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OPTICAL PROPERTIES OF Ti:Al_2O_3 SINGLE CRYSTAL

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ABSTRACT

Optical transmission and absorption spectra of Ti:Al_2O_3 single crystal have been determined in the region of UV-vis and infrared at room temperature. The main absorption peaks at 491 nm and 562 nm, the weak infrared absorption band at 650 nm and the strong UV absorption band below 300 nm are observed. The absorption coefficient α was determined in the visible range while the optical band gap have been determine using the relation of $\alpha^{1/2}$ vs ($h\nu$) plot. The refractive index is discussed in the vicinity of Fresnel's equation. In particular, the Sellmeier equation was determined in the range visible region by means on non-conventional method based on the measurement of refraction by using UV-visible spectroscopy. The refractive indices are forward to decrease from 3.71 to 1.28 in the wavelength range 400 – 800 nm.

***Keywords*:** Optical properties, Optical energy, Ti^{3+}:Al_2O_3, Refractive Index, UV-visible spectroscopy.

INTRODUCTION

Aluminum oxide (Al_2O_3) is an industrial material of great interest, both for fundamental studies and for applications mainly due to its hardness, good electrical insulation, useful optical properties, high surface area, and catalytic surface activity. The pure and doped single crystals of Al_2O_3 have long been known as excellent materials for optics, optoelectronics and laser applications [1]. Pure Al_2O_3 is a durable material with optical transmission spanning the range from UV to IR. Discovery of lasing action in Cr doped Al_2O_3 created a basis for modern laser technologies. This role has however been taken over by Ti:Al_2O_3 that is now successfully used as tunable laser material for near infrared spectra region of 0.7 – 1.1 μm [2]. It also exhibits a broad absorption band, located in the blue-green region of the visible spectrum that is associated with phonon-coupled excitation of the 3*d* electron of the Ti^{3+} ions [3].

The optical transition, optical band gap and band structure of crystalline and non-crystalline materials can be derived from the optical absorption spectra. The 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. There one, two types [4] of optical transition i.e. direct and indirect transitions which occur at the absorption edge. Due to the interaction of electromagnetic wave with a valence electron and raises it across the energy gap to the conduction band.

In this paper we describe the optical properties of Ti: Al_2O_3 in the visible and UV region. The optical energy gap of the single crystal Ti: Al_2O_3 were investigated. The reflectance and transmittance data at room temperature analyzed to determine the

refractive index of a single crystal Ti:Al_2O_3. The refractive index of a material is sensitive to crystal structure [5]. Atoms while are easily polarize, (i.e. electron are easily displaced), give rise to a high refractive index, while those with tightly bound electron give rise to a low refractive index.

EXPERIMENT PROCEDURE

In this study, titanium aluminum oxide (Ti: Al_2O_3) crystal was examined. The percentage of titanium doped is 0.1% in weight. The crystal is manufactured by RODITI International England. In preparation to measurement both opposite faces of the crystal were polished to optical quality. The optical absorption, transmittance and refractivity spectrum were taken using a Perkin Elmer UV-3101 Pc UV-VIS-IR spectrophotometer in the range 200-800 nm at room temperature.

RESULT AND DISCUSSION

Optical absorption

The absorption spectra of Ti: Al_2O_3 single crystal at room temperature is shown in Figure 1. The spectra exhibit two wide bands in the range 400 – 600 nm, associated with the transitions within different d-levels of the Ti^{3+} ions ($t_{2g} \rightarrow e_g$ transition) [6,7]. The main absorption is double structured band with overlapping peaks at 491 nm and 562 nm, due to transitions from the $^2T_2$ ground state of Ti^{3+} to the ^2E excited state. The results are similar to that reported by Yamaga *et.al* [8]. The visible band at 491 nm is due to the crystal field absorption band and corresponds to intra-configurationally transition $t_{2g} \rightarrow e_g$ of the d^1 configuration in the octahedral field approximation. The blue–green absorption band of Ti: Al_2O_3 is due to the vibronically broadened $^2T_2 \rightarrow {}^2E$ transition [3]. The weak infrared absorption band with the peak at 650 nm and the strong UV absorption band below 300 nm are observed in the crystal.

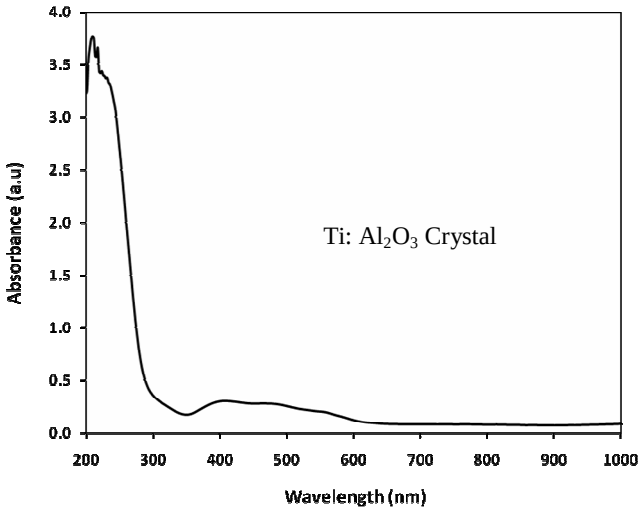

Figure 1: Absorption spectra observed at room temperature for Ti:Al_2O_3 single crystals

In the absorption spectrum of Ti:Al_2O_3 is the strong charge transfer absorption which sets in below 300 nm. Because the charge transfer absorption satisfies both spin and parity selection rules, it is strongly electric dipole allows, with oscillator strength. This strong absorption makes the observation of structure within the band using crystal of moderate dopant concentration and seasonable thickness very difficult. Lacovara [9] has studied the charge transfer bands of titanium (and other transition metals) in Al_2O_3, using low concentrations and thin samples. Tippins's spectrum of Ti:Al_2O_3 exhibits a hump in the UV absorption between 5.5 eV and 8.0 eV which is assigned to a charge transfer within Ti^{3+} and O^{2-}, and can be described as,

$$Ti^{3+} + O^{2-} \rightarrow Ti^{2+} + O^{-}$$

A weakened hump which appears between approximately 4.5 eV and 5.0 eV is assigned to the charge transfer within Fe^{3+} and O^{2}, and can be described as,

$$Fe^{3+} + O^{2} \rightarrow Fe^{2+} + O^{-}$$

In the UV part of spectra two strong absorption bands centered at 234 nm (5.30 eV) and 216 nm (5.74 eV). This observation indicates that the two bands have different origins. As a matter of fact, the so-called E-band centered at 5.30 eV in the absorption spectrum of Al_2O_3-Ti^{3+} bands are assigned to a bound excited of Ti^{3+}, whereas the 5.74 eV band is attributed to $2pO^2 \rightarrow 3dTi^{4+}$ charge transfer transitions [10].

The UV absorption edges for the crystals were observed at the 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 [11]. The dependence of absorption on photon energy is analyzed in the high absorption regions to obtain the detailed information about the energy band gaps [12]. The optical absorption coefficient (α) was calculated from the transmittance using the following relation

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

where T is the transmittance and d is the thickness of the crystal. The incident photon energy $h\nu$ and the optical energy gap E_g are related as in equation (2) [13], where α is the optical absorption coefficient.

$$(\alpha h\nu) = A(h\nu - E_g)^p \qquad (2)$$

where A is a constant that depends on the transition probability and p is the index that characterizes the optical absorption process, theoretically equal to 2 or ½ for a indirect or direct allowed transitions, respectively. The dependence of absorption coefficient α for the Ti:Al_2O_3 single crystals on $h\nu$ near the band edge is shown in Figure 2.

In a crystalline or polycrystalline material both direct and indirect optical transitions are possible depending on the band structure of the material [14]. Figure 2 shows the calculated room temperature coefficient α for Ti:Al_2O_3 in the photon energy range of 4.77 eV to 6.20 eV. The analysis of the experimental data shows that the absorption coefficient is proportional to $(h\nu - E_g)^p$ with p = 2 and ½ for the range between 4.77 eV to 5.64 eV and between 5.69 eV to 6.20 eV, respectively. Insets 1 and 2 for Figure 2

display the dependences of $(\alpha h\nu)^{\frac{1}{2}}$ and $(\alpha h\nu)^2$ on photon energy *hν*, respectively. Energy gap E_g can be calculated by the extrapolation of the linear part of $(\alpha h\nu)$ vs *hν* plot [15]. By extrapolation to $(\alpha h\nu)^{\frac{1}{2}}=0$ and $(\alpha h\nu)^2 = 0$, such plots inset 1 and 2 at Figure 2 give the values of the optical energy gap E_g for the indirect and direct band structure to be 4.69 eV and 5.57 eV respectively. Therefore, it is suggested that the colourless transparent Ti:Al_2O_3 single crystals have a direct band structure and an optical band gap of 5.57 eV.

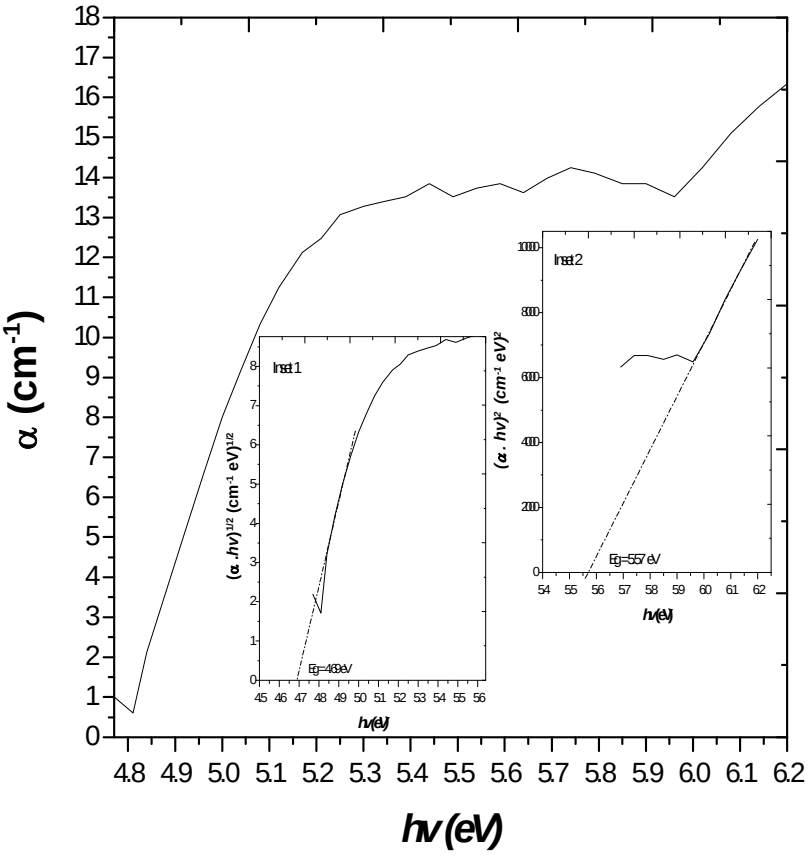

Figure 2: The variation of coefficient as a function of photon energy for the Ti: Al_2O_3 single crystal with doped Ti : 0.1 wt % at T= 300 K. Inset 1 and 2 represent the dependences of $(\alpha h\nu)^{\frac{1}{2}}$ and $(\alpha h\nu)^2$ on photon energy, respectively.

Determination of Refractive Index

The refractive indices of Ti:Al_2O_3 single crystal can be calculated from transmission spectrum in the wavelength region of 300 – 800 nm using the Fresnel equation [16],

$$R = \frac{(n-1)^2}{(n+1)^2} \qquad (3)$$

where R is reflectance and n is refractive index. The reflectivity can be calculated from transmittance spectrum with the following equation:

$$T = \frac{1-R}{1+R} \tag{4}$$

The transmission spectrum of Ti:Al_2O_3 single crystal is shown in Figure 3. The dispersion relations were calculated using Sellmeier's [17] refractive index dispersion distribution given as,

$$n^2 = A + \frac{B\lambda^2}{\lambda^2 - C} + \frac{D\lambda^2}{\lambda^2 - E} \tag{5}$$

where n is the refractive index, λ is the wavelength, and A, B, C, D, and E are know as Sellmeier parameters. The Sellmeier formula is selected since it facilitates more compact expression for the fitting equation than would generally be expected from a completely empirical formulation. Also, this formula often provides at least a rough guide to the values of certain other physical parameters of the optical material. Two term Sellmeier equation, as given in Eq (5), was used to fit the data consisting of the ordinary and extraordinary refractive index values measured at given wavelengths.

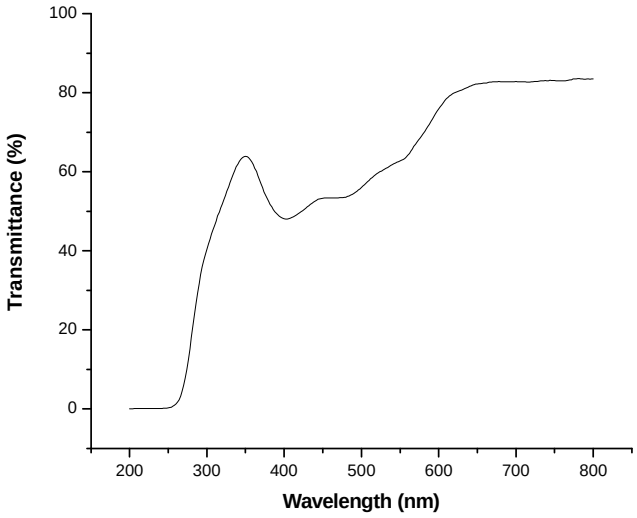

Figure 3: The transmittance spectrum of Ti: Al_2O_3 single crystal.

In the measured range, the Sellmeier equation can fit very well with the experimental values. The obtained fitting parameters are summarized in Table 1. The extrapolation to the short wavelength region, the Sellmeier fit is realistic, because the latter would imply that the material is transparent at wavelength shorter than the absorption edge, as can be observed in Figure 4. The Sellmeier equation, with double resonance frequencies (*B, D)* is accurate enough at short wavelengths. The refractive index for the extraordinary wave is larger than that of the ordinary wave, therefore, Ti:Al_2O_3 is an optically uniaxial positive crystal.

Table 1: Table Sellmeier coefficients from the fitting of measured refractive indices with Sellmeier equation. The corresponding curves are shown in Figure 3.

Sellmeier coefficients	n_e	n_o
A	1.78106	1.5586
B	1.27616	1.52365
C	0.01242	0.1097
D	0.33939	5.36043
E	17.03	325.66

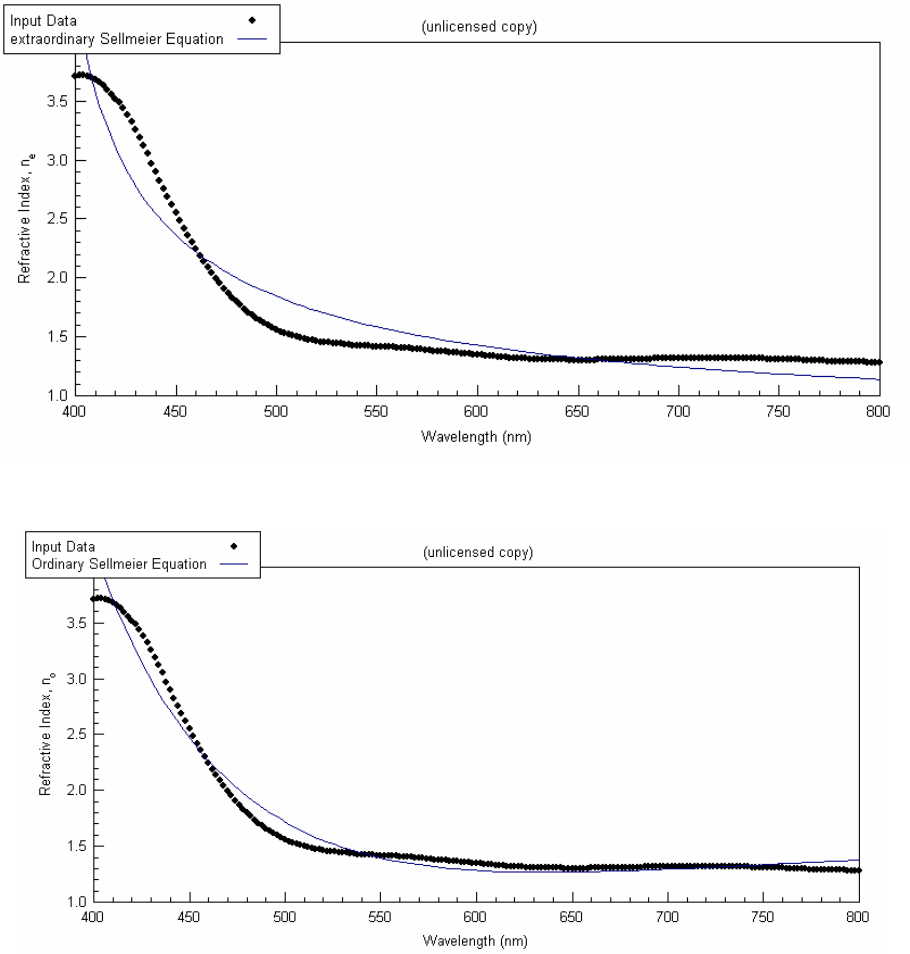

Figure 4: Measured extraordinary and ordinary refractive indices of Ti: Al_2O_3, n_e and n_o, respectively, and the calculated curve fit with the Sellmeier equation. The corresponding fitting coefficients are given in Table 1.

A typical result of refractive index obtained by using Sellmeier fitting methods is shown in Figure 3. It can be seen that the refractive index is depend on the wavelength. It is clear that the refractive index is decreased as the wavelength is increased. The accuracy of the reconstructed curve is very good, as it is also evidenced by the small absolute difference between experimental and interpolated values.

CONCLUSION

The Ti:Al_2O_3 single crystal has 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. The optical results indicated that the main absorption is due to isolated Ti^{3+} ion, whereas the parasitic infrared band is due to Ti^{3+} - Ti^{4+} pairs. The analysis of accurate measurements of the optical absorption in Ti: Al_2O_3 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 crystal of Ti: Al_2O_3 exhibit a direct band structure and the optical energy were found 5.57 eV for doped Ti: 0.1%. The refractive indices of Ti: Al_2O_3 single crystal as a function of wavelength has been determined by the Fresnel equation and the dispersion relations were calculated using Sellmeier's equation. The extraordinary refractive index is longer than the ordinary one, therefore Ti: Al_2O_3 is an optically uniaxial positive crystal.

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