Emission properties of YAG: Ce ceramics with barium fluoride flux

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Abstract. In this work, we investigated the luminescent properties of YAG, Ce ceramics with an addition of barium fluoride flux. The ceramic samples were sintered from obtained YAG: Ce, BaF_2 phosphor powder. Morphological, luminescent and decay time characteristics of YAG: Ce ceramics were investigated. The luminescence decay kinetics analysis of the ceramics showed that the decay time in phosphors and ceramics is different in the visual spectral range.

1. Introduction

Ceramics are of great interest for present photonic devices. These optical materials occupy an intermediate position between crystal materials and glass, and combine the best properties of crystals such as a high mechanical and thermal durability and glassy materials (the possibility of pressing, molding, and forming elements of different geometry). One of the last directions in technologies of converting emission in construction of white LED are luminescent ceramics application [1, 2].

Using luminescent ceramics as an emission converter makes it possible to rank LEDs by color temperature with a high precision. This is achieved by more precise proportioning of phosphors. Another advantage of ceramic materials is to produce LEDs with high color homogeneity, a thermal durability, and an elevated temporal stable.

Yttrium-aluminum garnet doped with trivalent cerium ions (YAG: Ce^{3+}) is often used as an inorganic phosphor in the manufacture of lighting and photonic devices. The maximum of emission spectrum of YAG: Ce^{3+} phosphors are in the visible spectral region from 530 to 560 nm. This is due to radiation transitions between 5d and 4f energy levels of Ce^{3+} ions [3].

The solid-state reaction method (SSR) has gained great popularity for the industrial production of YAG phosphors [4–6]. At the same time, the SSR method requires a rather long treatment of phosphors at the high temperatures (> 1600ºC) in an atmosphere of a gas mixture (N_2/H_2). A long-term high-temperature exposure leads to a partial sintering of the powder, and to the necessity for re-grinding the resulting solid-phase mixture.

Various sintering types of fluxes are used to improve the luminescent and morphological properties of phosphor powders obtained by SSR method [7, 8]. Fluoride materials (such as MgF_2, CaF_2, SrF_2, BaF_2, AlF_3) are often used as fluxes, which contribute well to the production of phosphor powders with a garnet structure [9, 10]. The authors of [9–13] are shown a positive effect of these fluxes on the ion diffusion, the crystallization process as well as on the formation of YAG host with a good crystallinity in the SSR method [9–13]. Obviously, under a radiation influence processes in ceramic materials differ from occurring processes in well-studied crystalline materials. In this regard, there is a growing of interest in the investigation of electron processes of excitation energy transfer (optical and

radiation) to the active center in these materials. Therefore, understanding the mechanisms of the relaxation processes in the ceramic materials, directly interacting with the ionizing emission in the optoelectronic devices, is the key to the development and creation of new materials with given luminescent properties. The recombination processes will eventually determine the light output of the radiating medium, the degradation resistance of optical materials. This makes possible to control the properties of optical materials by creating efficient non-radiative channels or radiative energy transfer to the various luminescence centers at the stage of development of new radiation-resistant or radiation-sensitive materials, prognostication changes in their properties during extreme impacts.

There is a need to study the processes of energy transfer in materials between dopant ions of various types. Obviously, the size effects will make a significant contribution to the processes of energy exchange and the defect formation processes under radiation influence, which is especially important for the luminescent and optical materials.

The purpose of this work is to study the structural and luminescent characteristics of YAG: Ce, BaF_2 ceramics.

2. Materials and methods

The synthesis of phosphor powders more detail described in [14]. YAG phosphors powders with a cerium content of 0.06 wt. % were used for ceramics preparation. Barium fluoride was used as a flux. The concentration of barium fluoride in samples was 0; 0.05; 0.1; 0.15 wt. %.

The ceramic samples were sintered from obtained YAG: Ce, BaF_2 phosphor powder.

For pressing the powder we used a uniaxially automatic press IP-500 AVTO ZIPO. In the result the samples with a diameter of 9 mm and a thickness of 1 mm after sintering in the air were obtained. The photographs of ceramic samples are shown in Figure1.
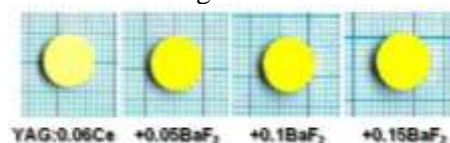
Figure 1. Sintered ceramic samples.

Integral spectral efficiency was measured by integrating sphere and spectrometer AvaSpec-3648 (integration time was 1 s, 200 – 1100 nm spectral range, 2.1 nm spectral resolution).At the first stage, the spectrum and emission flux of excitation source (LED) was measured. The next measurements were devoted to the emission spectrum of the investigated YAG:Ce^{3+} ceramics measurements.

The using of this method (Figure 2) made possible to subtract the measured spectrum of LED from the luminescence ceramic spectrum with a high precision. It allowed us to determine the reflected flux, the absorbed flux and the emission flux of the ceramic samples. The integral spectral efficiency determined as ratio of emission flux and absorption flux of sample.
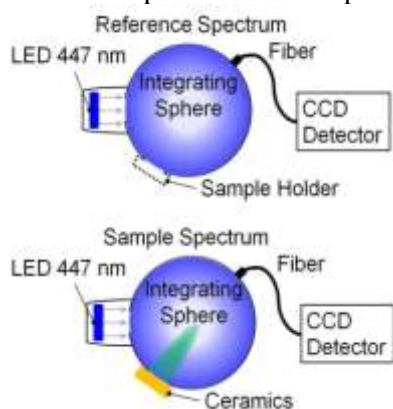
Figure 2. Method of measuring the energy efficiency.

For measuring pulse photoluminescence the LED (pulse duration $t_{1/2}$ ~15 ns, λ = 447 nm, FWHM-20 nm) as an excitation source was used. The luminescence decay kinetics were recorded with the monochromator MDR-204, and Hamamatsu H10720-20 photomultiplier tube and Tektronix DPO3034 (300 MHz) digital oscilloscope.

3. Results and discussion

3.1. SEM micro-images.
The SEM micro-images analysis of the investigated YAG:Ce^{3+} ceramics are shown in Figure3. The consolidation of particles with the formation of a high-density structure did not occur. Sintered ceramics are a porous monolith, which is confirmed by the results of scanning electron microscopy.

The sintering process is not complete until the end, consequently. The grain sizes remain at the level of the particle size of the initial powder, and the ceramics have a low density. YAG: 0.06Ce ceramics prepared with addition of 0.1 wt. % BaF_2 flux turned out with a smaller number of pores and more homogeneous than others one.
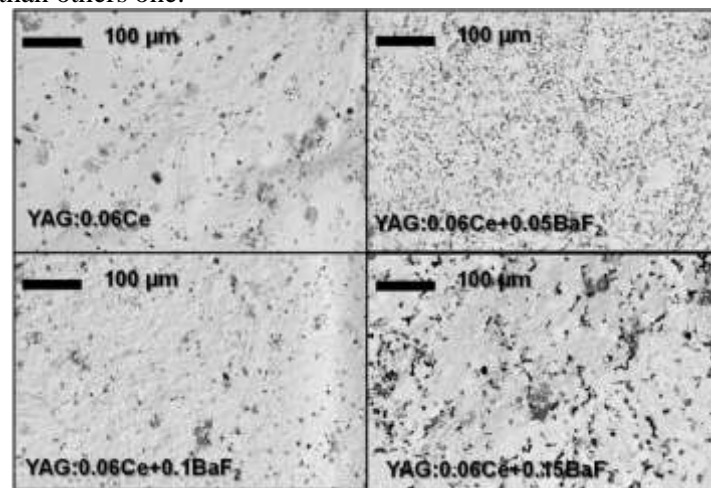

Figure 3. SEM micro-images.

3.2. Photoluminescence spectra and decay kinetics
There are two bands at 440 and 540 nm are recorded in the photoluminescence spectra excited by LED (λ_{ex} = 447 nm) ceramic samples. The results are represented in Figure 4. The photoluminescence spectra of synthesized YAG: Ce^{3+} ceramics with and without BaF_2 do not differ qualitatively.
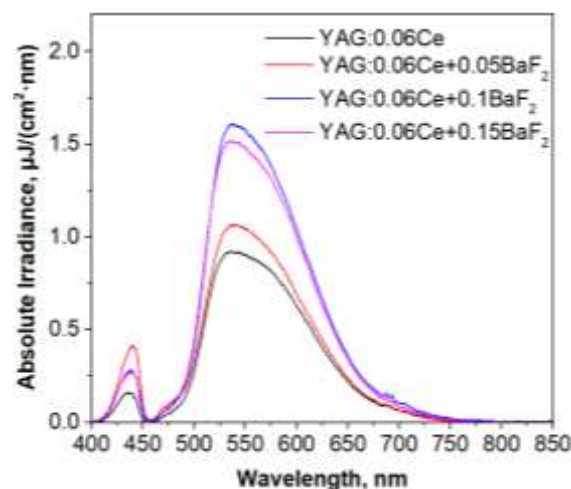

Figure 4. Photoluminescence spectra (λ_{ex}= 447 nm).

We suppose that the spin-orbit split ground state of Ce^{3+} ions determines the shape and the luminescence band position. The influence of YAG crystal field leads to the split of 5d energy level of Ce^{3+} ion into several sublevels. The emission occurs from the lower 5d sublevel into two splits states of the 4f level. This explains the luminescence double character of three valence cerium ion in YAG ceramics [15, 16].

Usually it is made experiments with the excitation by pulse laser radiation or by electron flux, but there are not results where as the excitation source used LED. According to [17], for YAG:Ce^{3+} nanocrystals short decay times (4 ± 3 ns and 17 ± 5 ns at 3.0 eV band) with excitation at 266 nm laser pulse is recorded. In our measurements we did not observe such short decay times (Figure 5). It can be explained by the pulse duration of excitation source. In our case the pulse duration was 30 ns and everything what was shorter than this time we could not observe.
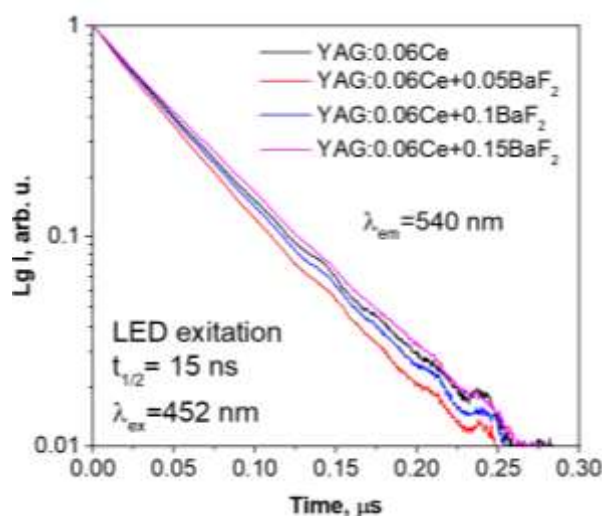

Figure 5. Luminescencedecaycurves.

Figure 5 shows the decay curves for 540 nm luminescence band. The character of the luminescence decay kinetics is explained by intra-center transitions. The radiative transition in each center occurs independently of the state of others and is determined only by its probability. The luminescence decay kinetics described by the single exponential function.

The results of measuring the decay kinetics showed that there is an effect of BaF_2 concentration on the luminescence decay time of YAG: Ce^{3+} ceramic samples (Figure 5).

Figure 6 shows the dependence of the decay times from barium fluoride flux. It can be seen that the lowest luminescence decay time corresponds to a concentration of 0.5 wt. % BaF_2. Also, it should be noted that the characteristic decay time for phosphors of similar composition, according to [14], averaged 60 ± 2 ns, while for ceramics 49 ± 2 ns.
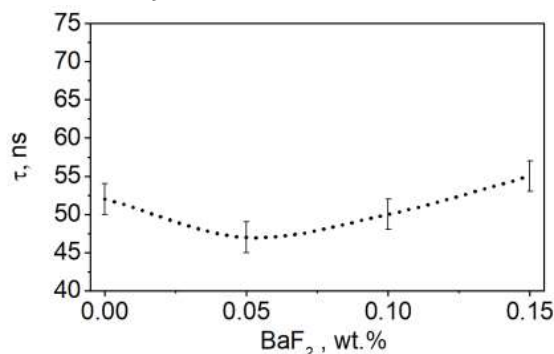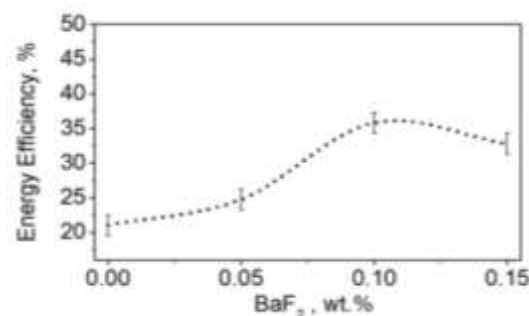

Figure 6. Dependence of decay times from barium fluoride flux.

3.3. Reflectance values and energy efficiency of YAG:Ce with barium fluoride flux

The results of a reflection measurement of the YAG:Ce^{3+} ceramic samples are shown in the Figure 7. The reflection values were measured for the band at 447 nm. It is shown the change of the reflection from 2 to 3% for the samples with different BaF_2 concentration. Often, the reflection of the materials is associated with the surface properties of ceramics. At the same time, we did not find a correlation between the dependence of the reflection on the concentration of barium fluoride with SEM images of the obtained ceramic samples.
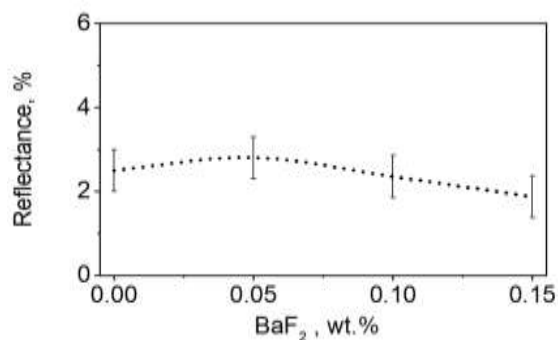
| **Figure 7.** Dependence of reflectance values from barium fluoride flux. | **Figure 8.** Dependence of energy efficiency from barium fluoride flux. |

Therefore, the change in the reflection values with the increasing barium fluoride concentration in the main absorption band of the obtained ceramics is apparently associated with a change of properties grain boundaries and changes in the processes of sample recrystallization.

The results of energy efficiency measuring are shown in Figure 8. Energy efficiency increases from 22 to 36% with increase of BaF_2 concentration from 0 to 0.1%, respectively. Then, with the increasing fluoride flux concentration the decrease of efficiency is observed. It should be noted that the increase of energy efficiency have a fairly good correlation with a surface quality of ceramic samples (an existence of pores, a homogeneity) (Figure 3). The maximum efficiency is obtained for the sample, which matches to the best quality of the surface (a few of the residual pores).

4. Conclusion

Such properties of samples as luminescent, optical and morphological have been studied. Also the influence of barium fluoride flux on the luminescent and decay characteristics was investigated.

From the obtained results was enucleate that by synthesis ceramics on the basis of YAG: Ce, BaF_2 phosphors the spectrum of photoluminescence did not change. However, an increase in the luminescence intensity is observed. It was experimentally shown that the optimal concentration of BaF_2 is 0.1 wt.%. Upon this concentration value the maximum of luminescence energy efficiency is achieved. This is probably related to the small number of pores and the high homogeneity of the obtained ceramics.

As a result of analysis the luminescence decay kinetics it was shown that the luminescence decay time in ceramics is significantly lower than in the phosphor of a similar composition.

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