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Growth, characterizations and highpressure studies of niobium sulphide single crystals

KEYWORDS: Crystal growth, EDAX, XRD, High pressure

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ABSTRACT *Single crystals of niobium sulphide (NbS2) having a layered structure were grown by chemical vapour transport technique (CVT) using iodine as transporting agent. The chemical composition of as grown crystals have been confirmed on the basis of energy dispersive analysis by X-ray. The structural analysis of as grown crystals have been accomplished by X-ray diffraction (XRD) analysis. The lattice parameters obtained from the XRD analysis were a = 3.33 Å & c =17.86 Å. The X-ray density was found to be 3.03 gm/cc and volume was calculated about 171.8 Å3.This crystal is found to possess hexagonal, layered structure. The resistivity measurements of the grown crystals were carried out within the temperature range of temperature 300 K to 423 K. The crystals were found to exhibit semiconducting nature in this temperature range. The behavior of the resistance under pressure is thoroughly studied using Bridgman anvil set-up upto 8 GPa. The nature of resistance found to be decreases with increasing pressure which indicate also semiconducting nature.*

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 [1-3]. 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 [4] and superconductivity [5-6]. 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 [7]. These materials except 2H-NbS_2 undergo the charge density wave (CDW) transition, then the metallic properties remain in the CDW phase [8]. 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 [9].

EXPERIMENTAL

Single crystal of NbS_2 has been 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 grown samples has been well confirmed by carrying out EDAX analysis as shown in Table 2.

The crystals under magnification revealed hexagonal spirals on the growing face as shown in Figure 1. 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 using CuK_a radiation.

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 graphical variation of logr with 1000/T is marked in Figure 2. The activation energy was calculated from the slop of this graph and is found to be 0.056 eV.

The high-pressure electrical resistance measurements were carried out at room temperature upto 8 GPa, using Bridgman opposed anvil apparatus. Pyrophillite and talk were used as materials for gasket and pressure transmitting medium, respectively.

RESULTS AND DISCUSSION

The chemical vapor transport technique has been used to grow single crystals of NbS_2 because it yields large single crystals with relative ease. The presence of hexagonal spirals on the face of the grown crystals suggests that growth involves a screw dislocation mechanism. The EDAX studies confirmed the NbS_2 single crystals are stoichiometrycally perfect. The values of lattice parameters a and c, unit cell volume (V) and X-ray density (ρ) determined from the X-ray diffractograms in Figure 2 are presented in Table 3. Values obtained by Xingcai [10] have also been listed for comparison.

The graph of log $r_{\wedge}$ vs $1000/T$ in Figure 3, shows that the resistivity decreases with the increasing temperature. The

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electrical dc resistivity is a function of pressures. Using Bridgman anvils author achieved pressure maximum upto 8 GPa. As shown in the Figure 4, resistance decreases continuously as pressure increases which shows the semiconducting behaviour of the as grown crystals. With increase in pressure samples becoming more conducting. No phase transition is found in these crystals upto 8 GPa pressure. The electrical resistance of the crystals has been found to be pressure dependent. It decreases with pressure by suggesting the presence of layered structure of the grown crystals.

CONCLUSION

The chemical (iodine) vapour transport (CVT) technique is most suitable for the growth of large size, layered single crystals of NbS_2. The optimum condition for the growth is given. The EDAX analysis of the as grown crystals shows that stoichiometry is nearly presented in these crystals. X-ray diffraction analysis of this crystal possesses hexagonal crystal structure. The lattice parameters are very well matched with the value obtained by earlier researchers. Surface morphology reveals the layer structure of these crystals. Growth Patten shows the hexagonal spirals are also shows the origin of the growth. The resistivity along the basal plane is decrease with increase in the temperature which indicates the semiconducting behavior of the as grown crystals. The resistance decreases with increases pressure upto 8 GPa for NbS_2 single crystals.

Table 1. Growth parameters of NbS_2 single crystal grown using chemical vapour transport technique.

Sample	Reaction temperature	Growth temperature	Physical characteristics of the crystals			
			Growth time hr	Plate area mm^2	Thickness mm	Color & appearance
NbS_2	1083	850	240	6	0.03	black shining

Table 2. The EDAX data for niobium sulphoselenide single crystals

Sample	Stoichiometric proportion (Wt%)		EDAX results (Wt%)	
	Nb	S	Nb	S
NbS_2	58.11	41.89	32.37	67.63

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[11]	171.8	3.03

Table4 The Hall coefficient, mobility and carrier concentration of niobium sulphoselenide single crystal at room temperature

Sample	Resistivity *r* (Ʊ×cm)	Conductivity *s*$(Ʊ\times cm)^{-1}$	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.

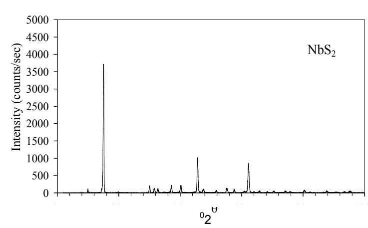

Figure 2 X-ray diffractogram of NbS_2 single crystal

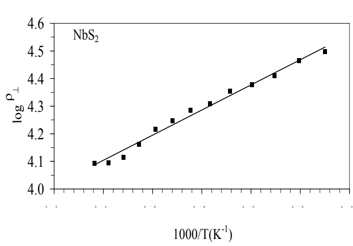

Figure 3 The plot of logr^ vs 1000/T for NbS_2 single crystal.

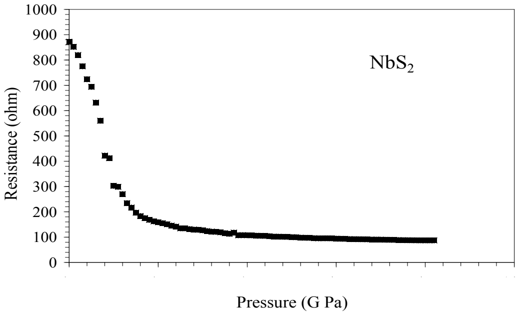

Figure 4 The variation of resistance with increase in pressure for NbS_2 single crystals

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