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Growth and characterization of $NbSe_2$ single crystals

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Abstract : Single crystals of niobium diselenide ($NbSe_2$) having a layered structure were grown by chemical vapour transport technique (CVT) using iodine as transporting agent. The energy dispersive analysis by X-ray (EDAX) gives the confirmation about the stoichiometry of the grown single crystal. X-ray diffraction (XRD) studies were performed for the structural characterization. The lattice parameters obtained from the XRD analysis were a = 3.49 ± 0.058 Å and c = 6.28 ± 0.058 Å. The $NbSe_2$ single crystals possess hexagonal crystal structure. The X-ray density was found to be 6.2869 gm/cm^3 and volume was calculated about 66.24 (Å)^3. The resistivity measurements of the grown crystals were carried out within the temperature range of 300 K to 423 K. The crystals were found to exhibit semiconducting nature in this range. The behaviour of the resistance under pressure is thoroughly studied using Bridgman anvil set upto 6.5 GPa. The resistance found decreasing as the pressure increases upto 6.5 GPa. The crystal shows semiconducting behaviour. The implications of the results have been discussed.

Keywords : Transition metal dichalcogenides, X-ray diffraction, Bridgman anvil set up, activation energy

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The work has been centered on the layered transition metal dichalcogenides of group V_B and VI_A. Niobium diselenide ($NbSe_2$) is a member of transition metal dichalcogenide (TMDC) group. Transition metal dichalcogenides (TMDC) have various characters of metal, semiconductor, magnetic substances and have been widely studied [1-3]. Among the TMDC's, $NbSe_2$ have layered crystal structure, which are formed of unit layers consisting of transition metal atoms sandwiched by chalcogen atoms [4]. Single crystals of the transition metal dichalcogenides (TMDC) have been prepared by chemical vapour transport technique using iodine or bromine as transporting agent [5-8]. The epitaxial growth of $NbSe_2$ thin film using the vacuum evaporation technique, has been reported [9]. In materials with a strong pressure dependence of superconductivity (such as $NbSe_2$), the strain-induced interaction affects the structure of the flux lattice. For the field parallel to the c-axis of $NbSe_2$, the flux lattice is locked on the crystal. The possible role of an harmonic elastic interactions of vortices is discussed [10]. The differential resistance in 2H-$NbSe^2$ single crystals at very low currents, have been probed [11]. The layered material $NbSe_2$ is a convenient material for studying the quantum oscillations in the vortex state [12]. A characteristic structure of the local density of the states observed in the layered hexagonal superconductor 2H-$NbSe_2$ by scanning tunneling microscopy (STM) [13]. The anisotropic superconductor 2H-$NbSe_2$ ($T_c \approx$ 7.1K) has attracted a great deal of attention over the last few years [14-20]. The production of $NbSe_2$- nanotubes by electron irradiation was reported [21]. The response of the incommensurate charge density wave modulation in the quasi-low dimensional 2H-$NbSe_2$, has been measured using X-rays scattering [22]. The results of a study of vortex arrangements in the peak effect regime of 2H- $NbSe_2$ by Scanning tunneling microscopy were presented [23].

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Single crystals of $NbSe_2$ were grown by a chemical vapour transport technique using iodine as transporting agent. A 5 gm mixture of Nb (Purity: 99.95 %, Make: Reachim, USSR) and Se(Purity: 99.99 %, Make: Aldrich, USA) was filled in the dried ampoule. Iodine of the quantity 5 mg/cc of the ampoule volume was sealed in the thin capillaries and placed in the ampoule as transporting agent. Then the ampoule was sealed at the pressure of 10^{-5} torr. The sealed ampoule was introduced into a two-zone furnace at a constant reaction temperature to obtain the charge of $NbSe_2$. 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

$NbSe_2$. The charge compositions and growth conditions are summarized in Table 1. The chemical composition of the grown samples has been well confirmed by carrying out EDAX analysis as shown in Table 2.

Table 1. Growth parameters for $NbSe_2$ single crystals 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 hr	Plate area mm^2	Thickness mm	Colour
250	22	1123	1073	240	6	0 03	Shining Black

Table 2. Weight % of elements taken for growth and obtained from EDAX analysis

Wt(%) of elements	$NbSe_2$	
	Nb	Se
Taken	37 04	62.96
From EDAX	34.38	65.62

For X-ray diffraction work, several small crystals were finely ground with the help of an agate mortar and filtered through 106-micron sieve to obtain grains of nearly equal size. X-ray powder patterns were recorded on X-ray Diffractometer (Make: Phillips, Holland and Model: X" Pert) using CuK_α radiation.

To study the effect of pressure on resistance of these single crystals, we used Bridgman opposed anvil set up. In Bridgman opposed-anvil system [24], the decrease in volume and therefore, the maximum pressure are limited by the flow of deformable gaskets in various geometries. The sample is in the form of a thin disk surrounded by pyrophyllite gasket [25] with talcum powder as pressure transmitting medium. A four-probe method is used to evaluate the resistance of the $NbSe_2$ sample up to 6.5 GPa pressure.

The high temperature four-probe resistivity set up manufactured by Scientific Equipments, Roorkee was used to study the variation of resistivity with temperature, in the range of 303 K to 423 K.

The shining black single crystals of $NbSe_2$ were obtained by chemical vapour transport (CVT) technique. The crystal structure of as grown crystal is hexagonal. The values of lattice parameters a, b and c, unit cell volume (V) and X-ray density (ρ) determined from the X-ray diffractograms are presented in Table 3. The X-ray data for $NbSe_2$ was used for the estimation of particle size using Scherrer's formula [26],

Table 3. Crystallographic data of $NbSe_2$ single crystals grown using chemical vapour transport technique.

Parameter	Present work
a =b (Å)	3.49 ± 0.058
c (Å)	6.28 ± 0.058
Unit cell volume (Å)^3	66.24
X-ray density (gm/cm^3)	6.2869

$$t = \frac{K\lambda}{\beta\cos\theta}$$

where t is the crystallite size as measured perpendicular to the reflecting plane, K the Scherrer constant whose value is taken to be unity assuming the particles to be spherical, λ the wave length of X-ray radiation, β the half intensity width measured in radians and θ is the Bragg angle. ($h\ k\ l$) values corresponding to prominent reflections, d-values, peak intensities and particle size for $NbSe_2$ single crystal are shown in Table 4.

Table 4. X-ray diffraction data for $NbSe_2$ single crystal

(h k l)	d-spacing (Å)	Peak intensity (counts /sec)	Particle size (Å)
002	6.4069	6174 55	297.34
004	3 1728	2885 43	303 47
101	2.9150	38.34	306 63
102	2 7127	46 96	307 27
103	2.4429	11.74	310.51
104	2.1722	32.71	314.83

The graph of resistance *vs* pressure for as grown crystals is at room temperature shown in Figure 1. The graph shows continuous decrease in resistance with increase in pressure The graphical variation of log ρ with $1000/T$ is marked in Figure 2. The activation energy was calculated from the slope of this graph and is found to be 0.056 eV.

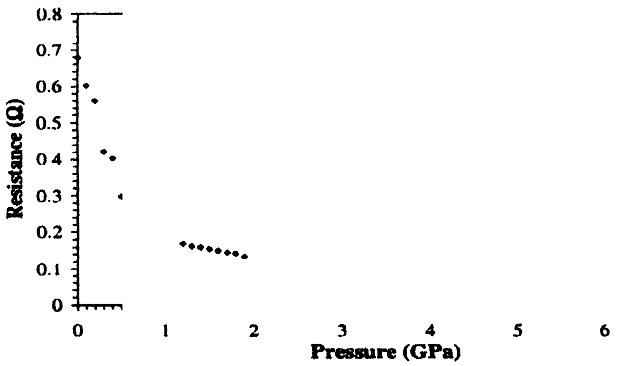

Figure 1. Plot of resistance *vs.* pressure for $NbSe_2$ single crystals at room temperature.

We conclude as follows :

(i) The chemical vapour transport technique has been used to grow the single crystals of $NbSe_2$. The optimum condition for the growth of $NbSe_2$ single crystal has been found out.

(ii) The EDAX and XRD study gives confirmation that $NbSe_2$ single crystals are stoichiometrically perfect and the crystal structure of $NbSe_2$ is hexagonal.

(iii) The resistance decreases as the pressure increases upto 6.5 GPa which shows the semiconducting nature of the as grown crystals. The sample becoming more conducting with increase in pressure.

(iv) The activation energy confirms that $NbSe_2$ behaves as extrinsic semiconductor in the temperature range of 303 K to 423 K.

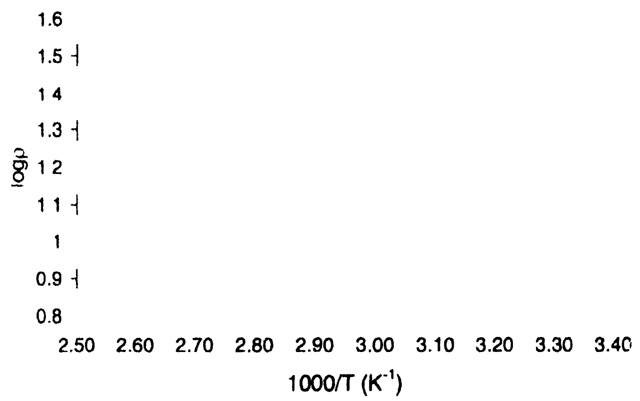

Figure 2. Variation of resistivity with inverse of temperature in the temperature range of 303 K to 423 K for $NbSe_2$ single crystals

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