Физика и техника полупроводников, 2007, том 41, вып. 5

Cathodoluminescence properties of yttrium alluminium garnet doped with Eu^{2+} and Eu^{3+} ions

© A.N. Trofimov¶, M.A. Petrova*, M.V. Zamoryanskaya

Ioffe Physicotechnical Institute, Russian Academy of Sciences,
194021 St. Petersburg, Russia
* Khlopin Radium Institute,
194021 St. Petersburg, Russia

(Получена 12 сентября 2006 г. Принята к печати 3 октября 2006 г.)

Yttrium aluminium garnet (YAG) doped with Eu^{2+} and Eu^{3+} ions is very interesting as a phosphor for conversion of light-emitting diode light for white light sources. Europium ion occupies the structural position of yttrium in yttrium aluminium garnet and has valence state Eu^{3+}. Our sample was doped with Zr^{4+}, that is why part of europium ions had valence state Eu^{2+}. As a rule luminescence of Eu^{3+} ions is observed in orange and red range of spectrum. The luminescence of Eu^{2+} in yttrium aluminium garnet is characterized by intensive broad band with maximum of intensity at about 560 nm (green color). In this work it was studied the intensity and decay time dependences on europium concentration, and the influence of excitation power density on cathodoluminescence of the sample. The more interesting result is the change of visible cathodoluminescence color in dependence on the density of exciting power.

PACS: 78.60.Hk, 71.55.Ht, 78.47.+p, 85.60.Jb

1. Introduction

Yttrium aluminium garnet (YAG) doped with Eu^{2+} and Eu^{3+} ions is very interesting as a phosphor for conversion of light-emitting diode light for white light sources. This phosphor has luminescence band in red and green region. Such phosphor conversion must have high efficiency. It is proposed that mixing of blue light from light-emitting diode and green and red luminescence from phosphor conversion allows to achieve a good „white“ illumination [1]. Eu^{3+} ion is well known as activator of efficient phosphors with red luminescence. Spectral position of Eu^{2+} ion emission band depends on a crystal host matrix. In YAG Eu^{2+} ions has luminescence maximum in green region. It was observed that visible color of cathodoluminescence (CL) depends on excitation power density. This color can be changed from red to green.

2. Experimental methods

Crystals of YAG doped with Eu were grown by the horizontal direct technique. The crystal growth was carried out in the fitting with Mo-armature. The growth camera was pumped to 10^{-4} mm Hg pressure and filled with hydrogen to 100 mm Hg pressure. The mixture of oxides Y_2O_3, Al_2O_3, Eu_2O_3 was molten and Mo-boat with the melt was pulled through crystallizing zone with rate 3–5 mm/h. The crystals doped with europium (0.5–0.8 at% with respect to yttrium) were colorless and contained only Eu^{3+}. Zirconium (Zr^{4+}) was used as a compensator to change the valence state of europium ions to Eu^{2+}. For this purpose 0.06–0.08 at% of zirconium was added to mixture.

The sample was polished and coated with carbon and then mounted in Wood's metal alloy.

The composition of the sample was studied by electron microprobe analysis (EPMA) using the electron microprobe Camebax (Cameca) under the following conditions: accelerating voltage 15 kV, electron beam current 10 nA. The cathodoluminescence was studied with the original spectrometer [2]. Cathodoluminescence spectrometer was installed on optical microscope port of Camebax electron microprobe. Spectrometer has automation unit linked with personal computer. Electronics and software allow to investigate the cathodoluminescence properties in different operating modes. The cathodoluminescence spectra were acquired under accelerating voltage 10 kV. Spectrum of YAG : Eu,Zr was acquired in stationary mode. In this mode the sample is continuously irradiated by electron beam. We used also time-resolution mode for study CL properties of the sample. Two cathodoluminescence spectra can be obtained simultaneously by using this mode. The first spectrum is being recorded during sample is exposed to electron beam, and the other spectrum is being measured within a given time after deflection of the beam from sample. This method is very useful for separating the peaks with different decay times. The equipment also permits to obtain dependence of CL intensity at chosen wavelength on time after turning on/off the electron beam with time resolution 0.1 μs. By use of this feature the decay times was measured.

3. Results and discussion

Microprobe analysis shows that the most part of the sample is stoichiometric yttrium aluminium garnet with small quantity of europium and zirconium ($Y_3Al_5O_{12}$: Eu, Zr). Concentration of Eu is about

---

¶ E-mail: trofimov.pti.@gmail.com

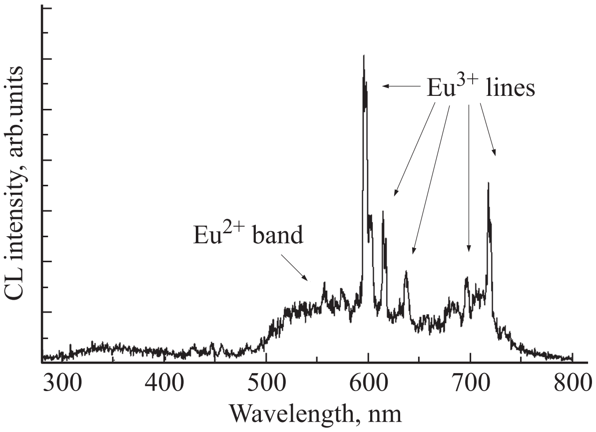

Figure 1. Cathodoluminescence spectrum of YAG : Eu,Zr.

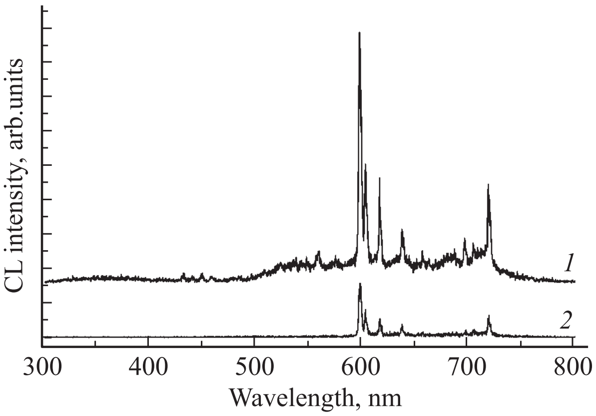

Figure 2. Time-resolved CL spectra of YAG : Eu,Zr. *1* — during excitation by electron beam, *2* — after electron beam deflection and 200 μs delay.

0.02–0.03 at% (or 0.13–0.2 at.% of Y). Distribution of Eu in most part of the sample is homogeneous. Concentration of Zr is close to the threshold of detectability for Zr, so we can only get upper estimation. We can say that concentration of Zr does not exceed 0.05 at%.

The sample also has heterogeneous regions and inclusions of phases with other compositions. Example of composition of such inclusion is Al $\sim$ 32 at%, O $\sim$ 60 at%, Eu $\sim$ 7 at%. In heterogeneous regions the composition is almost conform to YAG but the concentration of europium might vary in the range 0.015–0.4 at%. Existence of inclusions and heterogeneous regions explains the difference between amounts of eurpoium in the mixture and in most of the sample. Surplus amounts of Zr and Eu concentrate in these heterogeneous areas and inclusions. The spectrum of CL (Fig. 1) was obtained at 5 nA on homogeneous part of the sample. The sharp lines are related with transitions in Eu^{3+} ions ($^5D_0 \rightarrow {}^7F_x$) [3]. The broad band with maximum of intensity in green region belongs to Eu^{2+} ions. Time-resolved spectrum (Fig. 2) was obtained at 3 nA and with delay 200 μs. From these spectra we can see that Eu^{3+} lines have longer radiation time comparing with Eu^{2+} band. Time dependences of CL intensity were obtained for two lines of Eu^{3+} (716 and 595 nm) and for Eu^{2+} band (Fig. 3, *a, b, c*). Decay time values were found from this dependences: $\tau = 2.35$ ms, 2.7 ms and $\sim 1.2\,\mu$s, respectively. Dependences for 716 and 595 nm (Fig. 3, *a, b*) have fast decay at first time and then they decay with times 2.35 and 2.7 ms, respectively. The cause of this phenomenon is superposition of Eu^{3+} lines and Eu^{2+} band. The Eu^{2+} band makes significant contribution to 595 nm line intensity and small contribution to 716 nm line intensity.

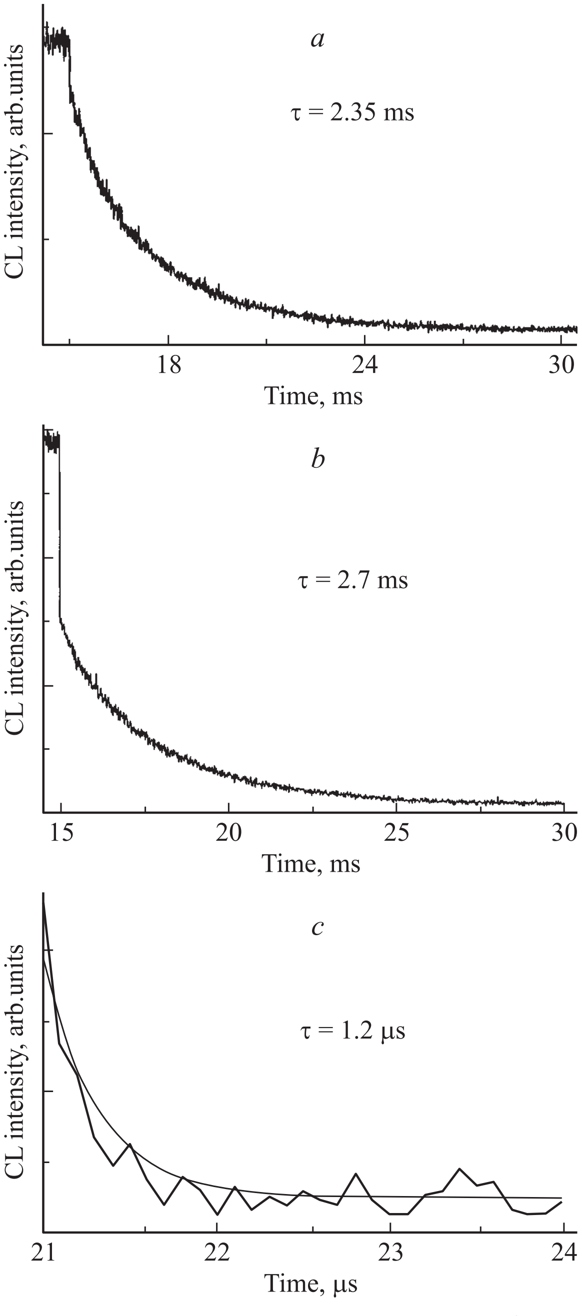

Figure 3. Time dependences of CL intensity for Eu^{3+} lines at 716 nm (*a*), 595 nm (*b*) and for Eu^{2+} band (*c*).

It was observed that brightness of CL vary in heterogeneous region. The dependence of CL intensity on Eu concentration was obtained (Fig. 4). We can observe decrease of CL intensity with increasing of Eu concentration. This phenomenon can be explained by the concentration quenching [4].

We obtained time dependences for Eu^{3+} line at 716 nm for areas of the sample with different Eu concentrations.

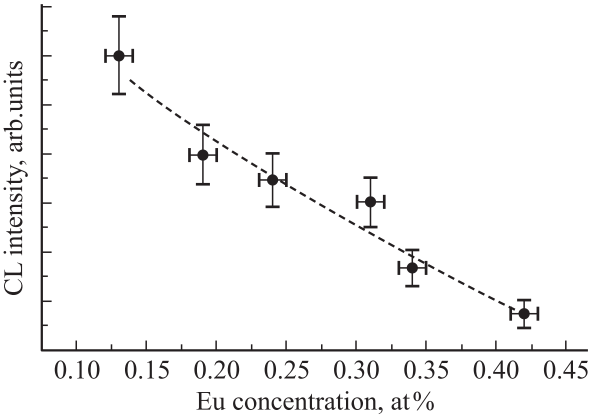

Figure 4. Dependence of CL intensity of Eu^{3+} 716 nm line on Eu concentration.

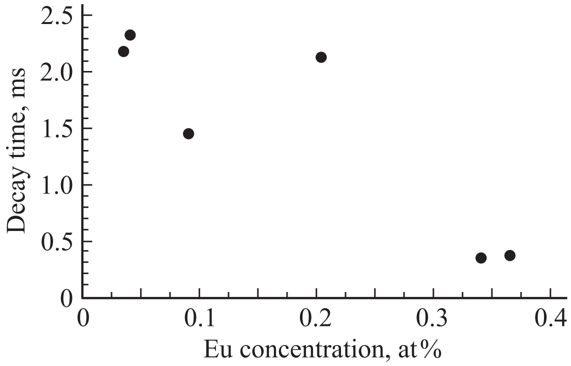

Figure 5. Dependence of decay time of Eu^{3+} 716 nm line on Eu concentration.

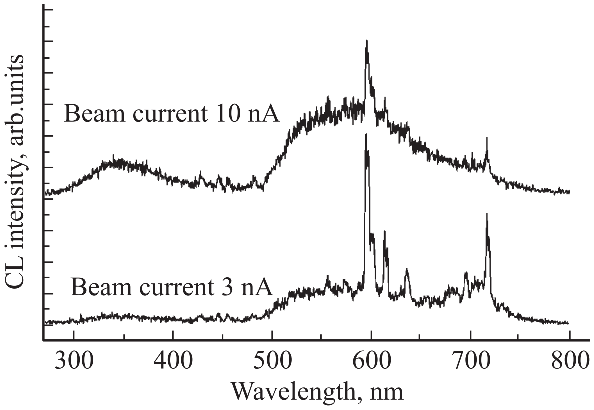

Figure 6. Spectra of CL obtained with different beam currents.

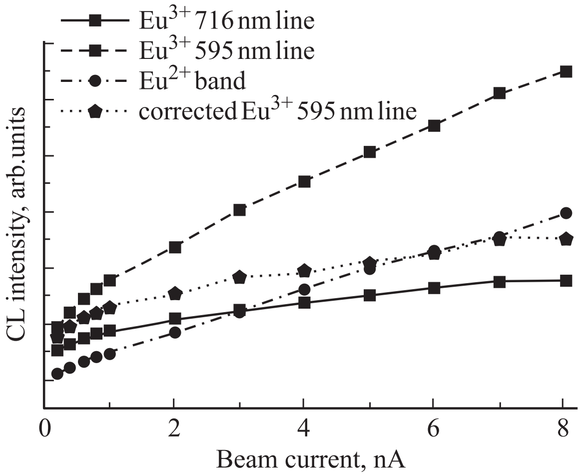

Figure 7. Dependence of CL intensity on beam current.

By this way we extracted dependence of decay time on Eu concentration (Fig. 5). In Fig. 5 we can see that the decay time decrease with rise of Eu concentration. The explanation of this phenomenon is growth of interaction between Eu^{3+} ions that leads to increase of nonradiative recombination probability.

It was observed that color of visible CL depends on exciting electron beam current. Two spectra were obtained with different electron beam currents, 3 and 10 nA (Fig. 6). We can see that ratio of intensities of any Eu^{3+} line and Eu^{2+} band is different for different electron beam currents.

The dependence of CL intensity on electron beam current for Eu^{3+} lines at 716 and 595 nm and Eu^{2+} band was obtained (Fig. 7). We can see that CL intensity of the line at 716 nm reaches saturation. CL intensity of Eu^{2+} band has almost linear growth.

CL intensity is proportional to population of excited levels of luminescence centers. The population of excited level n_1 is described by expression [5,6]

$$n_1 = \frac{LJN}{LJ + \tau^{-1}}, \qquad (1)$$

where L — CL output, J — excitation current density, N — concentration of radiating ions, τ^{-1} — probability of transition.

If $\tau^{-1} \ll LJ$ expression (1) will take the form

$$n_1 = N, \qquad (2)$$

then the intensity has saturation.

If $\tau^{-1} \gg LJ$ expression (1) will take the form

$$n_1 = LJN/\tau^{-1}, \qquad (3)$$

then the intensity has linear dependence on J.

From this considerations, it followes that the line at 595 nm must reach saturation. But we do not observe that. It is a result of overlapping of 595 nm line with Eu^{2+} band. Subtracting the intensity of Eu^{2+} band near the

595 nm peak from intensity of that peak we can obtain the corrected dependence of 595 nm line intensity on electron beam current, and so we can observe saturation of that dependence.

4. Conclusion

The results obtained from this study allow us to make following conclusions:

— visible CL color of our sample (YAG : Eu,Zr) depends on exciting electron beam current density;

— decay time of Eu^{3+} transition decrease with increasing of Eu concentration;

— CL intensity of Eu^{3+} transitions reaches saturation at high beam current density value;

— CL intensity of Eu^{2+} transition has linear growth in dependence on beam current.

References

[1] R. Mueller-Mach, G.O. Mueller, M.R. Krames, T. Trottier. IEEE J. Select. Top. Quant. Electron., **8** (2), 339 (2002).
[2] M.V. Zamoryanskaya, S.G. Konnikov, A.N. Zamoryanskii. Instruments and Experimental Techniques, **47** (4), 477 (2004).
[3] A.A. Kaminskii, L.K. Aminov, V.L. Ermolaev. *Physics and Spectroscopy of Laser Crystals* (Moscow, 1986) p. 272.
[4] D.L. Dexter. J. Chem. Phys., **22** (6), 1063 (1954).
[5] W.F. van der Weg, M.W. van Tol. Appl. Phys. Lett., **38** (9), 705 (1981).
[6] M.V. Zamoryanskaya, A.Ya. Valtere. Opt. Spectrosc., **76** (4), 546 (1994).

Редактор Л.В. Шаронова