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The recombination channels of luminescence excitation in YAG:Yb single crystalline films

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Abstract

Absorption and emission spectra, luminescence decay kinetics and thermostimulated luminescence of X-ray irradiated YAG:Yb single crystalline films were studied. Two emission bands peaked at 420 and 488 nm have been detected in the investigated films. The strong thermal quenching of luminescence band at 488 nm was observed above 160 K. The influence of growth conditions and annealing in air on the lifetime of Yb^{3+} ion excited state in the IR spectral region have been revealed. The recombination mechanisms of the f–f transition at Yb^{3+} ion excitation, as well as the mechanism of lifetime shortening for the excited Yb^{3+} luminescence have been discussed.

Keywords: Emission spectra; Decay kinetics; Thermal quenching; Thermostimulated luminescence

1. Introduction

The Yb substituted yttrium aluminium garnet $Y_3Al_5O_{12}$ (YAG) is considered for the last decade as a prospective material for high power solid-state thin disk lasers emitting in the near IR region (Giesen et al., 1994; Erhard et al., 1999; Shimoda et al., 2001). Yb:YAG crystals are also promising fast scintillators with charge transfer luminescence in UV and visible region (Guerassimova et al., 2001; Kamenskikh et al., 2003; Petermann et al., 2005). Studying the relaxation of excited states and the energy transfer from excited states are very important for both applications. In both cases these processes can be strongly affected by defects of crystal lattice and impurities that depend significantly on the synthesis conditions.

From this point of view the single crystalline films (SCF) of YAG:Yb were fabricated by liquid phase epitaxy technique and their optical and lasing properties were studied in Ubizskii et al. (2004) as an alternative to bulk single crystals owing to higher homogeneity and structure perfection of SCF what was shown in Zorenko et al. (2005). Further investigation made by Zakharko et al. (2005) revealed a correlation of the visible luminescence under X-ray excitation of the YAG:Yb SCF with Yb^{2+} ions. In order to study the relaxation processes with the participation of defects in SCF the X-ray excited luminescence in the visible and IR region and its temperature dependence are studied in this work along with the thermostimulated glowing of X-ray irradiated YAG:Yb SCF.

2. Experimental

Epitaxial films were grown at the R&D Institute for Materials, SRC "Carat" by means of routine isothermal liquid phase epitaxy technique in air. The single crystalline plates of pure YAG with a thickness of about 1 mm were used as substrates. Bi_2O_3 was used as a solvent. The content of the dissolved oxides (Y_2O_3, Al_2O_3 and Yb_2O_3) was calculated to obtain perfect epitaxial films of YAG:Yb with an ytterbium substitution level of about 10% relative to all Y sites in YAG. The Yb content in the grown films was estimated by means of measurement of

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Table 1
Characteristics of YAG:Yb epitaxial films

Sample number	h (μm)	Growth rate (μm/min)	Lifetime (μs)	Note
3L-6/1	16.3	0.8	270	Green light annealed in air at 1100 °C colourless with CaO, brown light
3L-6/2	16.3	0.8	808	
3L-14	131.5	0.44	866	
3L-24	37.8	0.63	665	

the characteristic Yb absorption in the 0.9–1.1 μm region. The final ytterbium content in the film estimated by the Yb^{3+} optical absorption was about 1.1×10^{21} cm^{-3} in all grown films. All the samples discussed here were grown sequentially from the same melt-solution. After growth of several samples the small amount CaO was added (e.g. film 3L-24) to prevent the Yb^{2+} creation that may be forced by Pt^{4+} impurity from the crucible. The grown films thicknesses were in the range from tens to about two hundreds micrometers. The main characteristics of the $(Yb, Y)_3Al_5O_{12}$ epitaxial films investigated in this work are presented in Table 1. Some samples were subjected to after-growth annealing in air at 1100 °C for 20 h. The optical transmission of the films was measured in the 0.2–1.1 μm wavelength range using a "Cary 5000" spectrometer. The luminescence lifetime was measured as described in Ubizskii et al. (2004).

To study the X-ray luminescence spectra and thermoluminescence glow curves a home-made spectral setup based on a quartz monochromator were used. The excitation was performed by a microfocused X-ray tube operated at 45 kV with a current of 0.3 mA. The thermostimulated luminescence (TSL) was measured in the linear heating regime with a temperature change rate of 0.2 K s^{-1}.

3. Results

The absorption spectra in the visible region of the as-grown YAG:Yb epitaxial films differ essentially corresponding to the growth conditions. As it ensues from Fig. 1, the light green-blue coloration is observed and there are two bands in the absorption spectrum at 375 and 625 nm in film 3L-6/1 grown with a higher growth rate. Annealing of sample in air leads to full bleaching of these bands (sample 3L-6/2). The inset in Fig. 1 represents a difference between the absorption for the as-grown (3L-6/1) and the annealed (3L-6/2) samples. The films with the same ytterbium content (e.g. 3L-14), obtained from Bi_2O_3 flux at a reduced growth rate were practical colourless in the visible spectral region. Addition of Ca^{2+} ion in an amount of 0.0032 at% to the melt leads to appearance of the broad absorption line in the UV range with a maximum near 350–400 nm. Similar absorption was observed earlier in garnets doped with two-valence cations that form probably complex defects containing Me^{2+} and oxygen vacancy (Vasyltsiv et al., 1993).

The strong absorption in the UV spectral region is characteristic for all the epifilms grown from Bi_2O_3-based flux and can be associated with entering uncontrolled bismuth impurity from the melt. It can be explained by the intra-centre transitions $^1S_0 \rightarrow {}^3P_1$ ($\lambda_{max} \sim 290$ nm) in Bi^{3+} (Zakharko and Andriychuk, 1983; Zorenko et al., 2002).

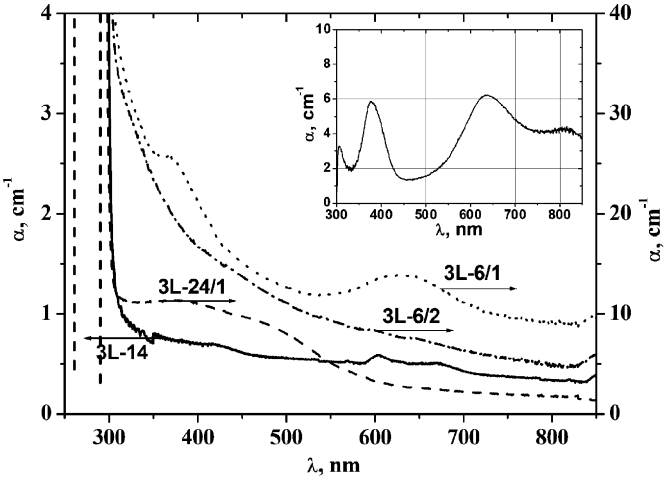

Fig. 1. Absorption spectra of the different YAG:Yb single crystalline films. Inset shows difference of absorption of the as-grown and annealed in air samples (3L-6).

The main emission bands at 1030 and 1049 nm, which correspond to the $^4F_{5/2} \rightarrow {}^4F_{7/2}$ inter-configuration transitions in Yb^{3+} ions are observed under optical excitation of all YAG:Yb epitaxial films. These transitions are observed under X-ray excitation as well. Furthermore, a broad emission band with maximum at 450 nm is observed in the X-ray luminescence spectrum of the epitaxial film 3L-14 at 90 K (Fig. 2). The emission peak varies in shape from sample to sample. This provided a reason to decompose the spectrum on elementary bands. The result of decomposition by gauss-shaped lines is presented in the inset. The corresponding sub-band maxima with half-width of about 0.5 eV are allocated at 2.95 eV (420 nm) and 2.54 eV (488 nm). The bands with the charge transfer luminescence occurring at 330 and 500 nm in YAG:Yb single crystals were not observed in the investigated SCF. We have established earlier (Zakharko et al., 2005) that such bands arise in SCF under more high content of ytterbium, specifically in YAG:40%Yb. The 2.54 eV band was revealed earlier in the YAG:Yb epifilms grown from PbO-based flux (Zakharko et al., 2005) and was attributed to the emission transitions in Yb^{2+} ions. The 2.95 eV band arises only in the epifilms grown from Bi_2O_3-based flux where the very intense absorption band at 290 nm is observed. This emission band might be related to the Bi-impurity in the garnet lattice.