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# Temperature dependence of the luminescence properties of $LaCl_3$:Ce crystal

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The optical properties of $LaCl_3$:Ce crystal are reported in this paper. Optical transmission spectrum, photoluminescence and time resolved photoluminescence spectra at different temperatures are investigated. It is found that optical transmittance is as high as 80% between 320 nm and 600 nm, and no obvious absorption band is found in this region. Emission intensity and decay time of photoluminescence are quite stable with the change of the temperature between 80 K and 500 K. No thermal quenching is present up to 500 K, and decay time keeps at $17 \pm 2$ ns. With the increase of the temperature, the whole emission bands and excitation bands present broadening and overlapping,leading to the strengthening of re-absorption of the $Ce^{3+}$ emission, which makes the emission spectra have a red shift trend.

**Keywords:** $LaCl_3$, scintillator, transmittance, photoluminescence, decay time, temperature dependence
**PACC:** 7855H, 2940M

## 1. Introduction

Most attention in the field of scintillation and luminescence application is paid to rare earth ions (especially $Ce^{3+}$) doped materials.[1−6] $LaCl_3$:Ce is a new inorganic scintillator, which belongs to $UCl_3$ type structure, space group $P6_3/m$. It has a density of 3.86 g/cm$^3$ calculated according to structure and lattice parameters and melts at 859°C.[7] Its high light yield (49000 ph/Mev), fast response (25 ns), excellent energy resolution and good time resolution (3.3% and 224 ps) make it a promising material in field such as medical imaging, nuclear physics, etc.[4−6,8−10]

However, up to now, the transmittance and temperature dependence of $LaCl_3$:Ce crystal have not been systematically investigated yet.

$LaCl_3$:Ce crystal with dimension of $\phi 25 \times 50$ mm was successfully grown in our laboratory by modified Bridgman method, which is a simple and effective method.[11,12] Its optical transmittance, temperature dependence of photoluminescence (PL) and temperature dependence of time resolved PL spectra are all characterized and discussed in this paper.

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## 2. Experiments and results

### 2.1. Transmittance

Transmittance was measured by Shimadzu UV - 2501 spectrophotometer. The systematic uncertainty in repeated measurements of transmittance was approximately 0.3%. The optical transmittance of $LaCl_3$:5%Ce crystal with the thickness of 5 mm at room temperature was shown in Fig.1. As is seen, the transmittance between 320 nm and 600 nm keeps as high as 80% without obvious absorption band, which denotes that oxygen contamination was effectively eliminated in the process of crystal growth by adding a kind of the deoxidizing agent. And at the same time, some special structure is also observed between 200 nm and 322 nm. According to the excitation spectrum of $LaCl_3$:5%Ce at 80 K, just as shown in Fig.2, five excitation peaks can be identified between 230 nm and 322 nm, peaking at 246 nm, 255 nm, 271 nm, 290 nm, and 312 nm respectively, which reflects the $4f \rightarrow 5d$ transition of $Ce^{3+}$ ions where the 5d is split into five levels. Therefore, the absorption bands appeared in the transmission spectrum between 225 nm to 322 nm are attributed to $Ce^{3+}$ ions absorption. In contrast to the transmittance spectrum of un-

doped $LaCl_3$ crystal shown in Fig.1(b), the absorption valley at 214 nm should be caused by the intrinsic absorption of the $LaCl_3$ crystal which transport the energy to the luminescence centre-$Ce^{3+}$.

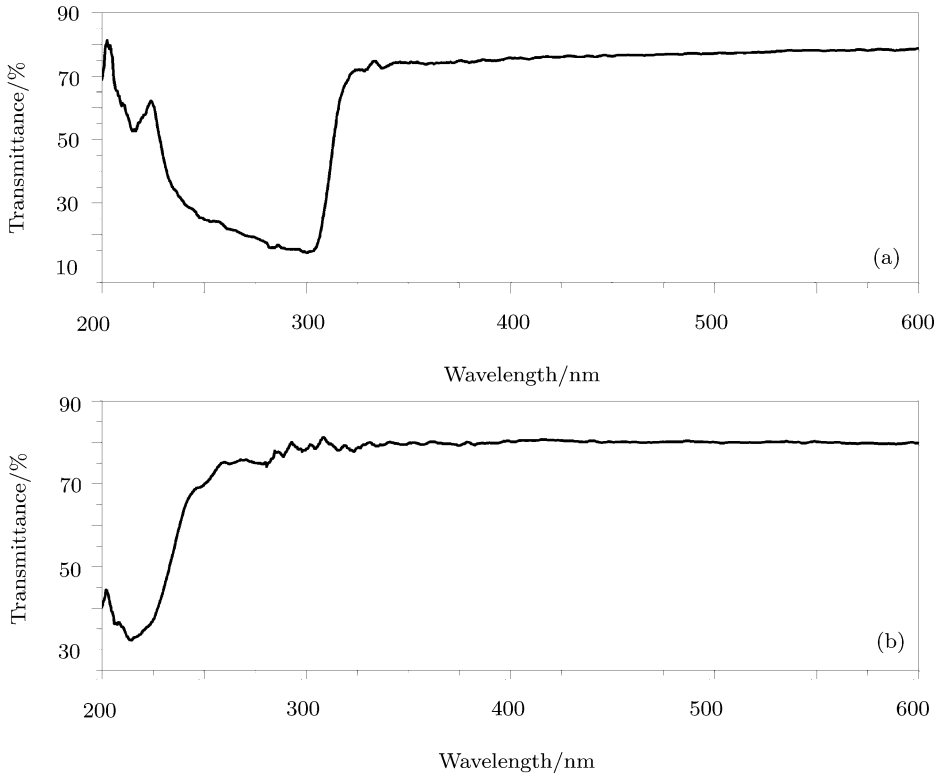



**Fig.1.** Transmittance of crystal with 5 mm thickness. (a) $LaCl_3$:Ce; (b)un-doped $LaCl_3$.

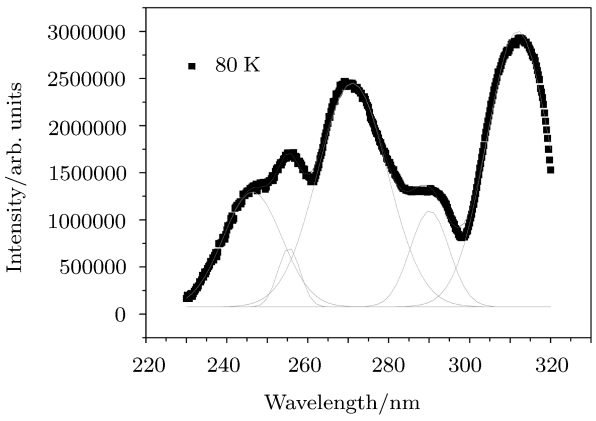



**Fig.2.** The excitation spectrum of $LaCl_3$:Ce crystal at 80 K.

## 2.2. The temperature dependence of PL

PL spectra of $LaCl_3$:5%Ce at different temperatures were measured by the single photon counting method with FLS920 spectrofluorimeter. The temperature varies from 80 K to 500 K in steps of 50 K. The 1.6 nm slit width was selected in the measurement of excitation and emission spectra. The spectral shapes are corrected for the grating efficiency and photomultiplier tube (PMT) quantum efficiency. The integral over all wavelengths can be used to estimate photoluminescent intensity.

Excitation spectra at different temperatures were shown in Fig.3. At the temperature of 80 K, excitation band of $Ce^{3+}$ is separated into five obvious bands, which can be fitted with five Gauss-shapes, just as shown in Fig.2, which are attributed to the 4f→5d transition of $Ce^{3+}$ ions where the 5d is split into five levels. However, with the rise of the temperature, the five excitation bands of $Ce^{3+}$ gradually become broadening and overlapping. Emission spectra present the similar change trend just as shown in Fig.4. At 80 K, emission spectrum of $Ce^{3+}$ is separated into two obvious narrow bands, maximum peaking at 332 nm and 356 nm respectively, resulting from transitions from the lowest 5d level to the two spin-orbit ground states, $^2F_{5/2}$ and $^2F_{7/2}$. However, with the rise of the temperature, the two narrow emission bands of $Ce^{3+}$ gradu-

ally become broadening and overlapping. This result is different from that reported by Guillot–Noël *et al*,[9] in which the full-width at half maximum (FWHM) of the two $Ce^{3+}$ emission bands under X-ray excitation were kept the same in fit between 135 K and 400 K. In addition, the maximum peaks of emission spectra have a little red shift as the temperature increases, which is probably caused by the self-absorption of $Ce^{3+}$ because of the small Stokes shift. Because the broadening of the excitation and emission bands with the temperature leads to the much more overlap between them, as a result, the $Ce^{3+}$ emission is more easily reabsorbed by another $Ce^{3+}$ centre resulting in the red shift of the maximum peaks of the emission spectra.

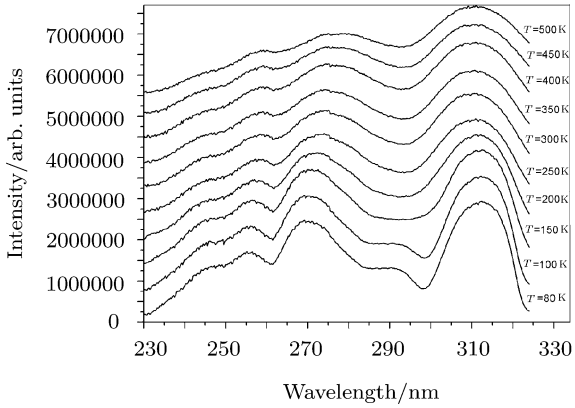



**Fig.3.** The excitation spectra of $LaCl_3$:5%Ce crystal at different temperatures.

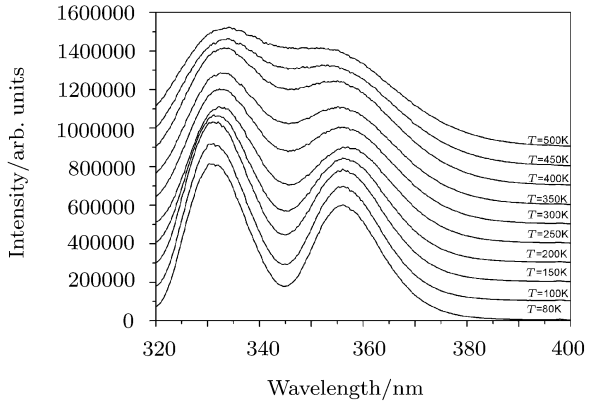



**Fig.4.** The photoluminescence spectra of $LaCl_3$ :5%Ce crystal at different temperatures.

The emission spectrum measured between 325 and 400 nm at different temperature can be fitted with three Gauss-shaped bands: peak1, peak2, and peak3. The peak1 and peak2 (around 332 nm and 356 nm respectively) are attributed to the 5d $\rightarrow^2 F_{5/2}$ and 5d $\rightarrow^2 F_{7/2}$ of $Ce^{3+}$, while for peak3, a new peak (around 370 nm), it is probably caused by the perturbed '$Ce^{3+}$'—when the $Ce^{3+}$ is next to the $Cl^-$ vacancy or $Cl^-$ ion in an interstitial position or the other impurity ions. The luminescence characteristics of $Ce^{3+}$ will be influenced by theses defects, resulting in the presence of the new emission peak. Similar phenomena were found in $CeF_3$ and $LaF_3$:Ce crystal.[13,14] However, its formation mechanism needs to be confirmed by further experiments.

The emission intensity of these three peaks and their total emission intensity with the change of the temperature were shown in Fig.5.

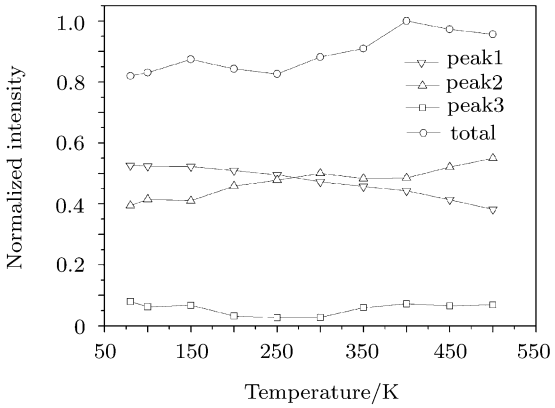



**Fig.5.** The emission intensity of three Gauss-shape peaks and total with the change of the temperature between 80 K and 500 K.

We can observe the following three facts. (1) As the temperature rises, emission intensity of peak1 is reduced, while that of the peak2 is enhanced correspondingly. Especially, at above 250 K, emission intensity of the peak2 exceeds that of the peak1. (2) The emission intensity of the peak3 has a slight change with the temperature. By the way, the intensity of the peak3 to the total emission is less than 10%. (3) However, the total emission intensity increases slightly with the temperature, and reaches maximum at 400 K, then turns to decline. On the whole, emission intensity at above room temperature is a little stronger than that below room temperature, which should be attributed to the improvement of energy transfer efficiency from self-trapped exciton (STE) to $Ce^{3+}$.

The variation of the temperature between 80 K and 500 K, almost has no influence on the energy level of the $Ce^{3+}$, but it changes the intensity ratio of the two emission bands of $Ce^{3+}$ ion (5d $\rightarrow^2 F_{5/2}$ and 5d

$\rightarrow^2 F_{7/2}$ ), which can be explained by Boltzmann distribution law, the equation is as fellows:

$$N_i/N_j = \mathrm{e}^{-\varepsilon_i/kT}/\mathrm{e}^{-\varepsilon_j/kT} = \exp(-(\varepsilon_i - \varepsilon_j)/kT)\,, \tag{1}$$

where, $N_i$ is the particle number in the energy level $\varepsilon_i$, $N_j$ is the particle number in the energy level $\varepsilon_j$, $k$ is a Boltzmann constant, $T$ is temperature.

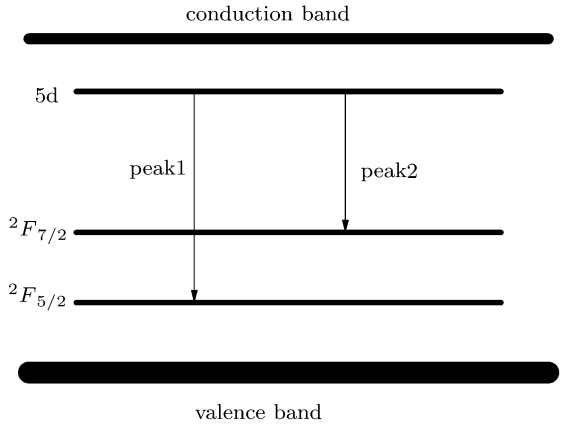



**Fig.6.** The energy level sketchy diagram of $Ce^{3+}$ in $LaCl_3$ crystal.

Energy level diagram of $Ce^{3+}$ in $LaCl_3$ crystal can be sketchily shown in Fig.6. According to Boltzmann distribution law described by Eq.(1), as the temperature rises, in a state of equilibrium, the probability of electron occupying $^2F_{7/2}$ energy is enhanced, on the contrary, occupying $^2F_{5/2}$ energy is reduced. As a result, the emission intensity of the $5d\rightarrow^2 F_{7/2}$ of $Ce^{3+}$ (around 356 nm) is increased, while that of $5d \rightarrow^2 F_{5/2}$ of $Ce^{3+}$(around 332 nm) is decreased with the rise of the temperature. In addition, the self-absorption of the $Ce^{3+}$ should also contribute to the change of $Ce^{3+}$ emission, peak1, and peak2 with the temperature.

## 2.3. The temperature dependence of time resolved PL spectra

The PL decay curves of $LaCl_3$:5%Ce from 80 K to 500 K temperature in steps of 50 K were measured by the single photon counting method with FLS920 spectrofluorimeter and fluorescence decay times were obtained from the decay curves using common deconvolution procedure. The decay time at different wavelengths can be measured by placing monochromator between the crystal and the photomultiplier. The measurement result was shown in Fig.7. Excitation wavelength was selected at 311.5 nm, emission wavelength at 332 nm. The slit width was set at 2.8 nm in the measurement. As can be seen the decay curves at different temperatures present single exponential decay. The decay times fitted with first order exponential decay are presented in Table 1.

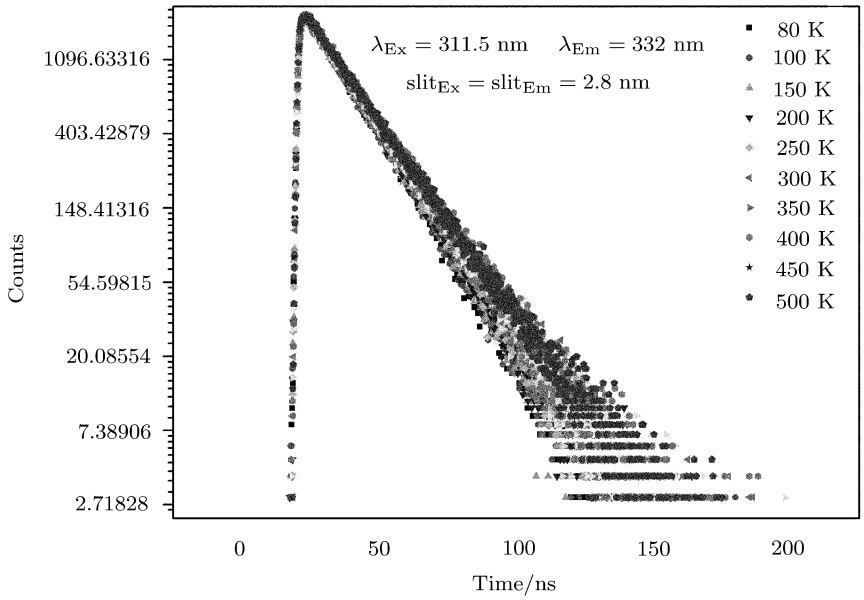



**Fig.7.** The time resolved PL spectra of $LaCl_3$:5%Ce with the change of the temperature between 80 K and 500 K in steps of 50 K.

**Table 1.** The fitted results of each temperature point by first order exponential decay.

| Temperature/K | 500 | 450 | 400 | 350 | 300 | 250 | 200 | 150 | 100 | 80 |
|---|---|---|---|---|---|---|---|---|---|---|
| Decay time/ns | 18.57 | 18.52 | 18.28 | 18.10 | 17.81 | 17.52 | 17.19 | 16.83 | 16.55 | 16.67 |
| $\chi^2$ | 1.002 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |

It is shown that decay time keeps quite stable, just has a slightly change trend (from about 15 ns to 19 ns) between 80 K and 500 K. On the whole, the decay curve of photo-excitation is different from the decay curve of the $\gamma$-ray excitation.[9] In the former, there is only an exponential component of $17 \pm 2$ ns, while, in the latter, there is not only exponential component of $20 \pm 2$ ns, but also a non-exponential component of 330±30 ns and a long component of 1.2 $\mu$s. It is because that the decay time under ultraviolet light excitation is due to the direct excitation of $Ce^{3+}$, while under $\gamma$-ray excitation, is not only due to the direct capture of electron–hole on $Ce^{3+}$, but also due to the energy transfer by binary electron–hole recombination, which leads to the non-exponential component of 330±30 ns and by STE diffusion leads to the long component.[6]

## 3. Conclusions

The optical transmittance of $LaCl_3$:Ce crystal grown by modified Bridgman method was first reported. It was found that the transmittance can reach to as high as 80% between 320 nm and 600 nm without obvious absorption. The emission spectra at different temperatures were measured and can be fitted with three Gauss-shaped bands- peak1, peak2 and peak3. Peak1 and peak2 are attributed to the two emission of the regular $Ce^{3+}$, while peak3 should be attributed to the "perturbed" $Ce^{3+}$. As the temperature increases, emission intensity of peak1 (around 332 nm) declines, the peak2 (around 356 nm) is enhanced correspondingly, and that of peak3 (around 370 nm) almost keeps the same. However, the total emission intensity is quite stable, without thermal quenching happening up to 500 K. It was found that the emission spectra had a red shift with the temperature, which should be caused by the re-absorption of the $Ce^{3+}$ emission. In addition, the FWHM of $Ce^{3+}$ emission bands becomes wider and wider with the increase of the temperature. The total emission intensity increases slightly between 80 K and 500 K, which should be attributed to the improvement of energy transfer efficiency: STE to $Ce^{3+}$ with the rise of the temperature. The decay time keeps at 17±2 ns between 80 K and 500 K. It can be clearly seen from above that $LaCl_3$:5%Ce crystal has excellent temperature stability which is very helpful for practical application at high temperature.

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