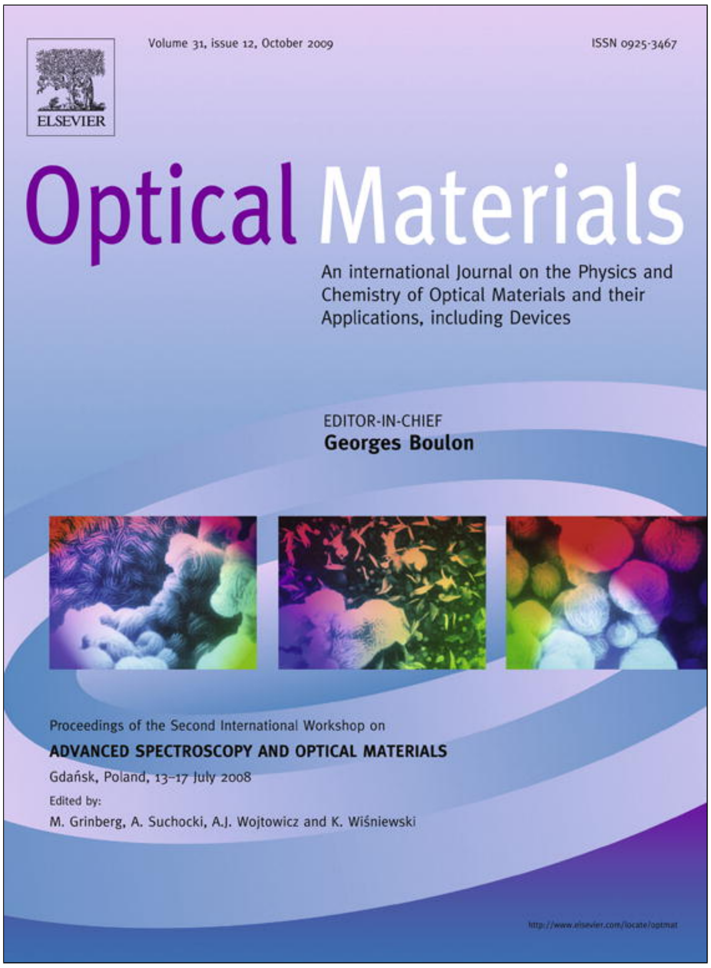

Volume 31, issue 12, October 2009
ISSN 0925-3467

Optical Materials

An international Journal on the Physics and Chemistry of Optical Materials and their Applications, including Devices

EDITOR-IN-CHIEF
Georges Boulon

Proceedings of the Second International Workshop on
ADVANCED SPECTROSCOPY AND OPTICAL MATERIALS
Gdańsk, Poland, 13–17 July 2008
Edited by:
M. Grinberg, A. Suchocki, A.J. Wojtowicz and K. Wiśniewski

http://www.elsevier.com/locate/optmat

Optical Materials 31 (2009) 1835–1838

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Time-resolved spectroscopy of intrinsic luminescence of $Y_3Ga_5O_{12}$ and $(LaLu)_3Lu_2Ga_3O_{12}$ single crystals

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ARTICLE INFO

Article history:
Received 30 September 2008
Received in revised form 29 October 2008
Accepted 26 November 2008
Available online 6 May 2009

PACS:
71.55.Ht
78.47.+p
78.55.Hx

Keywords:
Intrinsic luminescence
Excitons
$Y_3Ga_5O_{12}$ (YGG)
$(LaLu)_3Lu_2Ga_3O_{12}$ (LLGG) crystals

ABSTRACT

The nature of intrinsic luminescence of $Y_3Ga_5O_{12}$ (YGG) and $(LaLu)_3Lu_2Ga_3O_{12}$ (LLGG) single crystals grown from a melt was determined. In the case of a YGG single crystal containing Y_{Ga} antisite defects with a concentration of 0.25–0.275 at.% the intrinsic luminescence was considered as a superposition of luminescence of self-trapped excitons (STE), luminescence of excitons localized near antisite defects (LE(AD) centers) and luminescence caused by a recombination of an electron with a hole captured at Y_{Ga} antisite defects. Due to a large (2–3%) concentration of Lu_{La} antisite defects in LLGG single crystals the intrinsic luminescence was a superposition mainly of the LE(AD) center emission and the recombination luminescence of Lu_{La} antisite defects. The energy structure of the mentioned centers in YGG and LGGG hosts was determined from the excitation spectra of their luminescence under excitation by synchrotron radiation in the range of the fundamental absorption edge of these garnets.

1. Introduction

A peculiarity of the structural disorder of single crystals (SC) of $Y_3Ga_5O_{12}$ (YGG) and $(LaLu)_3Lu_2Ga_3O_{12}$ (LLGG) garnets that appears during their crystallization from a melt at high temperatures is a formation of antisite defects (AD); specifically, the Y^{3+} cations in the octahedral sites of Ga^{3+} cations (Y_{Ga}) in the YGG SC and the Lu^{3+} cations in the dodecahedral sites of the La^{3+} cations (Lu_{La}) in LLGG SC [1–5]. The concentration of AD of such type in YGG and LLGG SC reaches 0.2–0.275 at.% [1–3] and 2–3 at.% [4,5], respectively. The AD is an analogue of cation isoelectronic impurities and significantly contributes to the intrinsic UV luminescence of single crystals of garnet compounds [6].

The intrinsic luminescence of Ga-garnets, in particular the YGG and LLGG SC, has been recently studied in the papers [6–8] by conventional spectroscopic methods. It has been found that intrinsic luminescence of SC of these garnets is represented by broad complex bands in the UV spectral range which are a superposition of several components. The position and intensity of these components depend on the AD concentrations and temperature of measurements [6–8].

This work is devoted to further detailed investigation of the nature of the intrinsic luminescence of YGG and LLGG SC using the time-resolved luminescent spectroscopy under excitation in the range of fundamental absorption of these garnets.

2. Samples and experimental technique

The YGG and LLGG SC were grown by the Czochralsky method in Ir crucibles in Ar + 1.5% O_2 atmosphere at the National University of Lviv and the Institute of Technology of Electronic Materials in Warsaw, respectively. The Y_2O_3, Lu_2O_3, La_2O_3 and Ga_2O_3 oxides of 4 N purity were used as a charge. The crystal content was determined by the atomic emission spectroscopy. Plates cut from the upper part of crystals with (1 1 1) orientation of the growth axis that had $La_{2,6}Lu_{2,4}Ga_3O_{12}$ and $Y_{3,055}Ga_{4,945}O_{12}$ contents were used for investigating the luminescence properties.

The time-resolved intrinsic luminescence of YGG and LGGG SC was measured at 9–10 K under excitation by pulsed (0.127 ns with a repetition time of 200 ns) synchrotron radiation (SR), with an energy of 3.7–25 eV at the Superlumi experimental station (HASYLAB

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doi:10.1016/j.optmat.2008.11.024

at DESY). The emission and excitation spectra were measured in the integral regime over 1.2–10 ns and 150–200 ns time intervals, for fast and slow components, respectively. The luminescence decay was measured in the time range of 0–200 ns at 10 K.

3. Results and discussion

The intrinsic luminescence spectra of the YGG SC obtained under excitation by SR with two different excitation energies at 9 K are presented in Fig. 1. Similarly to the well-known $Y_3Al_5O_{12}$ (YAG) SC [9], the spectra of YGG SC are a superposition of the luminescence of self-trapped excitons (STE) with the band peaked at E_{max} = 4.13 eV, the luminescence of excitons perturbed at AD defects (LE(AD) centers) with the band peaked at E_{max} = 3.75 eV and the luminescence of Y_{Ga} AD with the band peaked at E_{max} = 3.27 eV originate from a radiative recombination of electrons of a conduction band with holes previously localized at these AD [6].

The intrinsic luminescence spectra of LLGG SC (the fast and slow components as well as the integrated spectrum) under excitation by SR with an energy of 6.45 eV in the range of LLGG fundamental absorption edge are presented in Fig. 2. LLGG SC is characterized by a substantially larger (by one order of magnitude) concentration of the Lu_{La} AD with respect to YGG SC, and therefore the intrinsic spectrum practically does not contain any STE luminescence even at 10 K (see also [8]). The luminescence of LLGG SC (Fig. 2) is a superposition of the emission band peaked at E_{max} = 3.59 eV related to the LE(AD) centers and the band peaked at E_{max} = 3.08 eV related to the recombination of the hole and the electron at Lu_{La} AD (see also [8]). The spectra presented in Fig. 2 are very close to those for the LuAG SC with a significantly large concentration of Lu_{Al} AD with respect to YAG SC [9].

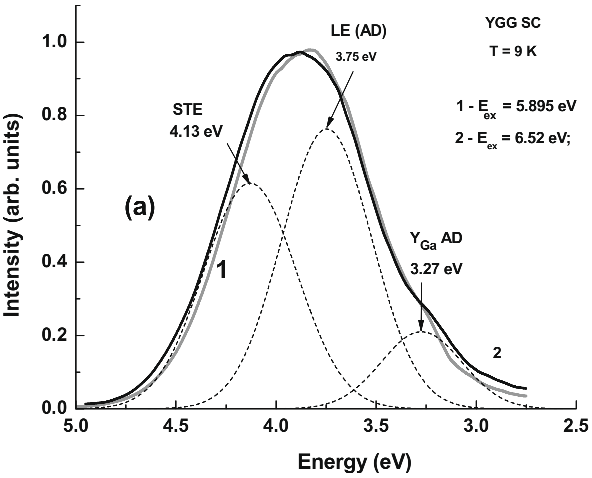

Fig. 1. Luminescence spectra of YGG SC at 9 K under excitation in the different part of a fundamental absorption range with an energy of 5.895 eV (1) and 6.52 eV (2). The fitting procedure for curve 2 is presented.

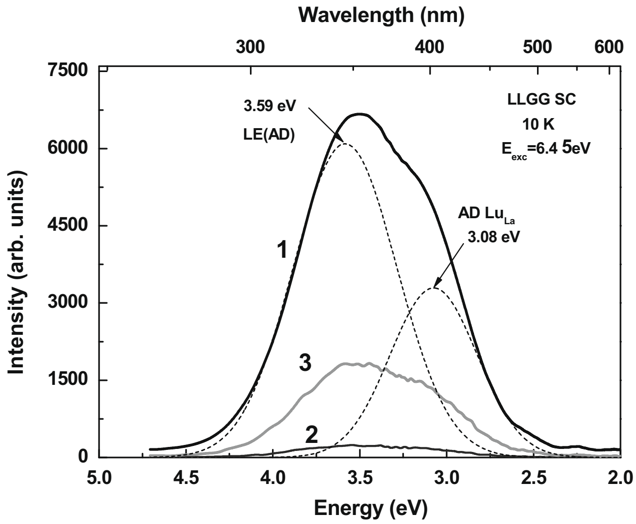

Fig. 2. Spectra of integral (1), fast (2) and slow (3) components of LLGG SC luminescence under excitation at 6.45 eV in the LLGG exciton range. The fitting procedure for curve 1 is presented.

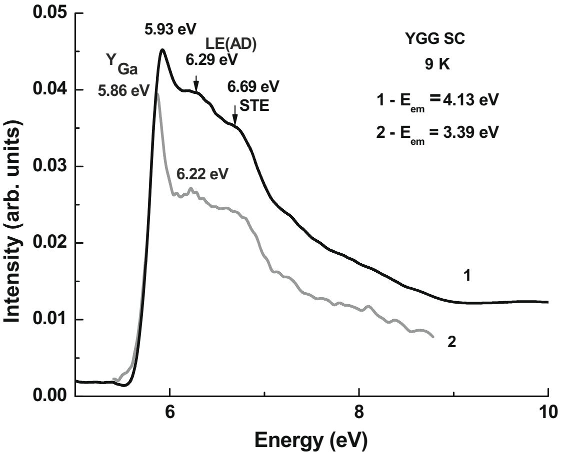

Fig. 3. Excitation spectra of different components of YGG SC luminescence under registration of emission at 4.13 eV (1) (dominance STE and LE(AD) luminescence) and 3.39 eV (2) (dominance of LE(AD) and Y_{Ga} AD luminescence).

The excitation spectra of the luminescence of YGG SC monitored at energies of 4.13 eV and 3.39 eV are shown in Fig. 3. Actually, the mentioned spectra are a superposition mainly of two different components of the intrinsic emission. Specifically, curve 1 presents a superposition of the excitation spectra of LE(AD) and the STE luminescence, whereas curve 2 presents a superposition of the excitation spectra mainly of LE(AD) and Y_{Ga} AD emission. In turn, the excitation spectra of all these components of the intrinsic emission show double structures with two peaks (Fig. 3). This phenomenon is typical for the excitation spectra of components of the intrinsic luminescence of Al-garnets [9] and caused by the transition from the ground state to singlet and triplet excited states of excitons related to the above mentioned centers.

Thus, the excitation spectrum of YGG SC (Fig. 3) allows the energies of STE formation to be estimated as equal to 6.69 eV and determines the energies of creation of the LE(AD) states (equal to 5.9 and 6.675 eV) (curves 1), as well as the energies of formation of excitons bound with the Y_{Ga} AD (equal to 5.855 and 6.22 eV) (curves 2). It is worth noting that due to a strong overlap of the excitation spectra of the emission of STE, LE(AD) and the Y_{Ga} AD centers, the positions of the excitation levels of STE must be defined more precociously. Specifically, this can be done by studying the STE luminescence in YGG single crystalline films where the AD and related luminescence centers are completely absent and the STE emission is a dominant component of the intrinsic luminescence [6,9].

The excitation spectra of LE(AD) and AD Lu_{La} emission components (the luminescence monitored at 3.695 eV and 2.88 eV, respectively) in LLGG SC are shown in Fig. 4. Both spectra are the superposition of the LE(AD) and AD Lu_{La} centers luminescence with the dominating content of one of them. The excitation spectra of both components of the intrinsic luminescence consist of two

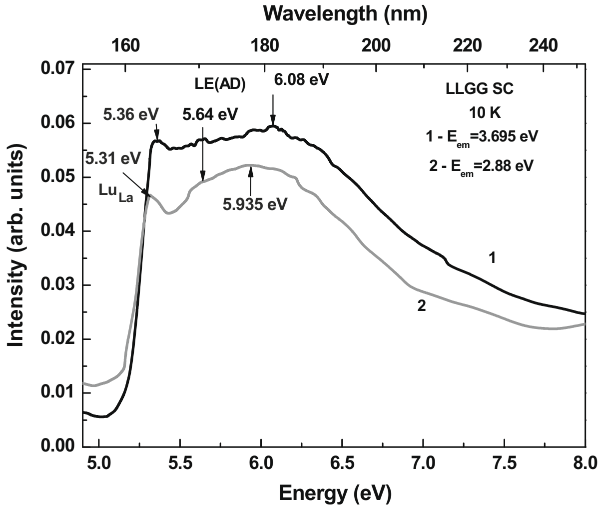

Fig. 4. Excitation spectra of components of LLGG SC luminescence under registration of emission at 3.695 eV (1) (dominance of LE(AD) centers luminescence) and 2.88 eV (2) (dominance Lu$_{La}$ AD centers luminescence).

characteristic peaks caused by the transition to the singlet and triplet excited states of excitons related to the LE(AD) and AD Lu$_{La}$ centers [9]. From these excitation spectra we determined the energies of formation of the LE(AD) states in LLGG (equal to 5.64 and 6.08 eV, Fig. 4, curve 1) and the energies of formation of the excitons bound with the AD Lu$_{La}$ (equal to 5.31 and 5.935 eV, Fig. 4, curve 2).

The decay kinetics of different components of the intrinsic luminescence of YGG and LLGG SC is shown in Figs. 5 and 6, respectively. All the decay curves have a similar shape. Generally, the decay curves of the intrinsic luminescence of YGG SC can be presented as a superposition of three components caused by the transition from the excited states of the STE, LE(AD) and excitons bound with the Y$_{Ga}$ AD in YGG. In the case of LLGG SC the decay curves of the intrinsic luminescence can be represented by a superposition of two components related to the LE(AD) and excitons bound with the Lu$_{La}$ AD. At the same time, using the appropriate energies of excitation and luminescence at the maxima of excitation and emission bands for different components of the intrinsic luminescence, it is possible to separate their dominant emission decay (Figs. 5 and 6). The parameters of fitting of the corresponding decay curves (shown in Figs. 5 and 6 by solid lines) are summarized in Table 1.

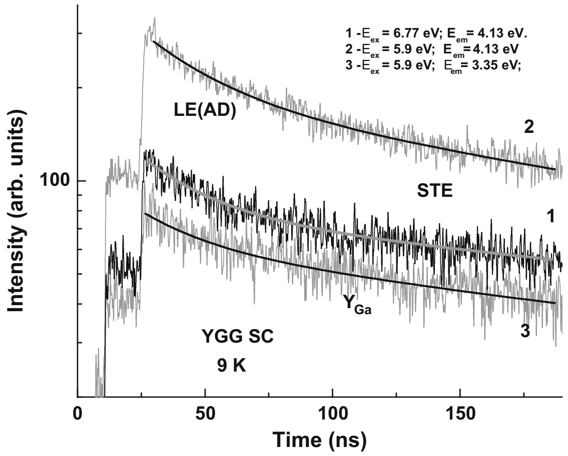

Fig. 5. Decay kinetics of different components of YGG SC intrinsic luminescence at 9 K under excitation by SR with an energy of 6.77 eV (1) and 5.9 eV (2, 3) and monitoring the emission at 4.13 eV (1, 2) and 3.35 eV (3).

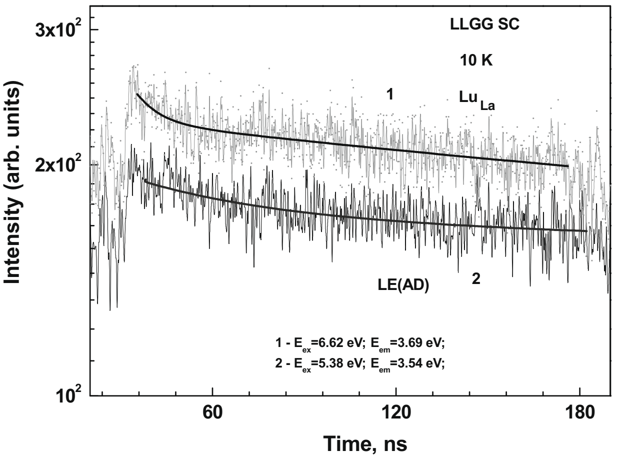

Fig. 6. Decay kinetics of different components of LLGG SC intrinsic luminescence at 10 K under excitation by SR with an energy of 6.62 eV (1) and 5.38 eV (2) and monitoring the emission at 3.69 eV (1) and 3.54 eV (2).

Table 1
Decay times of components calculated from the decay curves related to different centers of intrinsic luminescence of YGG and LLGG SC at 9–10 K.

Crystals	Centers type	Decay time		
		τ_1, ns	τ_2, ns	τ_3, ns
YGG	STE	9.5	47.6	410
	LE(AD)	4.1	49	471
	Y$_{Ga}$	2.1	31.1	494
LGGG	LE (AD)	17.8	98.2	1328
	Lu$_{La}$	7.3	65.1	893

As can be seen from Table 1, the complex decay kinetics of all components of the intrinsic luminescence of YGG and LLGG SC with the decay times of components in the ns, ten ns and hundred ns ranges, respectively suggests a radiative relaxation of different types of *triplet excitons* related to the above mentioned centers. This result matches well with the data for the decay of different emission components of the intrinsic luminescence in YAG and LuAG SC [9].

4. Conclusions

The nature of centers of the intrinsic UV luminescence of single crystals of $Y_3Ga_5O_{12}$ (YGG) and $(LaLu)_3Lu_2Ga_3O_{12}$ (LLGG) garnets obtained from melt has been considered. The intrinsic luminescence of YGG single crystals with a concentration of Y$_{Ga}$ antisite defects (AD) of 0.25–0.275 at.% is a superposition of luminescence of self-trapped excitons (STE), luminescence of excitons localized near antisite defects (AD) (LE(AD) centers) and recombination luminescence of centers formed by Y$_{Ga}$ AD. Due to a large (2–3%) concentration of Lu$_{La}$ AD in LLGG single crystals, the STE luminescence in these crystals is strongly diminished and the intrinsic luminescence presents a superposition mainly of the LE(AD) emission and the recombination luminescence of centers formed by Lu$_{La}$ AD.

The energy structure of the mentioned centers in YGG and LGGG garnet hosts is determined. The presence of two peaks in the excitation spectra, as well as the complex kinetics of the luminescence decay with the decay time of components respectively in the ns, ten ns and hundred ns ranges suggests the radiative relaxation of triplet excitons related to different components of intrinsic luminescence in the investigated materials.

The obtained results are consistent in the whole with the results of studying the nature of the intrinsic luminescence of single crystals of Al-garnets [9]. This indicates the universality of a model approach to the role of AD in a structure of intrinsic luminescence of oxides with a garnet structure [6,8,9].

Acknowledgements

The authors express their gratitude to Prof. Dr. G. Zimmerer and Dr. G. Stryganyk from the II Institute of Experimental Physics at the University of Hamburg for their assistance in carrying out the experiments in HASYLAB at DESY. The work was performed within the framework of HASYLAB II-05-105 research projects.

References

[1] M. Ashurov, Yu. Voronko, V. Osiko, A. Solol, Phys. Stat. Sol. (a) 42 (1977) 101.
[2] V. Lupei, A. Lupei, C. Tiseanu, S. Georgescu, C. Stoicescu, P.M. Nanan, Phys. Rev. B 51 (1995) 8.
[3] A. Lupei, C. Stoicescu, V.J. Lupei, Cryst. Growth 177 (1997) 207.
[4] T.H. Allik, S.A. Stevart, D.K. Sardar, G.J. Ouarles, R.C. Powell, C.A. Morrison, G.A. Turner, M.R. Kokta, W.W. Hovis, A.A. Pinto, Phys. Rev. B 37 (1988) 9129.
[5] J.B. Parise, R.L. Harlow, R.D. Shannon, G.H. Kwei, T.H. Allik, J.T.J. Armstrong, Appl. Phys. 72 (1992) 2152.
[6] Y. Zorenko, Phys. Stat. Sol. (c) 2 (2005) 375.
[7] S.K. Batygov, N.G. Margiani, N.N. Ryskin, V.V. Osiko, M.I. Timoshechkin, Y.K. Voronko, V.I. Strelov, Optica i Spectroskopia 67 (1989) 614.
[8] Yu. Zorenko, A. Voloshynovskii, V. Vistovsky, M. Grinberg, A. Kornylo, T. Łukasiewicz, M. Świrkowicz, Phys. Stat. Sol. (b) 244 (2007) 3271.
[9] Yu. Zorenko, A. Voloshinovskii, V. Savchyn, T. Vozniak, M. Nikl, K. Nejezchleb, V. Mikhailin, V. Kolobanov, D. Spassky, Phys. Stat. Sol. (b) 244 (2007) 2180.