International Journal of Physics and Mathematical Sciences ISSN: 2277-2111 (Online)
An Online International Journal Available at http://www.cibtech.org/jpms.htm
2012 Vol. 2 (3) July-September pp.47-51/Dave et al.
Research Article

STRUCTURAL CHARACTERIZATIONS OF NBS_2 SINGLE CRYSTALS

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ABSTRACT
Single crystals of niobium sulphide (NbS_2) having a layered structure were grown by chemical vapour transport technique (CVT) using iodine as transporting agent. The stoichiometry of the grown crystals was confirmed on the basis of energy dispersive analysis by X-ray (EDAX) and the structural characterization was accomplished by X- ray diffraction (XRD) studies. The crystals were found to possess hexagonal crystal structure. The lattice parameters, volume, particle size and X-ray density was carried out for this crystal. The grown crystals were examined under optical zoom microscope for their surface topography study. Hall Effect measurements were carried out on grown crystals at room temperature. The positive value of Hall coefficient implies that this crystal is p-type in nature. The results obtained are discussed in detail.

Key Words: *Crystal growth, semiconductor, EDAX, XRD*

PACS Nos.: *61.50.Nw, 61.10.Nz, 81.40.Tv*

INTRODUCTION
Transition metal dichalcogenides having general formula TX_2, where T is a transition metal and X is either S or Se, have been of considerable interest for the past two decades. They have unusual physical properties and can be intercalated with both Lewis bases and metals. The transition metal dichalcogenides, NbS_2 and $NbSe_2$ are layered compounds consisting of sandwiches with strong covalent/ionic intralayer bonds and weak van der Waals interlayer interactions. The stacking sequence of S and Nb are AcA BcB (2H- NbS_2 structure) or AbA BcB CaC (3R- MoS_2 structure) for $NbSe_2$ several more stacking sequences exist Lieth and Terhaell (1977); Boswell *et al.*, (1976) and Harper (1977). Structure elucidation of the hexagonal platelets yielded crystal structures in the space group $P6_3/mmc$ with NbS_2 layers, separated by intercalated alkali metals. The alkali metal niobium disulphides exhibit many interesting properties such as ionic/electronic conductivity McEwen and Sienko (1982) and superconductivity Gareh *et al.,* (1995); Dunn and Glaunsinger (1988)**.** Niobium disulfide has been synthesized using stoichiometric NbS_2 and has been investigated by X-ray powder diffraction, vapor pressure measurements, thermogravimetric analysis, differential scanning calorimetry and SQUID magnetometry Suzuki and Harima (2005)**.** These materials except 2H-NbS_2 undergo the charge density wave (CDW) transition and then the metallic properties remain in the CDW phase Subba and Shafer (1979)**.** Niobium disulfide (2H-NbS_2) is a material with a layered structure in which niobium atoms are linked covalently to six sulfur atoms in a trigonal prismatic coordination Xingcai *et al.,* (2004)**.**

MATERIALS AND METHODS
Single crystals of NbS2 were grown by a chemical vapour transport technique using iodine as transporting agent. Pure elements (purity 99.99%) of niobium and sulphur (purity 99.9%) in stoichiometric proportions and narrow capillary with I_2 (2 mg/cc) of ampoule volume were sealed in an evacuated (10^{-5} torr) quartz ampoule for compound preparation. The sealed ampoule was introduced into dual zone furnace at a constant reaction temperature to obtain the charge of NbS_2. The charge so prepared was rigorously shaken to ensure proper mixing of the constituents and kept in the furnace again under

appropriate condition to obtain single crystals of NbS_2. The charge composition and growth conditions are summarized in Table 1.

The chemical composition of the as grown crystals was confirmed with the help of energy dispersive analysis by X-ray (EDAX). The stoichiometric proportions of as grown crystals as well as the EDAX results are shown in Table 2.

Close examination of the surface composed of layers helps a great deal in understanding the mechanism by which a crystal grow. Therefore, it was thought worthwhile to make surface characterization of these grown crystals by optical microscopy. The surface microstructures of as grown crystals were examined by computer added optical zoom microscope (Make: Carl Zeiss, Model Axiotech 100HD). The surface microstructure on the face of as grown crystal is shown in Figure 1, which shows layered surface structures. For X-ray diffraction (XRD) work, several small crystals were finely grinded with the help of an agate mortar and filtered through 106-micron sieve to obtain grains of nearly equal size. The X-ray diffractograms were taken with Philips X-ray diffrractometer (model: PW1820) employing CuK_α radiation.

The room temperature resistivity of all crystals was determined using van derr Pauw's technique. The Hall Effect measurements were carried out to determine Hall coefficient, mobility and carrier concentration.

RESULTS AND DISCUSSION

The chemical vapor transport technique was used to grow single crystals of NbS_2 because it yields large single crystals with relative ease. The EDAX studies confirmed that NbS_2 single crystals are stoichiometrycally perfect. The presence of hexagonal spirals on the face of the grown crystals suggests that growth involves a screw dislocation mechanism. The X-ray diffractogram of as grown crystal is shown in Figure 2. The pattern consists of well-defined sharp diffraction peaks, indicating good crystallinity of the specimen.

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

$$\rho = \frac{\sum A}{V N} \qquad \text{...} \; (1)$$

Where $\sum$ A is the total weight of the atoms in the unit cell = MZ

M is the molecular weight and Z is the number of molecules/unit cell,

N is the Avogadro number and V is the volume of the unit cell for the hexagonal system given by

$$\frac{\sqrt{3}}{2} a^2 c \text{ Å}^3 = 0.866\, a^2 c \text{ Å}^3 \qquad \text{..} \; (2)$$

The values of lattice parameters a (Å), b (Å), c (Å), X-ray density ρ and unit cell volume V ($Å^3$) obtained from the diffraction data for as grown crystal of NbS_2 are presented in Table 3.

In order to obtain an idea about the grain size distribution in NbS_2 single crystal, the particle size was calculated using Scherrer's formula given as

$$t = \frac{k \lambda}{\beta_{2\theta} \cos \theta_0} \qquad \text{..} \; (3)$$

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 particles 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_o is the Bragg angle. A Table 4 records the crystallite size of grown crystal.

In the case of hexagonal close packed metals, it is possible to make a realistic estimation of the growth fault probability 'α' and the deformation fault probability 'β' 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

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faults whereas reflections for which h - k = 3n ± 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

$$(3\alpha + 3\beta) = \frac{\beta_{2\theta} \times \pi^2 \times c^2}{360 \times l \times d^2 \times \tan\theta} \quad \ldots\ldots (4)$$

where $\beta_{2\theta}$ is the full width at half the maximum intensity expressed in degrees, c = d_{002}, l is the Miller index in the (h k l) plane for which the estimation of 'α' and 'β' is being made, 'd' is the inter planer spacing for (h k l) reflection in question, θ is the Bragg angle corresponding to this (h k l) plane. The formula for (h k l) values with 'l' odd is given as

$$(3\alpha + \beta) = \frac{\beta_{2\theta} \times \pi^2 \times c^2}{360 \times l \times d^2 \times \tan\theta} \quad \ldots\ldots (5)$$

From the equations 4 and 5, it is clear that by measuring the half width β_θ for reflections with both even and odd values of 'l' it is possible to calculate the stacking fault probabilities α & β. In calculating the half width of the reflections, instrumental broadening is neglected. The results of estimation of α & β are given in Table 5. The Hall coefficient, carrier concentration and mobility of as grown crystals are listed in Table 6. The positive sign of Hall coefficients suggests that all crystals are p-type nature.

Table 1: Growth parameters of NbS_2 single crystal grown using chemical vapors transport technique

Sample	Reaction Temperature	Growth Temperature	Physical Characteristics of the Crystals			
			Growth Time hr	Plate Area mm^2	Thickness mm	Color and Appearance
NbS_2	1083	850	240	6	0.03	Black Shining

Table 2: The EDAX data NbS_2 single crystals

Sample	Stoichiometric Proportion (Wt %)		EDAX Results (Wt %)	
	Nb	S	Nb	S
NbS_2	59.16	40.84	58.11	41.89

Table 3: Structural parameters for NbS_2 single crystals

Sample	a = b (Å)	a = b (Å) Reported	c (Å)	c (Å) Reported	Volume (Å^3)	X-Ray Density (gm/cm^3)
NbS_2	3.33	3.33[11]	17.86	17.86[10]	171.8	3.03

Table 4: The h k l reflections, d- spacing, 2θ Values, Peak Intensity, $\beta_{2\theta}$ value and particle size for NbS_2 single crystals

(h k l)	d-Spacing	Angle 2θ (Degree)	Peak Intensity (cont/sec)	Tip Width $\beta_{2\theta}$	Particle Size (Å)
1 0 1	2.83	31.58	109.27	0.42	425.53
1 0 2	2.73	32.73	101.29	0.42	426.77
1 0 3	2.58	34.62	8.11	0.60	462.52
2 0 4	1.36	68.43	23.95	0.42	762.55

Table 5: Estimation of stacking fault probability of NbS_2 single crystals

(h k l)	$3\alpha + 3\beta$	$3\alpha + \beta$	α	β
1 0 1	-	0.007	0.033	0.499
1 0 2	0.838	-		
1 0 3	-	0.847		
2 0 4	0.729	-		

Table 6: The Hall coefficient, mobility and carrier concentration of NbS_2 single crystal at room Temperature

Sample	Resistivity r (W·cm)	Conductivity s $(W \cdot cm)^{-1}$	Hall Coefficient R_H $(cm^3/coul.)$	Mobility μ (cm^2/Vs)	Carrier Concentration N_c $(cm)^{-3}$
NbS_2	1.18	0.84	553.8	469.3	1.13×10^{16}

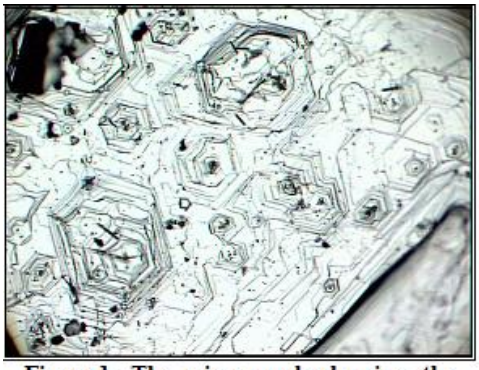

Figure 1: The micrograph showing the presence of growth layers with hexagonal spirals along the flat surface of NbS_2 single crystals.

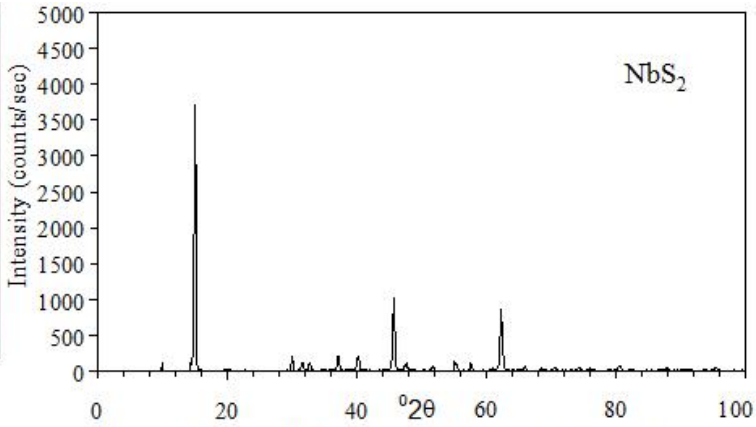

Figure 2: X-ray diffractogram of NbS_2 single crystal

CONCLUSION

- It is possible to grow large size single crystals of NbS_2 by chemical vapour transport technique using iodine as a transporting agent. A single crystal of NbS2 was found to grow in form of thin platelets showing a mirror like metallic luster.
- Growth and deformation fault probability are found which shows the layer structure of as grown crystals.
- From EDAX analysis stoichiometry of as grown crystal of NbS_2 is nearly preserved.
- X-ray diffraction analysis shows that the grown crystal possesses hexagonal structure.
- Surface morphology reveals the layer structure of these crystals.

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