

CHAPTER 1

EXISTING INFORMATION ON THE SOLID SOLUTIONS IN

$\text{MoS}_x\text{Se}_{2-x}$ SYSTEM

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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 MoS_2 are the end compounds of the $\text{MoS}_x\text{Se}_{2-x}$ system. Recently these compounds have found potential application in the fabrication of 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 $\text{MoS}_x\text{Se}_{2-x}$ in terms of their growth in the form of single crystals, their characterization by employing X-ray diffraction techniques, electrical properties measurements and photoelectrochemical properties etc. Growth of these intermediate compounds of the series $\text{MoS}_x\text{Se}_{2-x}$, in single crystalline form has not been reported, therefore it was thought worthwhile to grow and characterize 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 MoS_2 of $\text{MoS}_x\text{Se}_{2-x}$ series is presented here.

1.2 MoS₂ - Molybdenum Disulphides

MoS₂ is found in nature as molybdenite, and forms the most important ore of molybdenum. The greasy property of MoS₂ which led the ancients to confuse it with graphite gives it particular value as a solid lubricant in modern mechanical applications. The name molybdenite itself is derived from the Greek word 'molybdos' meaning graphite. The deposits of molybdenite at Climax, Colorado, is the largest which is now exploited for its molybdenum content. It is generally disseminated in granites or associated with tin-ore deposits. It is also found with the tin-ores of Schlaggenwald and Zinnwald in Bohemia, Czechoslovakia and at Altenberg in Saxony. In Norway it occurs in considerable amount in Telemarken, it is available in the form of fine specimens at Raads near Moss, at Brevik in Langesund district and at Armedal. It is also found in different localities of Australia, England, United States of America, U.S.S.R. and Quebec¹⁾.

Molybdenite can be prepared in the laboratory by various methods. The properties of natural and synthetic crystals correspond very closely.

1.2.1 Synthesis

In the system Mo-S various compounds exist,

i.e. Mo_2S_3 , MoS_2 , Mo_2S_5 , MoS_3 and MoS_4^2). Molybdenite has been made artificially by adding molybdic oxide to a fused mixture of potassium carbonate and sulphur, it is prepared also by heating a mixture of molybdates and lime in an atmosphere of hydrochloric acid and hydrogen sulphide¹⁾.

It is produced under atmospheric pressure and at a temperature of 425°C by the mixing of currents of H_2S and air containing vapour of oxyhalides of molybdenum³⁾. In 1951, Zelikman and Krien⁴⁾ reported the synthesis of MoS_2 by the reaction of sulphur with MoO_3 or CaMoO_4 in saline melt. The crystals thus obtained were having lubricating properties equal to those of natural crystals.

MoS_2 is synthesised in an autoclave under hydrothermal conditions, at a temperature of $300^\circ - 500^\circ\text{C}$ with a solution concentration of 50 g Mo/l and a pH of 8-12 regulated with NaOH. The sodium molybdate solution was converted into thiomolybdate solution by passing H_2S for 2 hours. The final component after prolonged passage of H_2S was the ion MoS_4^+ . The crystallization of MoS_2 from aqueous thiomolybdate began at $350^\circ - 400^\circ\text{C}$ and continued to $\geq 500^\circ - 550^\circ\text{C}$ ⁵⁾.

Chemical vapour transport method⁶⁻⁹⁾ has been reported as a reliable method of growing metal

dichalcogenide crystals. Brixner⁶⁾ has reported the synthesis of MoS₂ crystals by this method. Recently, Al-Hilli and Evans⁹⁾ have grown better crystals of MoS₂, by the sublimation method, without the use of a chemical transporting agent. Preparation and crystal growth data reported by various workers are presented in Table 1.1.

1.2.2 Crystal structure

MoS₂ belongs to the general family of group VI, TX₂ layer dichalcogenides. These TX₂ type layered materials in general arise from the stacking of hexagonally packed planes in the sequence shown in Fig. 1.1¹⁵⁾. 6:3 coordination results, that around the metal atoms being either trigonal prismatic or octahedral (Fig. 1.2).

The basic coordination unit for MoS₂ is the trigonal prism. Its structure consists of a hexagonal stacking of S-Mo-S sheets in which every Mo atom is surrounded by six S atoms in the trigonal prism^{16,17)}. The arrangement of such units in a single layer brings hexagonal symmetry (Fig. 1.3). The stacking sequences of trigonal and octahedral basic units define the polytypes and is either (AbA BaB)/(2H - polytypes) or (AbA BcB CaC)/(3R - polytypes) as shown in Figs. 1.3 and 1.4. Here A, B, C are the possible positions of X (chalcogen) atoms and a, b, c are that of central M (Metal) atoms. There

Table 1.1

Compound preparation and crystal growth techniques for MoS₂

Compound preparation procedures	Crystal growth techniques
<p>a. Direct synthesis from the elements at 1100°C, gives 2H MoS₂¹⁰⁾ at 600°C-700°C, for 24 H, followed by second firing at 1000°C-1050°C for 1-week in 220 x 22.5 mm tubes⁵⁾</p>	<p>Flux method^{2,11,12)} Br₂ transport T_H = 900°C → T_L = 800°C, tubes 120 x 10 mm, 0.05-0.1 millimoles cm⁻³, in 48 h^{8,6)}</p>
<p>b. Thermal degradation of higher sulfide, above 200°C in vacuum or inert gas yield 2H polytype^{2,10)}</p>	<p>Cl₂ transport¹⁰⁾ T_H = 1000°C - 1120°C → T_L = 810°C - 960°C, 5 mg Cl₂ cm⁻³, 3 days - 3.5 weeks, 2H-as source material. With 3R source in 1-3 weeks, gradient in T_H = 940°C - 1030°C → T_L = 820°C - 970°C yield is 2H + 3R - MoS₂</p>
<p>c. Flux method, carbonate melt at 900°C, gives 3R-modification^{2,21,12)} Ultra high pressure-high temperature (70 Kbar and</p>	

Table 1.1 (contd.)

Compound preparation procedures	: Crystal growth techniques
2000°C) gives the 3R type of MoS ₂ ¹³⁾	<u>Br₂ transport</u> ¹⁰⁾ T _H = 1050°C - 1080°C → T _L = 900° - 1030°C 5 mg Br ₂ cm ⁻³ , in 1-2 weeks with 2H source. Yield is 2H- and 3R-MoS ₂
	<u>I₂ transport</u> T _H = 830° - 1000°C → T _L = 795° - 875°C, 5 mg I ₂ cm ⁻³ , in 4-5 weeks with 2H- source pure 2H-MoS ₂ ^{7,10,14)}
	<u>Br₂ transport</u> T _H = 947°C → T _L = 890°C; 0.428 mg cm ⁻³ in 190 x 22.5 tubes ⁹⁾

are two molecules per unit cell in 2H form, Fig. 1.5(a)¹⁷⁾ and three molecules per unit cell in 3R form, Fig. 1.5(b)¹⁸⁾. In the 2H form the space group is D_{6h}^4 , (P6/mmc) with anions centered at $\pm (1/3, 2/3, 4)$, $\pm (2/3, 1/3, 1/2)$ and cations at $\pm (1/3, 2/3, 1/4)$ positions. In the 3R form the space group is C_{3v}^5 , (R_{3m}) with anions centered at (0, 0, 0), (0, 0, 1/2) and cations at (0, 0, 5/12). Fig. 1.6 shows these structures. The lattice parameters and relevant structural data are given in Table 1.2. The possible existence of several other structural modifications (polytypes) resulting from alternate combinations of the hexagonal and rhombohedral packing has been reported by Zelikman¹⁹⁾, Tackeychi and Nowacki²⁰⁾ and Zvyagin and Soboleva²¹⁾ from studies of synthetic and natural MoS₂ crystals.

1.2.3 Electrical properties

MoS₂ is a diamagnetic semiconductor. Its specific magnetic susceptibility at 16°C is reported both as -0.48×10^{-6} ²³⁾ and as 58.6×10^{-6} ²⁶⁾. The coefficient of thermal conductivity and dielectric constant were measured along c-axis by Salam²⁷⁾. The thermal conductivity was found to be 4.75×10^{-4} cal/cm. degree second at an average temperature of 80°C. The dielectric constant measured by a heterodyne beat method, was about 5.6 at a frequency of

Fig. 1.1 Sandwich of X-M-X sheets.

Fig. 1.2(a) Trigonal prismatic unit.

Fig. 1.2(b) Octahedral unit.

Fig. 1.3(a) Stacking of trigonal prismatic
units.

Fig. 1.3(b) Stacking of octahedral
units.

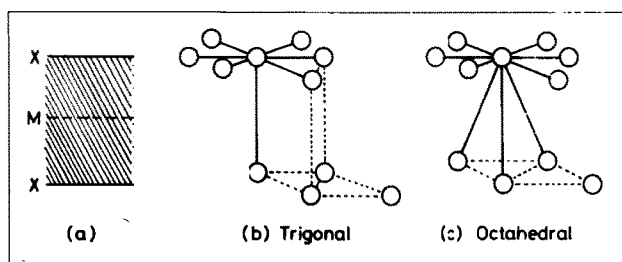


Fig. 1.1

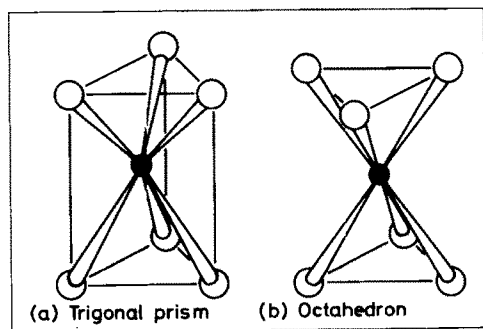


Fig. 1.2(a,b)

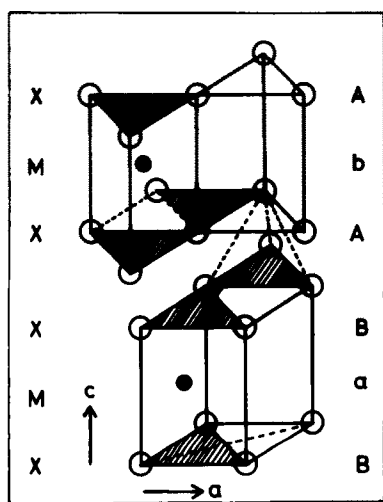


Fig. 1.3(a)

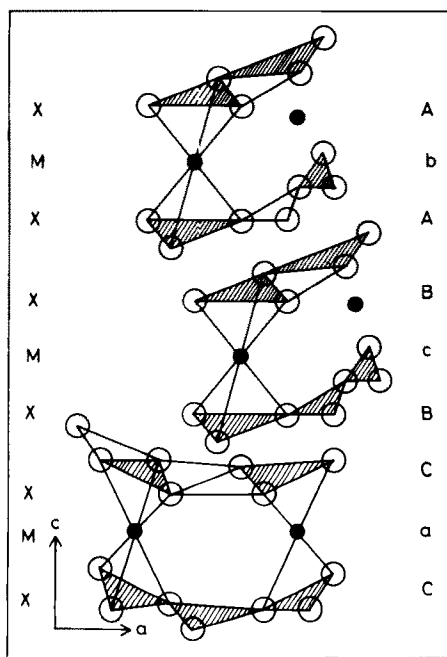


Fig. 1.3(b)

Fig. 1.4(a) Plane view of stacking in 2H-polytype.

Fig. 1.4(b) Plane view of stacking in 3R-polytype.

Fig.1.5(a) 2H-unit cell.

Fig.1.5(b) 3R-unit cell.

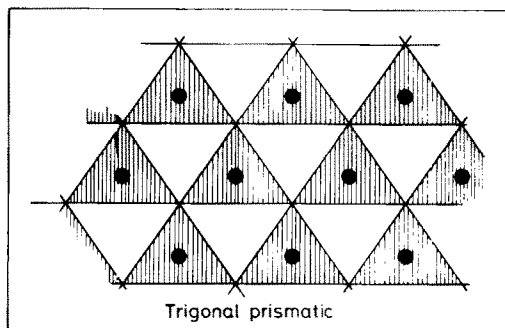


Fig. 1.4(a)

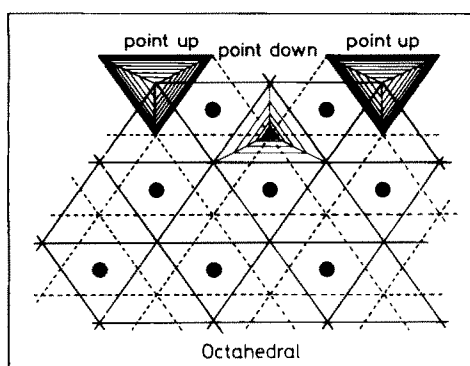


Fig. 1.4(b)

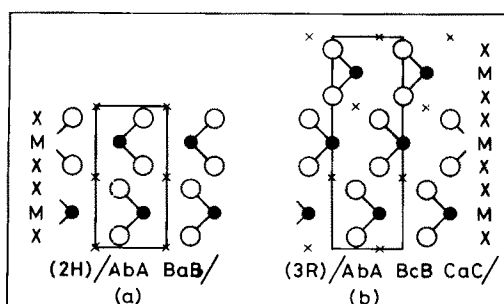


Fig. 1.5(a,b)

Fig. 1.6(a) Layer structure in 2H-polytype.

Fig. 1.6(b) Layer structure in 3R-polytype.

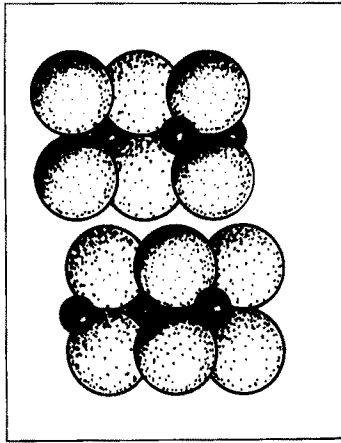


Fig. 1.6(a)

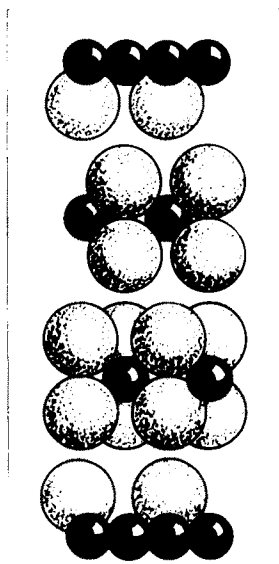


Fig. 1.6(b)

Table 1.2

The lattice parameters and the relevant structure
data of MoS₂

Luster	Metallic ²²⁾		
Colour	Gray-black ¹⁸⁾		
X-ray density g.ml ⁻¹	4.96 ¹¹⁾		
	4.92 ¹²⁾		
	5.024 ¹¹⁾		
Molecule per unit volume Z for 2 H	2		
	3 R	3	
Character	Covalent ²³⁾		
Group	P6 ₃ /mmc for 2 H		
	R _{3m} -C _{3v} ⁵ for 3 R		
Structure	Trigonal prismatic		
Lattice parameters in Å		'a'	'c'
	2H	3.160	12.294 ^{2,10)}
	3R	3.163	18.37 ^{2,10)}
	2H	3.16	12.29 ²⁴⁾
	3R	3.17	18.38 ²⁴⁾
	3R	3.16	18.37 ¹¹⁾
	2H	3.162	12.29 ²³⁾
	2H	3.14	12.327 ⁹⁾
	3R	3.165	18.37 ⁹⁾

about 8.00769 Mc/s. The electrical properties of MoS₂ have been studied by Brixner⁶⁾, Brixner and Teufer²⁸⁾, Wieting²⁹⁾, Mahalawy and Evans³⁰⁾, Fivaz and Mooser³¹⁾, Mansfield and Salam³²⁾, Evans and Young³³⁾, Wilson and Yoffe¹⁵⁾, Champion³⁴⁾, Revolinsky³⁵⁾, Canon et al³⁶⁾, Hick³⁷⁾ and Agarwal et al³⁸⁾. Various investigators have reported large variations in the electrical properties of molybdenite. These variations had been attributed to the larger anisotropies related to stacking faults³⁹⁾, thermal history of samples³⁶⁾, non-stoichiometry²⁸⁾, impurities^{39,40)} and independent nucleation during the growth of each crystals⁴¹⁾. The electrical properties of MoS₂ are given in Table 1.3.

1.2.4 Uses

MoS₂ is an important mineral of molybdenum. The usefulness of MoS₂ as a solid lubricant⁴²⁻⁴⁹⁾ has long been known. In modern mechanical applications it has got particular value as a lubricant. It is an effective lubricant reducing sliding and shearing friction, under severe conditions of temperature and load. It has been found to be superior to graphite for many applications.

Exhaustive comparative tests reported in the literature show performance of a variety of solid

Table 1.3

Electrical properties of MoS₂ Crystals

Electrical resistivity (ohm. cm)	10.50, 11.84 ³²⁾ 10.19 - 12.79 ³⁸⁾
Electrical conductivity (ohm ⁻¹ , cm ⁻¹)	0.078 ³³⁾ , 0.08 ³⁰⁾ 0.6 - 7.9 ²⁹⁾
Type	n ^{29,30,31)} p ^{3,32)}
Activation energy (ev)	0.87, 0.08 ³³⁾ 0.03 to 0.06 ³⁾
Seebeck coefficient (μv/°C)	+ 600 ³²⁾
Hall mobility μ_H	150 ³¹⁾ , 162 ³²⁾
Charge carrier density n (cm ⁻³)	6 x 10 ¹⁵ ³⁰⁾ 1.8 x 10 ¹⁷ ³²⁾
Paramagnetic susceptibility ¹⁵⁾ c. g. s. e. m. u. at 300° K	$\chi_{\perp} = - 50 \times 10^{-6}$ $\chi_{\parallel} = - 115 \times 10^{-6}$
Thermodynamic data ⁵⁰⁾	$\Delta H_{298}^{\circ} = - 65.8$ $S_{298}^{\circ} = 14.96$

lubricants under comparable conditions. MoS_2 has been used as a dry lubricant in forging metal parts, in the bearings of rotating anode X-ray tubes and in the space ships⁴⁹⁾. It is stable in the normal atmosphere or in absence of oxygen, over a wider temperature range and even under extreme pressures both high and low. It is especially useful in high vacuum. It is the chief source of molybdenum and its compounds. It is also used in the manufacture of steel and iron castings and in 'high speed' tools. Recently, it has been used in the fabrication of photoelectrochemical solar cells.

1.3 Molybdenum Diselenides

1.3.1 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 ¹⁰⁾ and at present only two polytypes of MoSe_2 are known 2H and 3R. In 1928, Wendehorst^{51a)} 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^{51b)} and Silverman¹³⁾ 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° to 1400°C , with the same pressures the resulting product was a mixture of 2H- and 3R- MoSe_2 . At 1700°C , under 47 Kbar and at 2000°C under 70 Kbar the complete reaction occurred. Heating the 3R modification, obtained under such conditions of temperature and pressure, in vacuum at 1000°C in quartz tubes resulted in a complete conversion into 2H-modification.

According to Al-Hilli's⁹⁾ 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 Wildervanck's experiments¹⁰⁾, only bromine and iodine were used. Both Mo and Se in powder form as well as the prereacted compound were employed as source material, with bromine, transport took place from $T_H = 995^\circ - 1100^\circ\text{C} \rightarrow T_L = 905^\circ - 1060^\circ\text{C}$. Reaction time varied between 4 days and one week. With iodine, a reaction

time of two days was needed to transport from $T_H = 1085^\circ\text{C} \longrightarrow T_L = 1030^\circ\text{C}$. In both cases halogen transport yielded 2H-MoSe₂. Preparation and crystal growth data reported by various workers are presented in Table 1.4.

1.3.2 Crystal structure

Molybdenum diselenide belongs to the general family of group VI TX₂ type layer dichalcogenides. The structure of MoSe₂ 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 MoSe₂ is same as that of MoS₂. The normal structure of MoSe₂ is hexagonal, with two molecules per unit cell, atoms are in special positions of space group P6₃/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 MoSe₂ 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 1.5 summarises the lattice parameters and relevant structure data pertaining to MoSe₂.

1.3.3 Electrical properties

The important data for electrical and

Table 1.4

Compound preparation and crystal growth techniques for MoSe₂

Compound	Compound preparation procedure	Crystal growth technique
MoSe ₂	<p>a) Direct synthesis from the elements at 900° - 1000° C gives 2H type¹⁰⁾ at 600° - 700° C, then at 1000° - 1050° C in 190 mm x 20.5 mm tube⁶⁾.</p> <p>b) U.H. Pressure, high temperature^{15, 51b)}</p> <p>c) Flux method is not valid¹⁰⁾</p>	<p>Br₂ transport conditions are analogous to those for MoS₂⁶⁾, T_H = 910° C → T_L = 730° C; 2 mg Br₂ cm⁻³, 2 days⁹⁾</p> <p>Transport without halogen¹⁰⁾ in temperature of 1070° C. T_H = 995° C - 1100° C → T_L = 905° - 1060° C; 4 days, 1 week, yields 2-H MoSe₂</p> <p>I₂ transport, T_H = 1085° C → T_L = 1030° C, 2 days gives 2H - MoSe₂¹⁴⁾</p>

Table 1.5

The lattice parameters and relevant structure data of MoSe₂

Luster	Highly shining	
Colour	Gray black	
X-ray density g. ml ⁻¹	6.98 ⁶⁰	
Pycn. density g. ml ⁻¹	6.90	
Mole. per unit cell Z	2	
Structure type	MoS ₂	
Character	Covalent	
Group	D _{6h} ⁴ P6 ₃ /mmc	
Structure	Trigonal prismatic layer structure	
Lattice parameters in Å	'a'	'c'
	2H 3.288	12.903 ¹⁰⁾
	3R 3.296	19.392 ¹⁰⁾
	2H 3.288	12.9 ⁶⁾
	2H 3.288	12.92 ⁹⁾
	3R 3.292	19.392 ⁹⁾

thermoelectrical properties obtained by different workers of MoSe_2 crystals are summarised in Table 1.6.

1.3.4 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.

1.4 Band Schemes of MoS_2 and MoSe_2

Detailed band calculations apparently do not yet exist for MoSe_2 . Sufficiently reliable information can, however, be deduced from theoretical work on MoS_2 ⁵²⁻⁵⁴.

In MoS_2 the conduction band is approximately 3 eV wide and based on four of the six Mo 4 d orbitals ($4 d_{xy}$, $4 d_{x^2-y^2}$), with anti-bonding admixtures of S 3p orbitals (Fig. 1.7). Separated by a hybridization gap⁵²) and approximately 1.75 eV below there is the energy band derived from the nonbonding Mo 4 d_z^2 orbital holding two electrons per MoS_2 . It is approximately 1 eV wide (the electrons in this energy band do not contribute to the transition metal dichalcogen bonding, however, the width of the band indicates that there is some bonding

Table 1.6Electrical properties of MoSe₂ crystals

Electrical resistivity (ohm. cm)	3.44 ⁶⁾ , 2.3 ²⁹⁾ , 5 ³⁰⁾ 1.38, 1.69 ³¹⁾ , 0.6 ³⁷⁾ .
Electrical conductivity (ohm ⁻¹ cm ⁻¹)	1.66 ³⁷⁾ , 1.3 - 3.1 ²⁹⁾
Type	n ^{30,31,34,35)} p ^{34,35)}
Activation energy (eV)	0.1 ³⁵⁾
Seebeck coefficient ($\mu\text{V}^\circ\text{C}$)	- 900 ^{6,28)} + 295 ³⁴⁾ + 400 ³⁵⁾
Hall mobility (cm ² /V.s)	100 ³¹⁾ 15, 99 ³⁷⁾
Charge carrier density n (cm ⁻³)	5 x 10 ¹⁶ ³¹⁾ , 5.6 x 10 ¹⁶ ³⁷⁾ 3.5 x 10 ¹⁶ ³⁰⁾ , 8 x 10 ¹⁶ ³⁷⁾
Thermodynamic data ⁵⁰⁾	$\Delta H_{298}^\circ = - 47$ $S_{298}^\circ = 21$

interaction among transition metal atoms). Below and slightly overlapping (0.1 eV) with the Mo d_{z^2} band is the principal 3p valence band. Optical excitation in the visible spectral range consequently involves d-d transitions, a fact which has been confirmed experimentally by parametric resonance measurements of holes⁵⁵⁾. Transitions from the sulfur 3p to the unoccupied molybdenum 4d bands are only expected to occur in the near ultraviolet region⁵²⁾. As verified experimentally⁵⁶⁾, it is seen that the main difference between the energy scheme of MoS₂ and MoSe₂ is that the hybridization gap in MoSe₂ decreases to approximately 1.4 eV and Mo d_{z^2} band is more narrow due to weaker atomic interactions. The simplified energy scheme of MoSe₂ is shown in Fig. 1.7 together with the scheme for MoS₂. Phototransitions in the near infrared and the red region of MoSe₂ have therefore to be expected to arise essentially from molybdenum d-d transitions. Light of shorter wavelength will in addition involve electron excitation from Se 4 p orbitals.

1.5 Solid Solution of MoS_xSe_{2-x} system

Importance of solid solutions of MoS_xSe_{2-x}

Fig. 1.7 Energy scheme of MoS_2 and MoSe_2 .

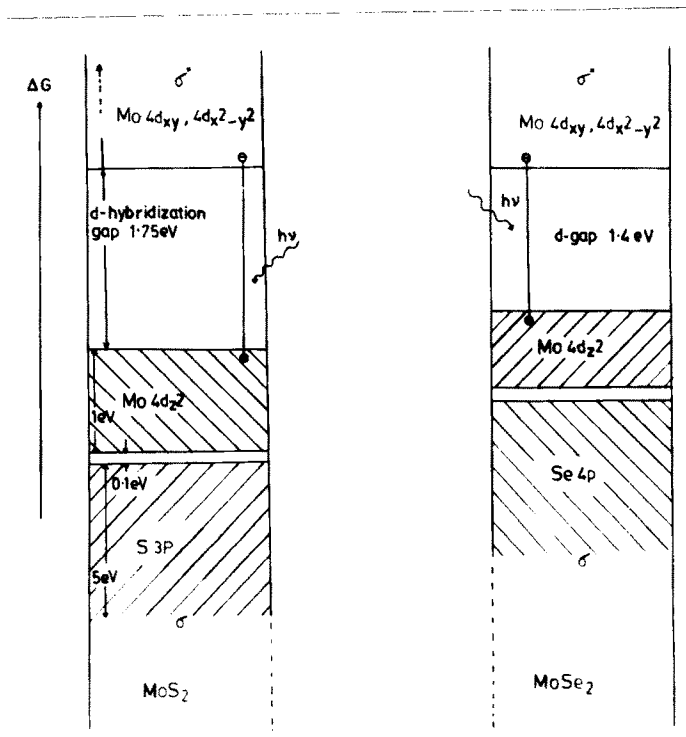


Fig. 1.7

system has already been pointed out in the introduction. While going through the literature it is felt that attempts have not been made so far to grow single crystals of these compounds by any method. In the present work, author has attempted to grow them successfully by using a 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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