



# Journal of Applied Sciences

ISSN 1812-5654

**science**  
alert

**ANSI***net*  
an open access publisher  
<http://ansinet.com>

## Optical Energy Gap of Ti:Al<sub>2</sub>O<sub>3</sub> Single Crystals

<sup>1,2</sup>Hamdan Hadi Kusuma, <sup>1</sup>Zuhairi Ibrahim and <sup>1</sup>Mohamad Khairi Saidin  
<sup>1</sup>Department of Physics, Faculty of Science, Universiti Teknologi Malaysia,  
81310 UTM Skudai Johor, Malaysia

<sup>2</sup>Department of Physics Education, Faculty of Education, IAIN Walisongo Semarang 50189,  
Central Java, Indonesia

---

**Abstract:** The optical absorption spectra of single crystals of titanium doped sapphire (Ti:Al<sub>2</sub>O<sub>3</sub>) with two different doping concentration (0.1% wt. and 0.25% wt.) have been recorded in the UV-visible spectroscopy at room temperature. It was observed that both crystals start to show strong absorptions around 325 nm. From this spectrum attempt was made to estimate the values of energy gap and the type of transition occurs in Ti:Al<sub>2</sub>O<sub>3</sub>. From the analysis it show that the optical energy gap are 5.57 eV for 0.1% wt. Ti and 5.94 eV for 0.25 wt.% Ti and it a direct band gap transition.

**Key words:** Ti:Al<sub>2</sub>O<sub>3</sub>, absorption, UV-visible, spectroscopy, energy gap

---

### INTRODUCTION

Sapphire (Al<sub>2</sub>O<sub>3</sub>) crystal is an important and widely used material in today's technology. It was used for optical and electro-optical applications. Sapphire crystal is being an important technological material as lasing material in solid state lasers, substrate for micro-electronic, radiation dosimeter and an insulator (Jheeta *et al.*, 2007). Doping Al<sub>2</sub>O<sub>3</sub> with foreign ions can be used to modify the optical properties and makes the system useful for large variation application, such us tunable solid state laser (Moulton, 1986; Blasse and Verweij, 1990) or optical waveguides (Townsend *et al.*, 1990; Crunteanu, *et al.*, 2003; Pollnau and Romanyuk, 2007). The pure and doped single crystal Al<sub>2</sub>O<sub>3</sub> has been known as an excellent material for optics, optoelectronics and laser applications (Mikhailik *et al.*, 2005). Pure Al<sub>2</sub>O<sub>3</sub> is a durable material with optical transmission spanning the range from UV to IR. This role has been taken over by Ti:Al<sub>2</sub>O<sub>3</sub> that is now successfully used as tunable laser material for near infrared spectra region of 0.7-1.1 μm (Moulton, 1986). It also exhibit a broad absorption band, located in the blue-green region of the visible spectrum that is associated with phonon-coupled excitation of the 3d electron of the Ti<sup>3+</sup> ions (Macalik *et al.*, 1992).

The optical transition, optical band gap and band structure of crystalline and non-crystalline materials can be determined using the optical absorption spectra. Particularly, measurement of the optical absorption

coefficient near the fundamental absorption edge is a standard method for the investigation of optically induced electronic transition in many materials. Generally, two types of optical transition i.e. direct and indirect occur at the absorption edge. Both of these transitions occur when an electromagnetic wave interacts with a valence electron and raises it across the energy gap to the conduction band. Previously, we studied the optical absorption of the Ti:Al<sub>2</sub>O<sub>3</sub> crystals (Kusuma *et al.*, 2010).

The purpose of the study is to present the fundamental optical absorption of Ti:Al<sub>2</sub>O<sub>3</sub> single crystal in the visible and UV region. The optical energy gap of the Ti:Al<sub>2</sub>O<sub>3</sub> single crystals were investigated.

### MATERIALS AND METHODS

The Ti:Al<sub>2</sub>O<sub>3</sub> crystals used in this study with doped Ti of 0.1% wt. (sample A) and 0.25 wt.% (sample B) were purchased from RODITI International Company (England) in 2008. The samples have both large faces polished to optical quality. The samples were transparent, free of pores, bubbles and grains. The absorption spectra were measured by using a Perkin Elmer UV-3101 PC UV-VIS spectrophotometer in the range 200-800 nm waveband at room temperature. The experimental absorption spectroscopy calibrated apparatus consists of a halogen lamp used as the light source for the measurement. The light beam is diffracted by a plane diffraction gratings attached to a step motor. From the results of absorption measurements which are used to determine an absolute

value of the absorption coefficient of crystals and the optical band gap was calculated by using absorption spectrum.

### RESULTS AND DISCUSSION

The optical absorption spectra of Ti:Al<sub>2</sub>O<sub>3</sub> single crystals with different doped titanium at room temperature are shown in Fig. 1. The spectrum represents the optical absorption of the Ti:Al<sub>2</sub>O<sub>3</sub> single crystal. Both the samples show two absorption peak (492 and 560 nm) that has been reported (Yamaga *et al.*, 1994) except for 374 nm (0.25 wt.%) and 389 nm (0.1 wt.%). 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<sub>2g</sub>→e<sub>g</sub> transition) (Wong *et al.*, 1995; Lupei *et al.*, 1986). 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>Ē</sup> excited state. The visible band at ~491 nm is the crystal field absorption band and corresponds to intra-configurationally transition t<sub>2g</sub>-e<sub>g</sub> 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 <sup>2</sup>T<sub>2</sub>-<sup>2</sup>E transition (Macalik *et al.*, 1992; Sanchez *et al.*, 1988). The weak infrared absorption band with the peak at 650 nm and the strong UV absorption band below 300 nm are observed in sample. For 0.1 %wt. sample, the abrupt increased in absorption started from 325 nm and show a shoulder at 234 nm before increase again at 216 nm. As for 0.25 wt.% sample, the sharp increased started at about the same point but show the abrupt increased of optical absorption spectra started from 325 nm. The sharp increased from 325 nm for both

samples can be attributed to fundamental optical absorption edge for the Ti:Al<sub>2</sub>O<sub>3</sub> single crystals.

The absorption spectrum beyond 200 nm cannot be obtained due to limitation of the instruments. The UV absorption edges for the crystals were observed at vicinity of 300 nm. The dependent of optical absorption coefficient with the phonon energy helps to study the band structure and the type of transition of electrons (Krishnan *et al.*, 2008). The dependence of absorption on photon energy is analyzed in the high absorption regions to obtain the detailed information about the energy band gaps (Goksen *et al.*, 2007). The optical absorption coefficient ( $\alpha$ ) was calculated from the transmittance using the following relation:

$$\alpha = \frac{1}{d} \log \left( \frac{1}{T} \right) \quad (1)$$

where, T is the transmittance and d is the thickness of the crystal. The incident photon energy hv and the optical energy gap E<sub>g</sub> are related as in Eq. 2 (Bang *et al.*, 1996), where  $\alpha$  is the optical absorption coefficient:

$$(\alpha hv) = A (hv - E_g)^p \quad (2)$$

In Eq. 2, A is a constant that depends on the transition probability and p is index that characterizes the optical absorption process and it is theoretically equal to 2 or 1/2 for a indirect or direct allowed transitions band structure, respectively. The dependence of absorption coefficient  $\alpha$  for the Ti:Al<sub>2</sub>O<sub>3</sub> single crystals on hv near band edge are shown in Fig. 2 and 3.

In a crystalline or polycrystalline material both direct and indirect optical transitions are possible depending on the band structure of the material (Tyagi and Vedeshwar, 2001). Figure 2 shows the calculated room temperature coefficient  $\alpha$  for sample A in the photon energy range 4.77 to 6.20 eV. Figure 3 shows the calculated room temperature coefficient  $\alpha$  for sample B in the photon energy range 5.34 to 6.20 eV. The analysis of the experimental data for sample A, shows that the absorption coefficient is proportional to (hv-E<sub>g</sub>)<sup>p</sup> with p = 2 and 1/2 for range (4.77-5.64) eV and (5.69-6.20) eV, respectively. While, that the sample B is in the range (5.34-5.69) eV and (5.74-6.20) eV. Insets 1 and 2 for Fig. 2 and 3 display the dependences of (αhv)<sup>1/2</sup> and (αhv)<sup>2</sup> on photon energy hv, respectively. The usual method of determining band gap is to plot a graph between (αhv)<sup>1/2</sup> and (αhv)<sup>2</sup> versus photon energy hv. The linear dependences were observed for the relations (αhv)<sup>1/2</sup> and (αhv)<sup>2</sup> versus hv. Energy gap E<sub>g</sub> was calculated by the extrapolation of the linear part (Krishnan *et al.*, 2008). By extrapolation to (αhv)<sup>1/2</sup> = 0

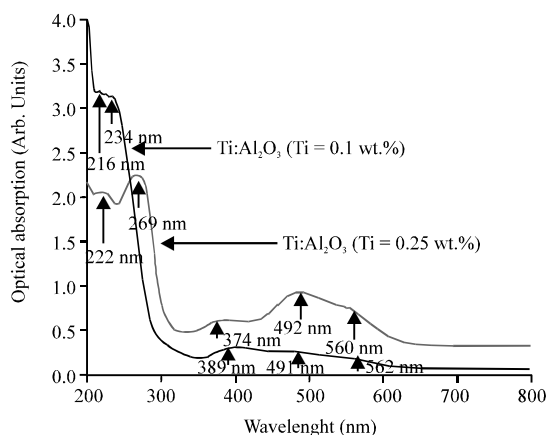


Fig. 1: Absorption spectra observed at room temperature for Ti:Al<sub>2</sub>O<sub>3</sub> single crystals

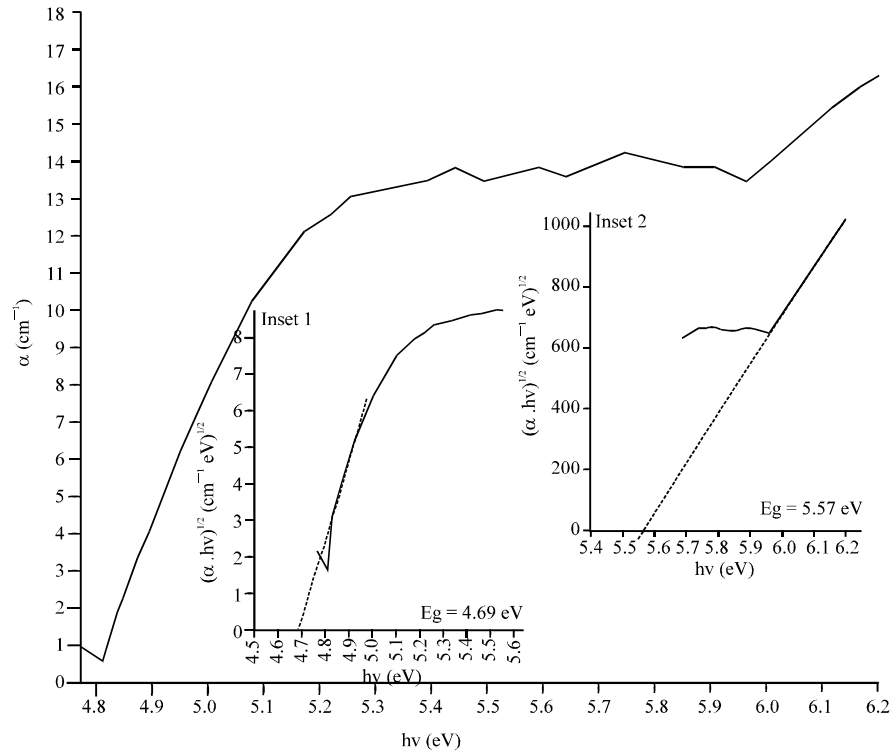


Fig. 2: The variation of coefficient as a function of photon energy for the Ti:Al<sub>2</sub>O<sub>3</sub> single crystal with doped Ti: 0.1 wt.% at T = 300 K. Inset 1 and 2 represent the dependences of  $(\alpha hv)^{\frac{1}{2}}$  and  $(\alpha hv)^2$  on photon energy, respectively

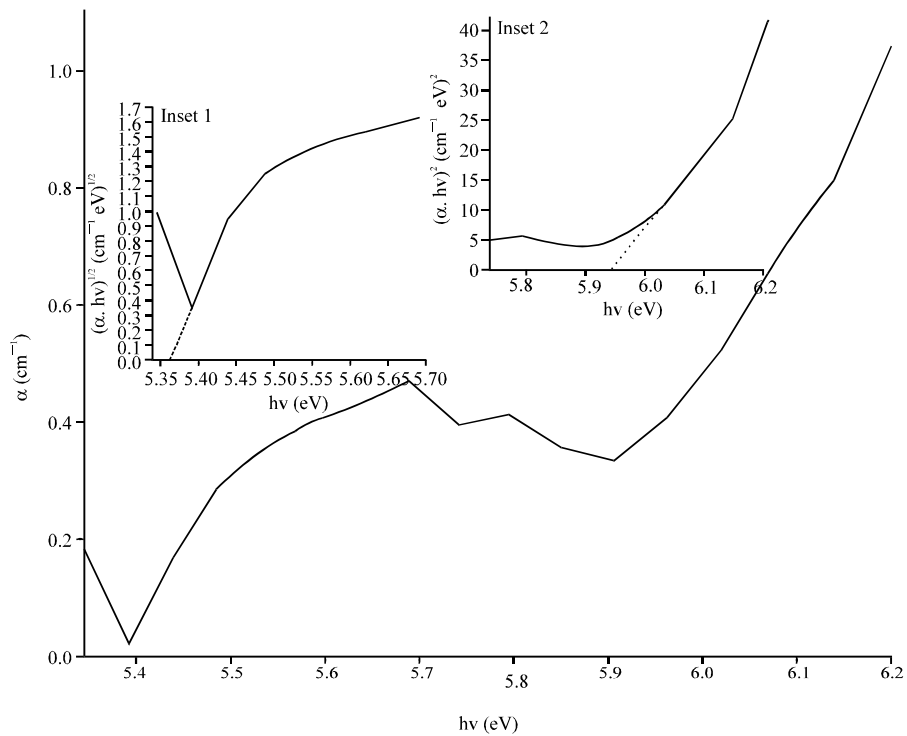


Fig. 3: The variation of coefficient as a function of photon energy for the Ti:Al<sub>2</sub>O<sub>3</sub> single crystal with doped Ti: 0.25 wt.% at T = 300 K. Inset 1 and 2 represent the dependences of  $(\alpha hv)^{\frac{1}{2}}$  and  $(\alpha hv)^2$  on photon energy, respectively

and  $(\alpha h\nu)^2 = 0$ , such plots inset 1 and 2 at Fig. 2 give the values of the optical energy gap  $E_g$  for the indirect and direct band structure to be 4.69 and 5.57 eV, respectively, while plots at Fig. 3 give the values of the optical energy gap  $E_g$  for the indirect and direct band structure to be 5.38 and 5.94 eV, respectively. Therefore, it is suggested that the colourless transparent Ti:Al<sub>2</sub>O<sub>3</sub> single crystals have a direct band structure and an optical band gap of 5.57 eV for Ti:Al<sub>2</sub>O<sub>3</sub> with doped Ti: 0.1% and 5.94 eV for Ti:Al<sub>2</sub>O<sub>3</sub> with doped Ti:0.25%. The direct and indirect band gap were found to increase as the Ti increases and the best for all the experimental points was observed in the case of  $(\alpha h\nu)^2$  vs.  $h\nu$  plot (Fig. 3).

### CONCLUSION

The analysis of accurate measurements of the optical absorption in Ti:Al<sub>2</sub>O<sub>3</sub> single crystals have shown that this material possesses both direct and indirect band gaps. The phonon assisted indirect transition is indirect allowed. The energies of the phonons have been determined. Further, The single crystals of Ti: Al<sub>2</sub>O<sub>3</sub> have a direct band structure and the optical energy were found 5.57 eV for doped Ti: 0.1% and 5.94 eV for doped Ti: 0.25%.

### ACKNOWLEDGMENT

The authors wish to thank the Ministry of Science, Technology and Innovation for their financial support via Science Fund No. 03-01-06-SF0572. We would also thanks to Universiti Teknologi Malaysia for the support on this project.

### REFERENCES

Bang, T.H., S.H. Choe, B.N. Park, M.S. Jin and W.T. Kim, 1996. Optical energy gap of CuAl<sub>2</sub>S<sub>4</sub> single crystal. *Semicond. Sci. Technol.*, 11: 1159-1162.

Blasse, G. and J.W.M. Verweij, 1990. The luminescence of titanium in sapphire laser material. *Mater. Chem. Phys.*, 26: 131-137.

Crunteanu, A., P. Hoffmann, M. Pollnau and C. Buchal, 2003. Comparative study on methods to structure sapphire. *Applied Surf. Sci.*, 208-209: 322-326.

Goksen, K., N.M. Gasanly and H. Ozkan, 2007. Dispersive optical constants and temperature tuned band gap energy of Ti<sub>2</sub>inGaS<sub>4</sub> layered crystals. *J. Phys.: Cond. Matter*, Vol. 19, No. 25.

Jheeta, K.S., D.C. Jain, R. Kumar and K.B. Garg, 2007. Effect of titanium ion irradiation on the surface and defect centre formation in sapphire. *Solid State Commun.*, 144: 460-465.

Krishnan, S., C.J. Raj, S. Dinakaran and S.J. Das, 2008. Investigation of optical band gap in potassium acid phthalate single crystal. *Cryst. Res. Technol.*, 43: 670-673.

Kusuma, H.H., Z. Ibrahim and M.K. Saidin, 2010. Optical absorption and refractive index study of Ti:Al<sub>2</sub>O<sub>3</sub> single crystal. *J. Chem. Chem. Eng.*, 4: 59-62.

Lupei, A., V. Lupei, C. Lonescu, H.G. Tang and M.L. Chen, 1986. Spectroscopy of Ti<sup>3+</sup>:  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. *Optic Commun.*, 59: 36-38.

Macalik, B., L.E. Bausa, J. Garcia-Sole, F. Jaque, J.E. Munoz Santiuste and I. Vergara, 1992. Blue emission in Ti-Sapphire laser crystals. *Applied Phys. B*, 55: 144-147.

Mikhailik, V.B., H. Kraus, M. Balcerzyk, W. Czarnacki, M. Moszynski, M.S. Mykhaylyk, D. Wahl, 2005. Low-temperature spectroscopic and scintillation characterisation of Ti-doped Al<sub>2</sub>O<sub>3</sub>. *Nucl. Instruments Methods Phys. Res.*, 546: 523-534.

Moulton, P.F., 1986. Spectroscopic and laser characteristics of Ti:Al<sub>2</sub>O<sub>3</sub>. *J. Opt. Soc. Am. B*, 3: 125-133.

Pollnau, M. and Y.E. Romanyuk, 2007. Optical waveguides in laser crystals. *Comptes Rendus Physique*, 8: 123-137.

Sanchez, A., A.J. Strauss, R.L. Aggarwal and R.E. Fahey, 1988. Crystal growth, spectroscopy and laser characteristics of Ti: Al<sub>2</sub>O<sub>3</sub>. *IEEE J. Quantum Electron.*, 24: 995-1002.

Townsend, P.D., P.J. Chandler, R.A. Wood, L. Zhang, J. McCallum and C.W. McHargue, 1990. Chemically stabilised ion implanted waveguides in sapphire. *Electron. Lett.*, 26: 1193-1195.

Tyagi, P. and A.G. Vedeshwar, 2001. Grain size dependent optical band gap of CdI<sub>2</sub> films. *Bull. Mater. Sci.*, 24: 297-300.

Wong, W.C., D.S. McClure, S.A. Basun and M.R. Kokta, 1995. Charge-exchange processes in titanium-doped sapphire crystals. I. Charge-exchange energies and titanium-bound excitons. *Phys. Rev. B.*, 51: 5682-5692.

Yamaga, M., T. Yosida, S. Hara, N. Kodama and B. Henderson, 1994. Optical and electron spin resonance spectroscopy of Ti<sup>3+</sup> and Ti<sup>4+</sup> in Al<sub>2</sub>O<sub>3</sub>. *J. Applied Phys.*, 75: 1111-1117.