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Crystal structure and band gap measurements of vanadium diselenide single crystals

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Abstract. Single crystals of layered single crystals of vanadium diselenide were grown by chemical vapour transport technique using iodine as transporting agent The stoichometry of the grown crystal was ascertained by EDAX analysis of as grown crystals. The structural characterization was accomplished by XRPD. The optical band gap of vanadium diselenide 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. The indirect transition was found to be allowed with two phonons involved in the process. The indirect and direct band gap for VSe_2 single crystals are 1.4 eV and 1.46 eV respectively.

Key words: Crystal growth, EDAX, XRPD and optical band gap.

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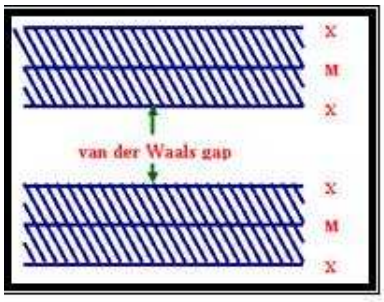
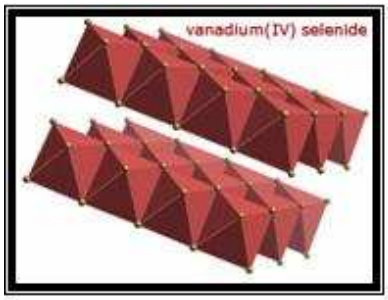
1 Introduction

Transition metal dichalcogenide (TMDC) layered crystals consist of stacks of hexagonally close-packed layers of transition metal atom (V) sandwiched between two layers of chalcogen atoms (Se) [Se–V–Se]. The stacking of hexagonally packed plane of MX_2 type dichacogenides and crystal structure of VSe_2 single crystal are shown in Fig. 1(a) & (b). The metal atoms are octahedrally coordinated and covalently or ionically bonded to the chalcogen atoms. Because of the weak van der Waals force acting between individual sandwiched layers, the van der Waals gaps exist in the layer stacking. TMDC layered crystals possess interesting physical properties, such as two dimensional metallic or semiconducting properties and allow the study of phenomena like charge density wave [1, 2]. Upon cleavage, TMDC crystals offer the possibility of studying fundamen-



(a) Stacking of hexagonally packed plane of MX_2 type dichalcogenides



(b) Crystal structure of VSe_2 single crystal.

Figure 1:

tal aspects of metal deposition onto flat substrate surfaces without any dangling bonds. The formation of self-assembled networks of linear nanostructures was reported for metal deposition onto cleaved layered transition metal dichalcogenide (TMDC) crystal surface [3, 4]. The local effect of the charge density wave in insitu Na-intercalacted 1T-VSe_2using scanning tunneling microscopy and spectroscopy between 300 K and 60 K were studied [5].

However, looking to the importance of optical band gap in this material and less availability of optical band gap details for this crystal, the authors have carried out a detailed study on determination of optical band gap of this material by optical absorp-

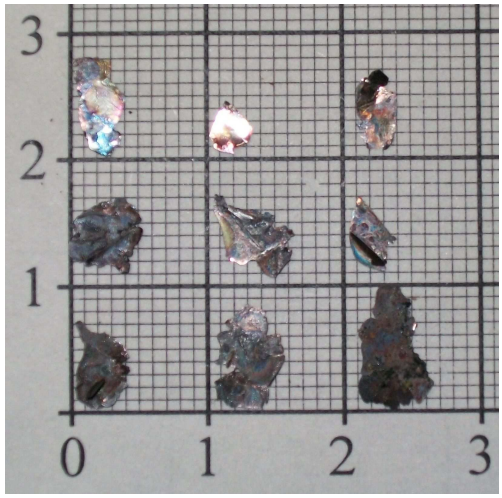


Figure 2: Photograph of grown crystals of vanadium diselenide.

tion within range 700 nm to 1400 nm. The results obtained are presented and discussed in this paper.

2 Experimental

The single crystals of vanadium diselenide (VSe_2) were grown by chemical vapour transport technique using iodine as a transporting agent. For the growth of VSe_2 single crystals, stoichiometric proportion of vanadium powder (Aldrich, Purity: 99%) and selenium powder (Chiti Chem, Purity: 99.95%) were taken in quartz ampoule. The ampoule containing the source material was evacuated to 10^{-5} torr pressure. The homogeneous mixture was properly distributed along the length of the ampoule and it was placed into the dual zone furnace. The temperature of furnace was increased slowly. The temperature was maintained at 800°C for three days to allow the reaction to be completed. After 3 days the furnace was slowly cooled down to room temperature. The charge so prepared inside ampoule was rigorously shaken to ensure the proper mixing of the constituents. For crystal growth the synthesized charge was transferred into another evacuated (10^{-5} torr) quartz ampoule with iodine (2 mg/cc) as a transporting agent filled in capillary tube. The sealed ampoule was introduced into the two zone

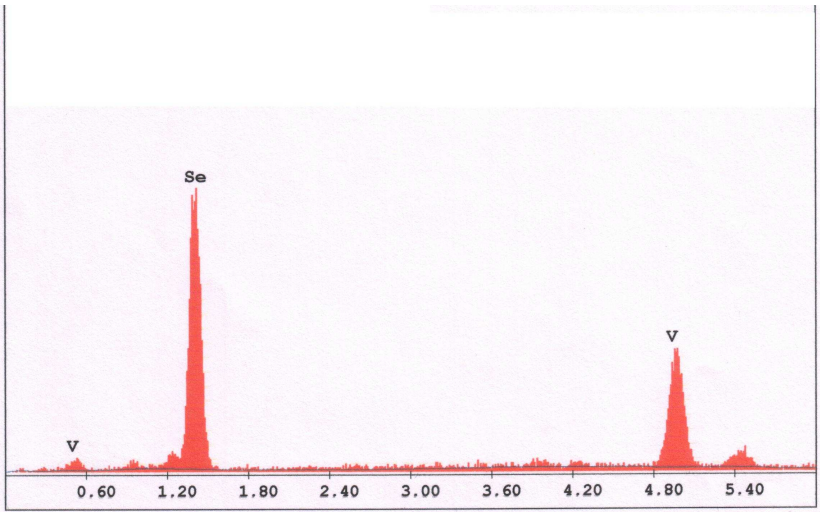


Figure 3: EDAX spectra of VSe_2 single crystals.

horizontal furnace with reaction zone at higher temperature and the growth zone at a lower temperature for a definite time period. The growth conditions along with the dimension of as grown crystals are presented in Table 1. The photograph of as grown crystals is shown in Fig. 2.

2.1 Structural characterizations

The chemical composition of the as grown crystals was confirmed on basis of energy dispersive analysis by X-ray (EDAX). The energy dispersive spectra of as grown sample of VSe_2 crystals is shown in Fig. 3 and their results are shown in Table 2. The structural characterization of this crystal was done by X-ray diffraction analysis. For X-ray diffraction study, several small crystals were finely ground 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 analysis. 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 X-ray diffractrogram of these crystals are shown in Fig. 4.

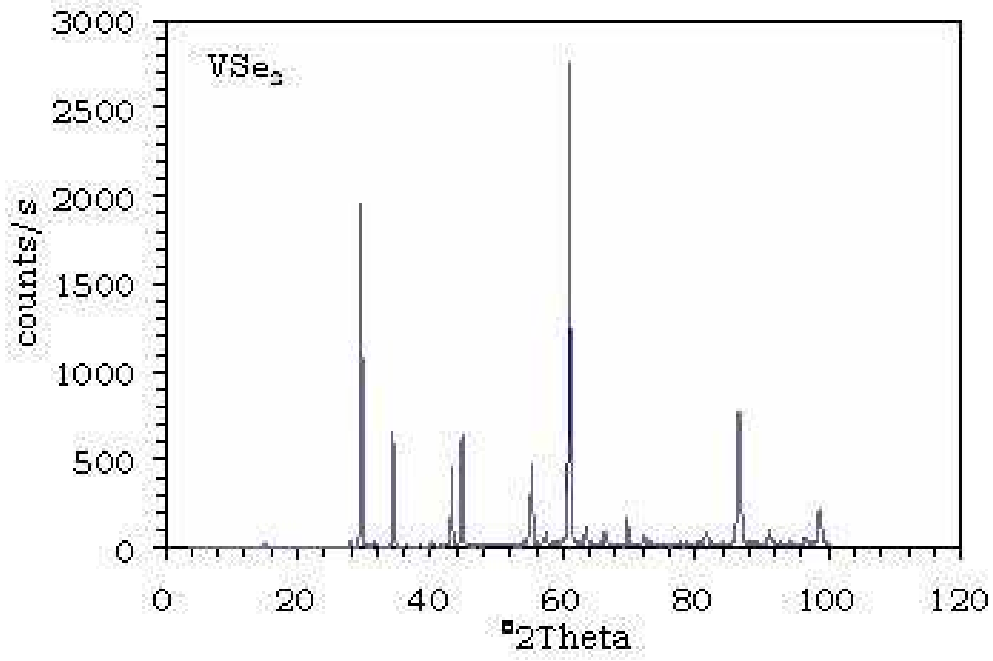


Figure 4: The X-ray diffractogram of VSe_2 single crystals.

2.2 Band gap measurements

The optical band gap of as grown crystals was obtained by optical absorption. The optical absorption spectra were taken by means of UV–VIS–NIR Spectrophotometer (Make: Perkin Elmer, Model: Lambda-19) in wavelength range of 700–1400 nm. The absorption spectra of as grown crystals are shown in Fig. 5. For obtaining the absorption spectra using UV-VIS-NIR spectrophotometer from single crystal specimens, thin flakes of as grown crystals were used. These flakes were pasted on a thick black paper with a cut exposing the crystal flake to the incident light. The reference used was a replica of the black paper, having the cut at exactly the same position as the crystal flake. This arrangement was necessary because the crystal size was smaller than that of the sample compartment. For determination of band gap for semiconducting materials, absorption of incident photon by semiconducting material is an important technique. In this technique, photons of selected wavelengths were bombarded on the sample and their relative transmission was observed. The photons with energies greater than the

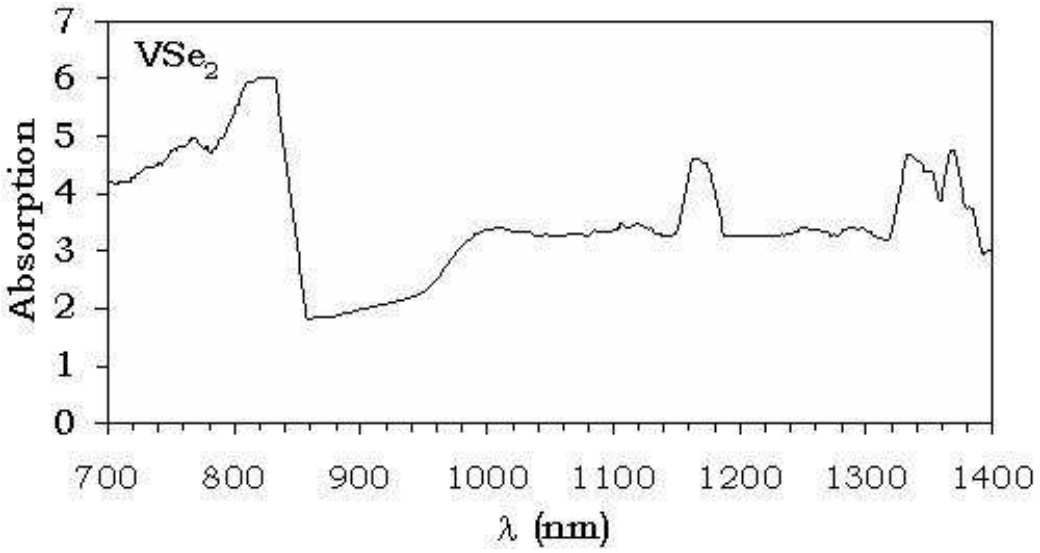


Figure 5: The absorption spectra of VSe_2 single crystals.

band gap were absorbed while photons with energies less than band gap were transmitted. For determination of energy band gap, the spectral variation of $(\alpha h\nu)^{1/2}$ vs $h\nu$ (for indirect band gap) and $(\alpha h\nu)^2$ vs $h\nu$ (for direct band gap) was studied and graphically the values of direct and indirect band gap were carried out. The absorption coefficient was calculated using the formula

$$\alpha = \frac{1}{t} \ln \left(\frac{1}{a} \right)$$

where t is thickness of the sample and a is the absorbance. A careful study of these spectra reveals the presence of absorption edges in the spectral range studied. In order to make an accurate determination of the points of discontinuities, authors followed the method earlier successfully used for layer compounds [6, 7, 8, 9].

3 Results

Single crystals of VSe_2 were grown by chemical vapour transport technique using iodine as a transporting agent. From the EDAX data, it is clear that the stoichometry of

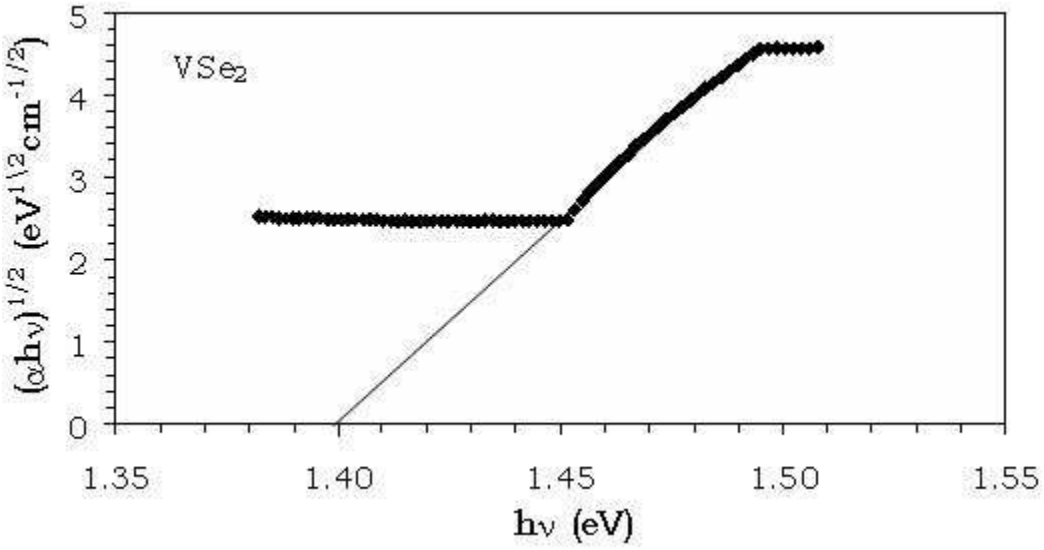


Figure 6: The graph of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ for VSe_2 single crystals.

as grown crystals are preserved. In Fig. 4, the pattern consists of well defined sharp diffraction lines, indicating good crystallinity of the specimen. The values of lattice parameter a, b and c, the unit cell volume (V) and X-ray density (ρ) obtained from the analysis of the diffractogram are presented systematically in Table 3. In Fig. 5, the curve indicates that discontinuous straight line is a possibility of indirect interband 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 [10]

$$\text{for direct band gap} \quad \alpha h\nu = A(h\nu - E_g)^r \tag{1}$$

$$\text{for indirect band gap} \quad \alpha h\nu = \sum_j B_j(h\nu - E_g' \pm E_{pj})^r. \tag{2}$$

Here α is absorption coefficient, $h\nu$ is the energy of the incident photon, E_g 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.

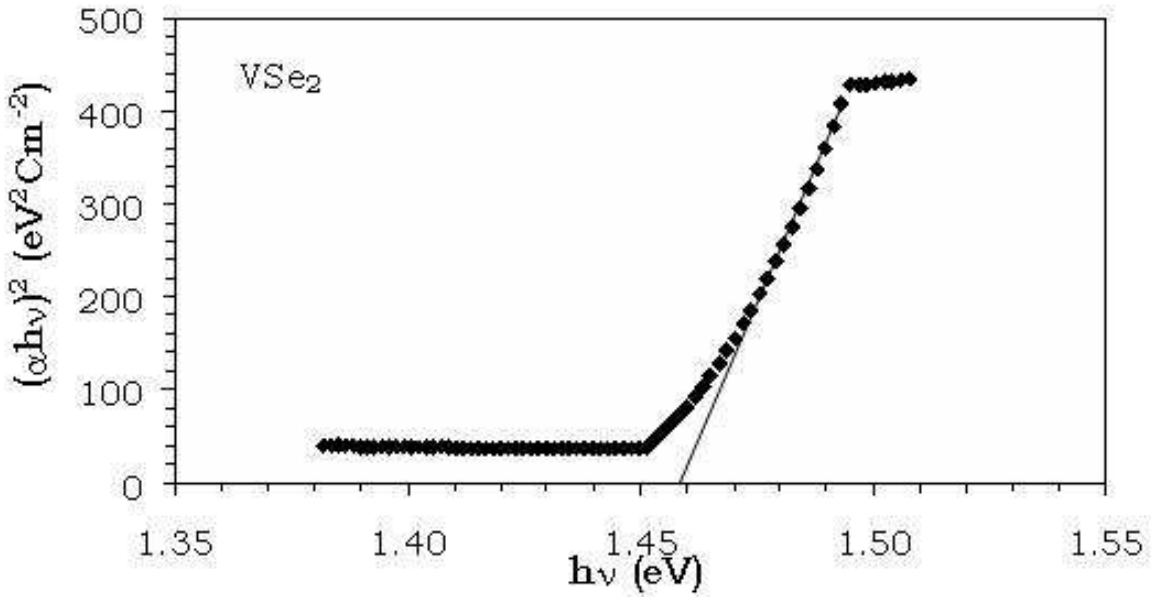


Figure 7: The graph of $(\alpha h\nu)^2$ vs. $h\nu$ for VSe_2 single crystals.

By plotting graph of $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ vs $h\nu$ as shown in Figs. 6 and 7, it is possible to determine the indirect as well as direct band gap respectively for VSe_2 single crystals. The dependence of the derivation $\delta(\alpha h\nu)^{1/2}/\delta h\nu$ on $h\nu$ has been shown in Fig. 8 for VSe_2 single crystal. It can be clearly seen from the Fig. 8 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 $E_4 < E$ given by

$$E'_g = \frac{E_1 + E_4}{2} = \frac{E_2 + E_3}{2} \tag{3}$$

and the phonon energies are given by

$$E'_p = \frac{E_4 - E_1}{2} \quad \text{and} \quad E^2_p = \frac{E_3 - E_2}{2}$$

the values of direct and indirect band gap and phonon energy thus obtained are presented in Table 4.

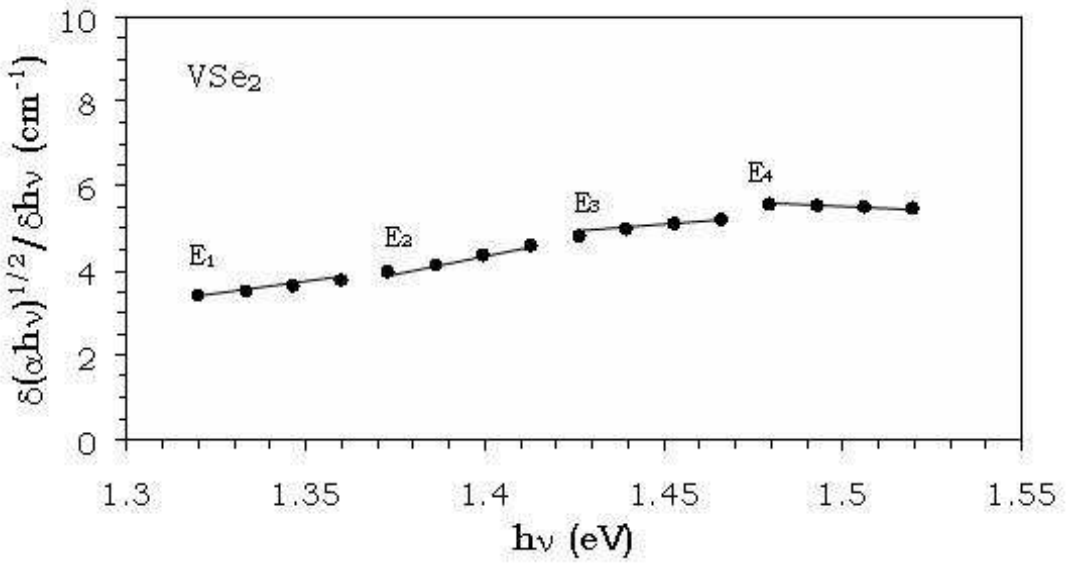


Figure 8: The graph of $\delta(\alpha h\nu)^2$ vs. $h\nu$ for VSe_2 single crystals.

4 Conclusion

The chemical vapour transport technique is most suitable for the growth of large size single crystals of vanadium diselenide. The X-ray diffraction analysis indicated that the grown crystal possesses hexagonal crystal structure. The vanadium diselenide 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.

Table 1: Growth parameters of VSe_2 single crystal grown using chemical vapour transport technique.

Sample	Reaction Temp. (K)	Growth Temp. (K)	Physical characteristics of the crystals			
			Growth time (h)	Plate area $l \times b$ (mm^2)	Thickness (mm)	Color & appearance
VSe_2	1073	1123	370	64	0.675	Silver shining

Table 2: The EDAX data of VSe_2 single crystals.

Elements	Stoichiometric proportion Wt %	From EDAX Wt %
V	24.39	25.53
Se	75.61	74.47

Table 3: The crystallographic data of VSe_2 single crystals.

Parameter	Calculated
$A = b$ (Å)	3.38
c (Å)	12.28
X-ray Density (gm/cc)	5.63
Volume V(Å^3)	121.7

Table 4: The values of band gap and phonon energies for VSe_2 single crystals.

Parameter	E_1 (eV)	E_2 (eV)	E_3 (eV)	E_4 (eV)	$E_g^{'}$ (C) (eV)	$E_g^{'}$ (E) (eV)	Ep_1	Ep_2	E_g (eV) (Direct)
Values	1.32	1.37	1.44	1.48	1.39	1.40	0.08	0.04	1.46

$E_g'(C) =$ indirect band gap from calculation.
$E_g'(E) =$ indirect band gap from extrapolation.

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