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Luminescence spectroscopy of the Bi^{3+} single and dimer centers in $Y_3Al_5O_{12}$:Bi single crystalline films

Y. Zorenko [a,*], V. Gorbenko [a], T. Voznyak [a], V. Jary [b], M. Nikl [b]

[a] *Laboratory of Optoelectronic Materials, Electronics Department of Ivan Franko National University of Lviv, 107 Gen. Tarnawskogo, 70017 Lviv, Ukraine*
[b] *Institute of Physics, AS CR, Cukrovarnicka 10,162 53 Prague 6, Czech Republic*

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ABSTRACT

Luminescence of the Bi^{3+} single and dimer centers in UV and visible ranges is studied in YAG:Bi (0.13 and 0.27 at% of Bi, respectively) single crystalline films (SCFs), grown by liquid phase epitaxy from a Bi_2O_3 flux. The cathodoluminescence spectra, photoluminescence decays, and time-resolved spectra are measured under the excitation by accelerated electrons and synchrotron radiation with energies of 3.7 and 12 eV, respectively. The energy level structure of the Bi^{3+} single and dimer centers was determined. The UV luminescence of YAG:Bi SCF in the bands that peaked at 4.045 and 3.995 eV at 300 K is caused by radiative transitions of Bi^{3+} single and dimer centers, respectively. The excitation spectra of UV luminescence of Bi^{3+} single and dimer centers consist of two dominant bands, peaked at 4.7/4.315 and 5.7/6.15 eV, related to the $^1S_0 \rightarrow {}^3P_1$ (A band) and $^1S_0 \rightarrow {}^1P_1$ (C-band) transitions of Bi^{3+} ions, respectively. The excitation bands that peaked at 7.0 and 7.09 eV are ascribed to excitons bound with the Bi^{3+} single and dimer centers, respectively. The visible luminescence of YAG:Bi SCF presents superposition of several wide emission bands peaking within the 3.125–2.57 eV range and is ascribed to different types of excitons localized around the Bi^{3+} single and dimer centers. Apart from the above mentioned A and C bands the excitation spectra of visible luminescence contain wide bands at 5.25, 5.93, and 6.85 eV ascribed to the $O^{2-} \rightarrow Bi^{3+}$ and $Bi^{3+} \rightarrow Bi^{4+} + e$ charge transfer transition (CTT) in Bi^{3+} single and dimer centers. The observed significant differences in the decay kinetics of visible luminescence under excitation in A and C bands of Bi^{3+} ions, CTT bands, and in the exciton and interband transitions confirm the radiative decay of different types of excitons localized around Bi^{3+} ions in the single and dimer centers.

1. Introduction

Bi^{3+}-doped single crystalline films (SCFs) of Y–Lu–Al garnets grown by the liquid phase epitaxy (LPE) method from melt-solutions based on a Bi_2O_3 flux attract attention due to the possibility of their applications for cathodoluminescence screens [1] and scintillators [2]. The condition of growth of these SCF by LPE method enables one to change in them the concentration of Bi^{3+} ions in a wide (from 10^{-4} to 10^{-1} at%) concentration range [1–3]. Depending on Bi^{3+} content in the SCF the dominant Bi^{3+} emission in UV (low Bi^{3+} concentration) or blue (high Bi^{3+} concentration) spectral ranges can be obtained [1–3]. Apart from practical applications, the Bi-doped SCFs of garnet compounds are also very useful model objects for basic research of the nature of Bi^{3+} luminescence in oxides [3–5].

In our previous works, we have studied the luminescence of Bi^{3+} ions in $Y_3Al_5O_{12}$:Bi (YAG:Bi) [2,3,5] and $Lu_3Al_5O_{12}$:Bi (LuAG:Bi) SCFs [2,4,5]. The luminescence spectrum of these garnets typically shows two main emission bands in the ultraviolet (UV) and visible (vis) spectral ranges caused by Bi^{3+} doping [6–10]. Relatively narrow UV band with a small Stokes shift is related to the radiative transition from the triplet $^3P_1$ and $^3P_0$ levels to the $^1S_0$ ground state of Bi^{3+} ions [2–10]. The origin of a broad visible emission band with a large Stokes shift is now still under research. This complex band consists of at least two (low and high-energy) bands, which were ascribed to the emission of exciton localized around Bi^{3+} single and dimer or clusters centers, respectively [4,5].

Not well established separation of luminescence of the Bi^{3+} single and dimer centers in the UV and visible ranges stimulated us to perform more detailed investigation of the Bi-doped SCF in a wide concentration range of the activator. In this work, we study the Bi^{3+} luminescence in YAG:Bi SCF. With respect to isostructural LuAG, the YAG host possesses a somewhat larger crystal field strength [10,11], which can be useful for spectral separation of

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* Corresponding author. Tel.: +3803229394205; fax: +380322448585.
E-mail address: zorenko@electronics.wups.lviv.ua (Y. Zorenko).

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luminescence of the Bi^{3+} single and dimer centers. For this purpose we study the luminescence characteristics of these centers under excitation by synchrotron radiation (SR) with energy in the exciton and fundamental absorption ranges as well as under excitation in the absorption bands of the Bi^{3+} single and dimer centers.

2. Samples and experimental technique

We studied two samples of YAG:Bi SCF with dimensions of $1.5\times1.8\,cm^2$ and thicknesses of 12 and 19 μm, labelled later as YAG:Bi1 and YAG:Bi2 samples, respectively. These samples (Table 1) were grown on (1 1 0) oriented YAG substrates at LOM, Lviv University, by the LPE method from a super-cooled melt-solution based on Bi_2O_3 oxide flux. The concentration of crystal-forming components (Y_2O_3 and Al_2O_3 oxides) with respect to the total content of melt-solution was 5.7 mol% (YAG:Bi1) and 6.8 mol% (YAG:Bi2). These values determine different temperatures of saturation of respective melt solutions $T_S=1023$–1025 and 1081–1086 °C as well as the ranges of SCF growth temperature $T_g=993$ and 1051 °C, respectively, see Table 1. The concentration of bismuth in both YAG:Bi SCF was determined using a JEOL JXA-733 electron microprobe analyzer and was found to be 0.13 and 0.27 at% in YAG:Bi1 and YAG:Bi2 samples, respectively, see Table 1. Due to the large ionic radius of Bi^{3+} (1.17 Å for 8-fold coordination) [12], Bi^{3+} ions are localized exclusively in the dodecahedral {c}-sites, replacing Y^{3+} cations in the garnet lattice.

The cathodoluminescent (CL) spectra of YAG:Bi SCF were measured at 300 K with a set-up based on a DMR-4A monochromator and a PMT FEU-106 under pulsed e-beam excitation (duration of pulse of 2 μs and frequency of 30–3 Hz) with an energy of electrons of 9 keV and a beam current of 100 μA. The CL spectra were corrected for the sensitivity of detection part of the set-up. The time-resolved photoluminescence (PL) of YAG:Bi1 and YAG:Bi2 SCFs was investigated at 10 and 300 K at the Superlumi station at HASYLAB under excitation by synchrotron radiation (SR) with an energy of 3.7–25 eV. The emission and excitation spectra were measured both in the integral regime and in time gates of 1.2–6 and 150–200 ns (called from now on as the fast and slow component, respectively) in the limits of SR pulse with a repetition time of 200 ns and duration of 0.127 ns. The excitation spectra were corrected for the spectral dependence of transmittance of Al-grating and intensity of SR beam, but emission spectra were not corrected. Using SR excitation the decay kinetics of the luminescence was measured in the time range of 0–50 ns at 10 K and 0–200 ns at RT. To follow the decay kinetics up to μs time scale the decay curves were further measured with a modified spectrofluorometer 199S (Edinburgh Instruments) under excitation with a nanosecond coaxial hydrogen-filled flashlamp using single grating monochromators. The detection was performed with a TBX-04 photomultiplier module (IBH Scotland) using the method of time-correlated single photon counting. A deconvolution procedure (SpectraSolve software package) was applied to extract true decay times using the multiexponential approximation.

3. Results and discussion

CL spectra of YAG:Bi1 and YAG:Bi2 SCF samples (Fig. 1a) show the typical ns^2-ions luminescence structure with two bands in the UV and vis spectral ranges peaked at 4.11 and 2.64 eV, respectively. Mutual intensity of emission in UV and vis bands strongly depends on Bi^{3+} concentration (Fig. 1a). In the previous works [1,2] we showed that the value of parameter K (equal to the ratio of intensities of the UV/vis bands) in YAG:Bi and LuAG:Bi SCF increases with decrease of Bi^{3+} content and vice versa. The rather different (8.0) and (4.2) K-values in the studied YAG:Bi1 and YAG:Bi2 SCFs, respectively, see Table 1, can be explained by varying concentration ratio of the Bi^{3+} single and dimer centers.

The dependence of shape and position of UV and vis bands on Bi^{3+} content in YAG:Bi SCF and energy of excitation can be studied from the difference in the CL spectra under e-beam excitation and PL spectra under excitation in A-absorption band of Bi^{3+} ions ($^1S_0\rightarrow{}^3P_1$ transitions; Figs. 1 and 2). The main differences in the CL (Fig. 2a) and PL (Fig. 2b) spectra of YAG:Bi1 and YAG:Bi2 SCFs, depending on Bi^{3+} concentration, are observed only in the 2.5–2.0 eV range. Specifically, the larger intensity of emission in this range in YAG:Bi1 SCF with lower Bi content can be caused by prevailing emission of Bi^{3+} single centers and partly by the emission of Ce^{3+} trace impurity emitting in YAG:Ce SCF just in the same spectral range in the band peaking at 2.34 and 2.17 eV [11].

The positions of UV emission band in YAG:Bi1 and YAG:Bi2 SCFs in CL spectra (Fig. 1a) are shifted towards the high-energy side to 4.11 eV with respect to the position of the same bands at 4.05 and 3.995 eV under excitation in the A band of single and dimer centers, respectively (Fig. 1b). In CL spectra the vis emission of YAG:Bi1 and YAG:Bi1 SCFs shows the dominant band at 2.64 eV (Fig. 1a) while under excitation in the A band of Bi^{3+} single and dimer centers, an additional strong emission band at 2.855 eV appears in both SCF (Fig. 1b).

Temperature dependence of the positions of UV and vis bands is shown in Fig. 2a. The UV luminescence of YAG:Bi1 with lower Bi content at 10–300 K under excitation in A band of Bi^{3+} ions presents a superposition of closely lying emission bands peaking at 4.045 and 4.0 eV caused by $^3P_{1,0}\rightarrow{}^1S_0$ radiative transitions in Bi^{3+} single centers (Fig. 2a; curves 1 and 2, respectively). These transitions show typical two-component decay kinetics of the Bi^{3+} ion luminescence in UV range (Fig. 3a). The decay curves measured in the 0–50 ns range (Fig. 3a) can be approximated by two-component expression $I(t)=A_1\exp(-t/\tau_{fast})+A_2\exp(-t/\tau_{slow})$ + background, where τ_{fast} and τ_{slow} correspond to the decay time of Bi^{3+} luminescence caused by prompt $^3P_1\rightarrow{}^1S_0$ and $(^3P_0\text{–}{}^3P_1)\rightarrow{}^1S_0$ radiative transitions, respectively.

Temperature dependences of decay kinetics (a) and decay time of the fast component (b) of UV luminescence of YAG:Bi2 SCF in the 8–300 K range are shown in Fig. 3. Two-step decrease of the fast component decay time of UV luminescence occurs from 250 ps at 8 K down to ~100 ps in 8–20 K range and to several tens-of-ps above 150 K. Relative intensity of the fast component with respect to the slow one is below 1%. The values and temperature dependence of decay time of UV luminescence in YAG:Bi SCF are similar to those in YGG:Bi [9].

Table 1
Growth conditions and luminescence properties of YAG:Bi SCF prepared by the LPE method from a Bi_2O_3 based flux. T_g-temperature of growth, h-SCF thickness, CL-intensity of ultraviolet (UV) and visible (vis) bands with respect to CL intensity of YAP:Ce reference crystal.

SCF sample	Bi content (at%)	T_g (°C)	h (μm)	CL intensity in UV–VIS bands	K=ratio of UV–VIS intensity
YAG:Bi 1	0.13	993	19	9.6/1.2	8.0
YAG:Bi 2	0.27	1051	30.5	7.5/1.8	4.2

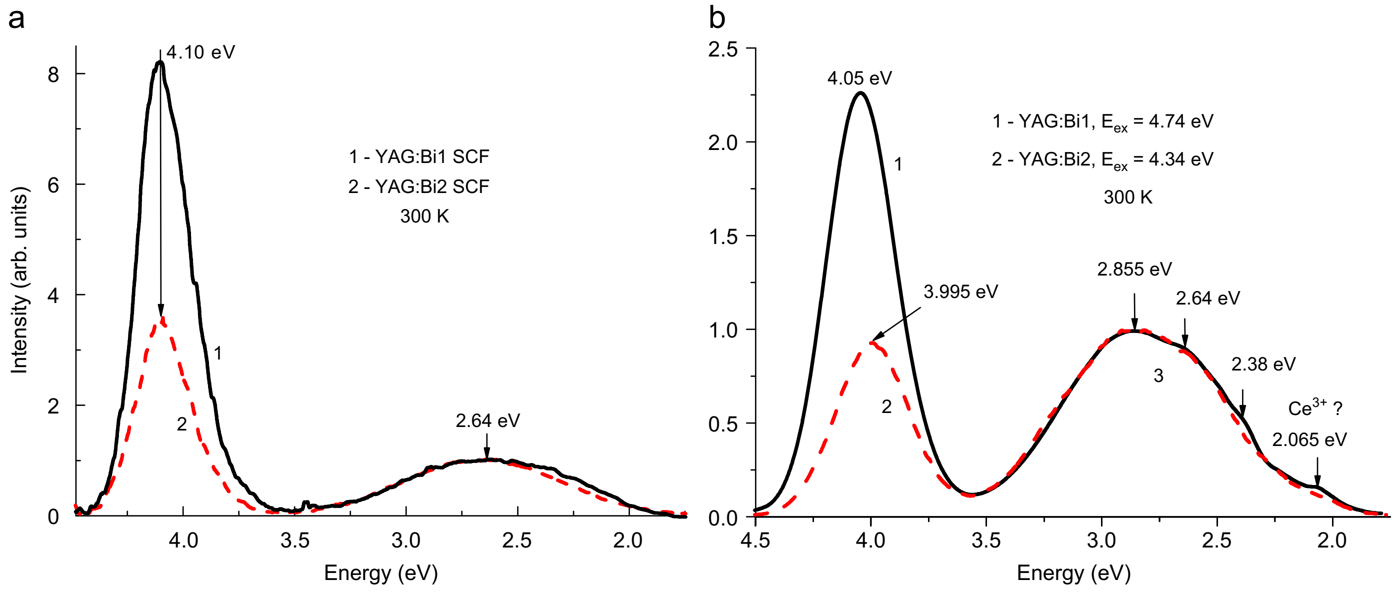

Fig. 1. (a)CL spectra of YAG:Bi1 (1) and YAG:Bi2 (2) SCF at 300 K and (b)luminescence spectra YAG:Bi1 (1) and YAG:Bi2 (2) SCF under excitation by SR in A and A′ bands of single (1) and dimer (2) centers at 4.74 and 4.34 eV, respectively. All spectra are normalized on the maximum intensity of the vis band.

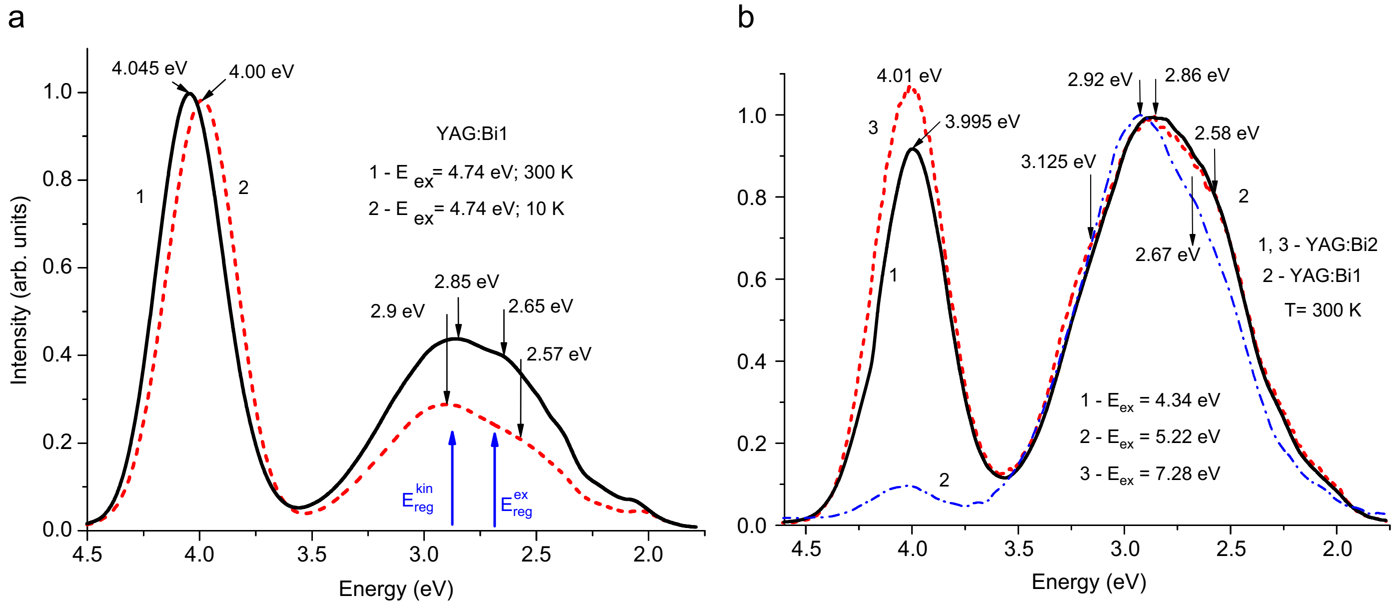

Fig. 2. (a)normalized emission spectra of YAG:Bi1 SCF under excitation by SR at 4.74 eV in A band of single Bi^{3+} centers at 300 K (1, 2) and 10 K (2) and (b)emission spectra of YAG:Bi2 (1, 2) and YAG:Bi1 (3) SCF at 300 K under excitation by SR at 4.34 eV in A′ band of Bi^{3+} dimer centers (1), at 5.22 eV in the band related to $O^{2-} \rightarrow Bi^{3+}$ CTT (2) and at 7.28 eV in exciton range (3).

The temperature dependence of slow emission component of UV luminescence was studied recently in detail in LuAG:Bi SCF [4] and in both LuAG:Bi and YAG:Bi SCFs in Ref. [5]. Below 80 K, its decay time is a constant of about 1 ms value . Above 150 K it starts to decrease. Evaluated in the 200 ns time interval, the decay times at 300 K are shown in Table 2, see also Fig. 5a.

The vis emission of YAG:Bi1 SCF (Fig. 2a) at 300 K under excitation in A band of Bi^{3+} of single centers at 4.74 eV consists of low and high-energy overlapped broad bands with larger FWHM and Stokes shift with respect to UV bands. The form of vis emission spectrum also depends on temperature. Specifically, the couple of bands peaking at 2.85 and 2.65 eV prevails in the spectrum of vis emission at 300 K (Fig. 2a; curve 1), whereas at 10 K they shift to 2.92 and 2.53 eV, respectively (Fig. 2b; curve 3). We previously assumed [4,5] that both vis bands have an exciton origin and are caused by emission of excitons localized around the Bi^{3+} single and dimer centers. Thus, the observed shift of vis emission bands with temperature (Fig. 2a) can be caused by (i) re-distribution of radiative transition from excited states of the *same* centers, responsible for vis emission, similar to changes observed in the position of UV bands and (ii) re-distribution of intensities of the radiative transition of exciton localized near the Bi^{3+} single and dimer centers.

In the present work, we found that the form of vis bands strongly depends on energy of excitation (Figs. 1 and 2). Specifically, under excitation in the A band of single centers at

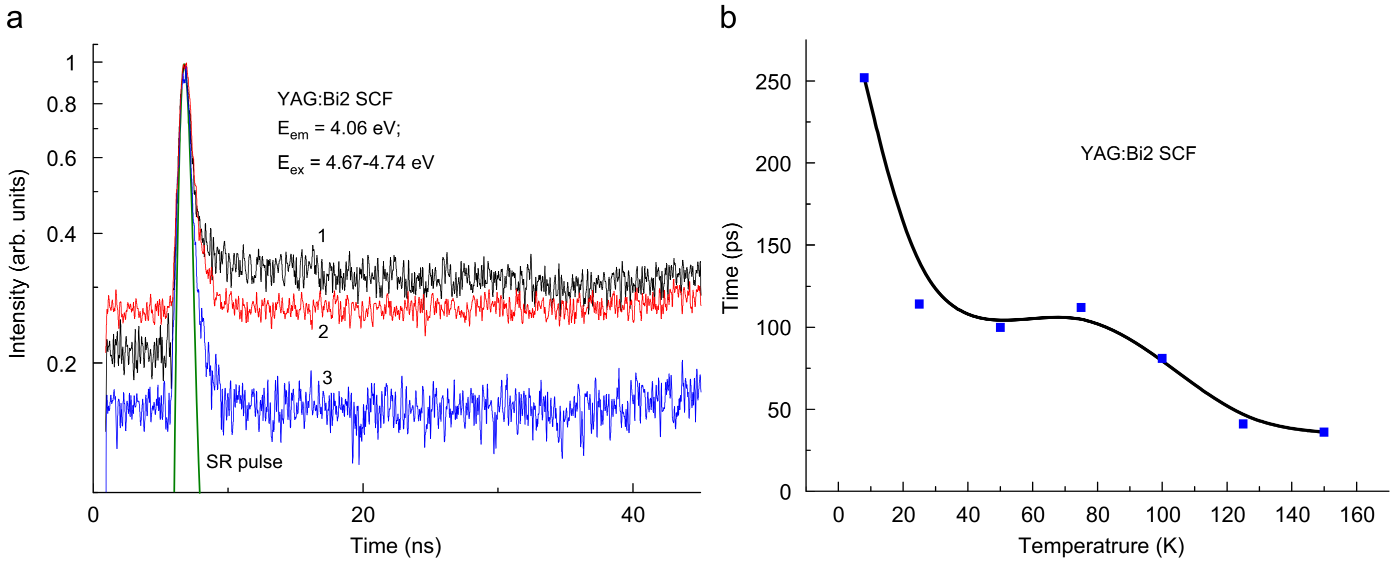

Fig. 3. Temperature dependence of decay kinetic (a) of UV emission related to the $^3P_{1,0}\rightarrow{}^1S_0$ transition measured in 0–50 ns time gate and (b) temperature dependence of fast components of UV luminescence of YAG:Bi2 SCF in the 8–300 K range.

Table 2
Parameters of the three-component approximation of decay curves presented in Fig. 5, YAG:Bi2 SCF, 300 K.

Curve number	E_{em} (eV)	E_{ex} (eV)	A_1	τ_1 (ns)	A_2	τ_2 (ns)	A_3	τ_3(ns)	A_0
1	4.06	4.27 (A′ band)	0.055	<0.03	0.003	22	0.27	488	0.0042
2	4.06	4.74 (A band)	2.9	0.08	0.04	14	0.25	395	0.0043
3	4.06	5.64 (C band)	2.7	0.11	0.04	10	0.34	462	0.0058
4	2.88	4.27 (A′ band)	0.85	0.35	0.25	5.2	0.59	729	0.11
5	2.88	4.74 (A band)	0.84	0.64	0.14	6.4	0.57	618	0.12
6	2.88	5.22 (CTT)	0.88	1.6	0.06	16	0.41	738	0.08
7	2.88	5.63 (C band)	0.87	0.824	0.17	9.7	0.48	491	0.09
8	2.88	5.95 (CTT)	0.9	1.4	0.17	19.6	0.35	389	0.05
9	2.88	6.88 (CTT)	1.1	1.5	0.17	16.8	0.18	211	0.02
10	2.88	11.79 ($E>E_g$)	1.7	0.87	0.31	4.1	0.02	182	0.003

4.74 eV, the couple of emission bands peaking at 2.85 and 2.65 eV prevails in the spectrum of vis luminescence of YAG:Bi1 SCF at 300 K (Fig. 2a; curve 1). However, under the excitation at 5.22 eV in the band related to $O^{2-}\rightarrow Bi^{3+}$ charge transfer transition (CTT) [13], another couple of emission bands peaking at 2.92 and 2.53 eV dominates (Fig. 2b; curve 3). Taking into account the rather large content of Bi^{3+} single centers in the studied sample, these results point to the possible existence of two different types of exciton localized around Bi^{3+} ions, which can be created under the above-mentioned excitations. They are labelled as Bi^{4+}-e and Bi^{2+}-h centers.

The excitation spectra of UV and vis luminescence in YAG:Bi1 and YAG:Bi1 SCFs at 10 K are shown in Fig. 4a and b, respectively. It is important to note that for recording the excitation spectra, we used reflection geometry of measurements and performed the investigation on very thin SCF samples. Therefore, any re-absorption effects were minimized. At the same time, we cannot exclude the existence of some perturbation of the excitation spectra in Fig. 4 due to re-absorption in the range of intensive A band.

The excitation spectra of UV emission band in YAG:Bi1 SCF with lower Bi content, monitored at 4.06 eV (Fig. 4; curve 1), show typical two-band structure related to the most intensive $^1S_0\rightarrow{}^3P_1$ and $^1S_0\rightarrow{}^1P_1$ transitions of Bi^{3+} single centers (A and C bands, respectively). The high-energy excitation band peaking at 7.0 eV corresponds to the creation of excitons bound at the Bi^{3+} single centers in YAG host. Apart from these bands, another strong A′ band, peaking at 4.31 eV, is present in the excitation spectra of UV emission. Most probably, this band is related to the A band of the Bi^{3+} dimer centers. If this conclusion is correct, the emission of dimer centers can be effectively excited via the luminescence of single centers due to the strong overlap of the corresponding emission bands of the former centers and the excitation bands of the latter in the UV range. This can be the reason for the observed non-exponential decay of UV luminescence in Y–Lu–Al garnets even at relatively low (~0.06–0.07 at%) concentrations of Bi^{3+} ions [2].

The excitation spectra of the vis emission in YAG:Bi1 and YAG:Bi2 SCFs (Fig. 4, curves 2 and 4, respectively) have completely different shapes with respect to those of UV emission (Fig. 4; curves 1 and 3). Apart from the A, A′ and C, C′ bands of the single and dimer centers, additional two or even three intensive excitation bands with large FWHM peaking around 5.25, 5.93, and 6.85 eV exist in excitation spectra of vis emission of these SCF samples. Most probably these bands are related to the $O^{2-}\rightarrow Bi^{3+}$ and $Bi^{3+}\rightarrow Bi^{4+}$ + e CTT in single and dimer centers, which provide alternative channels for the excitation of vis emission in YAG:Bi SCF [3]. It is worth noting that the CTT band peaking at 5.93 eV strongly overlaps with C and C′ bands of Bi^{3+} single and dimer centers. Intensity of the CTT bands markedly increases with rising Bi^{3+} content in the studied YAG:Bi SCF samples (Fig. 4; curves 2 and 4).

The decay of UV luminescence in YAG:Bi1 SCF sample, monitored at 4.06 eV at 300 K, under excitation in the A and C

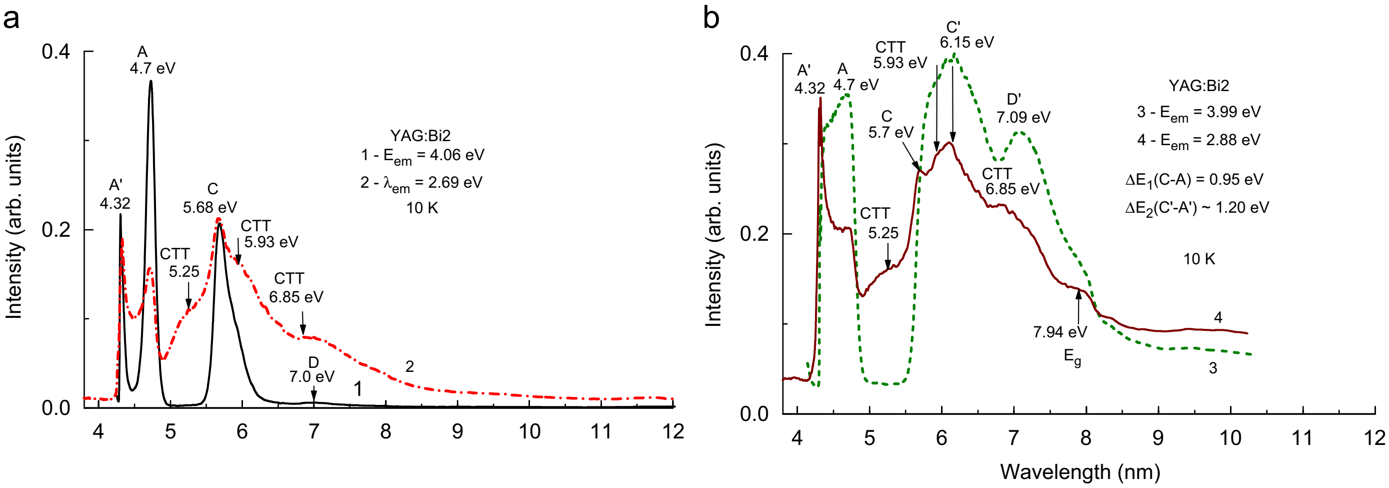

Fig. 4. Excitation spectra of UV (1, 3) and vis (2, 4) luminescence in YAG:Bi1 (1, 2) and YAG:Bi2 (3, 4) SCF at 300 K, registered at 4.06 eV (2), 3.99 eV (2), 2.69 eV (3) and 2.88 eV (4), respectively.

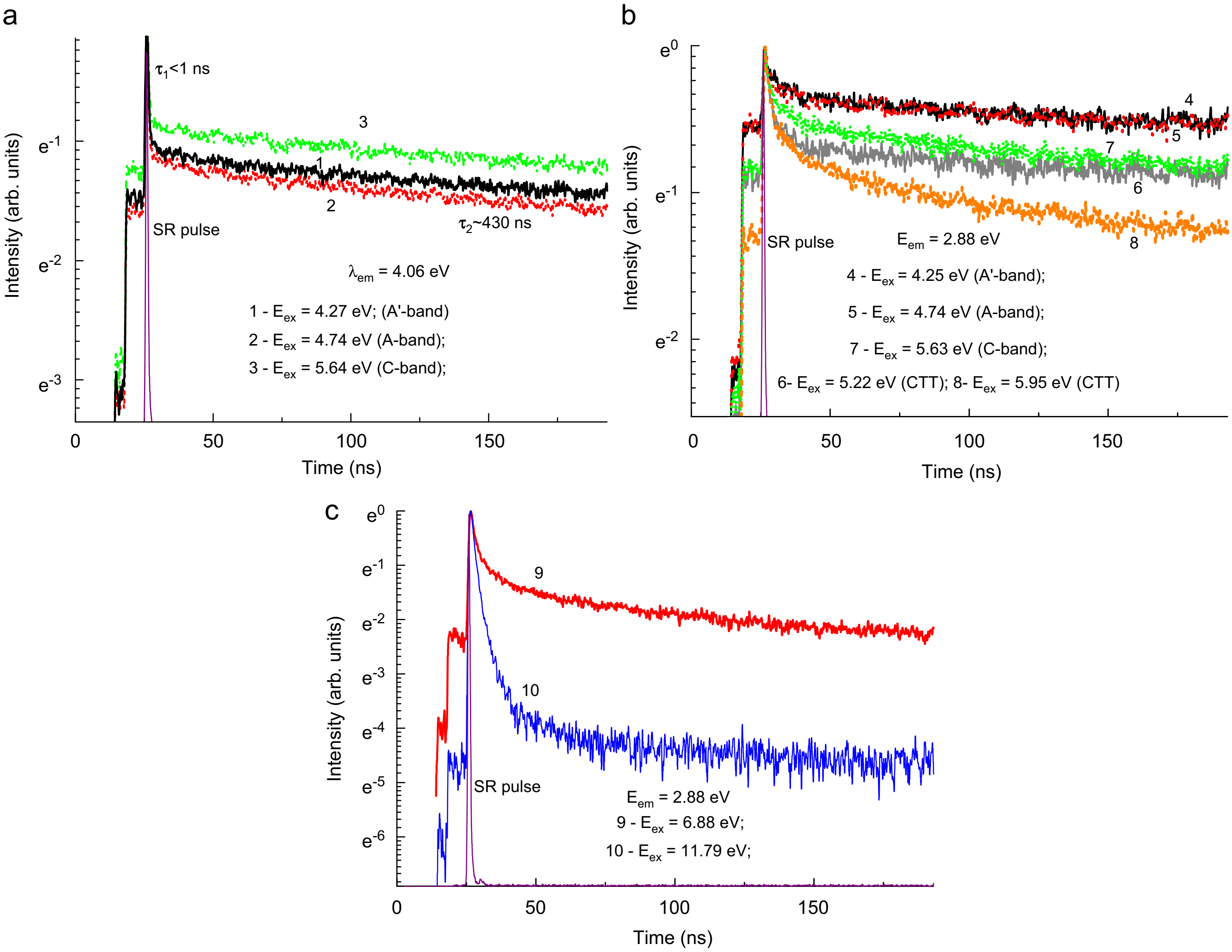

Fig. 5. Decay kinetics of UV emission at 4.06 eV (a) and vis emission at 2.88 eV (b, c) in YAG:Bi SCF at 300 K under excitation in A and C bands (a, b) and CTT bands (b) as well as in exciton range and range of interband transition (c) with the corresponding energies indicated in the legend of figures.

bands of Bi^{3+} single centers and A′ band of dimer centers, is presented in Fig. 5a. The parameters of three-component approximation of decay curves are shown in Table 2. Generally, the decay of UV luminescence of single and dimer centers at 300 K contains the very fast component with decay time $\tau_1 < 1$ ns arising from the prompt $^3P_1 \rightarrow {}^1S_0$ transition and the slow component with decay times τ_2 and τ_3 in the tens and hundred ns time range related to thermally populated $(^3P_0 \rightarrow {^3P_1}) \rightarrow {^1S_0}$ transition. It should be noted that the main slow component of UV luminescence of Bi^{3+} single centers is slightly faster ($\tau_3 = 395$ ns) than that in dimer center ($\tau_3 = 488$ ns) under excitation in the A and A′ bands, respectively (Table 2).

Due to the narrow time interval (200 ns) for the decay kinetics investigation under excitation by SR, we also performed measurements at a wider time scale using H_2-filled nanosecond flashlamp excitation in the A and A′ bands of single and dimer centers and emission registration at 260 and 320 nm, respectively (Fig. 6). Using such combination of the mentioned excitation/emission wavelengths we can better separate the decay of the Bi^{3+} single centers (close to curve 1 in Fig. 6a for YAG:Bi1 SCF) and dimer ones (close to curve 2 in Fig. 6b for YAG:Bi2 SCF). As can be seen from Fig. 6, the decay of Bi^{3+} single centers is systematically faster than that of dimer centers (curves 2). In agreement with data presented in [2], the slower decay of UV luminescence of Bi^{3+} single centers in YAG:Bi1 SCF (arising from $(^3P_0 – {^3P_1}) \rightarrow {^1S_0}$ transition) is the superposition of two components with decay times of 187 and 756 ns at 300 K (Fig. 6a; curve 1). The decay of UV luminescence of the Bi^{3+} dimer centers in YAG:Bi2 SCF arising from the same transition consists of two components with the decay times of 235 and 1324 ns at 300 K (Fig. 6b; curve 2).

The evolution of decay kinetics of vis luminescence in the YAG:Bi1 SCF sample, monitored at 2.88 eV at 300 K, depending on the excitation energy of SR radiation in the 4.25–11.8 eV range, is presented in Fig. 5b and c. These decay curves can be approximated by three components (Table 2). The decay of the vis emission under excitation in the A′, A and C bands in YAG:Bi1 SCF (Fig. 5b) is notably changed in comparison with that of UV luminescence (Fig. 5a). The shape of decay curves of vis luminescence under the intra-center excitation of the Bi^{3+} dimer centers in A and C band of single centers (curves 4 and 6, respectively) and A′ band of dimer centers (curves 5) confirms their exciton origin. Specifically, such a type of decay kinetics is typical for the radiative transition from the triplet state of excitons localized around Bi^{3+} single and dimer centers [2–5].

Under excitation in the CTT bands at 5.22, 5.93, and 6.85 eV the vis decay kinetics of the localized exciton emission (Fig. 5b; curves 6–8) is markedly changed with respect to that under excitation in A, A′ and C bands of single and dimer centers (Fig. 4b; curves 4 and 5, see also Table 2). It becomes much faster under excitation in the exciton absorption range (Fig. 5c; curve 9) and especially in the range of interband transitions (Fig. 5c; curve 10) in comparison with those under excitation in A and C bands (Fig. 5b; curves 4, 5) or CTT bands (Fig. 5b; curves 6–8). These results support our assumption concerning the formation of at least three different types of localized excitons related to the Bi^{3+} single and dimer centers under conditions of intra-center excitation of Bi^{3+} ions, excitation in the $O^{2-} \rightarrow Bi^{3+}$ CTT bands and interband transitions.

All the above-mentioned spectral-kinetic characteristics of the Bi^{3+} single and dimer centers as well as those of localized excitons are summarised in Table 3.

4. Conclusion

Luminescence of Bi^{3+}-related centers in YAG:Bi (0.13 and 0.27 at%) single crystalline film (SCF) grown by liquid phase epitaxy from a melt-solution based on the Bi_2O_3 flux was studied by means of cathodoluminescence spectra, photoluminescence decay, and time-resolved spectra under excitation within the 3.7–10 eV range and at 10 and 300 K temperatures.

Energy level positions regarding Bi^{3+} single and dimer centers were determined. UV luminescence of YAG:Bi (0.13 at% of Bi) SCF with a comparatively larger concentration of the Bi^{3+} single centers in the bands peaking at 4.045 and 4.0 eV is ascribed to the radiative transition from the $^3P_1$ and $^3P_0$ levels to the $^1S_0$ ground state of the Bi^{3+} single ions. Excitation spectra of UV emission of Bi^{3+} single centers show two intensive A- and C-bands peaking at 4.7 and 5.7 eV, related to $^1S_0 \rightarrow {^3P_1}$ and $^1S_0 \rightarrow {^1P_1}$ transitions,

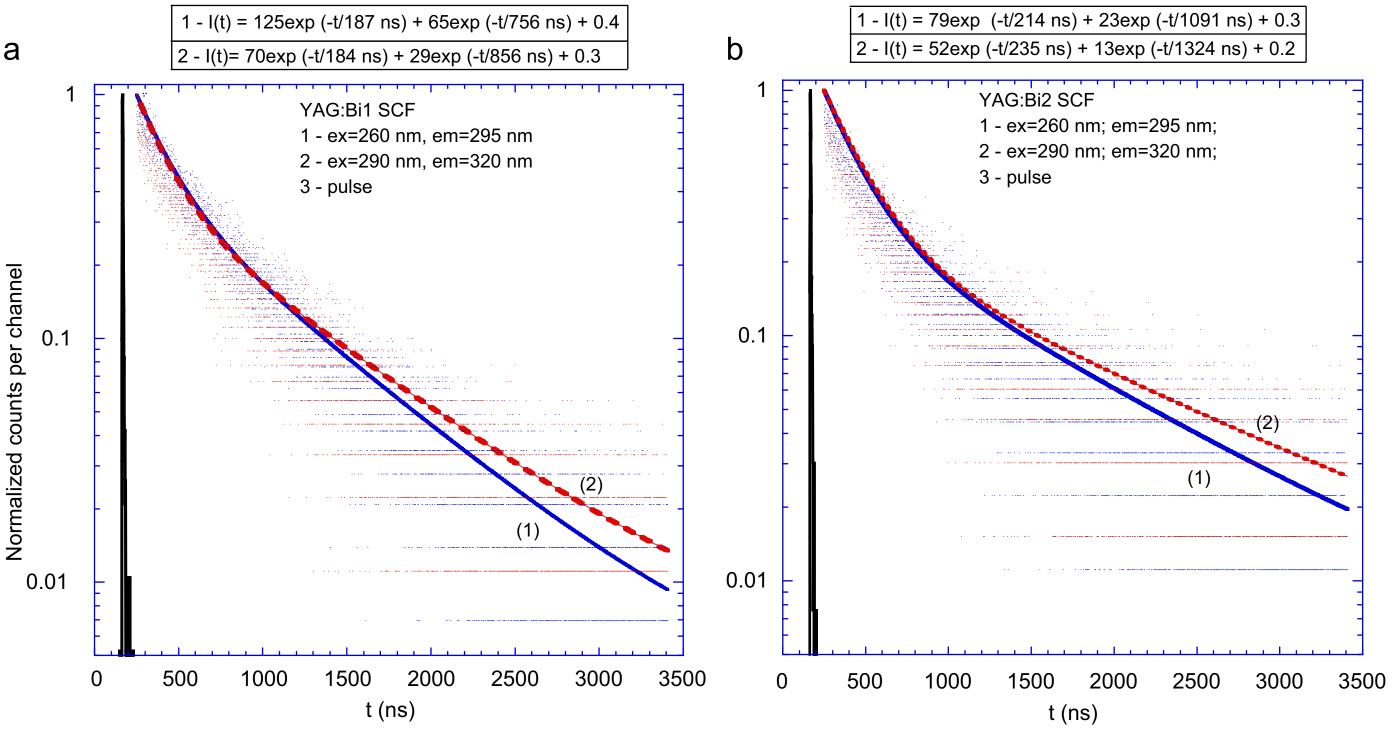

Fig. 6. Decay of Bi^{3+} single and dimer centers in YAG:Bi1 (a) and YAG:Bi2 (b) SCFs under excitation /registration wavelength of 260/295 and 295/320 nm (curves 1 and 2, respectively). The solid lines give the two-component approximation $I(t)$ of the decay curves shown above the figures.

Table 3
Spectral-kinetic characteristics of Bi^{3+}-related centers in YAG:Bi SCF at 10 K.

Type of centers	Position of emission band (eV)	Position of (A-, C-, D-) excitation bands (eV)	Position of CTT band (eV)	E_{ex}, E_g (eV)	Decay time (ns)
Single centers	4.0 (8 K);	4.7; 5.7, 7.0			0.25ns;
	4.045 (300 K)				< 0.1; 12 ± 2, 430 ± 35
Dimer centers	3.995 (300 K)	4.315; 6.15; 7.09	5.25; 5.93, 6.85		< 0.1; 22; 490
Localized exciton first type	2.65 (300 K)	4.315; 4.7; 5.7, 7.0	5.25; 5.93, 6.85		< 0.1; 6.4; 620
	2.85 (300 K)				< 0.1; 5.2; 730
	2.92; 2.53 (10 K)				
Localized exciton second type	2.92; 2.67 (300 K)		5.25		1.6, 16.0, 740
			5.93		1.4; 19.6; 390
			6.85		1.5; 16.8; 211
Localized exciton third type	3.125			7.28; 7.94 11.79	< 0.1, 4.1; 182

respectively, and a low-intensity band at 7.0 eV, corresponding to an exciton bound to the single Bi^{3+} centers.

The maximum of UV luminescence in YAG:Bi (0.27 at% of Bi) SCF at 3.995 eV at 300 K, corresponding to $^3P_{1,0} \rightarrow {}^1S_0$ radiative transition, is low energy shifted with respect the UV emission band of Bi^{3+} single centers due to dominant emission of the Bi^{3+} dimer centers in this sample.

Excitation spectra of UV luminescence of the Bi^{3+} dimer centers show two dominant bands peaking at 4.315 and 6.15 eV, related to $^1S_0 \rightarrow {}^3P_1$ and $^1S_0 \rightarrow {}^1P_1$ transitions, respectively, and a band at 7.09 eV, corresponding to an exciton bound around the Bi^{3+} dimer center. Luminescence of the Bi^{3+} dimer centers can be effectively excited via the single centers due to strong overlap of the corresponding emission bands of the latter and the excitation bands of the former centers in the UV range. This can explain the earlier observed non-exponential decay kinetics of the Bi^{3+} UV luminescence in Y–Lu–Al garnets even at a relatively low (0.06–0.07 at%) content of Bi^{3+} ions [2].

We show that the visible luminescence of YAG:Bi SCF is a superposition of several broad emission bands ascribed to excitons localized around the Bi^{3+} single and dimer centers. The shape of visible luminescence strongly depends on energy of excitation and temperature. The excitation spectra of visible luminescence in YAG:Bi SCF contain relatively narrow A and C bands, corresponding to $^1S_0 \rightarrow {}^3P_1$ and $^1S_0 \rightarrow {}^1P_1$ transitions, respectively, of the Bi^{3+} single and dimer centers. The excitation in these bands provides the *first* channel for the creation and radiation decay of excitons, localized around Bi^{3+} single and dimer centers, with emission maximum at 2.65 and 2.85 eV, respectively. The excitation within broad bands at 5.25, 5.93, and 6.85 eV corresponds to the charge transfer transition (CTT) between oxygen ligands and Bi^{3+} ions and Bi^{3+} ions and bottom of conduction band in both the Bi^{3+} single and dimer centers. The excitation in these bands provides the second channel for excitation of visible luminescence peaking at 2.92 and 2.67 eV at 300 K. Excitation around the host band edge results in the direct creation of excitons, localized around Bi^{3+} single and dimer centers, and provides the third channel for excitation of visible luminescence peaking at 3.135 eV.

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