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Intrinsic and Ce³⁺-related luminescence of YAG and YAG:Ce single crystals, single crystalline films and nanopowders

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ABSTRACT

A comparative analysis of the luminescent properties of YAG and YAG:Ce nanopowders (NP) in comparison with single crystalline film (SCF) and single crystal (SC) analogues was performed under excitation by a pulsed synchrotron and X-ray radiation. It was shown that the natural defects concentration in NP was between the SC with a large (~0.18–0.19 at.%) concentration of Y_{Al} antisite defects (AD) and SCF of these garnets where Y_{Al} AD were completely absent. At the same time, Ce³⁺ doped YAG NP showed luminescent properties close to those of YAG:Ce SCF.

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1. Introduction

Nanopowder (NP) ceramics of Y₃Al₅O₁₂ garnet (YAG) doped with rare-earth ions are currently considered as an alternative to single crystal (SC) analogues for scintillators and laser media applications [1]. The main differences concerning the properties of YAG-based NP are connected with the low-temperature preparation of this material by sol–gel methods [2,3]. Therefore, NP can possess, in principle, a lower concentration of the Y_{Al} antisite defects (AD) and vacancy-type defects (VD), first of all, oxygen vacancies, which are typical for high-temperature (1830 °C) melt-growth YAG SC [4,5]. The mentioned type of defects creates emission centers which significantly contribute to the intrinsic UV luminescence of YAG SC [6]. These centers are also involved in the processes of high-energy excitation of the Ce³⁺ luminescence in YAG:Ce SC [7]. In this respect, the behavior of Ce-doped YAG NP must be close to the YAG:Ce single crystalline films (SCF) obtained by the liquid phase epitaxy (LPE) method from melt-solutions at low (950–1050 °C) temperatures [6,7].

In this work, a comparative analysis of the time-resolved intrinsic and Ce³⁺-related luminescence of YAG and YAG:Ce NP, SC and

SCF was performed for the first time under excitation by pulsed X-ray and synchrotron radiation (SR).

2. Samples and experimental technique

YAG and YAG:Ce NP were prepared with the Pechini method in the University of Wrocław [3]. Al(NO₃)₃, Y(NO₃)₃ and Ce(NO₃)₃ initial compounds together with citric acid and ethylene glycol were dissolved in water and heated at 80–90 °C for condensation. After a few hours the temperature was slowly increased up to 200 °C to form a polymer resin. Afterwards, the precursor was heat-treated at 1000 °C in air. A portion of the YAG:Ce NP was additionally heat-treated at 600 °C in the N₂–H₂ (95–5%) atmosphere to reduce the Ce⁴⁺ fraction which could exist after the former heating at oxidizing conditions. The XRD patterns of the YAG and YAG:Ce NP proved a crystallographic purity of the products. The average size of NP crystallites calculated with the Scherrer formula reached 27–30 nm.

The SCF were crystallized from a melt-solution based on a PbO–B₂O₃ flux by the LPE method on YAG substrates in the University of Lviv [6,7]. The YAG and YAG:Ce SC were grown from the melt by the Czochralsky and Bridgman methods, respectively. Y₂O₃ and CeO₂ oxides of 5 N purity and Al₂O₃ oxide of 4 N purity were used for all the technological experiments.

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A comparative analysis of the time-resolved intrinsic luminescence of YAG and YAG:Ce NP, SC and SCF was performed at 10 K under excitation by pulsed (0.127 ns) SR with the energy $E = 3.7$ – 25 eV at the Superlumi station (HASYLAB, DESY) within the framework of II-05-105 research projects. The emission and excitation spectra were measured with an ARC monochromator and PMT Hamamatsu R6358P both in the integral regime and in the 1.2–6 and 150–200 ns time intervals (fast and slow components, respectively) in the limits of the SR pulse with a repetition time of 200 ns. The decay kinetics of the luminescence was measured in the time range of 0–200 ns at 10 K. The excitation spectra were corrected for the spectral dependence of the excitation energy; the emission spectra were not corrected.

3. Experimental results and discussion

3.1. VUV spectroscopy of intrinsic emission of YAG and YAG:Ce NP

The luminescence spectra of YAG NP at 10 K under excitation by SR in the exciton range are shown in Fig. 1 and compared with the corresponding behavior of YAG SC and SCF from our previous paper [6]. The complex UV emission band of YAG NP (Fig. 1a, curves 1 and 2) contains a dominant band peaked at 3.78 eV of Y_{Al} AD [6] and a defect-related band peaked at 3.27 eV that was observed only in

YAG NP with a small grain size [8]. The high-energy tails of emission spectra of YAG NP can be caused by the low-intensity bands peaked at 4.27 and 4.80 eV related to the luminescence of excitons localized around the AD (LE(AD) emission) and self-trapped excitons (STE) luminescence, respectively [6]. In the visible range, the emission spectra of YAG NP also contain two bands peaked at 3.05 and 2.675 eV caused by the luminescence of F^+ and F -centers (oxygen vacancy trapping one or two electron, respectively) [5] (Fig. 1a, curve 3).

The integral (b) and time-resolved (c) luminescence spectra of YAG:Ce NP in the UV region under excitation in exciton and inter-band transition ranges at 10 K present a complex low-intensity band which is a superposition of the STE and LE(AD) emission bands peaked at 4.88 and 4.27 eV, respectively (Fig. 1a). The low-energy wings of this complex band under excitation by SR with the energy $E = 7.74$ – 7.07 eV (Fig. 1b and c) also contain two low-intensity bands peaked at 3.78 and 3.27 eV caused by the emission of Y_{Al} AD and NP-defect centers, respectively.

The excitation spectrum of the integral and time-gated components of LE(AD) emission in YAG NP monitored at 4.76 eV indicates forming an exciton state with two excited levels at 7.12 and 7.49 eV, which dominates in the spectra of fast and slow components, respectively (Fig. 2a). These states correspond to the radiative transition from the singlet and triplet excited levels of LE(AD) centers with different probability of radiation transition [6].

The time-resolved excitation spectra of the NP defect-related band monitored at 3.095 eV show a separate band peaked at 6.04 eV in the range of YAG optical transparency, and two resolved peaks in the exciton range at 6.93 and 7.33 eV, corresponding to

Fig. 1. (a) Emission spectra of YAG NP at 10 K under excitation by SR with $E = 7.99$ (1), 4.27 (2) and 6.01 eV (3) in the exciton ranges. The arrows indicate the positions of emission bands of the corresponding centers in YAG SCF and SC [6]; (b) emission spectra of intrinsic UV luminescence of YAG:Ce NP at 10 K under excitation by SR with $E = 13.45$ eV (1) in the range of interband transition and 8.14 eV (2) and 7.74 eV (3) in the exciton range; (c) emission spectra of integral (1), fast (2) and slow (3) emission components of YAG:Ce NP under excitation by SR with $E = 7.07$ eV.

Fig. 2. Excitation spectra of integral (1), fast (2) and slow (3) components of STE (a), NP defect-related (b) and Ce^{3+} luminescence in YAG NP (a, b) and YAG:Ce NP (c) at 10 K in the bands peaked at 260 nm (a), 400 nm (b) and 530 nm (c).

the creation of bound-state excitons around NP-related defects, as well as a peak at 7.17 eV, most probably related to the Y_{Al} AD emission (Fig. 2b). The band peaked at 8.0 eV is close to the threshold of the YAG interband transition [6] (Fig. 2b, curve 1).

The decay kinetics of the LE(AD) and Y_{Al} AD luminescence under excitation by SR with $E = 8.14$ eV in YAG NP is shown in Fig. 3a, curves 1 and 2, respectively. Both decay curves can be presented by a superposition of the fast and slow components with the decay time in the ns and 100 ns– μ s ranges, respectively, which correspond to the radiative transitions from the singlet and triplet excited state of excitons related to the mentioned centers [6].

3.2. VUV spectroscopy of Ce^{3+} luminescence in YAG:Ce NP

The integral and time-gated excitation spectra of the Ce^{3+} emission in YAG:Ce NP monitored at 2.3 eV are shown in Fig. 2c. It should be noted that the position of the main band in the excitation spectra of the fast component of Ce^{3+} emission in YAG:Ce NP in the exciton range at 6.94 eV corresponding to the formation of excitons bound with the Ce^{3+} ions (Fig. 2c, curve 2) is very close to the position of a similar band in YAG:Ce SCF [7]. At the same time, the intensity of the fast components of the Ce^{3+} emission is very low with respect to the intensity of the slow components (Fig. 2c, curves 2 and 3, respectively). It is worth noting that the excitation spectra of the integral and slow components of the Ce^{3+} luminescence in the exciton range also contain two dominant bands peaked at 7.09 and 7.49 eV (Fig. 2c, curves 1 and 3). The positions of these bands are very close to the position of the main bands in the excitation spectra of the LE(AD) luminescence in YAG NP (Fig. 2a). This indicates that the LE(AD) and other AD-related centers which are located mainly on the boundaries of NP, participate in the excitation of the Ce^{3+} emission in YAG:Ce NP. The band

at 8.09 eV is related to the onset of recombination excitation of the Ce^{3+} luminescence by e/h pairs.

The decay kinetics of the Ce^{3+} emission in YAP:Ce NP under excitation in the Ce^{3+} absorption band at 5.58 eV (Fig. 3b, curve 1) is strongly non-exponential in agreement with [9] and faster than the corresponding decay of the Ce^{3+} luminescence in YAG:Ce SC and SCF. For the quantitative description this decay curve can be presented by a superposition of fast and slow components with lifetimes of 25.2 and 102 ns, respectively. Under excitation in the exciton and interband transition ranges (Fig. 3b, curve 2) the decay kinetics of the Ce^{3+} emission in YAG:Ce NP can be presented by a superposition of two components with decay times of 42 and 188 ns corresponding to the Ce^{3+} luminescence excitation by e/h pairs and a delayed energy transfer to Ce^{3+} ions from the defect-related centers, respectively. It should be noted that due to a significant participation of the AD and VD-related centers in the excitation of the Ce^{3+} luminescence mainly on the surface of YAG:Ce NP, the decay kinetics of the Ce^{3+} emission in YAG:Ce NP under excitation by SR with $E = 8.14$ eV in the onset of interband transitions possesses a larger content of slow components of 35.7% (presented by the value $\alpha = I_s/I_f \times 100\%$ in Fig. 3b, curve 2) in comparison with the corresponding values of 6.3% and 0.74% for YAG:Ce SC and SCF, respectively [7].

3.3. X-ray excited emission spectra of YAG:Ce NP

To compare the luminescent properties of YAG:Ce NP and SC we also studied their luminescence spectra and decay kinetics in a wider (3000 ns) time interval under excitation by pulsed

Fig. 3. (a) Decay kinetics of LE(AD) and Y_{Al} AD emission at a wavelength of 260 (1) and 340 nm (2) in YAG NP under excitations by SR with $E = 8.14$ eV; (b) decay kinetics of Ce^{3+} luminescence at 530 nm in YAG:Ce NP under excitations by SR with $E = 5.58$ eV in Ce^{3+} absorption band (1) and with $E = 8.14$ eV in the onset of interband transitions (2).

Fig. 4. Integral (1) and time-gated (0–5 ns) (2) X-ray excited emission spectra of YAG:Ce NP (a, curves 1 and 2) and SC (b) in comparison with CL spectra of YAG:Ce SCF (a, curve 3). Insert-decay kinetics of Ce^{3+} emission at 550 nm in YAG:Ce NP (1) and SC (2) under excitation by pulsed X-ray radiation at 300 K.

($\Delta t = 1.5\text{--}2\text{ ns}$) X-ray radiation ($W_{K\alpha}$, $E_{\text{eff}} = 60\text{ keV}$) at 300 K. The integral (1) and time-gated (0–5 ns) (2) X-ray excited emission spectra of YAG:Ce NP (a) and SC (b) in comparison with the cathodoluminescence (CL) spectra of YAG:Ce SCF (a, curve 3) are shown in Fig. 4. The integral and time-gated luminescence spectra of YAG:Ce NP at 300 K contain only the Ce^{3+} emission band peaked at 2.3 eV (Fig. 4a, curves 1 and 2). As distinct to YAG:Ce SC, the 4.27 and 3.78 eV bands related to the LE(AD) and Y_{Al} AD luminescence, respectively, strongly diminish in the spectra of YAG:Ce NP at 300 K (Fig. 4a).

The decay kinetics of the Ce^{3+} emission at 2.3 eV in YAG:Ce NP and SC in the time range 0–2000 ns under excitation by pulsed X-ray radiation at 300 K is shown in the insert of Fig. 4a. An increase in the penetration depth of the excitation beams in the case of X-ray radiation ($E = 60\text{ KeV}$) in comparison with SR excitation (8.3 eV) leads to shortening the decay kinetics of the Ce^{3+} luminescence of YAG:Ce NP (curve 1) in comparison with SC (curve 2). Specifically, in YAG:Ce NP there occurs a decrease in the lifetime of the main fast component of Ce^{3+} emission to a value of 43.6 ns in comparison with a typical lifetime of 64.3 ns for the Ce^{3+} luminescence in YAG:Ce SC at close values of medium (152 and 196 ns) and slow (7472 and 6426 ns) components, respectively.

4. Conclusion

A comparative analysis of the luminescent properties of YAG and YAG:Ce NP with respect to the SCF and SC analogues allows us to conclude that the properties of NP is situated between the properties of SC with large ($\sim 0.18\text{--}0.19\text{ at. \%}$) concentration of Y_{Al} AD and SCF of these garnets where Y_{Al} AD are completely absent. Specifically, the intrinsic luminescence of YAG NP mainly presents a superposition of the emission of defect centers: the luminescence of excitons, localized around Y_{Al} AD (LE(AD)); the

recombination luminescence of Y_{Al} AD; the luminescence of F- and F^+ -centers, as well as the luminescence of defects which are typical only for NP. Most probably the last type of defects are caused by aggregates of Y_{Al} AD and VD due to an increase in the concentration of these centers in the samples annealed in the reducing atmosphere.

At the same time, the Ce^{3+} doped YAG NP show luminescent properties close to those of YAG:Ce SCF. Similarly to SCF, the emission spectra of YAG:Ce NP at 300 K do not show the luminescence of AD and VD-related centers. The positions of excitation bands related to the creation of excitons bound with the Ce^{3+} ions in NP and SCF are close. This points to a high efficiency of the energy transfer to Ce^{3+} both by excitons and e/h pair ions in the main volume of YAG:Ce NP with a smaller concentration of Y_{Al} AD and VD with respect to SC. Meanwhile, the YAG:Ce NP possess a larger contribution of slow components of the Ce^{3+} emission under excitation in the threshold of the interband transitions in comparison with the SCF and SC analogues due to a significant involvement of the Y_{Al} AD and VD on the boundaries of NP as emission and trapping centers in the excitation of Ce^{3+} luminescence.

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