

Nanodefects in YAG:Ce phosphors

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Abstract. Since the mid-1990s, phosphors have played a key role in emerging solidstate white-lighting technologies that are based on combining a near-UV or blue solid-state light source with downconversion to longer wavelengths. Almost all of them used phosphorescreted a crystalline oxide, nitride, or oxynitride host that is appropriately doped with Gd, Ce or Eu. Activation of phosphors by rare earth elements, leads to the formation of defects in the lattice and due to the change in the luminescent properties. This paper presents the new original model of energy transfer in the YAG crystals, which is a good description of the possible luminescence transitions in crystals. The morphology, spectra and kinetics characteristics of the luminescence of industrial phosphor excited by electron and laser radiation were investigated. The obtained theoretical and practical data are good agreement with each other, and thus are of great interest for understanding the nature of luminescence.

1. Introduction

Scintillators and phosphors represent an extensive group of wide-band materials intended for visualizing high radiation fluxes and conversing ultraviolet (UV) radiation into visible radiation. The range of these materials is constantly expanding. It is due to the need to register a variety of radiation streams of various types and the energy of radiation fluxes, the need to increase the conversion efficiency of excitation energy into visible radiation and their wide application. For example, at the moment more than half of all the generated light energy is obtained by using luminescence and visualization of high radiation fluxes, which have been used in many areas of science and technology – from medicine to high-energy physics.

Most used materials as scintillators and phosphors are complex multicomponent compounds, which synthesis technology is complicated. The processes of conversion of excitation energy into visible radiation in phosphors and scintillators have been studied clearly insufficiently because of the complexity of the composition, different structures of the compounds and a wide variety of exist promising materials. Existing models assume that the luminescence centers in the lattice are uniformly distributed over the crystal. The luminescence centers in some elementary units are characterized by certain properties. The absorbed energy of the exciting radiation is transmitted from the matrix and the center of localized absorbed energy to the luminescence centers directly. This assumption is well confirmed by studies of radiation-stimulated processes in crystal phosphors with a perfect structure and a small concentration of activators, which made it possible to develop luminescence theory [1-5] and ensure the development of applications using luminescence.



However, in many cases, the crystal phosphors used in practice contain large concentrations of defects and activators, which made the crystal structure complexly and imperfectly. Therefore, it can be assumed that defects are introduced into such crystals during synthesis in the form of complicated complexes. The complexes could be the regions of the crystal with activators and together with other entered impurities and the intrinsic defects of the lattice, which can compensate the different charges between matrix and activator ions, and the elastic stresses in the activator region. A confirmation of the possible existence of such complexes was obtained by studying scintillation LiF crystals activated with polyvalent ions [5]. The possible composition of the complex defect in the activated by ions of polyvalent metals LiF crystals is described in [6]. Such complexes should have nanometer size and have been called nanodefekt in contrast to point defects.

The possible existence of nanodefekt is confirmed by studying the luminescence of scintillation materials based on tungsten zinc and cadmium [7-9].

The decay time of luminescence in nanocrystals is much less than in single crystals. It indicates that the size of nanodefekts is as same as the size of the nanocrystals. In this paper, the investigated results of phosphor based on YAG:Ce are presented to demonstrate the possible presence of nanodefekts in them.

2. Methods

In order to establish the possible existence of nanodefekts in phosphor based on YAG:Ce, the relationship between the luminescence characteristics of spectral and kinetic with the structure and composition of phosphor of different backgrounds were investigated. The luminescence of the samples was excited by stationary and pulsed fluxes of LED chips with $\lambda=265, 275, 280, 310, 365, 452$ nm, high-energy electrons, laser radiation with $\lambda=337$ nm. In stationary measurements, the luminescence and excitation spectra of phosphors were measured by Agilent's Cary Eclipse spectrophotometer. A pulsed xenon lamp was used as a source light. Registration of the integrated emission spectra was carried out by the optical spectrometers of AvaSpec-3648 and AvaSpec-2048 with the spectral range 200–1100nm.

The spectra and kinetics of the luminescence decay during excitation by electron and laser radiation were carried out by a photoelectric multiplier FEU-84-6 using a MDR-3 monochromator and a digital oscillograph LECROY 6030 (350 MHz). The time resolution of the measuring system was 7 ns. When excited by the chip radiation, the kinetics of luminescence decay was recorded through the monochromator MDR-204 PMT "Hamamatsu 10720-20" and the oscilloscope Tektronix DPO-3033 with a time resolution of 30 ns.

The elemental composition of phosphors was determined using a scanning electron microscope Quanta3D 200i with an energy dispersive X-ray analysis (EDAX) system. The morphology of the phosphors was studied using an optical microscope "Leica DM 6000 M" and an electron microscope Quanta3D 200i.

In this study, used phosphors were synthesized in NPO «Platan» (Moscow, Russia) «Billion Light Co., Ltd» (Taipei County, Taiwan), «Fultor Enterprises Co. Ltd» (Dalian, China).

3. Results and Discussion

3.1. Structure and composition of the investigated phosphors

Phosphors are finely divided powders of particles with sizes from 0.1 to 40 μm . The particle sizes in the range from 5 to 40 nm are considered optimal. The phosphor particles in the composite film should provide absorption of the excitation energy and partially pass the radiation flux of the chip. The more characteristic SEM images of the morphology of the investigated phosphors are shown in figure 1 as examples. It is clear that the phosphors have essentially different structures by the presented pictures. The phosphor SDL 2345 is a powder of particles with an almost amorphous structure. The SDL 3500 particles have pronounced planes, indicating that they have a high degree of crystallinity. All investigated phosphors have a wide dispersion in dispersion. The elemental compositions of the

investigated microcrystals of phosphors are very different. The results of the investigation of the elemental composition on the example of SDL type phosphors are given in table. 1.

In the designation of the phosphor type, the second digit means the year of manufacture. The difference in the elemental composition is observed not only in different phosphors, but even in the same phosphors, which were manufactured using the same technology at different times. In all investigated phosphors, the dominant elements are Y, Al, O, Ce, Gd. In the designation of the phosphor type, the second digit means the year of manufacture. The difference in the elemental composition is observed not only in different phosphors, but even in the same phosphors, which were manufactured using the same technology at different times. In all investigated phosphors, the dominant elements are Y, Al, O, Ce, Gd. Element Ce is contained in all investigated phosphors. The ideal YAG composition of the phosphor should correspond to the formula $Y_3(Gd_3)Al_5O_{12}:Ce$.

However, the actual elemental composition differs significantly from the stoichiometric composition. A description of the morphology of phosphors are given in table 1.

It is easy to see that there are characteristic diffraction peaks for the garnet structure (YAG phase) in all samples. The diffraction peak at 67.30° is observed only in the crystalline phases of the YAG [10]. In addition, the diffraction spectra show diffraction peaks that correspond to other phases: $YAlO_3$ (YAP) perovskite phase, Al_2O_3 – corundum, and possibly $Y_4Al_2O_9$ (YAM). Peak at 29.6° and $36.30\text{--}36.5^\circ$ is due to the phase of $Y_4Al_2O_9$ (YAM) [11]. The ratio of phases in different phosphors is different.

In this way, in addition to the intentionally introduced activators, all the investigated phosphors have a high concentration of other defects. It is confirmed by the studied results of morphology: the phosphor particles clearly differ in shape from the perfect crystal. The quantitative ratio of the elements in the composition of the investigated phosphors differs significantly from the stoichiometric one. In all the investigated phosphor substances, besides the basic YAG phase, there are also others coexisting. Additional defects introduced into the phosphor crystals during synthesis are obviously oxygen vacancies, ions in interstitial sites, antidefects that enter to compensate charges and elastic stresses caused by the difference in the sizes of the activator ions, other lattice defects.

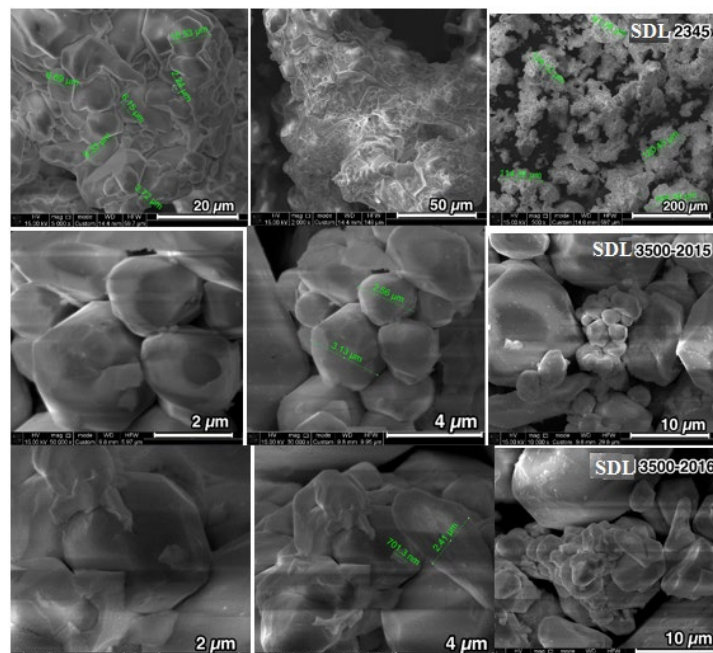
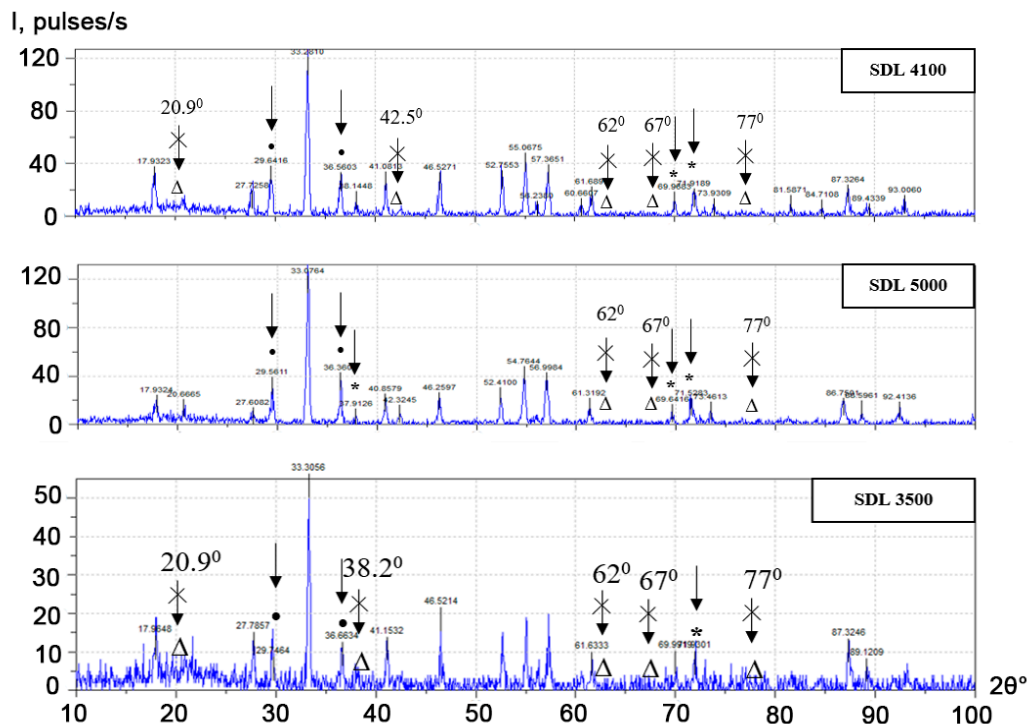


Figure 1. Morphology of the investigated phosphors.

Table 1. Elemental composition of investigated phosphors.

Phosphor	Content of metal ions in At (%)				Morphology
	Y	Al	Gd	Ce	
SDL 2700-2015	2.46	27.79	17.78	+	They consist of 20 micron crystals covered with small particles like fragments.
SDL 2700-2016	3.49	24.56	19.13	+	They have a porous non-international surface
SDL 3500-2015	10.83	27.45	3.42	1.01	They look like stuck together particles, the size is about 4 μm -25 μm
SDL 3500-2016	11.71	29.94	6.80	0.25	They have the appearance of small, non-crystalline particles, the size of which is larger than 30 μm
SDL 4000-2015	14.71	30.97	3.02	1.86	They have the appearance of stuck together granules, with cuts characteristic of crystals
SDL 4000-2016	13.79	26.00	2.45	0.44	They have a rounded shape and are covered with a layer of nanoscale particles

The results of the structure of YAG:Ce phosphors of SDL type are shown in figure 2. The investigations were carried out using the X-ray diffractometer DRON-7, Burevestnik.

**Figure 2.** XPD of phosphors of SDL type.

The following conclusion is significant. The ratio between the concentrations of the introduced defects in different phosphors differs sharply. This difference can reach several percent: it can be seen from the comparison of the relative elemental composition in different phosphors. Even in phosphors grown under identical technological regimes, there is a great difference in the level of introduced defectiveness. The amount and composition of introduced defects during the synthesis are determined

by synthesis technology. However, it is difficult to accomplish. Because the synthesis is carried out in extreme conditions like high temperatures, long processes of synthesis and annealing. Moreover, high concentrations of various defects in a crystal could agglomerate and then unify into complex defects. The energy efficiency of the chip radiation transformation into luminescence in the visible spectrum region was measured.

$$\eta = \frac{P_{lum}}{P_{diod}} \quad (1)$$

where P_{lum} is the radiation flux of a phosphor, P_{diod} is the absorbed radiation flux of a chip.

The measurements were performed using a photometric integrating sphere and an AvaSpec spectrometer with an integrated flux integration function:

$$P = \int_{300}^{1000} \phi \lambda d\lambda \quad (2)$$

The measurement results of the energy yield of the radiation conversion under chip excited with a radiation at 460 nm for SDL phosphors of different synthesis time are shown in table 2.

Table 2. The energy yield of the radiation conversion under chip excited $\lambda_{ex}=460\text{nm}$.

Phosphor	The energy yield of the excited radiation η $\lambda_{max}=460 \text{ nm}$
SDL 2700-2015	0.422
SDL 2700-2016	0.393
SDL 3500-2015	0.438
SDL 3500-2016	0.368
SDL 4000-2015	0.377
SDL 4000-2016	0.404

Nanodefekt as a complex defect could have a size of 2–3 nm. The expected form and composition of the nanodefekts are shown in figure 3.

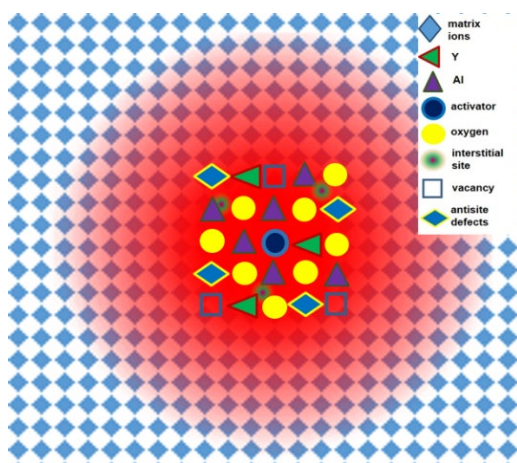


Figure 3. The expected form and composition of the nanodefekt in the YAG.

3.2. Luminescence regularities of YAG: Ce phosphors with different backgrounds.

Phosphors based on yttrium aluminum garnet, activated by cerium, have a high efficiency of converting the chip radiation into luminescence in the visible range. The characteristic luminescence

spectra of YAG: Ce phosphors under different excited sources are shown in figure 4. It can be found that broad mono band, centered in the region of 520–560nm. The band shifts toward to long wavelength by introducing Gd³⁺ as a modifier. Substitution of yttrium ions by gadolinium leads to an increase in the lattice parameter, and correspondingly, to a shift in the levels of the luminescence center [12, 13].

One of the main advantages of YAG phosphors is the good alignment of the luminescence excitation and emission bands in the region around 460 nm. The combination of chip-phosphor mode can provide the least Stokes losses and phosphor heating. [14, 15]

As shown in figure 4, the intense photoluminescence is obtained by excited radiation in the region of 340nm and 460 nm, which are attributed to the excitation of Ce³⁺ from 4f level to 5d states. In addition, the luminescence of the YAG: Ce phosphor can be excited by radiation in the region with $\lambda < 300$ nm. The excitation spectrum in this region is continuous. However, the structure of the spectrum differs somewhat in the phosphors with different background. It is known that the width of the forbidden band in crystals is about 6.45 eV [16].

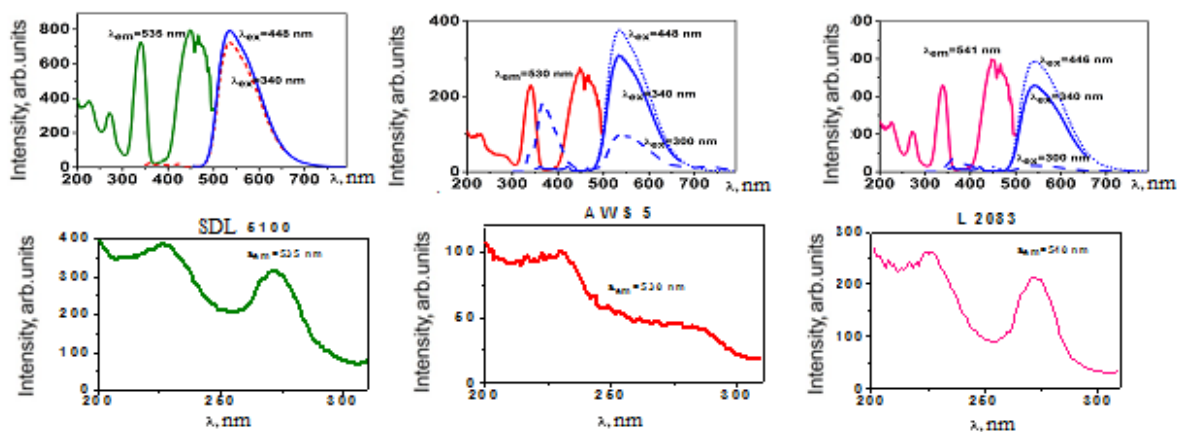


Figure 4. The luminescence and absorption spectra of SDL type YAG phosphor.

Luminescence of YAG: Ce phosphor under excitation by high-energy electrons also investigated. The luminescence spectra of SDL type YAG phosphor under excitation by a pulse of an electron beam with an energy of 250 keV are displayed in figure 5.

The cathodoluminescence spectra are close to optically excited by shape and position in all studied phosphors by us. The high-energy electrons energy is transferred to the material mainly for ionization. The cathodoluminescence intensity is large. Consequently, electron-hole pairs generated by hard radiation transmit their energy to the luminescence centers with high efficiency. Obviously, there is a capture of electronic excitations produced in the matrix in the region of the luminescence centers.

The main differences in the regularities of photo- and cathodoluminescence are the same for all the investigated phosphors and are as follows. The kinetics of luminescence decay during photoexcitation is characterized by a decay time, which is in the range 50–80 ns. With this characteristic decay time, the luminescence intensity decreases by almost two orders of magnitude. At least two components are observed in the cathodoluminescence kinetics decay: the characteristic decay time of the first component is in the range 50–120 ns, the second at 0.5–1.5 μ s.

Examples of the results of study of the decay kinetics are presented in table 3 and 4. From the results of the research presented in table. 4 it follows that the light sums of the two decay components can be comparable for each phosphor. But their ratio is differently in different phosphors. A significant difference in the kinetics decay of CL and PL is explained by the difference in excitation processes.

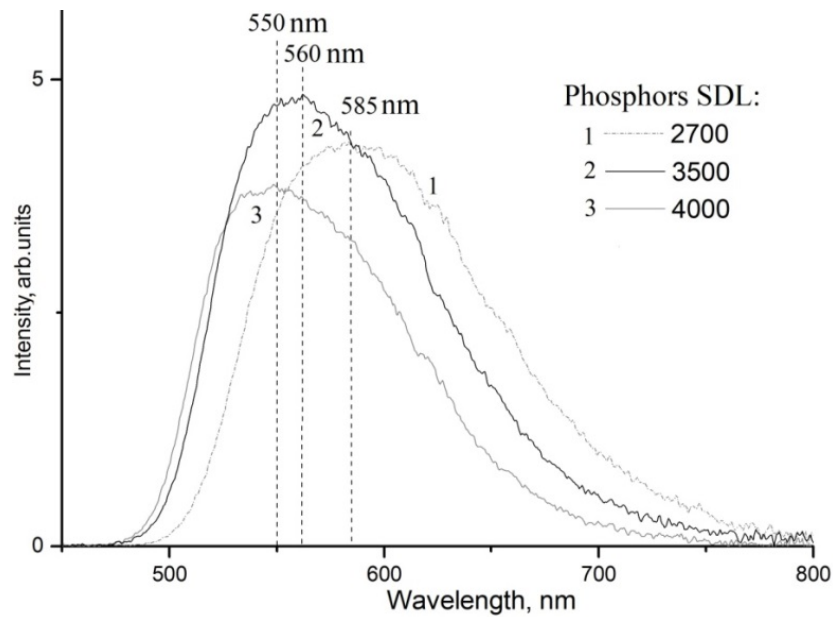


Figure 5. Cathodoluminescence spectra of SDL phosphors.

Table 3. Characteristic decay times of PL phosphors.

Phosphor	$\lambda_{ex}=452$ nm		τ , ns
	λ_{max} , nm	FWHM, eV	
SDL 3000	556±2	0.475	66
SDL 4000	532±2	0.468	61
SDL 4100	530±2	0.462	60
SDL 5000	517±2	~0.450	53

Table 4. Characteristic decay times of CL phosphors.

Phosphors (maximum band CL, nm)	A_1	τ_1 , ns	$A_1 \times \tau_1$	A_2	τ_2 , ns	$A_2 \times \tau_2$
SDL 3000 (575 nm)	3.47	103.98	360.81	0.630	687.8	433.31
SDL 4000 (535nm)	2.955	90	270	0.092	1070	980
SDL 4100 (535 nm)	1.886	78	147.11	1.2	1240	1490
SDL 5000 (534 nm)	0.926	61.39	56.85	0.031	502.22	15.57

The decay time is determined by the relaxation time of excitation luminescence center. In CL, the excitation energy is transferred to the matrix, then this energy is transferred through a combination of processes to the luminescence center. The following way of energy transfer seems most likely. The hole created by the electron-hole pair radiation is localized in the nanodefekt, where favorable conditions for autolocalization exist. The electron also appears in the nanodefekt [17]. The center of luminescence is excited when charges are transferred to the center of the glow.

4. Conclusion

The presented results fit quite well into the framework of ideas on the formation of nanodefects in phosphors during the process of synthesis. Microcrystals of YAG:Ce phosphors contain a large number of different structural defects. The nanodefekt in the microcrystal of the phosphor is a complex mixture defect. Besides the matrix ions, there are vacancies, ions in interstices, antidefects and coactivator in the composition of nanodefekt. The luminescence center is an element of the structure of nanodefekt, therefore, the main luminescence processes occur in the nanodefekt. It is found that in a couple of references [18], there are some similar nanodefeks and quantum dots existing in crystal phosphors. The difference is that the quantum dot appears to be a nanoscale region in a matrix with a certain elemental composition of the input phase. In nanodefekt, the structure and composition of a nanoscale complex defect are variable. The introduced nanodefekt into matrix can be considered as a separate formed conformation with its spatial and energy structure. The following arguments can serve as the basis for this assumption.

In the luminescence excitation spectra of YAG:Ce phosphors, the intrinsic absorption edge is observed at a region from $\lambda \sim 190$ nm to $\lambda \sim 300$ nm, which has a continuous form. Excitation at any wavelength of this region initiates a luminescence characteristic of the phosphors. It allows to assume that the transitions under excitation in this region realized between zones and not between specific levels of defects.

A set of nanodefeks in the microcrystal appear as the intrinsic valence and conduction bands. Therefore, the band scheme of the microcrystal phosphor can be represented as a nanodefected band structure which embedded in the band structure of the matrix (figure 5). Unfortunately, the concentration of nanodefeks is still difficult to estimate. There are no measurements of the absorption spectra in the UV region from 190 to 300 nm in real microcrystals and phosphor particles. There are measurements of the absorption spectra in macrocrystals, ceramics based on YAG:Ce. It is known that in ceramics, the absorption begins at 300 nm, with an absorption index greater than 20 cm^{-1} [19]

Obviously, the absorption coefficient of phosphor particles with high degree defects should be much higher in the UV region.

Figure 6 shows the proposed type of band structure of phosphor based on YAG:Ce. The diagram shows known absorbing and radiative transitions, The results of the CL studies fit well within the framework of the presented scheme. The difference between the CL kinetics decay from PL is explained by the fact that the energy transfer channels to the luminescent centers under these excitation methods are different. The existence of a multicomponent kinetics decay of CL is explained by the possible existence of a difference in the spatial mutual distribution of localized holes and electrons in traps.

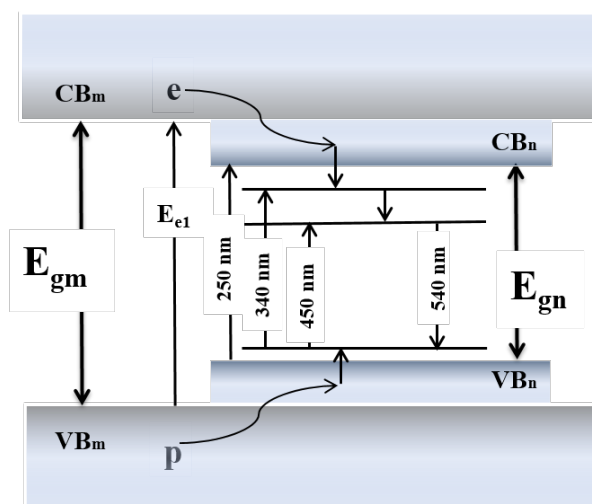


Figure 6. The proposed type of band structure of phosphor based on YAG:Ce.

Acknowledgments

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References

- [1] Levshin L V and Saletsky A M 1989 *Luminescence and its dimensions* Moscow State University p 56
- [2] Agranovich V M 1978 *Transfer of the electron excitation energy in condensed media* (Nauka)
- [3] Feofilov P P 1959 *Polarized luminescence of atoms, molecules, and crystals* (Fizmatgiz) p 1959
- [4] Ronda C R 2008 *Luminescence: From Theory to Applications* (WILEY-VCH) 273 p
- [5] Lisitsyna L A, Oleshko V I, Putintseva S N and Lisitsyn V M 2008 *Optics and Spectroscopy*. **05** 531
- [6] Lisitsyna L A and Lisitsyn V M 2013 *Physics of the Solid State* **55** 2297
- [7] Lisitsyn V M, Valiev D T, Tupitsyna I, Polisadova E F, Lisitsyna L A, Stepanov S A and Oleshko V I 2013 *Proceedings of high schools. Physics* **56** 75
- [8] Lisitsyn V M, Valiev D T, Lisitsyna L A , Tupitsyna I , Polisadova E F, Oleshko V I 2013 *Journal of Applied Spectroscopy* **80** 361
- [9] Lisitsyn V M, Valiev D T, Tupitsyna I A, Polisadova E F, Oleshko V I, Lisitsyna L A, Andryuschenko L A, Yakubovskaya A G and Vovk O M 2014 *J. Lumines* **153** 130
- [10] Zhao D, T W Coyle and K Chien 2013 *Surface & Coatings Technology* **235** 303
- [11] Zhou Y, Lu X, Xiang H and Feng Z 2015 *J. Advan Ceram* **4** 94
- [12] Hongling Shi, Chen Zhu, Jiquan Huang, Jian Chen, Dongchuan Chen, Wenchao Wang, Fangyu, Wang, Yongge Cao and Xuanyi Yuan 2014 *Optical Soc. of Amer.* **4** 649
- [13] Lisitsyn V M, Soshchin N P, Yang Yu, Stepanov S A, Lisitsyna L A, Tulegenova A T and Abdullin Kh A. 2017 *Russ. Phys. J.* **60** 5
- [14] Yangyang Ju, V M Lisitsyn and V S Lukash 2017 *Losses of Energy in Phosphor of LED at Transformation of Emission Spectrum* (APETC 2017)
- [15] Ju Yangyang, V M Lisitsyn and V S Lukash 2017 *Losses Of Energy In Phosphor Of Led At Transformation Of Emission Spectrum* (MATEC Web of Conferences) **110** 05023
- [16] Xian Qin, Xiaowang Liu, Wei Huang, Marco Bettinelli and Xiaogang Liu 2017 *Theoretical and Experimental Aspects. Chem. Rev* **117** 4488
- [17] Lisitsyn V M, Malishev A A and Yakovlev V Yu 1983 *Lokalizovannie primes'u eksitoni v sh.g.k. (FTT)* **25** 3356
- [18] Haiwei Chen, Juan He and Shin-Tson Wu 2017 *Journal of selected topics in quantum electronics* **23** 5
- [19] Tetsuhiko Tomiki, Yoshihiro Isa and Yashie Kadekawa 1996 *Journal of the Physical Society of Japan* **65** 1106