CHAPTER 1

LITERATURE SURVEY OF $MoSe_2$ AND $MoTe_2$ SINGLE CRYSTALS

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1.1 Scope of the Present Work

The subject of crystal growth has held a high level of interest both scientifically and technologically since long time. Nearly all basic solid materials of modern technology are made of crystals. Hence an understanding of how crystals are grown and study of their properties are important aspects of the science of materials.

$MoSe_2$ and $MoTe_2$ are the end compounds of the $MoSe_xTe_{2-x}$ system. Recently, these compounds have found potential application in the fabrication. PEC solar cells. Looking to their various applications and ever increasing importance, attention has been focussed on the constituents of these solid solutions of the system $MoSe_xTe_{2-x}$ in terms of their growth in the form of single crystals, their characterisation by employing X-ray diffraction techniques, electrical properties measurements and photoelectrochemical properties. Growth of these intermediate compounds of the series $MoSe_xTe_{2-x}$, in single crystalline form has not been reported, therefore it was thought worthwhile to grow and characterise them and then use them in the fabrication of PEC solar cells. A brief survey of existing information on the end compounds $MoSe_2$ and $MoTe_2$ of $MoSe_xTe_{2-x}$ series is presented here.

1.2 $MoSe_2$ - Molybdenum Diselenides

1.2.1 Synthesis

The material is not known to occur naturally and so has to be synthesised in the laboratory. It is a gray black substance, having covalent character and it is one of the best known layered transition metal dichalcogenide.

In the system Mo-Se three phases seem to be well established which are Mo_3Se_4, $MoSe_2$, $MoSe_3$[1] and at present only two polytypes of $MoSe_2$ are known 2H and 3R. In 1928, Wendehorste[2] reported a technique to grow $MoSe_2$ crystals by heating together MoO_3 and Se in a stream of hydrogen and by the reduction of $MoSe_3$ with hydrogen at red heat. The 3R modification has only been prepared by the high temperature high pressure method of Towel et al[3] and Silverman[4] with elemental Mo and Se in 1:2 atomic ratio mixtures, below 800°C and pressures between

17 and 78 Kbar only the hexagonal form was obtained. From 1100^{o} to $1400^{o}C$, with the same pressures the resulting product was a mixture of 2H and 3R - $MoSe_2$. At $1700^{o}C$, under 47 Kbar and at $2000^{c}C$ under 70 Kbar the complete reaction occured. Heating the 3R modification, obtained under such conditions of temperature and pressure, in vacuum at $1000^{o}C$ in quartz tubes resulted in a complete conversion into 2H - modification.

According to Al-Hilli's[5)] report, their growth experiments with bromine, resulted in a mixture of 2H and 3R crystals, whereas those grown without bromine were of 2H polytype only and showed well defined hexagonal growth spirals. In Widervanck's[1)] experiments, only bromine and iodine were used. Both Mo and Se in powder form as well an the prereacted compounds were employed as source material, with bromine, transport took place from $T_H = 995^{o} - 1100^{o}C \rightarrow T_L = 905^{o}-1060^{o}C$. Reaction time varied between 4 days and one week. With iodine, a reaction time of two days was needed to transport from $T_H = 1085^{o}C \rightarrow T_L = 1030^{c}C$. In both cases halogen transport yielded 2H-$MoSe_2$. Preparation and crystal growth data reported by various workers are presented in Table 1.1.

1.2.2 Crystal Structure

Molybdenum diselenide belongs to the general family of group VI TX_2 type layer dichalcogenides. The structure of $MoSe_2$ consists of hexagonal stacking of Se-Mo-Se sheets in which every 'Mo' atom is surrounded by six 'Se' atoms in trigonal prism. The crystal structure of $MoSe_2$ is same as that of MoS_2. The normal structure of $MoSe_2$ is hexagonal, with two molecules per unit cell, atoms are in special positions of space group $P6_3/mmc$ with cations at $\pm$ (1/3, 2/3, 1/4) and anions at $\pm$ (1/3, 2/3, 4), $\pm$ (2/3, 1/3, 1/2) positions. A second form of $MoSe_2$ is known to be rhombohedral in space group R_{3m} with atoms at sites (0, 0, 0) molybdenum and (0, 0, 1/12), (0, 0, 5/12) Selenium. Table 1.2 summarises the lattice parameters and relevant structure data pertaining to $MoSe_2$.

1.2.3 Electrical Properties

The important data for electrical and thermoelectrical properties obtained by different workers

Table 1.1

Compound Preparation and Crystal Growth Techniques for $MoSe_2$

Compound	Compound preparation procedure	Crystal growth technique
$MoSe_2$	a) Direct synthesis from the elements at 900°-1000°C gives 2 H type[1] at 600°-700°C, then at 1000°-1050°C in 190 mm x 20.5 mm tube[6]	Br_2 transport conditions are analogus to those for $MoSe_2$[6] T_H = 910°C T_L = 730°C, 2 mg $Br_2 Cm^{-3}$ 2 days[5]
	b) U. H. pressure, high temperature[7,3]	Transport without halogen[1] in temperature of 1070°C. T_H = 995° - 1100°C T_L = 905°-1060°C, 4 days, 1 week, yields 2 H $MoSe_2$
	c) Flux method is not valid[1]	I_2 transport T_H = 1085°C T_L = 1030°C, 2 days gives 2 H- $MoSe_2$[8]

Table 1.2

The Lattice parameters and Relevant Structure Data of $MoSe_2$

Luster	Highly shining	
Colour	Grey black	
X-ray density gm. ml^{-1}	6.98[6]	
Pycn. density gm. ml^{-1}	6.90	
Mole. per unit cell Z	2	
Structure type	MoS_2	
Character	Covalent	
Group	D^4_{6h} $P6_3/mmc$	
Structure	Trigonal prismatic layer structure	
Lattice parameters in Å	"a"	"c"
	2H 3.288	12.903[1]
	3R 3,296	19.392[1]
	2H 3,288	12.9[6]
	2H 3.288	12.92[5]
	3R 3.292	19.392

on $MoSe_2$ crystals are summarised in Table 1.3.

1.2.4 Uses

Molybdenum diselenide is a solid lubricant It can be used as sliding electrical contacts, thermoelectrical sources, battery cathodes and recently used in the fabrication of photoelectrochemical solar cells.

1.3 $MoTe_2$ - Molybdenum Ditelluride

1.3.1 Synthesis

The material is not known to occur naturally and so has to be synthesised in the laboratory It is a grey black substance,having covalent character.

In 1942 and 1944, Morette[17)] reported a technique to prepare $MoTe_2$ by mixing molybdenum with about twice the stoichiometric amount of telluride and then heating it in a sealed, evacuated silica tube at 600-700^{o}C for several days. Followig this the charge was placed in one end of another longer, evacuated silica tube and heated at 600-700^{o}C with the other end of the tube at room temperature. This resulted in the distillation of all

Table 1.3

Electrical Properties of $MoSe_2$ Crystals

Electrical resistivity (ohm. cm.)	3.44[6], 2.3[9], 5[10], 1.38 1.69[11], 0.6
Electrical conductivity (ohm^{-1} cm^{-1})	1.66[12], 1.3 - 3.1[9]
Type	n[10,11,13,14] p[13,14]
Activation energy (eV)	0.1[14]
Seeback coefficient (μ V °C)	- 900[6,15] + 295[13] + 400[14]
Hall mobility (cm^2/V.S.)	100[11], 15, 99[12]
Charge carrier density n (cm^{-3})	5×10^{16}[11], 5.6×10^{16}[12] 3.5×10^{16}[10], 8×10^{16}[12]
Thermodynamic data[16]	H^o_{298} = - 47 S^o_{298} = 21

the unreacted tellurium from the ingot, leaving the ditelluride as a single phase.

1.3.2 Crystal Structure

Molybdenum ditelluride belongs to the general family of group VI TX_2 type layer dichalcogenide. The structure of $MoTe_2$ consists of hexagonal stacking of Te-Mo-Te sheets in which every 'Mo' atom is surrounded by six 'Te' atoms in trigonal prism. The crystal structure of $MoTe_2$ is same as that of MoS_2. The normal structure of $MoTe_2$ is hexagonal, with two molecules per unit cell, atoms are in special positions of space group $P6_3/mmc$ with cations at ± (1/3, 2/3, 1/4) and anions at ± (1/3, 2/3, 4), ± (2/3, 1/3, 1/2) positions.

1.3.3 Electrical Properties

Electrical and thermoelectrical properties measurements on $MoTe_2$ was done by Bxixner[6], Revolinsky and Beernsten[14] and Champion[13].

1.3.4 Uses

Molybdenum ditelluride is a solid

lubricant. It can be used as sliding electrical contacts, thermoelectrical sources, and recently deals in the fabrication of photoelectrochemical solar cells.

1.4 Solid Solutions of $MoSe_xTe_{2-x}$ System

Importance of solid solution of $MoSe_xTe_{2-x}$ system has already been pointed out in the introduction. While going through the literature it is felt that attempts have not been made to grow single crystals of these compounds so far by any method. In the present work, author has attempted to grow them successfully by using a chemical vapour transport method. This thesis deals with the studies of growth, characterization and applications of these crystals in the fabrication of photoelectrochemical solar cells.

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