

Kinetic characteristics of the luminescence decay for industrial yttrium-gadolinium-aluminium garnet based phosphors

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Abstract. The spectral and decay kinetic characteristics of pulse cathodoluminescence and photoluminescence of phosphors based on yttrium-gadolinium-aluminum garnet were investigated using pulsed optical time resolved spectroscopy.

1. Introduction

LEDs based on InGaN heterostructures emitting in the near-UV (blue) spectral range are considered to be most promising to convert a portion of this radiation into light with the desired color characteristics using the phosphor. These heterostructures emit in the range of 430 ... 490 nm which corresponds to photon energies from 2.5 to 2.9 eV. To produce white light, radiation in the yellow-red spectral region is to be added to the blue radiation of the heterostructure [1–3]. The average photon energy in the visible spectral region is about 2.2 eV. Therefore, conversion of the blue light into yellow-red light is accompanied by low energy loss that provides high light efficiency of the LED light source and insignificant energy losses in device heating. Luminous efficiency currently achieved for “white” LEDs is 160 lm/W, while the theoretically maximum possible values are 240 ... 260 lm/W.

Further increase in light efficiency is mainly determined by the ability to improve the efficiency of phosphors. Radiative characteristics of phosphors to a large extent depend on the history: synthesis technology, quality of raw materials and composition of the resulting material defects. Therefore, optimization of phosphor properties to obtain the maximum light efficiency for the LED is challenging [1, 4, 5].

Lack of information on the processes of energy transfer to the luminescence centers, the characteristics of the luminescence decay kinetics hinders phosphor improvement. This paper addresses the study of the spectral and decay kinetic characteristics of the luminescence for a group of industrial phosphors based on yttrium-aluminum gadolinium garnet as promising phosphors for emitting in the visible range of spectrum.



2. The tasted samples and the experimental method

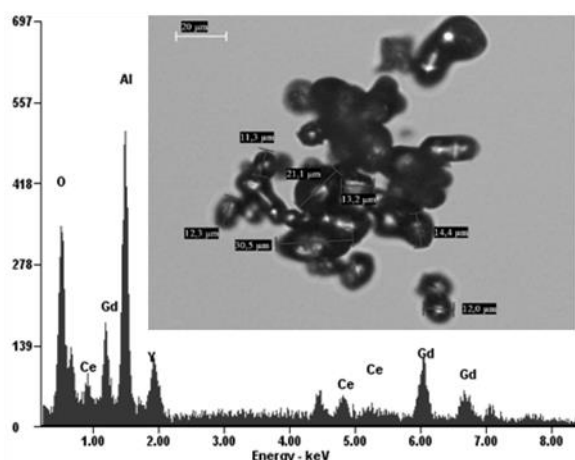


Figure 1. Elemental and particle size distribution of the FL-5049 phosphor

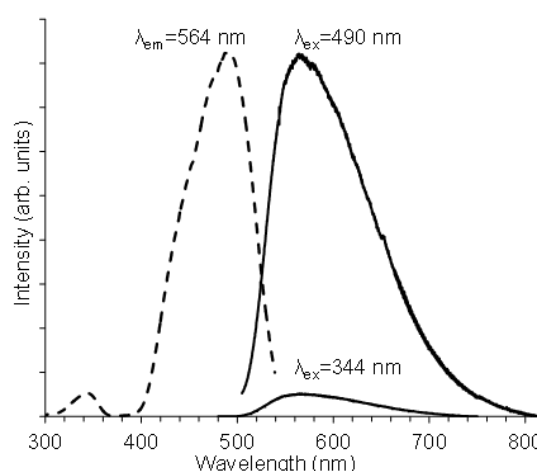


Figure 2. Excitation and luminescence spectra for FL-5049 phosphor

FL5049 (Y-Gd-Ce)₃Al₅O₁₂ phosphor doped with cerium has been provided by the INCOTEX Holding synthesized by Fultor Enterprises Co. Ltd, Dalian, China. Industrial phosphors manufactured by AWB3 (Billion Light Co., Taipei County, Taiwan) and LEUD 560 for were used to conduct the investigation as well. The elemental composition of the samples was determined using the scanning electron microscope Quanta 3D 200i. The images of the investigated powders were made using the Leica DM 6000 M optical microscope. The results obtained for the elemental composition of FL-5049 phosphor are presented in figure 1 as an example. The composition of the studied phosphors is provided in table 1.

FL-5049, AWB3 and LEUD 560 phosphors are similar in the composition of basic elements, but differ in their proportions.

Table 1. Phosphor composition

Element	FL5049		AWB3		LEUD 560	
	<i>Wt %</i>	<i>At %</i>	<i>Wt %</i>	<i>At %</i>	<i>Wt %</i>	<i>At %</i>
O	20.70	54.73	25.27	56.72	29.77	60.99
Al	16.64	26.09	21.17	28.18	19.53	23.73
Y	9.69	4.61	15.90	6.42	28.63	10.55
Ce	9.61	2.90	2.74	0.70	5.13	1.20
Gd	43.36	11.66	34.92	7.98	16.94	3.53

The sizes of the FL-5049 phosphor particles in measurement with the Leica DM 6000 M microscope vary from 12 to 30 μm. The luminescence and excitation spectra of the phosphor were measured with the AGILENT CARY ECLIPSE spectrofluorimeter and an optical complex based on two MDR-204 crossed monochromators. The xenon lamp was used as an excitation source. All the measurements were performed with allowance for the optical path spectral sensitivity.

Figure 2 shows the excitation and luminescence spectra for FL5049 phosphor. The luminescence spectrum of FL-5049 phosphor is a broad band with a maximum at 564 nm. The shape of the luminescence spectrum is independent of the excitation radiation. The luminescence is excited by radiation in the region of 400–540 nm, and it is weaker in the region of 310–360 nm. The excitation and luminescence spectra for the tested samples are characteristic of phosphor-based YAG with dopants [5]. The excitation and luminescence spectra for AWB3, LEUD 560 and FL-5049 phosphors are similar.

To investigate the time-resolved luminescence, four excitation sources were used: pulsed nitrogen laser with $\lambda = 337$ nm and pulse duration $\tau = 10$ ns (LR 337), pulse energy of 50 mJ; LED heterostructure with $\lambda = 395$ (Chip 395) and 450 nm (Chip 450) (pulse energy of 15 mJ, $\tau = 50$ ns), and high-current pulsed electron accelerator (PEF) with an average electron energy of 250 keV ($\tau = 10$ ns). The pulse luminescence of phosphors was investigated in the spectral range of 300–800 nm at room temperature within 10^{-8} – 10^{-3} s after the end of the excitation pulse. The luminescence and change in the optical absorption were recorded using FEU-106, FEU-84-6, digital oscilloscopes LeCROY (350 MHz bandwidth) and Tektronix TDS-2014 (100 MHz bandwidth), and monochromator MDR-204, MDR-3.

3. Experimental results

The results obtained for the luminescence decay kinetics in the range of 10^{-8} – 10^{-3} for the FL-5049 phosphor are shown in Fig. 3.

Excitation of FL-5049 phosphor by UV radiation flux ($\lambda = 390$ nm) does not cause sufficiently intense luminescence, as it can be expected from the excitation spectrum presented in Fig. 2. The luminescence is excited by heterostructure radiation (LED chip $\lambda = 450$ nm), and excitation by radiation with $\lambda = 337$ nm is not so efficient. However, high-power laser radiation is sufficient to excite intense luminescence. The short-time luminescence spectra are similar to those measured under steady state conditions: the maximum bandwidth accounts for 564 nm, and the band-width is equal to 0.44 eV.

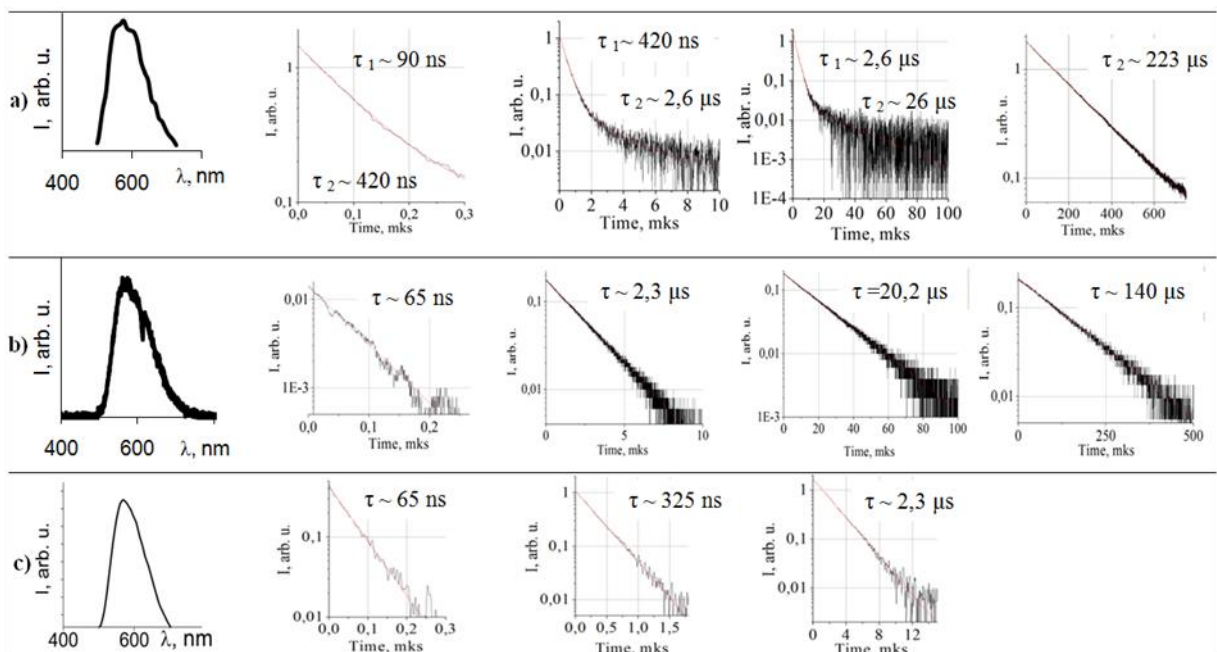


Figure 3. Spectral and decay kinetic characteristics of the luminescence for FL-5049 phosphor under different types of excitation: by electron beam (a), heterostructure radiation with $\lambda = 450$ nm (b), laser radiation flux with $\lambda = 337$ nm (c)

The luminescence decay kinetic curves in the maxima of the luminescence spectral bands for FL-5049 phosphor after excitation by PEF, radiation of LED Chip (450 nm) and laser radiation (337nm) are shown in figure 3. The measurements were performed in the time range from 10 ns to 1 ms. Within this time range, the luminescence intensity decreases by almost 10^6 times. To measure the luminescence decay within this time range, the measurement was performed with different temporal resolution (time window measurement). This allows identification of the main components of the

luminescence decay kinetics, but complicates kinetic curve matching. In the obtained decay kinetics, several components can be described by an exponential function. There are components of the nanosecond range: 65, 90 and 325 ns, and 420 ns. In the microsecond time range, there are components with characteristic times from 2.3 to 2.6 μs , from 20.2 to 26 μs and from 140 to 223 μs depending on the type of excitation. Note that the short-time decay component was observed in [6]. The contribution of each component to the total luminescence light sum is difficult to determine due to the uncertainty of the measurement of the amplitude values at the beginning of the decay kinetic curves. But it can be argued that the characteristic relaxation times are similar under different types of excitation.

From the results presented in table 2 it can be seen that the values of the characteristic luminescence decay times have are substantially similar for different excitation modes in all the investigated phosphors. The only difference is that no component with τ_2 can be observed under excitation by Chip 450. Lack of the components with τ_4 and τ_5 after excitation by laser radiation (LR 337) is due to the fact that the luminescence intensity of the phosphor is small and insufficient for recording in the large time domain. Note the difference in the quantitative characteristics of the luminescence decay in the studied phosphors under excitation by different sources. These differences are particularly distinct in the long lifetime components.

Table 1. Summarizes the values of the characteristic luminescence decay time τ_i for phosphors studied under different types of excitation

Phosphor	Excitation source	Luminescence decay time				
		τ_1 , ns	τ_2 , ns	τ_3 , μs	τ_4 , μs	τ_5 , μs
FL 5049	e-beam	90	420	2.6	26	223
	Laser radiation ($\lambda=337$ nm)	65	325	2.3		
	LED Chip ($\lambda=450$ nm)	65	-	2.3	20.2	140
LEUD560	e-beam	90	420	3.9	21	219
	LED Chip ($\lambda=450$ nm)	65	-	2.3	20.2	142
AWB3	e-beam	65	300	3.9	32	220
	LED Chip ($\lambda=450$ nm)	65	-	2.3	20.2	141

4. Discussion

Excitation of FL5049, AWB3 and LEUD 560 phosphors by energy pulses from different light sources: laser pulse with $\lambda_{\text{ex}} = 337$ nm, electron excitation with electron energy of 250 keV and LED chip with $\lambda_{\text{ex}} = 450$ nm cause burst of luminescence. The LED chip with $\lambda_{\text{ex}} 395$ nm does not excite the tested phosphors. Two characteristic properties of the pulsed luminescence in these phosphors have been found.

1. The pulse luminescence spectra of FL-5049, AWB3 and LEUD 560 phosphors under the excitation modes used in the experiment are of the same shape similar to that measured under steady-state conditions. Consequently, the same luminescence centers are excited by photon energies of 2.5 eV (LED Chip $\lambda_{\text{ex}}=450$ nm), 3.68 eV (LR 337 nm) and electrons (PEF).

2. The same centers are excited in FL-5049, AWB3 and LEUD 560 phosphors which are of insignificantly different quantitative elemental composition.

It is reasonable to explain the observed results as follows. During synthesis of phosphors based on yttrium-gadolinium-aluminum garnet doped with cerium, a large concentration of intrinsic lattice defects enters the crystals. High degree of stoichiometry in the crystal of complex composition cannot be provided during growing from salt mixtures at high temperatures. The crystal contains defects in the form of vacancies, interstitial ions, a variable dopant ion ratio, and a large diversity of defect complex. Apparently, in highly imperfect crystals (crystals containing large concentrations of various

defects accidentally or intentionally introduced during synthesis to provide activation), a set of processes initiated by external excitation should be different from those occurring in perfect crystals [8, 9]. In these crystals, the spatial and energy structure of the formed complexes and nanodefects differ from those in perfect crystals. In highly imperfect crystals doped with gadolinium yttrium-aluminum garnet, a nanodefekt substructure is formed. Therefore, in studying a set of the processes of emission excitation and generation, the possibility of processes in nanodefects is to be considered.

If we assume the existence of the nanodefekt substructure in phosphor crystals, the cumulative research results can be interpreted as follows. Exact coincidence of spectral characteristics (position and FWHM of the luminescence bands), satisfactory agreement of the luminescence decay kinetics characteristics indicate a similar structure of the luminescence centers. The emission center in these crystals can be Ce^{3+} ion [7]. In turn, the emission center is a component of the nanodefekt. Therefore, radiative characteristics do not depend (or weakly depend) on the change in elemental composition. The emission center may be a complex with a cerium ion in its composition.

The investigated phosphors provide high light yield of the conversion of the energy excited by laser, electron beam and LED Chip 450 radiation into luminescence. Consequently, the excitation energy is transferred to the luminescence centers with high efficiency, though energy from different sources is absorbed as a result of totality of different processes. The bandgap absorption of yttrium aluminum garnet crystals starts from 5.2 eV [11]. The photon flux of photons with energies of 2.5 eV, 3.68 eV excite either the luminescence center or the trap site which effectively transfers the energy to the luminescence center. The efficiency of energy transfer to the luminescence center is determined by spatial and energy correlation of the “trap-luminescence center” pair.

When excited by high-energy electron fluxes, the absorbed energy is spent mostly on creation of electronic excitations: electron-hole pairs and excitons in the host. It is highly probable that the resultant electronic excitations are trapped by nanodefects since their capture cross section is at least two orders of magnitude higher than that of the point defect. The electronic excitation captured by the nanodefekt cannot escape. It is highly likely that the energy is transferred to the luminescence center located in the same nanodefekt.

References

- [1] Nakamura S 1997 *Blue laser Diode* (Berlin: Springer)
- [2] Schubert F E 2006 *Light-emitting Diodes* (UK: Cambridge University Press)
- [3] Zorenko Yu, Gorbenko V, Konstankevych I, Voloshinovskii A, Stryganyuk G, Mikhailin V, Kolobanov V, Spassky D 2005 *J. Lumin.* **114** 85
- [4] Soshchin N P 2007 *SID-2007 Proceeding ECNU* 277
- [5] Briskina Ch M, Romyantsev S I, Ryzhkov M V, Soshchin N P, Spasskiy D A 2012 *Svetotekhnika* [in Russian] **5** 37
- [6] Zorenko Yu V, Savchin V P, Gorbenko V I, Wozniak T I, Zorenko T E, Puzikov V M, Dan'ko A Ya, Nizhankovskii S V 2011 *Fiz. tverd. tela* [in Russian] **53** 1542
- [7] Nishimira S., Tanabe S., Fujoka K., Fujimoto Y. // *Optical Materials*. - 2011.- N. 33.-P.688-691.
- [8] Lisitsyna L A, Lisitsyn V M 2013 *Fiz. tverd. tela* [in Russian] **55** 2183
- [9] Lisitsyn V M, Valiev D T, Tupitsyna I A, Polisadova Ye F, Lisitsyna L A, Stepanov S A, Oleshko V I 2013 *Izv. Vuz. Fizika* [in Russian] **56** 75
- [10] Tanner P A., Fu L, Ning L 2007 *J. Phys.: Condens.Matter* **19** 216213