OPTICAL, INFRARED AND LASER RAMAN STUDIES IN HEXAGONAL LAYER SEMICONDUCTING COMPOUNDS

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By

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PREFACE

The MX_2 (X = S, Se or Te) layer materials characterized by their high degree of anisotropy form a structurally and chemically well defined family known as dichalcogenides. Electrically however, they cover a wide spectrum of properties, from an insulator like HfS_2, through semiconductors like MoS_2 and semimetals like WTe_2 to true metals like NbS_2. During the past few years a wide spread interest in the structural, optical, electrical, magnetic and superconducting properties of these layer compounds has evolved as is evident from the recent literature survey. We concentrate here on four semiconducting compounds, three of which (MoS_2, $MoSe_2$ and $MoTe_2$) belong to group VI, whereas the fourth one ($SnSe_2$) is a IV-VI compound. These compounds have very weak interlayer van der Waal's binding and therefore found to be very useful as solid lubricants.[1,2] This interlayer gap can be increased to accept alkali metal atoms or ions.[3-5] Recently, in $SnSe_2$ a notable polarity dependent memory switching has been observed.[6] These further increased the interest of scientists in these materials. Although structure and semiconducting properties of these materials are known to some extent, there is a very little knowledge about their optical behaviour. The published work in electronic region is mainly concentrated on MoS_2[7-12] possibly because of its availability in nature. In case of $MoSe_2$ and $MoTe_2$ only a few papers are available at present. The data of $SnSe_2$ as reported by various workers[13-16] are very divergent in nature. The observation of lattice vibrations of any of these layer compounds have not been reported until the

work on natural MoS_2 was published.[17] No work has so far been done on infrared and Raman studies of $MoSe_2$, $MoTe_2$ and $SnSe_2$ crystals.

In the present investigation single crystals of MoS_2, $MoSe_2$, $MoTe_2$ and $SnSe_2$ were grown in our laboratory, the structures of these crystals were established and their electronic and vibrational spectra were extensively studied. The reported work has been divided in six chapters.

In Chapter I basic concepts and theories of optical infrared and Raman spectra are discussed in brief. Methods used in the thesis for calculating optical constants from the observed spectra are also explained

Chapter II deals with the experimental methods. Good large single crystals have been grown by using vapour phase transport technique with and without a transport agent. For MoX_2, bromine and for $SnSe_2$, iodine were the suitable transporters. The crystal structures are analysed using optical microscopy, X-ray analysis and electron microscopy. Most of the crystals were identified as 2H-polytypes. However, effect of various growth parameters has not been studied in detail because the main aim was to get good quality large single crystals rather than to establish the growth mechanism. Experimental techniques involved in cleaving thin crystals, measuring their thickness and in recording their optical (visible and near infrared), infrared (down to 50 μm) and He-Ne gas laser excited Raman

spectra are discussed in this chapter. A brief description of spectrophotometers used is also included. Since all the crystals were in the form of thin sheets, no measurements were possible for $\bar{E} \| \bar{C}$ orientation.

Chapter III describes the crystal structure and the symmetry of single crystals in detail. Group theoretical analysis of the Γ point lattice modes is applied to two space groups D_{6h} and D_{3d} of our interest.

Chapter IV gives our results on optical spectra in visible and near infrared regions. The work is mainly concentrated on transmission measurements on these compounds. The optical constants are calculated from transmission data and compared with the published results. The behaviour of exciton bands in $MoSe_2$ and $MoTe_2$ is found to be similar to that already reported in case of natural MoS_2. In $SnSe_2$ a detailed analysis of the shape of intrinsic absorption edge has been performed and the types of transitions responsible for it are identified. The existence of allowed direct transitions across an energy gap of 2.1 ev and forbidden indirect transition across an energy gap of 0.98 ev is established. However, the existence of two forbidden indirect transition energy gaps[13] is not found. Further, no existence of forbidden direct transitions as reported earlier[14] could be found. The wide differences among results of various workers on refractive index of $SnSe_2$ are thought mainly due to an inaccurate assignment of order number to an interference fringe.

Chapter V gives our results of infrared ($\ll 50\ \mu$m) studies of molybdenum dichalcogenides. To-date only the 'reflectivity' measurements in Reststrahlen region on single crystals of natural MoS_2[18] and on pressed pellets of MoS_2 and $MoSe_2$[19] are reported. We studied the infrared 'absorption' of single crystals of MoS_2, $MoSe_2$ and $MoTe_2$. The infrared absorption of their KBr pellets and reflection of pressed pellets of these compounds are also studied. The fundamental absorption bands of single crystals of MoS_2 and $MoSe_2$ are fitted to a damped classical oscillator model and the various parameters of oscillator are estimated. Besides fundamental, the infrared spectra of MoS_2, $MoSe_2$ and $MoTe_2$ showed a number of multiphonon absorption bands. In $MoSe_2$ an impurity band is also observed and attributed to oxygen impurity in the crystal. The index of refraction of MoX_2 (X = S or Se) in Reststrahlen region is determined from interference fringes and fitted to a theoretical curve of oscillator model.

Chapter VI gives our results of laser excited Raman studies of MoX_2 (X = S, Se or Te) and $SnSe_2$. In each case all the Raman active modes as predicted by theory have been identified. To-date Raman spectrum of MoS_2 is only available.[18] On comparing our infrared and Raman results we find a mode degeneracy in MoS_2 as well as in $MoSe_2$ and $MoTe_2$. $SnSe_2$ data however, show its absence as was expected from the difference between the two structures. Few elementary theoretical calculations of lattice vibrations of MoS_2 family are now available.[20,21] A comparison between theory and experiment is therefore made and some of force constants are evaluated.

The publications resulting from the above investigation are listed below.

1. Laser Excited Raman Spectra of Gr. VI Semiconducting Compounds.

   Solid State Communication, 12, 135 (1973).

2. Infrared Optical Properties of $MoSe_2$.

   Solid State Communication, 12, 1261 (1973).

3. Laser Raman Spectrum of $SnSe_2$.*

   (Communicated).

4. Optical Constants of $SnSe_2$.*

   (Communicated).

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CHAPTER II EXPERIMENTAL TECHNIQUES

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