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Scintillating properties of Bi-doped $Y_3Ga_5O_{12}$

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Abstract Shaped single crystals of Bi : $Y_3Ga_5O_{12}$ (Bi = 0.041, 0.047 and 0.061 mol%) were grown by the micro-pulling-down method. Optical absorption spectra show an absorption band at 288 nm ascribed to the lowest energy $6s^2 \rightarrow 6s6p$ transition of Bi^{3+}, while luminescence spectra demonstrate the band at 314 nm ascribed to the reverse radiative transition of the excited Bi^{3+} centres. At room temperature, dominant decay time component was found to be about 440 ns with a minor slower component 580 ns.

Key words Rare-earth garnet, Luminescent properties, Bi^{3+}

1. Introduction

Doped rare-earth garnets are well known media for optical applications. They are used as host media for solid state lasers, e.g. Nd-doped $Y_3Al_5O_{12}$ [1]. Other important area is scintillating application, where Ce-doped $Y_3Al_5O_{12}$ single crystals are widely employed [2], while luminescence and scintillation properties of Yb-doped $Y_3Ga_5O_{12}$ (YGG) have been reported [3].

Doping YGG with heavy ns^2 ions, particularly with Bi^{3+}, might be another way to obtain new scintillating materials. The Bi-containing iron garnet thin films were shown to be important for application in different magneto-optic devices [4]. Scintillating properties of Bi-doped $Gd_3Ga_5O_{12}$ have been demonstrated recently [5]. However, to our knowledge, there is no information about Bi-doped yttrium gallium garnets to be used for scintillating application.

In the present article, we report on the shaped single crystal growth of Bi-doped $Y_3Ga_5O_{12}$ by the micro-pulling-down (μ-PD) method as well as its optical and luminescence properties.

2. Experimental

Starting materials were prepared from the stoichiometric mixture of 4 N purity Y_2O_3, β-Ga_2O_3 and 3 N purity Bi_2O_3 powders. Shaped Bi:$Y_3Ga_5O_{12}$ single crystals were grown by the μ-PD method using an iridium crucible with a die [3]. The crucible was heated inductively at a frequency of 20 kHz. Growth rate was 0.05~0.3 mm/min. The <111> $Y_3Al_5O_{12}$ crystal was used as a seed. The growth atmosphere was mixture of Ar + O_2 (2%) to suppress the gallium oxides dissociation and evaporation.

To identify the obtained phase, powder X-ray diffraction analysis was carried out in air at room temperature with a RIGAKU RINT Ultima diffractometer using CuKα X-ray source (40 kV, 40 mA). The chemical composition was analyzed by electron microprobe analysis using JEOL JXA-8612MX.

Absorption spectra were measured with UV-VIS-NIR spectrophotometer Shimadzu UV-3101PC at room temperature. Measurements of radioluminescence were performed at room temperature using the Spectrofluorometer 199S (Edinburgh Instruments) equipped with a steady-state X-ray excitation source (35 kV, Mo-anticathode). Single grating emission monochromator and photomultiplier XP2233 in photon counting mode were used to detect the emission spectra. All the spectra were corrected for experimental distortions. Decay kinetics was measured at the same set-up using the nanosecond hydrogen-filled coaxial flashlamp and time-correlated single photon counting method.

3. Results and Discussion

Shaped single crystals of Bi : $Y_3Ga_5O_{12}$ were grown by

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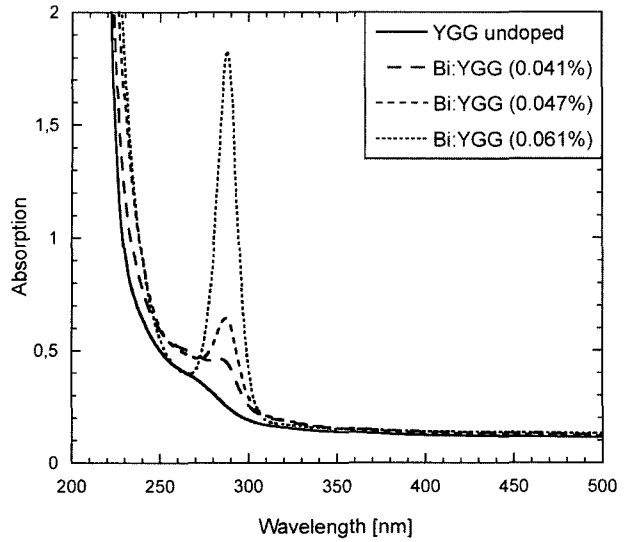

Fig. 1. Absorption spectra of Bi : $Y_3Ga_5O_{12}$ (Bi = 0.041, 0.047 and 0.061 mol%) samples at RT.

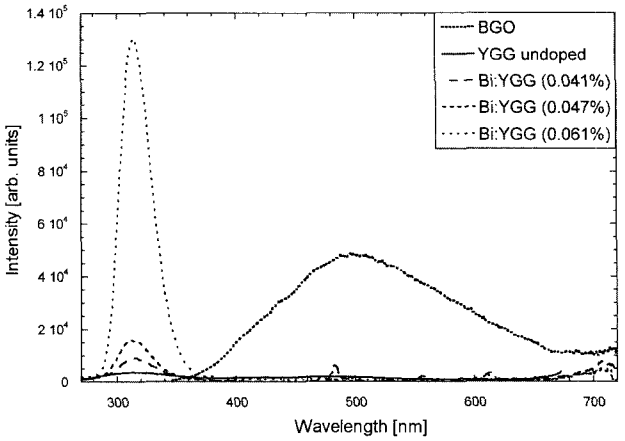

Fig. 2. Emission spectra of Bi : $Y_3Ga_5O_{12}$ (Bi = 0.041, 0.047 and 0.061 mol%) samples at RT, X-ray excitation. For comparison, spectrum of $Bi_4Ge_3O_{12}$ (BGO) standard sample is also given, spectra are comparable in an absolute way.

the μ-PD method. All samples under investigation were transparent, crack less and without visible inclusions. Single phase with garnet structure was observed with no impurity phases.

Chemical analysis showed strong evaporation of Bi during single crystal growth experiments. From starting compositions containing 0.5, 1 and 5 mol% of Bi, shaped single crystal of $Y_3Ga_5O_{12}$ containing 0.041, 0.047, 0.061 mol% of Bi were grown. As the μ-PD method is characterized by high homogeneity of the chemical composition [6], the dopant distribution analysis was not carried out. However, because of high volatilization of bismuth oxide, some axial Bi-concentration gradient in the case of long crystals could be expected.

Absorption spectra of Bi : $Y_3Ga_5O_{12}$ (Bi = 0.041, 0.047 and 0.061 mol%) samples show an absorption band at 288 nm increasing with Bi concentration in the crystals, see Fig. 1. In this spectral region it might be related to the lowest energy $6s^2 \rightarrow 6s6p$ transition of Bi^{3+} [7].

Luminescence spectra of Bi : $Y_3Ga_5O_{12}$ (Bi = 0.041, 0.047 and 0.061 mol%) samples shown in Fig. 2 demonstrate the band at 314 nm, which intensity strongly depends on the Bi concentration. We ascribe this band to the reverse radiative transition of the excited Bi^{3+} centres, in which two closely spaced excited state levels should be involved ($^3P_1$ and $^3P_0$ levels) and typical two-component decay kinetics is expected. Nonlinear dependency of the emission intensity on Bi content could be explained because of nonradiative energy transfer, mainly due to multipolar interactions, becoming more efficient with increase of dopant concentration.

It is interesting to note that despite of the same position of the absorption/excitation peak round 290 nm, there is a big difference in the position of the emission spectra of Bi-related bands in $Gd_3Ga_5O_{12}$ and $Y_3Ga_5O_{12}$ hosts, because in the former the emission band peaking at 470 nm was ascribed to Bi^{3+} emission [5]. However, it is well established that position of Bi^{3+} emission in different hosts can vary a lot because of local distortions of Bi-surrounding due to its excitation and resulting in extended relaxation processes. Stokes shifts (difference in energy between the absorption and emission band maxima) from 0.4 eV up to 2.4 eV were reported in the literature [8], so that Bi-doped $Y_3Ga_5O_{12}$ belongs to the compounds with smaller distortion of Bi-polyhedron, restricted relaxation of its excited state and Stokes shift is calculated of only 0.36 eV. Smaller Stokes shift usually results in higher energy barrier for thermal quenching and such compounds show luminescence up to very high temperatures as shown recently for Bi-doped YPO_4 [9].

Temperature dependence of the luminescence decay and intensity of Bi : YGG (Bi = 0.061 mol%) was followed between room temperature and 180°C. At room temperature it shows the dominant decay component of about 440 ns decay time with a minor slower component (580 ns decay time) in the tail, see Fig. 3. In Fig. 4 temperature dependence of the decay times is given, which were obtained from a single (tau1) or double (tau2) exponential approximations for the temperature up to 60°C and above 60°C, respectively.

Appearance of such a 2-components decay is typical for heavy ns^2 ions (Tl^+, Pb^{2+} and Bi^{3+}) [10]. The value of the dominant lifetime at RT is also very reasonable for a heavy ns^2 ion luminescence, for instance in BGO its

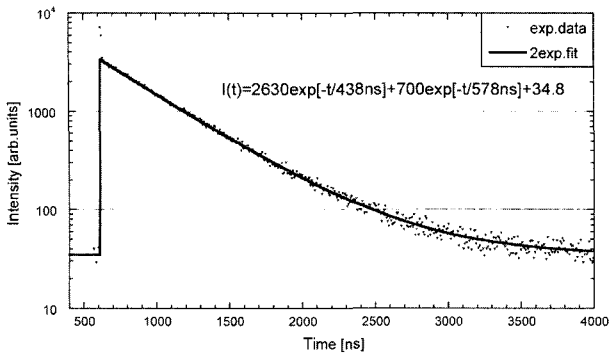

Fig. 3. Photoluminescence decay of Bi : $Y_3Ga_5O_{12}$ (Bi = 0.061 mol%) at RT, excitation at 290 nm and emission at 470 nm.

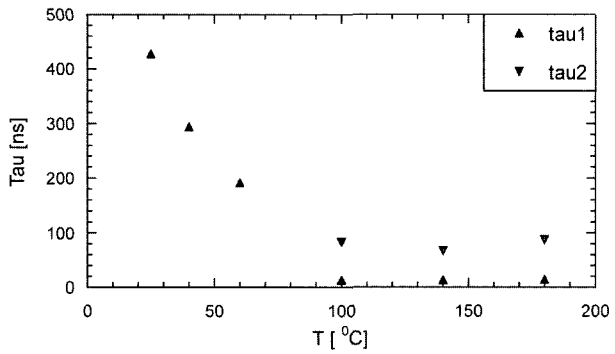

Fig. 4. Temperature dependence of the luminescence decay times of Bi : $Y_3Ga_5O_{12}$ (Bi = 0.061 mol%), excitation at 290 nm and emission at 470 nm.

value is about 300 ns. Temperature dependence up to 100°C shows higher speeding-up the decay time in comparison with emission intensity, so that it is not only thermal quenching, but also increasing thermalization between the radiative and metastable levels in the excited state of the Bi^{3+} centre [7], which can explain such dependences. Two-exponential (or non-exponential) course of the decay at RT may point to the presence of non-equivalent Bi-centres, e.g. due to some defects nearby. Measurement of the decay kinetics in an extended temperature region (down to 4 K) is necessary to determine the quantitative parameters of the Bi^{3+} excited state levels completely and will be the subject of the future investigation.

Scintillator based on the Bi-doped YGG (density 5.7 g/cm^3) provided uniform Bi-content and may appear as a possible competitor to BGO (density 7.13 g/cm^3) as its density can be noticeably increased by replacing the Y cations by heavier rare-earth ones. At room temperature, Bi-doped $Y_3Ga_5O_{12}$ shows about 2.6 times higher radioluminescence intensity, but only 1.5 times longer decay time respect to BGO. Finally, its emission intensity round RT is less temperature dependent (less quenched) with respect to BGO, which means that also scintillator parameters could be less temperature dependent round RT with respect to BGO.

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