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Exciton and recombination processes in YAG crystals

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Abstract. The excitation spectra of the recombination luminescence of YAG single crystals doped with isovalent impurities of Sc and La are studied. The excitation band of the excitons trapped near impurity ions is observed at 6.7 eV, adjacent to the YAG intrinsic absorption edge. The processes of energy transfer and storage as well as their relation to the problem of the origin of the 4.9 eV emission band (supposed to be self-trapped exciton emission) are studied and discussed. The overlapping of the spectral region of direct creation of excitons with the interband transition edge (causing a metastable character of excitons) is shown. The features of relaxation processes are discussed from the viewpoint of the specificity of the electron structure of complex oxides.

1. Introduction

The crystal of $Y_3Al_5O_{12}$ (YAG) is one of the representatives of a large class of crystals with a complex unit cell. The cubically symmetric unit cell of YAG contains 160 atoms, the local symmetry of ions being very low, especially for oxygen ions. The exciton and electron-hole processes observed in YAG crystals (as well as in a number of other similar crystals) exhibit several specific features [1, 2] contrasting with those for well investigated alkali halides, which are in a sense model objects of the study of crystals with strong electron-phonon coupling (i.e. with electron excitation self-trapping).

One such feature is connected with a bright low-temperature short-wavelength luminescence band at 4.9 eV. The main features of this emission are characteristic of self-trapped excitons (STEs), but this emission is not excitable in such recombination processes as thermoluminescence (TL), in contrast, e.g., to the STE emission of alkali halides. In addition, there are some facts indicating the possible existence of another independent branch of 'recombination' self-trapping, which gives rise to the 4.2 eV emission in undoped YAG crystals [2].

As far as unrelaxed exciton states in YAG crystals are concerned, their spectral separation from electron-hole continuum states is connected with certain difficulties. No typical resonant structure of exciton transitions is observable in absorption spectra, although the absorption in the region, hypothetically considered to be excitonic (see the step in the absorption spectra at about 7 eV in figure 1, curve 4), is sufficiently high (10^5 – 10^6 cm⁻¹ [3, 4]) to point out the direct character of the respective transitions. This phenomenon is characteristic of a number of other complex crystals and may supposedly be connected with the broadening of exciton resonances in the case when many different exciton states turn out to be concentrated in a relatively narrow area of the actual spectral region [3]. The effective excitation of the exciton luminescence (i.e. STE emission at 4.9 eV) takes place in such a 'strange' exciton absorption region. At the same time, the excitation efficiency of such luminescence decreases strongly in the shorter-wavelength region of intrinsic absorption,

which is usually related to large surface losses and to a relatively high mobility of the electron excitations created there. These electron excitations are usually considered to be electron-hole pairs.

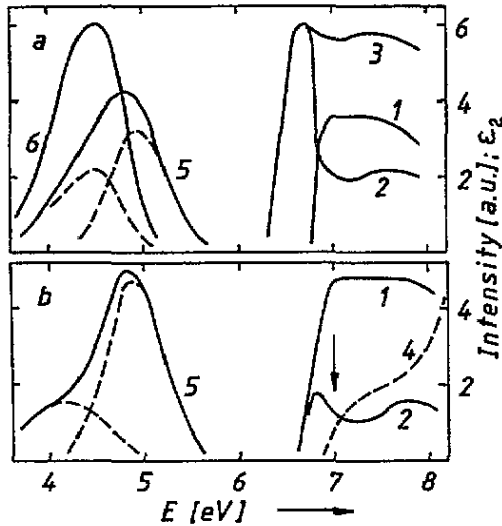


Figure 1. Luminescence and luminescence excitation spectra of (a) YAG:La (0.1 at.%) and (b) undoped YAG crystals. Excitation spectra for the 4.9 eV exciton emission (curves 1) and for recombination luminescence (curves 2 and 3) (4.5 eV for YAG:La and 4.2 eV for YAG) at 5 K (curve 3 at 300 K). Luminescence spectra at excitation at 5 K by photons of 7.7 eV (curves 5 and their distribution in elementary bands) and 6.7 eV (6). The ϵ_2 spectrum (4) at 300 K and the arrow indicating convergence point of the Urbach tail of intrinsic absorption are shown according to [3] and [4].

The situation becomes still more complicated, as the recombination processes seem to be excitable with a small (but non-zero) efficiency in the region of exciton absorption even at low temperatures. The precise separation of the exciton and the recombination processes taking place on photoexcitation in YAG crystals may have a wider significance, as such a situation (i.e. overlapping of the excitation spectra of different kinds of electron excitation) seems to be typical of a number of complex compounds.

A detailed study of transformation of the electron excitations created by photons in the region of intrinsic absorption will enable us to answer also a number of disputable questions about the origin of relaxed electron excitations giving rise to the UV luminescence of YAG crystals. It must be noted that the investigations connected with the latter problem have usually been done under x-ray or electron irradiation [5–8], when the relaxation processes of different electron excitations are observable in an averaged form, which complicates unambiguous interpretation of experimental results.

This work is devoted to a spectroscopic study of excitation spectra of both supposedly intrinsic and impurity-induced luminescence of YAG single crystals with the purpose of specifying the mechanism giving rise to the above-mentioned coexistence of different kinds of relaxation process in the exciton absorption region. Sc and La dopant ions, being isovalent to the Y and Al ions of the host crystal, induce bright bands of recombination luminescence (at 4.1 and 4.5 eV, respectively) [6,9] and, therefore, they can be used as suitable and

effective recombination centres to indicate the excitation of electron–hole processes in YAG crystals.

In addition, the investigation of the transfer of the energy of intrinsic excitations to the Sc and La luminescent centres gives us the possibility of modelling the influence of antistructural defects (ASDs) on the luminescent properties of garnets. These defects, being in some sense isovalent impurities, have spectroscopically been discovered via their influence on the emission of rare earth ions, [10, 11]. Their origin is connected with the incorporation of regular cations into the positions of second-kind cations and, according to an indirect estimation of their concentration, they may be the most essential defects of our crystals, that is, these defects are often assumed to be responsible for UV luminescence of YAG. The model similarity of Sc- and La-induced defects to ASDs is also confirmed by the circumstance that no such impurity ion has any optically active electrons in the actual spectral region.

2. Experimental details

The single YAG crystals investigated were grown by the method of directed horizontal crystallization at the General Physics Institute (Moscow); the concentration of the impurity ions in the crystals prepared was checked by x-ray probe microanalysis [12].

A hydrogen–deuterium discharge lamp and a vacuum grating monochromator were used in the excitation channel and a grating monochromator MUM, together with a photomultiplier tube FEU-39 in the registration one. The construction of a contact-type cryostat enabled us to replace the samples (up to three) during the experiment (for details see [13]). A pulsed x-ray source was used for time-resolved measurements [14].

Excitation spectra were measured in the temperature interval from 5 to 300 K by using traditional methods. The use of a monochromator in the registration channel enabled us to separate the excitation spectra of close-lying UV luminescence bands. Indeed, the spectral shapes of the respective elementary emission bands (thanks to their different decay times) were measured under pulsed x-ray excitation [9, 14] and, therefore, the distribution of the emission in elementary bands (as shown for curves 5 in figure 1) could be carried out sufficiently easily.

The TL excitation spectra were measured in a linear regime of the light sum storage to avoid the distortion of the spectra by trap saturation effects essential for a strong intrinsic absorption region [15].

3. Luminescence excitation spectra

For the Sc- and La-induced emissions well known from x-ray measurements, the single selective excitation band lying adjacent to the intrinsic transition edge was observed (see curve 2 in figure 1(a) and [16]). The Sc and La ions themselves cannot give any optical transitions in the actual spectral region and, therefore, the excitation band observed corresponds evidently to the transitions in the crystal lattice sites distorted by impurity ions (the so-called near-impurity excitations). This near-impurity excitation band is better observable at low temperatures when the energy transfer processes in the intrinsic absorption region are partially frozen up. Already at a 0.1 at.% concentration this band is clearly detectable in excitation spectra.

For undoped YAG crystals an analogous, but much weaker excitation band (for 4.2 eV emission) is detectable at low temperatures. This weak excitation band may represent here

the manifestation of residual isovalent defects of undoped crystals, including ASDs. Then the weakness of this band shows that the concentration of ASDs could be estimated to be much lower than 0.1 at.% in undoped YAG crystals. Thereby it must be noted that ordinary colour centres emitting at 3.1 eV have their excitation band in a longer-wavelength region [1, 17] and cannot be responsible for the emissions discussed.

In spite of a large number of dopant ions, the exciton-like emission at 4.9 eV is excitable by photons in doped crystals as well as in undoped ones. In contrast to recombination emissions, the excitation spectrum of the 4.9 eV emission lies without exception in the region of intrinsic absorption (defined by the Urbach edge [3, 4]) in both doped and undoped YAG crystals. From the long-wavelength edge of its excitation spectrum it is possible to estimate the value of impurity-induced additional absorption (giving rise to the competition between the exciton and dopant-induced excitation spectra) to be nearly 300 cm^{-1} at 0.1 at.% concentration of Sc or La ions. In undoped YAG crystals the residual absorption measured directly is about 50 cm^{-1} in accordance with the estimation of the defect concentration given above.

The concentrational quenching of the 4.9 eV emission studied at 80 K in a series of Sc-doped YAG crystals shows that the mobility of the exciton-like excitations is very low even in an unrelaxed state [16], being limited by the size of the unit cell. Therefore, the impurities (or ASDs) discussed cannot significantly suppress the emission of excitons created directly by photons even at 1 at.% dopant concentration. The relatively weak concentrational quenching of exciton emission seems to have a statistical character and not to be connected with any significant motion of excitons along the YAG lattice.

In doped YAG crystals, on excitation in the exciton absorption region, the energy transfer on impurity-induced centres is inefficient at low temperatures, despite the circumstance that these centres are, according to x-ray excitation data, the most effective recombination centres [9]. When the exciton emission starts quenching with the rise of temperature, the efficiency of energy transfer starts increasing, indicating a connection between the two processes. At room temperature, the excitation efficiency of the impurity-induced emission becomes nearly equal both in the intrinsic (exciton) and the dopant-induced (i.e. at direct excitation of the respective centres) absorption region. This shows that the migration losses are negligible here and, therefore, the excitation inefficiency of the impurity-induced emission observed at low temperatures in the exciton region is connected with the competition in the creation of excitations with different relaxation processes. The thermal redistribution observed at high temperatures is connected with the thermoionization of relaxed STEs (see below) and reflects, therefore, the secondary relaxation processes. Nearly the same thermal redistribution of relaxation processes is observable between two emissions (4.9 and 4.2 e) of undoped YAG crystals as well [15].

Thus, the similarity of thermal and spectral features of the excitation spectra of recombination emissions in the region of fundamental absorption is evidently connected with the circumstance that all these spectra reflect the creation and relaxation of the same intrinsic electron excitations. At the same time, the behaviour and the shape of the excitation spectrum of the exciton-like emission differ strongly from those of recombinational ones. This difference cannot be explained by competition in the trapping of the same unrelaxed electron excitation, but it reflects the creation of two different kinds of excitation in the exciton absorption region (the practically immobile excitons and, probably, the electron-hole pairs which are mobile and lead to an unfreezing mechanism of energy transfer). Indeed, if this competition were connected with the preferred trapping of electron excitation near some unknown shallow centres giving rise to the 4.9 eV emission, the concentration

of these centres would be (taking into consideration the high efficiency of excitation of this emission) improbably high (at least larger than 1 at.%).

In the case of ordinary one-photon excitation excitons are preferentially created, whereby at low temperatures the second kind of intrinsic excitation is represented much more weakly. The real existence of these second-kind excitations is more pronounced in two-photon excitation spectra, where the creation of excitons is suppressed by respective selection rules [18]. Nevertheless, the electron-hole origin of these second-kind electron excitations created in the exciton absorption region cannot be fully verified from luminescence excitation spectra. The study of TL excitation spectra can give us an answer about the spectral position of the interband transition edge in YAG crystals and, consequently, the independent determination of the spectral region of the creation of electron-hole pairs.

4. Thermoluminescence excitation spectra

The TL excitation spectra of undoped YAG crystals were investigated earlier [15, 19]. In the spectral region discussed above, a low efficiency of TL excitation was observed at low temperatures and this was related to the preferential creation of excitons in this region. Concerning the origin of this 'rest' efficiency, it was proposed to be connected either with the specificity of the intrinsic electron states located in the exciton absorption region [15] or with local trapping centres [19].

In the present work, the TL storage processes were investigated in YAG crystals doped by isovalent ions. If the TL excitation in the exciton absorption region is really induced by defects (e.g. by ASDs, considered to be the most probable defects of YAG crystals), the large number of isovalent impurities should significantly increase this efficiency. Indeed, there exist, in principle, two mechanisms of how local defect centres could cause the TL excitation in the exciton absorption region. The first mechanism is simply connected with the defect absorption which could overlap the exciton absorption. In the second case, the mobile excitons themselves could ionize the defect centres. Then the increase of the defect concentration must induce a respective increase of the TL excitation efficiency in both these cases. On the contrary, the TL excitation spectra observed in a series of doped YAG crystals show the opposite behaviour, as will be shown below.

Photoexcited TL spectra are similar to the ones observed earlier in the case of x-ray excitation [8, 12, 20, 21]. The TL spectra of both doped and undoped YAG crystals consist of a number of peaks, the lowest-temperature ones of these (at $T < 200$ K) being evidently formed on the recombination of delocalized electrons with localized holes. Indeed, the emission of, e.g., Ce ions—well known hole capture centres [20]—is observable in these low-temperature peaks [21]. The emission observable in the low-temperature TL peaks of Sc- and La-doped YAG crystals [9] consists mainly of impurity-induced luminescence (i.e. of 4.1 and 4.5 eV emission bands, respectively).

The origin of the electron capture centres responsible for these low-temperature TL peaks is not finally clear yet. These TL peaks are usually represented in all TL spectra of YAG crystals and, therefore, it is difficult to ascribe them to certain capture centres. TL excitation spectra were investigated in detail for the most intensive peaks at 80 K (for YAG:La) and at 120 K (for YAG:Sc), as it was possible to measure these spectra in an extremely large dynamic range. The excitation spectra of other, weaker L peaks exhibit mainly the same character.

The results obtained for doped YAG crystals show, in contrast to those discussed above, an increase of TL excitation efficiency in the short-wavelength part of the spectra, which

evidently reflects the increase of the number of trapping centres responsible for the capture of the intrinsic electron excitations created. The respective curves (1–3) in figure 2 are normalized on their short-wavelength side to exclude this dependence.

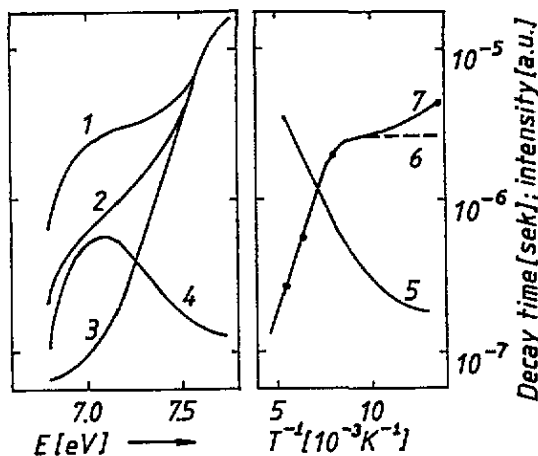


Figure 2. Excitation spectra of the TL peak at 120 K for undoped (1) and Sc-doped (curves 2 and 3 for the 0.1 and 1 at.% concentration, respectively) YAG crystals irradiated at 5 K and the spectrum of the ratio of the TL excitation spectra measured after irradiation at 160 K and at 80 K (4). The temperature dependence of the TL storage efficiency for the 220 K peak under 7.1 eV excitation (5), of the 4.9 eV luminescence intensity (6) and of this luminescence decay time under pulsed x-ray excitation (curve 7 for undoped and full circles for the 1 at.% Sc-doped YAG crystals).

In the course of the investigation of TL excitation spectra in alkali halides [22], the fast recombinations of the nearest electron-hole pairs (i.e. with small kinetic energy) were supposed to be responsible for the deformation of the shape of TL excitation spectra on excitation in the region of interband electron-hole transitions. These recombinations diminish the observed efficiency of TL storage on excitation near the interband transition edge: the stronger they are the higher the recombination centre concentration. In our case the behaviour of the TL excitation spectra points to the same mechanism as responsible for the observed evolution of the spectra studied.

When effect is taken into consideration, the corrected efficiency of the electron-hole pair creation on the long-wavelength side of the spectra will be somewhat higher. This correction cannot, nevertheless, change the situation where the observed edge of interband transitions extends over the whole exciton absorption region of YAG crystals. It is these interband transitions that seem to be responsible for the above-discussed excitation of recombination luminescence at low temperatures in the exciton absorption region of YAG crystals.

The amount of energy stored on the capture centres of YAG crystals is in our case estimated to be up to 10% of the luminescence energy emitted during irradiation. This amount of stored energy is small compared to exciton luminescence, but it forms a remarkable part of the second-kind (recombinational) luminescence, which shows once more that the recombination features are important in describing the excitation processes of this luminescence in the intrinsic absorption region.

Finally we discuss the dependence of TL excitation spectra on the temperature at which excitation and TL storage occur. With the rise of temperature the efficiency of TL excitation

starts to increase. This increase is better observable for high-temperature TL peaks (e.g. for a peak at 220 K, as was measured for undoped YAG crystals [15]). The ratio of the excitation spectra of the TL stored at different temperatures shows the correlation of this effect with exciton absorption (see curve 4 in figure 2). A comparison of opposite temperature dependences of both the increase of the TL excitation efficiency and the exciton emission quenching (which occurs via the decrease of the decay time [14]) shows that both processes have the same activation energy (70 meV) and are induced by thermal ionization of relaxed immobile STEs. Indeed, the independence of decay times of exciton luminescence on impurity concentration (see curve 7 in figure 2) shows that the thermal decay of excitons has intracentre character and cannot, therefore, be connected with possible hopping motion of relaxed STEs.

It must be noted that TL is unexcitable in the Sc- and La-induced luminescence excitation bands in the whole temperature interval investigated. This shows that the binding energy of respective trapped excitons (created directly by photons) is large enough. The temperature quenching of the respective luminescence bands takes place at much higher temperatures and is characterized by activation energy in the range of 0.2–0.3 eV [9]. These trapped excitons (in contrast to the excitons responsible for the 4.9 eV emission) are also the final states of recombination processes and represent here, probably together with the ones giving rise to the 4.2 eV emission of undoped YAG crystals, the second kind of trapping that is different from self-trapping of excitons as a whole (i.e. from self-shrinking, according to Sumi's classification—see details in [2] and [23]). The reason for such coexistence of different lattice relaxation processes may give complex low-symmetric surroundings of an oxygen ion in its crystal site.

5. Conclusions

The data obtained by different methods in YAG crystals show the energy spectrum of exciton states overlaps the states of the electron–hole continuum. This means that the excitons of YAG crystals are in fact metastable with respect to self-ionization. Such a situation may be typical of oxides with a complex unit cell, where oxygen ions are low coordinated and, correspondingly, the symmetry of their positions is very low. In fact, strong heterogeneity of the valence band of such oxides (connected with a tendency to form subbands of nonbonding oxygen orbitals on the top of the valence band, as show the calculations for relatively simple oxides of such a class, e.g., for sapphire [24]) may cause a situation when the excitons having holes from the lower part of the valence band (or, alternatively, from another subband) have the same energy as the electron–hole pairs with a hole originating from the subband of nonbonding oxygen orbitals. A strong structural difference of the holes of both types may be the cause of the low scattering efficiency between the above-mentioned two sets of states. Because of this, the creation of different kinds of electron excitation, having their own specific relaxation processes, can take place in a relatively wide area of the intrinsic absorption spectrum. Hypothetically such a situation was earlier discussed when interpreting luminescent features of complex compounds [2, 3, 25].

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