Luminescence centers in Y₃Al₅O₁₂:La single crystals

Y Zorenko, T Zorenko, T Voznyak

Laboratory of Optoelectronic Materials, Department of Electronics, Ivan Franko National University of Lviv, 107 Gen. Tarnavskyj Str., 79017 Lviv, Ukraine

E-mail: zorenko@electronics.wups.lviv.ua

Abstract The nature of luminescence centers created by La³⁺ isoelectronic impurities (IIs) in Y₃Al₅O₁₂ (YAG) crystals has been considered. The La³⁺ dopant in YAG crystals gives rise to intensive UV luminescence in the complex band peaked at 4.28 eV at 300 K with a decay time of the main component of 575 ns. It has been shown that the complex UV emission band in YAG:La crystals in the 10-300 K range is a superposition of the luminescence of excitons localized near La dopants (LE(La) centers), the recombination luminescence of La³⁺ ions in the positions of Y³⁺ cations (La₅Y centers) and the low-intensive recombination luminescence of Y₃Al antiseite defects in the bands peaked at 4.65-4.62, 4.29-4.25 and 3.86-3.84 eV, respectively. In the visible range the emission spectra of YAG:La crystals also consist of the luminescence of F⁺ and F-centers in the bands peaked at 3.1 and 2.69 eV with a decay time of the main components of 2.3 ns and in the μs-ms range, respectively. It has been shown that the luminescence of F⁺ and F-centers in YAG:La crystals can be excited by emission of LE(La₅Y) and La₅Y centers.

1. Introduction

Isoelectronic impurities (IIs) with respect to core cation (for example, La³⁺ and Y³⁺, Lu³⁺ or Sc³⁺ and Al³⁺) can effective localize low energy excitation (electrons and holes or excitons) at the expense of the non-Coulomb potential arising at substitution of core cation by IIs [1, 2]. For this reason IIs are being widely used for creation of luminescence materials based on Al₂O₃-Y₂O₃-Lu₂O₃ oxides of different structural types with radiation in the UV range (250-350 nm) [1, 3, 5-10]. One can also refer to analogues of IIs the antiseite defects (AD) of A₁II₃ type (A³⁺ cations in sites of B²⁺ cations) which are dominant type of defects in single crystals of complex oxides with the A₂B₁O₁₂ garnet and ABO₃ perovskite structure at their high-temperature (1800-2000 °C) crystallization from melt by the Czochralski and Bridgman methods [1, 2, 11-15].

Among the whole set of ions of III group, the Sc³⁺ and La³⁺ IIs possess the highest efficiency of radiative recombination in the Al₂O₃-Y₂O₃-Lu₂O₃ oxides of different structural types [2]. In this connection the luminescence of these two impurities has been studied in single crystals and single crystalline films of Al₂O₃:Sc sapphire [1, 3] and Y₃Al₅O₁₂:Sc [1-4], Lu₃Al₅O₁₂:Sc [6-9] and Lu₃Al₅O₁₂:La [9] garnets, as well as in single crystalline films of YAlO₃:Sc and YAlO₃:La perovskites [10]. At the same time, the luminescence of La³⁺ II in crystals and films of such widespread garnet as Y₃Al₅O₁₂ (YAG) has not been earlier investigated at all. Therefore, the aim of this work was detailed study of the nature of the luminescence formed by La³⁺ IIs in YAG crystals under excitation by synchrotron radiation (SR).

2. Samples and experimental technique

YAG:La crystals were grown by the Czochralski method in Ar +1.5 % O₂ atmosphere from the charge of 4N purity placed in Ir-crucible in the Institute of General Physics of RAS. The concentration of La₂O₃ impurity was 0.6 mole % in the melt. The La concentration in the crystal was 0.085 at. %; thus the segregation coefficient of La dopant amounted to 0.14. It should be noticed that large (1.165 Å) La³⁺ ions are localized in YAG crystals exclusively in the dodecahedral sites of Y³⁺ cations (1.01 Å).
forming La<sup>3+</sup> centers [16]. At the same time, Y<sup>3+</sup> cations besides the dodecahedral sites of garnet lattice can also substitute for the octahedral sites of Al<sup>3+</sup> cations (0.53 Å) forming Y<sub>Al</sub> AD (0.90 Å) [1, 2, 11-15]. This process is substantially stimulated by entering La<sup>3+</sup> large ions in the regular sites of Y<sup>3+</sup> cations what results in the so-called effect of “displacement” Y<sup>3+</sup> cations in the octahedral sites of Al<sup>3+</sup> cations with smaller dimensions [11].

Investigation of the luminescence of LuAG:La crystals at 10 and 300 K was performed under excitation by SR with an energy 3-25 eV at Superlumi experimental station in HASYLAB at DESY (Hamburg, Germany). The emission and excitation spectra were measured in both the integral regime and the 1.2-6 ns, 150-200 ns time intervals (fast and slow components, respectively) in the limits of SR pulse with a repetition time of 200 ns. The decay kinetics of the luminescence was measured in the time ranges 0-200 ns at 10 K. The excitation spectra were corrected for the spectral transmittance of Al-grating and the intensity of SR beam; but emission spectra were not corrected.

3. Experimental results and discussion

The La<sup>3+</sup> dopant causes in YAG crystals the intensive UV luminescence in the complex band peaked at 4.28 eV at 300 K (Fig.1 a). By analogy with studying LuAG:La single crystalline films [9], for analysis of the structure of this band in YAG:La crystals we have used the luminescence time-resolved spectroscopy under excitation by SR in the range of fundamental absorption of this garnet.

The the luminescence spectra of YAG:La crystals in the UV range at 10 K (Fig.1a) and 300 K (Fig.1b) under excitation by SR the YAG exciton range (7.6-6.45 eV) and in the range of the interband transitions (13.75 eV) contain superposition of two intensive bands with E<sub>max</sub>=4.65-4.62 and 4.29-4.24 eV, which by analogy with LuAG:La films [9] can be related to the emission of the excitons localized near La<sub>Y</sub> ions (LE(La) centers) and the recombination luminescence of La<sub>Y</sub> centers, respectively, as well as the low-intensity emission band of Y<sub>Al</sub> AD with E<sub>max</sub>=3.885-3.84 eV [17]. The luminescence of La<sub>Y</sub> center arises at the radiative recombination of electrons, preliminary localized at La<sub>Y</sub> centers, with holes in valence band [9], whereas the luminescence of Y<sub>Al</sub> AD is caused by the recombination of holes preliminary localized at these centers with electron of conduction band [1, 2]. In both these cases there occur formation and radiation relaxation of excitons bound on La<sub>Y</sub> and Y<sub>Al</sub> centers [9, 17]. The above mentioned components of UV luminescence of YAG:La crystals can be spectrally resolved only at 10 K (Fig.1b), whereas at 300 K certain structure of complex band of the UV luminescence can be observed only at the analysis of difference in emission spectra of YAG:La crystals obtained at different energies of excitation (Fig.1a, curve 3).

In the longer wavelength range the emission bands with E<sub>max</sub>=3.1 and 2.69 eV is also observed in the luminescence spectra of YAG:La crystals (Fig.1a) which are caused by the luminescence of F<sup>+</sup> and F-centers (an oxygen vacancy with trapped one or two electrons, respectively) [18].

The excitation spectra of different UV luminescence centers in YAG:La crystals in the exciton range at 10 K (Fig.2a) and especially at 300 K (Fig.2b) are complex superposition of excitation bands of the luminescence of LE(La), La<sub>Y</sub> and Y<sub>Al</sub> centers. Meanwhile, in the excitation spectra of the luminescence of YAG:La crystals at 10 K at registration of the luminescence in the vicinity of the corresponding emission bands we could spectrally extract two excitation bands of the LE(La) centers luminescence with E<sub>max</sub>= 6.95 and 7.64 eV (Fig.2, curve 1) and La<sub>Y</sub> centers with E<sub>max</sub>= 6.645 and 7.33 eV (Fig.2, curve 2). These bands correspond to the excited states of excitons (most probably singlet and triplet states) bound with the corresponding luminescence centers. Due to small intensity of the emission of Y<sub>Al</sub> AD at 10 K, the dominant band of the luminescence of these centers was observed in the form of a bump with E<sub>max</sub>=6.83 eV in the excitation spectrum of the luminescence of LuAG:La crystals monitored at 3.81 eV at 300 K (Fig.2a, curve 3). However, due to large overlapping of the excitation spectra of different emission centers in the exciton range the position of high-energy excitation bands of the Y<sub>Al</sub> AD centers luminescence could not be determined.

The excitation spectra of the F<sup>+</sup> and F-centers luminescence in YAG:La crystals are shown in Fig. 2c. The excitation spectrum of the F<sup>+</sup>-center luminescence (curve 1) contains the low-intensity band with E<sub>max</sub>=4.165 eV and the dominant band at 4.9 eV in the YAG transparency range, which correspond to the radiative 1B→1A transition in these centers [18], as well as two intensive bands in the exciton
Figure 1. Luminescence spectra (normalized) of LuAG:La crystals at 300 K (a) and 10 K (b) under excitation by SR in the range of interband transition (13.75 eV) (1a), in the exciton range at 7.595 eV (1b), 7.28 eV (2a, 2b) and 6.45 eV (3b) as well as in the range of F-center absorption (4.9 eV) (4b). Curve 3a shows difference between emission spectra 2a and 1a.

range with \( E_{\text{max}} = 6.57 \) and 6.93 eV. The excitation spectrum of the F-centers luminescence in the YAG transparency range besides of the intensive band with \( E_{\text{max}} = 4.9 \) eV contains also the spectrally-resolved band with \( E_{\text{max}} = 5.37 \) eV corresponding to the radiative \( ^3\!P \rightarrow ^1\!S \) transitions in these centers. The excitation spectrum of the F-center luminescence in the exciton range contains two intensive bands with \( E_{\text{max}} = 6.57 \) and 6.93 eV and the dominant band with \( E_{\text{max}} = 7.3 \) eV. Most probably, the position of the last excitation band corresponds to the energy of formation of exciton bound with F-center. On the whole, the positions of maxima of the excitation band of F” and F-center luminescence in YAG:La crystals well correlate with the analogous spectral characteristics of these centers in \( \text{Al}_2\text{O}_3 \) [19] and \( \text{YAlO}_3 \) [18] crystals with taking into account the difference in the forbidden gap of these oxides.

It should be noted that large overlapping of excitation spectra of the F’ and F-centers luminescence (Fig.2c) can be an evidence of the mutual photo-conversion of F” ↔ F center in YAG crystals which has been earlier observed in \( \text{Al}_2\text{O}_3 \) [19] and \( \text{YAlO}_3 \) [18] crystals. It is also worth to note that the excitation bands of the F’ and F-center luminescence in YAG:La crystals in the 4-5 eV range
Figure 2. Excitation spectra (normalized) of LE(La) (1a,1b), La\(_Y\) (2a, 2b), Y\(_{Al}\) (3a, 3b), F\(^+\) (1c) and F-centers (2c) luminescence monitored at 5.15 eV (1b) and 4.76 eV (1a), 4.24 eV (2a) and 4.125 eV (2b), 3.81 eV (3a, 3b), 3.1 eV (1 c) and 2.69 eV (2c), respectively, at 300 K (a) and 10 K (b, c) in LuAG:La crystals. The maxima of emission bands of LE(La) and La\(_Y\) centers are indicated by arrows in Fig.2c.
overlap to a great extent with the emission bands of LE(La) and LaY centers (Fig.2c). This results in excitation of the F$^+$ and F-center luminescence by the emission of the centers formed by La$^{3+}$. This fact is supported by the closeness of maxima of excitation bands of the F$^+$, F-centers luminescence and luminescence bands of LE(La), LaY centers in the 6.5-7.0 eV range (Fig.2c). Similar effect of the excitation of F$^+$- and F-center luminescence by the emission of Sc$^{3+}$ II has been earlier observed by us in Al$_2$O$_3$:Sc crystals and caused large deterioration of selectivity of the emission of this phosphor under long-duration excitation by electron beam [3].

The decay kinetics of different components of the UV luminescence of YAG:La crystals is shown in Fig.3a. All the decay curves have the similar shape. Generally, the decay curves of the UV luminescence of YAG:La crystals can be presented as a superposition of three components caused by the transition from the excited states of the LE(La) centers, and excitons bound with the LaY ions and Y$_{Al}$ ADs. At the same time, using the appropriate energies of excitation and registration of luminescence at the maxima of excitation and emission bands of different centers, it is possible to separate at 10 K the dominant emission decay of LE(La), LaY and Y$_{Al}$ centers (Fig.3a). The parameters of two-component fitting of the corresponding decay curves are summarized in Table 1.

Figure 3. Decay kinetics of luminescence of LE(1a, 4a), LaY (2a, 5a), Y$_{Al}$ AD (3a), F$^+$ (1b) and F-centers (2b) in LuAG:La crystals at 10 K (1a-3a, 1a, 2b) and 300 K (4a, 5a) under excitation by SR with different wavelengths in characteristic points of excitation spectra in Fig.2.
The nature of luminescence centers created by the La\(^{3+}\) isoelectronic impurities in \(Y_2Al_5O_{12}\) (YAG) single crystal grown from melt with La\(^{3+}\) content of 0.085 at. % has been considered. The UV emission of YAG:La crystal in the 10-300 K range is a superposition of the luminescence of the excitons localized near La\(^{3+}\) dopant in the positions of \(Y^{3+}\) cations (LE(La\(_Y\)) centers), the recombination luminescence of La\(_Y\) centers as well as the low-intensive recombination luminescence of \(Y_{Al}\) antisite defects in the bands with maxima at 4.65-4.62, 4.29-4.24 and 3.86-3.84 eV, respectively.

The energy structure of the mentioned emission centers in YAG:La crystal is determined. The presence of two peaks in the excitation spectra of the LE(La) center luminescence (6.95 and 7.64 eV) and La\(_Y\) centers luminescence (6.645 and 7.33 eV), as well as the complex decay kinetics of their emission with the decay time components in the ns and hundred ns ranges, respectively, suggest the radiative relaxation from the \textit{singlet} and \textit{triplet} state of excitons related to these centers in YAG:La crystals. The above mentioned results are consistent, on the whole with the results of studying the nature of isoelectronic impurities and antisite defects as special analogues of such dopants in single crystals of Al- and Ga-garnets [9, 10, 17, 20]. This indicates the universality of a model approach for the radiative relaxation of low-energy excitation in such a class of luminescent materials based on garnets compounds [2, 17, 20].

In the visible range the emission spectra of YAG:La crystal also consist of the luminescence of F\(^+\) and F-centers in the bands peaked at 3.1 and 2.69 eV with a decay time of the main components of 2.3 ns and in the \(\mu\)s-ms range, respectively. The overlapping the excitation band of the F\(^+\) and F-center luminescence in the 4.5-6 eV and 6.2-7.3 eV ranges presupposes the mutual photo-conversion of these centers. The excitation spectra of the F\(^+\) and F-center luminescence in YAG:La crystals in the 4.5 eV range overlap with the emission band of LE(La) \(\rightarrow\) La\(_Y\) centers what causes excitation of the F\(^+\) and F-center luminescence by emission of the centers created by La\(^{3+}\) impurity.

As can be seen from Table 1, the complex decay kinetics of all components of the UV luminescence of YAG:La crystal with the characteristic decay times of components in the ns and hundred ns ranges suggests the radiative relaxation from the \textit{singlet} and \textit{triplet} excited states of different types of the excitons related to the above mentioned centers. This result well matches to the data for the decay of different emission components of the intrinsic luminescence in single crystals of \(A_3B_5O_{12}\) (A=Y, Lu, La, Gd; B=Al, Ga) garnets [17, 20].

At the room temperature range the decay kinetics of LE(La), La\(_Y\) and \(Y_{Al}\) centers are strongly accelerated (Fig.3a). Specifically, at 300 K the main slow component of the La\(_Y\) center luminescence decays with a time of about 575 ns (Fig.3a, curve 4).

The decay kinetics of F\(^+\) and F-centers luminescence under excitation in the respective intrinsic transition of these centers, are shown in Fig.3b. Due to allowed character of the \(^3B\rightarrow^1A\) singlet-singlet transition in F\(^+\)-centers [18, 19], the main component of the luminescence of these centers decays with a time of 2.3 ns (Fig.3b, curve 1). This value well correlates with the decay time of the F\(^-\)-centers luminescence in \(YAlO_3\) crystals [18]. Due to forbidden character of the \(^3P\rightarrow^1S\) triplet-singlet transition in F-centers [18, 19], the main component of the luminescence of these centers decays in the ms range (Fig.3b, curve 2). Meanwhile, due to short time interval for the luminescence decay measurements (200 ns), the decay time of this component can not be evaluated anyway in our experiment.

### Table 1. The parameters of two-component fitting of the decay curves corresponding to luminescence of different centers in YAG:La crystal at 300 K and 10 K

| Type of center | \(\tau_1, \text{ns}\) | \(A_1\) | \(\tau_2, \text{ns}\) | \(A_2\) |
|---------------|-----------------|-------|-----------------|-------|
| 1 – LE(La), 300 K | 1.3             | 166   | 6560            | 139   |
| 2 – La\(_Y\), 10 K | 4.4             | 12    | 9.9x10\(^6\)   | 246   |
| 3 – Y\(_{Al}\), 10 K | 4.5             | 28.6  | 11x10\(^6\)    | 219   |
| 4 – LE(La), 300 K | 0.6             | 115.6 | 550             | 377   |
| 5 – La\(_Y\), 300 K | 0.65            | 49.28 | 575             | 473   |
| 1 – F\(^+\)- center, 10 K | 2.3             | 525.5 | 488             | 15    |
| 2 – F \(-\) center, 10 K | 4.6             | 111   | 12970           | 181   |

4. Conclusions

The nature of luminescence centers created by the La\(^{3+}\) isoelectronic impurities in \(Y_2Al_5O_{12}\) (YAG) single crystal grown from melt with La\(^{3+}\) content of 0.085 at. % has been considered. The UV emission of YAG:La crystal in the 10-300 K range is a superposition of the luminescence of the excitons localized near La\(^{3+}\) dopant in the positions of \(Y^{3+}\) cations (LE(La\(_Y\)) centers), the recombination luminescence of La\(_Y\) centers as well as the low-intensive recombination luminescence of \(Y_{Al}\) antisite defects in the bands with maxima at 4.65-4.62, 4.29-4.24 and 3.86-3.84 eV, respectively.

The energy structure of the mentioned emission centers in YAG:La crystal is determined. The presence of two peaks in the excitation spectra of the LE(La) center luminescence (6.95 and 7.64 eV) and La\(_Y\) centers luminescence (6.645 and 7.33 eV), as well as the complex decay kinetics of their emission with the decay time components in the ns and hundred ns ranges, respectively, suggest the radiative relaxation from the \textit{singlet} and \textit{triplet} state of excitons related to these centers in YAG:La crystals. The above mentioned results are consistent, on the whole with the results of studying the nature of the luminescence of isoelectronic impurities and antisite defects as special analogues of such dopants in single crystals of Al- and Ga-garnets [9, 10, 17, 20]. This indicates the universality of a model approach for the radiative relaxation of low-energy excitation in such a class of luminescent materials based on garnets compounds [2, 17, 20].

In the visible range the emission spectra of YAG:La crystal also consist of the luminescence of F\(^+\) and F-centers in the bands peaked at 3.1 and 2.69 eV with a decay time of the main components of 2.3 ns and in the \(\mu\)s-ms range, respectively. The overlapping the excitation band of the F\(^+\) and F-center luminescence in the 4.5-6 eV and 6.2-7.3 eV ranges presupposes the mutual photo-conversion of these centers. The excitation spectra of the F\(^+\) and F-center luminescence in YAG:La crystals in the 4-5 eV range overlap with the emission band of LE(La) \(\rightarrow\) La\(_Y\) centers what causes excitation of the F\(^+\) and F-center luminescence by emission of the centers created by La\(^{3+}\) impurity.
Acknowledgement
The authors thank Dr. N. Ryskin from the Institute of General Physics of RAS for LuAG:La crystals. The authors also express their gratitude to Prof. Dr. G. Zimmerer and Dr. G. Stryganyk from II Institute of Experimental Physics University of Hamburg for their assistance during our experiments in HASYLAB at DESY. The work was performed in the framework of HASYLAB II-05-105 research project.

References
[1] Valbis Ya A 1985 Isoelectrinic impurity centers and luminescence of ionic crystals (Extended Abstract of Doctoral Dissertation, Institut of Physics of Solid State, Salaspils, Latvia).
[2] Zorenko Yu 2005 Physica Status Solidi C 2 375.
[3] Zorenko Yu V 1997 Ukrainian Physical Journal 42 559.
[4] Rachko Z A and Yansons Ya L 1987 Optics and Spectroscopy 63 63.
[5] Valbis Ya A, Volzhenskaya L G, Dubov Yu G and Zorenko Yu V 1987 Optics and Spectroscopy 63 624.
[6] Ryskin N N, Dorenbos P, van Eijk C W E and Batygov S Kh 1994 J. Phys.: Condens. Matter 6 10423
[7] Zorenko Yu V, Konstankevich I V, Gorbenko V I and Yurchishin P I 2002 J. Applied Spectroscopy 69 665.
[8] Zorenko Yu, Gorbenko V, Voloshinovskii A, Stryganyuk G, Nedilko S, Degoda V and Chykova O, 2005 Phys. Stat. Sol.(c) 2 105.
[9] Zorenko Yu V 2006 Optics and Spectroscopy 100 572.
[10] Zorenko Yu, Gorbenko V, Voznyak T, Zorenko T, Nikl M and Nejezchleb K 2008 Journal of Luminescence 128 595.
[11] Ashurov M, Voronko Yu, Osiko V and Solol A 1977 Phys. Stat. Sol.(a) 42 101.
[12] Lupei V, Lupei A, Tiseanu C, Georgescu S, Stoicescu C and Nanan P M 1995 Phys. Rev. B 51, 8.
[13] Lupei A., Stoicescu C.and Lupei V. 1997 J. Cryst. Growth 177 207.
[14] Bo Liu, Mu Gu, Xiaolin Liu, Shiming Huang and Chen Ni 2009 Applied Physics Letter 94 121910.
[15] Kuklja M M 2000 J. Phys.: Condens. Matter 12 2953.
[16] Zorenko Y, Konstankevych I, Gorbenko V and Zorenko T 2002 Mol. Phys. Rep. 36 127.
[17] Zorenko Yu, Voloshinovskii A, Savchyn V, Vozniak T, Nikl M, Nejezchleb K, Mikhailin V, Kolobanov V and Spassky D 2007 Phys. Stat. Sol. (b) 244 2180.
[18] Zorenko Yu V, Voloshinovskii A S and Konstankevych I V 2004 Optics and Spectroscopy 96 532.
[19] Surdo A I, Kortov V S and Pustovarov V A 2001 Radiation Measurements 33 587.
[20] Zorenko Yu, Voloshynovskii A, Vistovsky V, Grinberg M, Kornylo A, Łukasiewicz T and Świrkowicz M 2007 Phys. Stat. Sol. (b) 244 3271.