STRUCTURAL AND OPTICAL PROPERTIES OF VANADIUM DISULPHIDE SINGLE CRYSTALS

*Kaushik R Patel

Biogas Research Center, Shri Mahadev Desai Gramseva Mahavidhyalaya, Gujarat Vidyapith, Sadra *Author for Correspondence

ABSTRACT

 VS_2 is a member of transition metal dichalcogenides (TMDC) group. Single crystals of vanadium disulphide were grown by chemical vapour transport technique using iodine as a transporting agent. The chemical composition of the grown crystals was confirmed with the help of energy dispersive analysis by X-ray (EDAX). The structural characterization was accomplished by X-ray diffraction (XRD) studies. Lattice parameters, unit cell volume and X-ray density were calculated using XRD data. The optical properties of VS₂ single crystals were observed using UV-visible spectrophotometer. The direct and indirect band gap of this single crystals were determined from the analysis of the absorption spectrum near the fundamental absorption edge at room temperature using light parallel to c-axis incident normally on the basal plane. Both direct and indirect transitions are involved in the absorption process.

Key Words: Crystal Growth, EDAX, XRD and Band Gap

INTRODUCTION

The transition metal dichalcogenides (including disulfide and diselenide) showed a wide variety of interesting physical properties, such as semiconducting, metallic, superconducting and magnetic behaviour (Tsuneta *et al.*, 2003; Salman *et al.*, 2007; Soto *et al.*, 2007 and Patel *et al.*, 2012). The vanadium diselenide single crystals have hexagonal crystal structure and have both direct and indirect band gap (Patel *et al.*, 2010). Electrochemical reactions of LiVS₂, Li₂FeS₄ and Li₄FeS₂ were investigated by using a Li⁺ ion conductive glass, $0.01Li_3PO_4$ - $0.63Li_2S$ - $0.36SiS_2$, as an electrolyte. They showed excellent electrode performance in the solid electrolyte system (Takada *et al.*, 2000).

However, looking at the important of optical band gap in this materials and because of the fact that no such information available for this compound, the author have carried out a detailed study on determination of optical band gap of this material by optical absorption method. The results are discussed in detail in this paper.

MATERIALS AND METHODS

The single crystals of vanadium disulphide (VS₂) were grown by chemical vapour transport technique using iodine as a transporting agent. The chemical composition of as grown crystals has been confirmed by using EDAX analysis. The energy dispersive spectrum of as grown crystal of VS₂ is shown in Figure 1. The stoichiometric proportion and EDAX data are given in Table 1. For X-ray diffraction analysis, several small crystals were finely grind with the help of an agate mortar and filtered through 100-micron sieve to obtain grains of nearly equal size. The powder obtained during the growth process was used for the X-ray diffraction study experiment. X-ray diffractometer (Make: Philips, Model: X'PERT MPD) was used to obtain the diffraction pattern in which wavelength used was 1.542 Å and Cu target X-ray tube was used as a source and all the measurements were taken with accuracy upto \pm 0.0025.

The absorption spectrum of as grown crystal was obtained by using UV-VIS-NIR spectrophotometer. 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.

International Journal of Physics and Mathematical Sciences ISSN: 2277-2111 (Online) An Online International Journal Available at http://www.cibtech.org/jpms.htm 2013 Vol. 3 (3) July-September, pp.74-80/Patel

Research Article

RESULTS

The chemical vapour transport technique is more suitable for obtaining large size single crystals of VS₂. From the Table 1 we can say the stoichiometry of as grown crystals are nearly preserved. The X-ray diffraction pattern of VS₂ is shown in Figure 2. The pattern consists of well-defined sharp diffraction lines, indicating good crystallinity of the specimen. The lattice parameter *a*, *b* and *c*, unit cell volume (*V*) and X-ray density (ρ) were calculated using XRD data and it systematically presented in Table 2.

The absorption spectrum of grown crystal is shown in Figure 3. In this figure, the curves indicated discontinuous straight line it is quit plausible that they are representing indirect interaband transition involving the emission or absorption of photons. The interpretations of experimental results, viz the dependence of absorption coefficient ' α ' in the term of the direct and indirect transitions is most often performed with the help of formula derived for three dimensional (3D) crystal their simplest form is as follows (Pankove, 1975)

For direct band gap

$$\alpha h \upsilon = A(h \upsilon - E_g)^r \tag{1}$$

For indirect band gap

$$\alpha h \upsilon = \sum B_{j} (h \upsilon - E'_{g} \pm E_{pj})^{r}$$
⁽²⁾

Here α is absorption coefficient hv is the energy of the incident photon, eg the energy for the direct transition, Eg' the energy for the indirect transition and E_{pj} the energy of the phonons assisting at indirect transition. A and B are parameters depending in the more complicated way on temperature, photon energy and phonon energies Ep.

However, for the analysis of the experimental results obtained at constant temperature, equations (1) and (2) are sufficient and they are most often used while interpreting results on absorption spectra obtained from semiconducting materials. The exponent 'r' in the above equations depends upon whether the transition is symmetry allowed or not and the constants A and B will assume different values for the allowed and forbidden transitions. For indirect transitions the detailed form of equation (2) (Elkorashy, 1986; Vlachs *et al.*, 1976) is given as,

$$\alpha_{i} = \sum_{i=1}^{2} \left\{ \frac{B_{ai}}{E} \left(\frac{1}{e^{\theta_{i}/T} - 1} \right) (E - E'_{g} + k\theta_{i})^{r} + \frac{B_{ei}}{E} \left(\frac{1}{1 - e^{\theta_{i}/T}} \right) (E - E'_{g} - k\theta_{i})^{r} \right\}$$
(3)

Where B_{ai} and B_{ei} are coefficients associated with absorption and emission of *i*th phonon. *E* the photon energy, E'_g the indirect energy gap and θ_i is a phonon equivalent temperature defined by the equation,

$$\theta_i = \frac{E_{_{pi}}}{k} \tag{4}$$

Where E_{pi} being the i^{th} phonon energy and k is the Boltzman constant.

In these cases the density of states is a constant independent of the energy and the expressions showing the dependence of α in terms of direct and indirect transitions get modified (Elkorashy, 1986) as

$$\alpha = A'(hv - E_{g})^{r} \tag{5}$$

For direct transition and

$$\alpha_{i} = \sum_{i=1}^{2} \left\{ B_{ai}' \left(\frac{1}{e^{\theta_{i}/T} - 1} \right) (E - E_{g}' + k\theta_{i})^{r} + B_{ei}' \left(\frac{1}{1 - e^{\theta_{i}/T}} \right) (E - E_{g}' - k\theta_{i})^{r} \right\}$$
(6)

For Indirect Transition (Goldberg et al., 1975)

The graph of $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ vs hv are as shown in Figures 4 & 5 respectively. Using this graph we can determine the indirect as well as direct band gap respectively for VS₂ single crystals. The dependence

Research Article

of the derivation δ (α hv) ^{1/2}/ δ hv on hv has been shown in Figure 6. It can be clearly seen that the derivation are step function of energy with four steps well defined in the rang $E_1 < E < E_2$, $E_2 < E < E_3$, $E_3 < E < E_4$ and $E_4 < E$. Form Figure 6, we can also determine the indirect band gap using the formula of $Eg' = \frac{E_1 + E_4}{2} = \frac{E_2 + E_3}{2}$ (7)

and the phonon energies are calculated by using question (8).

$$Ep' = \frac{E_4 - E_1}{2}$$
 and $Ep^2 = \frac{E_3 - E_2}{2}$ (8)

The values of direct band gap, indirect band gap and phonon energy and phonon equivalent temperature are presented in Table 3.

Table 1: The EDAX data of VSe2 single crystals			
Elements	Stoichiometric proportion Wt %	From EDAX Wt %	
V	44.27	44.19	
S	55.73	55.81	

Table 2: The crystallographic data of VS₂ crystals

Parameter	Result	
a = b (Å)	3.38	
c (Å)	12.28	
X-ray Density (gm/cc)	1.57	
Volume V(Å) ³	121.49	

Table 3: The optical parameters for VS₂ single crystals

Parameter	VS_2
$E_1 (eV)$	1.32
$E_2 (eV)$	1.37
E ₃ (eV)	1.43
$E_4 (eV)$	1.48
E'_{g} (C) (eV)	1.40
E'_{g} (E) (eV)	1.396
E _{p1} (eV)	0.08
$E_{p2} (eV)$	0.03
Θ_1 (K)	928.02
$\Theta_2 \left(\mathrm{K} ight)$	348
E _g (e V) (Direct)	1.444

International Journal of Physics and Mathematical Sciences ISSN: 2277-2111 (Online) An Online International Journal Available at http://www.cibtech.org/jpms.htm 2013 Vol. 3 (3) July-September, pp.74-80/Patel Passaarah Articla





Figure 2: X-ray diffractogram for VS₂ single crystals

International Journal of Physics and Mathematical Sciences ISSN: 2277-2111 (Online) An Online International Journal Available at http://www.cibtech.org/jpms.htm 2013 Vol. 3 (3) July-September, pp.74-80/Patel

Research Article



Figure 3: UV absorption spectrum for VS_2 single crystals



Figure 4: The graph of $(\alpha hv)^{1/2} \rightarrow hv$ for determination of indirect band gap of VS₂ single crystals



Figure 5: The graph of $(\alpha hv)^2 \rightarrow hv$ for determination of direct band gap of VS₂ single crystals

International Journal of Physics and Mathematical Sciences ISSN: 2277-2111 (Online) An Online International Journal Available at http://www.cibtech.org/jpms.htm 2013 Vol. 3 (3) July-September, pp.74-80/Patel

Research Article



Conclusion

The single crystals of vanadium disulphide were successfully grown by chemical vapour transport technique. The X-ray diffraction analysis indicated that the grown crystal possesses hexagonal crystal structure. The vanadium disulphide single crystals have both direct and indirect band gap. The accurate analysis of the data has shown that the indirect transition represented by the absorption curves is indirect allowed involving two different phonons. The energies of these phonons have been determined.

REFERENCES

Elkorashy AM (1986). Optical absorption in tin monoselenide single crystal, *Journal of Physics and Chemistry of Solids* 47(5) 497.

Elkorashy AM (1986). Indirect forbidden fundamental absorption edge in germanium selenide single crystals, *Physica Status Solidi* (b) 135(2) 707.

Goldberg AM, Beal AR, Levy FA and Davis EA (1975). The low-energy absorption edge in 2H-MoS₂ and 2H-MoSe₂, *Philosophical Magazine* **32**(2) 367-378.

Pankove JI (1975). Optical Processes in Semicondcuctors, New York: Dover Publications Inc. 1.

Patel CA, Patel KR and Patel KD (2012). Structural characterization of tungsten diselenide single crystal, *International Journal of Physics and Mathematical Sciences* **2**(4) 17-26.

Patel KR, Vidya RD, Dave MS and Patel SG (2010). Crystal structure and band gap measurements of vanadium diselenide single crystals, *Sciencia Acta Xaveriana* 1 5-15.

Salman Z, Wang D, Chow KH, Hossain MD, Kreitzman SR, Keeler TA, Levy CDP, MacFarlane WA, Miller RI, Morris GD, JParolin T, Saadaou H, Smadella M and Kiefl RF (2007). Magnetic-Field Effects on the Size of Vortices below the Surface of NbSe2 Detected Using Low Energy β -NMR. *Physical Review Letter* **98**(16) 167001–167004.

Soto F, Berger H, Cabo L, Carballeira C, Mosqueira J, Pavuna D, Toimil P and Vidal F (2007). Electric and magnetic characterization of NbSe2 single crystals: Anisotropic superconducting fluctuations above *TC. Physica C* **460** 789.

Takada Kazunori, Inada Taro, Kajiyama Akihisa Kajiyama, Kouguchi Masaru, Kondo Shigeo and Watanabe Mamoru (2001). Research on highly reliable solid-state lithium batteries in NIRIM, *Journal of Power Sources* 97-98 762-764.

International Journal of Physics and Mathematical Sciences ISSN: 2277-2111 (Online) An Online International Journal Available at http://www.cibtech.org/jpms.htm 2013 Vol. 3 (3) July-September, pp.74-80/Patel **Research Article**

Tsuneta T, Toshima T, Inagaki K, Shibayama T, Tanda S, Jui S, Ahlslog M, Harkonen P and Paalanen (2003). Formation of metallic NbSe2 nanotubes and nanofibers. *Current Applied Physics* **3**(1) 473-476.

Vlachs SV, Lambros A P, Thanailakis A and Economou N A (1976). Anisotropic Indirect Absorption Edge in GeSe, *Physica Status Solidi (b)* 76(2) 727-735.