Synthesis and characterization of 2D $NbSe_2$

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Abstract: *Two-dimensional van der Waals (vdW) materials possess novel physical properties and promising applications. A wide range of 2D vdW materials having been obtained via the chemical vapor transport (CVT) method. In this work, we develop the controllable growth meyhod of 2H-$NbSe_2$ single crystals via the CVT method. The quality of fabricated crystals was characterized by X-ray diffraction, and electron dispersive spectrometry (EDS) measurements. Crystals of the best quality were successfully grown under selected temperature/time schedule.*
Keywords*: TDMC, CVT (CHEMICAL VAPOR TRANSPORT), NBSE2, SINGLE CRYSTAL, STRUCTURE*

1. Introduction

In recent years, interest in the synthesis and applications of transition metal dichalcogenides MX_2 (M: Mo, W, X = S, Se, Te) nanomaterials has steadily grown because of their unique structure and superior properties [1]. Transition metal dichalcogenides have a sandwich interlayer structure formed by the stacking of the X–M–X layers, which are loosely bound to each other only by van der Waals forces and are easily cleaved. Moreover, MX_2 exhibits unique physical, optical and electrical properties correlated with their layered structure. In addition, their electronic structure is such that band-edge excitation corresponds largely to a metal centered d-d transition. Owing to these features, TMDCs materials have numerous applications such as sensors, detectors, solid lubricants, catalysis, electrocatalysis, high-density batteries and optoelectronic devices [2].

Niobium diselenide ($NbSe_2$) is transition metal dichalcogenide layered compound, and it is exceptionally attractive because of its super conductivity and the formation of a charge-density-wave (CDW) state [3]. 2H-phase niobium diselenide (2H-$NbSe_2$) is a superconducting vdW (Van der Waals) crystal with charge density wave (CDW) and Weyl semimetal properties. It has a superconducting critical temperature of ~7.8K and charge density wave behavior at ~34K. It has layered structure (lamellar) with weak interlayer coupling. $NbSe_2$ displays metallic and superconducting behavior.

2. Experimental details

Chemical vapour transport (CVT), a technique / process where a condensed phase, typically a solid is volatilized in the presence of a gaseous reactant (transport agent) and deposited elsewhere in the form of crystals. Typical transport agents include halogens and halogen compounds. The setup consists of a 2-zone furnace, the reactant and transport agent sealed in an ampoule. The various parameters that must be optimized for a successful CVT are growth temperature, transport direction, rate of the mass transport, choice of the transport agent and the free energy of the reaction.

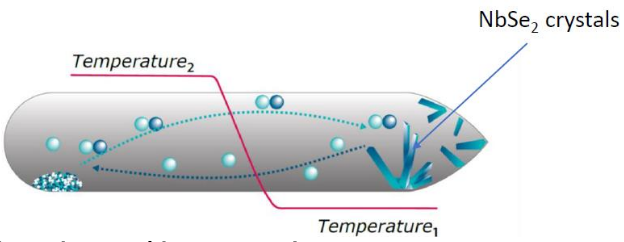

Fig. 1 *Schematic of the experimental setup.*

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 %, Alfa Aeser, Germany) and Se (purity: 99.99 %, Alfa Aeser, Germany) was filled in a dried ampoule. Iodine of the quantity 5-6 mg/cc of the ampoule volume was sealed in the thin capillary 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 constant reaction temperatures 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 experimental conditions for crystals growth are shown in Table 1.

Table 1: *Growth parameters for $NbSe_2$ single crystals using chemical vapor transport technique.*

	Length (mm)	ID (mm)
Ampoule dimensions	300	25
	Hot zone (K)	Cold zone (K)
Temperatures	1123	1053
	Time (hours)	
Growth time	240	

Powder X-ray diffraction (XRD) patterns were gathered within the 2Θ range from 20 to 80° with a constant step 0.02° on a Bruker D8 Advance diffractometer with a Cu Kα radiation and LynxEye detector. Phase identification was performed with the Diffracplus EVA using the ICDD-PDF2 Database.

3. Results and discussions

$NbSe_2$ is Molybdenite-like structured and crystallizes in the hexagonal $P6_3$ /mmc space group. The structure is two-dimensional and consists of two $NbSe_2$ sheets oriented in the (0, 0, 1) direction. Nb^{4+} is bonded to six equivalent Se^{2-} atoms to form distorted edge-sharing $NbSe_6$ pentagonal pyramids. All Nb–Se bond lengths are 2.62 Å. Se^{2-} is bonded in a 3-coordinate geometry to three equivalent Nb^{4+} atoms.

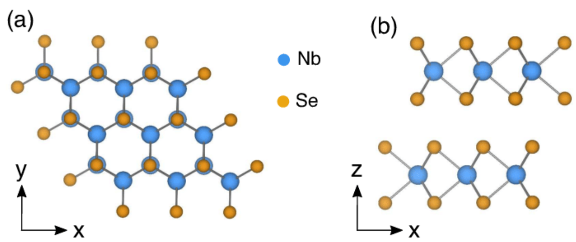

Fig.2 *(a) Crystal structure of bulk $NbSe_2$ illustrating the (a) top view and (b) side view of the structure. The x, y and z axes denote the cartesian axes*

Many methods have been developed to improve the crystalline quality of superconducting $NbSe_2$, for example: (a) exfoliation from bulk single-crystal $NbSe_2$ by the electrochemical exfoliation method [4]; (b) growth by salt-assisted CVD [5]; (c) growth by molecular beam epitaxy (MBE) under ultra-high vacuum [6]; and (d) growth of a wafer-scale $NbSe_2$ film in oxygen-free conditions by a two-step vapor deposition method [7]. However, most of the above preparations of $NbSe_2$ have either a lot of point defects or a small grain size, which reduces its environmental stability or Tc. Therefore, it is still challenging to develop a reliable strategy to grow 2D $NbSe_2$ with a large area, high crystalline quality, and high repeatability.

The CVT single crystals growth was chosen due to the advantages of bulk single crystals as large crystals to measure basic properties: structural, optical, electrical; nearly-perfect state of material: purity, no grain boundaries, less structural defects, stress, etc. The tunability of bulk properties: control of phase stoichiometry, doping level, alloy composition is readily obtained. The layered crystals as $NbSe_2$ are easily of exfoliation and stacking of heterostructures. In the CVT process, metallic niobium (Nb) and selenium (Se) are mixed together with a small amount of a halogen gas in a sealed quartz tube. The mixture is heated to high temperatures, typically between 800-1100°C, causing the halogen gas to vaporize and transport the Se from the hot zone to a cooler region in the tube. The Se reacts with the Nb to form $NbSe_2$, which deposits on a cooler surface in the tube. The halogen gas also plays a crucial role in preventing the formation of impurities and defects in the $NbSe_2$ crystal.

The overall reaction can be written as:

$$Nb + Se + X_2 \text{ (X=Br or I)} \rightarrow NbSe_2 + X_2 \text{ (transport)} \quad (1)$$

The use of halogen gas as a transport agent in CVT synthesis allows for the growth of high-quality, single crystals of NbSe2 with controlled stoichiometry and low defect density.

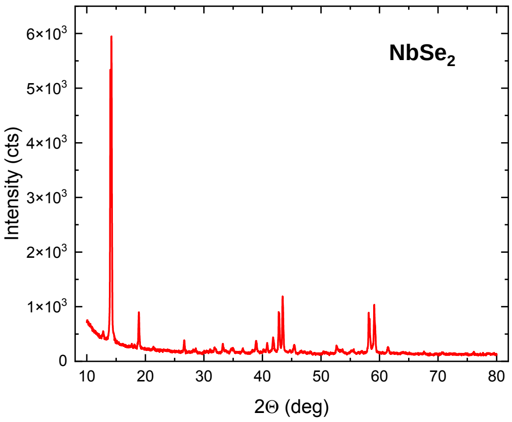

Fig.3 *XRD patterns of $NbSe_2$ single crystal*

The crystallinity, structure, and phase purity of the prepared samples were confirmed by XRD and EDS. As shown in Fig. 1a, all observed diffraction peaks can be exactly indexed to the hexagonal phase of $NbSe_2$ with lattice constants a = 3.445 Å and c = 12.55 Å (PDF No. 65-7464). No characteristic peaks were observed, and the sharp diffraction peaks imply a good crystallinity of the obtained $NbSe_2$ products under current synthesis conditions. The Energy-dispersive X-ray Spectrometry (EDS) result demonstrates that the samples are consisted of elements Nb and Se, while no other elements were observed. Photoluminescence spectra are presented at Fig.4. Broad response around 2.5 eV was observed.

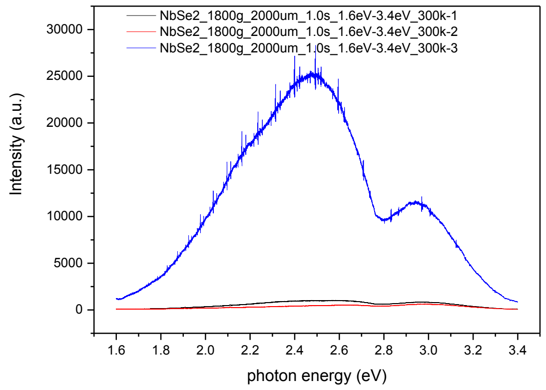

Fig.4 *Photoluminescence spectra of $NbSe_2$*

4. Acknowledgements

We are grateful for the financial support from Bulgarian Science Fund project number КП-06-КОСТ/13 and COST Action CA17123 - Ultrafast opto-magneto-electronics for non-dissipative information technology (MAGNETOFON)

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