International Journal of Physics and Mathematical Sciences ISSN: 2277-2111 (Online)
An Open Access, Online International Journal Available at http://www.cibtech.org/jpms.htm
2016 Vol. 6 (1) January-March, pp. 11-16/Patel and Lakhataria.
Research Article

SYNTHESIS AND STRUCTURAL ANALYSIS OF $NBSE_2$ SINGLE CRYSTALS

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ABSTRACT
The transition metal dichalcogenides NbS_2 and $NbSe_2$ are layer compounds consisting of sandwiches with strong covalent/ionic intra layer bonds and weak Van der Waals interlayer interactions. The $NbSe_2$ single crystals were grown by chemical vapour transport technique (CVT) using iodine as transporting agent. The chemical compositions of the grown crystals were confirmed with the help of energy dispersive analysis by X-ray (EDAX). The structural properties were studied by X- ray diffraction analysis (XRD). The crystals were found to possess hexagonal crystal structure. The lattice parameters, unit cell volume, grain size and X-ray density were computed for this crystal. The results obtained are discussed in detail.

Keywords: *Crystal Growth, Semiconductor, EDAX, XRD, Lattice Parameters*
PACS Nos.: *61.50.Nw, 61.10.Nz, 81.40.Tv*

INTRODUCTION
The transition metal dichalcogenides, NbS_2 and $NbSe_2$ are layered compounds consisting of sandwiches with strong covalent/ionic intra layer 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 *et al.,* 1977; Boswell *et al.,* 1976; 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 and Dunn and Glaunsinger, 1988).
The superconducting properties of the transition-metal dichalcogenides TaS_2, $TaSe_2$, NbS_2 and $NbSe_2$ have been studied as a function of structural disorder induced by heavy-ion bombardment and by deintercalation at temperatures between 300 K and 800 K (Tsang *et al.,* 1975). The band structure of 2H-NbS_2 the 3s state of sulphur (S) dominate the four bands with lowest energy. These bands are separated by a gap of 5.3 eV from the highest valence bands, which consists mainly of S 3p orbitals (Fang *et al.,* 1995).
The transition metal (V, W, Nb, Mo & Ta) diselenide single crystals were synthesized by chemical vapour transport and direct vapour transport techniques by various researchers (Patel *et al.,* 2012; Patel *et al.,* 2010; Patel *et al.,* 2012 and Mehul Dave *et al.,* 2005). The structural properties of NbS_2 single crystals have been carried. Growth and deformation fault probability were determined by Dave *et al.,* (2012).

Experimental
From literature survey it is observed that Niobium diselenide is important because of its usefulness in various applications like lubricating materials, switching device, electrode for photo electro chemical solar cell etc. The method of chemical vapour transport was found to be suitable for growing large size single crystals of layered chalcogenides.
In this regards authors were used chemical vapour transport technique and iodine was used as transporting agent. For the growth of $NbSe_2$ single crystals the pure elements (purity 99.99%) of niobium and selenium (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. After sealing the loaded ampoule, the powders taken in stoichiometric proportion were thoroughly mixed by vigorous

shaking and the mixture was distributed along the length of the ampoule. The sealed ampoule was introduced horizontally into the furnace.

The temperature was slowly increased to 1073 K. The ampoule was left at this temperature for 72 hours. Then the furnace was shut down and allowed to cool at room temperature. A shining dark powder resulted from the reaction. The charge thus prepared was well mixed up by vigorously shaking the ampoule. The charge was then transferred into another quartz ampoule with iodine as a transporter. The charge along with iodine was kept at one end of the ampoule and the ampoule was kept in the coaxially set furnace as shown in Figure 1.

The furnace temperature in both the zones was increased slowly as was done for the charge preparation to the required final temperature for growth. The optimum growth conditions are presented in Table 1. Figure 2 shows in general the temperature profile maintained along the ampoule after the required period of growth the furnace was cooled down up to room temperature with the rate of 50K/hr.

The ampoule was broken and crystals were found to be grown at the cooler end of the ampoule. The physical properties of as grown crystals are given into the Table 1. The photographs of as grown crystals are shown in Figure 3.

Table 1: Optimum Condition for the Growth $NbSe_2$ Single Crystals and the Physical Parameters of as Grown Crystals

Sample	Reaction Temperature	Growth Temperature	Physical Characteristics of the Crystals			
			Growth Time hr	Plate Area mm^2	Thickness mm	Color & Appearance
$NbSe_2$	1123	1073	192	9	0.05	Silver shining

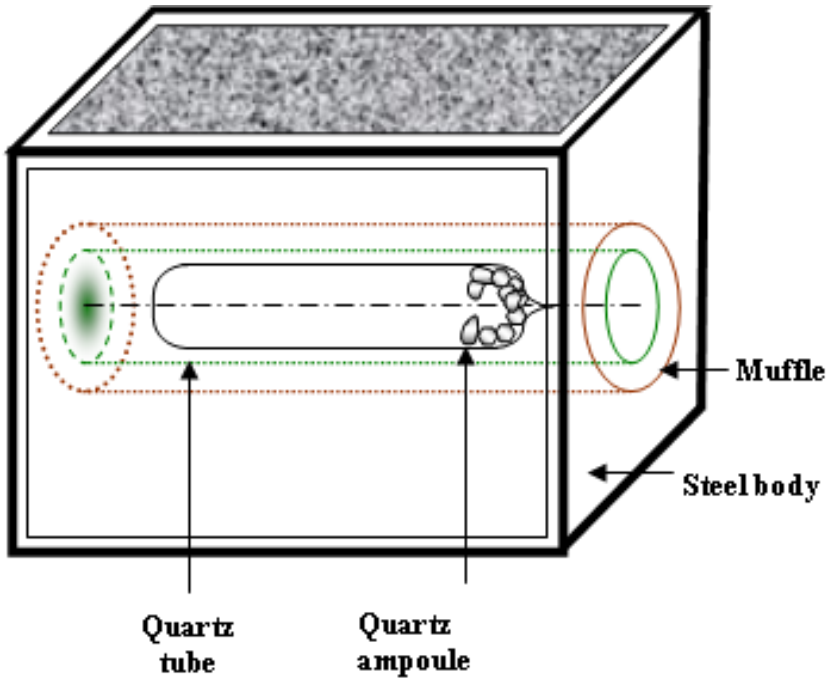

Figure 1: Coaxially Set Ampoule in the Furnace

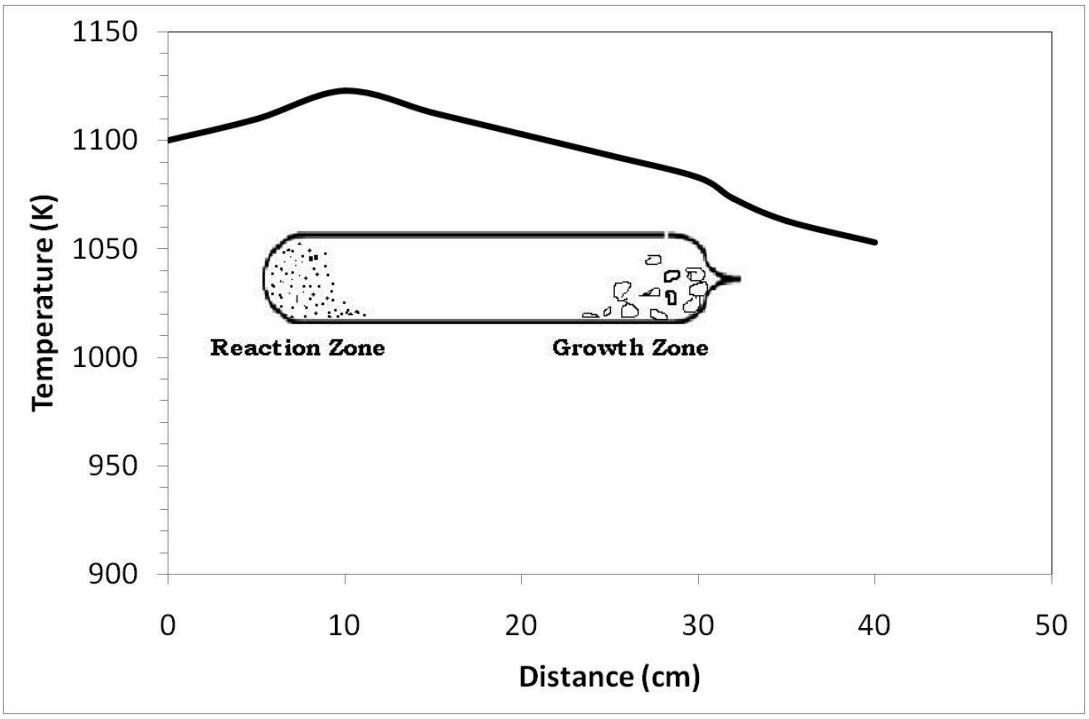

Figure 2: Temperature Profile for the Growth of $NbSe_2$ Single Crystals

Figure 3: The Photograph of as Grown Crystals of $NbSe_2$ Single Crystals

The stoichiometry of the as grown crystals was confirmed on the basis of energy dispersive analysis by X-ray (EDAX). The stoichiometric proportion of as grown crystals and the EDAX results is shown in Table 2. 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.

Table 2: The Stoichiometric Proportion and EDAX Results of $NbSe_2$ Single Crystals

Stoichiometric Proportion (%)		**EDAX Result (%)**	
Nb	**Se**	**Nb**	**Se**
37.04	62.96	37.15	62.85

RESULTS AND DISCUSSION

The chemical vapor transport technique is more suitable for the growth of large size single crystal The EDAX results confirmed that $NbSe_2$ single crystals are stoichiometrycally perfect. The X-ray diffraction pattern of as grown crystal is shown in Figure 4. The pattern consists of well-defined sharp diffraction peaks, indicating good crystallinity of the specimen.

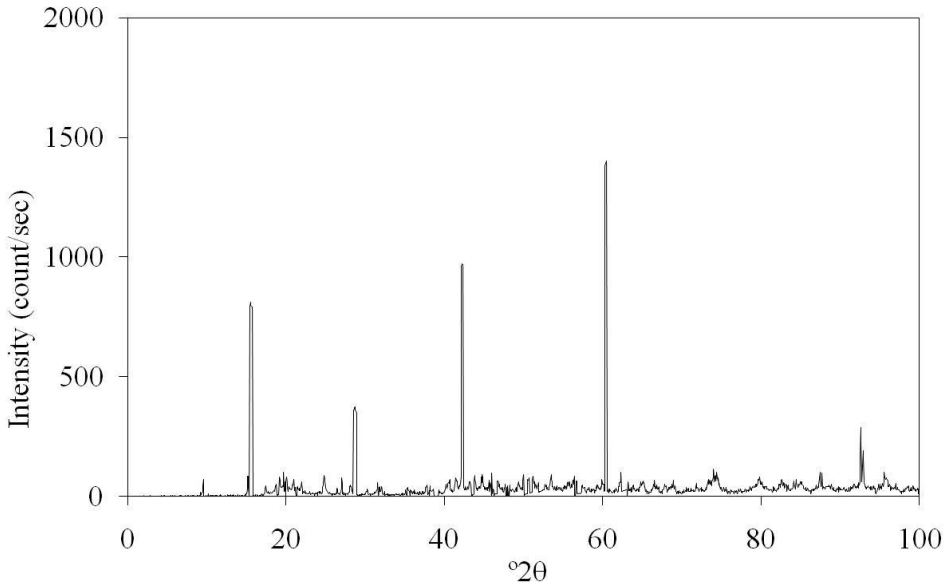

Figure 4: The X-Ray Diffraction Pattern of $NbSe_2$ Crystals

Lattice Parameters

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

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

Where, ∑ 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

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

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 $NbSe_2$ are presented in Table 3.

Table 3 Structural Parameters for $NbSe_2$ Single Crystals

Parameter	Obtained	Reported
a = b (Å)	3.444	3.443 (Murphy *et al.*, 2003)
c (Å)	12.553	12.54 (Murphy *et al.*, 2003)
Volume (Å^3)	129.4	-
X-ray Density (gm/cm^3)	6.43	-

Particle Size Determination

In order to obtain an idea about the grain size distribution in $NbSe_2$ single crystal, the particle size was calculated using Scherrer's formula given as

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

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 wave length 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.

Table 4: The h k l Reflections, d- Spacing, 2θ Values, Peak Intensity, $\beta_{2\theta}$ Value and Particle Size for $NbSe_2$ Single Crystals

(h k l)	d-Spacing	Angle 2θ (Degree)	Peak Intensity (cont/sec)	Tip Width $\beta_{2\theta}$	Particle Size (Å)
1 0 2	2.16	41.78	1540.47	0.18	1009.83
1 0 3	1.72	53.16	377.52	0.15	981.73
2 0 1	1.48	62.70	44.11	0.30	641.57
2 0 2	1.39	67.46	25.79	0.30	767.61

Estimation of Growth and Deformation Fault Probabilities

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 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

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

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

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

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.

Table 5: Estimation of Stacking Fault Probability of NbS_2 Single Crystals

(h k l)	3α + 3β	3α + β	α	β
1 0 3	-	0.036	0.0162	0.0131
2 0 1	-	0.090		
1 0 2	0.055	-		
2 0 2	0.126	-		

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

1. Single crystals of $NbSe_2$ have been grown by the chemical vapour transport technique, they are observed to be larger in size suitable for characterization and transport property measurement studies.
2. The presence of iodine contamination on the surface of single crystals was found which was removed immediately by keeping the crystals in hot air oven at 373 K for few hours.
3. Single crystals of $NbSe_2$ were found to grow in form of thin platelets showing a mirror like metallic luster.
4. From EDAX analysis grown crystal were stoichiometrically perfect.
5. X-ray diffraction analysis shows that the grown crystal possesses hexagonal structure.
6. The lattice parameters are very well matched with the value obtained by earlier workers.
7. Particle sizes for some (h k l) planes of the as grown crystals are found.
8. Growth and deformation fault probability are found, which shows the layer structure defects of as grown crystals.

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