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Study of chemical vapour transport (CVT) grown $WSe_{1.93}$ single crystals

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A R T I C L E I N F O

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A B S T R A C T

In the present study, the single crystals of $WSe_{1.93}$ were grown by chemical vapour transport (CVT) technique. Iodine was used as transporting agent. The purity and stoichiometry of the as-grown $WSe_{1.93}$ single crystals were determined by energy dispersive analysis of X-ray (EDAX). The structural characterization was done by X-ray diffraction (XRD) technique. The scanning electron microscopy (SEM) of the as-grown single crystal surfaces showed that the crystal growth took place by layer growth mechanism. The thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analysis (DTA) of as-grown $WSe_{1.93}$ single crystal in inert N_2 atmosphere showed two stages decomposition. The thermal parameters like activation energy (E_a), Arrhenius constant (A), enthalpy change (ΔH), the entropy change (ΔS) and the free energy change (Gibbs function) (ΔG) were calculated using Kissinger method. The optical bandgaps were determined from the optical absorption spectrum. The d.c. electrical resistivity measurements in the temperature range of 303–483 K showed that the resistivity value decreases with increase of temperature, in line with semiconducting behavior. The p - type semiconducting nature of the sample was confirmed by Hall effect and thermoelectric power (TEP) measurements. The obtained results are discussed in details.

1. Introduction

Transition metal dichalcogenides (TMDCs) have a general formula, MX_2, where M is a transition metal from IVB, VB and VIB groups (i.e. M=W, Mo, Zr, Nb, …) of periodic table and X is one of the chalcogen (i.e. *S*, Se, Te). These materials are regarded as prototype for two dimensional solids, characterized by two dimensional sandwich units of X-M-X atomic layered along the crystallographic axis [1,2]. These compounds has been used as switching devices, lubricants, electrode in photo-electrochemical (PEC) solar cells, etc [3–5]. They have also been used as a battery cathode in rechargeable secondary cells [6], as selective oxidation and reduction agents [7], as a SQUID detector [1] and as catalyst in reaction such as hydrogenation [8,9]. The literature survey shows that in last few decade, lots of work on photo conversion using WS_xSe_{2-x}[10], WSe_{2-x}, $MoSe_2$ [11], WSe_2 [2,5,9,11–13] materials, transport and optical properties studies of indium intercalated $MoSe_2$ [14] and WSe_2 [15–18] have been studied in details. The physical properties of TMDCs are predominantly sensitive to intrinsic and extrinsic defects. The chalcogen vacancies and dopants gives rise to intrinsic [19,20] and extrinsic [21–23] defects, respectively. In reduced dimensional TMDCs especially in 2D structure studies, tailoring of physical properties by doping has proven to be a challenge, leaving option of compositional variation only [24]. Looking to the literature survey of TMDCs, it appears that very limited amount of work has been carried out on the off stoichiometric crystals of molybdenum/ tungsten selenides. Therefore the authors decided to carry out comprehensive characterization of one of the off stoichiometric TMDC crystals, $WSe_{1.93}$, i.e. x=0.07 from the series of WSe_{2-x} single crystals. Literature reports that WSe_2 single crystals have been grown by different vapour transport techniques, like direct vapour transport (DVT) [19], sublimation [25] and chemical vapour transport (CVT) employing $SeCl_4$ as transporting agent [26]. Here the off stoichiometric $WSe_{1.93}$ single crystals were grown by chemical vapour transport (CVT) technique employing iodine as transporting agent.

2. Experimental details

2.1. Crystal growth

Firstly, the compound of $WSe_{1.93}$ was prepared by taking pure elemental powders of tungsten (99.999%) and selenium (99.999%) (Koch-Light Laboratories Ltd., UK) in off stoichiometric proportion and sealing in an evacuated (~10^{-3} Pa) quartz ampoule. The ampoule was of length 20 cm and inner diameter of 2.2 cm. The vacuum sealed ampoule was thoroughly shaken for mixing of the individual precursor powders. After thorough mixing, the powder was evenly spread all

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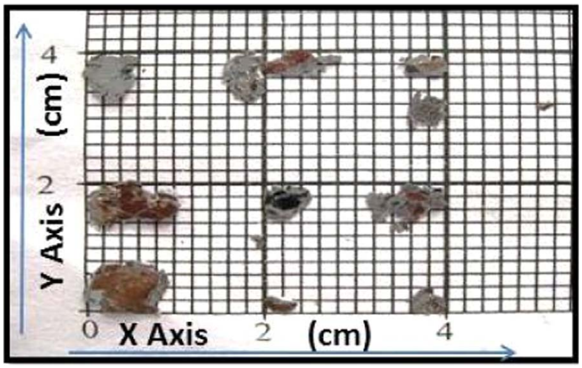

Fig. 1. Photograph of the as-grown $WSe_{1.93}$ single crystals.

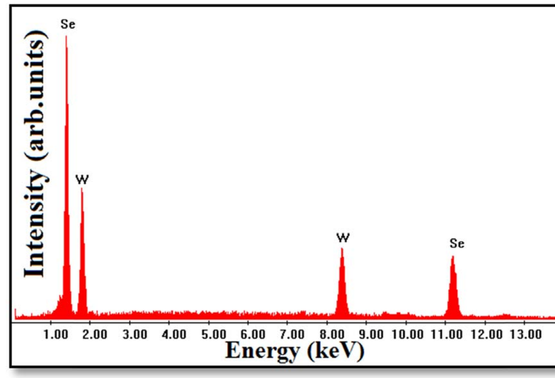

Fig. 2. The EDAX spectrum of the as-grown $WSe_{1.93}$ single crystals.

throughout the length of the ampoule. The ampoule was placed in a two-zone horizontal furnace having a linear temperature of 1073 K along the length of the ampoule. After 72 h, the ampoule was allowed to cool down to room temperature. The synthesized compound was then homogenized by grinding and was identified to be single phase $WSe_{1.93}$ by X-ray diffraction (XRD).

The synthesized compound powder thus prepared was then transferred into another evacuated ($\sim10^{-3}$ Pa) quartz growth ampoule having length of 20 cm and inner diameter of 2.2 cm. along with 4 mg/c.c. iodine transporter. The sealed ampoule was then loaded in a two-zone furnace. The charge powder along with iodine was at one end of the ampoule known as the reaction zone kept at a higher temperature of 1253 K and the other empty end of the ampoule known as growth zone was at a lower temperature of 1183 K. The single crystal growth was performed for a period of 168 h. After the single crystal growth run, the temperature of the ampoule was slowly decreased to room temperature. Slow cooling was done to avoid crack in the as-grown single crystals. The as-grown single crystals were in the form of opaque platelets and shining silver in colour, Fig. 1.

2.2. Characterizations

The stoichiometric composition and surface topography of the as-grown single crystals were studied with the help of energy dispersive analysis of X-ray (EDAX) and scanning electron microscopy (SEM) using the Philips ESEM having 10–20 KeV energy range of the beam, respectively. The crystallographic lattice parameters of the as-grown CVT single crystals were determined by X-ray diffraction (XRD) using a Philips X-ray diffractometer X′Pert-MPD employing CuK_α radiation. The thermogravimetry (TG), differential thermogravimetric (DTG) and differential thermal analysis (DTA) curves were recorded at three different heating rates of 10 K/min, 15 K/min and 20 K/min in inert N_2 atmosphere using Seiko SII-EXSTAR TG/DTA-7200. The optical properties of as-grown $WSe_{1.93}$ single crystals were studied using Perkin Elmer Lambda −19 UV–vis–NIR spectrophotometer in the wavelength range of 200–1500 nm. The four probe d. c. electrical resistivity perpendicular to c-axis in the temperature range 303–483 K was carried out on the four probe setup Model-DFP-02 developed by Scientific Equipment Services (SES), Roorkee, India. The Hall effect measurements at room temperature using van der Pauw method were carried out on the Hall set-up Model-DHE-22 and constant current source Model-DPS175 developed by Scientific Equipment Services (SES), Roorkee, India. The variation of thermoelectric power ‘S′ as a function of temperature in the temperature range of 303–433 K with temperature gradient of 10 K was measured on thermoelectric power measurement setup developed by Supernova Technology, Vithal Udyognagar, Gujarat, India.

3. Results and discussion

3.1. Composition

The chemical composition of as-grown $WSe_{1.93}$ single crystals was determined by EDAX technique for confirming stoichiometry. The obtained spectrum is shown in Fig. 2. The EDAX data of weight % of $WSe_{1.93}$ single crystals along with standard values shown in bracket are; W: 54.62% (54.67%) and Se: 45.38% (45.33%). The data clearly states that the as-grown CVT single crystals have chemical composition of $WSe_{1.93}$ and they are free from any impurity.

3.2. Crystal structure

The XRD of $WSe_{1.93}$ single crystals is shown in Fig. 3. The XRD pattern analysis showed that the crystal possessed hexagonal structure. All the peaks could be indexed and the determined lattice parameters are, a=3.28 Å and c=12.98 Å with space group *P*6$_3$/*mmc*. The determined XRD data are in good agreement with the standard (JCPDS Card No. 38–1388) and reported values [15]. In the XRD spectrum, no evidence of any other phases was detected indicating that the product is of high purity. The XRD pattern clearly shows that (002) reflection is of the maximum intensity and thereby indicates the presence of a well-stacked layered structure [16].

3.3. Microstructure

The surface analysis of as-grown $WSe_{1.93}$ single crystals was done by SEM technique. The SEM analysis gives the mechanism and condition of crystal growth. The commonly visible features seen on the surfaces with low and high magnification are shown in Fig. 4**(a–d)**. The surfaces are flat all throughout the crystal, Fig. 4**(a–c)**, with layer edges and no other features except some small island growth visible. It clearly states that the crystal growth has taken place by layer growth

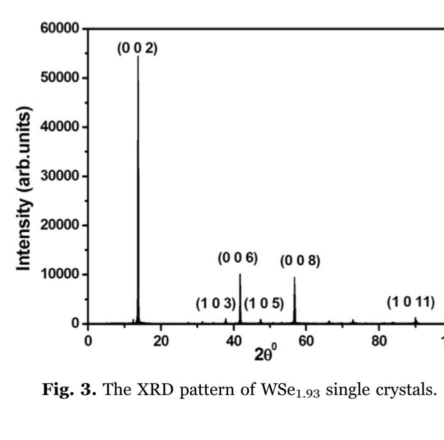

Fig. 3. The XRD pattern of $WSe_{1.93}$ single crystals.

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