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Abstract. The photoluminescence of Ti-doped sapphire (Ti : Al_2O_3) crystals excited using the second (532 nm) and fourth (266 nm) harmonics of a high power pulsed Nd : YAG laser has been investigated. Excitation at 532 nm into the crystal field band of Ti^{3+} produces the well known broad infrared emission band corresponding to the $e_g \rightarrow t_{2g}$ transition in the octahedral field approximation. However, this emission can also be excited with ultraviolet light together with an additional blue emission via a two-photon excitation process. This has two lifetime components of 600 and 21 μs. The mechanism of excitation for the infrared emission band when it is excited via ultraviolet radiation has been studied: it is shown that the excited state of the Ti^{3+} ions is populated via an intermediate state (here labelled as X) which clearly correlates with the shortest lifetime component of the blue emission.

1. Introduction

After demonstration of the Ti : Al_2O_3 (Ti–sapphire) system as a broadly tunable solid state laser [1] research into the optical spectroscopy of this material has attracted considerable attention [2–10]. Ti^{3+} shows a broad visible absorption band, centred at $\approx$490 nm, within which the pumping of the laser action can be performed. This broad absorption is unambiguously associated with the $t_{2g} \rightarrow e_g$ transition, between the levels of the d^1 configuration of this ion split by the octahedral crystalline field. Excitation into this band produces a broad fluorescence band in the IR region ($\approx$750 nm) which is responsible for the tunability. However, it has been reported recently that this luminescence can also be excited with high intensity light lying inside the strong UV absorption edge in which the oxygen–titanium charge transfer bands are present [5].

In this work a systematic study on the luminescence of titanium in Al_2O_3 crystals under high excitation intensity in the UV region is reported. Such experiments have become necessary to get a more detailed understanding of the possible excited states as well as to explore alternative mechanisms for pumping the laser emission. The results are compared with those obtained under direct excitation in the crystal field transition.

2. Experimental

The Ti : Al_2O_3 crystal samples used in this work were grown by the Verneuil method at the Institute of Low Temperature and Structure Research (Wroclaw, Poland). The concentration of Ti^{3+} ions was estimated from the absorption spectrum to be 0.01 wt%.
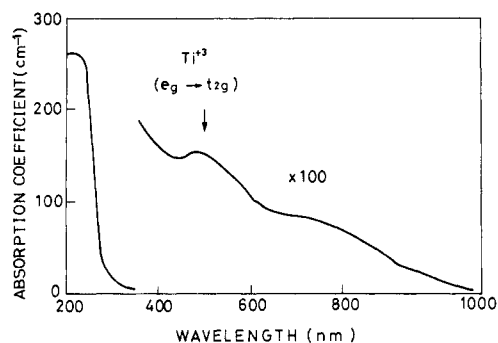
Figure 1. *RT* absorption spectrum of our Ti–sapphire crystal.

To carry out the emission experiments the 266 nm quadrupled and 532 nm doubled lines of a high power pulsed Nd : YAG laser (Spectra Physics model DCR 2/2A3378) were used to excite electrons in the charge transfer absorption edge and in the crystal field transition band. The emitted pulses were sent to a photomultiplier tube RCA 7102 followed by a boxcar integrator PAR model 162 through which the shape of the fluorescence decay time curves were analysed. Time-resolved emission spectra were obtained with a spectral resolution of 5 nm. To perform the measurements of emission versus excitation laser intensity the power of our Nd : YAG laser was varied by changing the pumping intensity. The excitation intensity had previously been calibrated. At the same time some additional continuous fluorescence measurements (see text) were made using a conventional spectrofluorimeter, Jovin Ivon model JY3CS, which were to be compared with results obtained under Nd : YAG excitation.

3. Experimental results and discussion

The optical absorption spectrum of our Ti : Al_2O_3 crystal (see figure 1) agrees with that previously reported for this material [2]. It consists of a broad visible absorption band at 490 nm, a strong absorption UV edge beginning around 300 nm with a shoulder at $\simeq$240 nm and a broad absorption band peaking around 780 nm, which is a spurious absorption related to either Ti^{4+}–Fe^{2+} or Ti^{3+}–Ti^{4+} pairs [11, 12].

The visible band at 490 nm (indicated by an arrow in the figure) is the crystal field absorption band and corresponds to the intra-configurational transition $t_{2g} \rightarrow e_g$ of the d^1 configuration in the octahedral field approximation.

On the other hand, the strong UV absorption edge, which appears at lower energy than that corresponding to the intrinsic absorption edge of the material (about 9.4 eV), is related to the ligand–metal charge transfer absorption bands of Ti^{3+} or Ti^{4+}, which can both be incorporated inside the crystal host, although the presence of trace ions such as Fe^{3+} and Cr^{3+} could also be contaminating this edge [4, 5, 13]. The origin of these O–Ti charge transfer bands may be understood in terms of molecular orbital theory for the TiO_6 complexes. At first it seems reasonable to assign the greater part of the absorption at 240 nm (5.16 eV) to charge transfer bands between the oxygen and Ti^{4+} ions in accordance with the reflectivity spectrum of the rutile phase and molecular orbital theory calculations for the TiO_6 complex [14]. Information is scarce for the ligand–Ti^{3+} charge transfer band but it has been proposed that it occurs at 190 nm (6.2 eV) [15] too.
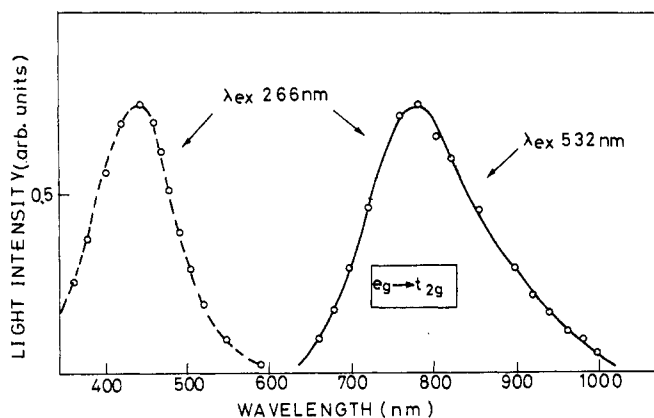
Figure 2. LNT emission spectra obtained under both UV and green excitation. Wavelengths are displayed on the figure. Emission bands have been normalized.
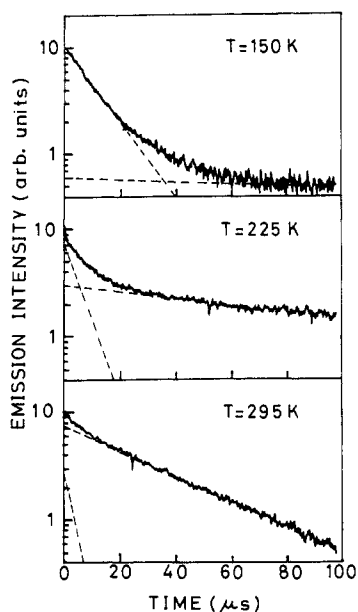

Figure 3. Normalized fluorescence decay time curves of the blue emission ($\lambda_{emi} = 430$ nm) at three different temperatures.
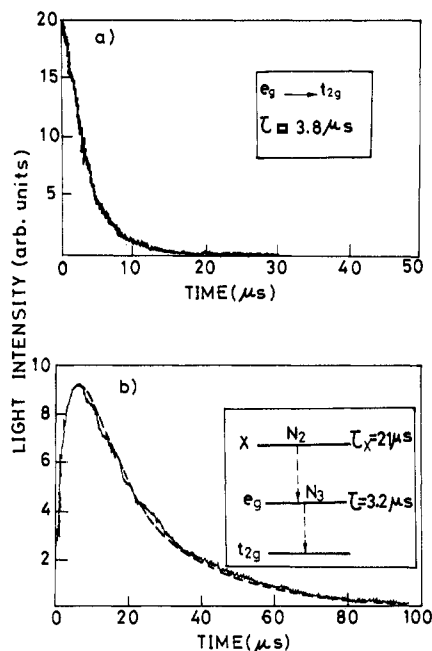

Figure 4. LNT fluorescence decay time of the IR emission ($\lambda_{emi} = 760$ nm). (a) $\lambda_{exc} = 532$ nm, (b) $\lambda_{exc} = 266$ nm. Inset of (b) includes a quantitative scheme of responsible levels.

Figure 2 shows the liquid nitrogen temperature (LNT) emission spectrum obtained under excitation in this charge transfer absorption edge ($\lambda = 266$ nm). Two emission bands are observed: a blue luminescence peaking at 430 nm and near-IR luminescence of the Ti^{3+} ions ($e_g \rightarrow t_{2g}$ transition) centred at 780 nm. This last band (with the same

spectral distribution) is also obtained under direct excitation into the crystal field $e_g \rightarrow t_{2g}$ band (530 nm). In order to perform these measurements the total area under the emitted pulse was recorded. This result is consistent with that reported by Powell *et al* [5] for their Czochralski Ti : Al_2O_3 crystals.

In order to characterize the origin of these two emissions (blue and IR) their decay times were systematically analysed.

For the blue luminescence the decay time (at LNT) consists basically of one component with a lifetime of 21 μs. However, with increasing temperature the shape of the fluorescence decay curve changes substantially and a new component is observed at about 150 K with a lifetime of 600 μs. Above this temperature the decays of the blue emission can be well described as a sum of two exponential decays. The time-resolved emission spectra of both components were very similar giving (inside our experimental spectral resolution) the same emission spectrum of figure 2.

Figure 3 shows, as an illustrative example, three normalized decay time curves for three different temperatures. Both blue emissions lifetimes decrease with increasing temperature but their corresponding intensities behave quite differently. While the intensity associated with the short component decreases monotonically with increasing temperature, the intensity associated with the long component grows as the temperature is raised from LNT to 220 K. So, at LNT the emission is basically due to the short component while at room temperature the long component predominates, having a room temperature lifetime value of 35 μs. This second emission should be associated with Ti^{4+} centres because it disappeared after thermal annealing at high temperatures ($\approx 1800\,^{\circ}$C) when a reduction of the Ti^{4+} ions to Ti^{3+} took place [5]. At the same time this assignation agrees with previous results in which a similar blue luminescence has been reported for several crystalline oxides doped with Ti^{4+} ions [16–18] as a consequence of exciting in
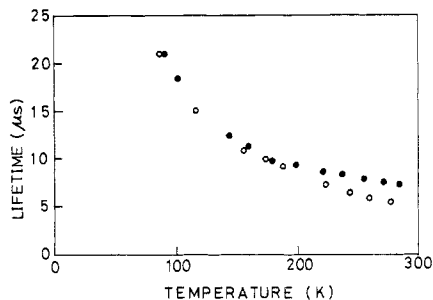
Figure 5. Temperature dependence of the short blue component (open circles) and the decay time, τ_X, of the X level populating the IR emission (full circles), see figure 4(b).
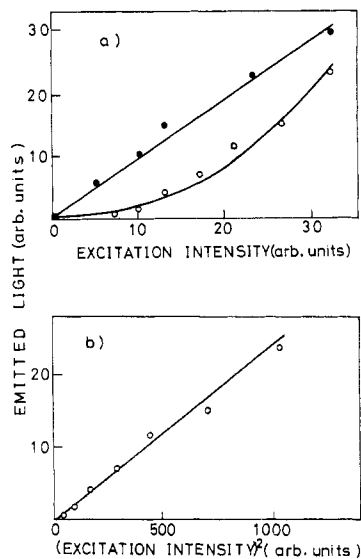
Figure 6. (a) Intensity of the IR emission ($\lambda_{emi} = 780$ nm) as a function of the laser excitation intensity. Open circles, $\lambda_{exc} = 266$ nm; full circles, $\lambda_{exc} = 532$ nm. (b) Quadratic dependence observed under UV excitation.

the UV region, where charge transfer from oxygen ions to Ti^{4+} ions can occur. On the other hand, it is important that the short component (21 μs at LNT), which is predominant at low temperatures, has not been reported up to now, probably due to the experiments being performed at room temperature only. As we will see later this emission, which seems to be correlated with Ti^{3+} centres, plays an important role in the UV excited IR emission.

Regarding the IR emission observed under excitation in the UV region, it is important to point out that its fluorescence decay time is different from that obtained for this emission ($e_g \rightarrow t_{2g}$) when it is directly excited into the crystal field transition.

Figure 4 shows the LNT decays observed for both visible and UV excitation. The decay time observed under excitation into the crystal field band (532 nm) consists of a single exponential decay associated with a radiative lifetime of 3.8 μs (see figure 4(a)) as has been reported for the frozen electric dipole $e_g \rightarrow t_{2g}$ transition induced by the crystal field.

On the other hand, when this emission is excited via UV light the decay time is different (see figure 4(b)) showing an initial rise time followed by a decay which seems to be slower than that observed in figure 4(a). However, the shape of this decay can be reproduced well considering the third additional level responsible for an indirect population of the upper level, e_g, of Ti^{3+}. A simple scheme of levels proposed for the mechanism of excitation of the IR emission under UV light is displayed on the inset of figure 4(b). Within this model UV excitation would cause direct population of the X level and its relaxation should produce a populated e_g level. The time evolution of the e_g population can be obtained using the rate equations for the levels involved:

$$\frac{dN_3}{dt} = -N_3(t)p_{3n}$$

$$\frac{dN_2}{dt} = -N_2(t)p_{21} + N_3(t)p_{32} \tag{1}$$

where p_{21} represents the de-excitation rate from level e_g to level t_{2g}, p_{32} the rate from X to e_g and p_{3n} the sum of the rates from level X to possible ground levels n (including the t_{2g} one). N_2 and N_3 are the instantaneous populations for the e_g and X levels respectively.

Solution of (1) with the initial conditions $N_3(0) = N_{03}$ and $N_2(0) = 0$ gives the time evolution for N_2, as follows:

$$N_2(t) = \frac{N_{03}p_{32}}{p_{21} - p_{3n}} [\exp(-p_{3n}t) - \exp(-p_{21}t)]. \tag{2}$$

The best fit for the decay time curve of figure 4(b) is represented by the broken curve and corresponds to the values $\tau_X = 21$ μs and $\tau_2 = 3.2$ μs obtained from expression (2) for LNT. The value for the lifetime of the e_g level agrees with that observed when exciting directly into the crystal field band although it now appears slightly shortened. On the other hand, the lifetime obtained for the X level is the same as that observed for the short component of the blue emission; it occurs across the whole temperature range (77–300 K) investigated in this work, as shown in figure 5. This fact strongly suggests that the X band is also the excited level for the short component of the blue emission.

Further investigation is required into how the X level is reached in order to obtain more detailed information on the mechanism of the UV excited $e_g \rightarrow t_{2g}$ emission of Ti^{3+}. In fact the continuous excitation spectrum of the IR emission band showed no trace of the UV excitation band. This indicates that the emission spectrum cannot be obtained

with low intensity UV excitation and therefore population of the X level can only be reached with high intensity UV excitation, probably via a two-photon absorption process. In order to confirm this assumption the IR emission spectrum was studied as a function of excitation intensity.

Figure 6(a) shows the dependence of the 780 nm emission band on excitation intensity for both UV (266 nm) and green (530 nm) excitation wavelengths. Direct excitation into the $t_{2g} \rightarrow e_g$ absorption band produced linear behaviour as expected for a one-photon process whereas a non-linear dependence was clearly observed for UV excitation. This indicates that higher photon absorption processes are involved in the population of the $e_g^1 t_{2g}^0$ excited state of Ti^{3+}. Figure 6(b) reveals that this dependence is better described by a quadratic process showing that two photons of 266 nm are being absorbed earlier to reach the e_g excited state.

At this point we mention that the short component of the blue emission ($\tau = 21 \mu s$ at LNT) additionally showed a non-linear dependence on the excitation intensity. Further, it is important to point out that the shapes of the fluorescence decay time pulses for both blue and IR emission bands remained unchanged as the excitation intensity was increased and therefore no new levels set in when the excitation intensity increases.

In order to understand the mechanism of UV excitation of the IR emission band the possible excited states of Ti^{3+} should be taken into account. In fact, as reported previously [5], the UV excited IR luminescence increased under a high temperature annealing (1800 °C) treatment, which reduced Ti^{4+} to Ti^{3+}, so that the possibility of excitation of Ti^{4+} centres leading to IR emission should be disregarded†. Therefore we may consider that two photons of 266 nm are being simultaneously absorbed from a Ti^{3+} ion, which then reaches a higher energy state at $\simeq 133$ nm (9.3 eV) far from the t_{2g} level. This excited state could de-excitate giving both the blue and IR emissions.

Other possibilities, involving impurities or colour centres, should not be disregarded. In this scheme the excitation (via a two-photon process) should be localized on these defects and then transferred to the Ti^{3+} ions. In fact, it is known that a number of emission bands correlated with colour centres appear under UV excitation [19]. These colour centres could also be responsible for the short decay time component of the blue emission. The colour centres could transfer their energy to the Ti^{3+} ions, in accordance with the strong overlapping between the blue emission and the $t_{2g} \rightarrow e_g$ absorption band. The quadratic dependence observed for the UV laser excited emission could also be explained as a consequence of including the rate of formation of defects.

In any case, it is risky to make a definitive assignation for both centres and energy levels involved in the population of the e_g excited state of the IR emission, particularly if one takes into account that gap energies are involved. Excited state levels probably need to be studied using excited state absorption techniques as well as photoconductivity measurements to increase our understanding. Moreover experiments on samples co-doped with other impurities should be very useful. In any case the proposed mechanism of the observed UV excited IR luminescence of Ti^{3+} in sapphire is well supported by experimental results and correlation between the blue and IR emission is evident.

Acknowledgments

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† The possible occurrence of some $Ti^{4+} \rightarrow Ti^{3+}$ energy transfer at temperatures higher than 200 K should not be disregarded. In fact, it could explain the small difference between the temperature dependence of the short blue component and that of the decay time of the X level.

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