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Electroluminescence of Y_2O_3:Eu and Y_2O_3:Sm films[*]

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Electroluminescence of Y_2O_3:Eu and Y_2O_3:Sm films, as well as the films coactivated with Eu and Sm, is studied. The electroluminescence spectra are measured. The physical mechanism of electroluminescence is analyzed It is shown that the increase in the heat treatment temperature and the content of doping impurities of the films enhances the intensity of electroluminescence. Additional doping of Y_2O_3:EuF$_3$ films by the SmF$_3$ impurity, practically does not influence the emission spectrum.

Keywords: *electroluminescence; film luminophors; spectra; hot electrons*

1. Introduction

The development of high-luminance film electroluminophors comparable with ZnS films doped by Mn [1, 2] in terms of emission intensity and the efficiency, but different in spectral characteristics, is a quite urgent task aimed at the creation of full-color electroluminescent indicators. Oxide and oxysulfide luminophors, which are distinguished by their high stability, have attracted a significant attention of researchers and developers for a long time and are considered as an alternative to sulfide luminophors, which are less stable [3–8]. Y_2O_3 films belong to the most stable luminophors [9–11]. It seems interesting to use the methods increasing the luminance at the expense of the processes of sensibilization [12, 13] and high-temperature thermal treatment [14, 15] for the creation of the luminophors based on Y_2O_3:Eu film.

2. Experimental

The Y_2O_3 films were obtained by electron-beam evaporation of pellets produced by pressing a pow-
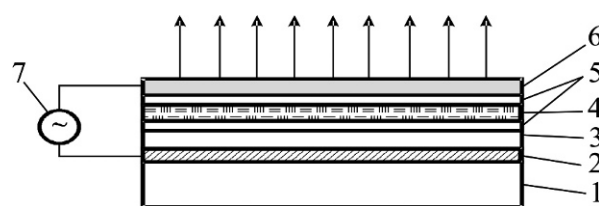

Fig. 1. Structure of a thin-film electroluminescent indicator: 1 – ceramic substrate, 2 – built-in metal electrode, 3 – layer of ceramics VS-2, 4 – electroluminescent layer Y_2O_3, 5 – dielectric layer, 6 – transparent conducting ITO electrode, 7 – source of the sinusoidal voltage.

der consisting of Y_2O_3 and EuF$_3$ with various concentrations of the latter, from 1 to 5 wt.%. As a co-doping impurity, we added a powder of SmF$_3$ to the input material. The temperature of a substrate during the deposition was $120 \div 200$ °C.

The annealing of the specimens was carried out in air and in the oxygen-argon atmosphere for one hour at temperatures of 600, 750, 900, and 1050 °C.

The electroluminescent structure under study is presented in Fig. 1. It includes a ceramic substrate with built-in metal electrodes and the working layer of ceramics, 40 μm in thickness, on the basis of BaTiO$_3$ with the dielectric permittivity $\varepsilon = 24\,000$ [5, 15]. The luminescent layer was positioned between thin-film dielectric layers, $0.05 - 0.1$ μm in
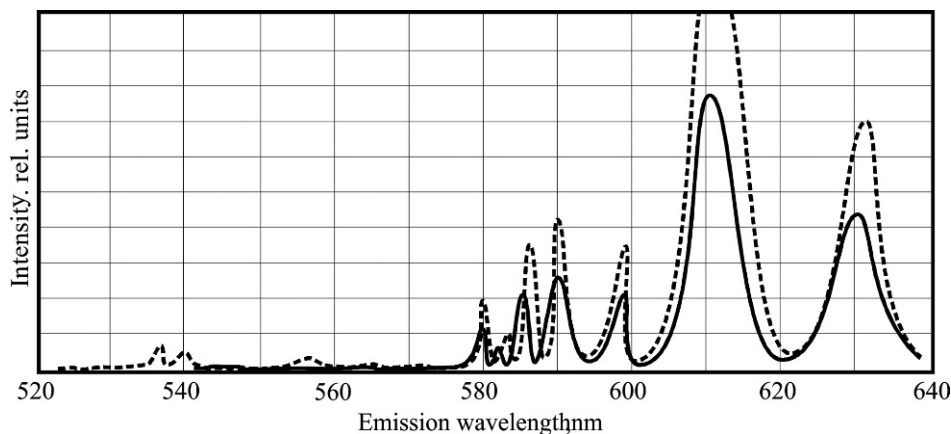
Fig. 2. Spectral characteristics of electroluminescence of Y_2O_3 films: solid line - doped by EuF_3 (2.5 %), dotted line – doped by EuF_3 (2.5 %) + SmF_3 (2.0 %).

thickness; on the top, the layer of a transparent ITO electrode was placed [5, 6].

The emission spectra were registered with a diffraction luminscence spectrometer SDL-2, and the emission luminance was measured with the help of FPI and FPCh-BPU photometers. The excitation of the electroluminescence was realized by a pulse generator with adjustable frequency, on-off ratio, pulse duration, and amplitude.

The stability of emission was determined after 1, 5, 10, 50, and 100 h of the operation at the excitation by the sinusoidal voltage with a frequency of 2 kHz and the 100 V amplitude.

The crystal structure of the films was studied by X-ray diffraction with a spectrometer DRON-3M. The investigation of the surface morphology of the films was performed with an atomic-force microscope (NanoScope 3000 Digital Instruments).

3. Results

In Fig. 2, we present the electroluminescence spectrum of a Y_2O_3:Eu film (solid line) after the annealing for 1 h at a temperature of 600 °C under an alternating voltage of 200 V with a frequency of 2 kHz. As is seen, the basic emission color is red with the bands at 611 and 630 nm, which correspond to the transitions $^5D_0 \rightarrow {}^7F_j$. The remaining emission bands corresponding to the yellow-orange spectrum with the peaks at 600, 592, 588, and 581 nm have significantly lower intensity.

The dotted line in Fig. 2 represents the electroluminescence spectrum of Y_2O_3:Eu, Sm film after annealing under the same conditions. As is seen, the spectral composition of the emission has not changed, but the electroluminescent emission intensity has increased approximately by a factor of 2.5. The ratio of the intensities of the bands remains the same. However, the additional emission bands at 532 and 537 nm, corresponding to the green region of the spectrum, caused by the transitions $^5D_1 \rightarrow {}^7F_j$ have appeared. These bands could not be identified in the spectrum of Y_2O_3:Eu film due to their low intensity.

In Fig. 3a, we show the volt-luminance characteristics (VLC) of the initial electroluminescent structures on the basis of Y_2O_3 films doped by EuF_3 and EuF_3+SmF_3 at the excitation by an alternating voltage with a frequency of 2 kHz and those after the thermal treatment at temperatures of 600, 750, 900, and 1050 °C. Fig. 3b demonstrates similar characteristics at the excitation by 20-µs pulses with alternating signs supplied with a frequency of 60 Hz.

As is seen, the electroluminescence luminance increases when the annealing temperature grows from the initial one to 900 °C, attaining 7800 cd/m^2 at a frequency of 2 kHz. This value was obtained for the samples with an electroluminescent Y_2O_3 film doped by Eu and Sm. The samples of Y_2O_3 films doped only by Eu had the maximum luminance up to 3200 cd/m^2.
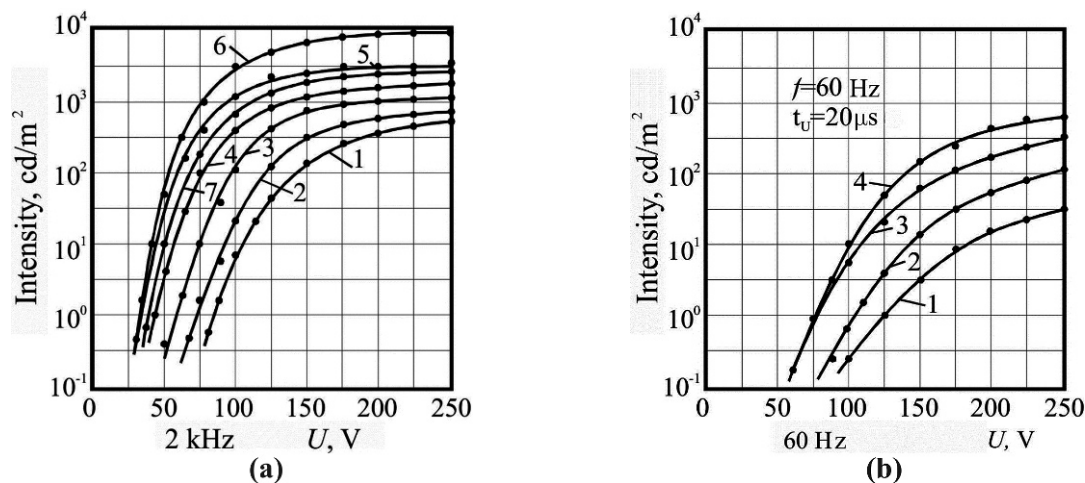
Fig. 3. a) electroluminescent emission intensity of Y_2O_3 films at a voltage frequency of 2 kHz; samples 1, 2, 3, 4, 5, 7 – doped by EuF_3, 6 – doped by $EuF_3 + SmF_3$, 1 – before thermal treatment, 2 – after thermal treatment at 600 °C, 3 – at 750 °C, 4 – at 1050 °C, 5, 6, 7 – at 900 °C; b) electroluminescent emission intensity of Y_2O_3 films at a voltage frequency of 60 Hz, $t_p = 20$ μs for the samples thermally treated at different temperatures: 1, 2, 3 – doped by EuF_3, 4 – doped by $EuF_3 + SmF_3$, 1 – before thermal treatment, 2 – after thermal treatment at 750 °C, 3, 4 – at 900 °C.

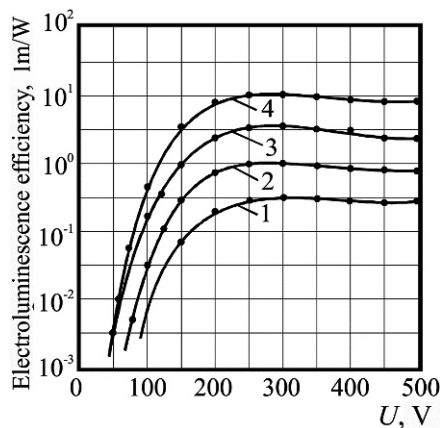Fig. 4. Electroluminescence efficiency of Y_2O_3 films doped by EuF_3 (1, 2, 3) and doped by $EuF_3 + SmF_3$ (4) versus voltage at different annealing temperatures: 1 – before thermal treatment, 2 – after thermal treatment at 750 °C, 3, 4 – at 900 °C.

The maximum values of luminance, 680 cd/m^2 for Y_2O_3 specimens doped by Eu and Sm and 260 cd/m^2 for Y_2O_3:Eu specimens, were obtained at the excitation by a pulse voltage with a frequency of 60 Hz.

In Fig. 4, we show the dependence of the electroluminescence efficiency under pulse voltage with a frequency of 60 Hz on the voltage at different annealing temperatures for the specimens with an electroluminescent Y_2O_3 film doped by Eu and Sm. As is seen, the electroluminescence efficiency at a voltage of 200 V attains 10 lm/W, which is comparable with that of the ZnS:Mn luminophor, the best at the present time.

The image of the Y_2O_3:Eu film surface obtained with AFM is shown in Fig. 5. As is seen from Fig. 5, the size of grains (microcrystals) depends on the annealing temperature. For example, the size of grains, which is tens of nanometers in the as-produced film, varies from 100 to 300 nm after the annealing at a temperature of 750 °C, and is comparable with the thickness of the electroluminophor layer after the annealing at a temperature of 900 °C (700 ÷ 800 nm). We have observed also the dependence of the size of grains in the initial films produced by the deposition of Y_2O_3 on a ceramic substrate in vacuum on the temperature. We demonstrate this dependence in Fig. 7.

In the subsequent studies, we used only the specimens of initial films with the largest grain size, which were produced by the deposition on a substrate at a temperature of 200 °C. We did not apply higher temperatures of the substrate, since this could
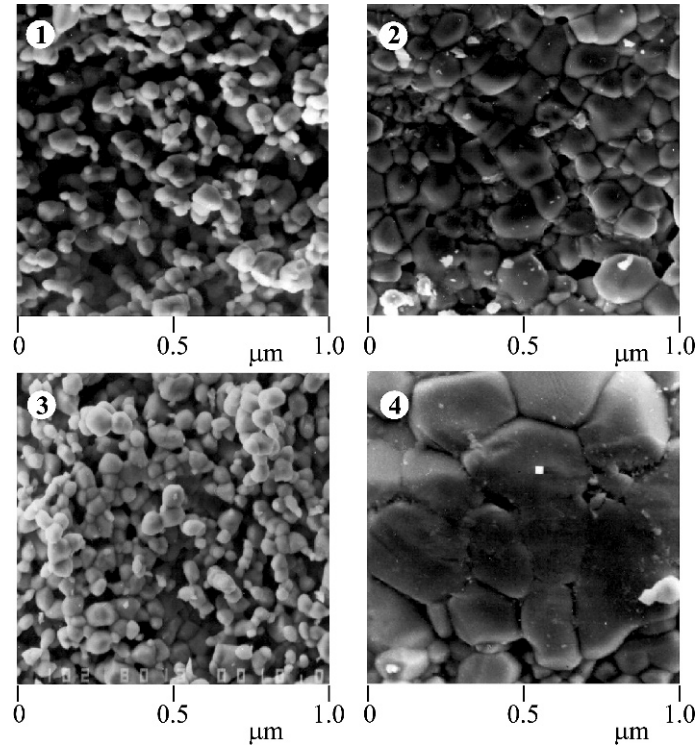
Fig. 5. AFM images of Y_2O_3:EuF_3 films: 1, 2 – initial films (deposition temperature 1 – 80 °C, 2 – 200 °C), 3, 4 – Y_2O_3:EuF_3+SmF_3 films (3 – deposition temperature 100 °C, 4 – after annealing at a temperature of 1000 °C for 1 h).
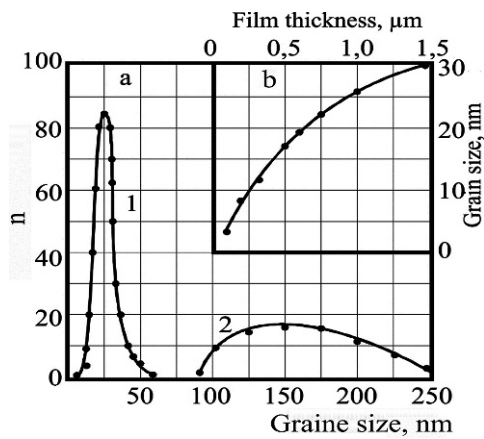

Fig. 6. Size distribution of grains in a Y_2O_3:EuF_3 film on a ceramic substrate after deposition in vacuum at temperatures: 1 – 100 °C, 2 –250 °C.
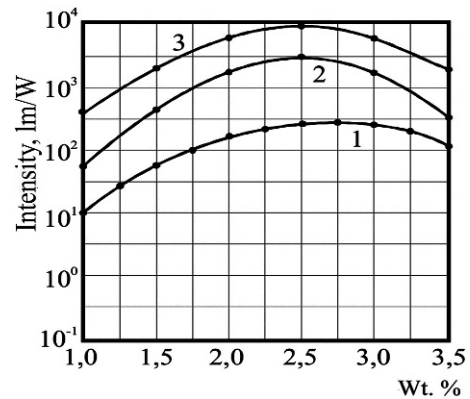
Fig. 7. Dependence of luminescence intensity on EuF_3 dopant, 1 – Y_2O_3:Eu film before thermal treatment, 2 – Y_2O_3:Eu film annealed at 900 °C; 3 – Y_2O_3:Eu,Sm film annealed at 900 °C.

cause a noncontrolled change in the composition and the amount of a doping impurity.

In Fig. 7, we demonstrate the dependence of the luminescence intensity on the concentration of the EuF_3 dopant. As is seen, 2.5 wt.% concentration of EuF_3 is optimum, though the intensity is practically unchanged in the EuF_3 interval of 2 ÷ 3 wt.%.

Fig. 8. Shift of the luminance characteristics in the stabilization process of VLC of Y$_2$O$_3$:Eu,Sm films: 1 – initial specimen,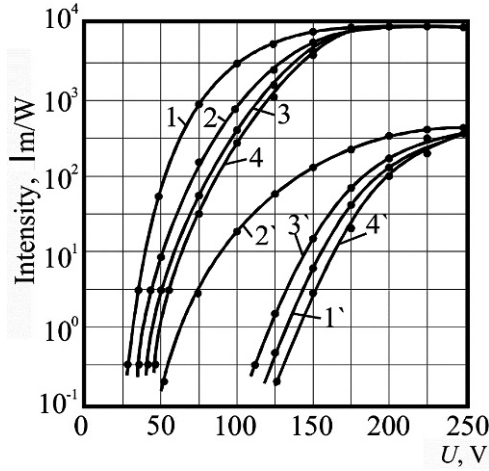 after thermal treatment at 900 °C for: 2 – 20 h, 3 – 100 h, 4 – 1000 h; 1′ – initial specimen, after thermal treatment at 500 °C for 2′ – 20 h, 3′ – 100 h, 4′ – 1000 h.

In Fig. 8 we demonstrate the shift of the luminance characteristics in the process of stabiliza-tion for different temperatures of thermal treatment (900 °C and 500 °C) and different annealing times.

4. Theory of electroluminescence

Consider briefly the theory of electrolumines-cence. In the case where ions Eu^{+3} are excited by means of direct intertaction with "hot" carriers, the luminescence intensity for these ions is given by the formula [21]:

$$J(\lambda) = P(E)J_{\text{Eu}^{3+}}(\lambda) \tag{1}$$

where $P(E)$ is the probability of the excitation of Eu^{+3} ion by a "hot" electron depending on the electric field strength in Y$_2$O$_3$; and $J_{\text{Eu}^{3+}}(\lambda)$ is the luminescence intensity of the excited ion of europium at the wavelength λ.

For the given mechanisms, the probability of the excitation of a rare-earth ion by a "hot" electron with regard to their inelastic interaction can be written with the use of the Boltzmann kinetic equation as:

$$P(E) = \frac{\int_{3\text{Б}p} Nn\sigma[W_0(k) + eEx]^{3/2} \exp\left[-\frac{3}{2}\frac{W_0(\kappa) + eEx}{W_T + eEX}\right]\rho_{ba}d^3k}{\int_{3\text{Б}p}[W_0(k) + eEx]^{3/2} \exp\left[-\frac{3}{2}\frac{W_0(\kappa) + eEx}{W_T + eEX}\right]d^3k} \tag{2}$$

where the integration in the momentum space of electrons is carried out in the Brillouin zone, $W_0(k)$ – initial energy of electrons; k – wave vector, W_T – energy of thermal motion of electrons; e – electron charge; n – concentration of electrons in the conduction band; σ – area of a scattering center, *i.e.*, the europium ion (we take $\sigma_{Im} = 3.2 \times 10^{-14}$ cm^2); ρ_{ba} – probability of the excitation of a separate ion of thulium from the state b to state a; N – concentration of europium ions (2.9×10^{18} cm^{-3}); x – mean free path of electrons with energy W_0 in the electric field with strength E given by the formula:

$$x = \frac{4\varepsilon^2 W_0^2}{\pi Ne^4} \frac{1}{1 - \frac{4\varepsilon^2 w_0 E}{\pi Ne^3}} \tag{3}$$

where ε – dielectric permittivity equal to $10^{-5} \div 10^{-6}$. The probability ρ_{ba} was calculated [24] with the use of multielectron molecular orbitals.

Let us consider the problem of the concentration of "hot" electrons as a function of the electric field strength in Y$_2$O$_3$. For the low electric field strength ($\sim 10^3$ V/cm), the concentration of charge carriers is determined by the formula [17]:

$$n = \frac{L}{3\sqrt{\pi}\mu E\tau_T}e^B Z^{-\frac{3b}{2Z_{cb}}} \int \exp\left[-Z + B + \left(\frac{3b}{2Z_{cb}} + \frac{1}{2}\right)\ln Z\right]dZ \tag{4}$$

where $B = \frac{9(1-b)}{4Z_{cb}Z}$, $Z_{cb} = \frac{W_n}{kT}$, $W_n = W_0 + eEx$, $b = 0.007$, $Z = \frac{W_0}{RT}$ R – universal gas constant, T – ab-

solute temperature, μ – mobility of electrons, τ_T – duration of the thermoluminescence of electrons.

For strong and intermediate fields, the concentration of charge carriers is given by the formula [19]:

$$n = n_0 \exp(\alpha L) \qquad (5)$$

where L – thickness of the Y$_2$O$_3$ layer; α – coefficient of impact ionization; and n_0 – number od electrons entering the force field.

For the fields with a strength of $\sim 10^6$ V/cm, the coefficient of impact ionization

$$\alpha = \frac{C_1}{E} \exp\left(-\frac{C_2}{E^2}\right) \qquad (6)$$

The transition probabilities for Eu^{3+} and Sm^{3+} ions are calculated by methods given in [19, 23, 24]. The peaks in Fig. 2a and 2b are caused by the transitions of ions Eu3 and the influence of the coactivation of Eu^{3+} and Sm^{3+}, respectively. The saturation observed in Figs. 3 and 4 is related to the fact that all rare-earth ions are excited practically at some value of electric filed strength, and the emission intensity cannot exceed the luminescence intensity of all excited ions.

5. Discussion of results

It is seen from Figs. 2a and 2b that the spectral composition of the emission from Y$_2$O$_3$:EuF$_3$ films has not changed.

The increase in the emission intensity was accompanied only by the manifestation of extremely weak emission bands at 532 and 537 nm caused by the transitions $^5D_1 \rightarrow {}^7F_j$. In our previous work [12], we observed such an increase in the electroluminescent emission intensity of SrS films doped by Eu under their additional doping by the impurity of Sm and explained this effect by the sensibilization, whereas the emission was caused by the $^5D_0 \rightarrow {}^7F_0$ transitions at Eu centers. The additional doping of films ZnS, ZnO:Cu by Ga and their high-temperature annealing [16–18] caused an increase in the luminescence luminance, the significant increase in the electroluminescent emission intensity, and some shift of the emission spectrum. The increase in the emission intensity was related to the

addition of Ga and the high-temperature annealing, which induced the significant increase in the size of crystals and a decrease in the amount of structural defects on the grain boundaries.

In our case, no changes in the spectrum composition occurred. Earlier, the cluster mechanism of electroluminescence was proposed [19–21]. According to this mechanism, under "strong" fields where the energy of an electron is sufficiently high to cause the ionization of atoms at the sites of the lattice, the avalanche-like increase in the number of carriers occurs. In this case, there happens the direct excitation of clusters containing an ion responsible for the emission spectrum and "blue" centers transferring their excitation energy to the clusters by the resonance mechanism.

It is worth noting the increase in the electroluminescent emission intensity with the annealing temperature and the significant decrease in the levels of the initial and working voltages (Figs. 4a,b).

As is known [20, 21, 23], the free path of electrons increases in the region of medium fields ($1.5 \cdot 10^4 \div 10^5$ V/cm) and reaches $20 \div 25$ nm, so that the "hot" electrons can attain energies of about $0.2 \div 0.3$ eV. At such energy, the "hot" electrons interact intensively with the ions of lattice matrix, by losing most of their energy. Moreover, in view of the fine-grained structure of a film and the presence of a high number of grain boundaries (Figs. 5 and 4), the appearance of the electroluminescence requires the fields as high as 10^6 V/cm. As the annealing temperature increases, the size of the grains in the film grows. Under the thermal treatment at 1000 °C, it becomes comparable with the film thickness, which causes a decrease in the working voltage and the appearance of the threshold electroluminescence at the fields of $10^5 \div 2 \cdot 10^5$ V/cm (25 V).

At voltages of the order of $150 \div 250$ V and the corresponding fields of $10^6 \div 2 \cdot 10^6$ V/cm, the electroluminescent emission intensity is 3000–4000 cd/m^2. At the additional doping by SmF$_3$, it increases up to 8000 cd/m^2, and the efficiency (at an excitation frequency of 60 Hz and $t_p = 20$ μs) becomes 10 Lm/W.

The decrease in the electroluminescence emission intensity with the increase in the annealing temperature up to $1050 - 1100$ °C was earlier re-

ferred to a deterioration of characteristics of the ceramic layer [22]. However, the measurements of the dielectric permittivity (ε) of the ceramics did not indicate the complete correspondence of the variations of ε and the electroluminescent emission intensity (especially, in the zone of the threshold electroluminescence). It is known that the structure of bulk monocrystalls of Y_2O_3 at a temperature of $1300 - 1400$ °C is changed and becomes cubic. The most probable additional reason for the decrease in the electroluminescent emission intensity is the onset of a rearrangement of the thin-film structure of Y_2O_3 already at the temperature of $1050 \div 1100$ °C.

In Fig. 8, we show the stability of electroluminescent indicators on the basis of an Y_2O_3 film. As is seen, the structure after a high-temperature thermal treatment manifests a high stability during the operation as long as 1000 h.

This is related to the more uniform distribution of impurities in the process of high-temperature thermal treatment as compared with that of the specimens with fine-grained structure, where a part of impurities is accumulated during the operation near the grain boundaries and does not take part in the processes of electroluminescence.

6. Conclusions

The increase in the temperature of a thermal treatment of Y_2O_3:EuF_3 films up to 1000 °C caused an increase in the electroluminescent emission intensity up to 4000 cd/m^2 at the excitation by the sinusoidal voltage with a frequency of 2 kHz and up to 350 cd/m^2 with an efficiency of 3.5 lm/W at the excitation by 20-μs pulses with alternating signs with a frequency of 60 Hz. In this case, the threshold of "ignition" of the electroluminescence was ~ 25 V in the first case and 60 V in the second case. This was related to the increase in the grain sizes in the crystal structure of Y_2O_3 films from $25 \div 30$ nm to $500 \div 600$ nm and to the corresponding change in the conditions for acceleration and multiplication of "hot" electrons participating in the process of electroluminescence. The additional doping by the SmF_3 impurity allowed us to increase the electroluminescent emission intensity up to 8000 cd/m^2 at the excitation at a frequency of 2 kHz and up to

700 cd/m^2 at the excitation by 20-μs pulses with a frequency of 60 Hz at efficiencies up to 10 lm/W.

Additional doping of Y_2O_3:EuF_3 films by the SmF_3 impurity did not cause any changes in the emission spectrum. This testifies that the main channel of emission is realized through the centers including Eu.

At the high-temperature thermal treatment, the stability of VLC increased significantly. In this case, a shift of the threshold voltage did not exceed 15 V and was completely absent at exciting voltages above 170 V.

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