JOURNAL OF MATERIALS SCIENCE 27 (1992) 3693–3705

Review
Preparation, structure and properties of transition metal trichalcogenides

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In recent years, the transition metal trichalcogenides (TX_3) of Group IVB, VB and VIB have received much more attention because of the considerable diversity in their physical properties. The most striking feature of these compounds is that the structure here may be classified into three types depending on the number of different TX_3 chains present in the unit cell. Thus $ZrSe_3$, $TaSe_3$ and $NbSe_3$ are the representative compounds having one, two and three types of chain based on the different bond lengths for the $(X_2)^{2-}$ pairs in the base of the TX_3 trigonal prismatic framework. A similar model is also applicable in the case of NbS_3, with the addition of a 2*b*-superstructure associated with the formation of niobium pairs. The chain structure also facilitates the process of intercalation which has been most effectively used in secondary batteries. These compounds exhibit the superconductivity phenomena and charge density wave, etc. and also find application in photoelectrochemical cells. An attempt has been made here to review the up-to-date chemistry of transition metal trichalcogenides related with their preparation, structure and properties such as physical and chemical, thermodynamic, electrical, magnetic and optical properties, intercalation and use in the photoelectrochemical cells.

1. Introduction

Transition metal trichalcogenides TX_3, (T is a transition metal of Group IVB, VB and VIB, X is a chalcogen, S, Se, Te) constitute structurally and chemically a well-defined family of compounds. These trichalcogenides are thin fibrous ribbons and offer several interesting phenomena originating from their strong anisotropy. The electronic structure of these compounds is of considerable interest both from the experimental and theoretical points of view. They possess a pseudo one-dimensional structure where there is an infinite chain of trigonal prismatic $[TX_6]$ units extending parallel to the *b*-axis and share upper and lower faces. The chains with strong ionic covalent (or metallic) bonding are separated by a relatively large distance and interchain bonding, and are weak. Thus *a*- and *c*-planes perpendicular to the chain axis in TX_3 crystals are more compressive than in more ordinary metals, alloys or compounds. As a result, these compounds exhibit marked anisotropy in most of their physical properties, which accounts for the great interest in this family of compounds. In addition, the chain-type structure in TX_3 results in the formation of intercalation compounds. These compounds also exhibit superconductivity and charge density wave (CDW) phenomena. The attemps have also been made to study the photoelectrochemical behaviour in these compounds.

The main purpose of this review is to present the up-to-date chemistry of the transition metal trichalcogenides concerned with their preparation, structure and properties, e.g. physical, chemical, thermodynamic, magnetic, electrical, optical and intercalation, and their use in photoelectrochemical cells. It is hoped that the present article will help research workers in selecting methods for growth of crystals with desired properties, in order to stimulate further research in the domain of transition metal trichalcogenide chemistry.

2. Experimental procedure

2.1. Group IV

TiS_3 can be prepared by passing a mixture of $TiCl_4$ and H_2S vapours in a pyrex tube in the temperature range 480–540 °C [1]. The product is mainly TiS_2 which is further subjected to an excess of sulphur in a vacuum-sealed tube for 3 days at 600 °C. The product still contains chloride and so is further heated to about 600 °C for 2 days. This results in the formation of TiS_3 and some unreacted sulphur which is mainly removed by distillation at 400 °C. Another simple method to prepare a chlorine-free product is from the direct union of the elements in a vacuum-sealed tube at 650 °C for 4 days [2]. Recently, TiS_3 has been prepared by the reaction of $TiCl_4$ and organic sulphurizing agents, e.g. hexamethyldisilthane, simply by heating the obtained amorphous powder or by heating this powder in the presence of sulphur at 300 °C [3]. Oshima *et al.* [4] synthesized it from the elemental constituents in appropriate proportion at 600–750 °C and 10–20 MPa [5].

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TiS_3 is a black crystalline powder with a density of 3.22 g cm^{-3}. It is unaffected by hydrochloric acid and is converted to dioxide hydrate by nitric acid, with the release of sulphur. TiS_3 reacts rapidly with boiling 5 N NaOH solution. It forms TiO_2 on heating in air.

The trisulphides of zirconium, in general, and hafnium, in particular, have been less studied than that of titanium. The preparative methods for ZrS_3 are very similar TiS_3, i.e. by reacting $ZrCl_4$ vapours with H_2S or from elements in the temperature range 600–800 °C. ZrS_3, in general, and HfS_3, in particular, have been less studied than that of titanium. The preparative methods for ZrS_3 are very similar to TiS_3, i.e. by reacting $ZrCl_4$ vapour with H_2S or from elements in the temperature range 600–800 °C. $ZrTe_3$ thin films were also deposited by a sputtering technique using Zr–Te targets on various substrates e.g. glass, Si, Mo, etc. [5]. ZrX_3 and HfX_3 decompose, when heated in air, to the corresponding ZrO_2 and HfO_2 [6].

2.2. Group V

An exhaustive study on the Nb–S system has been carried out by Kodyk and Jellinek [7]. NbS_3 and TaS_3 can be prepared directly from the elements in a stoichiometric proportion with a slight excess of sulphur at 700 and 750 °C, respectively. NbS_3 can also be obtained in a similar way when heated at 700 °C for 15 days [17]. Kikkawa *et al.* [8, 9] used for the first time the high pressure–high temperature techniques to synthesize TaS_3, NbS_3, $TaSe_3$ and $NbSe_3$. The procedure involved the mixing of respective powdered metal and chalcogen to give the desired composition which was then subjected to 700 °C temperature and 2 GPa pressure for 30 min. All the products were black sintered masses. This method has not been used for other trichalcogenides and therefore requires further attention. $NbTe_3$ and $TaTe_3$ are not known to exist.

TaS_3 remains unaffected by hydrochloric acid and sodium hydroxide, but is rapidly oxidized by nitric acid. It decomposes to TaS_2 and sulphur when heated at 650 °C in a vacuum.

2.3. Group VI

Opalovskii and Fedorov [10] were the first to review the chemistry of molybdenum chalcogenides. MoS_3 is one of the sulphide molybdenums which is well established. Its direct synthesis from the elements is not feasible from the thermodynamic point of view. MoS_3 can be prepared by saturating alkali molybdate with H_2S or dissolving MoO_3 in alkali sulphide and then decomposing the thiomolybdate thus formed with dilute hydrochloric acid [10, 11]. MoS_3 thus prepared is reported to have variable compositions, e.g. $MoS_3 \cdot 2H_2O$ [12, 13], $MoS_3 \cdot H_2O$ [14], $MoS_{3+x} \cdot yH_2O$ [$(0 < x < 1)$; $(y > 0)$] [15], $3MoS_3 \cdot H_2O \cdot H_2S$ [16, 17]. Pure MoS_3 can be obtained by thermal decomposition of $(NH_4)_2MoS_4$ crystals in the temperature range 150–280 °C [14]. A solid state reaction between MoO_3 and thiourea at 130 °C has also been reported [18]. In recent years, thin films of MoS_3 have been deposited by electrochemical methods from aqueous and non-aqueous solutions of $(NH_4)_2MoS_4$ [19]. The chemical vapour deposition technique from MoF_6 and hexamethyldiseathiane at 200–250 °C has also been successfully employed [20].

MoS_3 is a brownish-black product. Prolonged heating at 1100 °C in vacuum is necessary to convert MoS_3 to well-crystallized MoS_2 [21–24]. In air it loses water of hydration at about 200 °C but does not become oxidized below 390 °C [13, 15]. It was reported that the conversion of nonstoichiometric MoS_3 to MoO_3 during heating in air proceeds through amorphous and crystalline MoS_2 and partially MoO_2 [25].

WS_3, $MoSe_3$ and WSe_3 can be prepared in a similar manner to MoS_3 from ammonium thiomolybdate and thioselenate, respectively [26]. The solubility of WS_3 in water depends on temperature. It is soluble in a cold concentrated solution of CO_2, indicating its acidic character. It is also soluble in basic solutions. Above 1700 °C, WS_3 dissociates to WS_2 and sulphur. Hydrogen reduces WS_3 to WS_2 and then metallic tungsten, unlike MoS_3, which is reduced to metallic molybdenum via the formation of first MoS_2 and then Mo_2S_3 [27]. WSe_3 is a black solid and soluble in concentrated hydrochloric acid. It is decomposed to WSe_2 at 220 °C.

2.4. Single-crystal growth

Successful attempts have also been made to grow single crystals for some of transition metal trichalcogenides [28–31]. The crystals are grown from the vapour phase, slow cooling producing sublimation, or by mineralization. But the chemical transport techniques have been used more frequently by using I_2, ICl_3, S_2Cl_2 or $TeCl_4$ as transporting agents. Levy and Berger [32] reviewed the most important results on the crystal growth of these transition metal trichalcogenides. The crystals are in the shape of platelets and ribbons or needle-type for Group IVB and VB, respectively. No crystalline materials could be prepared for Group VIB compounds. Table I records the most suitable preparative conditions to grow the single crystals of larger size and best quality.

3. Crystal structure of transition metal trichalcogenides

The crystal structure of transition metal trichalcogenides has received much more attention in the last few years [33–36]. The crystal structure, in general, possess the same structural unit, i.e. TX_6 trigonal prisms stacked in order to form TX_3 trigonal prismatic chains, which develop parallel to the *b*-axis of the monoclinic cell (Fig. 1). As a result, there is a tendency in these chalcogenides to attribute one-dimensional characteristics. However, they differ from each other in shape and packing of trigonal prism chains. Such differences result in a large variation in electrical properties. Wilson [37] classified these trichalcogenides into three structural types based on [TX_3] chains which may not be equivalent due to the difference in chalcogen–chalcogen bonds in the trigonal prismatic

TABLE I Conditions to grow single crystals of transition metal trichalcogenides by chemical transport reactions

Crystals	Temperature (°C)		Transporting agents	Best conditions	
	Source	Growth		(°C)	Agent
TiS_3	600–500	500–450	I_2, S_2Cl_2, ICl_3, S	550–500	ICl_3
ZrS_3	850–650	800–600	I_2, S_2Cl_3, ICl_3	750–730	S_2Cl_3
				650–600	I_2
	950–750	725–550	I_2	650–600	I_2
$ZrSe_3$	750–650	700–600	I_2, Se_2Cl_2	650–600	I_2
$ZrTe_3$	800–650	700–600	I_2, $TeCl_4$	650–600	I_2
HfS_3	850–650	800–600	I_2, S_2Cl_2	650–600	I_2
$HfSe_3$	700–650	650–600	I_2, Se_2Cl_2	650–600	I_2
NbS_3	700–650	700–600	I_2, S_2Cl_2, S	670–610	10%S
$NbSe_3$	750–650	700–600	I_2, S_2Cl_2, Se, ICl_3	720–710	10%Se
				680–660	ICl_3
TaS_3	700–650	550–450	I_2, S_2Cl_2, S	550–500	S_2Cl_2, 30%S
$TaSe_3$	750–650	710–600	I_2, ICl_3, Se	700–680	10%Se

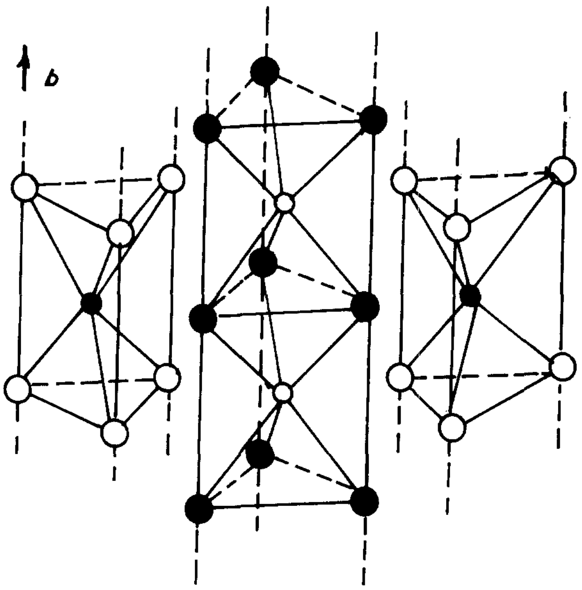

Figure 1 Schematic general representation of transition metal trichalcogenides.

base of the trigonal prismatic rearrangements. This classification is primarily based on the relative position of $[TX_3]$ chains. Thus the transition metal trichalcogenides which exhibit one, two or three types of chain may be represented by $ZrSe_3$, $TaSe_3$ and $NbSe_3$, respectively.

The crystal structure of $ZrSe_3$ shows the presence of one type of chain with an Se–Se bond length of 0.234 nm, which corresponds to the formation of $(Se_2)^{2-}$ pairs (Fig. 2a) [38, 39]. Further studies based on X-ray spectroscopy also confirmed the $(X_2)^{2-}$ pairing in the trigonal base [40]. The figure shows that in the $ZrSe_3$ prism, two or more selenium atoms in the base of each prism are bonded at a distance comparable to pure selenium (0.230 nm) while other Se–Se distances are considerably larger. The prisms share their tops and bottom with each other, forming columns of $ZrSe_6$ along the *b*-axis. The columns are displaced by *a*/2 with respect to each other. Each metal has two selenium neighbours in adjacent columns at distances scarcely longer than those of its six intracolumn ligands. The one-dimensional columns are linked with the intercolumn bonds forming successive layers by van-der Waal's gaps. The crystal structure of NbS_3 may also be discussed on the same grounds. Here, the S–S distance corresponds to the formation of $(S_2)^{2-}$ anions. However, the presence of 2*b*-superstructure has also been observed and is associated with the formation of niobium pairs [41].

The structure of TiS_3 is isostructural with $ZrSe_3$ [42]. It shows that parts of the chalcogen atoms form pairs so that the compound may be recorded as a polysulphides $Ti^{4+}S^{2-}(S_2)^{2-}$, which was further confirmed by X-ray photoelectron spectral studies [43]. The cation is surrounded by four S^{2-} ions and two $(S_2)^{2-}$ groups. The crystal structure of ZrS_3 and HfS_3 has been much less studied than that of TiS_3. These may also be regarded as having the same polysulphide structure.

The structure of $TaSe_3$ is monoclinic having two types of regular chain (Fig. 2b) [44]. The Se–Se bond lengths are 0.258 and 0.291 nm, respectively, exceeding the value of $(Se_2)^{2-}$ pairs.

$NbSe_3$ possess three kinds of chain in unit cell corresponding to a short (0.237 nm) (III), a mean (0.248 nm) (I) and a long 0.291 nm (II) Se–Se bond in the base of trigonal prismatic chains (Fig. 2c) [45–47]. The short bond length, 0.237 nm, is due to $(Se_2)^{2-}$ pairs as in $ZrSe_3$, and would correspond to a weakening of the Se–Se bond and a strengthening of the Nb–Se bond. This would bring about an intermediate situation for the niobium atoms (between Nb^{4+} and Nb^{5+}).

TaS_3 exists in an orthorhombic modification whose structure is not well established [48]. The unit cell is large and contains 24 chains. The formation of monoclinic phase [8, 49, 50] has also been reported. It is isostructural to $NbSe_3$ with a little difference in interatomic distances (Fig. 2d). It possess here three kinds of six chains. There are two short distances, S–S = 0.207 (III) and 0.211 nm (I) leading to a covalent bonding $(S_2)^{2-}$, and a long one of 0.284 nm (II) in Columns I and III, respectively, and they are interconnected through Column II.

Band structure calculations have been made for some of the transition metal trichalcogenides in order

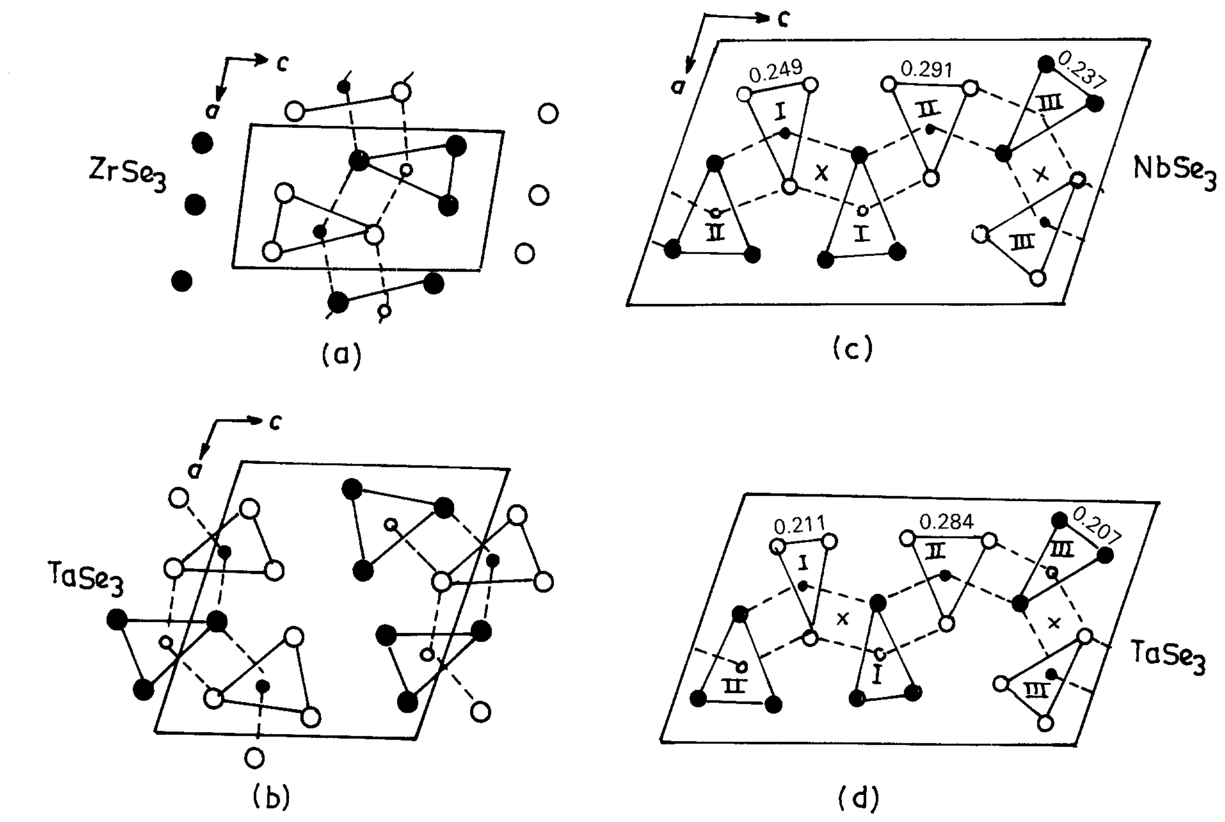

Figure 2 Projection along [0 1 0] of the monoclinic (a) $ZrSe_3$, (b) $TaSe_3$, (c) $NbSe_3$, (d) TaS_3 structure. $\begin{pmatrix} O & T \\ O & Se \end{pmatrix} y = \frac{1}{4}$.

to explain the change in their properties based on the crystal structure differences [51–56]. The photoelectron spectroscopic studies have also been used for TiS_3, NbS_3 and TaS_3 in order to obtain information about their valency band structure [57]. The presence of stacking disorder in NbS_3, and $ZrSe_3$ has also been investigated [58].

MoS_3 and WS_3 are amorphous towards X-rays [59]. The earlier studies on MoS_3 provided no conclusive evidence that it is a definite chemical compound rather than an intimate mixture of sub-crystalline MoS_2 and amorphous sulphur [60–62]. However, it was concluded from X-ray photoelectron spectral measurements that MoS_3 is an intimate association of subscrystalline MoS_2 and amorphous sulphur [63]. Diemann [64] studied extensively the structure and properties of MoS_3 and its related non-crystalline trichalcogenides, and concluded that these trichalcogenides are compounds in their own right, and not a mixture, as suggested by previous studies [60–63]. Liang *et al.* [65], based on their experimental observations, proposed a chain-type structure similar to crystalline trichalcogenides of neighbouring IVB and VB group elements where adjacent metal atoms are bridged with three sulphur atoms along the chain. The structure has two metals paired up with a shorter metal–metal distance and one polysulphide atom in the chain bond in every other sulphur triangle. As a result, these amorphous trichalcogenides may be regarded as $T(V)(S_2)^{2-}_{1/2}(S_2)^{2-}$. Raman spectra studies of MoS_3 also confirmed the presence of polysulphide bonds and supported the chain-type structure for amorphous MoS_3, similar to that of crystalline MS_3 (M = Ti, Zr, Hf, Nb, Ta) [66]. The other workers [64, 67–69] also investigated MoS_3 and suggested that MoS_3 is in the reduced state, probably Mo(V). Goodenough [69], while reviewing the solid state chemistry of molybdenum compounds, also concluded that the oxidation state of molybdenum in trisulphide is indeed Mo(V), and that the molecular formula is $(Mo^{5+})_2S_2^{2-}(S^{2-})_4$. ESR [70] and EPR [71] spectral studies on MoS_3 have also been reported.

Table II records the structural type, space group and lattice parameters of various transition metal trichalcogenides [72–92].

4. Properties of transition metal trichalcogenides

4.1. Thermodynamic properties

Thermodynamic properties, e.g. heat of formation, entropy, free energy function, etc. for some of the transition metal trichalcogenides are recorded in Table III, together with their densities [59, 93–99].

4.2. Magnetic, electrical and optical properties

Transition metal trichalcogenides TX_3 (T = Ti, Zr, Hf, X = S, Se) and TS_3 (T = Nb, Ta) are diamagnetic semiconductors (Table II). TiS_3 has a Seebeck coefficient, α, of $-500\,\mu V\,C^{-1}$, $E_g = 0.9$ eV (optical absorption) and $e_d = 0.14$ eV (resistivity–temperature curve) [73]. It is a semiconductor with metallic lustre and has a maximum value of electrical conductivity at around 200 K [73]. In order to investigate the possibility of Pierles transition in TiS_3, Kikkawa *et al.* [100] conducted conductivity measurements along the *b*-axis in the temperature range 77–400 K, and elec-

TABLE II Magnetic and electrical properties and crystallographic data for some transition metal trichalcogenides

Compound	Magnetic and electrical properties	Structural type	Space group	Lattice parameter					References
				a (nm)	*b* (nm)	*c* (nm)	β (deg)	*V* (10^3 nm^3)	
TiS_3	Diamagnetic semiconductor	Monoclinic	$P2_1$ or $P2_1/m$	0.501	0.3400	0.8800	98.4	–	[74–76]
	[72, 73]	Monoclinic	$P2_1/m$	0.4958	0.3400	0.8778	97.32	146.8	[77]
		Monoclinic	–	0.4940	0.3404	0.8826	97.3	–	[78]
		–	–	0.4973	0.3443	0.8714	97.3	–	[79]
ZrS_3	Diamagnetic semiconductor	–	C^2_{2h} [80]	0.5124	0.6244	0.8980	97.28	165.4	[77]
	[72, 73]			0.4990	0.3633	0.8988	97.3	–	[78]
$ZrSe_3$	Diamagnetic semiconductor	Monoclinic	–	0.5411	0.3749	0.9444	97.48	189.9	[77]
	[72–74]	Monoclinic	–	0.5409	0.3746	0.9439	97.30	–	[78]
$ZrTe_3$	Metallic [81]	–	–	0.5894	0.3926	1.0100	97.82	231.5	[77]
HfS_3	Diamagnetic semiconductor [72, 74]	–	–	0.5092	0.3525	0.8967	97.38	162.8	[77]
$HfTe_3$	–	Monoclinic	–	0.5388	0.3722	0.9405	97.80		[78]
		–	–	0.5879	0.3902	1.0056	97.98	228.5	[77]
NbS_3	Diamagnetic semiconductor	Monoclinic	–	0.9680	0.3370	1.4830	109.90	454.3	[9]
	[6, 82]	Triclinic	$P\bar{1}$	0.4963	0.673	0.9144	97.14	303	[41]
		Triclinic	–	0.4949	0.6684	0.9148	97.2 ($\alpha = \gamma = 30$)	–	[78]
		Monoclinic	–	1.5635	0.3474	0.9986	109.3	–	[78]
		Monoclinic	C^2_2–$P2_1$ or C^2_{2h}–$P2_1/m$	0.4940	0.6740	1.8100	97.5	–	[83]
$NbSe_3$		–	–	0.4980	2×0.338	0.913	97.5	–	[84]
	–	Monoclinic	–	1.002	0.3470	1.563	109.5	512.8	[9]
		Monoclinic	$P2_1/m$	1.000	0.3480	1.5629	109.47	513.3	[85]
		Monoclinic	$P2_1/m$	1.0478	0.3478	1.5626	109.50	513.3	[86]
TaS_3	Diamagnetic semiconductor	Monoclinic	–	0.9520	0.3350	1.4920	110.00	446.8	[8]
	[28, 82, 86]	Orthorhombic	$C222_1$, $C222$ or C_{mmm}	3.6804	1.5173	0.3340	–	186.5	[48–87]
		Monoclinic	$P2_1/m$	0.9515	0.3341	1.4912	109.99	445.0	[88, 89]
$TaSe_3$	Diamagnetic metallic	Monoclinic	–	1.002	0.348	1.565	109.6	513.4	[9]
	[28, 90]	Monoclinic	C^3_{3h}–$P2_1/m$	1.0421	0.3494	0.9836	106.36	–	[28]
		Monoclinic	–	1.0384	0.3500	0.9790	106.3	–	[78]
		Monoclinic	–	1.0374	0.3501	0.9827	106.11	–	[91]
		Monoclinic	$P2_1/m$	1.0402	0.3495	0.9829	106.26	350.0	[92]
MoS_3	Amorphous								[59]
WS_3	Amorphous								[59]

TABLE III Thermodynamic data and density of some of the transition metal trichalcogenides

Compound	Molecular weight	Heat of formation, H^0 (kcal mol^{-1}) at 298 K	Entropy, S^0 (cal deg K^{-1} mol^{-1}) at 298 K	Free energy function	Density[a] (g cm^{-3})	Reference
TiS_3	144.09	− 102.7, − 99.2, − 99.7	21.7 ± 3	30.2 at 800 K 32.0 at 900 K	3.233	[77, 93–97]
ZrS_3	187.4	− 150 ± 15, − 151.6, − 158 ± 10	21.7	29.0 at 298 K 32.4 at 1000 K	3.751	[77, 93, 98]
$ZrSe_3$	328.1	− 100 ± 20	24.0 ± 3	–	5.708	[93, 98]
$ZrTe_3$	474.2	− 70 ± 20	33.0 ± 5	–	6.788	[77, 93]
HfS_3	274.68	− 149 ± 20	23.0 ± 4	33.4 at 900 K	5.573	[77, 93, 99]
$TaSe_3$	417.83	− 86 ± 10	22.0 ± 4	–	7.913	[96]
MoS_3	192.13	− 74 ± 5, − 61.48	18.0	–	–	[93]
WS_3	280.04	− 70 ± 5	− 18.5 ± 2.5	–	–	[93]

[a] HfS_3, 7.312 [77]; $HfTe_3$, 8.205 [77], NbS_3, 4.15 [8]; $NbSe_3$, 6.41 [8, 45]; TaS_3, 6.18 [7], 5.92 [48]; $TaSe_3$, 8.11 [8], 8.08 [48].

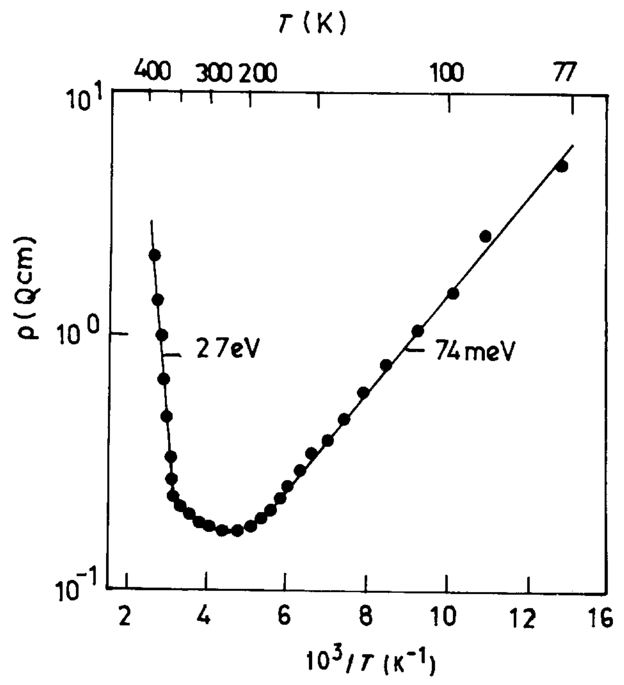

Figure 3 Temperature dependence of ρ for TiS_3 [100].

tron diffraction studies at room temperature (Fig. 3). It is seen that below 200 K resistivity increases with decreasing temperature with an activation energy of 74 meV and may be explained as due to a semiconducting extrinsic transition. It showed a minimum at room temperature ($\sigma = 2 \times 10^{-1}\ \Omega$ cm). After that it increased with temperature in the range 320–400 K with an activation energy of 2.7 eV. Such a change in conductivity suggested the posssibility of Pierles transition. Liang *et al.* [101] also measured conductivity and Seebeck coefficient between 40 and 335 K for TiS_3 and noted that the conductivity is non-exponential and temperature independent below its maximum value at 165 K, and frequency dependent. This, together with dependence of Seebeck coefficient, suggested the disorder effects in TiS_3. Gorochov *et al.* [79] found a room-temperature Hall coefficient value of 2×10^{18} electron cm^{-3}.

The electrical properties of compact as well as single crystals of zirconium trichalcogenides have also received attention. Perluzzo *et al.* [102] carried out resistivity, Hall coefficient, mobility and Seebeck coefficient measurements along the chain *b*-axis in the temperature range 100–500 °C on ZrS_3 crystals. This is a semiconductor with a room-temperature value of 15 Ω cm (Fig. 4a), which is 10^4 times lower than that of powder-compressed pellet, with an activation energy of 0.20 ± 0.02 eV. The Hall coefficient data are shown in Fig. 4b and can be fitted with the expression

$$R_H = 0.13 \exp(2400/T) \qquad (1)$$

over the entire temperature range, resulting in an activation energy of 0.20 eV. The variation of mobility with the temperature is shown in Fig. 4c and is based on the data from Fig. 4a and b. It is evident from the figure that at low temperatures, mobility is limited by ionized scattering and is given by $6.5 \times 10^{-3} T^{-3}$ cm^2 V^{-1} s^{-1}. The room-temperature

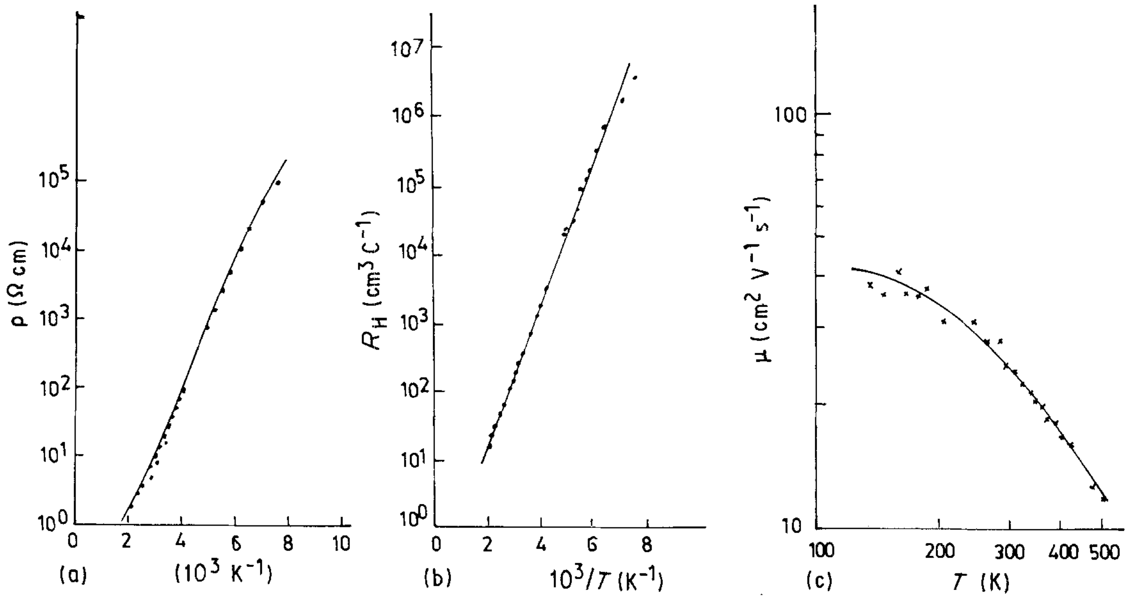

Figure 4 (a) ρ versus $10^3/T$, (b) R_H versus $10^3/T$ (the straight line represents a carrier activation energy of 0.02 eV, (c) μ versus T (the line represents the contribution of both ionic impurities and phonons) for ZrS_3 [102].

Seebeck coefficient value is $-850\ \mu V\ K^{-1}$, which is quite close to that already reported [7]. It decreased with decreasing temperature showing thereby a typical semiconducting behaviour (Fig. 5a, b).

The electrical transport properties data for single-crystal $ZrSe_3$ in the temperature range 100–400 K have also been investigated [103]. It is a semiconductor having a resistivity of $9 \times 10^2\ \Omega$cm. The Hall coefficient, R_H, is negative and the electron carrier concentration is $1.6 \times 10^{16}\ cm^{-3}$. The room-temperature mobility is $0.45\ cm^2\ V^{-1} s^{-1}$, which is very much smaller compared to ZrS_3 [102]. The mobility decreases and follows a simple power law of $T^{-1.5}$, which suggests that the scattering mechanism is dominated by photons. The room-temperature Seebeck coefficient value for $ZrSe_3$ is $-820\ \mu V\ K^{-1}$ and it increased linearly with reciprocal of temperature. $ZrTe_3$ shows a metallic behaviour [81, 103, 104]. The Group IVB transition metal trichalcogenides have also proved very attractive materials for photo-electrochemical measurements [79, 105, 106].

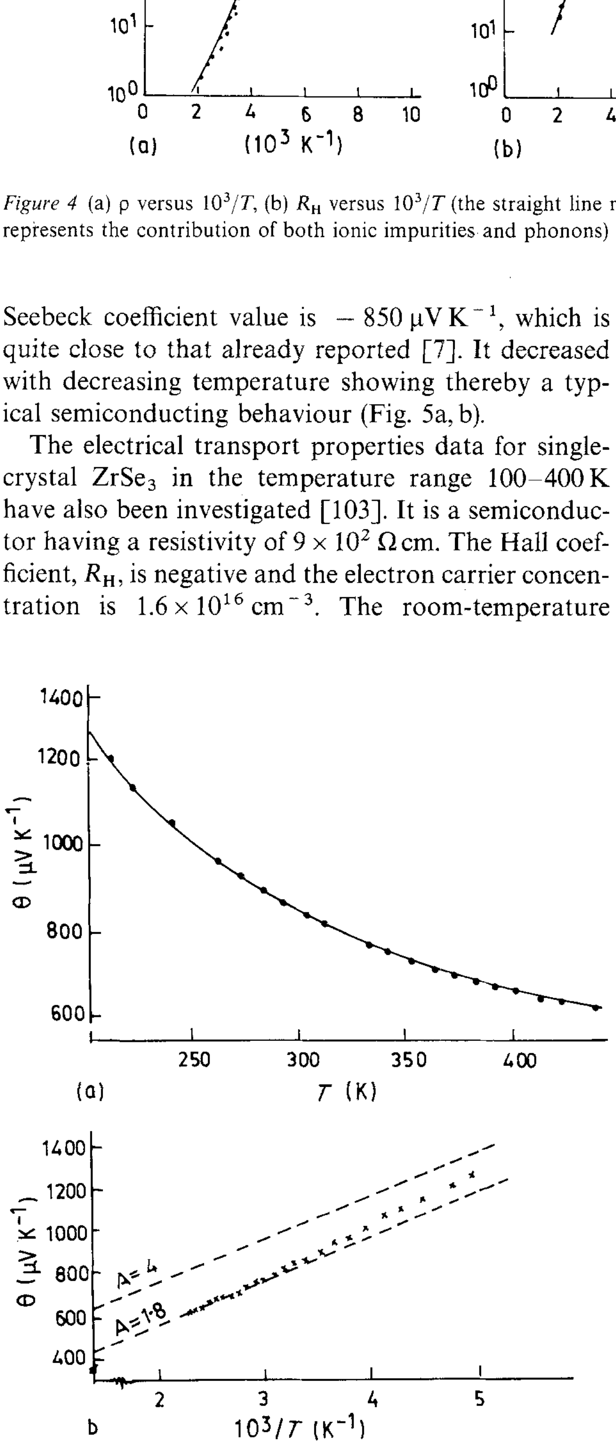

Figure 5 (a) Variation of the thermoelectric power with temperature for ZrS_3, (b) variation of thermoelectric power with reciprocal of temperature. (– – –) A carrier activation energy of 0.2 eV. When the phonons limit the mobility $A \approx 1.8$ and when ionic impurities dominate $A = 4$ [102].

NbS_3 exhibits semiconducting behaviour with a room-temperature resistivity of the order 10^2–$10^3\ \Omega$cm [6, 8, 83]. However, the electrical properties of $NbSe_3$ received much more attention [107, 108] where it showed the presence of two phase transitions at 145 and 59 K [109–112]. The room-temperature resitivity value for $NbSe_3$ is of the order 600 μΩcm. The temperature variation in the range 2–300 K is shown in Fig. 6. Above 145 K, ρ decreased

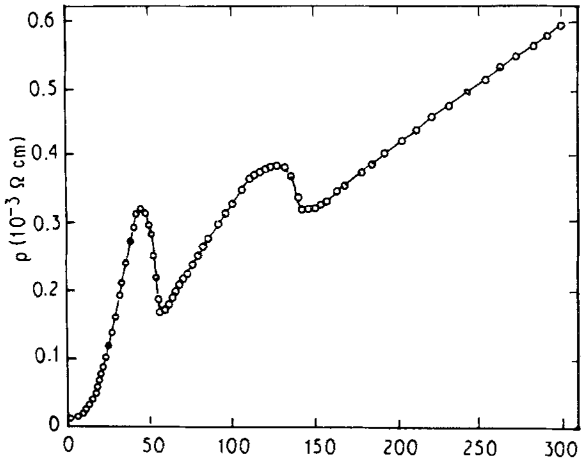

Figure 6 ρ versus T along the b-axis for $NbSe_3$ showing two phase transitions at $T_{c_1} = 145$ K and $T_{c_2} = 59$ K. The resistivity minima are at 125 and 49 K [109].

slightly with a slight curvature when the temperature was lowered, showing thereby a metallic behaviour. Below 10 K, resistivity appeared to saturate to a value limited by the defects. The most interesting features here are the two strong anomalies which appeared at $T_{c_1} = 145$ K with a maximum at 125 K and T_{c_2} with a maximum at 49 K, before resuming the metallic behaviour. The specific heat measurement also showed an anomaly at the same initial temperature, T_{c_1}, where resistivity increased very sharply. At T_{c_2}, it presents no pronounced anomalies (Fig. 7). These anomalies are strongly supressed by the applied electric field [113] and microwave field of 9 GHz [112]. This phenomenon has been interpreted in terms of charge density waves (CDW) as in many other low-dimensional conductors. Strong support for this hypothesis has been attained using electron and X-ray diffraction studies [46, 113–115]. Various models have been proposed dealing with CDW in $NbSe_3$ [116–118]. Briggs *et al.* [119] observed that T_{c_1} and T_{c_2} and the amplitude of the resistivity anomalies decreased with pressure. The resistivity measurements on $NbSe_3$ prepared by the high-pressure synthesis method, also confirmed the presence of two anomalies at 120 and 40 K [8], which are very similar to that already reported. Hall measurements [120–122] and further studies on thermoelectric power experiments [123] have also been made.

The electrical properties of TaS_3 also received much attention in the last few years [29, 50, 127–134]. Fig. 8 shows the temperature variation of resistivity in the range 77–480 K on a single crystal of an o-TaS_3 [29]. The room-temperature value for σ is of the order 3×10^{-4} Ω cm. It exhibits metallic behaviour above 270 K, whereas below 270 K a steep rise in resistivity is observed. It was therefore concluded that TaS_3 undergoes a metal–semiconductor transition at 270 K [29]. Further studies also confirm the presence of this transition but near room temperature [127], and it was explained in terms of Peirles instability [128]. Another form of TaS_3 is monoclinic, which undergoes transition at 212 and 161 K [131]. Kikkawa *et al.* [98] reported that the o-TaS_3 phase is semiconducting and not metallic, as reported earlier. The effect of pressure on transport properties of TaS_3 has also been studied and it showed a pressure dependence of metal–semiconductor transition [135–137]. The temperature variation of Seebeck coefficient on TaS_3 and $TaSe_3$ has also been studied and two types of carrier transport process in these compounds have been suggested [138, 139]. $TaSe_3$ is metallic (σ 300 K = 2×10^{-3} Ω cm) in character below room temperature, as shown in Fig. 9.

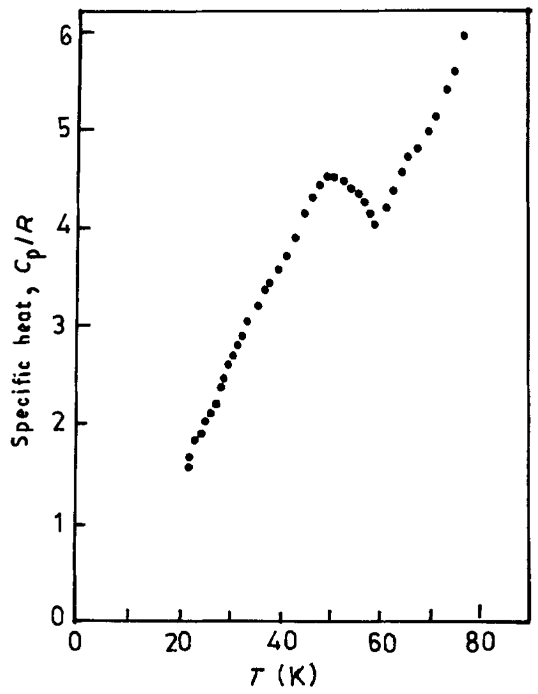

Figure 7 Heat capacity of $NbSe_3$ showing an anamoly at the same temperature (59 K) as ρ [110].

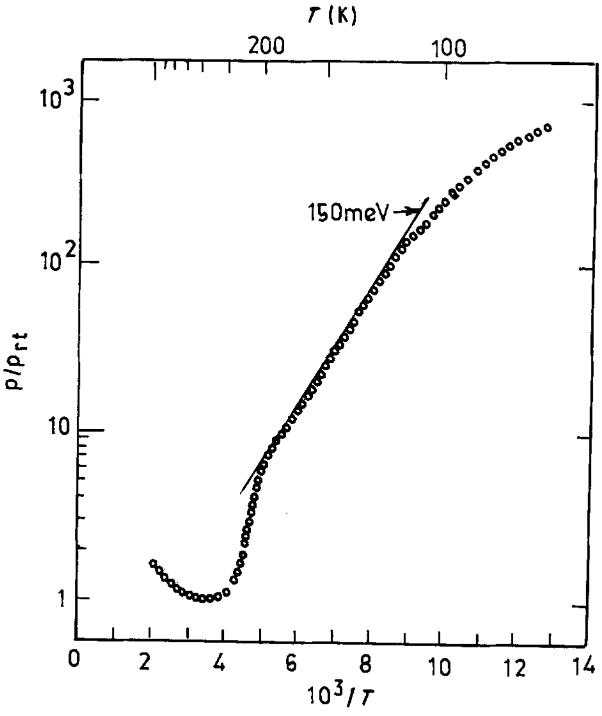

Figure 8 Electrical resistivity of TaS_3 [29].

Magnetic susceptibility measurements were carried out on $NbSe_3$ [140] and on $TaSe_3$ [140–145]. $NbSe_3$ is diamagnetic and showed a decrease in susceptibility beginning above its charge density transition at 144 K, but no change is observed near the transition at 59 K [140]. $TaSe_3$, however, showed a temperature-independent susceptibility with a classical metallic behaviour [109].

NbS_3 has also been found to be superconducting with a transition temperature, $T_c = 2$ K [146]. However, a great deal of interest was focussed on $NbSe_3$ [147–151]. It was noted that a small pressure is necessary for superconductivity to occur at 4.2 K. TaS_3 [151], $TaSe_3$ [141] and $ZrTe_3$ [152, 153] are also superconducting below 2 K.

4.3. Optical properties

The optical properties of layered transition metal trichalcogenides have received much less attention in contrast to their dichalcogenides analogue, which has been studied extensively by Wilson and Yoffe [154]. Grimmeiss *et al.* [73] made preliminary optical absorption measurements on $ZrSe_3$ and HfS_3 and obtained a direct band gap of 2.8 and 3.0 eV and an indirect band gap of 2.0 and 2.1 eV, respectively.

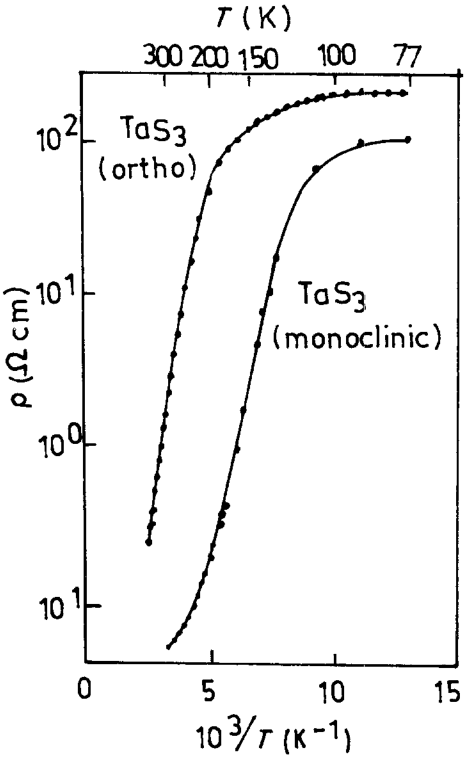

Figure 9 Temperature dependence of orthorhombic and monoclinic TaS_3 [8].

Further work on growth and the optical absorption spectrum of these compounds was done by Schairer and Schafer [31] and their results are shown in Fig. 10, which shows a very good similarity between them. The common features here in the high absorption region are a strong and weak absorption peak in both $k_{\|}$ and $k_{\perp}$ polarization parallel and perpendicular to the *b*-axis of these layered compounds. The peaks are sharper and more intense at 80 K than at room temperature. No further change in absorption is observed even at much lower temperature (4.2 K). The two compounds differed appreciably in their absorption in the low-temperature region. The fundamental optical gap energies were also estimated from the optical data and were in good agreement, as reported earlier [73]. ZrS_3, HfS_3 [36] and $ZrSe_3$ [155] have also been shown to exhibit dichroism. Kurita *et al.* [156] studied the absorption behaviour near the absorption edge for ZrS_3 and $ZrSe_3$ single crystals, and found that ZrS_3 has a direct band gap of 2.56 eV. The indirect band gaps of 2.055 eV ($E_{\|b}$) and 2.085 eV ($E_{\perp b}$) for ZrS_3 and of 1.535 eV ($E_{\|b}$ and $E_{\perp b}$) for $ZrSe_3$ are obtained at liquid helium temperature.

4.4. Intercalation

Transition metal trichalgonides TX_3 (T = Ti, Zr, Hf; X = S, Se) form intercalation compounds [157–173] when reacted with *n*-butyl lithium or by an electrochemical method [157–171] as follows

$$x\text{Li} + xe^- + \text{TX}_3 \rightarrow \text{Li}_x\text{TX}_3 \qquad (2)$$

The optical, infrared and X-ray diffraction studies confirmed the formation of intercalation compounds.

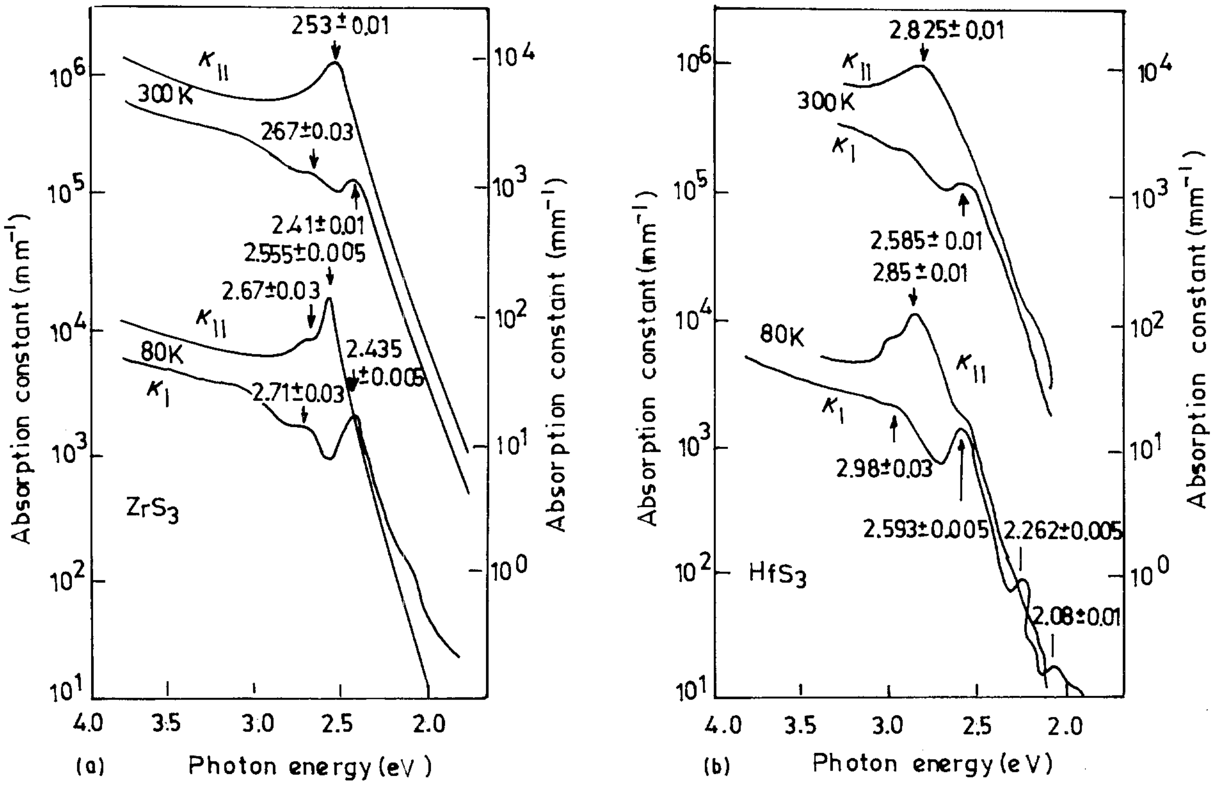

Figure 10 Absorption spectrum of (a) ZrS_3, (b) HfS_3 at 300 K (upwardly shifted right-hand scale, and 80 K (left-hand scale), $k_{\|}$ and $k_{\perp}$ refer to the polarizations parallel and perpendicular to the *b*-axis of the layer compound [31].

TALBE IV Lattice expansion of Li_3TX_3 intercalation compounds[a]

Compounds	Pure TX_3				Li_xAX_3			
	a (nm)	b (nm)	c (nm)	β (deg)	Δa (nm)	Δb (nm)	Δc (nm)	Δβ (deg)
Li_3TiS_3	1.111	0.346	0.912	98.0	0.12	+ 0.006	0.034	0.7
Li_3ZrS_3	1.12	0.359	0.922	100	0.10	− 0.003	0.024	0.7
Li_3ZrSe_3	1.18	0.376	0.968	99.1	0.10	+ 0.001	0.024	1.6
Li_3HfS_3	1.21	0.352	0.924	100	0.19	− 0.008	0.027	2.6
Li_3HfSe_3	1.15	0.371	0.952	98.2	0.07	− 0.001	0.009	0.7
Li_3NbS_3	1.70	0.348	1.15	98.1	0.14	0.000	0.140	12.7

[a] Δa, Δb, Δc and Δβ are the differences in lattice parameters and Bragg angles between the pure and lithiated trichalcogenides.

During this process, three lithium atoms are incorporated into the host crystal, while the TX_3 chains remain intact. Such reactions are accompanied by minimum structural changes, and often only by a small lattice expansion, and are reversible by appropriate thermal or chemical treatments. The diffraction pattern in such cases could be indexed on the basis of an expanded monoclinic lattice with the b-axis (chain axis) remaining constant.

Studies were also made to discover how the three lithium atoms are intercalated in the host MX_3 [158, 169]. A two-step mechanism has been proposed to explain the results of electrochemial intercalation [158, 159, 164] as follows:

$$MX_3 + 2Li \rightarrow Li_2MX_3 \qquad (3)$$

and

$$Li_2MX_3 + xLi \rightarrow Li_{2+x}MX_3 \quad (0<x<1) \qquad (4)$$

It is believed that the first step is responsible for breaking X–X bonds in MX_3 (i.e. $X\text{–}X^{2-} + 2e^- \rightarrow 2X^{-2}$) whereas the second step is believed to reduce the metal ($M^{4+} + e^- \rightarrow M^{(4-x)+}$). The electrochemical and diintercalation studies on Li_xMX_3 also show that the reaction is reversible only for ($2 < x < 3$). The irreversible behaviour for the composition range $0 < x < 2$ has been interpreted in terms of structural changes from prismatic to octahedral coordination [161] which the metal atom is presumed to undergo during the first step of the intercalation process. However, according to Canadell *et al.* [173], this mechanism cannot be used to explain the results for chemical intercalation of MX_3 with n-BuLi. For chemical intercalation, a one-step mechanism has been proposed. During the process of intercalation of MX_3 with x Li ($x < 3$), there are always two phases Li_3MX_3 and MX_3, as if a metal atom is affected by three lithium atoms at a time [160, 172]. The X-ray analysis shows that all the parameters change from a, b and c in MX_3 to approximately $2a + 1$, b and $c + 0.3$ in Li_3MX_3, and this does not support the proposal of a prismatic to octahedral coordination change as a reason for irreversibility of lithium intercalation in Li_xMX_3 ($0 < x < 2$). The infrared and Raman studies [172] on Li_3MX_3 show that lithium intercalation of MX_3 does indeed break the X–X bond.

The transition metal trichalcogenides of Groups IVB, VB and VIB also possess a marked difference towards electrochemical reversibility. For example, in TiS_3, low reversibility compared to $NbSe_3$ may be associated with a less stable trigonal prismatic coordination around the metal atom. A tendency to exhibit the octahedral coordination would lead to an irreversible situation. Thus it may be possible to make a battery having an energy density three times higher than is possible using TX_2 (Table V).

In recent years, MoS_3 has been proved to be a relatively more effective cathode material in making a battery by its reaction with lithium, but most of the information is guarded by patents [174–199]. The theoretical energy density of lithium cells based on reaction by the n-BuLi technique and electrochemically to form Li_4MoS_3 is significantly higher (Table V) than is reported for crystalline transition metal sulphides. Whittingham *et al.* [200] proposed a mechanism for lithium insertion in MoS_3 and TiS_3 and observed high reversibility in the former and poor in the latter case. The X-ray absorption spectroscopic studies have been made to determine the structure of MoS_3, WX_3, (X = S, Se) [201] and their lithium intercalation compounds [202]. It shows that the fully lithiated structure of Li_4MoS_4 [Mo–Mo = 0.266(3) nm, Mo–S = 0.250(3) nm] consists of an octahedral Mo_6 cluster analogous to those found in Chevrel phase materials. Similar clusters may be formed on lithium intercalation of WS_3 and WSe_3 with metal–metal, metal–chalcogen distances for intercalation compounds Li_4WS_3 and Li_5WSe_3 of 0.264(3), 0.247(3), 0.267(3) and 0.261(3) nm, respectively.

In addition, the formation of sodium intercalation compounds of TiS_3, NbS_3 and TaS_3 have also been reported [203]. These results demonstrated that TiS_3 disproportionate to TiS_2 and NbS_3 gradually under-

TABLE V Cell e.m.f. and energy density for some Li/TX_3 couples

TX_3	Cell e.m.f. (V)	Energy density $(\mathrm{Wh\,K\,g^{-1}})$
TiS_3	1.7	840
ZrS_3	1.2	450
$ZrSe_3$	1.7	390
$HfSe_3$	1.3	240
NbS_3	1.6	10
$NbSe_3$	1.5	340
TaS_3	1.6	430
$TaSe_3$	1.7	310
MoS_3	2.0	1040

goes irreversible transformation that decreases the amount of niobium which can be reversibly inserted, whereas TaS_3 is found to be most suitable. TaS_3 also forms an intercalation compound with hydrazine where the transition temperature is suppressed from 2.2 K to 1.5 K [204]. No attempts have been made to undertake similar studies on other transition metal trichalcogenides.

Conclusion

The preparative methods and crystal structures of transition metal trichalcogenides are described. The properties, such as physical, chemical, thermodynamic, magnetic, electrical, optical and intercalation, etc., are reviewed.

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Received 2 September
and accepted 10 September 1991