

Review

Layer type tungsten dichalcogenide compounds: their preparation, structure, properties and uses

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Tungsten dichalcogenides constitute a well defined family of compounds which crystallize in a layer type structure. These compounds find a wide range of applications in the field of catalysis and as a lubricant at high temperatures and pressures. They have also been investigated successfully as cathode and anode materials in photoelectrochemical cells for solar energy conversion. The layered tungsten dichalcogenides also exhibit superconducting behaviour when intercalated with alkali or alkaline earth metals and different divalent rare earth metals. In the present paper an attempt has been made to review the preparation, crystal structure and band models of tungsten dichalcogenides. Furthermore, we have tried to incorporate the physical, chemical, optical and electrical properties along with intercalation, thermal stability and uses of these compounds.

1. Introduction

During recent years, the transition metal dichalcogenides of Group IVB, VB and VIB elements have received a fair amount of attention [1-9]. The most striking feature of these compounds is that they crystallize in a quasi two-dimensional structure consisting of a sheet of metal atoms sandwiched between two sheets of chalcogens, which are held together by relatively weak van der Waals forces. Within a layer the bonds are strong, while between adjacent layers, they are weak. As a result, these compounds exhibit marked anisotropy in most of their physical properties which accounts for the great interest in this family of materials. The layer type structure also facilitates the process of intercalation by a variety of foreign atoms, ions or neutral molecules to form new compounds. These transition metal dichalcogenides are also very attractive semiconducting materials for use in photoelectrochemical energy conversion processes as they are not as susceptible to photodecomposition as are many other materials

whose band gaps are in the region of maximum solar energy efficiencies.

The main purpose of this review article is to present an up-to-date chemistry of tungsten dichalcogenides mainly concerned with their preparation, structure, properties and important uses. The range of literature relevant to this field is very large, but no attempt has been made so far to deal with tungsten dichalcogenides specifically. The general survey for this review article has been made from the literature available up to 1984. It is hoped that the present article will help research workers in selecting preparative and crystal growth methods and stimulate further research work into the properties of tungsten dichalcogenides.

2. Method of preparations

Tungsten dichalcogenides constitute structurally and chemically a well defined family of compounds having a general formula TX_2 , where T represents tungsten metal and X is a chalcogen S, Se or Te. The methods of preparation of

different tungsten dichalcogenides are discussed below.

2.1. Tungsten disulphide

Tungsten disulphide is one of the most metal-rich sulphides of tungsten which exists in only two types of polymorphs, namely, two layer hexagonal form (2H) and three layer rhombohedral form (3R).

Tungsten disulphide was first synthesized by Glemser *et al.* [10] from the thermal decomposition of WS_3 at 800°C for 24 h, whereas Wildervanck and Jellinek [11] obtained WS_2 by heating WS_3 at 1100°C . Voorhoeve and Wolters [12] observed that decomposition of WS_3 is an irreversible process which leads to the product $W_{1-x}S_2$, where x decreases with increasing decomposition temperature. The procedure of Zeilkman *et al.* [13] involved decomposition of ammonium thiotungstate in the temperature range of 300 to 600°C with final heating at 800°C .

Van Arkel [14] synthesized WS_2 from the direct union of elements at 800 to 900°C in a pure N_2 atmosphere. It can be obtained by calcination of WO_3 with CS_2 at 1000°C [15] or by the reaction of WO_3 and metal sulphide MS ($M = \text{Zn, Cd, Mg}$), when heated in the temperature range of 500 to 1200°C in an argon atmosphere [16]. Sulphurization of the powdered tungsten metal at $\approx 400^\circ\text{C}$ [17] or WO_3 at 1400°C has also been used [18, 19]. When H_2S reacted with WO_3 [20] or WCl_6 heated to 375 to 550°C [21], tungsten disulphide is formed. However, in the latter case it is possible that WS_2 may be incorporated with chlorine and has to be purified by heat treatment with excess sulphur. Reaction of WO_3 with H_2S at a low pressure yielded WS_2 having a lamellar-type structure [22]. In order to obtain a WS_2 compound of high purity, its synthesis from the elemental tungsten and sulphur, when placed in a quartz tube and vacuum sealed, seems to be the most convenient procedure, which always yields the 2H-polymorph. Thus according to differential thermal analysis (DTA) studies WS_2 is formed at a temperature always higher than 400°C , although to obtain a well crystallized product without any stacking disorders a temperature of 900 to 1000°C is preferred [23].

A hydrothermal method for WS_2 has also been reported, where WS_2 crystallized from

strongly reducing sulphide solution containing $\geq 2 \times 10^{-3} \text{ M W}$. The synthesis of WS_2 was also studied for 0.02 to $1 \text{ M Na}_2\text{WO}_4$ solutions, 0.5 to $0.02 \text{ M H}_2\text{S}$ and 1 to 4 M HCl at 88 to 500 atm and 300°C in a titanium autoclave [24].

The rhombohedral polymorph of WS_2 was synthesized by Wildervanck and Jellinek [11] by the carbonate melt method, where the WO_3 reacts with sulphur in a flux of an alkali carbonate at about 900°C . The yield was found to be quite low and further attempts on its improvements resulted in the product having a larger degree of stacking disorder. Silverman [25] successfully employed high pressure-high temperature for the synthesis of rhombohedral WS_2 . When an elemental mixture of tungsten and sulphur was compressed at 45 kbar and heated to 1800°C for 2 to 3 min , a silver-grey coloured product was formed which was completely rhombohedral.

However, the most interesting feature concerned with the synthesis of WS_2 is the growth of single crystals, which are needed for the study of the various physical properties. The first attempt in this direction was made by Nitsche [26] who suggested that under carefully controlled temperature conditions, transport reactions may be used for the growth of single crystals in particular for materials where the classical melt techniques fail because of high melting points or pressure decomposition. Thus he was able to synthesize WS_2 single crystal using Br_2 as a transport agent. Wildervanck [27] obtained it by halogen transport using Cl_2 , Br_2 , I_2 and NH_4Cl and observed that in the latter case transport was incomplete. The preparative techniques used by Shafer *et al.* [28, 29] have shown the possibility of sulphur assisted transport of WS_2 . They further investigated the influence of water on the I_2 transport method for WS_2 and suggested that the transportation proceeds via gaseous oxyiodide WO_2I_2 formation. The oxygen here is being obtained from H_2O which is liberated from the walls of the quartz tube. It may be stated here that crystals grown by all these methods were not only very small, but also incorporated the transport agent. Agarwal *et al.* [30] reported that single crystals of WS_2 can be grown from polycrystalline WS_2 powder by a sublimation method without the addition of a transporting agent. Very recently, Baglio *et al.* [31] synthesized WS_2 single crystal from the chlorine and bromine transport technique. It

TABLE I Conditions to grow single crystals of tungsten dichalcogenides

Crystal	Workers	Temperature ($^{\circ}$ C)		Transport agent	Duration	Remarks
		Source	Growth			
WS ₂	Nitsche [26]	900	800	Br ₂	48 h	Product is 2H-WS ₂ Yields 2H as well as 3R-WS ₂ Yields 2H + 3R-WS ₂ Transportation was incomplete; yields 2H-WS ₂ 15 mm \times 10 mm \times 25 mm large platelets 2H-WS ₂ } source yields good quality crystal W + S } Bright shining n-type. 2H-WS ₂ crystals having shape of hexagonal plates
	Wildervanck [27]	960-1030 865-1090	875-945 787-1009	Cl ₂ Br ₂	10 days-2.5 week 1-2 week	
		830-930	800-870	I ₂	2-4 week	
		900	800	NH ₄ Cl		
	Agarwal <i>et al.</i> [30]	1055	1035	Without transport	5 day	
	Baglio <i>et al.</i> [31]	1200 1175	1140 1125	Cl ₂ Br ₂	100 or 160 h 120 h	
WSe ₂	Brixner [33]*	800-850 1055	750 890	Br ₂ I ₂	10 g of the sample could be transported during 10-15 h	
	Wildervanck [27]	800-850 1055	750 890	Br ₂ I ₂	2.5-3 week 2.5-3 week	
	Al-Hilli and Evan [32]	800	700	Without transport	4-day	
WTe ₂ *	Agrawal <i>et al.</i> [39]	1000	960	With Br ₂ transport Without transport	10 day	2H-WSe ₂ thin small crystals p-type, 2H-WSe ₂ plates with well defined hexagonal growth features Thin buckled crystals with obvious surface Shining platelets, 17 mm \times 12 mm \times 14 mm size crystal No transportation of WTe ₂ occurred Thin long sheets of WTe ₂
	Al-Hilli and Evan [32]	900	700	Br ₂ Without Br ₂	4 day	

*Conditions reported by Brixner [33] for WSe₂ (without transport) is also applicable for WTe₂.

was concluded from their studies that the quality of the single crystals was strongly affected by the temperature of the growth process but not strongly dependent on either the nature or the concentration of the transporting agents. Table I summarizes the most important results on growth of Tungsten disulphide single crystal.

2.2. Tungsten diselenide

The earliest attempt to synthesize WSe_2 was made by Glemser *et al.* [10] by thermal decomposition of WSe_3 which was obtained by saturating an aqueous solution of alkali tungstate with H_2Se and subsequently precipitating it by the addition of dilute acid. Synthesis of polycrystalline WSe_2 was also made directly from the elements in the stoichiometric ratio [28, 32–36]. The DTA experiments indicated that WSe_2 is formed at $\approx 480^\circ C$, however most of the procedures utilized high temperatures. A self propagating high temperature synthesis from the elements at < 400 atm pressure and temperature $1770^\circ C$ has also been used [37]. The physicochemical properties of WSe_2 prepared by this method were found to be similar to those obtained by the usual synthetic methods. Obolonchik and Prokoshina [38] synthesized WSe_2

by heating finely powdered WO_3 at 900 to $1300^\circ C$ in a stream of H_2Se .

The ultra high pressure–high temperature synthesis was carried out by Silverman [25] but the application of 70 kbar pressure and $2400^\circ C$ temperature gave only hexagonal modification of WSe_2 .

Successful attempts on single crystals of WSe_2 have also been made with [28] and without [32] halogen transport. The sublimation method has also been reported by Agarwal *et al.* [39]. Table I records growth conditions and characteristic feature of the resulting WSe_2 single crystals.

2.3. Tungsten ditelluride

The synthesis of WTe_2 has been reported by various workers from the direct union of elements at high temperature [32, 33, 40, 41]. DTA measurements have shown that the temperature of formation from the elements lies at $\approx 630^\circ C$ [23]. It can also be obtained by passing tellurium vapours in a hydrogen atmosphere over tungsten or tungsten trioxide powder heated at $800^\circ C$ for 4 h [42]. Silverman's [25] high temperature–high pressure technique failed to give rhombohedral modification of WTe_2 .

The growth of WTe_2 single crystal has been

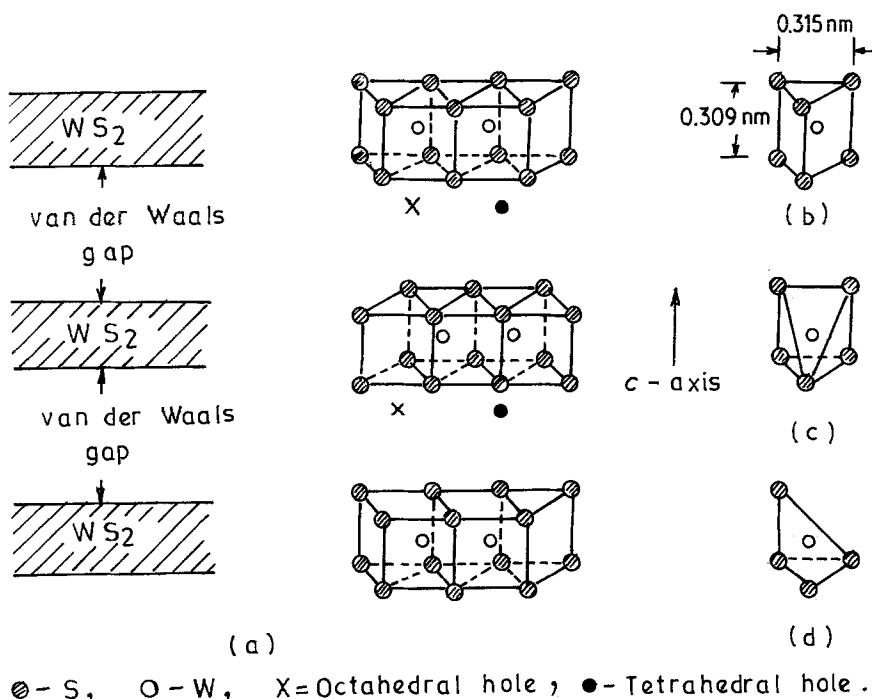


Figure 1 The structure of tungsten disulphide [44] (a) stacking of layers illustrating the position of holes. Site symmetry of tungsten ion (b) in the bulk, (c) in the surface, and (d) on an edge parallel to the c -axis.

achieved by Al-Hilli and Evan [32], Brixner [33] and Brown [43] using halogens as the transporting agent. The experiments of Al-Hilli and Evan [32] without bromine vapours failed to yield WTe_2 (Table I). Brown [43] carried out structure determination studies on this bromine transported WTe_2 crystal.

3. The structure of tungsten dichalcogenides

Tungsten disulphide crystallizes into a layer type structure similar to $C7(MoS_2)$ (Fig. 1) [44]. Within each layer there is a trigonal prismatic co-ordination between tungsten and sulphur atoms. The structure of WS_2 is characterized by the presence of W^{2+} and S^{2-} sheets, but each W^{2+} sheet is sandwiched between two S^{2-} sheets. The sandwiches are held together by weak van der Waals forces. The variation in the stacking sequence of layers leads to the formation of hexagonal (2H) or rhombohedral (3R) polymorphs.

The structure of WSe_2 was found to be similar to WS_2 with a trigonal prismatic co-ordination of the metal surrounded by selenium atoms [45, 46].

The structure of WTe_2 was first thought to be closely related to the $C7(MoS_2)$ type [40] but further studies have shown that WTe_2 is a layer type compound with a distorted octahedral co-ordination about the tungsten atom, which is isostructural to the high temperature form of $MoTe_2$ [43].

The lattice parameters for tungsten dichalcogenides are recorded in Table II.

4. Approach towards the band model

Considerable interest in the band structure of

layered transition metal dichalcogenides has been shown by various workers. The general features of the band structures are similar to molybdenum dichalcogenides. It consists of a valency band made up of chalcogen s and p orbitals, above which is a broad antibonding or conduction band made up of metal s and p orbitals and in between a nonbonding band made mostly of metal d-character. If the metal atom is in trigonal prismatic co-ordination, a narrow d_{z^2} band is lowest in energy. The energy difference between the valency band and low lying d_{z^2} band as well as electron occupancy will determine the optical and electrical properties of the transition metal dichalcogenides. The d_{z^2} band is full for WS_2 and WSe_2 and the materials exhibit diamagnetism and semiconducting behaviour. Wilson and Yoffe [51] assigned this d_{z^2} band in the gap between the valency band and the Fermi level, E_f (Fig. 2a). Huisman *et al.* [52] placed it at the top of the valency band as shown in Fig. 2b. McMenamin and Spicer [53] and William and Shepherd [54] from their photoemission studies concluded that this band is somewhere in between these two positions, the top of the band falling above the top of the valency band, with the bottom at or slightly below the top of the valency band as shown in Fig. 2c. Recently electron loss spectroscopic measurements have also been made to study the electronic state of tungsten dichalcogenides, providing the information about the conduction band, mainly that of WS_2 [55]. Wood and Pendry [56] suggested the application of the layer method for the calculation of the band structure of WS_2 , whereas Bromley and co-workers [57, 58] calculated the band structure in a two-dimensional approximation on the basis of a semiempirical tight bonding method.

TABLE II Lattice parameters for tungsten dichalcogenides

Compound	<i>a</i> (nm)	<i>b</i> (nm)	<i>c</i> (nm)	<i>c/a</i>	Reference
WS_2 (2H)	0.3155		2×0.6195	1.957	[11]
(3R)	0.3162		3×0.6117	1.935	[11]
(2H)	0.3161		2×0.6179	1.955	[47]
WSe_2 (2H)	0.3286		2×0.6488	1.974	[11]
	0.3282 ± 0.0004		2×0.6488	1.976	[32]
	0.3286		2×0.6492	1.975	[33]
	0.3286		2×0.6492	1.976	[47]
	0.3285 ± 0.0001		2×0.6468	1.968	[48]
	0.3285		2×0.6489	1.975	[49]
WTe_2	0.6270	0.3495	1.4028		[33]
(orthorhombic)	0.6282	0.3496	1.4073		[43, 50]

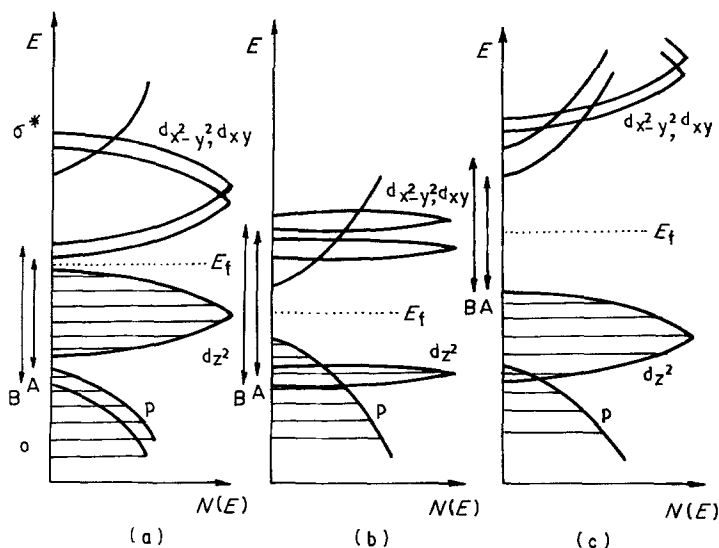


Figure 2 Band structure of trigonal prismatic dichalcogenides as suggested by (a) Wilson and Yoffe [51] (b) Huisman *et al.* [52] (c) McMenemy and Spicer [53] and William and Shepherd [54].

Mattheiss [59] used an argued plane wave (APW) calculation for the band structure of a C7(MoS₂) type of layered transition metal dichalcogenides. Apart from their quantitative aspects, the results of this method provide useful information about the correct band ordering and effect of hybridization between states and different atomic symmetry properties.

5. Properties of tungsten dichalcogenides

5.1. Physical properties

Some of the physical properties of tungsten

dichalcogenides are listed in Table III. There is disagreement in the literature with regard to the numerical values of some of the properties, which may be due to the different methods by which the dichalcogenides have been prepared.

5.2. Chemical properties

WS₂ is insoluble in water. Mineral acids have no action on WS₂ but it reacts readily with the mixture of nitric acid and hydrofluoric acid or hydrochloric acid. It is oxidized by aqua regia to H₂SO₄ and WO₃. It is readily soluble in molten alkali hydroxide and alkali carbonate in the

TABLE III Physical properties of tungsten dichalcogenides

Properties	WS ₂	WSe ₂	WTe ₂
Mol wt (g)	247.98	344.77	439.05
Colour	Black	Grey-black	Grey-black
m.p. (°C)	1150° (d)* [61] 1200° (d) [62, 63]	800° C(d)	970°(d) [64]
Density (g cm ⁻³)	7.5 [63]	9.35 [33] 9.40 [34]	9.51 [43]
Crystal structure and polymorph	Trigonal prismatic layer structure 2H and 3R	Trigonal prismatic layer structure 2H	Distorted octahedron
Space group and stacking sequence	2H: P6 ₃ /mmc BaB AbA 3R: R3 _m BcB CaC AbA	2H: P6 ₃ /mmc BaB AbA	Pnm2 ₁
Magnetism	Diamagnetic	Diamagnetic	Diamagnetic
Heat of formation [63] k cal mol ⁻¹	-64 ± 4 [63] -36.71 [65]	-45 ± 15 [63]	-32 ± 15 [63]
Entropy [63] cal k ⁻¹ mol ⁻¹ at 298 K	15.5 ± 1.5	21.5 ± 3	25.0 ± 3
Heat capacity [63] (cal k ⁻¹ mol ⁻¹)	7.81 (in the temperature range of 298-623 K)	-	-

*Decomposition temperature (d).

presence of an oxidation agent. Fluorine at ordinary temperatures reacts with WS_2 to form the fluoride, whereas chlorine at $400^\circ C$ yields the hexachloride. It is attacked by bromine at $700^\circ C$. Both WS_2 and WSe_2 have been found to be stable in dilute non-oxidizing acids at room temperature but dissolve on heating. WTe_2 is inert towards water, ammonia, hydrochloric acid and sulphuric acid.

5.3. Magnetic properties

Tungsten dichalcogenides with the trigonal prismatic co-ordination are diamagnetic [66]. In contrast WTe_2 [67], where the metal atoms have essentially octahedral co-ordination, is metal or semimetal with temperature independent paramagnetism. The effects of temperature (2 to 300 K) on a single crystal of WS_2 have indicated that magnetic susceptibility is temperature independent and strongly anisotropic [68].

5.4. Optical properties

The study of the optical properties of solids gives a good deal of information on the electronic properties and band structures of both metals and semiconductors. Wilson and Yoffe [51] interpreted the optical spectra of transition metal dichalcogenides having trigonal prismatic co-ordination based on the interband transition. Liang [69] studied the reflectivity spectra of 3R- WS_2 and 2H- WSe_2 grown as such by bromine transport, at 77 K and is shown in Fig. 3. The transmission spectra of iodine grown crystals

have also been measured by Beal *et al.* [70]. The general feature of the spectra are characterized by the presence of absorption peaks A, B, C, D, α , β etc. in the direction of increasing photon energy. Furthermore, the spectra may be subdivided into regions at low energy which are dominated by sharp excitonic transitions (e.g. A and B) on an otherwise relatively low absorption background and a region of strong absorption at higher energies where the absorption coefficient rises to a maximum (e.g. C, D and beyond). In the case of 2H- WSe_2 two subsidiary peaks are also observed. It may be noted here that all these measurements were made with light incident normal to the layer plane i.e. with the light electric vector $E_{\perp c}$, the hexagonal crystal (optic) axis. Liang [71] therefore, further made reflectance measurements on 3R- WS_2 and 2H- WSe_2 parallel to the crystal c -axis at liquid nitrogen temperature and room temperature, where crystals were grown by bromine transport. Fig. 4 shows the reflectivity spectra of these crystals at a given temperature (a) with $k_{\parallel c}$, $E_{\perp c}$ taken from layer plane surface (b) with $k_{\perp c}$, $E_{\perp c}$ and $k_{\perp c}$, $E_{\parallel c}$, taken from the edge-plane surface, where k denotes the wave vector of the incident light. It appears from the figure that the average value of reflectivity for $E_{\parallel c}$ is about half of that for $E_{\perp c}$, and there is usually a prominent but broad peak in the reflectivity spectra for $E_{\parallel c}$ followed by a low reflectivity window 1.0 to 1.5 eV wide at higher energies.

The ϵ_1 and ϵ_2 spectral variation ($E_{\perp c}$) for

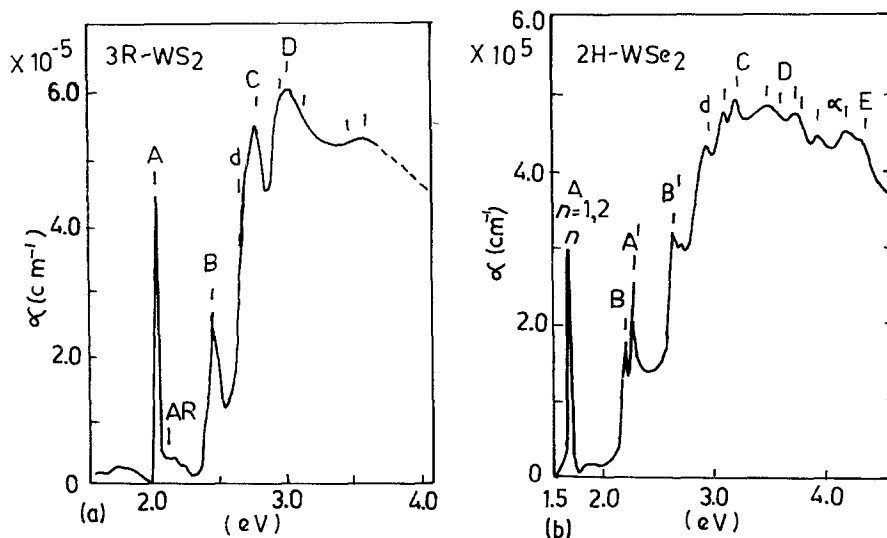


Figure 3 Transmission spectra of (a) 3R- WS_2 and (b) 2H- WSe_2 [70].

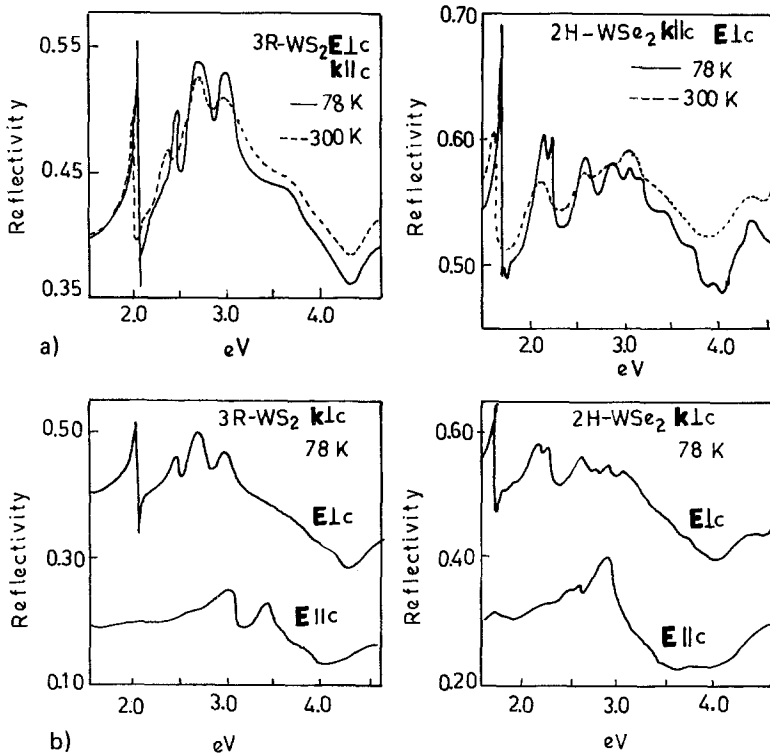


Figure 4 Reflectance spectra of 3R-WS₂ and 2H-WSe₂ [71] with light incident (a) normal to the layer plane, (b) normal to the edge plane.

p-type WSe₂ at 77 K is shown in Fig. 5 [72]. The 2H-WSe₂ single crystal for this purpose was grown directly from the powder. The ϵ_2 (imaginary part of dielectric constant) spectrum of WSe₂

initially shows the presence of two sharp excitonic peaks A_1 (1.7380 eV) and B_1 (2.150 eV). On the high energy side of A_1 the ϵ_2 spectrum showed the presence of a shoulder A_2 . Exciton band B_1

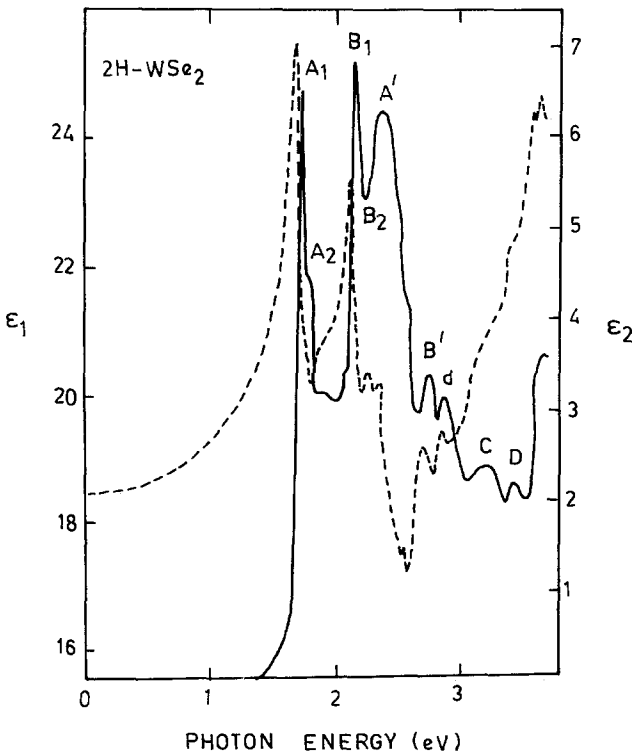


Figure 5 Spectral variation of ϵ_1 (dashed line) and ϵ_2 (full line) for 2H-WSe₂ (77 K) E_{1c} [72].

is sharply defined and a shoulder B_2 is also observed. On the high energy side of B_1 , exciton peaks labelled as C_1 , D_1 and E_1 and F_1 occurred.

The optical spectra of WSe_2 has also been studied in the 1.5 to 3.2 eV range by wavelength and temperature modulated photovoltaic effects from 4.1 to 300 K [73]. The resulting spectra was interpreted with the help of the known band structure of the isomorphous compound MoS_2 .

5.5. Electrical properties

WX_2 ($X = \text{S, Se}$) are found to be diamagnetic semiconductors, whereas WTe_2 with the octahedral co-ordination of a metal exhibits metallic or semimetallic behaviour. Band gaps for WS_2 and WSe_2 are presented in Table IV.

The electrical properties of tungsten dichalcogenides have been studied in detail by various workers. Table V records the electrical data e.g. carrier type, resistivity ($\Omega \text{ cm}$) Hall coefficient R_H ($\text{cm}^3 \text{ cb}^{-1}$), carrier concentration n (cm^{-3}), Hall mobility μ ($\text{cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$) and Seebeck coefficient S ($\mu \text{ V}^\circ \text{ C}^{-1}$) for various dichalcogenides of tungsten.

The effect of pressure on resistivities and structure of WS_2 and WTe_2 has been studied at ≤ 65 kbar [88]. A smooth decrease in resistivity with increasing pressure was observed. Mahalawy and Evan [89] carried out further experiments on the dependence of electrical conductivity in p-type 2H- WSe_2 in the temperature range 300 to 870 K and at pressures upto 30 kbars. The derived values for pressure dependent activation energy were interpreted in terms of the existing band models.

TABLE IV Band gap of tungsten dichalcogenides

Compound	Conductivity type	Band gap	Reference
WS_2	—	1.1	[74]
	n	1.78*	[75]
		1.34 [†]	
	p	1.34 [†]	[76]
1.3 [†]		[77]	
WSe_2		1.60 [†]	[77]
		1.57 [†]	[78]
	n	1.35	[79]
	n	1.4	[80]
		1.57*	[81]
	n	1.16 [†]	[82]
	n	1.78*; 1.34 [†]	[75]
	p	1.2 [†]	[82, 83]

*Direct, [†]indirect

5.6. Intercalation

Layered transition metal dichalcogenides, due to their unique structure, exhibit a variety of interesting properties, one of which is that they can accommodate atoms, ions or organic molecules in the van der Waals gap of weakly bonded S–W–S layers. The changes in structural and physical properties accompanying this intercalation process have been extensively investigated over the past few decades. In most of the cases, the observed changes have been explained on the basis of a model which assumes that host band structure remains unchanged and electrons are transferred from the intercalate to a conduction band of the host crystals.

Rüdorff and co-workers [90–92] were the first to prepare intercalated compounds of tungsten dichalcogenides by its reaction with alkali or alkaline earth metal in liquid ammonia at -40°C . It was concluded that WSe_2 intercalated to a lesser extent than WS_2 whereas no intercalated compound of WTe_2 is known. Subba Rao *et al.* [93, 94], Schafer *et al.* [95] also investigated alkaline earth metal and divalent rare earth (Eu and Yb) metal intercalation of tungsten disulphide. Further studies have shown that butyl lithium when used in a solution of hexane provides an excellent way to affect the intercalation of lithium into tungsten dichalcogenides under mild conditions [96]. Highly crystalline and uncontaminated stoichiometric products were obtained by this method. It was observed that these intercalated compounds exhibit superconducting behaviour and are very susceptible to air or moisture.

Very recently, Srivastava *et al.* [97] reported a synthesis for an indium intercalation compound of molybdenum disulphide, In_xMoS_2 ($0 \leq x \leq 1$) and studied their various physicochemical properties. These properties were found to be quite interesting and encouraging and therefore Srivastava and Avasthi [98] extended their studies on synthesis and characterization of indium intercalation compounds of tungsten disulphide, In_xWS_2 ($0 \leq x \leq 1$). All these compounds were shining black in colour and unlike their alkali and alkaline earth metals analogues were found to be stable on exposure to air. Such a stability behaviour is similar to that reported for intercalation compounds of $\text{M}'\text{MCh}_2$ ($\text{M}' =$ unsolvated metal including transition and post transition elements) where it was assumed that

TABLE V Electrical data for tungsten dichalcogenides

Compound	Workers	Carrier type	Resistivity ρ (Ω cm)	Hall coefficient R_{Hl} ($\text{cm}^3 \text{cb}^{-1}$)	Carrier concentration n (cm^{-3})	Hall mobility μ ($\text{cm}^2 \text{V}^{-1} \text{sec}^{-1}$)	Seebeck coefficient S ($\mu \text{V}^\circ \text{C}^{-1}$)
WS ₂	Baglio <i>et al.</i> [31] Agarwal <i>et al.</i> [84] Brixner [33] Brixner and Teufer [85] Hicks [36] Revolinsky and Beerntsen [41] Champion [48] Kershaw <i>et al.</i> [45] El Mahalaya and Eyan [86] Spán <i>et al.</i> [87] Fivoz and Mooser [66]	n (p by Nb doping)	33.33 (300 K)	—	—	105 (300 K)	—
		p	Semiconducting $E_g = 0.14 \text{ eV}$ (300–620 K)	—	1.057×10^{16}	1.347×10^3	—
		p	0.5 (300 K)	—	—	—	+990 (300 K)
		p	15 (77 K)	—	—	—	+700 (300 K)
		p	0.72 (300 K)	—	—	—	+560 (100° C)
		p	120 (77 K)	78 (25° C)	8.0×10^{16} (25° C)	99	+527 (600° C)
		p	0.570 (100° C)	—	—	—	+600 (300 K)
		p	0.780 (600° C)	—	—	—	—
		p	$\approx 10^3$ (300 K)	—	—	—	—
		p	≈ 10 (550 K)	—	—	—	—
WTe ₂	Brixner [33] Revolinsky and Beerntsen [41]	p	$E_g \sim 0.09 \text{ eV}$ 400 (300 K)	—	—	—	+600 (300 K)
		p	≈ 5 (300 K)	—	—	—	—
		p	≈ 30 (100 K)	—	—	—	—
		p	0.166 (300 K)	—	3.88×10^{17} (300 K)	μ (300 K) ~ 121.5 ($> 300 \text{ K}$) $\sim T^{-2.7}$	—
		n	0.8 (298 K)	—	7.4×10^{16} (298 K)	105 (298 K)	—
		p	0.38 (298 K)	—	7.0×10^{16} (298 K)	236 (298 K)	—
		n	≈ 1.23 –1.33 (300 K)	100 (300 K)	1×10^{17} (100 K)	μ (300 K) ~ 100	—
		n	(300 K)	—	5×10^{16} (300 K)	$\alpha T^{-2.4}$ (or greater)	—
		n	2.87×10^{-3} (25° C)	—	1×10^{12} (80 K)	$> 120 \text{ K}$	—
		p	0.30×10^{-3} (–196° C)	—	—	—	–57 (25° C)
	2.5×10^{-3} (25° C)	—	—	—	—	+30 (130° C)	

guest–host bonding is fairly strong with the result that de-intercalation is difficult [99]. The interesting feature of the X-ray diffractogram in In_xWS_2 ($0 \leq x \leq 1$) intercalated compounds is their marked similarities to that of 2H-WS_2 (Fig. 6) as was the case with the previously reported In_xMoS_2 ($0 \leq x \leq 1$) intercalation compounds. It may therefore be concluded that even upon intercalation the arrangement of W and S atoms remains same as in 2H-WS_2 excepting a slight expansion of the van der Waal gap due to incoming intercalated metal atoms (Table VI). Room temperature magnetic susceptibility and

thermo-electric power experiments suggested that like host WS_2 , In_xWS_2 ($0 \leq x \leq 1$) intercalation compounds were diamagnetic with p-type conductivity (Table VI). The two-probe electrical conductivity data for the temperature range 150 to 300 K indicated that all In_xWS_2 intercalated compounds possess semiconducting behaviour similar to pure 2H-WS_2 . Furthermore, it was observed that conductivity increased with increasing indium content in WS_2 , whereas activation energy followed the reverse order. Such a behaviour was found to be contrary to the usual metallic and paramagnetic behaviour

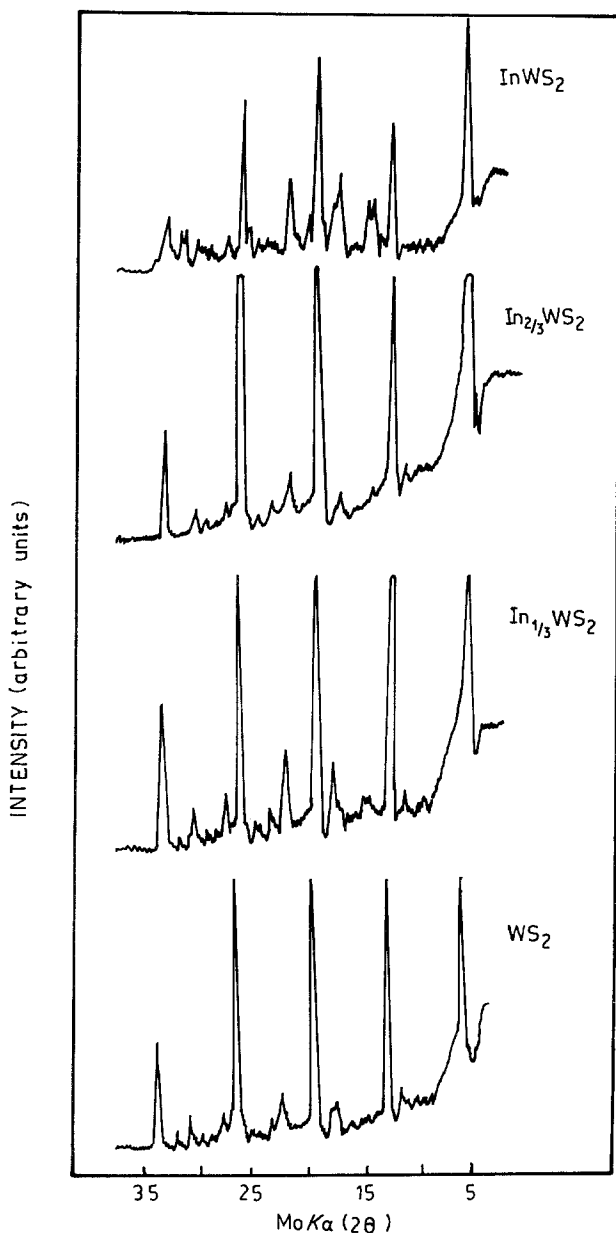


Figure 6 X-ray diffractograms of the In_xWS_2 ($0 \leq x \leq 1$) compound [98].

TABLE VI Characterization of In_xWS_2 ($0 \leq x \leq 1$) compounds

Compound	Lattice parameter (nm)		Seebeck coefficient S ($\mu\text{V}^\circ\text{C}^{-1}$)	Room temperature conductivity σ (Ωcm) ⁻¹	Activation energy E_g (eV)	Magnetic susceptibility x_g ($\times 10^{-6}$ cgs emu)
	a	c				
WS_2	0.3152	1.2350	+330	1.79×10^{-3}	0.0961	0.350
$\text{In}_{1/3}\text{WS}_2$	0.3154	1.2356	+211	1.5×10^{-2}	0.0776	0.110
$\text{In}_{2/3}\text{WS}_2$	0.3154	1.2360	+37.47	0.165	0.0326	0.135
InWS_2	0.3150	1.2366	+40.4	51.49	0.0091	0.378

of alkali and alkaline earth metal intercalate of WS_2 . Thus it was concluded that the charge transfer model does not seem to be applicable for all intercalated layered transition metal dichalcogenides. These findings were found to be in agreement with the results of Trichet *et al.* [100] and Srivastava *et al.* [97], who from their studies on I_xZrS_2 ($\text{I} = \text{Fe}, \text{Co}, \text{Ni}$) and In_xMoS_2 respectively concluded that these compounds retained the semiconducting behaviour even upon intercalation. Rouxel [101] proposed that in some intercalation compounds, the electrons given up by the intercalated atoms may get trapped in certain sites rather than being delocalized in the conduction band of the host crystal. Very recently, Yacobi *et al.* [102, 103] made fundamental absorption edge measurements on I_xZrS_2 , I_xHfS_2 ($\text{I} = \text{Cu}, \text{Fe}$ for $x \leq 0.22$) and Ni_xZrS_2 ($x \leq 0.15$) and suggested that the intercalated atom might be regarded as analogous to deep level impurities leading to an additional energy level near the top of the valency band, or, alternatively a modification of the host crystal valency band might occur due to interaction between the intercalate and sulphur atoms. The superconductivity behaviour of these indium intercalated compounds is yet to be investigated.

The thermal stability behaviour of In_xWS_2 ($0 \leq x \leq 1$) intercalation compounds in an inert atmosphere of argon indicated that the stability of WS_2 is maximum and is decreased with increasing indium content [104, 105].

Table VII records the intercalation compounds of tungsten dichalcogenides reported so far.

5.7. Thermal stability

The thermal stability of tungsten disulphide is still not clearly understood. At temperatures below 1150°C no sign of decomposition was noticed and WS_2 was found to sublime slowly but in weighable amounts e.g. in a zone from

1000 to 900°C . The product consisted of a well crystallized WS_2 [106]. When heated in vacuum, decomposition of WS_2 takes place at a temperature above 1150°C [61, 62]. It undergoes marked changes with temperature in an atmosphere of hydrogen. It reduced disulphide completely to tungsten metal at 800 to 900°C .

Thermal behaviour of WSe_2 prepared by the reaction of WO_3 in a current of H_2Se has been powdered as well as in compressed form in vacuum (10^{-4} to 10^{-5} torr) [107]. It was observed that the powdered and compressed form dissociated at 900°C and 1200°C respectively. Gladohenko *et al.* [108] further investigated the thermal dissociation of WSe_2 obtained directly from the elements, in vacuum (10^{-4} to 5×10^{-6} torr). These observations have led to the conclusion that it is stable at $\leq 800^\circ\text{C}$, but decomposes rapidly into W and Se at higher temperatures.

Yanaki and Obolonchik [109] studied the thermal stability of WTe_2 which is potentially useful as an antifriction material in vacuum, hydrogen and helium. The stability was found to be highest in an inert atmosphere and lowest in vacuum. In each case, loss of tellurium started at 400 to 600°C . The gradual loss of tellurium resulted in the formation of compounds corresponding to lower homogeneity limits and was stable at 850 to 1000°C . The loss of tellurium was followed by the formation of free metal.

TABLE VII Intercalation compounds of WX_2 ($\text{X} = \text{S}, \text{Se}$)

WS_2	WSe_2	Reference
$\text{I}_{0.8}\text{WS}_2$ ($\text{I} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$)	$\text{K}_{0.5}\text{WSe}_2$	[90–92]
$\text{Sr}_{0.2}\text{WS}_2$	$\text{Sr}_{0.2}\text{WSe}_2$	[93, 94]
Eu_xWS_2^*	$\text{Eu}_x\text{WSe}_2^*$	[95]
In_xWS_2^*		[98]

* x = varies from 0 to 1.00

The oxidation products of thermal decomposition of tungsten dichalcogenides are stable tungsten oxide and volatile chalcogen oxides. The kinetics of oxidation of WS_2 have also been investigated [110].

6. Uses

The catalytic effects of WS_2 in various chemical reactions have been known for decades [111]. It has been used as a catalyst in hydration, hydrogenation, hydrogenolysis, hydrodesulphurization and isomerization reactions either in pure form or supported on carriers. The most significant property of WS_2 is that it is widely used for removing sulphur compounds from petroleum or coal derived liquids.

Tungsten disulphide and diselenide possess very good antifriction properties, since the coefficient of friction, k_f , is 0.05 to 0.01 in vacuum and 0.1 to 0.2 in air at 1 kg cm^{-2} pressure and 0.025 in vacuum at a pressure of 1000 kg cm^{-2} . Due to their good adhesive characteristics and stability against moisture they are extensively employed as a solid lubricant. The lubricating properties of WS_2 at high pressure ($< 80 \text{ kbars}$) and temperature ($< 200^\circ\text{C}$) have also been investigated [112].

During the last few years, several efforts have been made to investigate new semiconducting materials for their use in photoelectrochemical (PEC) solar cells. The primary problem concerned with these semiconducting electrodes is their susceptibility towards photocorrosion, which in fact has presented a major difficulty in cell developments. But very recently under the impetus of modern energy studies throughout the world, the semiconducting transition metal dichalcogenides with special reference to WS_2 [113, 114] and WSe_2 [115–129] have been proved quite efficient electrodes for their use in photochemical devices for the conversion of sunlight into electricity or chemical energy. These materials are not as susceptible to photocorrosion as many other electrode materials whose band gap lies in the maximum for solar energy conversion efficiencies. Tributsch [129] suggested that the conduction band in transition metal dichalcogenides are primarily d in character and the absorption of photons with energy greater than their band gap could therefore result in d–d transition which could not tend to break the bond between the metal and chalcogen atoms.

This explains the enhanced stability of these materials over other semiconductors with more polar bonding, such as CdS and GaAs, in which promotion of an electron from the valency band to the conduction band tends to break metal – anion bonds resulting in photocorrosion.

7. Conclusions

Preparation methods, crystal structures and band models of tungsten dichalcogenides have been described. Physical, chemical, optical and electrical properties, intercalation and thermal stability behaviour of these compounds have been reviewed. Some important uses of tungsten dichalcogenides have also been mentioned.

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Received 28 December 1984
and accepted 31 January 1985