Dispersion characteristic of photoluminescence decay times of phosphor YAG: Ce, Gd

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Abstract: The dispersion of the characteristic decay times of gadolinium co-doped yttrium aluminum garnet doped with cerium phosphors were studied. In the present work, an ultraviolet semiconductor laser (λ_{em}=375 nm, τ = 1 ns) was used as excitation source for measuring kinetics characteristics of phosphor groups based on YAG with different content of cerium.

1. Introduction

Phosphors based on yttrium aluminum garnet doped cerium ($Y_{3-x}Al_5O_{12}$: Ce_x^{3+}) have been found to be an efficient phosphor material, which are used for the conversion of ultraviolet or blue emission from LEDs into white light emitting LEDs. [1-6] On account of the 4f–5d transition of the Ce^{3+} ion, which shows a maximum absorbance in the blue region thus converting InGaN based blue LED radiation into a broad intense yellow emission band. White light is then a result of the combination of this yellow emission with the non-absorbed blue emission from the blue LED. In order to improve the color rendering index (CRI) of white light emission, co-activators are doped to change the composition of the matrix, and accordingly the luminescence spectrum also changes.

It is assumed that the change of luminescence spectrum is due to the lattice distortion formed in the region of luminous center of ion Ce^{3+}. In [7] suggested that the luminous center has a complex structure. Additional information about luminous centers can be obtained from kinetic characteristics of luminescence decay time. Luminous centers with different structures should have different kinetic characteristics.

2. Experimental details

Industrial phosphors SDL4000, SDL2700 and SDL3500 which are characterized by the different ratio of the elemental composition were used for this research. Among them, SDL2700, SDL3500 contain gadolinium and cerium in amounts of 6.22%, 1.26% and 0.68%, 1.29% of the total composition, respectively. SDL4000 does not contain gadolinium and cerium in amounts which are available for measurement by X-ray photoelectron spectroscopy (XPS).

The photoluminescence spectra of the phosphor samples were recorded by using FLS980 spectrometer with a xenon lamp (250-1000 nm) as the excitation source. Ultraviolet semiconductor laser (λ_{em} = 375 nm, τ = 1 ns) was used as the excitation source for the measurement of the kinetics of decay time

3. Experimental results

3.1. Photoluminescence properties and energy transfer

The excitation spectra (λ_{em} = 560 nm) of phosphor samples were measured in the region between 300 and 550 nm. The excitation spectrum allocated 2 peaks at 344 nm and 454 nm. The excitation peak at 454 nm agrees well with the peak of blue emission band of chip based on InGaN. Therefore, the studied YAG phosphors can efficiently absorb blue emission from chip and then convert it into a more long-wavelength region. Photoluminescence (PL) emission spectra of YAG and YAG:Ce were co-doped with Gd at a fixed excitation wavelength of 340 nm and 460 nm. The measurement results obtained from the spectral characteristics of the studied phosphors are summarized in Table 1. Spectra of SDL2700 and SDL3500 phosphor compared to SDL 4000 phosphor present a broader and shift to the red region.

Table1. Measurement results obtained for the luminescence spectra and excitation of phosphors: peak value position and half band-width

Phosphor	Luminescence				Excitation			
	λ_{ex} = 460 nm		λ_{ex} = 340nm		In the region of 340nm		In the region of460nm	
	ΔE, eV	λ_{Max}, nm	ΔE, eV	λ_{Max},nm	ΔE, eV	λ_{Max}, nm	ΔE, eV	λ_{Max}, nm
SDL2700	0.487	584	0.489	582	0.264	336	0.450	459
SDL3500	0.484	560	0.487	558	0.294	339	0.390	459
SDL 4000(1)	0.435	539	0.486	540	0.313	339	0.396	456
SDL 4000(2)	0.447	541	0.504	542	0.324	339	0.426	456

3.2. Kinetics curves of the luminescence decay

The kinetics curves of the luminescence decay were excited by pulsed laser radiation with λ = 375 nm. The results are shown in Figure 1.

The luminescence decay kinetic curves in nanosecond time domain are well described by a sum of two exponential functions.

$$I = A1 \exp(-t / \tau 1) + A2 \exp(-t / \tau 2) + I0 \qquad [1]$$

Where A1 and A2 represent respective initial intensity; I0 represents the intensity of background, which is independent of the test range time; $\tau 1$ and $\tau 2$ - characteristic luminescence decay times in the nanosecond range.

Kinetic curves in the nanosecond time domain are well described by a sum of two exponential functions. The measurement results of the spectral dependence of the characteristic decay time phosphors are shown in Figure 1. From these results it can be concluded that investigated phosphors have different kinetic luminescence decay curves. The inset in Figure 3 shows the luminescence kinetic curves in semilogarithmic scale at different wavelengths. Results of the studied kinetic luminescence decay curves are summarized in Table 2.

Table2. Summarizes the values of the characteristic luminescence decay time τ for studied phosphors under pulsed laser excitation with λ = 375 nm

| №	phosphor	τ_1 (ns)	Rel.%1	τ_2 (ns)	Rel.%2	τ (ns)
1	SDL2700	4.2	10.4	66.1	89.6	59.6
2	SDL3500	1.5	12.3	60.5	87.7	53.4
3	SDL4000(1)	3.0	12.7	61.8	87.3	54.4
4	SDL4000(2)	2.9	9.1	59.8	90.9	54.6

Short-time decay component in the nanosecond range for the investigated phosphors changes from 1.46 to 4.15 ns, long lifetime component is in the range of 59.8 - 61.8 ns. Long lifetime component accounts for 87.3% - 90.9% of total radiation. Averaged decay time τ is in the range of 53-59 ns, which corresponds to the measurement results with large duration excitation pulse about 60 ns in other working time.
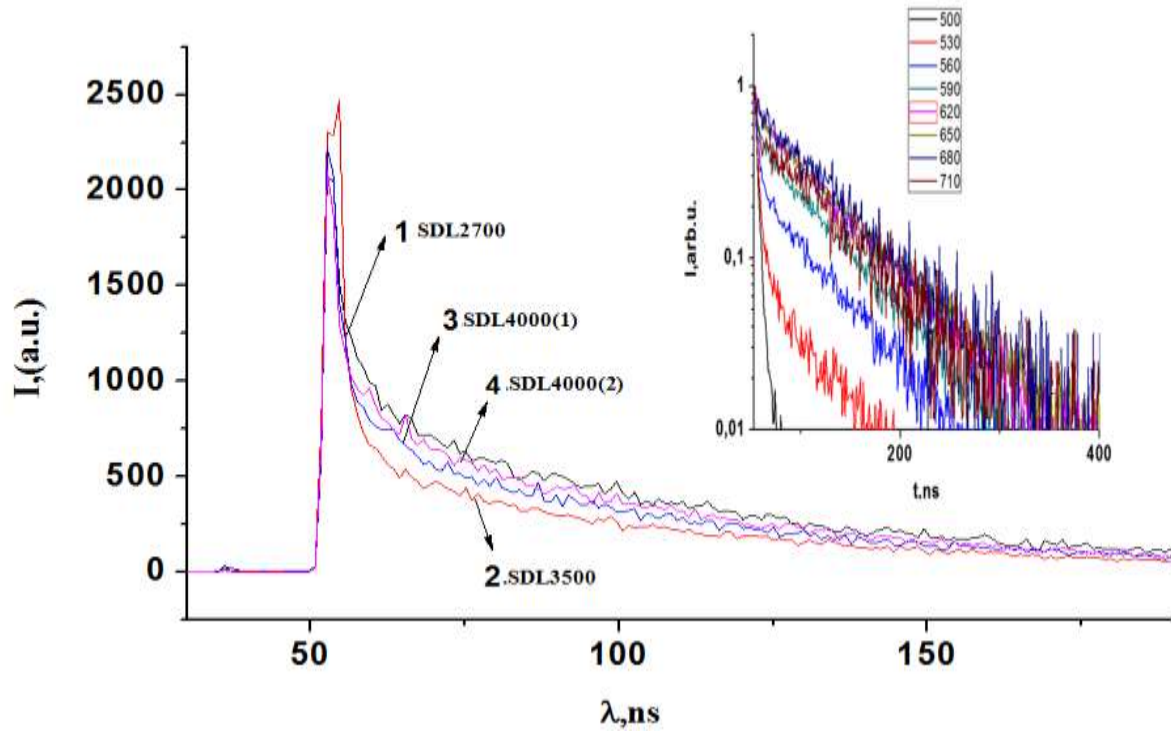
Figure1. Decay kinetic characteristics of the luminescence for investigated phosphors under pulsed laser excitation with $\lambda = 375$ nm

3.3. The kinetic curves dispersion of the luminescence decay
As shown in Figure 1, the kinetics of luminescence decay depends on the wavelength at which it is measured.
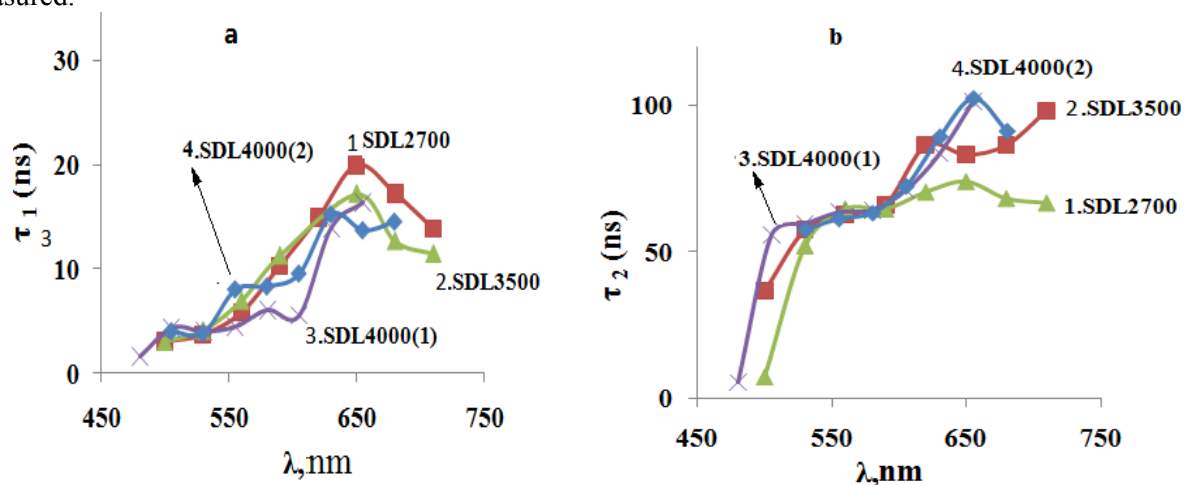
Figure 2.The dispersion of the characteristic decay times.

The dependence of the luminescence delay time with the excitation wavelength in the nanosecond range was studied. According to the measurement results, characteristic decay times were calculated to build a diagram of relationship between time and wavelength (dispersion characteristic times). The measurement results are shown in Figure 2: short –time component (2a) and long time component (2b).

As shown in Figure 2, the dispersion curve can be divided into three sections. Within a short time in the spectral region up to 500 nm is mainly recorded radiation of chip. Photoluminescence duration of two components is lower than at longer wavelengths in the region up to 610 nm. The emergence of this phenomenon may be caused by different luminous centers, or luminous centers are in different environments.

4. Conclusions

The investigation results make it possible to suggest the following conclusions: from the research of kinetic curves dispersion, it can be seen that characteristic decay times in the range of 480 - 610 are different from those in the range of 610 - 700 nm. This indicates that there are two kinds of luminous centers responsible for the luminescence of all investigated phosphors, luminescence independent on the content of cerium. The changes in the ratio of two types of luminous centers lead to a change in the luminescence spectrum of investigated phosphor. It is difficult to ensure compliance with stoichiometry during the crystal formation with a complex structure. Therefore, native defects are introduced in the crystal at the synthesis. Native defects together with activators and co-activators can form complex defects which are called nanodefects [7] Doped activators (Ce^{3+}) and co-activators (Gd^{3+}) result in changes in spatial and energy structure of nanodefects. As a result, the luminescence spectrum and kinetic characteristics change accordingly.

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