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1991 J. Phys.: Condens. Matter 3 5457

(http://iopscience.iop.org/0953-8984/3/28/021)

J. Phys.: Condens. Matter 3 (1991) 5457–5461. Printed in the UK

LETTER TO THE EDITOR

Polarization of luminescence of colour centres in YAG crystals

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Received 27 March 1991

Abstract. The polarization diagrams of the luminescence at 400 nm of colour centres in YAG crystals have been measured under excitation in absorption bands at 370 and 235 nm. The results suggest that the centre is most likely to be a one-electron centre involving an oxygen vacancy and a perturbing agent in the adjacent Al_{O_h} site.

Although there are a considerable number of papers devoted to colour centres in YAG ($Y_3Al_5O_{12}$) crystals the nature of the centres is not clear. A particular type of centre is often observed in crystals obtained or treated under a reducing atmosphere. It has the main absorption band at 370 nm and the corresponding luminescence band at 400 nm [1–6]. A necessary condition for obtaining considerable concentrations of the above-mentioned centres is the deficiency of Al_2O_3 (or excess of Y_2O_3) in the YAG crystals [2, 4]. In principle the main constituent of the centre could be either an interstitial cation or an anion vacancy with one or two trapped electrons.

To obtain more information about the nature of these centres we performed optical measurements including those of luminescence polarization of the centres under consideration.

Several different samples were studied and the highest concentrations of centres were observed in crystals grown from the melt with excess Y_2O_3 under the reducing conditions. Other samples were made from initially transparent crystals treated in CO atmosphere or in Al or Y vapours at ≃1500 °C. For the polarization measurements the crystals were cut as small platelets with surfaces in the (100) plane.

The typical optical spectra at 290 K are shown in figure 1. At low temperature the phonon structure can be seen both in the excitation (370 nm) and luminescence spectra in accordance with previous observations [6]. Besides the main 370 nm band there are other bands in the shorter-wavelength region of the excitation spectrum (figure 1). In accordance with the results concerning the intrinsic optical properties [7, 8] we suggest that the excitation of luminescence in the spectral regions with $\lambda < 155$ nm and around 175 nm involves band-to-band transitions with subsequent recombination and exciton energy transfer, respectively. This is substantiated by the fact that under excitation in the region from 150 to 200 nm several other luminescence bands are also excited and weak thermostimulated luminescence is accumulated at room temperature with the main peak at about 500 K. The excitation bands at 235 and 370 nm correlate with

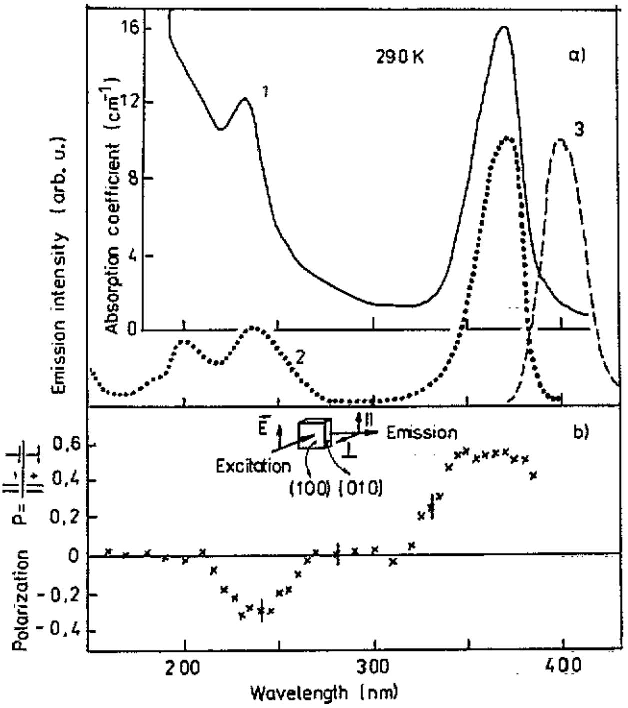

Figure 1. Room temperature optical spectra of YAG crystal grown in a reducing atmosphere from the melt with excess Y_2O_3. (*a*) Absorption (1), excitation (2), luminescence (3) spectra. (*b*) Degree of polarization spectrum; inset—the geometry of the measurements of the degree of polarization.

pronounced absorption bands and these are most likely the main bands of the centres under consideration.

The fast decay of the 400 nm luminescence ($\tau = 3$ ns at RT [6]), the small Stokes shift and the nearly symmetric shape of the emission and excitation bands lead to the conclusion that we have to deal with an allowed electric dipole transition with almost equal transition probabilities for the absorption and luminescence. Using Einstein's relations for allowed transitions and the refraction coefficient of YAG, the decay time constant and the luminescence yield of the 400 nm band from [6] we calculated the oscillator strength for unpolarized light in the 370 nm band to be 0.4 (±20%). The absorption coefficient was 15 cm^{-1} in the 370 nm band of one of the YAG crystals grown from the melt with Y_2O_3. Using Smakula's formula and the estimated oscillator strength we determined the concentration of the corresponding centres as 6×10^{16} cm^{-3} (±25%). Taking into account the dispersion of the refraction coefficient and the absorption coefficient in the 235 nm band, 6 cm^{-1} (ignoring the background), we obtained the oscillator strength for the 235 nm band as 0.2 (±30%). The total oscillator strength, 0.6, for the main 235 and 370 nm bands is reasonable for a single-electron centre. So far we do not have a definite judgement on whether the excitation band at 200 nm belongs to the same 400 nm luminescence centres because of the strong background absorption in this region and the recombination processes excited in this band. Assuming that it belongs to the same centre, nevertheless we estimate the oscillator strength to be between 0.1 and 0.2 from the relative intensities of the excitation bands.

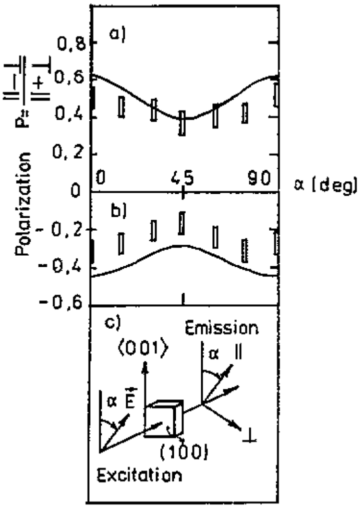

Figure 2. Experimental azimuthal polarization relations (bars) for the 400 nm luminescence under the excitation with (*a*) 365 nm and (*b*) 240 nm light at 290 K. Theoretical azimuthal polarization relations (full curves) (*a*) for absorbing and emitting dipoles oriented in the ⟨0, 1, 2⟩ direction and (*b*) for an absorbing circular oscillator with its normal coinciding with the direction of the emitting oscillator ⟨0, 1, 2⟩. (*c*) The geometry of the experiment.

The main experimental work was devoted to the study of the polarization of the photoluminescence at 400 nm. The degree of polarization within the luminescence band was measured under the excitation in all excitation bands (figure 1). The luminescence is unpolarized under excitation in the 150 to 200 nm region. This supports the view that in this case energy transfer processes are involved during which the anisotropy of the excitation is lost and, as a result, the luminescence is unpolarized. Under excitation in the 235 and 370 nm bands the 400 nm luminescence is polarized and the degree of polarization is negative and positive, respectively. We also measured the azimuthal polarization relations of the 400 nm luminescence for excitation with 235 and 365 nm polarized light (figure 2). The luminescence was observed in the corresponding direction as the excitation light beam and the polarization degree $P(\alpha) = (\| - \perp)/(\| + \perp)$ was determined, where ∥ and ⊥ stand for the intensity of luminescence polarized ∥ and ⊥ to the $\boldsymbol{E}$ vector of the exciting light, respectively and α is the angle between the crystal ⟨001⟩ axes and the $\boldsymbol{E}$ vector of the exciting light (figure 2).

The experimental results are compared with theoretical relations calculated as in [9] for dipole moments of the transitions having coordinate directions $\langle h, k, l\rangle$ in the crystalline structure of YAG. The calculations were based on the following considerations. (i) The direction of the dipole moment of the absorption transition at 370 nm and the radiative transition at 400 nm is the same. (ii) The angle between the directions of the dipole moments of the 400 nm transitions and the 235 nm absorption transitions is nearly 90°. This consideration is based on the analogy of the spectral dependence of the degree of polarization with that of the colour centres in simple cubic crystals [9] and the dichroism and the polarization of the luminescence of the single-electron F^+ centres in α–Al_2O_3 [10].

The polarization relations were calculated for many directions of dipoles. From all the relations only those that had the same shape as the experimental ones and did not differ by more than ±30% from the absolute value of the experimental degree of polarization (the accuracy of the direction measurements was ±10° as determined from the accuracy of the cutting of the crystals with respect to their crystallographic planes, the orientation of the crystal and the measurement errors) were considered. From this comparison we conclude that the transitions giving rise to 370 nm absorption and 400 nm luminescence can be related to dipoles oriented in the ⟨0,1,2⟩ direction but the 235 nm absorption is related to dipoles lying in the plane perpendicular to this direction. The experimental data are still not sufficient to allow determination of the exact orientation of the dipole in this plane. If we assume that the centre has two absorption bands, then the 235 nm band can be bound to the degenerate excited state and the polarization relations reflect the circular oscillator (two phase-conjugated mutually perpendicular dipoles)—the centre is axial with the axis in the ⟨0, 1, 2⟩ direction. In another case it can be suggested that the centre has a third absorption band at around 200 nm. Then the shape of the azimuthal relation of the polarization under 235 nm excitation would be like that observed experimentally but the absolute values would differ by about three times. Unfortunately, for the above-mentioned reasons the azimuthal polarization relations could not be measured under the 200 nm excitation; however, it seems that under the 235 nm excitation the difference between the experimental and calculated relations is too large in this case.

The direction ⟨0, 1, 2⟩ in the YAG structure corresponds to one of the oxygen–oxygen directions, thus suggesting that two adjacent oxygen vacancies could form the basis of the centre responsible for the 400 nm luminescence band. However, the observed concentration of the centres ($\sim 10^{17}$ cm^{-3}) seems to be too high for a bivacancy centre. Besides, one expects that the absorption peak of a bivacancy, similarly to those in other oxides, should be at lower energy.

From the analysis of the results reported above we suggest as the possible model for the centre emitting the 400 nm luminescence band a perturbed F$^+$ centre. An unperturbed F$^+$ centre would be an anion vacancy with one localized electron in the irregular tetrahedron formed from two $Y^{3+}_{D_2}$ ions and an $Al^{3+}_{O_h}$ ion and $Al^{3+}_{T_d}$ ion.

Because of the low symmetry (point group C_1) of the anion vacancy, the degenerate p-like excited states of the F$^+$ centres are split by the crystal field and there should be three absorption bands. On the grounds of a certain analogy with F$^+$ centres in α–Al_2O_3 crystals, several peculiarities of the polarization of analogous centres in YAG can be predicted. In particular, the azimuthal relations of polarization should be similar to those calculated in our work for the case of three absorption bands. However, it should be noticed that the concentration of the centres emitting 400 nm luminescence is considerably higher in reduced crystals grown from the melt with excess Y_2O_3. It is known that all YAG crystals prepared from the melt have a non-stoichiometric composition due to the incorporation of some portion of the Y^{3+} ions into $Al^{3+}_{O_h}$ sites [4, 11, 12]. The concentration of such 'antisite' defects can reach 10^{20} cm^{-3} and it seems possible that such a high concentration of the $Y^{3+}_{O_h}$ could be found in crystals grown from the melt with excess Y_2O_3. It is reasonable to assume that the formation of the oxygen vacancy is energetically favourable if the adjacent octahedral site is occupied by an Y^{3+} ion rather than in the regular oxygen site. In this case the three Y^{3+} ions surrounding the vacancy form a plane nearly perpendicular to the ⟨0.3, 1, 2⟩ direction, which is close to the ⟨0, 1, 2⟩ direction. It seems probable that the lower-energy p-like orbital of the perturbed F$^+$ centre is in this direction, thus determining the nearly axial configuration of the F$^+$ centre and the polarization properties of the 400 nm luminescence under 370 nm excitation.

Taking into account several theoretical speculations about the energy level position in F$^+$ centres and perturbed F$^+$ centres [13], one should not anticipate significant differences between the two cases in YAG—regular F$^+$ centres and F$^+$ centres with three adjacent Y^{3+} ions. With this in mind we used the Mollwo–Ivey relation to determine the approximate position of F$^+$-centre absorption bands in YAG [14]. As the p-like excited state is fully split (as it is also in corundum crystals), the energy given by the Mollwo–Ivey relation should be the weighted average from two (or three) absorption bands. The Mollwo–Ivey relation gives 4.8 eV as the absorption transition energy for F^+ centres in YAG, which is close to the weighted average (4.94 eV) from the energies of the bands at 370 nm (3.35 eV), 235 nm (5.28 eV) and 200 nm (6.2 eV). The weighted average energy from the first two bands is 4.64 eV if we assume that the 235 nm band corresponds to a doubly degenerate level.

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