Bull. Mater. Sci., Vol. 1, No. 2, October 1979, pp. 107–112, © Printed in India.

Growth and characterisation of TaS_2 single crystals

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MS received 20 July 1979

Abstract. Single crystals of tantalum disulphide have been grown by a sublimation or direct vapour transport method. Crystals as large as $15 \times 10 \times 0{\cdot}05\ mm^3$ grew in the form of platelets and needles above the charge which was kept well distributed within the ampoule. Characterisation of the as-grown cyrstals has been carried out at room temperature by x-ray diffraction. Electrical conductivity and magnetic susceptibility measurements have also been made.

1. Introduction

Tantalum disulphide is one of the members of the family of transition metal dichalcogenides which grow in layer structure. Recently, this compound has acquired importance as its properties depend on its structure. It is semiconductor in the lT-structure and superconducting in the 2H-form and is a mixture of both in the 4H (b)–TaS_2 type. The discovery of intercalation of these compounds with metals and organic molecules has further spurred a great deal of interest in them.

Single crystals of tantalum disulphide are not found in nature and were therefore prepared with iodine as the transporting agent by Brouwer and Jellinek (1974), Revelli and Phillips (1974), Conroy and Pisharody (1972) and by Schafer *et al* (1968) with the aid of sulphur vapour. Revelli and Phillips produced crystals of 2H variety which were grey black in colour. Howe er crystals of 3R variety have not been reported so far. Recently, Di Salvo *et al* (1973) have grown 4H (b)–TaS_2 crystals by using iodine as a transporting agent. Crystals of $4 \times 4 \times 2\ mm^3$ sizes have been reported by these workers.

It also appears that most workers used a transporting agent for growing single crystals of TaS_2. Iodine when used as a transporting agent always contaminates the crystals (Schafer *et al* 1968). Incorporaion of iodine or bromine affects the electrical conductivity due to addition of high concentration of electronic carriers (Gamble and Thomson. This paper reports our attempts to evolve a method of growing the crystals by sublimation method without using any transporting agent.

2. Experimental Procedure

Stoichiometric proportions of the specpure tantalum and sulphur were taken in a transparent quartz tube (internal diameter 22 mm) closed at one end. The tube, evacuated and sealed at the other end, was mechanically stirred for nearly an hour. The mixture was kept well distributed within the ampoule. The ampoule was then placed in a horizontal furnace and heated uniformly at a constant temperature of 800° C for 5 days. It was then cooled to room temperature over a period of 20 hr. This resulted in the growth of perfect single crystals of TaS_2 ($15 \times 10 \times 0 \cdot 05$ mm^3) at the central portion of the ampoule and sporadically distributed over a well-arranged charge.

The experimental conditions and the size of the crystals grown are given in table 1. It may be mentioned that: (i) the size of the crystals once grown at 800° C does not increase if the same tube is kept again at a temperature higher than 800° C. (ii) Under the conditions mentioned in table 1, increase in the period of growth does not affect the crystal size. (iii) No crystals grow if the powder once used is again used for further growth under identical conditions.

3. Characterisation

The x-ray diffraction pattern of the powdered crystals gave d values which agree with the values reported in ASTM data cards. The pyknometer density of the crystals determined at room temperature also agreed with the theoretically calculated value.

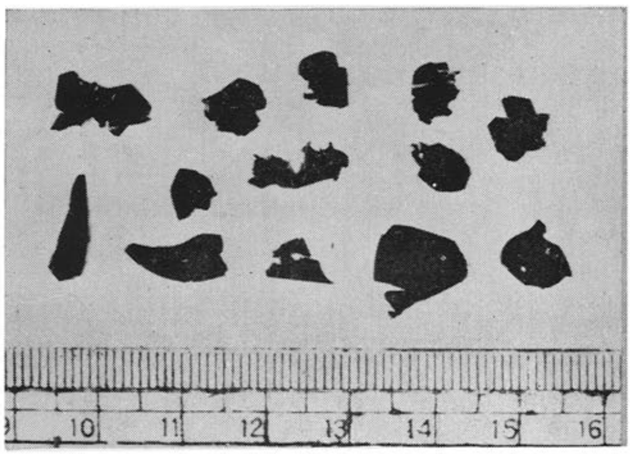
The TaS_2 crystals grown were in the form of thin platelets and ribbons and could be used for taking oscillation photographs. An analysis of the (a-axis 15° oscillation) diffraction pattern indicates the crystal to be 1T type with $a = 3 \cdot 426$ Å and $c = 5 \cdot 927$ Å. The absence of arcing and streaks in the diffraction pattern indicates that the crystals are perfect. The diffraction pattern of the crystals heated to 600° C for 60 min results in the formation of rings thus indicating that heating the single crystal has turned it into a pol crystalline material. This change may be attributed to the oxidation of TaS_2 in air. This was also confirmed when the crystals were heated in vacuum at 10^{-5} torr at 600° C for 1 hr. The pattern of this sample showed no arcing or streaking but in addition to the 1T-spots, faint spots corresponding to 2H-spots were observed. Thus the heating has changed the crystal from 1T structure to a mixture of 1T and 2H structures. Phase transformation in these crystals are now being studied.

Optical examination of the (0001) face of ribbons and platelets showed absence of spirals and indicate that the crystals must have been grown by two-dimensional nucleation. Figure 1 is a photomicrograph of the as-grown (0001) face of the crystals in which the edges of the growth layers are clearly seen.

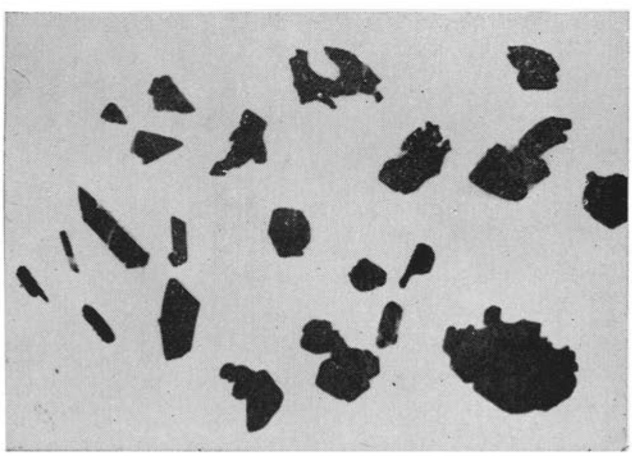
Crystals could be grown in the form of platelets and ribbons of various forms, straight and kinked, narrow and wide, round and straight edged, single or branched (figures 2a and 2b).

The electrical resistivity of the crystals was measured by using the standard four-probe Van-der-Pauw technique. Cold silver contacts were made on the edges of the crystals and were checked for ohmicity prior to resistivity measurements.

(1)



(2a)



(2b)

Figures 1–2. 1. Growth layers on the as-grown face of the crystal. **2 a.** Single crystal of TaS_2, scale in mm. **2 b.** TaS_2 crystals of various shapes.

Table 1. Crystals of TaS_2 grown at 800° C in quartz tube of length 215 mm and internal diameter 22 mm

Sr. No. of ampoule	Temp. °C	Weight (g)		Total weight of Ta and S (g)	Growth duration (days)	Representative size (mm)	Length of the tube (mm)	ID of the tube (mm)	Remarks
		S	Ta						
1.	800	3·8	10·7223	14·5223	7	2 to 3	210	23	Crystals grew more at the top. No change observed when same ampoule kept for further five days with sides reversed. No improvement in the results even at 850° C still for further four days.
2.	800	5·0	14·1083	19·1083	4	5 to 6	210	24	No change in the result seen when same ampoule kept for further four days.
3.	800	5·0	14·1083	19·1083	5	10 to 15	215	22	Very good crystal growth, more at the top and centre of the ampoule. Same ampoule kept for further five days, but no further improvement.
4.	900	5·0	14·1083	19·1083	7	..	210	20	Crystals not grown
5.	1020	5·0	14·1083	19·1083	7	..	220	22	Crystals not grown

Resistivity of several samples of different dimensions when measured at room temperature gave values between $13 \cdot 22 \times 10^{-4}$ and $14 \cdot 55 \times 10^{-4}$ ohm cm.

Magnetic measurements using Gouy balance yielded dimagnetic susceptibility of 0·7471 Böhr magneton which was independent of the field strength.

The electron microprobe analysis confirmed the crystals to be TaS_2 without any impurities within the limits of the sensitivity of the microprobe (<5%).

Acknowledgements

We are grateful to Prof. A R Patel for the valuable discussion and keen interest in the work. One of us (JVP) is indebted to the University Grants Commission for a Fellowship and to the Principal and management of Shree Jayendrapuri Arts and Science College, Broach, for study leave.

References

Brouwer and Jellinek F 1974 *Mater. Res. Bull.* **9** 827
Conroy L E and Pisharody K P 1972 *J. Solid State Chem.* **4** 345
Di Salvo F J, Bagly B G, Voorhoeve J M and Waszczak J V 1973 *J. Phys. Chem. Sol.* **34** 1357
Gamble F R and Thomson A H Private communication
Revelli J F and Phillips W A 1974 *J. Solid State Chem.* **9** 176
Schafer H, Wehmeier F and Trenkel M 1968 *J. Less-Common Met.* **16** 290