

## UV-SPECTROSCOPY AND BAND STRUCTURE OF Ti: Al<sub>2</sub>O<sub>3</sub>

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### ABSTRACT

Spectroscopic properties and excited-state absorption (ESA) of Ti<sup>3+</sup> doped Al<sub>2</sub>O<sub>3</sub> were investigated in detail. Absorption spectrum was carried in the range of 200-800 nm by UV-Vis NIR spectrometer, and the emission spectra in the range 200–900 nm was recorded by a Perkin Elmer LS 55 luminescence Spectrometer. The excitation spectra of these emissions were measured and interpreted using a band model for the Ti: Al<sub>2</sub>O<sub>3</sub> system.

*Keywords: Ti<sup>3+</sup>:Al<sub>2</sub>O<sub>3</sub>; Absorption; Charge-transfer transitions; UV-spectroscopy*

### INTRODUCTION

Titanium doped sapphire (Ti<sup>3+</sup>:Al<sub>2</sub>O<sub>3</sub>) is a very important crystal for tunable solid state laser. After demonstration of the Ti<sup>3+</sup>:Al<sub>2</sub>O<sub>3</sub> system as broadly tunable solid state laser by Moulton [1], research into the optical spectroscopy of this material has attracted considerable attention many researcher [2-6]. The laser active ion Ti<sup>3+</sup> shows a board visible absorption band at about 490 nm, within which the pumping of the laser action can be performed. This band corresponds to the  $t_{2g} \rightarrow e_g$  transition inside the d<sup>1</sup> electronic configuration of the trivalent ion. The reverse transition  $e_g \rightarrow t_{2g}$  leads to a very broad emission band centered at about 750 nm, which provides a wide wavelength range for tunability. In addition, this material shows a blue emission band at 420 nm (at room temperature) which is excited with ultraviolet (UV) light [7, 8].

The study of the origin of the blue band in Ti:sapphire becomes a very interesting problem because excitation with UV laser light also leads to the  $e_g \rightarrow t_{2g}$  infrared band of Ti<sup>3+</sup> [4].

In this paper we report the absorption spectrum and the luminescence behavior of different concentration of titanium in Al<sub>2</sub>O<sub>3</sub> crystals under variable excitation intensity in the UV region. The excitation spectra of these emissions are measured and

interpreted in a band model for the Ti: Al<sub>2</sub>O<sub>3</sub> system.

## EXPERIMENT DETAILS

A crack-free and perfect Ti:Al<sub>2</sub>O<sub>3</sub> single crystal with size of (23–25) mm was successfully obtained by the Czochralski technique. The pulling and rotation rates were, respectively selected in the range of 0.75–1.5 mm/h and 15 rpm depending on the growth condition. The as-grown Ti:Al<sub>2</sub>O<sub>3</sub> crystal taken out from the furnace is transparent with slightly pink color. By using Perkin Elmer UV-3101 PC UV-VIS-IR spectrophotometer, the absorption spectra for p polarization in the range 200–800 nm waveband were recorded. The emission spectra were carried in the range 200–900 nm by Perkin Elmer LS 55 luminescence Spectrometer. The excitation spectra of these emissions are measured and interpreted in a band model for the Ti: Al<sub>2</sub>O<sub>3</sub> system. The experiments were both performed at room temperature.

## RESULTS AND DISCUSSION

### *Absorption spectrum of Al<sub>2</sub>O<sub>3</sub> and Ti<sup>3+</sup>: Al<sub>2</sub>O<sub>3</sub> crystals*

The optical absorption of Al<sub>2</sub>O<sub>3</sub> and Ti<sup>3+</sup>: Al<sub>2</sub>O<sub>3</sub> crystals grown by Cz technique have been recorder and presented in Figure 1. Its consists of a broad visible absorption band at 490 nm, and a strong absorption UV edge beginning around 300 nm with a shoulder at ~240 nm and, which is a spurious absorption related to either Ti<sup>4+</sup>-Fe<sup>2+</sup> or Ti<sup>3+</sup>-Ti<sup>4+</sup> pairs [9].

The spectra exhibit two wide bands in the range 400 – 600 nm, associated with the transitions within different d-levels of the Ti<sup>3+</sup> ions ( $t_{2g} \rightarrow e_g$  transition) [6, 10]. The main absorption is double structured band with overlapping peaks at 491 nm and 562 nm, due to transitions from the <sup>2</sup>T<sub>2</sub> ground state of Ti<sup>3+</sup> to the <sup>2</sup>E excited state. The results are similar to report by Yamaga *et al.* [11]. The visible band at 491 nm is the crystal filed absorption band and corresponds to intra-configurationally transition  $t_{2g} \rightarrow e_g$  of the d<sup>1</sup> configuration in the octahedral field approximation. The blue–green absorption band of Ti: Al<sub>2</sub>O<sub>3</sub> is due to the vibronically broadened  ${}^2T_2 \rightarrow {}^2E$  transition [2]. The weak infrared absorption band with the peak at 650 nm and the strong UV absorption band below 300 nm are observed in sample. In the absorption spectrum of Ti: Al<sub>2</sub>O<sub>3</sub> is the strong charge transfer absorption which appears in below 300 nm. Due to charge transfer absorption satisfies both spin and parity selection rules, it is strongly electric dipole allowed, with oscillator strength [5]. This strong absorption makes the observation of structure within the band using crystal of moderate dopant concentration and seasonable thickness very difficult. Tippins in reported Lacovara [5] has studied the charge transfer bands of titanium (and other transition metals) in Al<sub>2</sub>O<sub>3</sub>, using low concentrations and thin samples. Tippins's spectrum of Ti: Al<sub>2</sub>O<sub>3</sub> assigns a hump in the UV absorption between 5.5 eV and 8 eV to the charge transfer



in good agreement with simple theory. A weakened hump appears between approximately 4.5 eV and 5 eV is assigned to the charge transfer

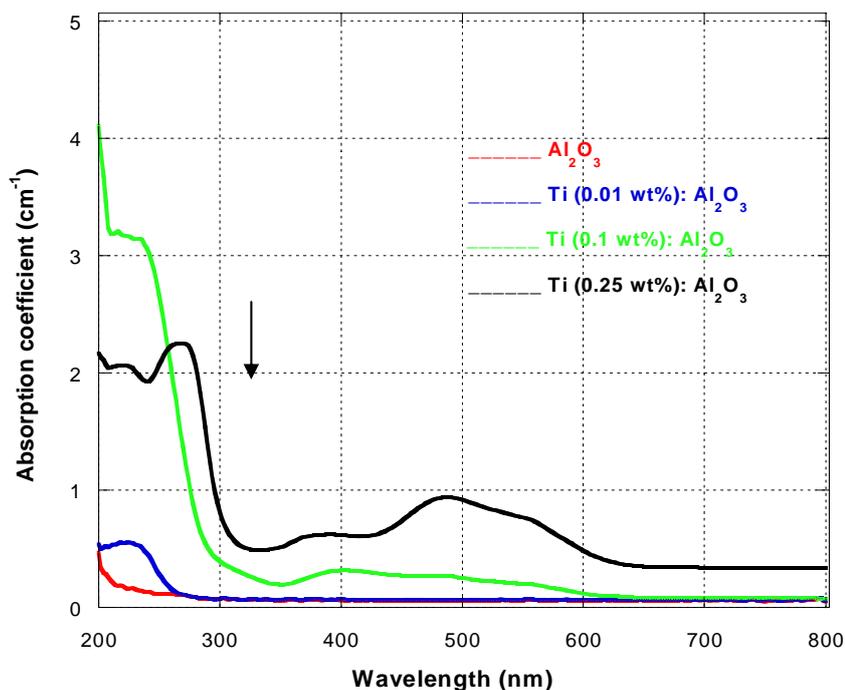


Figure 1: Absorption spectra observed at room temperature (300K) for  $\text{Al}_2\text{O}_3$  and  $\text{Ti}^{3+}:\text{Al}_2\text{O}_3$  single crystals

As shown in Figure 1, the intensity of optical absorption of crystal  $\text{Ti}^{3+}:\text{Al}_2\text{O}_3$  in the range 200 – 300 nm was stronger than that of crystal  $\text{Al}_2\text{O}_3$ . The variation of the intensity of the absorption band in the range 200 – 300 nm was closely related to the concentration of the impurity.

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  $\text{Ti}^{3+}$  or  $\text{Ti}^{4+}$ , which can both be incorporated inside the crystal host, although the presence of trace ions such as  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  could also be contaminating this edge [13]. The origin of these O-Ti charge transfer bands may be understood in terms of molecular orbital theory for the  $\text{TiO}_6$  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  $\text{Ti}^{4+}$  ions in accordance with the reflectivity spectrum of the rutile phase and molecular orbital theory calculations for the  $\text{TiO}_6$  complex [14].

*Photoluminescence study*

Optical excitation in the UV-absorption band for these samples produces a broad emission band at 300 nm -500 nm. Figures 2 and 3 show the blue emission band of  $\text{Al}_2\text{O}_3$  and  $\text{Ti}:\text{Al}_2\text{O}_3$  with different titanium concentration under excitation at 232 nm and at 266 nm respectively. The excitation at 266 nm wavelength of  $\text{Ti}:\text{Al}_2\text{O}_3$  almost coincides with the excitation maximum reported for the blue band [8]. From Figure 2, the emission band maximum is at ~365 nm for  $\text{Al}_2\text{O}_3$  while  $\text{Ti}:\text{Al}_2\text{O}_3$  at ~410 nm. The emission band with excitation 266 nm (see Figure 3) is at 352 nm for  $\text{Al}_2\text{O}_3$ , and for  $\text{Ti}:\text{Al}_2\text{O}_3$  are about at ~400 nm. The excitation with light of 266 nm (4.66 eV) has to produce photoionization of  $\text{Ti}^{3+}$  ions [15]. The emission band is the same as previously reported, whose intensity strongly increase with increase concentration of the impurity. The effect of concentration of impurity will be cause different intensity of emission peaks.

Using 232 nm (or 266 nm) ultraviolet light to pump these samples, a strong emission emerges around 410 nm (420 nm [3, 4, 14], 425 nm [5, 6], 430 nm [7, 8]).

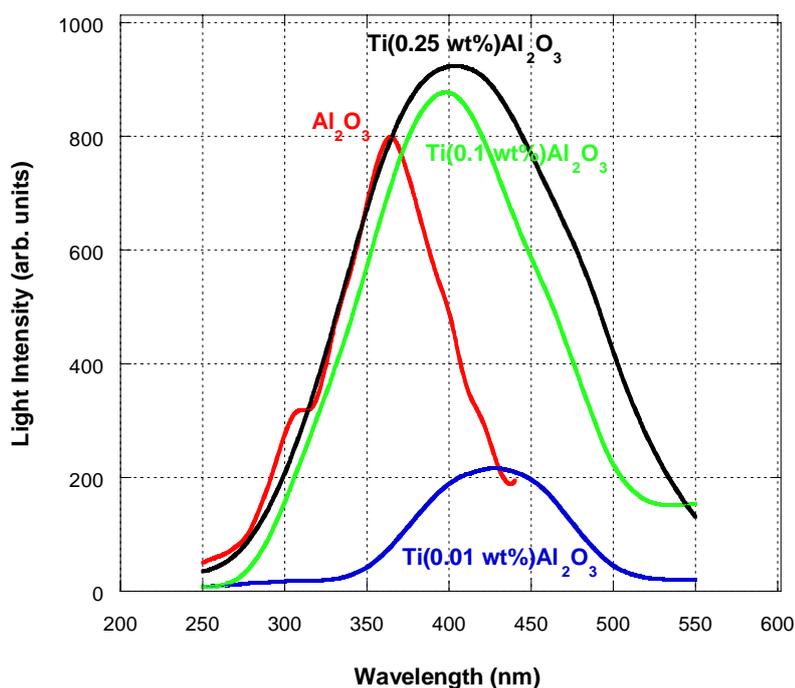


Figure 2: The 232 nm excited emission spectra of  $\text{Ti}:\text{Al}_2\text{O}_3$  at room temperature (300K)

From Figures 2 and 3, its can be seen that the blue emission can be excited by the 232 nm and 266 nm excitation band. This indicates that the 232 nm (or 266 nm) excitation center must be connected with the blue emission center. Simultaneously, the excitations between 280 and 340 nm did not bring about any emission in the blue region. Consequently, it is reasonable to assume that no energy transfer is operating here. In

fact, no reference reported the occurrence of energy transfer for the blue emission in titanium doped sapphire [3–8, 14]. Thus, a 266 nm excitation center is identical with the blue emission center.

The fact that no other excitation bands were found between the 266 nm excitation band and the 410 nm blue emission band still means that both of them probably result from the lowest excited state ~at least a lower state of the blue emission center. In addition, we are convinced that there must be a 266 nm absorption band corresponding to that 266 nm excitation band. According to above reasons, we speculate that a few absorption bands may be observed in the energy region higher than 4.7 eV (266 nm). If we obtain some information concerning the upper excited states of the blue emission center, we can deduce its origin. The purpose of this letter is to observe and interpret these possible higher energy absorption bands.

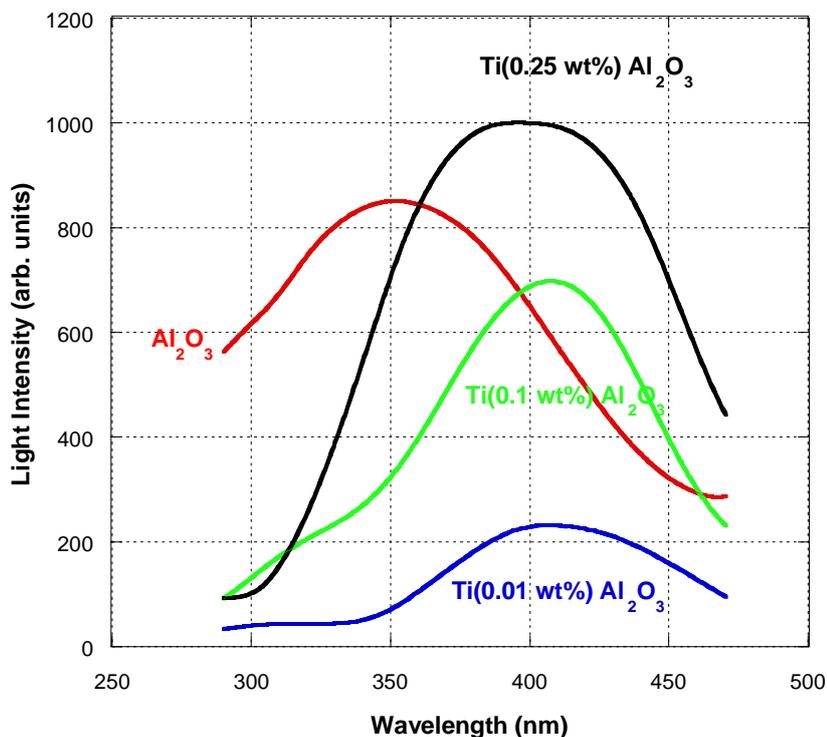


Figure 3: The 266 nm excited emission Spectra of Ti:Al<sub>2</sub>O<sub>3</sub> at room temperature (300K)

The 410 nm band of Ti:Al<sub>2</sub>O<sub>3</sub> is usually assigned to the characteristic emission of Ti<sup>4+</sup> that is stimulated through charge-transfer transitions. Provided that Ti<sup>3+</sup> is an efficient donor of electrons one might expect that the oxygen vacancies gain the outer electron of a Ti<sup>3+</sup>, hence creating (Ti<sup>4+</sup>-F<sup>+</sup>) or (Ti<sup>4+</sup>-F) spatially correlated complexes. Given the proximity of the impurity and the defect it is very likely that F and/or F<sup>+</sup>-centres are involved in the luminescence excitation processes. Then the energy transfers from the

defect centres to  $Ti^{4+}$  that will lead to the appearance of the blue emission. In this case the excitation spectrum of  $Ti^{4+}$  will represent a superposition of the charge transfer band and of the excitation bands of the F and/or  $F^+$ -centres. At the same time present results provide the reasons to suggest other possible scenario, namely that the 410 nm band can also be caused by the emission of F-centres. A model for such a process could include the photoionization of  $Ti^{3+}$  ions and the creation of the conduction electrons. These electrons can migrate and finally are captured by  $F^+$  centres that will trigger a recombination process according to the scheme:  $F^+ + e^- \rightarrow F^* \rightarrow F + h\nu$  (410 nm), where  $F^*$  stands for an excited F-centre.

The excitation spectra of these emission are measured of  $Ti:Al_2O_3$  single crystal are interpreted in a band model system. Figure 4 shows the band model for with the different excitation band.

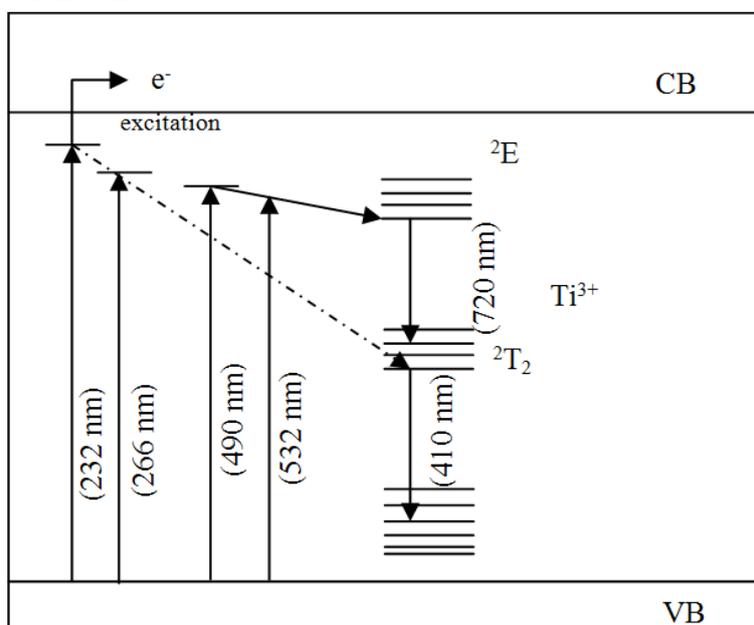


Figure 4: Band model for  $Ti:Al_2O_3$  showing the different excitation mechanism

### CONCLUSION

The  $Ti:Al_2O_3$  single crystal have main double-structured absorption peaks at 491 nm and 562 nm, the weak infrared absorption band with the peak at 650 nm and the strong UV absorption band at 234 nm. In summary, blue emission bands have been identified in  $Ti$ : sapphire laser crystals using UV excitation. The band at 410nm is the reported charge transfer band of  $Ti^{4+}$  ions.

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