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Scintillation Properties of $LaCl_3$：Ce Crystal with Low Radioactivity Background

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Abstract: 10% Ce^{3+}-doped lanthanum chloride ($LaCl_3$：Ce) crystals with low-radioactive background have been prepared using raw materials with low content of U-series isotopes. The radioactive background was estimated to be about 0.713 counts·s^{-1}·cm^{-3} resulted from the natural U-series radioactive isotopes in the prepared $LaCl_3$：Ce crystal. The energy resolution (FWHM) of the $LaCl_3$：Ce crystal was 3.3% for 662 keV γ-rays. Moreover, the peak-to-valley ratio, relative light output and peak count rate of the $LaCl_3$：Ce crystal were approximately 2.61 times, 87.88% and 1.96 times of that of NaI：Tl crystal with the same size of Ø25 mm× 50 mm, respectively. The effects of crystal size on the scintillation properties of the prepared $LaCl_3$：Ce crystal were discussed.

Key words: $LaCl_3$：Ce; scintillation crystal; background count rate; energy resolution
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Cerium-doped lanthanum chloride ($LaCl_3$：Ce) crystal is a type of excellent scintillator discovered by Guillot *et al.* in 1999[1]. It has a hexagonal structure with $P6_3/m$ space group, a density of 3.86 g/cm^3 and a melting temperature of 859 ℃[2-4]. So low melting temperature allows the growth of $LaCl_3$：Ce crystals in sealed quartz ampoules by using the Bridgman crystal growth technique. Before $LaCl_3$：Ce crystal grow, the raw materials must be subjected to anaerobic dehydration treatment to prevent forming of oxide impurities. The scintillation properties of $LaCl_3$ crystals with different Ce^{3+} concentrations have fully studied, and it was found that the $LaCl_3$ crystal doped with 10% Ce^{3+} shows higher light output, shorter decay time and good energy resolution[2,5]. The best energy resolution reported was 3.2% for 662 keV γ-rays obtained for a small sample with a volume of 1 cm^3[3]. In generally, it is considered that the higher isotopes of ^{138}La and U-series contained in the raw materials, which limited the application of the $LaCl_3$：Ce crystals in 1 460 keV and above 1.6 MeV, due to its high radioactive background. Therefore, high-performance $LaCl_3$：Ce crystals could be obtained by reducing the content of uranium(U)-series isotopes in raw materials. Recently, high-quality $LaCl_3$：Ce crystals were obtained with Bridgman method by using starting materials, $LaCl_3 \cdot 7H_2O$ and $CeCl_3 \cdot 7H_2O$, with low-radioactive background at Beijing Glass Research Institute.

In this work, the scintillation properties of the $LaCl_3$：Ce crystal with low-radioactive background

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were measured.

1 Experimental Setup and Results

Two pieces of $LaCl_3$: Ce crystal with different sizes, Ø25 mm×25 mm and Ø25 mm×50 mm, were cut from one crystal ingot. One piece of Ø25 mm×50 mm NaI : Tl crystal was also prepared as a reference. Fig.1 shows photographs of above three crystal samples. The energy resolution, photofraction, relative light output, linearity and count rate of the samples were measured and compared. Moreover, the effect of the thickness of $LaCl_3$: Ce crystal on its scintillation properties was also discussed.

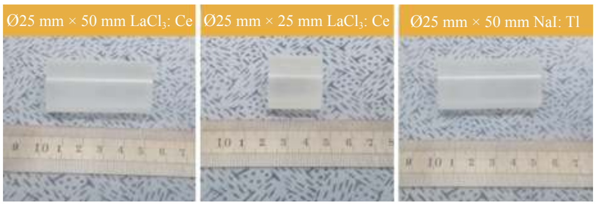

Fig. 1 Three $LaCl_3$: Ce and NaI : Tl crystal samples

A high-voltage power supply (Ortec 556), an amplifier (Ortec 672), a preamplifier (Ortec 113), and a multichannel analyzer (Ortec 926 MCB) are used to set up an energy spectrum measurement system. The crystal samples were optically coupled with a 50 mm -diameter Hamamastu R6231-100 super bialkali photomultiplier (PMT) with a quantum efficiency of 35% at 350 nm[6]. 5 mm-thick white polytetrafluoroethylene film was used to cover the surfaces of the crystal samples except the faces coupled to the PMT to ensure the effective collection of the scintillation light from the samples. Furthermore, the light emitting surface of sample was optically coupled to the optical window of PMT with a silicone oil with a dynamic viscosity of 20 000 mm^2/s (20 000 cSt) at 25 ℃. To prevent the crystal from hydrating, all handling was done in a dry nitrogen glove and the ambient temperature was 20 ℃. The working voltage of the PMT is positive 700 V. Four radioactive sources (^{241}Am, ^{22}Na, ^{137}Cs, and ^{60}Co) are used in the measurements.

1.1 Energy resolution and photofraction

Fig.2 shows the distribution of the energy resolution (full width at half maximum over the peak position) of full absorption peaks of 59.5, 511, 662 keV, 1 173.2 keV and 1 332.5 keV γ-rays. At less than 200 keV, the energy resolution of $LaCl_3$: Ce crystal is not as good as that of NaI : Tl crystal. However, the energy resolution of $LaCl_3$: Ce crystal has a significant advantage compared with NaI : Tl in the γ-ray energy range of 200 ~ 1 332.5 keV.

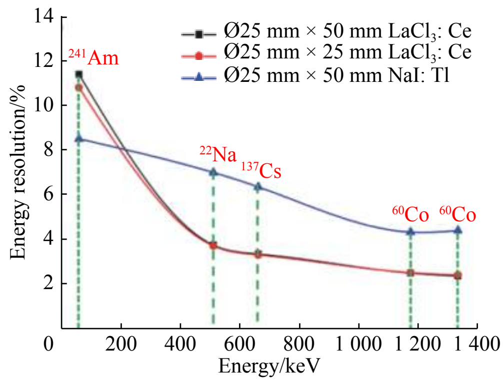

Fig. 2 Energy resolution (FWHM) of $LaCl_3$: Ce and NaI : Tl samples versus energy for ^{241}Am, ^{22}Na, ^{137}Cs and ^{60}Co γ-rays

Fig.3 shows the energy spectra of three samples under irradiation of the γ-rays from ^{241}Am, ^{57}Co, ^{22}Na and ^{137}Cs radioactive sources. The 59.5 keV γ-ray full-energy peak of the ^{241}Am source is shown in Fig.3(a). The energy resolution (E.R.) of the Ø25 mm×50 mm $LaCl_3$: Ce sample is 11.39%, while the Ø25 mm×50 mm NaI : Tl sample can reach 8.51%, which is better than that of $LaCl_3$: Ce. The energy resolution of the Ø25 mm×25 mm $LaCl_3$: Ce sample is 10.80%. As can be seen a smaller crystal size resulted in a better energy resolution. The 662 keV γ-ray full-energy peak of the ^{137}Cs source is shown in Fig.3(b). The energy resolution of the Ø25 mm×25 mm $LaCl_3$: Ce sample is 3.33%, and those of $LaCl_3$: Ce and NaI : Tl samples with the same size of Ø25 mm×50 mm are 3.37% and 6.37%, respectively. The results are better than that reported by Balcerzyk[7] and Alexiev[8], which may be attributed to the improved quality of the obtained $LaCl_3$: Ce crystal. As shown in Fig.3 (c) and 3(d), the energy resolutions of the Ø25 mm×50 mm $LaCl_3$: Ce for 511 keV, 1 173.2 keV and 1 332.5 keV γ-rays are 3.37%, 2.52% and 2.39%, respectively.

The peak-to-valley (p/v) ratio is a convenient parameter for evaluating the energy resolution of a scintillation detector. It does not affected by any possible shift in the signal. It can be calculated by obtaining the p/v ratio between two γ peaks or by taking the ratio between the low energy peak and the PMT (electronic noise). For further analysis of the measured energy spectra, the p/v ratio of the samples can be calculated from the energy spectra for ^{60}Co source in Fig.3(d). For $LaCl_3$: Ce and NaI : Tl crystal samples with the same size of Ø25 mm×50 mm, the count ratio of the peak (1 332.5 keV) to the valley between 1 332.5 and 1 173.2 keV is 40.5 and 15.5, respectively. The p/v ratio of the Ø25 mm×25 mm $LaCl_3$: Ce crystal sample is 42.8. There exists a correlation between the obtained results and the energy resolutions of the samples. Therefore, The difference in energy resolution between different samples can be evaluated by examining the p/v ratio conveniently.

Photofraction is an important parameter describing the γ-ray response of the detector. It is defined as the ratio of the full-energy peak count to the total spectrum count measured at a specific γ-ray energy[7,9-10]. The photofraction results of three crystal samples for 511 keV and 662 keV γ-rays are given in Tab. 1. For comparison, Tab. 1 also gives the σ-ratio of the photoelectric absorption cross section to the total cross section including coherent scattering, which are calculated by XCOM program[11]. The results of two scintillation crystals are very close, but the σ-ratio of NaI : Tl crystal is higher than that of $LaCl_3$: Ce crystal. The photofraction of $LaCl_3$: Ce is related to the size of the crystal, the value of larger crystal is higher. This may due to a more significant Compton scattering and photoelectric absorption, which makes the contribution of the full-energy peak in the energy spectrum more obvious. The photofraction and σ-ratio of two scintillators have the same trend, which is higher at 511 keV γ-rays, due to increasing in the photoelectric absorption cross section with the decrease of the energy of the rays.

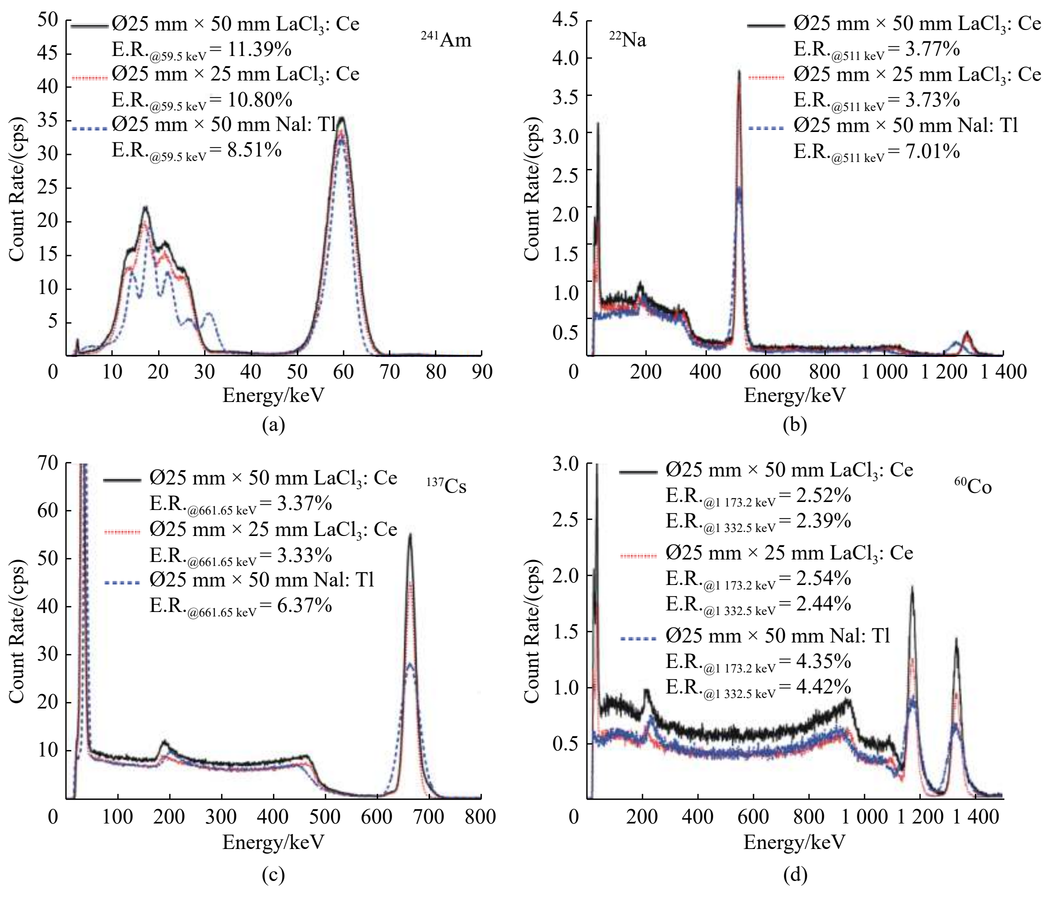

Fig. 3　Energy spectra of ^{241}Am, ^{22}Na, ^{137}Cs, and ^{60}Co sources measured with three samples

Tab. 1 Photofraction and σ ratio for three samples

Crystal	Size/mm	^{22}Na 511 keV		^{137}Cs 662 keV	
		Photofraction /%	σ- ratio/%	Photofraction/%	σ- ratio/%
NaI : Tl	Ø25×50	30.1	17.4	23.3	11.4
$LaCl_3$: Ce	Ø25×50	25.1	14.8	22.0	9.6
	Ø25×25	22.7		20.2	

1.2 Relative light output and linearity

The charged particles or γ-rays with energy E are incident on the scintillator, and the energy is deposited in the scintillator, and N photons with an average energy of ε are excited[12]. The luminous efficiency of the scintillator is:

$$\eta = \frac{N \times \varepsilon}{E} \tag{1}$$

In actual measurement, the photon number N and the average photon energy ε are difficult to measure at the same time. Considering the sensitivity of the measuring instrument and other factors, the light output of the scintillator is usually evaluated by the relative light output. For calculating the value of relative light output, the full-energy peak pulse height (corresponding to the channel) of three crystal samples for 59.5 keV, 511 keV, 662 keV, 1 173.2 keV, and 1 333.5 keV γ-rays were measured.

The results of relative light output are shown in Tab. 2. When the ^{137}Cs source was used, the relative light output of the Ø25 mm×25 mm $LaCl_3$: Ce sample is 108% higher than that of the Ø25 mm×50 mm $LaCl_3$: Ce sample. At 511 ~ 1 332.5 keV, the relative light output of the Ø25 mm×50 mm sample is 86% ~ 88% of the NaI : Tl reference sample. Due to the self-absorption of fluorescence of the crystal, the thin crystal with the same diameter has weaker self-absorption, and its relative light output is thus higher.

Tab. 2 Relative light output statistics of $LaCl_3$: Ce and NaI : Tl crystals

Crystal	Size/mm	Relative light output/%				
		@59.54 keV	@511 keV	@661.65 keV	@1 173.24 keV	@1 332.5 keV
NaI : Tl	Ø25×50	100.00	100.00	100.00	100.00	100.00
$LaCl_3$: Ce	Ø25×50	74.27	86.04	87.88	87.83	88.04
	Ø25×25	80.47	93.64	95.16	96.10	96.33

Linearity means that the total light output of the scintillation crystal is proportional to the energy of the absorbed γ-ray photons[7,13]. The linear response can be defined as Eq.(2):

$$\mathrm{LR} = \frac{\mathrm{PH}}{E} \times \frac{661.65}{\mathrm{PH}_{137_{\mathrm{Cs}}}} \tag{2}$$

where E is the energy of γ ray, PH is the pulse height corresponding to the ray of energy E, and the measurement data is normalized with the data points of ^{137}Cs source 662 keV γ-ray[14].

Fig.4(a) presents the light yield linearity of the samples. The results plotted show very linear energy behaviour for the samples in the test. It can be intuitively judged that the light output of $LaCl_3$: Ce crystal, which measures the same energy, is lower than that of NaI : Tl reference crystal by comparing the slope of each line.

Fig.4(b) shows the calculation results of linear response. The pulse height of 662 keV γ-ray from ^{137}Cs is defined as 1. The nonlinearity that appear at measured energy range is noted. The dashed straight line in Fig.4(b) indicates the ideality of the scintillation crystal. The measured values are distributed around the ideal value, showing a certain linearity. From 511 keV to 1 332.5 keV, the linearity of the crystal samples are all within 3%, and there is no significant difference between $LaCl_3$: Ce and NaI : Tl scintillation crystals. For energy less than 511 keV, all samples show obvious

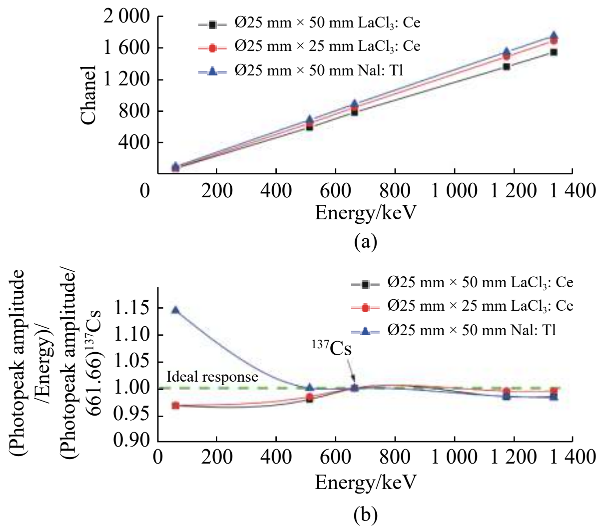

Fig. 4　Linear response of $LaCl_3$: Ce and NaI : Tl crystals

nonlinearity. The linearity of NaI : Tl crystal at 59.5 keV is 15% higher than that at 662 keV. It is worth noting that $LaCl_3$: Ce crystal has more stable linearity and more suitable for low energy ray detection with higher linear requirements. The obvious non-linear response appears under low energy rays, and which is mainly because of the non-radiative electron-hole pair recombination in the high ionization density part of the ionization track of the γ rays. And that means close to the track (<5 nm), with the decrease of the electron velocity (or energy E), the energy loss of the ionized electrons is increasing so the composite loss is highest at the end of the main track[15-16].

1.3　Count rate and background

Tab. 3 shows the statistical results of the count rates of the samples. $Ratio_{LC/NI}$ represents the ratio of the count rates of the Ø25 mm×50 mm $LaCl_3$: Ce sample to that of the Ø25 mm×50 mm NaI : Tl. Comparing the total energy spectra count rates from low energy to high energy, the spectrum count rates of $LaCl_3$: Ce crystal is 3% ~ 25% higher than that of NaI : Tl reference crystal, and the ratios of the peak count rate of the two samples are 1.09 ~ 2.31.

Tab. 3　Count rate of the samples for different radioactive source

Crystal	Size/mm	Spectrum count rates / (counts·s^{-1}·cm^{-3})				Peak count rates / (counts·s^{-1}·cm^{-3})				
		^{241}Am	^{22}Na	^{137}Cs	^{60}Co	59.5 keV	511 keV	662 keV	1 173.2 keV	1 332.5 keV
$LaCl_3$: Ce	Ø25 × 25	6 243.43	474.09	8 450.34	808.70	32.20	2.28	28.20	0.83	0.63
	Ø25 × 50	6 415.52	530.62	8 863.69	1 014.16	35.25	3.83	55.23	1.83	1.41
NaI : Tl	Ø25 × 50	6 077.39	482.86	7 973.67	744.11	33.69	3.59	45.05	1.33	0.91
$Ratio_{LC/NI}$		1.03	1.12	1.05	1.25	1.09	1.68	1.96	2.20	2.31

$LaCl_3$: Ce contains natural radionuclides, of which La contains about 0.09% of ^{138}La. 66.4% and 33.6% of ^{138}La, after half-life of 1.02×10^{11} years, undergo two types of decay processes, electron capture and β-, respectively, and decay to steady-state ^{138}Ba and ^{138}Ce, respectively[17]. γ-rays with an energy of 1 436 keV and characteristic X-rays of 32 keV are released by the electron-capture decay, and γ-rays with an energy of 789 keV are released through the β-decay process.

Fig.5 presents the background spectra of $LaCl_3$: Ce and NaI : Tl with the same size measured by PMT in a lead chamber with a wall thickness of 15 cm. For the background spectrum of $LaCl_3$: Ce crystal, the count rate of (20 ~ 255) keV X and β rays is 1.038 counts·s^{-1}·cm^{-3}, the count rate of 760 keV ~ 1 MeV γ and β rays is 0.051 counts·s^{-1}·cm^{-3}, and ^{138}La and ^{40}K (in PMT and aluminum) interact at 1 468 keV γ and X rays count rate is 0.075 counts·s^{-1}·cm^{-3}. The count of α particles produced

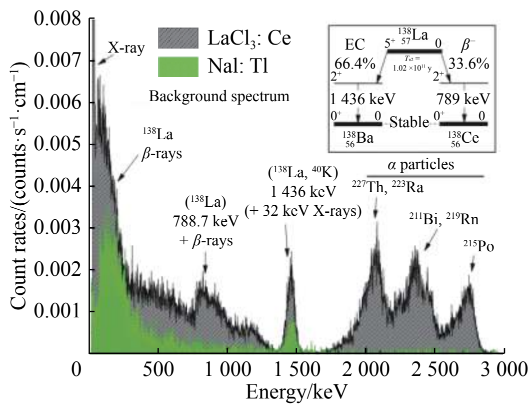

Fig. 5　Background spectra of $LaCl_3$: Ce and NaI : Tl crystals

by the decay of U series isotopes ^{227}Ac and its progeny in the background spectrum of $LaCl_3$: Ce is also measured. As can be seen, the back-ground count rate is 0.713 counts·s^{-1}·cm^{-3} in 1.6 ~ 3 MeV. Compared to NaI : Tl, the background spectrum of $LaCl_3$: Ce crystals in unit time and unit volume is 4 times that of the NaI : Tl reference crystal.

2 Conclusions

The prepared $LaCl_3$: Ce samples show excellent energy resolution, very good linearity, high count rate, and similar light output and photofraction. The U series background count rate of the prepared $LaCl_3$: Ce crystal is 0.713 counts·s^{-1}·cm^{-3} at 1.6 MeV ~ 3 MeV, which is far lower than that of the previous reported results. The energy resolution of the $LaCl_3$: Ce crystal is 3.3% for 662 keV γ-ray. The size effects of $LaCl_3$: Ce crystal on its scintillation properties were discussed. As the thickness of sample increase from 25 mm to 50 mm, the photofraction of $LaCl_3$: Ce crystal increases by 8.9%, the light output decreases by 7.7%, the peak count rate increases by 22.6%, and the energy resolution and linearity are also improved. The prepared $LaCl_3$: Ce crystals can be applied to high energy physics, nuclear physics test, nuclear medicine, and environmental monitoring equipment which require high energy resolution, light output, and counting rate.

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（编辑 陈 红）

低放射性本底 $LaCl_3$: Ce 晶体闪烁性能

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摘 要：使用锕系同位素含量低的原料制备了具有低放射性本底的 10% Ce^{3+}掺杂氯化镧（$LaCl_3$: Ce）样品。在制备的 $LaCl_3$: Ce 晶体中，天然锕系放射性同位素的放射性本底约为 0.713 counts·s^{-1}·cm^{-3}。对于 662 keV γ 射线，$LaCl_3$: Ce 晶体的能量分辨率（FWHM）为 3.3%。此外，与相同尺寸Ø25 mm×50 mm 的 NaI : Tl 晶体相比，$LaCl_3$: Ce 晶体的峰谷比、相对光输出和峰值计数率分别为 2.61 倍、87.88%和 1.96 倍，并对晶体尺寸对 $LaCl_3$: Ce 晶体的闪烁性能的影响进行了讨论。

关键词：$LaCl_3$: Ce；闪烁晶体；本底计数率；能量分辨率
中图分类号：O734 **文献标志码**：A

张明荣(1964-)，博士，教授级高级工程师，北京玻璃研究院总工程师，北京一轻“首席专家”，兼任中国硅酸盐学会人工晶体生长与材料分会理事、中国稀土学会稀土晶体专业委员会委员、全国仪表功能材料标准化技术委员会(SAC/TC419)委员、中国材料与试验团体标准委员会光电材料及产品领域委员会(CSTM/FC60)委员等。长期从事新型闪烁晶体材料与辐射探测器件的研究和开发以及光功能材料的改性和应用研究，作为项目负责人主持和完成了国家部委级、省市级等各类科研项目十多项，开发了多种非氟卤化物新产品，发表学术论文 40 余篇，获得 6 项国家专利，编制行业标准和国际标准 7 项。

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