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TIME-RESOLVED LUMINESCENCE EXCITED WITH N_2 LASER OF YAG:CE CERAMICS FORMED BY ELECTRON BEAM ASSISTED SYNTHESIS

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In this paper, an attempt to synthesize the phosphor using powerful hard radiation fluxes. White light-emitting diodes (LEDs) are considered a good lighting devices due to their unsurpassed qualities, such as energy saving and long service life. The synthesized ceramics has the characteristic properties of YAG: Ce, YAGG: Ce phosphors. In total, 10 types of phosphors were chosen for research. Phosphors differed in the presence of Ce2O3 and gadolinium ions incorporated as a modifier.

Keywords: white LEDs, yttrium-aluminum garnet, phosphor, ceramics, synthesis in the radiation field.

Introduction

OnYAG:Ce based phosphors are the most promising for use in LEDs [1-2]. Phosphors are crystalline multicomponent systems [3-4]. The synthesis of YAG:Ce phosphors is carried out by different methods: solid-state reactions, [5], laser ablation [6], sol-gel method [7], hydrothermal [8], pyrolytic spraying [3], coprecipitation [9], using combustion [10] and others. The most common is the synthesis using solid-phase reactions. But this method, as well as the others listed, requires to use a high temperatures. The melting points of the components are from 2455 °C in Y_2O_3 to 2075 °C in Al_2O_3. Therefore, the reproducibility of the synthesis results is low: the elemental composition of microcrystals differs significantly from that included in the mixture, the composition of different batches of phosphor even during synthesis under the same conditions, and the same initial composition of the mixture are changes [11-13]. This also affects to the luminescent properties of phosphors. Therefore, work is constantly ongoing to improve synthesis technologies. In this work, we present the results of studies YAG:Ce based phosphors synthesized in a radiation field.

1. Experimental technique

The samples were synthesized by high-power electron beam generated electron accelerator ELV-6. The possibility of using such a method was first demonstrated in [13-14]. Synthesis in the radiation field should obviously contribute to the occurrence of solid-phase reactions. In the present work, phosphors of different compositions were synthesized with a Y_2O_3 charge content of 22 to 36 wt%, Al_2O_3 ~56 to 62 wt%, Ce_2O_3 ~4.8 to 9.1 wt%, and Gd_2O_3 ~0 to 12 wt% (Table 1).

The structure and elemental composition of these samples were described in [15]. The luminescence spectra of samples and the luminescence excitation spectra were measured using an Cary Eclipse (Agilent) fluorescence spectrophotometer. The photoluminescence kinetics was registrated by a Hamamatsu PMT through a monochromator when excited by a nitrogen laser at a wavelength of 337 nm.

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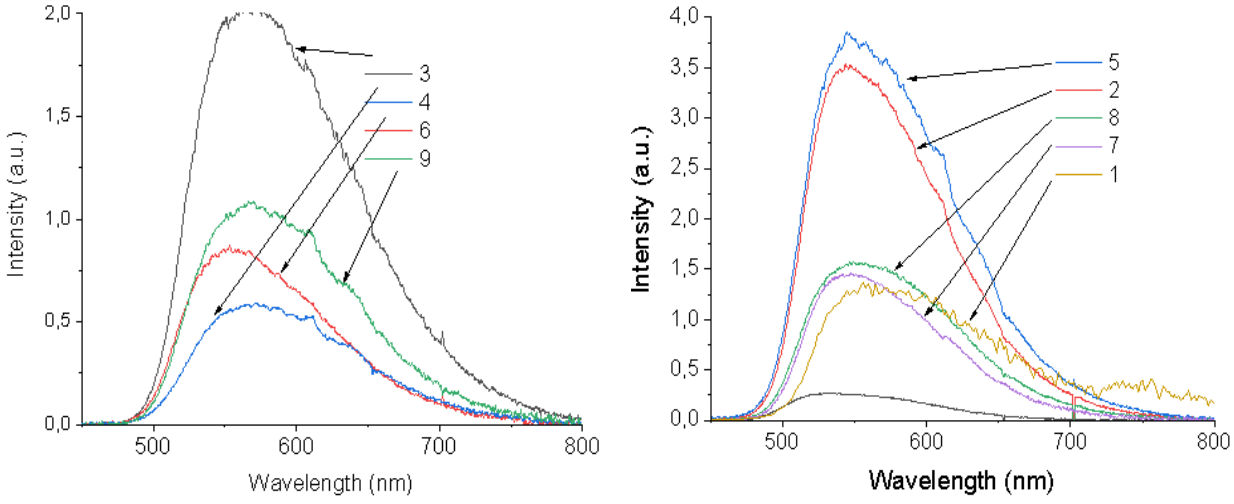
Table 1. The initial composition of the synthesized samples

No.	Compositions	Sample number
1	Al_2O_3 (59.5%) + Y_2O_3(35.7%)+ Ce_2O_3(4.8%)	1
2	Al_2O_3(56.8%) + Y_2O_3(34.1%)+ Ce_2O_3(9.1%)	2
3	Al_2O_3 (59.5%) + Y_2O_3(23.8%) + Gd_2O_3(11.9%) + Ce_2O_3(4.8%)	3
4	Al_2O_3 (56.8%) + Y_2O_3(22.7%)+ Gd_2O_3(11.4%) + Ce_2O_3(9.1%)	4
5	Al_2O_3(56.8%) + Y_2O_3(34.1%)+ Ce_2O_3(9.1%)	5
6	Al_2O_3(59.5%) + Y_2O_3(23.8%)+ Gd_2O_3(11.9%) + Ce_2O_3(4.8%)	6
7	Al_2O_3(59.5%) + Y_2O_3(35.7%)+ Ce_2O_3(4.8%)	7
8	Al_2O_3(56.8%) + Y_2O_3(34.1%)+ Ce_2O_3(9.1%)	8
9	Al_2O_3(56.8%) + Y_2O_3(22.7%)+ Gd_2O_3(11.4%) + Ce_2O_3(9.1%)	9

2. Results and Discussion

The synthesized samples were ceramic balls with a diameter of 3-6 mm of a characteristic yellow color. The samples were crushed into powder, photoluminescence spectra were measured upon excitation by laser radiation λ 337 nm. Excitation spectra and decay kinetics were also measured. It was established that the main luminescent characteristics of the synthesized ceramic samples are mainly similar to those known for the solid-phase synthesis of phosphors obtained by traditional methods [16]. Fig. 1 shows the results of study the luminescence spectra of powdered samples of different compositions; the luminescence spectra have the form of a monopole by exciting on 337 nm.



a b

Fig. 1. Luminescence spectrum of YAG (a) and YAGG (b) ceramics samples excited by 337 nm.

A comparison of results of measuring the characteristics of the spectra gives the following. There is a large variation in the positions and half-widths of the luminescence bands. In YAG:Ce ceramic samples the positions of bands are in the range from 546 to 563 nm, the half-width is from 0.42 to 0.49 eV. In YAGG:Ce from 548 to 570 nm and from 0.44 to 0.48 eV, respectively. In general, tendency is: the entering of gadolinium leads to a band shift to the red region. The wide variation in the band characteristics is explained by the following. In strongly defective systems, which are YAG:Ce ceramics samples, the luminescence center is an element of a nanodefect, a complex defect [17]. Nanodefect is formed during the synthesis. The formation does not have time

to complete at a high rate of ceramic synthesis. Therefore, small differences in the synthesis conditions, primarily during the preparation of mixtures, can lead to deviations in the structure of the nanodefect. This is manifested in a change in the characteristics of the spectrum due to differences in environment of luminescence center. The maxima position, the half-width of the spectra, the kinetic parameters at a wavelength of registration of 540 nm pulsed photoluminescence are presented in table 2.

Table 2. The maxima position, the half-width of the spectra, the kinetic parameters at a wavelength of registration of 540 nm

Sample number	λ_{ex}=337 nm		Photoluminescence kinetics parameters at λ = 540 nm			
	ΔE, eV	λ_{max}	τ_1, ns	A_1	τ_2, ns	A_2
1	0.494371	563	38.78	0.51	70	0.6
2	0.427453	545			62.34	
3	0.477145	570	28	0.5	64.29	0.6
4	0.459989	548	21.44	0.85	60	037
5	0.441487	546			65	
6	0.441029	554	29	0.4	62	0.69
7	0.422713	548			67.71	
8	0.456703	550			70	
9	0.484883	570	37.16	0.475	68.37	0.6

Figure 2 (a,b)shows the results of study of the luminescence decay kinetics of synthesized ceramic samples after excitation by a nanosecond laser measurement pulse at 337 nm.

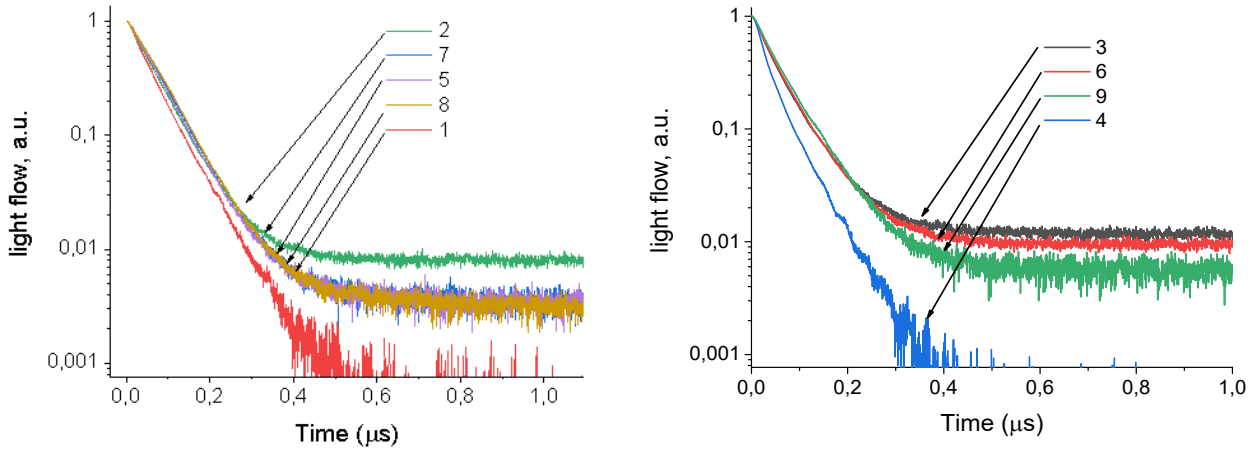


Fig. 2. Photoluminescence kinetics of YAG ceramics excited by a 337 nm nitrogen laser

In the majority of studied ceramic samples, at least two stages of decay with characteristic times ~ ns and long in the microsecond range take place. For some samples, the decay pattern is described by a single exponent. There is a difference in the decay amplitude ratios in the first stage

Conclusion

The luminescent characteristics of YAG: Ce ceramic samples synthesized in a radiation field were studied. In general terms, the spectral and kinetic characteristics of ceramics luminescence are similar to those known for YAG: Ce phosphors and ceramics obtained using the solid-state reaction method. Therefore, the radiation method for the synthesis of luminescent ceramics which differ

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fundamentally from the existing one, can be considered as an alternative. It was shown that the luminescence characteristics of the synthesized samples have a large variation. This is explained in the framework of the notion that the luminescence center, cerium ion, are elements of nanodefects which formed during the synthesis. In the synthesis of samples, the radiation field, which takes 1 s, does not complete the formation of nanodefects. Subsequent annealing of the samples is required to complete their formation.

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