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Structural Property Measurement of Vanadium Ditelluride Single Crystals Grown by CVT Technique

KEYWORDS: Crystal growth, chemical vapour transport (CVT) technique, EDAX, XRD, structural properties

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ABSTRACT *Vanadium Ditelluride (VTe_2) is one of the important members of transition metal dichalcogenides (TMDC) group. Single crystals of VTe_2 were grown by the chemical vapour transport (CVT) technique for the purpose of study of its structural properties measurements. Here, iodine was used as a transporting agent. The chemical composition of grown crystals was confirmed on the basis of Energy Dispersive Analysis by X-ray (EDAX). The structural properties of grown crystals have been studied using X-ray diffraction (XRD) analysis. The lattice parameters, unit cell volume and X-ray density have been determined for grown crystals. The as grown crystals were revealed to possess hexagonal structure. Growth and deformation fault probability have been calculated.*

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, Patel C. A. et al., 2012, 2014 and M. D. Dave 2012). The vanadium diselenide and vanadium disulphide single crystals have hexagonal crystal structure and have both direct and indirect band gap (Patel et al., 2010 and Kaushik R Patel 2013). Electrochemical reactions of $LiVS_2$, Li_2FeS_4 and Li_4FeS_2 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).

It has been observed that relatively less work have been done on the growth of VTe_2 single crystals and its different properties. Research work presented here is an attempt to study the growth and determination of structural properties of as grown crystals.

EXPERIMENTAL

The single crystals of vanadium ditelluride (VTe_2) were grown by chemical vapour transport technique using iodine as a transporting agent. For the growth of VTe_2 single crystals, stoichiometric proportion of vanadium powder (99% pure) and telluride powder (99.95% pure) were taken in quartz ampoule. The ampoule containing the source material was evacuated at 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 to avoid any explosion, which might occur due to the strongly exothermic reaction between the elements. The temperature for then maintained at 800° C temperature was three days to allow the complete reaction. After 3 days the furnace was slowly cooled with the rate of 20 °C/hr up to 500°C and after that cooled it with the rate of 50°C/hr up 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) and evacuated at 10^{-5} torr pressure. The sealed ampoule was introduced into the dual zone horizontal furnace with reaction zone at higher temperature and the growth zone at a lower temperature for a definite time period. The optimum growth condition and physical parameters of as grown crystals are shown in Table 1.

Table 1. Growth parameters of VTe_2 single crystal grown using chemical (iodine) vapour transport technique.

Ampoule dimension		Temperature distribution		Physical characteristics of crystals			
Length (mm)	ID (mm)	Hot zone (K)	Cold zone (K)	Growth time (h)	Plate area (mm^2)	Thickness (mm)	Colour and Appearance
250	22	1123	1073	192	45	0.09	Silver Shining

The stoichiometry of the as grown crystals has been confirmed with the help of EDAX analysis. The energy dispersive spectra for determining the chemical composition of as grown sample of VTe_2 crystals is shown in Figure 1.

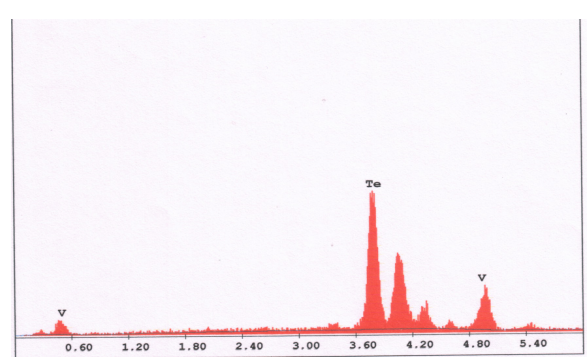

Figure 1: EDAX spectra of VTe_2 single crystal.

For X-ray diffraction study, 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

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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 ± 0.0025.

RESULTS AND DISCUSSION

The stoichiometric proportion of the constituent elements taken for the growth and results obtained from the EDAX are shown in **Table 2**, with chemical formula. The EDAX analysis shows that the grown crystals are stoichiometrically perfect without any extra impurities.

Table 2 The stoichiometric proportion and EDAX data of VTe_2 single crystals

Element	Stoichiometric proportion (Wt %)	From EDAX (Wt %)
Vanadium (V)	1.6640	1.6642
Telluride (Te)	8.3360	8.3358

The X-ray diffraction pattern obtained for VTe_2 is shown in Figure 2. The pattern consists of well-defined sharp diffraction lines, indicating good crystallinity of the specimen.

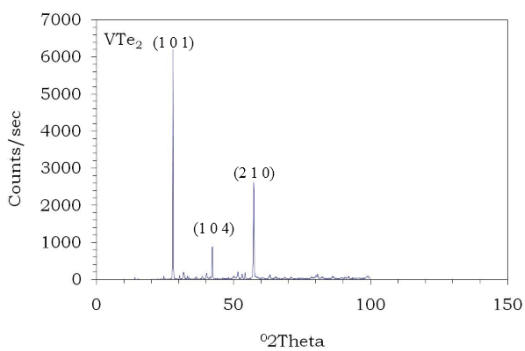

Figure 2: The X-ray diffraction pattern of VTe_2 crystal

The lattice parameters for the hexagonal structure have been computed, using the equation (1), i.e.

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2} \qquad (1)$$

where d is the inter planar spacing obtained from the diffractogram, h, k, l are the miller indices and a & c are the unit cell dimensions. Substituting the values of inter planar spacing parameter d corresponding to the planes having index {00l}, the value of lattice the parameter 'c' has been determined. Substituting the value of c and d for the rest of the planes, lattice parameters for rest of all the planes have been calculated. Using the values of lattice parameters a, b, c the unit cell volume (V) has been calculated with the help of the equation (3). It is found that there is no significant variation in the values of lattice parameters a and c.

Volume, in terms of lattice constants a, b, c and angleso,α and β is given as

$$V^2 = a^2b^2c^2\left(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha - \cos\beta - \cos\gamma\right) \qquad (2)$$

For hexagonal system, $\gamma\ \alpha = \beta\ 90^0$, = $=120^0$ and a = b ≠ c,

Substituting above values in equation (2), the unit cell volume is given as,

$$V = \frac{\sqrt{3}}{2}\ a^2c\ (Å)^3 = 0.866\ a^2c\ (Å)^3 \qquad (3)$$

The density ρ of the grown crystals was calculated by the formula,

$$\rho = \frac{\sum A}{VN} \qquad (4)$$

Where, ΣA is the total weight of the atoms in the unit cell = MZ. Here M is the molecular weight and Z is the number of molecules/unit cell, N is the Avogadro number and V is the unit cell volume. The quadratic form of the Bragg equation for a Hexagonal system, of MX_2 is given as [Cullity, (1978) and Suryanarayana, (1998)],

The values of lattice parameters a, b, c, X-ray density (ρ) and unit cell volume (V) have been calculated from the XRD data for as grown crystals of VTe_2 it given in **Table 3**.

Table 3: The crystallographic data of VTe_2 crystals.

Parameter	Calculated
a = b (Å)	3.64
c (Å)	6.58
X-ray Density (gm/cc)	6.70
Volume V(Å)^3	75.8

Particle size determination

In order to obtain an idea about the particle size distribution in VTe_2 single crystals, the particle size was calculated using Scherrer's formula [Al-Hilli and Evans, 1972] given as

$$t = \frac{k\lambda}{\beta_{2\theta}\cos\theta} \qquad (5)$$

Where t is the crystallite thickness as measured perpendicular to the reflecting plane; k is Scherrer's constant whose value is chosen as unity assuming the particle to be spherical; λ is the wavelength of the X-ray radiation, $\beta_{2\theta}$ is the width at half the maximum intensity measured in radians, and θ_0 is the Bragg angle. **Table 4** records the crystallite size for $Sn_{0.5}Se_{2.5}$single crystals. The intense and sharp peaks reveal the excellent crystallinity of the products and confirm their stoichiometric nature. The reflections corresponding to the observed peaks indicate the formation of single-phase material.

Table 4 The h k l reflections, d- spacing, 2γ Values, Peak Intensity, $q_{2\beta}$ value and particle size for VTe_2 single crystals.

(h k l)	d-spacing	Angle 2θ (degree)	Peak Intensity (cont/sec)	Tip Width$q_{2\theta}$	Particle Size ($_{Å}$)
0 0 1	6.2858	14.0778	72.26	0.18	864.23
1 0 2	2.9440	30.3355	99.23	0.18	887.6
0 0 3	2.8303	31.5852	142.48	0.24	667.61
1 1 0	2.7955	31.9888	166.18	0.24	668.77
1 1 2	2.3288	38.6303	77.44	0.36	453.87
2 0 2	1.9698	46.0393	38.97	0.24	697.99
114	1.7223	53.1327	125.22	0.30	574.65

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The particle size of as grown crystals is found to be in the range of 450 Å – 864 Å as shown in Table 4. The intense and sharp peaks reveal the excellent crystallinity of the products and confirm their stoichiometric nature. The reflections corresponding to the observed peaks indicate the formation of single phase material.

Estimation of growth and deformation fault probabilities

Perfect crystalline structure is an ideal concept since perfect crystals are neither available in nature nor can be grown in the laboratory. Several types of defects are always present in crystal e.g. point defects, stacking fault etc. The study of stacking fault is very important because it plays a fundamental role in the description of defects. The enhanced conduction of the stacking faults along the c-axis is difficult to understand because of the extreme two-dimensional character of the MX2 layer compounds. The only way to understand this conduction is by supposing the presence of stacking faults in these crystals [Vora A M, 2007]. In the case of hexagonal close packed metals, it is possible to make a realistic estimation of the growth fault probability 'θ' and the deformation fault probability 'θ' by measuring the half width of X-ray diffraction lines. Reflections for which h - k = 3n where 'n' is an integer, are independent of stacking faults whereas reflections for which h - k = 3n θ 1 and l ± 0 depend upon the faults in the crystal structure. An estimation of the deformation and growth fault probability can be obtained from the following formula for (h k l) values with 'l' even

$$(3\neq+3\alpha)\ \beta \qquad \frac{\beta_{2\theta}\times\pi^2\times c^2}{360\times l\times d^2\times\tan\theta}$$

where =2β is the full width at half the maximum intensity expressed in degrees, c = d002, l is the Miller index in the (h k l) plane for which the estimation of 'θ' and 'α' is being made, 'd' is the inter planer spacing for (h k l) reflection in question, β is the Bragg angle corresponding to this (h k l) plane.

The formula for (h k l) values with 'l' odd is given as

$$(3\alpha+\beta)=\frac{\beta_{2\theta}\times\pi^2\times c^2}{360\times l\times d^2\times\tan\theta} \qquad (7)$$

From the equations 6 and 7, it is clear that by measuring the half width qβ for reflections with both even and odd values of 'l' it is possible to calculate the stacking fault probabilities θ & α. In calculating the half width of the reflections, instrumental broadening is neglected. The results of estimation of β & α is presented in Table 5.

Table 5:Estimation of stacking fault probability of VTe_2 single crystals.

(h k l)	3β + 3α	3β + α	β	α
0 0 1	-	0.0437	0.01067	0.01078
0 0 3	-	0.0419		
1 0 2	0.0454	-		
2 0 2	0.0833	-		

From the Table 5, it can be seen that there is a significant variation shown in the deformation fault probability (α) and growth fault probability (β) may be due to small off-stoichiometry as observed by EDAX. The calculations of the stacking faults may be considered as one of the guide lines for further detailed study of defects and various properties of crystals.

CONCLUSION

The chemical vapour transport technique is more suitable for the growth of large size, good quality single crystals of vanadium ditelluride. Single crystals of VTe_2 were found to grow in form of thin platelets showing a mirror like metallic luster. The EDAX analysis of the as grown crystals shows that stoichiometry is nearly preserved in this crystal. The X-ray diffraction analysis indicated that the grown crystal possesses hexagonal crystal structure (a = b ≠ c). Growth and deformation fault probability are found which shows the layer structure of as grown crystals.

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