PREFACE

It is a group of transition metal dichalcogenides which has currently attracted many research workers, on account of the interesting properties of the compounds of this family. Their marked anisotropy in many physical properties led to an intensive investigation in the field of solid state research. The experimental development of successfully growing perfect single crystals in laboratories of most of these compounds opened the doors to careful examination of their extremely fascinating properties. Many of these compounds possess layered structures. At the juncture of the rapid scientific and technical development of the modern age, these compounds have gained unique importance, particularly for their potential applications in the area of semiconductors, superconductors, photo-electrochemical cells, solid lubricants, optical windows, etc.

In these layered compounds the bonding within a layer is strong, while the interlayer forces are weaker. This leads to the remarkable cleavage perpendicular to their axis of symmetry making such materials anisotropic both mechanically and electrically. This enables one to introduce metal atoms or molecules of organic compounds into Van der Waal's gap between the layers. In general, the compounds of this group can be represented by the formula of the type MX_2 where M is one of the transition metals from group IV B, V B or VI B of the periodic table and X is any one of the chalcogens, sulphur, selenium or tellurium. The structure and the physical properties of this broad group of materials have been reviewed by Wilson and Yoffe.

Among the different transition metal dichalcogenides, tantalum disulphide has aroused much interest on account of its striking properties observed in different forms : from semiconducting in the 1T-structure and superconducting in the 2H-form to a mixture of both in 4H(b) - TaS_2 type. They often individually show transitions as a function of temperature, pressure or doping.

Literature reveals that so far the transition metal dichalcogenide crystals have been grown by using transporting agents, such as bromine or iodine. The crystals thus grown are likely to suffer from the contamination of the transporting agent and thus adversely affect some of their interesting properties. It was therefore considered worthwhile to attempt to grow single crystals of TaS_2 without using transporting agent and then investigate their properties. The experimental work thus carried out and the studies made on the crystals grown are presented here in the form of a thesis.

The thesis has been divided into three parts. Chapter 1 of the part I deals with the survey of the literature and the existing information of TaS_2. The experimental techniques employed are briefly described in Chapter 2. A brief review of growth and dissolution of different crystals is given in

Chapter 3. In the beginning of the chapter 4 the essential features of a chemical vapour transport method are described while the later part of it deals with a brief account of a direct vapour transport technique.

In chapter 5 of part II a direct vapour transport technique and the sublimation method, avoiding contamination of the grown crystals by the transporting agent, established in this department has been described. By this method crystals as large as $15 \times 10 \times 0.05\ mm^3$ have been grown successfully. The crystals have been characterised by X-ray diffraction technique and their magnetic susceptibility has been determined by Gouy balance.

Chapter 6 deals with the studies made on the microstructures on different faces of the crystals by using optical microscopy and an attempt is made to explain the growth by two dimensional layer mechanism.

A reliable dislocation etchant and the morphology of etch pits are reported in chapter 7. The effect of etching time, etchant concentration and temperature on the selective etch rate have also been studied and described. The activation energy determined gives an indication that the etching in chromic acid is a diffusion control. The relation for the dependence of etch rate, activation energy and pre-exponential factor on the etchant concentration is established. Polytypism in TaS_2, the arcing phenomena observed in the a-axis X-ray oscillation photographs are explained in Chapter 8. An estimation of dislocation density has been made from these photographs.

In Chapter 9, electrical and thermoelectrical properties of TaS_2 single crystals are described. The temperature dependence of resistivity and Seebeck co-efficient are also studied.

Part III deals with TEM studies of TaS_2 crystals. The general theory is described in Chapter 10. It is observed that the dark field electron micrographs taken in weak diffracted beams significantly improve the structure of the lattice defects. In this case the dislocations appear as very narrow bright lines against low intensity background. TEM study of the crystals using weak beam microscopy is given in chapter 11.

The observations of the extended and contracted nodes described in Chapter 11 make it possible to estimate quantitatively the ratio (γ/μ)

which is proportional to the stacking fault energy γ. γ/μ is calculated using the separation of the partials of an edge dislocation and is presented in chapter 12.

The presence of hohlstellens, loops, crystallites and zone-axis patterns are observed, their types and the details of a possible cause of their formation are given in Chapter 13.

The phase transformations as studied by electron diffraction at different temperatures are discussed and described fully in chapter 14. Variation of lattice parameter 'a' with temperature, in $2H\text{-}TaS_2$ has been studied and the defect formation energy determined is reported in Chapter 15.

Review of the present work and the scope for the future work are given at the end of the thesis.