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X-ray excited luminescence of ytterbium containing YAG single crystalline films

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Luminescence properties of ytterbium ions in of $Y_3Al_5O_{12}$ (YAG) epitaxial films have been investigated. The influence of growth conditions on the change of activator ions charge state and the luminescence in visible spectral region has been demonstrated. It has been established that emission bands with maxima at 480 and 580 nm are attributed to the $5d$-$4f$ transitions of Yb^{2+} ions. The emission bands with maxima at 330 nm and 500 nm correspond to transitions from charge transfer state to $^2F_{7/2}$ and $^2F_{5/2}$ state of Yb^{3+} ions, respectively.

Проведено исследование люминесцентных свойств ионов иттербия в эпитаксиальных пленках $Y_3Al_5O_{12}$ (YAG). Показано влияние условий выращивания на изменение зарядового состояния ионов активатора и его свечения в видимой области спектра. Установлено, что люминесценция в полосах с максимумами при 480 нм и 580 нм в эпитаксиальных пленках YAG:Yb приписывается $5d$-$4f$ переходам ионов Yb^{2+}. Полосы свечения с максимумами при 330 и 500 нм отвечают переходам из состояния переноса заряда соответственно на уровни $^2F_{7/2}$ и $^2F_{5/2}$ ионов Yb^{3+}.

Bulk single crystals and epitaxial films of ytterbium containing yttrium-aluminum garnet (YAG:Yb) are considered as promising materials for high power lasers [1, 2]. An important factor that decreases the performance thereof is the presence of divalent Yb^{2+} ions being responsible for the shortening of the Yb^{3+} excited state lifetime. The YAG:Yb films grown by liquid phase epitaxy (LPE) technique have several advantages in comparison with YAG:Yb single crystals. The fabrication technology thereof provides a homogeneous material with perfect structure, suitable thickness, and composition that is important from point of view of this material practical use [2]. In recent years, there is an increasing interest to luminescence and scintillation properties of YAG single crystals activated with Yb^{3+} ions. The very fast luminescence in ultra violet (UV) and visible spectral regions associated with charge transfer transitions offers new application possibilities for these materials in experiments for detection of neutrinos and other high-energy particles [3, 4]. The aim of this work was to investigate the influence of growth conditions and heat treatment of YAG:Yb epitaxial films on the optical absorption and luminescence emission thereof under X-ray excitation.

The YAG epitaxial films activated with ytterbium ions were grown by LPE technique from $PbO–B_2O_3$ and Bi_2O_3 melt-solution in air as described in [2]. Single crystal plates of (111) oriented YAG of about 1 mm thickness were used as substrates. The

Table. Characteristics of the $(Yb,Y)_3Al_5O_{12}$ epitaxial films

Sample No.	h, μm	Grown from flux	Ytterbium ion substitution of Y sites, %
5-01	32.3	$PbO–B_2O_3$	10
5-03	62.0	$PbO–B_2O_3$	10
2-03	65.0	Bi_2O_3	12
2-24	128	Bi_2O_3	12
2-49	106	Bi_2O_3	40

change of ytterbium concentration was realized by successive additions thereof into the melt. The general tasks of the melt composition selection were to obtain a necessary doping level and to minimize the lattice parameters misfit between the substrate and the epitaxial film. The growth rate was controlled by means of the growing temperature. The thickness of layers grown was 30 to 260 μm. The characteristics of the $(Yb,Y)_3Al_5O_{12}$ epitaxial films mentioned thereafter in this work are presented in Table. Some samples were annealed in a reducing atmosphere (H_2 flow) at 800°C for 6–7 hours to stabilize the divalent state of Yb ions.

Optical absorption spectra of the samples were computed from transmission spectra recorded by double-beam spectrophotometer "Specord-M40" (Carl Zeiss, Germany) at room temperature (RT). A home-made spectral setup based on the SF-4A quartz monochromator was used to study the X-ray luminescence spectra. The excitation was performed by microfocused X-ray tube operated at 45 kV with a current of 0.3 mA. The emission spectra were corrected for the monochromator dispersion and detector spectral response.

The absorption spectra in the UV and visible regions of the grown YAG:Yb epitaxial films differ essentially depending on the melt composition and growth conditions. As it is seen from Fig. 1, the sharp increase of absorption coefficient in UV spectral region starts at shorter wavelengths for the films grown from lead oxide based flux as compared to those grown from bismuth oxide one. This is observed in both cases at wavelengths shorter than 300 nm and can be associated with doping with uncontrolled lead or bismuth impurities, depending on the melt composition. The absorption of garnet epitaxial films in UV spectral region is explained by intra-center

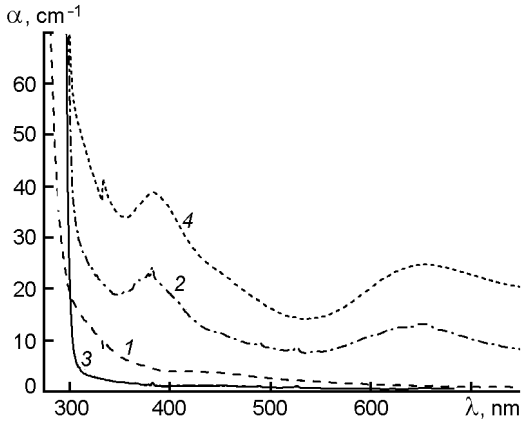

Fig. 1. Absorption spectra of the YAG:Yb epitaxial films in UV and visible region. Film Nos. 5-01 (*1*), 2-03 (*2*), 2-24 (*3*), 2-24 (*4*), reduced in H_2 (*5*).

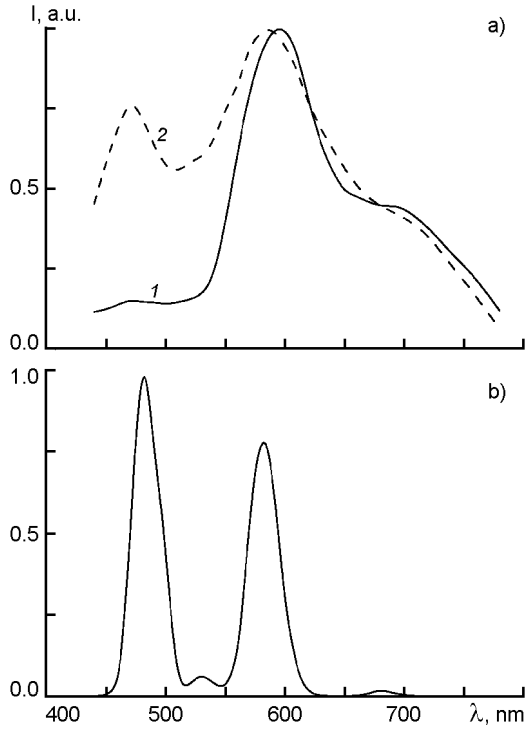

Fig. 2. Emission spectra of YAG:Yb single crystalline films under X-ray excitation. a) films grown from lead oxide based flux: No. 5-01 (*1*), No. 5-03 (*2*); b) film grown from bismuth oxide based flux (No. 2-03).

transitions $^1S_0 \rightarrow {}^3P_1$ (λ_{max} ~ 260–270 nm) in Pb^{2+} and Bi^{3+} Hg-like ions with high oscillator strength as well as by charge transfer between impurity levels and conductivity band [5, 6]. A broad maximum at 450 nm and increasing absorption at about 310–350 nm are observed in absorption spectrum of the films grown from $PbO–B_2O_3$ melt (curve 1, Fig. 1). The absorption

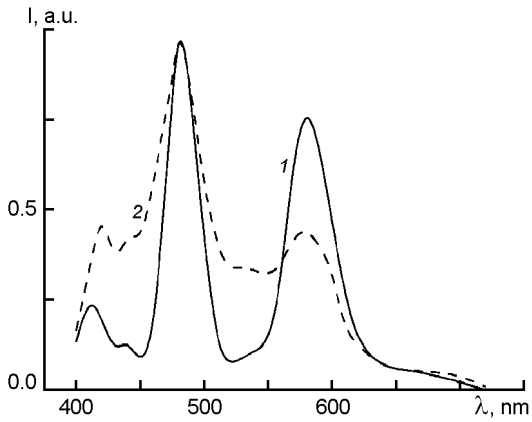

Fig. 3. Emission spectra of reduced YAG:Yb single crystalline film No. 2-24 under X-ray excitation: *1*, room temperature, *2*, liquid nitrogen temperature.

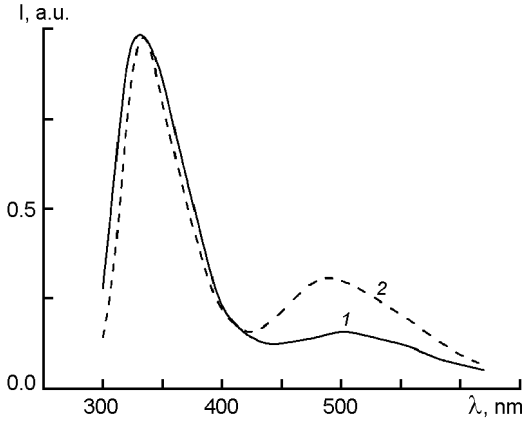

Fig. 4. Emission spectra of reduced YAG:Yb single crystalline film No. 2-49 under X-ray excitation: *1*, room temperature, *2*, liquid nitrogen temperature.

increases almost by one order and the distinct maxima at 390 and 650 nm are observed for the films with near the same ytterbium contents grown from Bi_2O_3 melt. The films with the same ytterbium content obtained from Bi_2O_3 flux at much reduced growth rate were essentially colorless in the visible spectral region. But the same absorption bands as in film No.2-03 arise therein after the annealing in H_2 atmosphere (800°C, 6–7 h). The analogous bands were observed in absorption spectra of YAG:Yb single crystals grown in reducing atmosphere with addition of quadrivalent impurities (Si, Zr) for charge compensation [7]. It allowed to connect these bands with $4f$-$5d$ optical transitions in Yb^{2+} ions.

The X-ray luminescence spectra of the grown epitaxial films differ considerably depending on the melt composition. Fig. 2a represents the emission spectra of two films obtained from lead containing melt at somewhat different growth rates. A pronounced luminescence band with a maximum at 580 nm and a long-wave shoulder in the 650–750 nm range is observed in both films. The relative intensity of another luminescence band in blue spectral region with maximum at 480 nm changes from sample to sample and increases with the film growth rate. The main emission intensity increases by several times in films grown from bismuth based flux (Fig. 2b) and there are two well divided narrow bands with maxima at 480 and 580 nm. Fig. 3 represents the luminescence spectra of the film No.02-24 annealed in reducing atmosphere under X-ray excitation at the room and liquid nitrogen temperatures. It can be seen that bands with maxima at 480 and 580 nm prevail also in luminescence spectra of this film but there are weak maxima at 410, 440, and 530 nm as well. After the temperature is decreased from 293 to 100 K, the intensity of main bands becomes approximately halved and a change in the relative intensity thereof is observed. At the same time, the intensity of background lines which can be associated with presence of rare earth impurities increases.

As to the nature of luminescence bands at 480 and 580 nm observed in films with relatively low ytterbium contents, we can assume that those are connected with divalent Yb^{2+} ions. These bands can be attributed to intra-center transitions in $5d$-$4f$ configuration of Yb^{2+}. The changes in relative intensity of emission bands at 480 and 580 nm may be caused by different mechanisms of excited states population recombination processes resulting in the luminescence. The emission spectrum of the YAG:Yb films with increased ytterbium concentration (up to 40 at.%) differs qualitatively and new broad bands with maxima at 330 and 500 nm arise (Fig. 4). Decreasing temperature results in increase of both bands and change in relative intensity thereof. No luminescence was observed after annealing of YAG-40 % Yb films in hydrogen atmosphere.

In epitaxial films with high ytterbium content, the absence of Yb^{2+} attributed luminescence can be connected with concentration quenching. The luminescence in the bands at 330 and 500 nm observed before in YAG:Yb single crystals [3, 8] is caused by charge transfer transition. It is necessary to study the time and temperature charac-

teristics of luminescence to confirm such suppositions. Kinetic study of the luminescence associated with divalent ytterbium ions can be of use for specification of relaxation mechanisms of excited Yb^{3+} ions states in complex oxides.

To conclude, the luminescence bands with maxima at 480 nm and 580 nm observed in the YAG:Yb epitaxial films under X-ray excitation are attributed to $5d$-$4f$ transitions associated with Yb^{2+} ions. Changes of growth conditions, impurities and structural vacancy-type defects concentration results in variations of the relative intensity of these emission bands. The broad emission bands with maxima at 330 and 500 nm in YAG:Yb epitaxial films as well as in YAG:Yb single crystals are caused by the charge transfer transitions.

References

1. A.Giesen, H.Hügel, A.Voss et al., *J.Appl.Phys.*, **B 58**, 365 (1994).
2. S.B.Ubizskii, A.O.Matkovskii, S.S.Melnyk et al., *Phys.Stat.Sol.*, **A 201**, 791 (2004).
3. N.Gherassimova, N.Garnier, C.Dujardin et al., *Chem.Phys.Lett.*, **339**, 197 (2001).
4. P.Antonini, S.Belogurov, G.Bressi et al., *Nucl.Instr.and Meth.in Phys.Res.*, **A 486**, 220 (2002).
5. G.B.Scott, J.L.Page, *Appl.Phys.*, **48**, 1342 (1977).
6. Yu.V.Zorenko et al., *J.Appl.Spectr.*, **49**, 514 (1988).
7. M.Henke, J.Perbon, S.Kuck, *J.Luminescence.*, **87–89**, 1049 (2000).
8. L.van Pieterson, M.Heeroma, E.de Heer et al., *J.Luminescence.*, **91**, 177 (2000).

Рентгенолюмінесценція монокристалічних плівок ІАГ з домішкою ітербію

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Проведено дослідження люмінесцентних властивостей іонів ітербію в епітаксійних плівках $Y_3Al_5O_{12}$ (YAG). Показано вплив умов вирощування на зміну зарядового стану іонів активатора та його свічення у видимій області спектра. Встановлено, що люмінесценція в смугах з максимумами при 480 нм і 580 нм приписується $5d$-$4f$ переходам іонів Yb^{2+}. Смуги свічення з максимумами при 330 і 500 нм відповідають переходам зі стану перенесення заряду відповідно на рівні $2F_{7/2}$ і $2F_{5/2}$ іонів Yb^{3+}.