**Effect of Annealing Treatments on Optical and Luminescence Properties of Lu\(_{1.8}Y_{0.2}\)SiO\(_5\):Ce Single Crystal**

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**Abstract.** LYSO:Ce crystal is one of efficient scintillation materials with high light output and short decay time. LYSO:Ce crystal grown by Czochralski method can be affected byannealing treatments. In present work, annealing treatments in different atmosphere (air, N\(_2\) and H\(_2\)) were carried out on the LYSO:Ce crystals to investigate the effect on the optical and luminescence properties after annealing. The optical transmittance, excitation and emission spectrum, and the decay time have been attained at room temperature. Luminescence efficiency has been presented by the integrated area of emission spectra under ultraviolet (UV) excitation. It is found that annealing treatments almost do not affect the optical transmission. Annealing in N\(_2\) atmosphere has no noteworthy effect on the luminescence intensity of LYSO:Ce crystals, but increases much annealing in H\(_2\) atmosphere, dramatically decreases the luminescence intensity after annealing in air. In addition, the decay time of LYSO:Ce crystals are affected by annealing treatment either in air or in H\(_2\) atmosphere.

**Introduction**

Ce-doped lanthanide oxyorthosilicate single crystals have excellent scintillation properties. Much attention has been paid to Ce-doped Lu\(_2\)SiO\(_5\) (LSO:Ce) amongst them because of its high density and high atomic number, high light output, short decay time [1]. Owing to these properties, it has been widely used in computed tomography (CT), positron emission tomography (PET), detecting the gamma ray in nuclear physics and geological exploration [2, 3]. LYSO:Ce crystal shows the similar scintillation properties with LSO:Ce, and is proposed as an interesting alternative to LSO:Ce [4-6]. Introducing Y\(^{3+}\) into the matrix reduces the bath temperature during the Czochralski method growth by ~50\(^\circ\)C, also reduces amount of defects in the crystals. Hence the cost during growing will be lower. LYSO:Ce is particularly suitable for PET application due to the shorter decay time and very good time resolution [7, 8].

There are many methods to further improve the properties of LYSO:Ce crystal, annealing process has been proved to be a very important and effective method. It is found that annealing treatment can improve the properties of tungstate (PWO) [9] and cerium doped lutetium pyrosilicate (LPS:Ce) [10]. Bruce chai found that annealing treating in an containing oxygen atmosphere can improve the scintillation properties of LSO:Ce and LYSO:Ce in proper condition [11]. In this paper, we investigate the effect of annealing treatment in different atmosphere (air, N\(_2\) and H\(_2\)) on optical and luminescence properties of the LYSO:Ce crystals obtained by Czochralski method. Based of the analysis of the crystal’s spectra before and after annealing treatments, the effects of different annealing atmosphere have been discussed.

**Experimental procedures**

LYSO:Ce crystal was grown by Czochralski method in induction heating furnace, then flawless crystals (colorless and clear) were obtained. The samples with dimensions of 15 × 15 × 2 mm\(^3\) were cut from the LYSO:Ce crystal boule and polished before annealing treatments. The samples were annealed in different atmosphere (air, N\(_2\) and H\(_2\)) at 1500\(^\circ\)C for 3 h.
Optical transmittance spectra were measured at room temperature (RT) by using a HITACHI U2910 PC spectrophotometer. The ultraviolet (UV)-excitation and emission spectra were tested by SHIMADZU RF-5301 fluorescence spectrometer at RT. Decay curves were recorded by FLS920 steady-state fluorescence made by Edinburgh Instrument. Experimental conditions and geometry were kept carefully the same when the test is taken to compare the effect of before and after annealing treatments. Besides, the luminescence intensity of the crystal was presented by the integration area of the emission spectra under UV excitation.

Results and Discussion

The transmittance spectra before and after annealing of LYSO:Ce crystal were shown in Fig. 1. The transmittance is an important index of the optical property of crystal. It is obvious that there is no absorption for the wavelength ranging from 400-800 nm and the transmittance reach to 74%. That is to say, the LYSO:Ce crystals grown by Czochralski method own good optical property. The transmittance has little change before and after annealing in air atmosphere at the long wavelength. As presented in the Fig. 1, the absorption peaks are at 264 nm, 295 nm. Obviously absorption band can be seen ranging from 343-374 nm, as report in papers [12, 13], which cause from the charge transfer between Ce$^{4+}$ and O$^{2-}$ ion in the crystal.

Fig. 2 shows the UV-excitation and emission spectra of LYSO:Ce crystals before and after annealing in air atmosphere. By comparing the spectra before and after annealing treatment, we find that the peaks positions are the same. The excitation spectra are due to the transition of 4f level to 5d level and the emission spectra owe to the transition of the lowest energy level of 5d to the subbands of 4f ($^{2}F_{5/2}$, $^{2}F_{7/2}$). It is clear that the luminescence intensity decreases a lot after annealing in air. By comparing the integral intensity of emission spectra, the luminescence intensity reduced by 42% after annealing in air. Annealing in air atmosphere, on the one hand, helps to reduce the content of electron traps which possibly result from the oxygen vacancy and then increase the luminescence intensity. On the other hand, it also will oxidize Ce$^{3+}$ into Ce$^{4+}$, which is a nonradiative center and then reduces the luminescence intensity. In conclusion, the later plays a dominant role, so the luminescence efficiency decreases a lot after annealing treatment in air.

Fig. 3 shows the optical transmittance of LYSO:Ce crystal before and after annealing treatments in N$_2$ atmosphere. In the wavelength ranging from 400-800 nm, we find that the transmittance reduces a little. Fig. 4 shows the UV-excitation and emission spectra of LYSO:Ce crystal before and after annealing treatments in N$_2$ atmosphere. Annealing treatments in air has little effect on the luminescence spectra. This is to say, annealing in inert atmosphere will not improve the intensity of luminescence. When annealing in inert atmosphere, it does not work on the factor (Ce ion, oxygen vacancy [7] and Ir$^{3+}$ [14]) which affect the luminescence efficiency.
Fig. 5 shows the transmittance of LYSO:Ce crystal before and after annealing in H$_2$ atmosphere. Transmittance curve after annealing treatment is almost the same with that before annealing in the wavelength ranging from 400-800 nm.

<table>
<thead>
<tr>
<th>annealing</th>
<th>Peaks</th>
</tr>
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<tbody>
<tr>
<td>Before</td>
<td></td>
</tr>
<tr>
<td>Position(eV)</td>
<td>2.80</td>
</tr>
<tr>
<td>Integral intensity</td>
<td>28.3</td>
</tr>
<tr>
<td>Intensity ratio</td>
<td>2.1</td>
</tr>
<tr>
<td>After</td>
<td></td>
</tr>
<tr>
<td>Position(eV)</td>
<td>2.79</td>
</tr>
<tr>
<td>Integral intensity</td>
<td>40.5</td>
</tr>
<tr>
<td>Intensity ratio</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Fig. 6 shows the emission spectra of LYSO:Ce crystal before and after annealing in H$_2$. Integral intensity of emission spectrum has increased by 45% after annealing in H$_2$ comparing with that before annealing. The emission spectra can be fitted with three Gaussian bands with peak positions at 3.11 eV (399 nm), 2.95 eV (420 nm) and 2.80 eV (444 nm), which are marked with A, B and C, respectively.
The emission peaks are due to the transition of 5d to 4f of Ce$^{3+}$, and the peak positions are in agreement with previous work [15]. Bands A and B correspond to the luminescence of Ce1 (7-oxygen-coordinated), while band C correspond to the luminescence of Ce2 (6-oxygen-coordinated) [16, 17]. As shown in Table 1, the percentages of the areas with bands A and B comparing with C before and after annealing in H$_2$, i.e., the ratio of Ce1 and Ce2 emission intensity are almost the same after annealing treatment. It indicates that the annealing treatment in H$_2$ can increase concentrations of Ce1 and Ce2 at same time when Ce$^{4+}$ reduced to Ce$^{3+}$.

Fig. 7 shows the luminescence decay curves of LYSO:Ce crystal before and after annealing treatments and the decay time shows in Table 2. The decay time becomes shorter after annealing in H$_2$ and longer in air atmosphere comparing with that of the as-grown LYSO single crystal. The decay time is associated with the oxygen vacancy in crystals, it suggests that the amount of electron traps increase annealing in H$_2$ while decrease in air.

![Decay curves of LYSO:Ce crystal](image)

**Table 2** Decay time of LYSO:Ce crystal before and after annealing in different atmosphere fitted by equation of $Y = A_0 \exp \left(-\frac{x}{t}\right) + y_0$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Decay time (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1# (as-grown)</td>
<td>33</td>
</tr>
<tr>
<td>2# (air)</td>
<td>35</td>
</tr>
<tr>
<td>3# (H$_2$)</td>
<td>31</td>
</tr>
</tbody>
</table>

**Summary**

The optical and luminescence properties of LYSO:Ce crystal with annealing treatments in different atmosphere were studied. It is sure that the annealing treatments almost do not affect the transmittance. We find that the annealing treatments in N$_2$ atmosphere do not change the luminescence efficiency of LYSO:Ce crystal. When annealing in air, on the one hand, some oxygen...
vacancy of LYSO:Ce crystal were eliminated, which decreases the host lattice defect and lengthens the decay time. On the other hand, the annealing treatment in air the Ce$^{3+}$ will be oxidized into nonradiative center Ce$^{4+}$, which makes the luminescence intensity decreases. What’s more, it is clear that the luminescence intensity increases a lot when annealing in H$_2$ atmosphere because of Ce$^{4+}$ reduced to radiative center Ce$^{3+}$. Emission spectra annealing in H$_2$ fitted by Gaussian function suggests that the ratio of Ce1 (seven-oxygen-coordinated) and Ce2 (six-oxygen-coordinated) has little change comparing with that before annealing in H$_2$ when Ce$^{4+}$ reduced to Ce$^{3+}$. In addition, the annealing treatment in H$_2$ atmosphere will shorten the luminescence decay time of LYSO:Ce single crystal. All in all, only annealing treatment in reduction atmosphere (H$_2$) is good for increasing of luminescence intensity and decreasing of luminescence decay time of LYSO:Ce single crystal scintillator.

References