PART II

CHAPTER 5

GROWTH AND CHARACTERISATION OF TaS_2 SINGLE CRYSTALS

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5.1 Introduction

Different techniques for synthesises of different types of polytypes of TaS_2 and their importance have already been described in Chapter 1. This chapter deals with the details of the experimental techniques employed for growing the crystals by sublimation method without using any transporting agent and the description of the various growth parameters which yield large single crystals. Characterisation of the as grown crystals using X-ray diffraction techniques as well as magnetic susceptibility measurements using Gouy balance have been carried out and the results obtained are described and discussed.

5.2 Experimental Procedure

Stoichiometric proportions of the spec - pure tantalum and sulphur powders (both from Johnson Mathey Chemicals Ltd., England) were taken in a transparent quartz ampoule closed at one end, cleaned and dried as outlined in the previous chapter. It was evacuated and sealed at the other end, at a pressure of 10^{-5} torr.

The mixture in the ampoule was mechanically stirred for nearly an hour and was well distributed in the ampoule. The ampule was then placed in a horizontal furnace described in chapter 4. The temperatures of the two zones of the furnace were slowly increased (50° C/ 30 min) until it attained a uniform constant temperature of 800° C. Figure 5.1 shows the position of the ampoule and the profile of the temperature in the region in which the ampoule was kept in the furnace.

The ampoule was kept in the constant temperature furnace for 5 days. It was then cooled to the room temperature over a period of 20 hr. This resulted in the growth of perfect single crystals of TaS_2 (15 x 10 x 0.05 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 5.1. It may be mentioned that :

(i) the size of the crystals once grown at 800°C does not increase in the size if the tube is kept again for a longer period at a temperature higher than 800° C.

(ii) under the conditions mentioned in Table 5.1 increase in the period during which the growth takes place does not affect the crystal size.

(iii) the crystals do not grow if the powder once used is used again for growing the crystals in the same conditions.

For growing crystals ampoules of various dimensions were tried. However, the best results were obtained in an ampoule having a length of 215 mm and internal diameter 22 mm.

5.3 Characterisation

The crystals were characterised by X-ray diffraction technique using Debye-Scherrer powder patterns of the crushed crystals obtained with

Table 5.1

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.in °C	Wt.of S in gms.	Wt.of Ta in gms.	Total wt. of Ta and S in gms.	Growth duration in days.	Representative size in mm	Length of the tube in mm	I.D.of the tube in mm.	Remarks
1.	800	3.8	10.7223	14.5223	7	2 to 3	210	23	Crystals grew more at the top. Same ampoule kept for further five days with sides reversed, no change observed. Even at 850°C still for further four days, no improvement in the result.
2.	800	5.0	14.1083	19.1083	4	5 to 6	210	24	Same ampoule when kept for further four days, no change in the result seen.
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.

a Phillips 114.6 mm diameter camera at 25° C. The samples were sealed in 0.2 mm diameter lithium borate glass capillaries (as they have small X-ray absorption) and were exposed to the $K\alpha$ radiation of copper (λ = 1.5418 Å) for five to six hours. The representative diffraction pattern obtained is shown in Fig. 5.2. The calculated d values together with the standard ones are given in Table 5.2. The values of 'a' and 'c' parameters calculated from the data with the help of IBM 1620 computer were a = 3.426 Å and c = 5.927 Å. These values agree with those reported in ASTM data cards.

The X-ray density, ρ was calculated using the following formula

$$\rho = 1.66020 \sum \frac{Z}{V} n$$

where Z = atomic wt.
n = number of stacking layers per unit cell,
and V = volume of the unit cell.

Now the volume of the hexagonal unit cell is given by

$$V = 0.866 \ a^2 c$$

where a and c are lattice parameters.

Table 5.2

I_{ASTM}	d_{ASTM} A°	$d_{cal.}$ A°	$I_{observed}$
100	6.01	6.067	VVS
80	2.96	2.963	W
60	2.63	2.636	VW
60	2.092	2.059	M
80	1.978	1.973	S
20	1.693	1.689	VVW
70	1.637	1.624	M
20	1.426	1.446	VW
60	1.319	1.312	W
40	1.285	1.273	M
60	1.182	1.189	S
10	1.177	1.167	VVW
80	1.096	1.089	W
50	1.009	1.013	W
40	0.967	0.968	M
100	0.933	0.935	M
60	0.919	0.916	W
50	0.884	0.866	W
40	0.850	0.852	W
20	0.809	0.809	M

Thus substituting the values of 'a' and 'c' obtained above, the X-ray density ρ becomes

$$\rho = 6.754 \text{ gm/cc.}$$

This value is in good agreement with the pyknometer density determined at room temperature.

To compare the observed intensities of the different lines in the diffraction pattern, with those given in ASTM data cards, the X-ray reflections on the photograph were divided into different grades. The line with the highest observed intensity, was graded as very very strong (VVS). Several such other grades were made such as very strong (VS), strong (S), medium (M), weak (W), very weak (VW), very very weak (VVW). The relative intensities observed for different lines are given in Table 5.2.

The crystals grown were in the form of platelets and ribbons of various forms, straight and kinked, narrow and wide, round and straight edged, single and branched (Figs. 5.3 and 5.4).

The electron microprobe analysis confirmed the crystals to be TaS_2 without any impurities within the limits of the sensitivity of

the microprobe.

Optical examination of the (0001) faces of ribbons and platelets of the as grown crystals has been carried out and described in the next chapter.

The various properties studied for characterisation of TaS_2 single crystals are represented in Table 5.3. The details of these studies are explained and discussed at the relevant places in different chapters of this thesis.

5.4 Magnetic Susceptibility Measurements

There are two commonly used methods of measuring magnetic susceptibilities :

(i) Gouy method

(ii) Faraday method

In the Gouy method, the force integrated over a large field gradient is measured, whereas in the Faraday method, the force on a very small specimen is measured directly.

5.4.1 Gouy method

For the experimental purpose of magnetic susceptibility measurements Gouy method was employed. The Gouy method[1-3] consists essentially of suspending

Table 5.3

Sr. No.	Properties studied	TaS_2 single crystals
1.	maximum size obtained	15 x 10 x 0.05 mm^3
2.	colour	pale yellow
3.	luster	highly shining metallic
4.	faces developed	(0001)
5.	unit cell dimensions	a = b = 3.426 Å c = 5.927 Å
6.	X-ray density	6.754 gm. ml^{-1}
7.	Pyknometer density	6.748 gm. ml^{-1}
8.	cleavage planes	(0001)
9.	estimated dislocation density	1.869 x 10^6 cm^{-1}
10.	magnetic susceptibility	0.7471 Bohr Magneton
11.	electrical resistivity	13.88 x 10^{-4} Ω cm.
12.	polytypes	1T (Ramsden notation)

a cylindrical sample of a substance in a nonhomogeneous magnetic field with the lower end in the region of maximum field and the upper end in a region of effectively zero field and measurement of the force acting on the sample is obtained by the conventional weighing technique.

The Gouy set up should be calibrated[3-7] in terms of a substance of known susceptibility. The required properties for a calibrant are,

(i) readily available purity,

(ii) an accurately known and moderate susceptibility ($\chi_g \approx 10^{-5}$),

(iii) stability in moist air,

(iv) χ_g must vary in a known and simple way, at least at room temperature, and

(v) easily and reproducibly packable into the Gouy tube.

Many substances have been used for this purpose. Some of them are distilled water, benzene, aqueous nickel chloride solution, copper sulphate, etc.

The magnetic susceptibility measurements in the present work, were made at room temperature using a Gouy balance (sartorius, semi-micron).

For experimental purposes TaS_2 single crystals were finely ground to give fairly small, roughly uniform particles and were carefully packed into a pyrex Gouy tube, introducing a small quantity at a time and tapping it down after each addition; this procedure was repeated until the sample filled the tube upto a fixed mark. The tube was then suspended in such a way that its bottom remained at the centre of the gap between the pole faces of the electromagnet. It was then weighed with and without application of the magnetic field and the difference in the weight of tube (ΔW) containing W gm. of sample was determined. The volume of the sample in the tube was determined in order to apply correction due to air displaced by the sample. The Gouy set-up was calibrated using water (χ_g = -0.02 x 10^{-6} c.g.s. units) and mercury tetrathocyanato cobaltate, $[HgCo(CNS)_4]$, (χ_g = 16.44 x 10^{-6} c.g.s. units at 20° C and 0.05 x 10^{-6} c.g.s. units decrease per °C rise)[5] as the standards. The Gouy tube constant, β was checked by calculating μ_{eff} of highly pure copper sulphate. The difference in the weight of the empty tube, (δ), was also determined at the same field strength. The gram susceptibility or specific

susceptibility was calculated using the expression

$$10^6 \cdot \chi = \frac{\alpha + \beta \cdot dW}{W}$$

where α = correction due to displaced air,
= + 0.029 x 10^{-6} c.g.s. units x volume of air

β = Gouy tube constant

dW = $\Delta W - \delta$, here ΔW is apparent change in weight (in mg) of the tube containing W grams of the sample on application of the field and δ is difference in the weight of the empty tube on application of the field

W = weight of the sample in grams.

In order to minimize errors due to packing of the solid into the tube the observation with each sample was repeated three to four times, each time with fresh packing and average change in weight was considered.

The gram susceptibility was multiplied by the molecular weight to obtain the molar susceptibility.

χ_m. A correction was applied for diamagnetism of of the ligands and anions using Pascal's constant[8-10] to give corrected molar susceptibility, χ'_m. The effective magnetic moment, μ_{eff}, was then calculated from the expression,

$$\mu_{eff} = 2.84 \, (\chi'_m \times T)^{1/2}$$

T is absolute temperature (^{o}K).

In the case of TaS_2 single crystals, the susceptibilites obtained at room temperature, by this method are represented in Table 5.4, however it may be mentioned that the value of χ_g (specific susceptibility) determined at 4 ampere and 6 ampere current was 0.9356×10^{-6} and 0.9272×10^{-6} e.m.u. resply. suggesting thereby that χ_g is almost independent of the current used.

Table 5.4

Magnetic susceptibility measurements

1.	Specific susceptibility χ_g	0.9356×10^{-6} e.m.u.
2.	Molar susceptibility χ_m	229.2×10^{-6} e.m.u.
3.	$\mu_{effective}$	0.7471 Bohr Magneton

5.5 Conclusions

TaS_2 single crystals grown by direct vapour transport method, without using transporting agent are of the maximum size 15 x 10 x 0.05 mm^3. The 'a' and 'c' parameters determined by X-ray diffraction technique are 3.426 Å and 5.927 Å respectively. X-ray density as calculated from the X-ray data comes out to be 6.754 gm. ml^{-1} which shows a close resemblence with that determined by pyknometer method. Magnetic susceptibility as estimated for these crystals is 0.7471 Bohr Magneton.

5.6 References

1. French, C. M., and Harrisen, D.
   J. Chem. Soc. (1953) 2538.

2. Hilal, O. M. and Fredericks, G. E.
   J. Chem. Soc. (1954) 785.

3. (a) Figgis, B. N. and Nyholm, R.S.
   J. Chem. Soc. (1959) 331.

   (b) Idem, Ibid, (1958) 4190.

4. Curtis, N. F.
   J. Chem. Soc. (1961) 3147.

5. Selwood, P. W.
"Magnetochemistry", Interscience, New York,
Edn. second (1956) 3-31.

6. Eranshaw, A.
"Introduction to Magnetochemistry"
Acad. Press, New York, (1968) 84-86.

7. Mulay, L. N.
"Magnetic Susceptibility"
John Wiley and Sons, Interscience,
New York, (1963).

8. Kortum, G. and Kortum, Seiler
K. Naturforsch. 2a (1947) 652.

9. Kortum, G. and H., Scholtler
Z. Electrochem. 57 (1953) 357.

10. Griffiths, T. R., Lott, K. A. K. and
Symons, M.C.R.
Anal. Chem. 31 (1959) 1338.

Captions of the figures

Figure 5.1 Schematic view of the furnace showing the position of the ampoule inside the two-zone furnace during crystal growth.

Figure 5.2 X-ray powder diffraction pattern of TaS_2.

Figure 5.3 Single crystals of TaS_2, scale in mm.

Figure 5.4 TaS_2 crystals of various shapes.

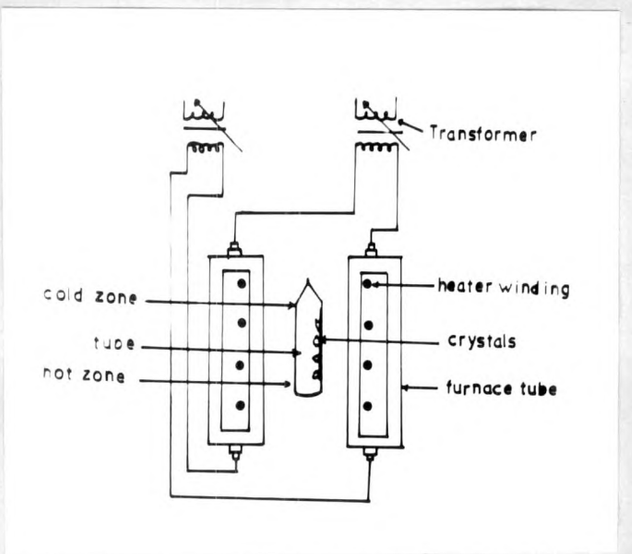
Transformer
heater winding
cold zone
crystals
tube
furnace tube
hot zone

Fig. 5.1

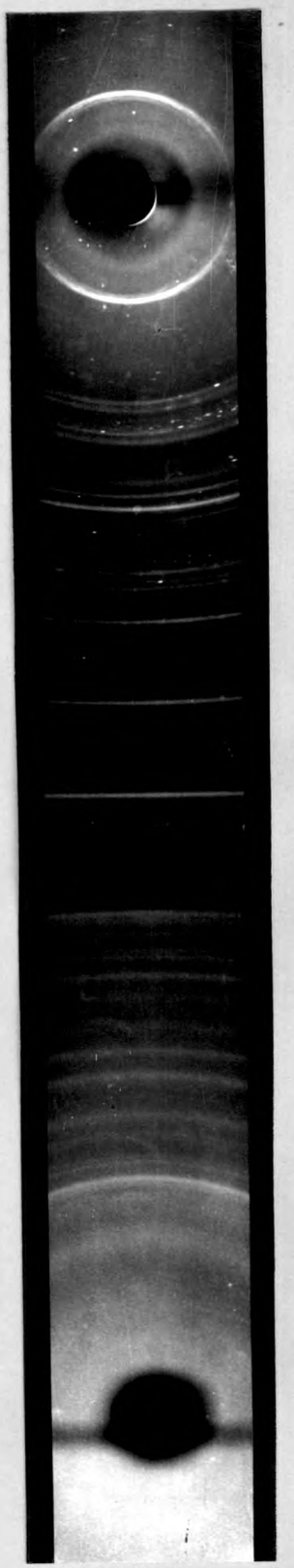

Fig. 5.2

Fig. 5.3

Fig. 5.4