

Laser-excited spectra of $\text{Lu}_2\text{SiO}_5\text{:Ce}$ scintillator

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Abstract

The emission spectra of $\text{Lu}_2\text{SiO}_5\text{:Ce}$ single crystal under the excitation of 266 nm laser were investigated. The emission spectra of LSO single crystal show no temperature quenching from 20 to 300 K, under the excitation of 266 nm laser with 2 mJ pulse energy. With rising temperature, the Ce1 emission is slightly decreased, while the Ce2 emission is slightly increased. These results show the emissions of Ce1 and Ce2 is not only dependent on the concentration ratio but also influenced by the possible energy transfer processes, including Ce1 to Ce2, intrinsic STHs to Ce2 and the phonon-assisted transfer processes. The spectral thermal broadening and the spectral overlap become evident at high temperature, leading to the enhancement of energy transfer. When the excitation power lowers, the ratio of Ce1 and Ce2 emission increases, and is close to the Xe lamp ultraviolet (UV) excitation, suggesting that the energy transfer from Ce1 center to Ce2 center may be also dependent on the excitation power.

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1. Introduction

Cerium-doped lutetium oxyorthosilicate ($\text{Lu}_2\text{SiO}_5\text{:Ce}^{3+}$ or LSO) with excellent light yield ($\sim 30,000$ photons/MeV), short-decay time (~ 40 ns), high density (7.4 g/cm^3) is of considerable research interest as a promising medical scintillator in positron emission tomography (PET) for medical imaging [1–5].

The scintillation light of LSO is ascribed to the parity-allowed electric dipole $5d \rightarrow 4f$ transition of the Ce^{3+} ion that is strongly affected by the crystal field. The host of LSO belongs to monocline structure with the space group of C2/c. The Lu ions occupy two crystallographically independent sites with oxygen coordination number of six and seven, and the average nearest-neighbor distances of 2.22 and 2.32 Å, respectively. Ce^{3+} ions can substitute for the Lu^{3+} ions, thus occupying two crystallographically independent sites. It is established that the Ce^{3+} lumines-

cence in LSO exhibits two distant types of excitation and emission spectra under ultraviolet excitation, contributing from two luminescence centers Ce1 and Ce2. A typical Ce1 center emission peaks at 393 and 422 nm and the double structure for the Ce1 emission is ascribed to the transition of Ce^{3+} from the lowest 5d level to the two 4f levels ${}^2\text{F}_{7/2}$ and ${}^2\text{F}_{5/2}$ due to the spin–orbit splitting. While Ce2 center emission peaks at about 450 nm without double structure even at low temperature. The energy transfer from Ce1 center to Ce2 center can occur and be enhanced by the rising temperature, which was revealed by the luminescence spectra under the synchrotron radiation vacuum ultraviolet (VUV)–UV excitation [6].

The possibility of substitutional and interstitial occupation by Ce ions was proposed by Naud et al. [7] based on the fact that the spin–orbit splitting of the Ce^{3+} 4f ground state was found in the Ce1 emission spectra, while no such splitting can be observed in the Ce2 emission spectra even at low temperature. However, Suzuki et al. [8] proposed that the two centers are substitutional sites rather than one substitutional and one interstitial, which was also

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supported by Cooke et al. [9]. The coexistence of the two luminescence centers Ce1 and Ce2 at room temperature in LSO crystal is a possible reason of degradation energy resolution of LSO in medical imaging application [10]. The emission from Ce2 centers should be controlled as possible in order to reach the requirement of practical application.

In the present paper, the temperature and excitation power-dependent emission spectra of LSO single crystal under the 266 nm laser excitation were investigated. Under the high-density excitation of laser, the emission of Ce1 and Ce2 could exhibit different characteristic, compared with low-density excitation. This work also provides the insight into the luminescence properties of Ce1, Ce2 and their energy transfer process in LSO host under laser excitation with different power.

2. Experimental

The LSO single crystals were grown from the raw materials Lu_2O_3 , SiO_2 , CeO_2 (with purity of at least 99.99%) by the Czochralski technique. The detailed method of growth was described in Ref. [11]. The Ce^{3+} concentration in the melt was 0.25 at% relative to Lu^{3+} . The crystal sample was polished to slices $10 \times 10 \times 1 \text{ mm}^3$ in size. The light yield of LSO crystal used in the present work is 32,000 photons/MeV with ^{137}Cs source, and the decay times obtained under optical excitation and gamma excitation are 30 and 41 ns, respectively [11]. Such scintillation properties suggest that the crystal is of high quality.

The luminescence spectra were measured under 266 nm laser from Nd:YAG with the pulse duration of 10 ns and the pulse energy of 2 mJ. A JOBIN YVON HRD1 double-grating monochromator was used as the emission monochromator. The emission spectra were detected by a Hamamatsu R456 photomultiplier. Appropriate filters were used to decay the power of the incident laser. The temperature of measurement is from 20 to 300 K. The emission spectrum measured by a Hitachi 850 fluorescence spectrometer with a Xe lamp (150 W) was also present for comparison.

3. Experimental results and discussion

The 266 nm laser-excited emission spectra at different temperatures were shown in Fig. 1. All the emission spectra can be decomposed into two bands peaking at 3.20 eV (389 nm) and 3.04 eV (408 nm) due to the Ce1 center emission and one band peaking at 2.78 eV (446 nm) due to the Ce2 center emission, shown in Fig. 2. The double structure for the Ce1 center emission is ascribed to the transition of Ce^{3+} from the lowest 5d level to the two 4f levels $^2\text{F}_{5/2}$ (Ce1-I emission, 3.20 eV) and $^2\text{F}_{7/2}$ (Ce1-II emission, 3.04 eV) due to the spin-orbit splitting. The emission intensity is nearly stable at different temperatures without observing temperature quenching effect, which is different from those excited by X-ray [12] and synchrotron

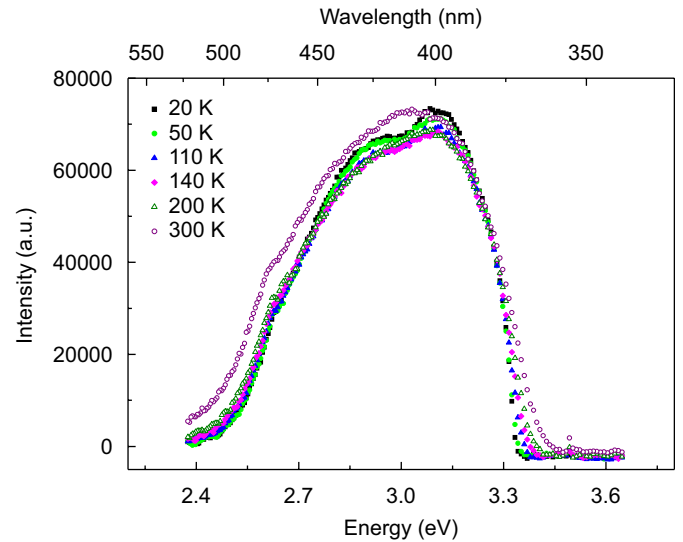


Fig. 1. Emission spectra of LSO single crystal under the excitation with 266 nm laser at various temperatures.

radiation VUV–UV [6]. The spectral integral intensities for Ce1, Ce2 and their sum are depicted in Fig. 3 as a function of temperature. With the rising temperature, the Ce1 emission intensity is slightly decreased, while the Ce2 emission intensity is slightly increased. The sum of Ce1 and Ce2 is nearly constant below 200 K but slightly increases at 300 K.

As the temperature rises, the spectra are thermally broadened. At low temperatures of 20 and 50 K, for instance, the spectral splitting is evidently observed. After Gaussian-fitting for the spectra, the full-width at half-maximum (FWHM) at different temperatures can be obtained. The FWHM should obey the relation [13]

$$W(T) = W(0) \left[\coth \left(\frac{\hbar\omega}{2k_B T} \right) \right]^{\frac{1}{2}}, \quad (1)$$

where $W(T)$ is the FWHM at absolute temperature T ; $W(0)$ is the FWHM at 0 K; $\hbar\omega$ is the energy of the lattice vibration (or phonon) that couples with the electronic transition and k_B is the Boltzmann constant.

For a Gaussian line shape it can be written as

$$W(T) = \hbar\omega \left[8S \ln 2 \coth \left(\frac{\hbar\omega}{2k_B T} \right) \right]^{\frac{1}{2}}, \quad (2)$$

where S is Huang–Rhys factor [14], showing the electron–lattice coupling magnitude.

The FWHM for Ce1 and Ce2 emission at different temperatures is present in Fig. 4 and the data are fitted according to formula (2). Therefore, we can extract the $W(0)$, ω , and S values for Ce1-I, Ce1-II and Ce2 emissions are shown in Table 1. The S values for the three emissions are close and more than 5, suggesting the strong coupling between the Ce^{3+} ion and lattice vibrations. The lattice vibration energy of $\hbar\omega$ for Ce2 (465 cm^{-1}) is much larger than those of Ce1 (329 and 312 cm^{-1} for Ce1-I and II, respectively), indicating that the Ce2 has a stronger

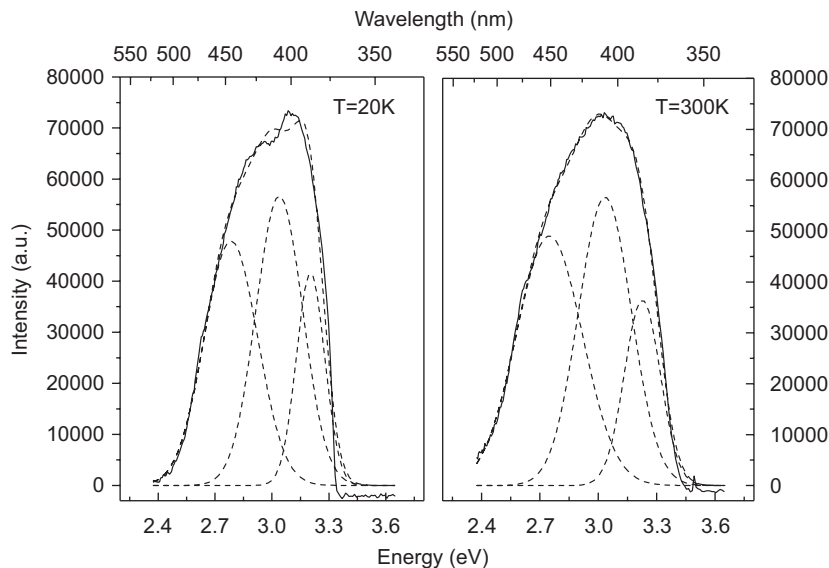


Fig. 2. Emission spectra of LSO single crystal excited by 266 nm laser (solid lines) and their Gaussian-fitting results (dashed lines) at 20 and 300 K.

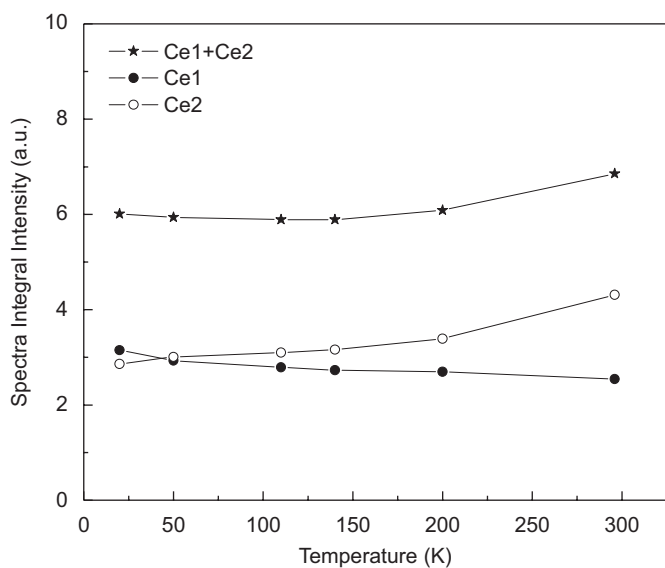


Fig. 3. Temperature dependence of the spectra integral intensity of LSO single crystal for Ce1 emission, Ce2 emission and their sum.

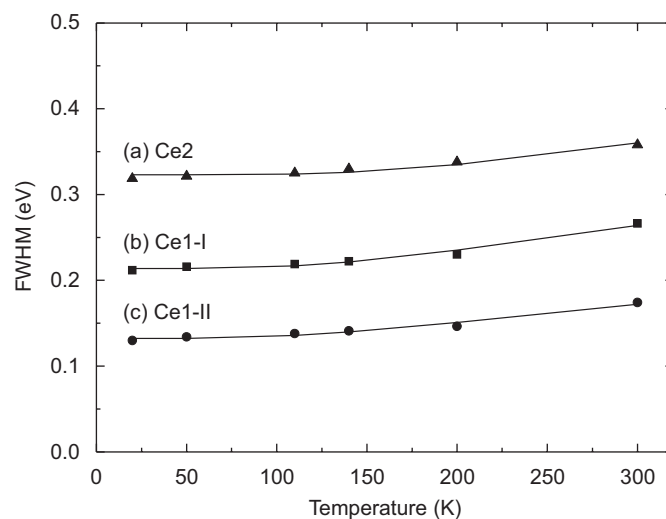


Fig. 4. Temperature dependence of FWHM for the LSO emission spectra. (a), (b) and (c) refer to the emission peaks for Ce2, Ce1-I and Ce1-II, respectively.

electron–lattice interaction. The similar thermal broadening effect for the absorption spectra of LSO single crystal was also reported by Cooke et al. [9]. But, we obtain somewhat different S and ω values, indicating that the energy and the number of the phonons involved in the electron–lattice interaction may be different for the absorption and emission processes.

Under the excitation of 266 nm laser with 2 mJ power, the Ce2 emission intensity is close to the Ce1 emission intensity. This result is quite different from that under the lower density excitation, such as Xe lamp UV and synchrotron radiation VUV–UV. In order to investigate the influence of excitation power on the Ce1 and Ce2

Table 1
Electron–lattice coupling parameters

Emission	$W(0)$ (eV)	ω (10^{13} s^{-1})	$\hbar\omega(\text{cm}^{-1})$	S
Ce1-I $5d \rightarrow 4f$ (${}^2F_{5/2}$)	0.215	6.18	329	5.02
Ce1-II $5d \rightarrow 4f$ (${}^2F_{7/2}$)	0.212	5.86	312	5.44
Ce2	0.323	8.74	465	5.67

emissions, we measured the emission spectra under the different excitation power with appropriate filters. The emission spectra excited by 266 nm laser with 2, 1 and 0.1 mJ are shown in Fig. 5(a)–(c), respectively. For

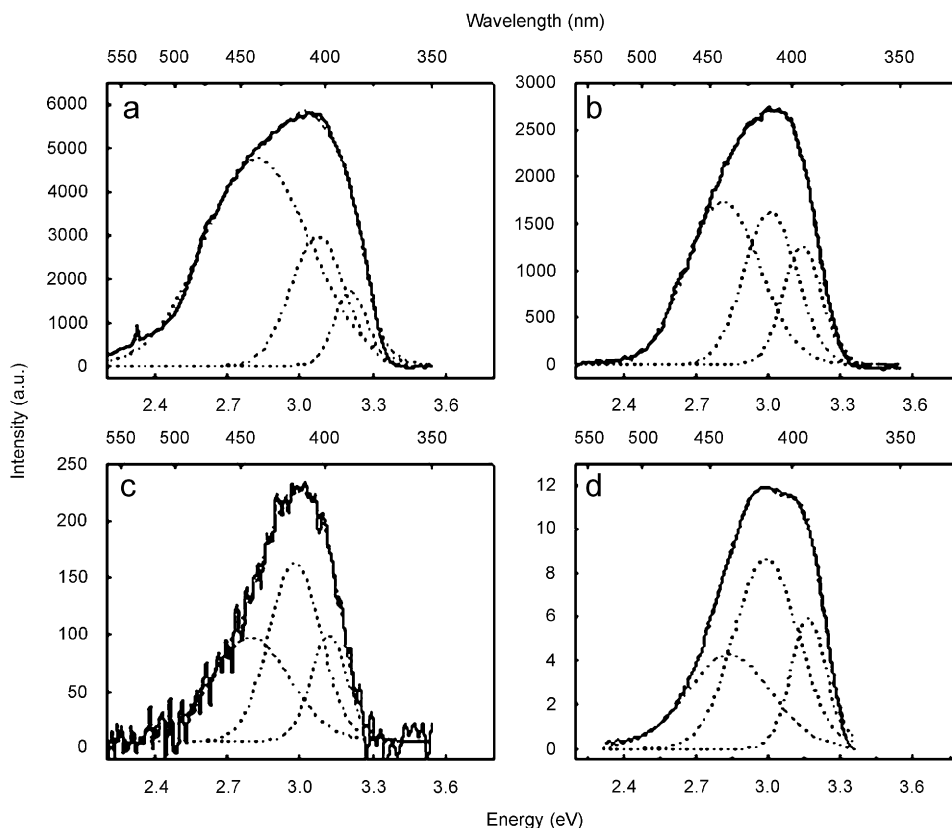


Fig. 5. The emission spectra LSO under the different power excitation of 266 nm laser (a) 2 mJ, (b) 1 mJ, (c) 0.1 mJ and (d) 266 nm excitation from Xe lamp. Notice that the intensities of (a), (b) and (c) for the laser excitation have the same scale and are comparable.

comparison, the emission spectra excited by Xe lamp 266 nm UV are also shown in Fig. 5(d). When the laser power decreases, the emission intensity is decreased but the emission ratio of Ce1 to Ce2 increases. At the lowest power of 0.1 mJ, the ratio is nearly equal to that excited by the Xe lamp 266 nm. In fact, under the 266 nm excitation, the Ce1 and Ce2 centers are both effectively excited. At the same time, the energy transfer from Ce1 center to Ce2 center should be considered. It is probable that the energy transfer from Ce1 center to Ce2 center becomes more efficient when the excitation power increases.

The ratio of Ce1 and Ce2 emissions is dependent on not only the concentration ratio of Ce1 and Ce2 but also temperature and the excitation intensity. Although electron paramagnetic resonance (EPR) study indicated that the relative concentration of Ce^{3+} at each site to be 95% for Ce1 and 5% for Ce2 [15], or the ratio of the Ce1 and Ce2 was suggested to be 4:1 [9] when the doped Ce concentration was 0.25 at% relative to Lu^{3+} in the melt, the Ce2 emission shows a comparative intensity with Ce1 emission at room temperature in the present experiment, which is analogous with our previous research [6,12] and others reported on Refs. [10,11]. The energy transfer process should be taken into account for the explanation of the relation between Ce1 and Ce2. In addition, we may also consider the influence of intrinsic luminescence from LSO

host that consists of the self-trapped excitons (STEs) emission at 256 nm and self-trapped holes (STHs) emission at 315 and 331 nm [5]. In fact, only the STHs emission may occur under the 266 nm excitation. The energy of excited STHs could be transferred to the Ce2 center leading to the enhancement of the Ce2 emission since the emission of STHs at 315 and 331 nm can cause effectively excitation for the Ce2 center [6]. Such influence may only dominant below 100 K because the STHs cannot survive at a higher temperature. The distinct temperature effect of Ce1 and Ce2 is also probably due to the energy transfer from Ce1 center to Ce2 center. The energy transfer from Ce1 to Ce2 can occur with the dipole–dipole interaction, which is highly efficient due to the parity-allowed electric-dipole transition of Ce^{3+} $5d \rightarrow 4f$. The transfer efficiency is enhanced by rising temperature because the spectral overlap is increased due to the thermal broadening effect [6]. For such strong electron–lattice coupling system suggested by the Huang–Rhys factor S larger than 5, the phonon-assisted energy transfer may also happen, which is strongly dependent on the temperature. It is evident that the multi-phonon process, and thus the phonon-assisted transfer probability, is significantly enhanced by rising temperature. Therefore, the energy transfer from Ce1 to Ce2 could be enhanced by the rising temperature, leading to the different temperature dependence effect.

4. Conclusion

Under the excitation of 266 nm laser with 2 mJ pulse energy, the emission spectra of LSO single crystal show no temperature quenching from 20 to 300 K. The Ce1 emission is slightly decreased and the Ce2 emission is slightly increased with the rising temperature, showing that the possible energy transfer from Ce1 center to Ce2 center. The spectral thermal broadening is observed. When the excitation power lowers, the ratio of Ce1 and Ce2 emission increases, and is close to the Xe lamp UV excitation, showing the energy transfer from Ce1 center to Ce2 center is also dependent on the excitation power. These results show the emissions of Ce1 and Ce2 is not only dependent on the concentration ratio but also influenced by the possible energy transfer processes, including Ce1 to Ce2, host to Ce2 and the phonon-assisted transfer processes. It is obvious that when such energy transfer is enhanced, the Ce2 emission can be increased, resulting in degradation of the energy resolution.

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