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Band Gap Determination of VT_{E2} Single Crystals

KEYWORDS: Crystal growth, chemical vapour transport (CVT) technique, EDAX, XRD, optical properties, direct & indirect band gap

Rajiv D. Vaidya

Sheth P. T. Arts and Science College, Godhra

ABSTRACT *The study of optical properties of solids gives a good deal of information on the electronic properties and band structures of both metals and semiconductors. The optical band gap of semiconducting materials plays an important role in deciding the photoelectric properties of the optoelectronic devices. The optical properties of VTe_2 single crystals were studied using UV-visible spectrophotometer. Both direct and indirect band gap of this single crystal were determined from the analysis of the absorption spectrum near the fundamental absorption edge at room temperature. It has been found that both direct and indirect transitions are involved in the absorption process.*

Introduction:

Vanadium compounds, particularly vanadium oxides and some of their complexes are known to show semiconducting properties and have potential to be used for the fabrication of different kinds of devices. The excessive use of heating and cooling systems in extreme climates results in an extensive use of energy which in turn leads to several environmental problems as well as global warming. The solar control coating is a technology of great interest for researchers due to the necessity of improving the energy efficiency of buildings, with a view to avoiding excessive energy consumption for cooling and heating systems. The latest approach is based on the use of thermochromic coatings on the smart windows. These coatings possess the ability of actively changing their optical properties (transmission, reflection and absorption) as a consequence of a reversible structural transformation when going through a critical temperature. The thermochromic properties of VO_2 thin films for advanced smart window glazing were investigated [1,2]. VO_2 has insulating to a metal state transition at 68 ^{0}C, while the V_2O_5 undergoes a similar phase transition at 257 ^{0}C [3]. It has been shown that vanadium dioxide thin films prepared by chemical vapor deposition from vanadium (III) acetylacetonate exhibit optical and electrical switching behavior that strongly depends on film thickness [4].

Lead-telluride-based doped materials are used in IR optoelectronics to fabricate lasers and photodetectors because they offer a small band gap, high carrier mobility, and high radiation hardness. These applications take advantage of unusual impurity states produced in IV–VI compounds by doping and associated with the formation of impurity centers of different valences. For example, doping with In and Ga results in properties atypical of PbTe, such as Fermi-level pinning, a semiinsulating state, and delayed photoconductivity at low temperatures [5]. It is of interest to dope lead telluride with vanadium because vanadium and tellurium form several stable compounds in which vanadium can be in different oxidation states. In an earlier study [6], PbTe <V> samples were shown to be in a semi-insulating state near liquidhelium temperature, which is attributable to different valence states of vanadium in PbTe.

Experimental:

The samples of VTe_2 were grown by the chemical vapour transport technique. Since the crystals grew in the form of thin platelets, as grown samples were used to obtain the absorption spectra. The absorption spectrum of as grown crystal was obtained by using UV-VIS-NIR spectrophotometer in the range 700 nm to 1400 nm. For obtaining this spectrum thin flake of as grown crystal was used. This flake is pasted on a thick black paper with a cut exposing the crystal flake to the incident light. For reference the replica of the black paper was used and it cut at exactly the same position as the specimen. This arrangement is necessary because the crystal size is smaller than that of the sample compartment. Blank glass slides can also use as replica. All measurements were taken at room temperature with the incident beam normal to the basal plane i.e. along the c-axis of the grown flakes. Measurement along the c-axis could not be observed since the specimens were too thin to be mounted along this direction.

Result and Discussion:

The absorption spectrum was taken over the spectral range of 700 - 1400 nm. The optical absorption spectrum of as grown crystals is shown in Figure 1. A careful study of this spectrum reveals the presence of absorption edges in the spectral range 820 nm to 900 nm.

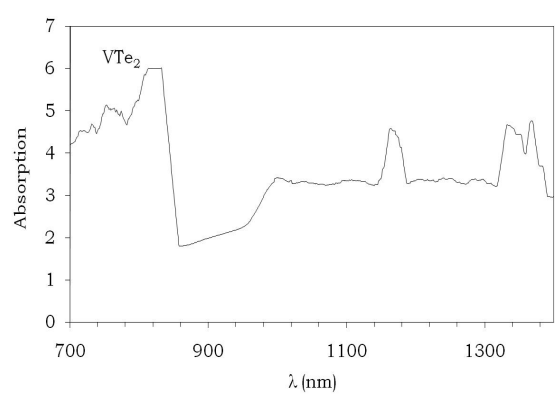

Figure 1: Absorption spectra of VTe_2 single crystals

The interpretation of experimental results, viz the dependence of absorption coefficient 'α' in terms of the direct and indirect transitions is most often performed with the help of formula derived for three dimensional (3D) crystals.

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Their simplest form is as follow [7],

For direct band gap.....(1)

$$\alpha h\upsilon = \sum_j B_j (h\upsilon - E_g' \pm E_p)^r$$

$$\alpha h\upsilon = A(h\upsilon - E_g)^r$$

For indirect band gap.....(2)

Here 'α' is absorption coefficient, calculated as a function of photon energy from absorption vs wavelength curve. hν is the energy of the incident photon, E_g the energy for the direct transition, E_g' the energy for the indirect transition and E_{pj} the energy of the phonons assisting at indirect transition. From E_{p1} & E_{p2} phonon equivalent temperatures θ1 & θ2 are defined as $\theta = E_{pi}/k$. A and B are parameters depending in the more complicated way on temperature, photon energy and phonon energies E_p.

Figure 2 shows the spectral variation of $(\alpha h\nu)^{1/2}$ vs hν. Since the curve indicates a discontinuous straight line it is quite possible that it represents indirect interband transition involving the emission or absorption of phonon. In order to make an accurate determination of the points of discontinuities, the method used which was adopted by earlier researchers [8]. The band gap was obtained by extrapolating the linear part to the energy axis for zero absorption. The graph of $\delta(\alpha h\nu)^{1/2}$ / dhν versus hν has been shown in **Figure 3**. It can be clearly seen that the derivation are step function of energy with four steps well defined in the range $E_1 < E < E_2$, $E_2 < E < E_3$, $E_3 < E < E_4$ and $E_4 < E$. The values of E_1, E_2, E_3 and E_4 indicate the points of discontinuities and shown in the plot of $\delta(\alpha h\nu)^{1/2}$ / dhν versus hν. The indirect energy gap obtained from these values of E_1, E_2, E_3 and E_4 are given by

$$E_g' = \frac{E_1 + E_4}{2} = \frac{E_3 + E_2}{2} \quad \textbf{(3)}$$

and the phonon energies are given by

$$Ep_1 = \frac{E_{p1} - E_1}{2}$$

And (4)

$$Ep_2 = \frac{E_3 - E_2}{2}$$

The obtained values of indirect band gap, phonon energies and phonon equivalent temperature are shown in **Table 1**.

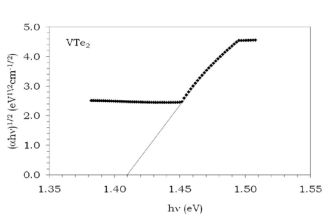

Figure 2: The graph of $(\alpha h\nu)^{1/2}$ vs hν for determination of indirect band gap.

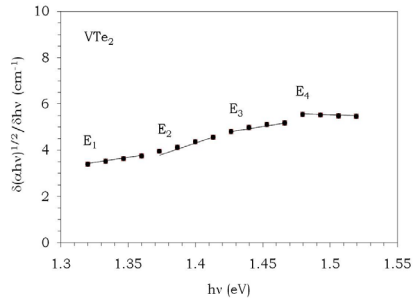

Figure 3 The spectral variation of $\delta(\alpha h\nu)^{1/2}/dh\nu$ versus hν for as grown crystals.

For the determination of direct gap, the best fit of all the experimental points was observed in the case of a $(\alpha h\nu)^2$ vs hν plote which is shown in Figure 4. The values of E_g obtained from the intercept of the straight line portion of the curve on the 'hν' axis are as shown in Table 1.

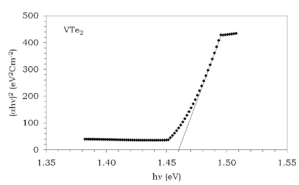

Figure 3: The graph of $(\alpha h\nu)^2$ vs hν for determination of direct band gap.

Table 1: The values of band gap and phonon energies of VTe_2 single crystals

Parameter	Obtained values
E_1 (eV)	1.32
E_2 (eV)	1.37
E_3 (eV)	1.42
E_4 (eV)	1.47
E_g' (C) (eV)	1.40
E_g' (E) (eV)	1.41
E_{p1} (meV)	79.8
E_{p2} (meV)	26.6
θ_1 (K)	926.39
θ_2 (K)	308.79
E_g (e V) (Direct)	1.47

Using absorption spectra, transmission and reflection coefficients have been computed by equations (6) and (7).

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$$\%T = (1/A) \times 100 \quad (6)$$

$$R = 1- (T+A) \quad (7)$$

where symbols have their usual meaning. The relation between T, R and A in graphical form is shown in Figure 5. From Figure 5 it implies that transmittance and reflection possess almost the same trend. But the value of reflectance in percentile is more than that of the absorption. The reflectance data confirms the shining surface of the crystal under investigation. The inset of Figure 5 indicates that crystals are transparent in the range 1.0-1.4 eV less than the energy gap ($E<E_g$) representing the urbach tail [9].

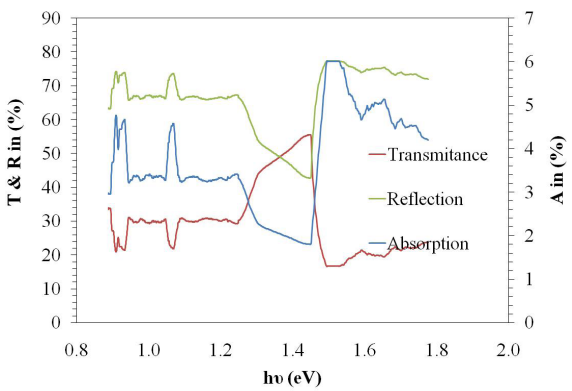

Figure 5: The transmittance, reflectance and absorbance spectra of VTe_2 single crystals.

CONCLUSION

It is quite clear from the analysis of the absorption data presented here that both direct and indirect symmetry allowed transitions give a good account of the absorption edge in the VTe_2 crystals. The value of direct band gap found was 1.46 eV and that of indirect band gap was 1.41 eV. It has been observed that the indirect transitions were phonon assisted.

The fact that formulae based on three dimensional model are capable of giving a consistent explanation for the absorption spectra suggests that VTe_2 is not truly two dimensional but can be considered as pseudo two dimensional.

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