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Excited State Absorption of $Ti^{3+}:YAlO_3$*

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Abstract. Spectroscopic properties and excited-state absorption (ESA) of Ti^{3+} doped $YAlO_3$ are investigated in detail. The fluorescence band is centered at 623 nm with a room-temperature lifetime of 11.4 µs and a quantum efficiency nearby one. Till now laser action could not be detected because of strong excited-state absorption into a charge transfer band located 45500 cm^{-1} above the Ti^{3+} ground state. At the Ar-laser pump wavelength the ESA cross-section is determined to be $\sigma_{ESA} = 1 \times 10^{-18}$ cm^2. This value is a factor of 44 higher than the ground-state absorption cross-section. Consequently the pumping efficiency is decreased by one or two orders of magnitude. The $Ti:YAlO_3$ results are compared with the spectroscopic data of $Ti:Al_2O_3$.

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Ti-doped sapphire is a well known solid-state laser material in the red to near infrared spectral range [1]. With $YAlO_3$ (YAP) the fluorescence wavelength can be shifted into the yellow region with a room-temperature lifetime of 11.4 µs, which is four times longer than the value for sapphire. This longer lifetime would be advantageous in case of flashlamp-pumping and for all purposes of energy storage, for example Q-switching. So far, we could not achieve laser action of $Ti^{3+}:YAlO_3$ under cw pumping or pulsed conditions although Kvapil et al. have published some hints at stimulated emission [2]. However, the estimated power efficiency of 4.4×10^{-4} under laser pumping is extremely low. In this paper we report on excited-state absorption (ESA) measurements of $Ti^{3+}:YAlO_3$ and investigate the process on which this transition is based upon. For comparison the ESA properties of $Ti^{3+}:Al_2O_3$ are also reported.

Spectroscopic Properties

$YAlO_3$ crystallizes in a perowskite type structure with space group Pbnm. The Al sites – also occupied by the Ti ions – are surrounded by oxygen octahedra, which are distorted to triclinic site symmetry C_i.

Figure 1 shows the ground-state absorption (GSA) spectrum of this system. Two broad bands peaking at 432 nm and 491 nm are observed corresponding to transitions from the ground-state to the Jahn-Teller split ^2E excited state. By microprobe analysis the Ti concentration was evaluated to be 1.7×10^{19} cm^{-3}, which gives an absorption cross-section $\sigma_a(488\,nm) = 2.3 \times 10^{-20}$ cm^2 at the Ar-laser pump wavelength of 488 nm and a peak value $\sigma_a(432\,nm) = 2.9 \times 10^{-20}$ cm^2.

Another very broad band not yet identified is located in the near infrared region around 950 nm. This band is very similar to a parasitic absorption in

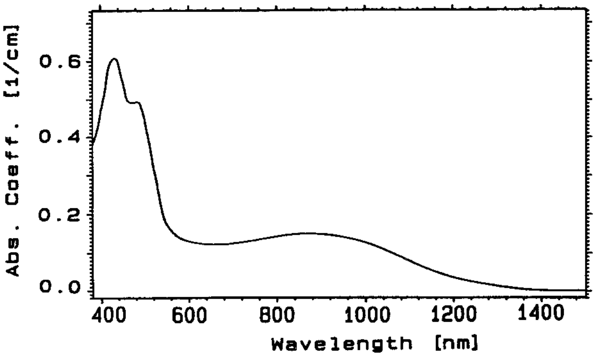

Fig. 1. Ground-state absorption spectrum (GSA) of $Ti:YAlO_3$ at 300 K

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* Dedicated to Prof. Dr. Herbert Welling on the occasion of his 60th birthday

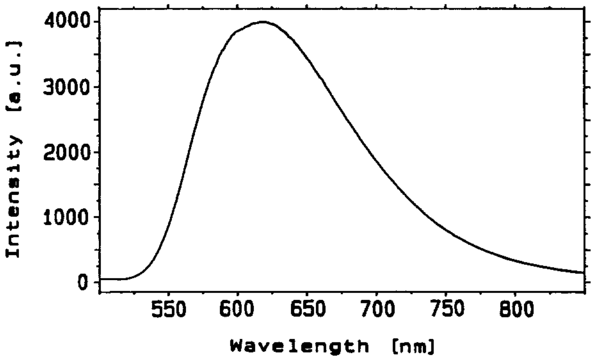

Fig. 2. 300 K fluorescence spectrum of $Ti^{3+}:YAlO_3$ at 488 nm Ar laser excitation

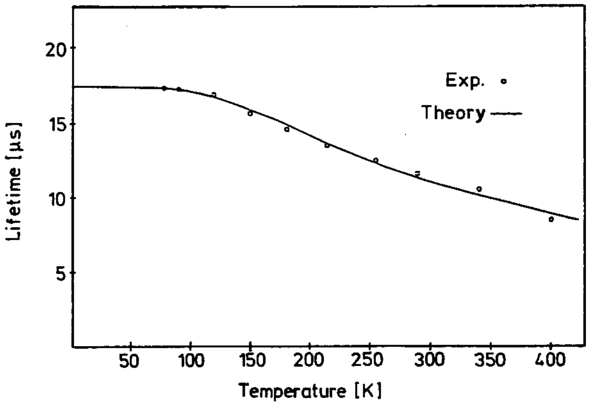

Fig. 3. Temperature dependence of the fluorescence lifetime

$Ti:Al_2O_3$, where it is attributed to a Ti^{3+}/Ti^{4+} complex center [3]. But in contrast to sapphire it was not possible to remove this band by annealing in reducing atmosphere. Also the Ti^{3+} absorption bands at 432/491 nm were not influenced by this heat treatment. Therefore we conclude, that practically all Ti ions are in the trivalent state. In the UV region a charge transfer band is measured at 220 nm, which will be discussed in detail in the ESA section of this paper.

In Fig. 2 the broad-band fluorescence spectrum is shown with maximum wavelength at 623 nm and 3310 cm^{-1} FWHM, which is a bandwidth very similar to $Ti:Al_2O_3$. The corresponding transition is from the ^2E excited state to the crystal-field and probably also Jahn-Teller split ^2T ground state. The Stokes shift of 4360 cm^{-1} is somewhat smaller than in $Ti:Al_2O_3$ (5360 cm^{-1}).

For calculation of the effective emission cross-section σ_e at peak wavelength the method of McCumber [4] was used involving the integrated fluorescence curve, the index of refraction $n = 1.9$ [5] and the room-temperature emission lifetime $\tau = 11.4$ µs. We obtain $\sigma_e = 3.7 \times 10^{-20}$ cm^2 which is in accordance with the ground-state absorption cross-section given above.

Fluorescence lifetime measurements were carried out by the photon-counting method. The results are shown in Fig. 3 as a function of temperature. All decay curves are single exponential, i.e. only one type of Ti^{3+} center is present in the host crystal. At low temperatures, the lifetime increases up to 17.5 µs, as given in Fig. 3. The experimental data can be fitted by the following equation [6, 7]:

$$\tau_{rad}^{-1} = \tau_{stat}^{-1} + \tau_{vib}^{-1} \cdot \coth(h\nu/2kT).$$

Here the total radiative transition rate consists of a stationary part τ_{stat}^{-1} caused by the static crystallographic site symmetry (inversion symmetry yields parity forbidden $d-d$ transitions); the temperature dependent vibronic part $\tau_{vib}^{-1} \cdot \coth(h\nu/2kT)$ is caused by coupling an increasing number of asymmetric phonons resulting in an additional dynamical distortion of the Ti site. Consequently the lifetime is decreasing with temperature. In Fig. 3 the fit yields $\tau_{stat} = 952$ µs, which is a reasonable value for a site of C_i symmetry; also the value for $\tau_{vib} = 17.8$ µs and the effective phonon energy $h\nu = 310\,cm^{-1}$ is obtained. This curve demonstrates, that up to a temperature of 400 K nearly no nonradiative transitions occur, i.e. the quantum efficiency is nearby one. For comparison the quantum efficiency of Ti-doped sapphire is about 0.8 at room temperature.

Laser Experiments and Excited-State Absorption

For our laser pumped experiments we used $Ti:YAlO_3$-crystals of 2 and 6 mm thickness with good optical quality in a nearly concentric cavity. Two sets of high reflecting mirrors with 5 or 10 cm radius were used. As pumping source an Ar ion laser at 488 and 514 nm wavelength as well as in the multiline mode was employed. The laser tests were carried out as quasi-cw experiments to minimize thermal loading of the crystal.

An estimation shows that the infrared band of the ground-state absorption causes round-trip losses of 16% at the emission peak wavelength. Assuming additional cavity losses of 2% a threshold inversion of 24% and a threshold pump power of 1.1 W is calculated. Though the maximum absorbed pump power in our experiments was 4 W, which is nearly a factor 4 above threshold, we could not get the $Ti:YAlO_3$ lasing.

$Ti:YAlO_3$ crystals have also been investigated by Heumann [8]. He performed pulsed experiments with a frequency-doubled Nd:YAG laser as pumping source. Till now these laser tests were unsuccessful too despite the high pulse energy of about 80 mJ at 30 ps pulse duration (single-shot experiments).

Excited-state absorption (ESA) was supposed to be the reason for strong additional losses. Therefore we

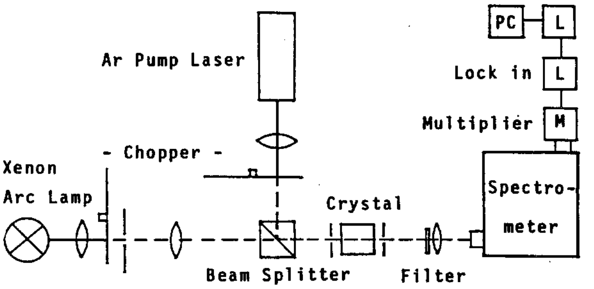

Fig. 4. Experimental setup for excited-state absorption (ESA) measurements

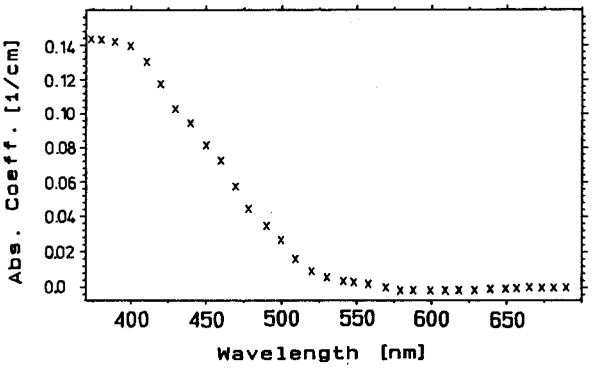

Fig. 5. ESA spectrum of Ti^{3+} : $YAlO_3$

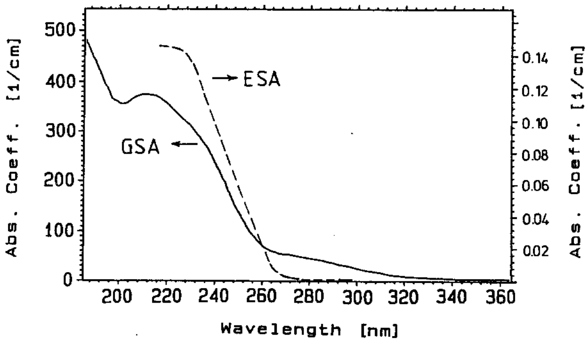

Fig. 6. UV ground-state absorption spectrum of a 78 μm-platelet and ESA spectrum shifted by the zero-phonon energy of Ti^{3+} : $YAlO_3$

have carried out ESA measurements in the whole visible spectral range. The experimental set up is shown in Fig. 4. The probe beam is provided by a Xenon arc lamp or a halogen lamp and the inversion of the Ti^{3+} ions is produced again by the Ar ion laser at 488/514 nm wavelength. To obtain well matched overlap of the two beams, they are superimposed by a beam splitter and focused through two 150 μm diameter pinholes with the crystal in between. The pump light is blocked by a filter, while the probe beam is passed through a spectrometer and is detected by a S1 photomultiplier. Signal processing is performed with two lock-in amplifiers. By this technique the probe beam difference spectrum for the pumped and unpumped condition is recorded giving the ESA spectrum directly. Spectrometer control and data storage are accomplished by a Personal Computer.

The ESA measurements have been carried out from 370 nm to 1 μm. The resulting spectrum in Fig. 5 yields a very strong ESA effect for wavelengths shorter than 550 nm. In the emission range no ESA could be detected. After adding the Ti^{3+} : $YAlO_3$ zero-phonon energy ($18500\,cm^{-1}$) to the measured ESA spectrum the dashed curve in Fig. 6 is obtained, which now can be compared with the ground-state absorption of a 78 μm thick platelet also shown in Fig. 6. The 280 nm band of the GSA spectrum is ascribed to Fe impurities [9]. The broad band around 230 nm is attributed to a $Ti^{3+} \rightarrow Ti^{4+}$ charge transfer transition, because this absorption does not appear in the undoped material and higher *d*-levels do not exist in Ti^{3+}. In accordance with Weber [10] the band edge of $YAlO_3$ can be located around 190 nm.

By comparing both, the ESA and GSA spectrum, it can be concluded that the Ti charge transfer band is giving rise to the strong excited-state absorption. Using the pumping conditions an ESA cross-section $\sigma_{ESA}(488\,nm) = 1 \times 10^{-18}\,cm^2$ is calculated for the 488 nm Ar wavelength and $\sigma_{ESA}(432\,nm) = 1 \times 10^{-17}\,cm^2$ for the peak cross-section, which matches well the expected value of a charge transfer band. The 488 nm σ_{ESA}-value is nearly two orders of magnitude higher than the Ti^{3+} ground-state cross-section σ_a. As a consequence the pumping efficiency ε is drastically reduced especially at high pump intensities:

$$\varepsilon = \frac{\sigma_a \cdot n_1}{\sigma_a \cdot n_1 + \sigma_{ESA} \cdot n_2}$$

with ground-state population n_1 and excited-state population n_2. This formula clearly indicates that a pump efficiency of 6.8×1 has to be expected for the Ti : $YAlO_3$ laser at three.

Comparison with Ti^{3+} : Al_2O_3

The fact that Ti^{3+}-doped sapphire is an efficient laser rises the question about excited-state absorption in this system. The GSA spectrum of Ti:Al_2O_3 shown in Fig. 7 is quite similar to that of Ti : $YAlO_3$. At 220 nm a charge transfer band is observed again and at 275 nm a second UV band, which is caused also by the Ti^{3+}/Ti^{4+} complex center mentioned above. If now the zero-phonon energy of $16200\,cm^{-1}$ (618 nm) is subtracted from the charge transfer band, an ESA-band ranging from 300 to 390 nm would be expected. But this wavelength range is well out of the Ti^{3+} ground-state absorption bands (400 to 600 nm) and does not match the wavelengths of the mostly used Ar

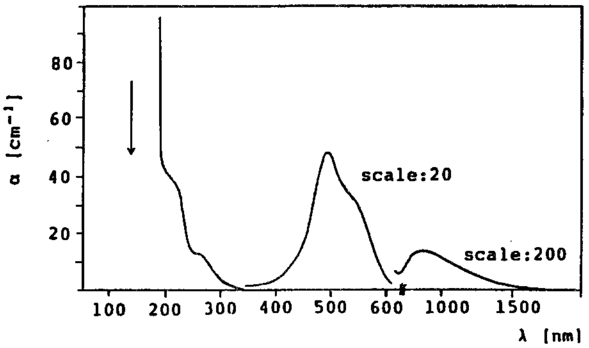

Fig. 7. Ground-state absorption spectrum of Ti : Al_2O_3 at 300 K; the band edge is indicated by an arrow

or doubled Nd : YAG pump sources. Indeed no ESA effect could be detected between 370 nm and 1 μm wavelength. Consequently it is just the property of the $YAlO_3$ host lattice, i.e. the shift of the Ti^{3+} emission to shorter wavelengths, which prevents laser action of this system.

Conclusion

In summary, we have observed strong excited-state absorption of Ti^{3+} : $YAlO_3$ overlapping the pump band, but no ESA was found in the emission wavelength range. As a consequence the pump efficiency is decreased drastically by nearly two orders of magnitude especially at high pump intensities. Therefore we conclude that it is very unlikely to obtain laser action with this material, and if so, the efficiency will be very low.

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