by comparing them with anthracene. The photo-peaks are clearly separated from the backgrounds, and the spectra of the three samples extend up to the 3500 channels which are much higher than the corresponding channels of anthracene. The spectra which extend to high channels indicate large fluctuations in scintillation light transmission. In addition, the figure also indicates that the light output increases with increasing dopant concentration, and clearly the sample doped with 5 at% Ce whose relative light yield is around 37.1 compared with that of anthracene is the best at scintillation.

Table 1. Relative light yields with the excitation of α particles.

sample:Ce	photo-peak position	relative light yield
anthracene	∼1503	100
$LiYSiO_4$:1at%	∼422	∼28.1
$LiYSiO_4$:2at%	∼484	∼32.2
$LiYSiO_4$:5at%	∼557	∼37.1

Figure 2(b) depicts the energy spectra of samples with a 1.5 mm thickness and the NaI excited by the X-rays of ^{241}Am. The background is centered at around channel No. 70 and No.87 for the $LiYSiO_4$ samples and the NaI scintillator, and the photo-peaks of the three samples are shown to be overlapping at channel No. 400. The full energy photo-peak positions of the 59.5 keV in the NaI scintillator are at around channel No. 1300. After subtracting the contributions of the background and assuming that the light yield of the NaI as 100, each sample light yield is around 27.2. The three Ce^{3+} concentrated samples nearly have the same light output when X-rays are used to excite the samples.

3.2 Thickness effects

At present, transparency needs to be improved further for $LiYSiO_4$ to avoid multiple reflection and self-absorption of scintillation light in the samples. The light output here is still influenced by the thickness choice. Specifically, the light output, like the ZnS, decreases with increasing thickness of the sample layer.

By using the ^{239}Pu radiation, Fig. 3, as an example, shows the spectra of samples with 5 at% dopant in Fig. 3(a) and the spectra of samples with 2 at% dopant in Fig. 3(b). In Fig. 3(a) the photo-peak positions are around Channel No. 561 and No. 407 for 1 mm and 1.5 mm thicknesses respectively, thus the position is shifted towards lower channels as the thickness increases. In specific applications, high light yield and high detection efficiency are both desirable in most experiments, thus it forces users to make compromises between light yield and detection efficiency in some detections like neutron imaging convertors. Fig. 3(a) also shows that the fluctuation of light output becomes smaller with the thickness increasing because many photons are not able to transmit out of the samples for thick samples.

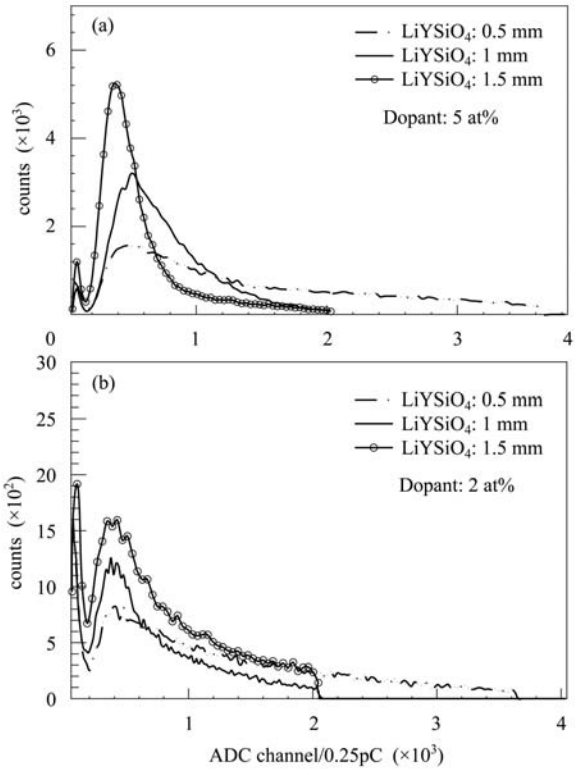

Fig. 3. The different thickness pulse height spectra excited by ^{239}Pu.

However, unlike the 5 at% Ce doped sample, Fig. 3(b) shows the variation of photo-peak positions of the samples with 2 at% Ce doped. The difference of photo-peak positions is not obvious for the thickness of 1 mm and 1.5 mm samples, whose channel numbers are all around No. 410 with ∼140 less than that of the sample with a thickness of 0.5 mm.

3.3 Timing behavior

It is the timing behavior of emission which governs how frequently the scintillator response can be achieved. The timing behavior is determined by two independent factors: one is the excitation/ de-excitation duration which concerns the host lattice trapping/detrapping processes and the other is the decay time of the scintillation light.

To examine the timing behavior of $LiYSiO_4$:Ce, the samples are measured using both the ^{239}Pu and the ^{241}Am (X-rays). Since the spectrum of $LiYSiO_4$:Ce has the main characteristics of the emission band of Ce^{3+} 5d-4f transitions, the radiative lifetime of the Ce^{3+} excited states is determined by the crystal field at the ion site. The fast dipole allowed emission is characteristic of a lifetime of about 15 to 70 ns [3].

Figure 4(a) and (b) show the pulse shapes recorded by the oscilloscope of the sample with a thickness of 0.5 mm and dopant concentration of 5 at% by using ^{239}Pu and ^{241}Am irradiation respectively. Overall, the shapes of the two main pulses are both fast and big, and their amplitude differences may be caused by the different energy depositions. There exist many small pre-pulses before the main pulse of the sample irradiated by ^{241}Am, which may be caused by the Compton effect in the PMT because of the X-rays escaping from the sample, and they are not shown in Fig. 4(a). We should notice the pulsing following the main pulses in Fig. 4(a) and (b). Besides the after-pulse of PMT, there are slow components which are caused by the re-trapping of the auto-ionized electrons of Ce^{4+} followed the $5d$-$4f$ transition (see Ref. [4]). The intensity of such slow components, however, is very low compared with the typical pulse of $5d$-$4f$ emission, therefore, it cannot influence the sample as a kind of fast scintillator.

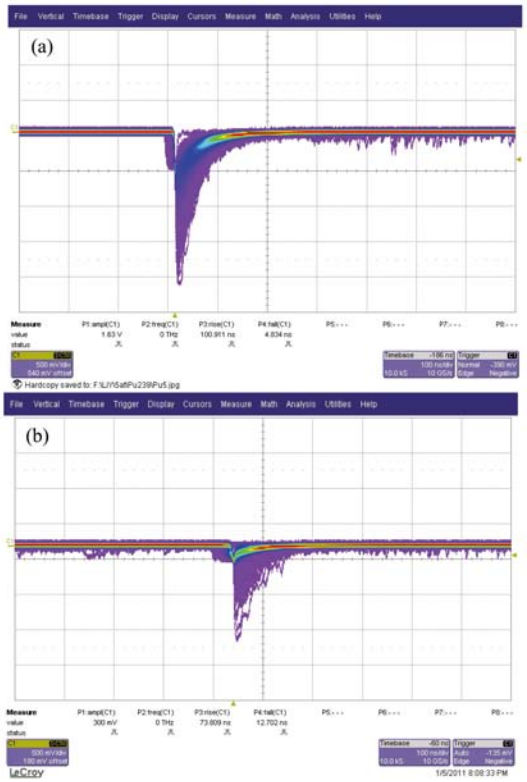

Fig. 4. Pulse shape sampled with an oscilloscope irradiated by ^{239}Pu (a) and ^{241}Am (b).

The decay time of the scintillator is defined as the time between the maximum of the pulse amplitude and its $\frac{1}{e}$ time position. Fig. 5(a) and (b) show the decay time curves of the samples irradiated with α particles and X-rays respectively. There are a few comparatively slow components >100 ns, but the intensities are too low and such components can be ignored. In addition, the initial decay of each sample

is faster than the intrinsic life-time of Ce^{3+}, and this contribution is caused by $LiYSiO_4$ itself. The decay time curves are fitted by Gaussian functions, and the fitted mean values plus the fitted σ values are shown in Table 2. It indicates that the decay time is around 30 ns which is the typical time of the fast dipole allowed $5d$-$4f$ emissions.

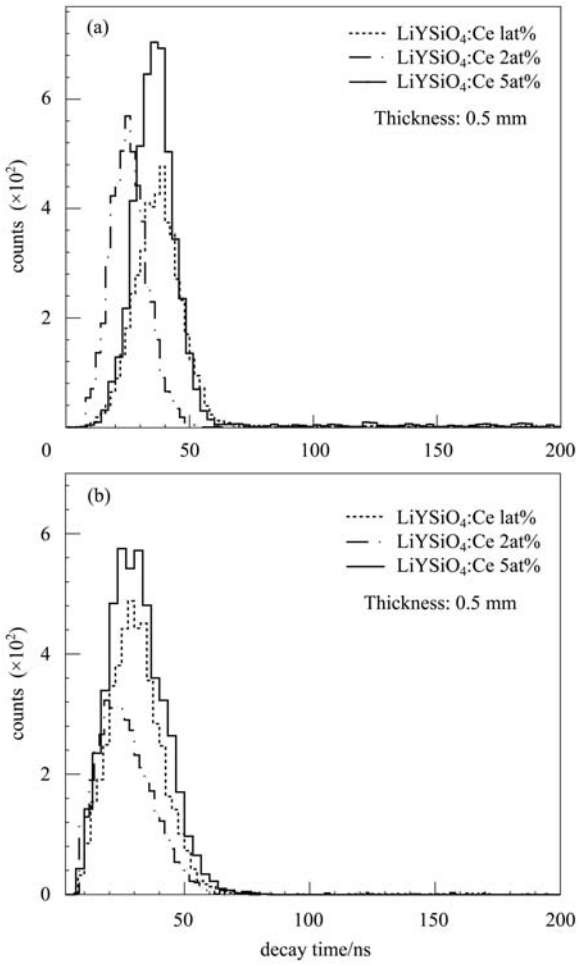

Fig. 5. The decay time curves of different concentrations of $LiYSiO_4$ excited by (a), ^{239}Pu, and (b), ^{241}Am.

Attention should be paid to some specific points given in Table 2. It shows that the fitted mean values of decay time vary with the concentration of Ce doped in the samples. By irradiating with α particles and X-rays, the decay time of the sample with 2 at% dopants is less than 38 ns for both cases as reported in Ref. [3]. Furthermore the decay time of samples irradiated with ^{241}Am is a little longer than that of samples irradiated with ^{239}Pu. For the other two samples, the decay time is around 38 ns, and the mean values of the samples excited by ^{239}Pu are larger than the values of those excited by ^{241}Am. In addition, unlike the other two samples, the sample with 2 at% Ce doped has fewer slow components (>60 ns) under irradiation with ^{239}Pu which is shown in Fig. 5(a). The results reveal that the concentration of Ce influences the time of electron trapping/de-trapping processes in $LiYSiO_4$, and it speeds up the scintillating transition faster at the 2 at% dopant concentration than at the other two concentrations.

Table 2. Decay times of samples measured by ^{239}Pu and ^{241}Am.

sample:Ce	^{239}Pu/ns	^{241}Am/ns
$LiYSiO_4$:1at%	36.9±9.3	29.9±10.5
$LiYSiO_4$:2at%	25.2±7.5	27.4±9.6
$LiYSiO_4$:5at%	36.7±7.9	30.4±11.2

4 Conclusion

In this paper, the $LiYSiO_4$:Ce samples are prepared with three concentrations, and their light yields are around 28.1%–37.1% compared with that of an anthracene scintillator using α particle radiation and 27.2% compared with a NaI scintillator using X-rays radiation. Under α particle radiation, the sample with 5 at% Ce dopant has a larger light output than the other two kinds of dopants. The $LiYSiO_4$:Ce light yield is influenced by sample thickness, and using a thin film sample, one can get a higher light yield but a poor resolution of the energy spectrum. As far as the timing behavior is concerned, the intensity of the slow component is low and it can be ignored. The decay time, around 30 ns, changes with dopant concentration, and the sample with 2 at% dopant has the advantage of a fast response time.

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