

## VAPOR TRANSPORT CRYSTAL GROWTH OF THE TRANSITION METAL DICHALCOGENIDE COMPOUNDS $Nb_{1-x}Ta_xSe_2$

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Techniques are described for growing single crystals of the transition metal dichalcogenide compounds  $Nb_{1-x}Ta_xSe_2$  ( $0 \leq x \leq 0.20$ ). Both iodine and selenium vapor transport have been used. A portion of the phase diagram has been determined, in order to produce the desired 2H polymorph for all compositions of interest. Measurement of the superconducting transition temperature is shown to be a useful tool for diagnosis of the crystal growth process.

### 1. Introduction

The transition metal dichalcogenides (TMDC's) are a class of compounds of interest because of the novel physical properties imparted by their layered crystal structure [1]. This Paper reports the techniques which we have developed for growing high quality crystals of the 2H polymorph of the compounds  $Nb_{1-x}Ta_xSe_2$  over the composition range ( $0 \leq x \leq 0.20$ ). Both iodine and selenium vapor transport have been used. The compounds  $Nb_{1-x}Ta_xSe_2$  are superconducting metals and provide an interesting system for studying anisotropy effects [2] in the upper critical field  $H_{c2}(T)$ .

A number of researchers have investigated the phase diagram of the Nb–Se system [3–5]. However, to produce 2H crystals of the alloy compounds  $Nb_{1-x}Ta_xSe_2$ , it was necessary to determine a portion of the phase diagram. Determination of the polymorph type was done using X-ray powder diffraction and measurement of the superconducting transition temperature. A complication is that in addition to the dichalcogenide phase, trichalcogenides can form in the presence of excess chalcogen, if the crystal growth temperature is too low [3].

The TMDC's can be formed by a direct reac-

tion of the elements. However, the result of this reaction is a powder of small, intergrown crystallites, with crystallite diameters typically less than 100  $\mu\text{m}$ . To produce larger, single crystals the vapor transport technique is the standard method used [6] Iodine is the most commonly used transport agent for growing TMDC crystals [7,8]. A potential problem with iodine vapor transport (IVT) is that a small amount of iodine is incorporated into the crystal structure during growth. Iodine concentrations reported for IVT  $NbSe_2$  vary, but are typically a few hundred parts per million [9–11]. An attractive alternative procedure is to use the chalcogen itself as the transport agent. This is referred to as direct vapor transport (DVT). Published comparisons of  $NbSe_2$  crystals produced by both IVT and DVT methods indicate that DVT crystals are of higher quality [11–13], although high quality TMDC crystals can be grown by the IVT method, at least for some systems [14].

There are a number of published reports of DVT growth of TMDC crystals [11,15,16]. However, in all these published reports, stoichiometric amounts of the elements were used, so it is not clear if crystal growth occurred as the result of sublimation, or by chemical vapor transport promoted by an unintentional excess of chalcogen. Such an unintentional excess can occur if the metal reacts with adsorbed water or oxygen in the growth tube.

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In the Nb<sub>1-x</sub>Ta<sub>x</sub>Se<sub>2</sub> system it appears that true sublimation growth does not occur at the crystal growth temperatures usually used. As a test, several tubes containing prereacted Nb<sub>1-x</sub>Ta<sub>x</sub>Se<sub>2</sub> powder were placed in a tube furnace in a temperature gradient. The end containing the powder was held at 776°C and the cooler end was held at 707°C. After seven days, no transport had occurred. Lewis [17] made a detailed study of DVT growth of NbSe<sub>2</sub>, including the effects of intentionally adding excess Se. Lewis used unreacted Nb and Se as his starting material. He concluded that the DVT crystal growth mechanism was indeed chemical vapor transport involving unreacted Se.

Our DVT technique differs from Lewis's in two important respects. First, we have always used a prereacted, stoichiometric powder of Nb<sub>1-x</sub>Ta<sub>x</sub>Se<sub>2</sub> crystallites as the starting material, with a known quantity of excess Se (or, for IVT, iodine) as the transport agent. Second, in our experiments crystal growth takes place in a temperature gradient which occurs along the length of the growth tube, similar to the method used for IVT. Lewis used a furnace which had a nominally uniform temperature.

This paper will begin with a brief discussion of the techniques used for powder synthesis. Then the vapor transport procedures will be considered. Finally, the phase diagram will be discussed.

## 2. Powder synthesis

All the crystals have been grown using 99.9999% Se pellets and 99.95% Ta powder (Atomergic Chemetals Corp.). Two types of Nb have been used: a 325 mesh powder (Atomergic Chemetals Corp.) and a coarse powder having a grain size of ~ 1 mm ("Specpure", Johnson-Matthey). The finer powder was originally used to ensure a complete reaction. However, as discussed below, it is possible to obtain a complete reaction using the coarser Nb powder. This powder is purer, and has a much smaller surface area per unit mass, which minimizes adsorption of water vapor. (The 325 mesh metal powder will adsorb a measurable amount of water vapor if exposed to the air.)

Powder synthesis is carried out in sealed quartz

tubes (15 cm long, 1 cm ID). These tubes are cleaned by soaking them in a 75%HF–25%HNO<sub>3</sub> solution (for ~ 1 h) followed by several rinses with de-ionized water. Before filling, the tubes are heated to 1000°C for 24 h. This is done to drive off any volatile impurities present in the quartz. It is known that water and other volatile impurities can be given off by quartz at temperatures above 700°C [6,18]. (This cleaning procedure is also used for vapor transport tubes.) The powder synthesis tubes are filled in a dry air atmosphere. The total charge is ~ 5 g. A very slight excess of Se is always included (typically 0.3% of the charge) to ensure stoichiometry in the resulting crystals [19]. For NbSe<sub>2</sub>, it is known that any excess metal present will intercalate into the Van der Waals gap between the layers [3,20]. Excess Se is not incorporated into the dichalcogenide crystal structure, but will condense onto the tube wall as elemental Se when the tubes are finally cooled down (unless triselenides are formed, see below). The tubes are evacuated with a liquid-nitrogen-trapped diffusion pump to typically  $2 \times 10^{-5}$  Torr and sealed.

The powder synthesis tubes are heated in a nominally uniform temperature box furnace. The reaction between the Nb and Ta and the Se occurs at approximately 500°C; this reaction is strongly exothermic [21]. To avoid thermal runaway, the tube temperature is increased slowly over the temperature range 400 to 550°C at a rate of 4°C/h. Then the temperature is turned up to 900°C in 50°C increments. The temperature remains at 900°C for typically 5 days to ensure that the reaction is complete [3,15,21]. Nb and Ta can react with quartz at elevated temperature, and the mobility of the metal atoms can be enhanced by excess Se which acts as a transport agent. The reaction between the metal atoms and the quartz is promoted by the presence of water vapor [6,15]. With proper preparation of the quartz tubes, reaction with the tube is not a problem at 900°C, however, a noticeable reaction can occur at 1000°C. If 2H powder is desired, the reacted powder must be annealed at a lower temperature, as discussed below. Tubes removed from the furnace should contain a free-flowing, sparkling, black powder.

### 3. Vapor transport crystal growth

Vapor transport crystal growth has been carried out using both IVT and selenium vapor transport (DVT). Most of our studies have involved DVT. DVT has the practical advantage that Se is easy to load into the crystal growth tube; Se pellets can simply be dropped into the tube. To add iodine for the IVT process, we have used small, fragile, quartz ampules, which are separately filled with iodine and then evacuated and sealed. One ampule is placed into each crystal growth tube. The ampule is broken open using a magnetically controlled weight after the tube has been evacuated and just before it is sealed. Some iodine is lost through this procedure, but the amount of iodine actually included in the crystal growth tube is not crucial.

The quartz tubes used for vapor transport typically have an ID of 16 mm and a length of 40 cm. The vapor transport tubes are loaded with a 5 g charge of prereacted powder and the transport agent. For both IVT and DVT, we have used  $\sim 5$  mg of transport agent per  $\text{cm}^3$  of tube volume [7]. A four-zone tube furnace is used. Before the tubes are placed in the furnace the entire charge is shaken to one end of the tube. The furnace is initially turned on with a reverse temperature gradient, in order to remove, by vapor transport, any small crystallites stuck to the tube wall in the crystal growth zone [7]. The reverse temperature gradient is applied for 3–4 days, and then the furnace is set to a uniform temperature and the crystal growth gradient is slowly turned on. During this process, the growth-zone temperature is kept as constant as possible, and the temperature of the charge end of the tube is raised at the rate of  $2^\circ\text{C}/\text{h}$  (to prevent polynucleation). The final temperature difference between the charge and growth zones is  $20\text{--}30^\circ\text{C}$ .

Fig. 1 shows a typical furnace profile, used for both IVT and DVT. The region over which the vapor transported crystals are found is shown. The bulk of the transported crystals grow in the region of the tube between the hot end and the point where the temperature is a minimum. We believe this is caused by the sequence of gradual temperature increases used for establishing the final temperature profile. At the cooler end of the tube the

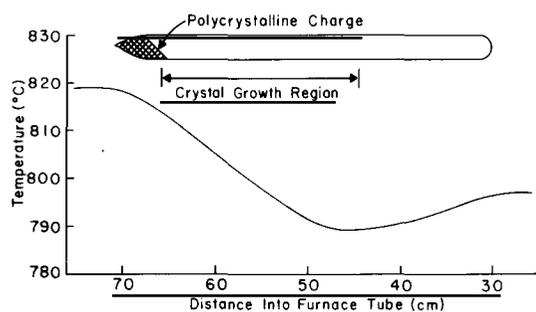


Fig. 1. The temperature profile used for a typical vapor transport experiment, showing the region of the tube over which transported crystals are found.

temperature rises slightly. This has been recommended to prevent nucleation of crystals on the extreme end of the tube [7]. Crystal growth occurs for approximately one week. After this time the furnace is shut off and the furnace-tube endplugs are removed to ensure a rapid cooldown. This is done to preclude the formation of triselenides, which can easily form if excess Se is present and the furnace is left plugged and allowed to cool slowly.

Using the heating schedule described above, a small fraction of the charge will be transported towards the cooler end of the tube, forming crystals with diameters on the order of 1–2 mm. This size is optimum for our superconductivity experiments. Since only a small fraction of the charge is transported, even if Nb and Ta are transported at different rates, the composition of the growing crystals will not change significantly during the growth process.

Measurements of the superconducting transition temperature provide a sensitive and convenient check on the composition and quality of the transported crystals. The transition temperature  $T_c$  of  $Nb_{1-x}Ta_xSe_2$  varies fairly rapidly as a function of composition [2] as shown in fig. 2. The data shown in fig. 2 were determined using bulk measurements of homogeneous powder samples of each composition. Measuring  $T_c$  of individual transported crystals allows us to determine any deviation from the composition of the starting powder. The width of the superconducting transition serves as a measure of crystal quality and uniformity of composition [22].

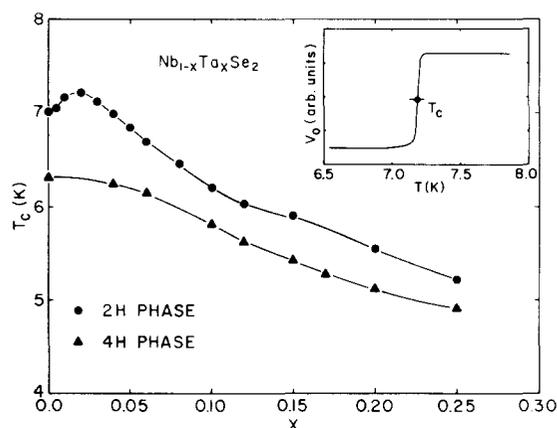


Fig. 2. The transition temperature as a function of composition for the 2H and 4H phases.  $T_c$  is measured using an RF susceptibility technique.  $T_c$  is defined by the midpoint of the observed transition, as shown in the inset.

The range of  $T_c$  values observed in crystals from a typical vapor transport tube corresponds to a composition variation of several tenths of an atomic percent of Ta. The average  $T_c$  of the crystals from a given transport growth tube also displays a slight shift relative to the  $T_c$  of the starting powder, again corresponding to a composition difference of several tenths of an atomic percent. The direction of this shift varies randomly from one growth tube to another. Thus we observe small but measurable differences in stoichiometry between the starting powder and the transported crystals. The  $T_c$  measurements allow us to select high quality crystals with the correct composition.

#### 4. $Nb_{1-x}Ta_xSe_2$ phase diagram: 2H–4H boundary

In order to obtain the desired 2H crystal structure for all compositions of interest, it was necessary to determine a portion of the phase diagram of the  $Nb_{1-x}Ta_xSe_2$  system (for  $0 \leq x \leq 0.20$ ). For  $NbSe_2$ , the 2H polymorph is stable up to  $\sim 900^\circ C$  [5,23]. However, as Ta is added substitutionally, the phase boundary between the low-temperature-stable 2H phase and the higher-temperature-stable 4H polymorph decreases. This behavior is similar to that seen in the  $Nb_{1-x}Ti_xSe_2$  system [24].

The phase diagram was determined using X-ray

and  $T_c$  measurements made on powder samples. (Both the 2H and 4H polymorphs are superconductors.) The powder synthesis tubes used for this work were quenched in air by rapidly removing them from the box furnace. The  $T_c$  measurements have sufficient resolution to detect the transition of a thin hexagonal platelet  $50 \mu m$  in diameter and  $10 \mu m$  thick [25]. The X-ray measurements were made at room temperature with a standard diffractometer, using  $Cu K\alpha$  radiation. 2H crystals tend to form as thin hexagonal platelets. 4H crystals are also hexagonal, but tend to be thicker, and have a faceted appearance. Unfortunately, polymorph identification solely on the basis of optical inspection can be ambiguous, especially for very small crystallites. In addition, optical inspection cannot detect the presence of two phases in a single crystal.  $T_c$  measurements can do this.

Fig. 3 shows the phase boundary between the pure 2H region stable at low temperatures and a mixed 2H–4H region found at higher temperatures as a function of composition. Each point shown results from a separate powder synthesis experiment. In the mixed 2H–4H region, individual crystals may either contain both phases, or may be purely of one polymorph. The phase boundary depends somewhat on the amount of excess Se present, since excess Se stabilizes the 4H polymorph of  $NbSe_2$  [5]. We have not quantified this dependence. The boundary shown in fig. 3 must therefore be interpreted as the phase boundary in the presence of the slight excess of Se used in the powder growth experiments.

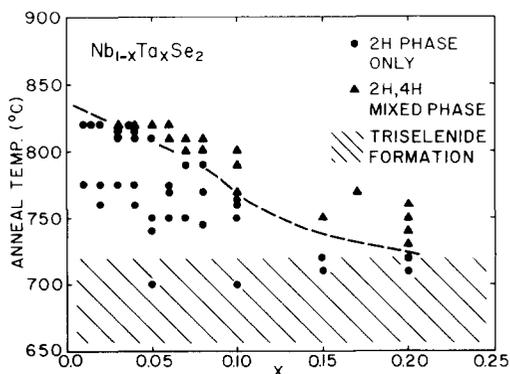


Fig. 3. The portion of the  $Nb_{1-x}Ta_xSe_2$  phase diagram determined in this work.

An important reason for determining the phase boundary is that triselenides can grow at lower temperatures if any excess Se is present.  $Nb_{1-x}Ta_xSe_3$  forms thin, needle-like crystals which can easily be recognized by visual inspection. The triselenides are only stable below a certain temperature. This temperature does not appear to be a function of composition. For the slight excess of Se used in the powder growth experiments, the triselenide phase becomes stable at temperatures  $\sim 720^\circ\text{C}$  and below. The temperature region over which 2H crystals can be grown in an environment containing excess Se is therefore bounded from below by the temperature at which the triselenide phase becomes stable. As shown in fig. 3, it may not be possible to use Se vapor transport to grow 2H crystals of  $Nb_{1-x}Ta_xSe_2$  for all compositions. However, we find that it is possible to grow 2H crystals by Se vapor transport up to at least  $x = 0.20$ .

The only previous information pertaining to the phase diagram of the  $Nb_{1-x}Ta_xSe_2$  system is in the work of Ikebe et al. [26]. They grew  $Nb_{1-x}Ta_xSe_2$  crystals of several compositions at  $750^\circ\text{C}$  using IVT. The polymorphs found by Ikebe et al. are in agreement with the phase diagram shown in fig. 3.

## 5. Conclusions

Techniques have been discussed for growing high quality crystals of the compounds  $Nb_{1-x}Ta_xSe_2$ . It has been shown that selenium can be used, in the same manner as iodine, to produce single crystals by vapor transport. The formation of triselenides at lower temperatures is a limitation on the composition range for which this technique may be used. For the  $Nb_{1-x}Ta_xSe_2$  system, measurements of the superconducting transition temperature provide very useful information for establishing the phase diagram and also provide a sensitive indicator of stoichiometry and crystal quality.

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