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Relaxation of electronic excitations in YAG and YAP crystals

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One- and two-photon spectroscopy is used for the investigation of the nature of the lowest electronic excitations and their relaxation in YAG and YAP crystals. The coexistence of two types of electronic states (the metastable excitons and the electron–hole continuum) having different relaxation ways has been observed in the exciton absorption region. The peculiarities of the electronic state spectrum observed are supposed to be connected with the complexity of the electron structure of the oxides investigated.

1. Introduction

$Y_3Al_5O_{12}$ (YAG) and $YAlO_3$ (YAP) crystals are the most investigated oxide crystals with a complex unit cell. In spite of that, the nature of the electronic excitations appearing in the bright ultraviolet luminescence and in other electronic processes is not clear yet. The optical and luminescent properties of YAG and YAP crystals are distinctive for a number of oxides having a complex unit cell and, therefore, studying these may be of some heuristic importance for a large intermediate class of crystals lying between single model crystals containing 1–2 atoms in a unit cell and glassy solids.

The unit cells of YAG and YAP crystals contain 160 and 20 atoms, respectively. Because of such a complexity of the unit cell some new peculiarities can be expected in the nature of electronic excitations and in relaxation processes. Indeed, the large number of nonequivalent atoms in the unit cell leads to the circumstance that a number of energy bands having strongly different origins may actually be even in the low-energical part of the spectrum of intrinsic electronic excitations. For oxides one of the most important features of the electronic structure which can determine this is connected with the tendency to form subbands in the valence band which are induced by bonding and nonbonding orbitals of oxygen, as it has been calculated for several relatively simple oxides [1,2]. Taking exciton effects into consideration, the situation will be still more complicated.

The topic of our interest was the origin of the intrinsic electronic excitations determining absorption and relaxation processes in the complex oxides under investigation. One-photon investigations were carried out with traditional methods of VUV spectroscopy by using hydrogen discharge lamps. In the present work, the methods of two-photon spectroscopy were used for the first time to investigate electronic excitations in YAG and YAP crystals. The second harmonic of the emission of an excimer-pumped dye laser was used for excitation. The 2ω-absorption regime was achieved in the spectral region up to 260 nm by focusing the laser beam into the crystal at temperatures of 80–300 K. The power of the laser beam and the two-photon absorption were controlled by photodiodes. The luminescence was observed perpendicular to the laser beam direction by using a monochromator and time-resolved registration. The luminescence intensity was proportional to the square of the laser beam power in accordance with theoretical predictions.

2. Experimental results and discussion

2.1. One-photon spectroscopy

As we can see from the absorption spectra obtained by the Kramers–Kronig relations (Fig. 1, curve 4), the fundamental absorption of YAG and YAP crystals begins with a hardly distinguishable step. As the Urbach tail measurements show, the electron–phonon interaction in our crystals is strong and perhaps therefore all the thresholds in the absorption spectra are sufficiently broad, which aggravates the determination of their exact positions. The above-mentioned steps in the absorption spectra lay between 7 and 8 eV in YAG and near 8 eV in YAP crystals and they were supposed to be due to exciton absorption [3,4]. On the other hand, these steps can be formed by pairs of thresholds of interband transitions. Because of this, the nature of these peculiarities is not finally clear and it is not

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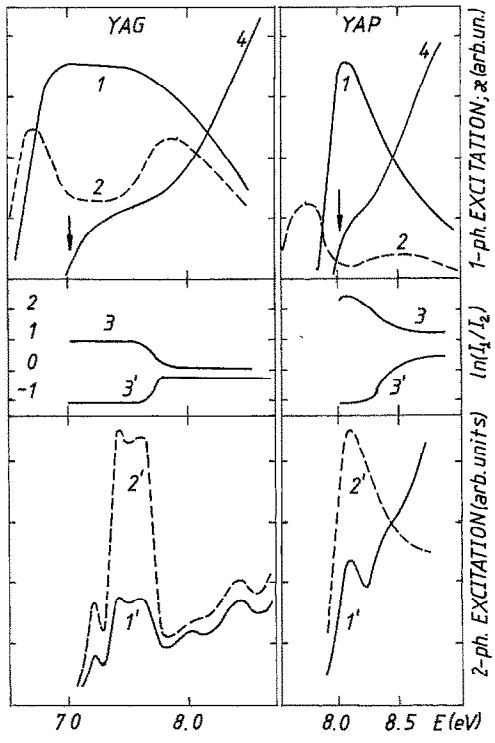

Fig. 1. Luminescent and optical properties of YAG and YAP crystals. Excitation spectra of I_1 (1, 1′) and I_2 (2, 2′) emission bands and the spectra of the ratio of the intensities of these bands (3, 3′) on one- (1–3) and two-photon (1′–3′) excitation at LNT; one-photon absorption spectra x (4) at 300 K. The curves of I_1 emission correspond to 4.9 eV emission bands for YAG and 5.9 eV for YAP, the curves of I_2 emission, to 4.2 eV in both cases. The energetical scale of two-photonic spectra corresponds to the double photon energy. The arrows indicate the position of the Urbach edge E_0 (see the text).

possible to determine it by absorption measurements only, as it can be done in the case when the resonant structure of exciton absorption is observable (as, e.g., in alkali halides).

The investigation of the luminescence of both crystals shows that there are pairs of characteristic emission bands having a strongly different nature in each type of crystal. The short-wave bands (4.9 eV in YAG and 5.9 eV in YAP) are exciton-like, whereby the long-wave ones (4.2 eV in both crystals) have a recombinational character, as the latter are observable in a such typical recombinational process as thermoluminescence. Both kinds of emission bands are excited only in the fundamental absorption region and, therefore, they can be considered as the luminescence of intrinsic excitations [3,5].

We will not discuss here in detail the nature of the relaxed states responsible for these emissions. It must be noted that because of the sufficiently high mobility of the electronic excitations responsible for recombinational luminescence the influence of the impurity- or defect-induced trapping on the final stage of relaxation is not excluded. At the same time, the mobility of the exciton-like excitations created in our crystals is very low. As it has been shown for YAG crystals, the imperfections (e.g. the dopant ions) cannot significantly suppress this exciton emission and on the whole the exciton relaxation branch on direct creation of excitons by photons even when crystals contain on the average up to one dopant atom in the unit cell [6]. In this case the sphere of the interaction of the exciton with imperfections seems to be less than the unit cell volume. These "strange" excitons are practically immobile and are barrierlessly self-trapped. Therefore their (noncharged intrinsic excitations of the crystal) participating in the energy transfer in our crystals is insignificant. These excitons seem to be "strange" only because of the large size of the unit cell (1.2 nm for YAG), while the spatial size of their interaction sphere is nearly of the same order as in some alkali halides, where the barrierless self-trapping of excitons takes place also. The absence of the strong resonant structure in our crystals characteristic of traditional absorption of direct excitons, may therefore be connected with the circumstance, that such an exciton is located during all its lifetime in such a small region where the crystalline structure is not yet pronounced. In this case, our exciton seems to be more glass-like than the crystalline one.

Both kinds of emissions, being excited in the fundamental absorption region only, have different excitation spectra. The exciton-like emission is excitable with high efficiency namely in the region of the above-discussed step in the absorption spectra (Fig. 1, curve 1) at low temperatures where this emission is not quenched yet. Because of this, the assumption about the exciton nature of these peculiarities of absorption spectra seems to be true. The excitation spectrum of the second kind of emission – the recombinational one (Fig. 2, curve 2) shows a non-zero efficiency of excitation in the same region of exciton absorption. The excitation spectra of other kinds of recombinational processes (such as energy transfer to rare-earth ions and thermoluminescence storage) have an analogous character in the intrinsic absorption region. Therefore, we can assume that all these processes have common initial states, i.e. the states of electron–hole continuum, and we will use the 4.2 eV emission as an indicator of the continuum state excitation. The excitation of these recombinational processes in the exciton region takes place even at 5 K.

Together with the unfreezing mechanism of excitation of recombinational processes in the exciton region there is another one, which starts working at higher temperatures. When the temperature rises over the

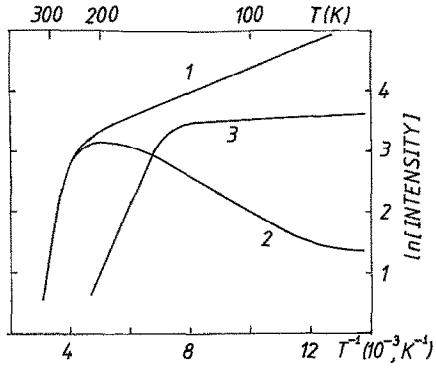

Fig. 2. Temperature dependence of 4.2 eV (1,2) and 4.9 eV (3) emission intensities on one- (2,3) and two-photon (1,3) excitation in the exciton region (7.3 eV) of YAG crystals.

quenching temperature of the exciton emission (see Fig. 2 for YAG), the exciton energy transforms into the energy of the recombinational branch of relaxation, which is expressed in the respective addition in the excitation spectra as well [6]. As it was shown for YAG [7], the quenching of the exciton emission causes the rise of thermoluminescence excitation efficiency. This process, assumed to be the process of thermoionisation of relaxed (self-trapped) excitons, seems to be the primary process determining the temperature-induced redivision of energy relaxation between the exciton and the recombinational branch. Concerning the unfreezing part of excitation efficiency, it is not clear whether the creation of the recombinational-type excitation in the exciton region is caused directly by autoionisation or by ionisation during relaxation of excitons (like in case of defect creation in alkali halides on self-trapping of excitons).

At low temperatures the relative excitation efficiency of both kinds of processes, the exciton and the recombinational ones, can be reflected by the spectrum of the ratio of two emission intensities. This spectrum seems to be more informative as it is less disturbed by possible surface losses. As can be seen, this ratio changes strongly on moving from the exciton region to that of more higher energies of exciting photons. Therefore, the threshold observed here seems to represent the short-wave edge of the exciton absorption region. Because of the higher mobility of the excitations, responsible for recombinational emission, we can suppose that the observed threshold would be even stronger if we take into consideration the possible surface losses. As will be shown later, this threshold (or edge) is clearly observable in two-photon spectra as well.

2.2. *Two-photon spectroscopy*

A number of problems connected with the possible influence of surface effects (traditionally actual on the interpretation of one-photon excitation data in crystals with large values of absorption coefficients) can be overcome in case of two-photon excitation, when absorption takes place entirely in the crystal. Both kinds of the above-discussed emissions are observable on two-photon excitation in the same region of crystal energetical spectra, which shows that their origin is not connected with any surface effects.

The spectra of two-photon excitation are given by curves 1′ and 2′ in Fig. 1 for a constant power of the laser beam and, therefore, they reflect partially the structure of two-photon absorption. Two-photon excitation takes place in the whole region of the intrinsic absorption of the crystals. The excitation spectra of the two kinds of emissions are different (like also in the case of one-photon excitation). The difference between the long-wave edges of one- and two-photon excitation spectra is due to an additional contribution from the states of the Urbach tail in the one-photon case. These states are located at $E < E_0$ (E_0 is the parameter of the Urbach rule) and they will not be discussed here. A much more important feature is clearly observable in the spectra of the ratio of two emission intensities. Curves 3 and 3′ in Fig. 1 illustrate the main peculiarity: in the excitonic region in the case of one- and two-photon absorption at the same energy mainly excitonic or electron–hole processes, respectively, are excited. This dependence on the excitation manner is lower on excitation at higher energies. The energy distribution between both relaxation branches differs for two-photon excitation in the exciton region from that for one-photon excitation. This fact is expressed also in the temperature dependence of recombinational luminscence (Fig. 2). As the exciton excitation efficiency is much lower for two-photon excitation than for one-photon excitation, the exciton relaxation branch cannot significantly disturb the temperature dependence of recombinational branch in this case.

3. Conclusions

It is known that in one- and two-photon cases the selection rules are different and, therefore, different electronic states may be excited in these two cases. A comparison of the data of one- and two-photon spectra shows that for two-photon excitation in the exciton region the excitation of the recombinational branch prevails strongly, whereas in the one-photon case the excitonic one is prevalent. Such a fact may be a direct evidence of the existence of two types of initial states (the metastable excitons and the electron–hole continuum) in the exciton region, which leads to specific branching of relaxation. These states can be excited almost separately, and they are the initial states for two branches of relaxation. The processes of interstate

Table 1

	Crystals	
	YAG	YAP
Structural properties		
Lattice constant (Å)	12.008	$a = 5.176$ $b = 5.307$ $c = 7.355$
Atoms in unit cell	160	20
Symmetry group	O_h^{10}	D_{2h}^{16}
Symmetry of oxygen positions	C_1	C_1
Optical properties		
Convergence point of the Urbach tail (E_0 threshold, eV) according to refs. [8,9]	7.012	8.018
Edge of the strong electron-hole-transitions (see threshold on Fig. 1) (eV)	7.6–7.7	8.2–8.3
Absorption in exciton region		
One-photon (10^5 cm^{-1}) at 300 K	3	2
Two-photon (cm/GW) at 80 K	1	
Luminescent properties according to refs. [5,10]		
Exciton-like luminescence		
Position of emission band (eV)	4.9	5.9
Quantum yield at 5 K	0.5	0.3
Recombinational luminescence		
Position of emission band (eV)	4.2	4.2
Quantum yield at 250 K	0.5	0.3

scattering seem to be strong only for the electronic excitations of a higher energy, where the dependence on the excitation manner disappears and the branching of relaxation is, evidently, determined mainly by intrinsic processes. We relate the observed peculiarities in the spectrum of electronic excitations of our crystals with the manifestation of at least two electron–hole continua having holes from different subbands of the nonhomogeneous valence band. In such a case the observed excitonic states, which have the same energies as do the states of the lowest continuum, must be associated with the electron–hole continuum of a higher energy. The specificity of electronic excitations and their relaxation branching observed in YAG and YAP crystals may be characteristic of a large number of complex oxides and may give the dependence of radiation effects not only on the excitation energy, but also on the manner of selective excitation.

YAG and YAP crystals are very suitable for the investigation of such a coexcistence, as both branches are observable simultaneously via different bands of bright luminescence. Some features of the crystals discussed above are given in the Table 1.

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References

[1] M. Causa, R. Dovesi, C. Roetti and E. Kotomin, Chem. Phys. Lett. 140 (1987) 120.
[2] Y.P. Li and W.Y. Ching, Phys. Rev. B 31 (1979) 2172.
[3] A.I. Kuznetsov, B.R. Namozov and V.V. Myurk, Fiz. Tverd. Tela. 27 (1985) 3030.
[4] T. Tomiki, F. Fukudome, M. Kaminao, M. Fujisawa and Y. Tanahara, J. Phys. Soc. Jpn. 55 (1986) 2090.
[5] A.I. Kuznetsov, V.N. Abramov, V.V. Mürk and B.R. Namozov, Trudy Inst. Fiz. Akad. Nauk Est. SSR 63 (1989) 19.
[6] V. Mürk and N. Yaroshevich, Phys. Status Solidi, B 181 (1994).
[7] K.M. Ismailov and V.V. Myurk, Fiz. Tverd. Tela 34 (1992) 311.
[8] T. Tomiki, F. Fukudome, M. Kaminao, M. Fujisawa, Y. Tanahara, and T. Futemma, J. Phys. Soc. Jpn. 58 (1989) 1801.
[9] T. Tomiki, F. Fukudome, M. Kaminao, M. Fujisawa, Y. Tanahara and T. Futemma, J. Luminesc. 40/41 (1988) 379.
[10] A.I. Kuznetsov, V.N. Abramov, V.V. Myurk and B.R. Namozov, Fiz. Tverd. Tela 33 (1991) 2000.