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journal homepage: www.elsevier.com/locate/optmat 5d–4f luminescence of Er³⁺ in YAG:Er³⁺Eduard Aleksanyan^{a,b,*}, Vachagan Harutunyan^b, Radik Kostanyan^c, Eduard Feldbach^a, Marco Kirm^a, Peeter Liblik^a, Vladimir N. Makhov^{a,d}, Sebastian Vielhauer^a^a Institute of Physics, University of Tartu, 142 Riia Str., 51014 Tartu, Estonia^b Yerevan Physics Institute, 2 Alikhanian Brothers Str., 0036 Yerevan, Armenia^c Institute for Physical Research, Armenian National Academy of Sciences, 0203 Ashtarak-2, Armenia^d Lebedev Physical Institute, 53 Leninskii Prospect, 119991 Moscow, Russia

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ABSTRACT

Interconfigurational $4f^{10}5d \leftrightarrow 4f^{11}$ transitions of the Er³⁺ ion in the YAG host were studied under both VUV photon (synchrotron radiation) and electron beam excitation. It was found that the lowest low-spin 5d level of the Er³⁺ ion has a rather large energy gap to the next lower $4f^2D(2)_{5/2}$ crystal-field level, which results in a relatively low rate of nonradiative transitions from this 5d level leading to the appearance of weak spin-allowed 5d–4f luminescence at low temperature. The lowest high-spin 5d level, from which spin-forbidden 5d–4f radiative transitions could occur potentially, is situated only at $\sim 500\text{ cm}^{-1}$ above the $^4D_{1/2}$ level. Such close location allows fast depopulation of the 5d level resulting in the absence of spin-forbidden 5d–4f luminescence and appearance of $^4D_{1/2}$ 4f–4f luminescence.

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1. Introduction

Wide bandgap materials doped with trivalent rare-earth (RE) ions, which show radiative interconfigurational $4f^{n-1}5d-4f^n$ (hereafter abbreviated as 5d–4f) transitions, have potential applications as fast scintillators, as media for solid state lasers in UV and vacuum UV (VUV) regions, as new efficient VUV-excited phosphors for plasma display panels and mercury-free fluorescent lamps. Only some trivalent RE ions possess radiative decay from the lowest level of $4f^{n-1}5d$ electronic configuration (5d level) to the ground state or some excited levels of $4f^n$ electronic configuration of the RE³⁺ ion, namely Ce³⁺, Pr³⁺, Nd³⁺, Gd³⁺, Er³⁺, Tm³⁺ and Lu³⁺ (see e.g. [1] and references therein). For the first half of the lanthanide series, transitions from the lowest 5d level into the 4f levels are spin-allowed and 5d–4f luminescence is fast with typical lifetimes in the nanosecond range. As it is now commonly accepted [2], in the second half of series, transitions from the lowest 5d state (so-called high-spin 5d state) are spin-forbidden, and such 5d–4f luminescence is slow with lifetimes in the microsecond range. However, depending on the particular ion, the host, and the temperature, spin-allowed luminescence from the higher-lying, so-called low-spin 5d state can coexist with spin-forbidden luminescence.

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Y₃Al₅O₁₂ (YAG) single crystals doped with RE ions are attractive materials for practical applications because of their advantageous thermal, chemical and mechanical properties. YAG:Ce³⁺ is an efficient yellow phosphor widely used, in particular, in phosphor-converted light-emitting diodes [3]. YAG doped with Pr³⁺ is considered as promising fast scintillator [4]. YAG:Nd³⁺ is a well known laser medium but laser action (at 1.06 μm) in this material is achieved on intraconfigurational 4f–4f transitions of Nd³⁺. Nevertheless, luminescence in the deep UV region due to interconfigurational 5d–4f transitions has been observed recently from Nd³⁺ doped into YAG [5]. 5d–4f luminescence was observed also from Tm³⁺ doped into YAG [6], but this kind of luminescence was not revealed so far from Er³⁺ ions in YAG. Although, YAG:Er³⁺ is widely used in IR lasers and optical communication techniques [7], where 4f–4f transitions of Er³⁺ are utilized, interconfigurational 4f–5d transitions of Er³⁺ in YAG were only fragmentarily investigated [6]. In this paper, we report on low temperature luminescence studies of Er³⁺ doped into YAG host under VUV photon and electron beam excitation (cathodoluminescence).

2. Experiment

Photoluminescence experiments were carried out at the SUPER-LUMI station of HASYLAB at DESY using for excitation 3.75–20 eV synchrotron radiation from the DORIS storage ring [8,9]. The excitation spectra were recorded with an instrumental resolution of $\sim 0.3\text{ nm}$. Emission in UV/visible spectral range was detected by

using a 0.3 m Czerny–Turner monochromator-spectrograph SpectraPro-308i (Acton Research Inc.) equipped with a photomultiplier tube (R6358P, Hamamatsu), which was used for excitation spectra measurements, and a liquid nitrogen cooled CCD detector (Princeton Instruments Inc.) used for emission spectra measurements. VUV luminescence was recorded through a 0.5 m Pouey-type VUV monochromator equipped with a solar-blind photomultiplier tube (R6836, Hamamatsu). The typical spectral resolution of UV/visible monochromator (with CCD detector and a 300 grooves/mm grating) was ~ 1 nm, whereas that of VUV monochromator ~ 2 nm. Measured emission spectra were not corrected for the spectral response of the detection system.

YAG:Er³⁺ single crystal was grown by the Czochralski technique. The concentration of Er³⁺ in the studied crystal was estimated by the comparison of intensities of Er³⁺ 4f–4f absorption lines (in the range of 250–850 nm) in absorption spectra measured for this sample and for another YAG sample with known Er³⁺ concentration. The respective estimation gives the value of $\sim 20\%$. The RE³⁺ ions occupy in YAG the Y³⁺ sites with D₂ point symmetry, and each site is coordinated to eight oxygens. The crystals were cleaved prior to the mounting onto a copper sample holder attached to a cold finger of a flow-type liquid helium cryostat. The orientation of crystallographic axes of the crystal was arbitrary with respect to polarization vector of exciting synchrotron radiation. All measurements were performed under ultrahigh vacuum conditions.

Cathodoluminescence (CL) experiments were carried out with a special setup at the Institute of Physics, University of Tartu [10]. CL was detected in the region of 4–12 eV through a double vacuum-grating monochromator equipped with a photomultiplier tube Hamamatsu R6838. The CL spectra were measured in the temperature range of 5–420 K. The characteristics of the electron gun are: tuneable electron energy 1–30 keV and electron current 10–100 nA, a typical spot size ~ 0.5 mm².

3. Results and discussion

Figs. 1 and 2 show emission and excitation spectra of YAG:Er³⁺ measured at low temperature. Emission spectra of YAG:Er³⁺ in the UV/visible spectral range were analysed before [6,11] and the lines observed in the spectra were assigned to transitions originating from the ²P_{3/2}, ⁴D_{1/2} and ⁴S_{3/2} multiplet terms. The excitation spectrum of ⁴D_{1/2} 4f–4f luminescence at 9 K shows an intense broad band with the onset at ~ 6.3 eV, which is assigned to the edge of interconfigurational spin-allowed 4f–5d transitions in Er³⁺. The methodology proposed by Dorenbos [12] allows estimating the energy of the lowest 4f–5d transition in the RE³⁺ ion doped into a particular host if the value of this energy is known for some other RE³⁺ ion. As it was shown in [5] the lowest zero-phonon 4f–5d (spin-allowed) transition of Nd³⁺ in YAG:Nd³⁺ is at 236 nm (5.25 eV). The calculations show that the lowest zero-phonon spin-allowed 4f–5d transition energy of Er³⁺ in YAG:Er³⁺ is at ~ 6.2 eV, which agrees well with our experimental results.

The intensity of ⁴D_{1/2} luminescence is strongly reduced at excitation photon energies above the edge of YAG host absorption at $h\nu > 6.7$ eV, where mainly ²P_{3/2} 4f–4f luminescence is observed (Fig. 2). In the case of the host absorption an effective host – Er³⁺ (²P_{3/2}) energy transfer takes place. Obviously the ⁴D_{1/2} level lies well above the energy range, where intrinsic excitonic luminescence of YAG occurs and, therefore the excitonic mechanism of the energy transfer to this level is not realised because of energetic reasons in contrast to the efficient energy transfer to the lower lying ²P_{3/2} multiplet term of Er³⁺. The excitation spectrum of ²P_{3/2} 4f–4f luminescence also shows the band with the onset at ~ 6.3 eV, but in this case there are no drastic changes in the spectrum above the edge of the host absorption energy at $h\nu > 6.7$ eV, only small in-

Fig. 1. Emission spectra of YAG:Er³⁺ under the 4f–5d excitation (lower curve, $h\nu_{\text{ex}} = 6.7$ eV) and the host excitation (upper curve, $h\nu_{\text{ex}} = 7.5$ eV), recorded at 9 K with UV/visible monochromator. The assignments of emission lines to the corresponding Er³⁺ 4f–4f transitions are indicated.

Fig. 2. Cathodoluminescence spectra of YAG:Er³⁺ (1) and “pure” YAG (2). Emission spectrum of YAG:Er³⁺ under the 4f–5d excitation (3, $h\nu_{\text{ex}} = 6.7$ eV) recorded with VUV monochromator and excited by synchrotron radiation. Excitation spectra of YAG:Er³⁺ monitoring Er³⁺ ⁴D_{1/2}–⁴F_{9/2} emission at $\lambda = 317.4$ nm (4) and Er³⁺ ²P_{3/2}–⁴I_{13/2} emission at $\lambda = 404$ nm (5). Excitation spectrum of STE emission at $h\nu = 4.9$ eV from “pure” YAG (6).

crease of intensity confirms the efficient energy transfer process from the host to $^2P_{3/2}$ multiplet of Er^{3+} . For comparison, the excitation spectrum of excitonic emission from “pure” YAG is also shown. However, in the CL spectrum of YAG:Er at 6 K both $^2P_{3/2}$ and $^4D_{1/2}$ 4f–4f luminescence is observed, the intensity of the latter emission being by an order of magnitude weaker. This indicates that the energy transfer from the YAG host crystal to Er^{3+} ions with the excitation of Er^{3+} to high-lying $^4D_{1/2}$ level really takes place, but with the decreased efficiency than excitation to $^2P_{3/2}$. The $^4D_{1/2}$ level of Er^{3+} can be populated by impact excitation mechanism due to hot secondary electrons, which formed in the course of relaxation of exciting primary beam. Such impact mechanism have been analysed in detail for s^2 ions in alkali halides [13] and also shown to act on rare earth ions doped into fluoride host [14].

In addition to narrow-line Er^{3+} 4f–4f luminescence fast broadband emission at 6.2 eV has been detected under both VUV photon and electron beam excitation (Fig. 2). This emission was assigned to $4f^{10}5d\text{--}4f^{11}$ interconfigurational spin-allowed transitions (from the lowest low-spin $4f^{10}5d$ level to the ground $4f^{11}$ multiplet term) in the Er^{3+} ion. Under photoexcitation the intensity of this emission was very weak, which prohibited us to record its excitation spectrum. The ratio between rates of radiative and nonradiative decay from the 5d level of Er^{3+} in YAG (at 9 K) is estimated to be less than 1%, which was deduced from the ratio of integrated intensities of 5d–4f luminescence and $^4D_{1/2}$ 4f–4f luminescence.

The necessary condition for the observation of 5d–4f radiative transitions in RE^{3+} is the existence of large enough energy gap between the lowest 5d level and the closest lower-lying excited levels of $4f^n$ configuration. Otherwise 5d–4f luminescence will be completely quenched due to nonradiative transitions from the lowest RE^{3+} 5d level to 4f levels. The only exception is Gd^{3+} ion [15], where the direct 5d–4f nonradiative transitions are heavily spin-forbidden and intense 5d–4f luminescence is observed at low temperatures in spite of the fact that there are many Gd^{3+} 4f levels overlapping with lowest 5d state. In the case of the Nd^{3+} ion in YAG, the energy gap between the lowest Nd^{3+} 5d level and the closest crystal-field level of the lower-lying $4f^2F(2)_{7/2}$ multiplet term is $\sim 2670\text{ cm}^{-1}$ [5] that results in competing radiative and nonradiative transitions from the 5d level with comparable rates. For the Tm^{3+} ion in YAG the lowest low-spin 5d level (from which spin-forbidden 5d–4f luminescence has been detected in [6]) is situated at $\sim 50,000\text{ cm}^{-1}$, i.e. is strongly above the closest crystal-field level (situated at $\sim 38,200\text{ cm}^{-1}$) of the highest-energy $4f^3P_2$ multiplet (we do not consider $4f^1S_0$ level which is located at very high energy $\sim 75,000\text{ cm}^{-1}$), that excludes possible nonradiative relaxation processes from 5d to 4f levels and results in the appearance of well-recognized 5d–4f luminescence.

The energy of the lowest low-spin 5d level of Er^{3+} (i.e. the energy of zero-phonon 4f–5d transition) can be located in the middle between 6.2 eV emission band and first excitation band of 4f–4f emission, i.e. at $\sim 6.3\text{ eV}$. From Er^{3+} ion's 4f energy level diagram [16,17] it is seen (see Fig. 3), that the lowest low-spin 5d level has a considerable energy gap ($\sim 1600\text{ cm}^{-1}$) to the next lower $4f^2D(2)_{5/2}$ crystal-field level (situated at $\sim 49,200\text{ cm}^{-1}$), which results in a relatively low rate of nonradiative transitions from the 5d level at low temperatures, leading to the appearance of weak 5d–4f luminescence. At higher temperatures nonradiative processes depopulate 5d level and no 5d–4f luminescence can be detected. In this case relaxation occurs to the $^4D_{1/2}$ level, from which the nonradiative transitions will have very low rate because of significantly larger ($\sim 3400\text{ cm}^{-1}$) energy gap to the next lower 4f level. Therefore luminescence from the $^4D_{1/2}$ level can be observed.

Estimations based on data from [12] show that the lowest high-spin 5d level of Er^{3+} in YAG should be situated in the same energy range as crystal-field levels of the $^2L_{15/2}$ multiplet term and only at

Fig. 3. Energy level diagram illustrating the relative positions of 4f and 5d levels of Er^{3+} in YAG and intrinsic absorption edge of the host crystal. Solid arrows mark radiative decay and dashed arrows nonradiative transitions.

Fig. 4. Temperature dependencies of Er^{3+} 5d–4f luminescence (6.2 eV) and STE emission (4.9 eV) from YAG:Er $^{3+}$ under excitation with 5 keV electron beam.

$\sim 500\text{ cm}^{-1}$ above the $^4D_{1/2}$ level. Such an energetic location allows fast nonradiative depopulation channel of the 5d level, which results in complete absence of spin-forbidden 5d–4f luminescence.

In Fig. 4 the temperature dependence of Er^{3+} 5d–4f luminescence intensity is shown. At temperatures higher than 40 K the emission intensity is significantly reduced. This thermal quenching is due to circumstance that at higher temperatures mainly nonradiative depopulation of 5d level takes place, whereas at low temperatures radiative transitions clearly compete with nonradiative decay. However, after the strong decrease of intensity at $T > 40\text{ K}$ the emission intensity does not reach zero value, and there is a plateau of intensity up to $\sim 200\text{ K}$ after which the emission at 6.2 eV becomes completely quenched. The reason of such “two-stage” behaviour of temperature dependence is still not completely clear. It was verified that in the temperature range 40–200 K the shape of emission spectrum is the same (STE plus 6.2 eV emission bands), i.e. emission from some other optical centers does not contribute to emission intensity at 6.2 eV. As can be seen from Fig. 4, there is an anti-correlation between the temperature dependencies of 6.2 and 4.9 eV (STE) emissions, namely the decrease of the 6.2 eV luminescence intensity at $T > 40\text{ K}$ is accompanied with the increase of STE emission intensity in the same temperature range. This effect arises from a competition between two processes: energy transfer to Er^{3+} (with its excitation to 5d level) and thermally activated formation of STEs. Such anti-correlated behaviour confirms also that excitonic mechanism of the energy transfer from the host to Er^{3+} does not lead to the excitation of Er^{3+} ions to 5d

level. Thermal quenching of STE emission (due to thermally induced ionization of STEs [18]) takes place at $T > 120$ K whereas for 6.2 eV luminescence the second stage of the intensity decrease at $T > 200$ K is tentatively assigned to the process of thermal quenching of Er^{3+} $5d-4f$ luminescence.

4. Conclusions

Fast UV luminescence at 6.2 eV has been detected at low temperature from Er^{3+} doped YAG under both photon and electron beam excitation. This luminescence was assigned to $5d-4f$ spin-allowed radiative transitions in Er^{3+} . Under the YAG host absorption the $^2P_{3/2}$ $4f-4f$ luminescence of Er^{3+} is efficiently excited whereas under the Er^{3+} $4f-5d$ excitation the radiative transitions from the $4f^4D_{1/2}$ level dominate in the emission spectrum.

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