JOURNAL OF MATERIALS SCIENCE 23 (1988) 388–394

Structure, properties and morphological studies of indium intercalation compounds of tungsten disulphide, In_xWS_2 ($0 \leqslant x \leqslant 1$)

S. K. SRIVASTAVA
Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, India

A detailed investigation of crystal structure, properties and morphological characteristics of indium intercalation compound of tungsten disulphide, In_xWS_2 ($0 \leqslant x \leqslant 1$) is reported. X-ray analysis shows that intercalated compounds, like the host 2H–WS_2, also possess hexagonal symmetry with a small but continuous increase in c-lattice parameter. Room-temperature thermoelectric power experiments and low-temperature (150 to 300 K) conductivity measurements indicate that intercalated compounds also exhibit p-type semiconducting behaviour similar to base material WS_2. Thermal stability behaviour of these compounds in air and argon atmosphere has been studied and based on the X-ray data of oxidized products, formation of tungsten bronzes has been proposed. Results of the SEM study are also reported.

1. Introduction

Recently, the properties of solids with layer-type structure have received a considerable attention. Probably, much more interest has been focused on transition metal dichalcogenides, TCh_2 (T = metal, Ch = chalcogen, sulphur, selenium, tellurium) of groups IVB, VB and VIB and which constitute as such a structurally and chemically well-defined family of compounds [1–10]. The valency state and d-electron configuration of the metal bonded to the chalcogen are responsible for diverse electrical, magnetic and optical properties of these compounds, whereas their quasi two-dimensional layer-type structure imparts substantial anisotropy in most of their physical properties. These layered transition metal dichalcogenides crystallize basically in a hexagonal or rhombohedral structure where as sheet of metal atom (T) is covalently bonded to and sandwiched between the two layers (hexagonally packed) of chalcogens (Ch) (Fig. 1a). The coordination of the metal atom may either be octahedral or trigonal prismatic. These Ch–T–Ch sheets are weakly bonded to other slabs presumably through van der Waal forces of attraction and are stacked together in the c-direction to give rise to the observed hexagonal structure similar to graphite and many other silicate minerals. The other interesting feature of these compounds is that there exist vacant lattice sites which are potential holes (Fig. 1b) and can be filled partially or completely by extra metal atoms, ions or molecules to give rise to stoichiometric or nonstoichiometric intercalation compounds [1–14]. The bonding between the intercalate to the slabs may be weak. These transition metal dichalcogenides and their intercalation compounds finds a wide range of application, e.g. in the fields of catalysis [15], high temperature–high pressure lubricants [4], solid state electrolyte batteries [16], long-life photo-electrochemical solar cells [17], hydrogen storage devices, ionic/electronic conductors [11], SQUID detectors [18] and as superconducting materials [13].

Tungsten disulphide, WS_2, is one such representative which displays a characteristic layered structure and is a most promising material for modern uses [19]. Earlier studies have shown that WS_2 could be successfully intercalated with alkali and alkaline earth metals [20–23]. Thus upon intercalation a remarkable change in host from diamagnetic semiconducting behaviour to metallic and superconductivity was observed. The results were explained on the basis of a band model which assumes that electrons are being transferred from the intercalate to the conduction band of the host crystal [1]. Recently, we have reported for the first time, the synthesis of intercalation compounds of WS_2 with a post-transition metal indium [24]. In this paper, we report, the X-ray study of these compounds using CuK_α radiations for structure determination and crystallite size calculation, room-temperature Seebeck coefficient measurements, low-temperature (150 to 300 K) conductivity measurements, thermal stability behaviour in air and argon atmosphere, and X-ray study of the oxidized products and scanning electron micrographs, etc.

2. Experimental details

2.1. Sample preparation

The preparative methods of In_xWS_2 ($0 \leqslant x \leqslant 1$) compounds were similar to those already been reported [25]. A high-purity semiconducting grade tungsten powder, sulphur powder and indium metal were taken in stoichiometric proportion to obtain the desired composition. The constituents were then placed inside a quartz tube, vacuum sealed and heated first at 700° C for 40 h and finally to 1000° C for 48 h followed by slow cooling to room temperature.

0022–2461/88 $03.00 + .12

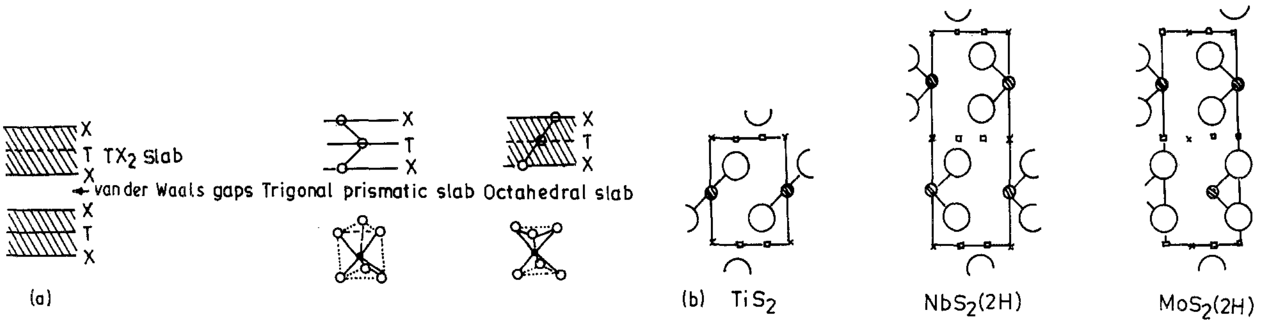

Figure 1 (a) Basic features for a schematic representation of lamellar dichalcogenides. (b) TiS_2, NbS_2, 2H–MoS_2 structural types (1 1 2 0 section) (○), Ch, (×) octahedral hole, (□) tetrahedral holes.

2.2. Characterization

Powder diffraction patterns of the samples were taken in a Phillips diffractometer using a monochromatic CuK_α radiations ($\lambda = 0.15404\,nm$) and MoK_α radiations ($\lambda = 0.0711\,nm$). For qualitive identification of the phases present, the patterns were taken from $5° < 2\theta < 50°$ with a scan rate of $2°\ 20\,min^{-1}$ and a chart speed of $1\,in.\,min^{-1}$ ($2.54\,cm\,min^{-1}$). The scan rate used to obtain X-ray patterns for precision cell constant determination was $0.25°\ 2\theta\,min^{-1}$ with a chart speed of $1\,in.\,min^{-1}$. All parameters were determined by least square refinements of the reflections. The crystallite size was determined by Sherrers method and a shape factor of 1.00 was applied.

Room-temperature Seebeck coefficient values were determined by simple thermoelectric power experiments. Low-temperature (150 to 300 K) conductivity measurements were made using a two-probe technique on compressed circular pellets. For this purpose, a constant current source was used to supply current to the sample and the voltage across it was measured using a Keithley Model 1602B microvoltmeter.

Thermal analysis in air and in argon atmosphere were carried out by MOM derivatograph, Paulik–Paulik, Hungary (Model no. 874373), over a temperature range of 1000° C. A linear heating rate of $10°\,C\,min^{-1}$, sensitivity of DTA = 1/10 and TG = 200 mg were maintained in all the samples. The oxidized products were also identified by X-ray analysis.

The SEM studies were made using an ISI-60 (USA) unit. The samples for this purpose were compressed into a pellet form and a thin film of gold was deposited by a sputtering method prior to study by SEM.

3. Results and discussion

Fig. 2 shows the X-ray diffractogram of indium intercalated compounds of tungsten disulphide, In_xWS_2 ($0 \leqslant x \leqslant 1$). A striking similarity in the diffraction pattern of these intercalated compounds with pure 2H–WS_2 indicates an unaltered arrangement of tungsten and sulphur atoms in tungsten disulphide even upon intercalation. Therefore, the structure can be referred to the same space group as in the host 2H–WS_2, namely, $P6_3/mmc$ and a layer stacking sequence as given by BaB AbA. In all In_xWS_2 ($0 \leqslant x \leqslant 1$) compounds, the 0 0 2 reflections in the low-angle region were found to be of maximum intensity indicating a strong orientation along the *c*-axis, an observation already inferred when $MoK\alpha$ radiation was used for X-ray analysis [23]. However, the reflections corresponding to higher harmonics 0 0 4, 0 0 6, 0 0 8, 0 0 1 0 were relatively of much lower intensity for a copper target and may account for respective absorption and polarization factors involved therein. The 1 0 *l* and 1 1 *l* reflections in all In_xWS_2 ($0 \leqslant x \leqslant 1$) compounds were more or less constant in intensity. The diffractograms of these compounds were thoroughly scanned in order to ascertain the presence of any extra phases due to either free indium or tungsten metal or binary sulphides, e.g. InS, In_2S_3, In_7S_6, etc., and were absent. Formation of ternary compounds similar to $InMo_6S_8$ [25], $InMo_6Se_8$ [26], have been reported but such compounds with tung-

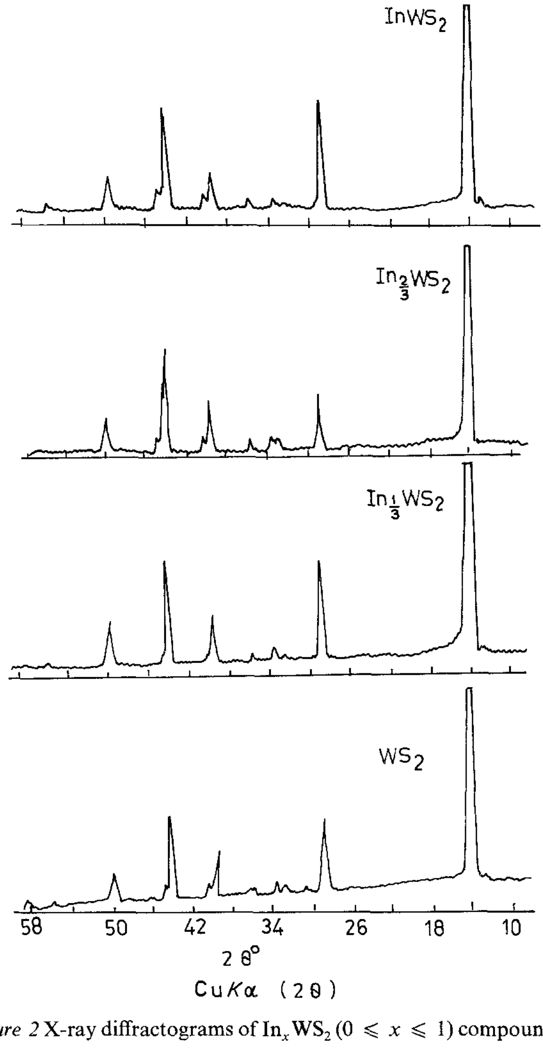

Figure 2 X-ray diffractograms of In_xWS_2 ($0 \leqslant x \leqslant 1$) compounds.

TABLE I Indexing of diffraction patterns for In_xWS_2 ($0 \leqslant x \leqslant 1$) compounds

		WS_2		$In_{1/3}WS_2$		$In_{2/3}WS_2$		$InWS_2$	
	hkl	*d* (nm)	I/I_0	*d* (nm)	I/I_0	*d* (nm)	I/I_0	*d* (nm)	I/I_0
00*l*	002	0.61800	100	0.61849	100	0.61856	100	0.61875	100
	004	0.30891	20	0.30921	5	0.30940	15	0.30901	25
	006	0.20604	22.5	0.20612	5	0.20621	5	0.20626	22.4
	008	0.15451	15.2	0.15462	< 5	0.15463	10	0.15472	10
	010	0.12362	< 5	0.12351	< 5	0.12361	< 5	0.12332	< 5
hko	100	0.27311	< 5	0.27331	< 5	0.27304	< 5	0.27331	< 5
	110	0.15780	< 5	0.15802	< 5	0.15781	< 5	0.15802	< 5
hol	101	0.26671	< 5	0.26672	< 5	0.26732	< 5	0.26672	< 5
	102	0.24981	< 5	–	–	–	–	–	–
	103	0.22700	15	0.22841	5	0.22783	15	0.22801	10
	105	0.18332	10	0.18371	5	0.18323	10	0.18402	10
	106	0.16451	< 5	0.16442	< 5	0.16441	< 5	0.16510	< 5
	107	0.14832	< 5	0.14831	< 5	0.14830	< 5	0.14331	< 5
	108	0.13451	< 5	0.13441	< 5	0.13450	< 5	0.13482	< 5
	109	0.12272	< 5	0.12281	< 5	0.12250	< 5	0.12250	< 5
	1010	0.11274	< 5	–	–	–	–	–	–
	1011	0.10340	5	0.10401	5	0.10399	5	0.10406	5
hkl	118	0.11060	< 5	0.11051	< 5	0.11050	< 5	0.11060	< 5

sten are not known and hence not verified. Therefore taking all these points into consideration, it may conclude that WS_2 retains the same hexagonal structure even upon indium intercalation. The d-bands in indium metal seem to play an important role in bonding contribution thereby stabilizing a trigonal prismatic coordination of indium metal with respect to the surrounding sulphur atoms. However, in alkali and alkaline earth metals these bands are absent, and allow octahedral coordination to be more stable. The *d*-values for In_xWS_2 ($0 \leqslant x \leqslant 1$) compounds were calculated from Fig. 2 and are recorded in Table I.

Lattice parameters and other characteristic features of these compounds are presented in Table II. It is noted that indium intercalation produced a small increase in *c*-lattice parameters, unlike its alkali or alkaline earth metal analogue [27], where a large increase in *c*-parameter was observed. The structural studies on some other layered transition metal dichalcogenides, e.g. Cu_xNbS_2 [28, 29], Cu_xNbSe_2 [29, 30], Al_xTaS_2, Zn_xTaS_2 [31], In_xMoS_2 [32] and some other intercalation compounds, e.g. Li_xYCl, Li_xGdCl [33], revealed that the process of intercalation not necessarily produces a characteristic sharp increase in *c*-parameter and is thought to be dependent on the size, concentration and electronic configuration of the incoming guest atom and the structure of the host crystal as well. The calculations of the crystallite size for these compounds confirmed that there exists an isotropy towards the crystallite size (Table II).

Room-temperature thermoelectric power experiments have shown that those In_xWS_2 ($0 \leqslant x \leqslant 1$) intercalated compounds like host $2H-WS_2$ possess a p-type conductivity (Table II). Two-probe low-temperature (150 to 300 K) conductivity measurements indicated that these compounds were semiconducting [24], a behaviour contrary to the usual alkali and alkaline earth metal analogue of WS_2 [19], and can be explained on the basis of band model of WS_2 [1]. The main feature of this band structure is the valence band primarily based on chalcogen s- and p-orbitals, the conduction band made up of metal s and p orbitals and in between a non-bonding band based on its d and p orbitals (Fig. 3). The Fermi level lies in the gap of dz^2 and d/p band. Upon intercalation with alkali/alkaline earth metals their conduction band overlaps with unfilled d/p bands of WS_2 and as a result of which these compounds become metallic with a large increase in free electron density over pure WS_2. However, the semiconducting behaviour in indium intercalated compounds in our case leads to the conclusion that the charge transfer band model is not

TABLE II Crystallographic data and other properties of In_xWS_2 ($0 \leqslant x \leqslant 1$) compounds

	WS_2	$In_{1/3}WS_2$	$In_{2/3}WS_2$	$InWS_2$
Colour	Shining black	Shining black	Shining black	Shining black
Cell parameter				
a (nm)	0.3152	0.3154	0.3154	0.3150
c (nm)	1.2350	1.23556	1.23560	1.2366
c/*a*	3.388	3.3920	3.394	3.397
$v\,nm^3$	0.142095	0.141930	0.141898	0.141889
Crystallite size (nm)	42.5	46.0	45.0	43.0
Seebeck coefficient ($\mu V\,^{\circ}C^{-1}$)	+330	+211	+37.4	+40.4

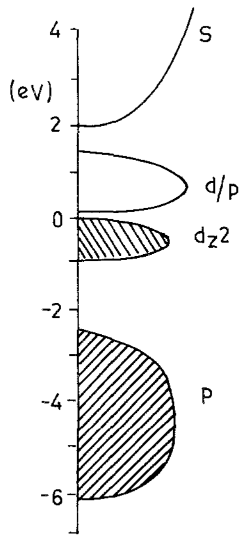

Figure 3 Energy band structure of WS_2.

applicable in the present case. It may be that higher ionization potential of indium hinders the delocalization of electronic charge transfer. A similar type of behaviour has also been observed by other workers: there are few layered transition metal dichalcogenide host crystals which remain semiconducting even upon intercalation [32, 34–36].

Rouxel [34] suggested that in certain cases the electrons given by the intercalate may be trapped in certain sites rather than being delocalized in the conduction band of the host crystal. Recent measurements on the absorption edge on T_xZrS_2 and T_xHfS_2 (T = copper, iron; $0.22 \leqslant x$) revealed that these compounds retained semiconducting behaviour [35, 36]. It was proposed that in such cases the intercalated atoms might be regarded as analogous to deep-level impurities, leading thereby to an additional energy level near the top of the valence band or, alternatively, it may be regarded as a modification of the energy band of the host crystal due to the interaction between the intercalate and sulphur atoms.

Fig. 4 shows the variation of room-temperature conductivity (σ) and activation energy (E_a) with the composition x in In_xWS_2. It was observed that conductivity increases first with increasing indium content and becomes almost constant beyond $x = 2/3$ whereas the activation energy follows the reverse trend. The initial increase in conductivity with composition x is due to the increase in carrier concentration due to the indium incorporation which donates its extra electrons. However, the saturation beyond $x = 2/3$ suggested a decrease in carrier mobility because conductivity (σ) is proportional to both carrier concentration (pe) and carrier mobility (μ). The room-temperature thermoelectric power experiments for In_xWS_2 showed remarkably similar behaviour where increasing indium content in WS_2 first decreases the Seebeck coefficient value and then becomes almost constant beyond $x = 2/3$ (Table II).

Thermograms of pure and indium intercalated compounds of WS_2 in air atmosphere are shown in Fig. 5. The general feature of the DTA curve is the presence of a shallow exothermic peak at ≈ 660, 630 and 560° C in WS_2, $In_{1/3}WS_2$ and $In_{2/3}WS_2$, respectively, whereas in $InWS_2$ a sharp, but narrow, exothermic peak occurred at 580° C. Thermogravimetric analysis (TG) of these compounds indicated a constant weight gain above ≈ 380° C. For WS_2, $In_{1/3}WS_2$ and $In_{2/3}WS_2$ this weight gain was maximum when the exothermic peak appeared in thermograms, whereas in $InWS_2$ weight gain continues up to 700° C even though an exothermic peak appeared at 580° C in the thermogram. This weight gain is further followed by a continuous weight loss and is less prominent at higher temperature (≥ 800° C). The initial weight gain in TG demonstrated the possibility of high surface coverage with oxygen for these compounds, but the subsequent weight loss in TG may be attributed to the oxidation of these compounds under prevailing experimental conditions. The calculations based on weight loss in TG suggested that the oxidation product of In_xWS_2 ($0 \leqslant x \leqslant 1$) are nothing but In_xWO_3 ($0 \leqslant x \leqslant 1$) compounds. Further, to identify the oxidized products so formed, each In_xWS_2 ($0 \leqslant x \leqslant 1$) compounds

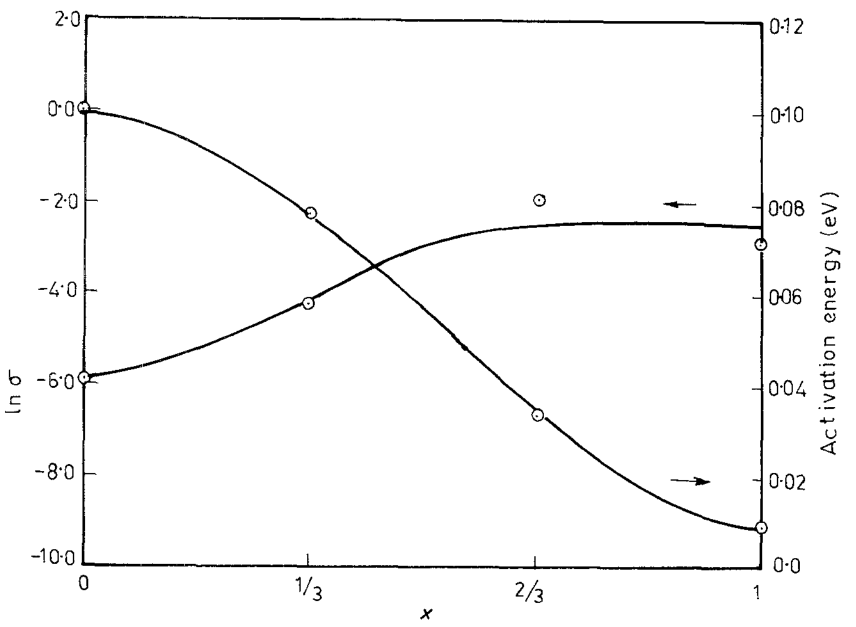

Figure 4 Variation of room-temperature electrical conductivity and activation energy with composition x in In_xWS_2 compounds.

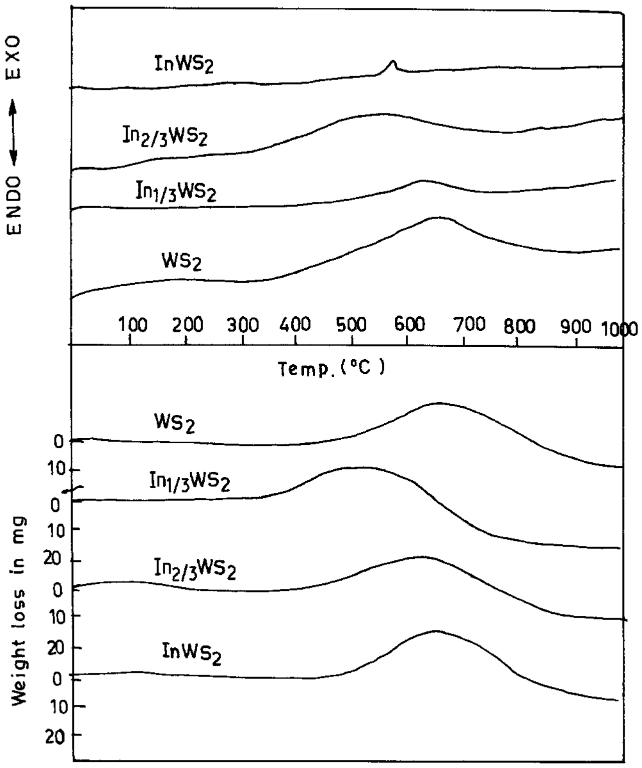

Figure 5 Thermograms of In_xWS_2 ($0 \leqslant x \leqslant 1$) in air.

were heated separately at ≈800° C for 2 h and their X-ray studies were made (Fig. 6, Table III). This confirmed that the oxidation product of WS_2 is WO_3 [37]. The diffraction pattern of In_xWS_2 ($0 \leqslant x \leqslant 1$) oxidation products showed a good resemblence to the host tungsten trioxide, WO_3. The d-lines were calculated for each samples which did not agree with the existing binary indium oxide, In_2O_3 [38] or ternary indium tungsten oxides [39] in In_xWS_2 ($0 < x \leqslant 1$) oxidized products (Table III).

Tungsten trioxide, WO_3, is monoclinic at room temperature and orthorhombic at ≥ 710° C, but both these forms constitute a host lattice which is characterized by a system of intersecting channels, a distorted version of ReO_3 lattice structure (perovskite structure) built up of chains of WO_6 octahedra linked by shaired corners extending three-dimensionally [40]. The similarity in diffraction pattern of these In_xWS_2 ($0 \leqslant x \leqslant 1$) oxidized compounds further confirmed the conclusion infered from TG analysis that tungsten bronzes In_xWO_3 ($0 \leqslant x \leqslant 1$) are formed where indium occupies positions in between the intersecting channels. The literature reveals that the structure adopted in WO_3 bronzes is controlled to a considerable degree by ionic radii of the guest atoms [11, 41] and their preparative methods as well. The results were explained on the basis of corner sharing of WO_6 octahedra where tunnels are formed by stacking of sheets of WO_6 octahedra that contain holes. These openings, depending on their size, are broadened by either four, five or six WO_6 octahedra. The guest then resides in these cavities. The radii of these cavities are 0.096, 0.129 and 0.163 nm for four, five and six tunnels, respectively. The ionic radius of In^+ is 0.132 nm and hence it can be anticipated that it stabilizes the same monoclinic structures of WO_3 with five-sided tunnels in all In_xWO_3 compounds.

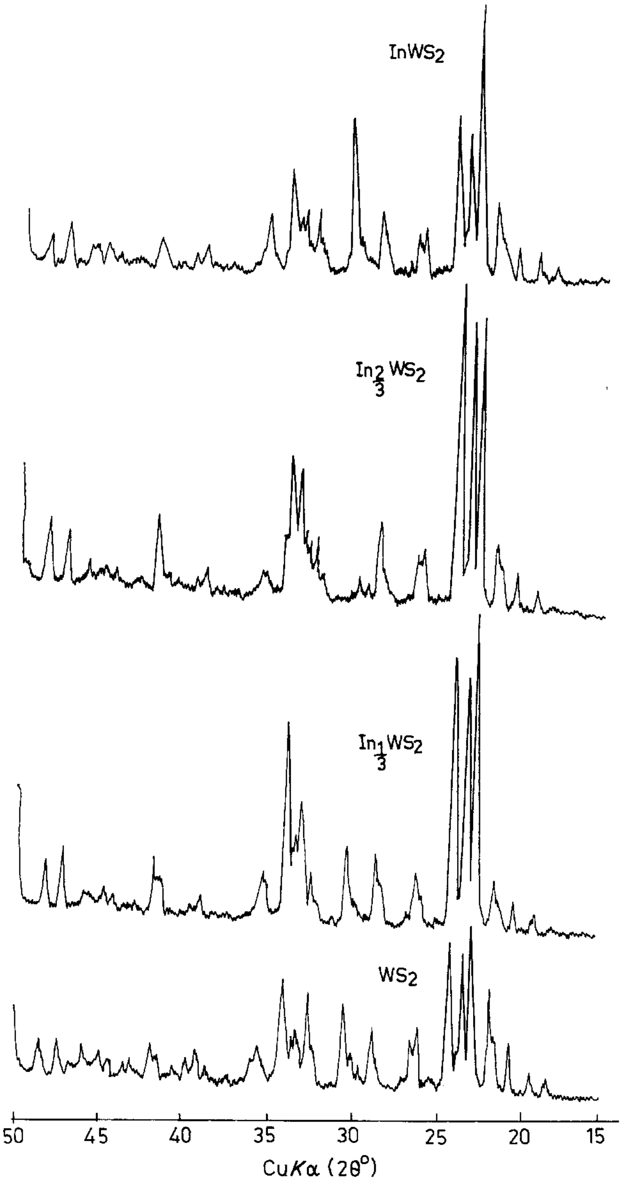

Figure 6 X-ray diffractograms for oxidized products of In_xWS_2 ($0 \leqslant x \leqslant 1$) compounds.

The oxidation products in all these In_xWS_2 ($0 \leqslant x \leqslant 1$) compounds are light greenish/yellow in colour. However, a substantial variation in the intensity of colour was observed with increasing concentration of indium in WO_3.

Thermal behaviour of WS_2 in inert (argon) atmosphere indicated its stability up to ≈ 1000° C. However, thermograms for In_xWS_2 ($0 < x \leqslant 1$) suggested a decrease in the stability of these compounds with increasing indium content in WS_2. Thus $In_{1/3}WS_2$, $In_{2/3}WS_2$ and $InWs_2$ decomposed at 900, 870 and 880° C, respectively, and subsequently formed sulphur defficient compounds, as was evident from their small, but continuous, weight loss in TG up to 1000° C.

The SEM studies for pure and indium intercalated compounds are presented in Fig. 7, which shows the presence of hexagonal flakes in all the compounds. However, electron micrographs of In_xWS_2 when compared with In_xMoS_2 analogues [42] clearly revealed that in the former case there was little change in the morphological characteristics of the crystals. This suggested that the effect is less prominent in In_xWS_2 than In_xMoS_2 intercalation compounds for

TABLE III X-ray data for the oxidation products of In_xWS_2 ($0 \leqslant x \leqslant 1$) compounds

WS_2^*				$In_{1/3}WS_2$		$In_{2/3}WS_2$		$InWS_2$	
d_{obs}	d_{rep}	*hkl*	I/I_1	d_{obs}	I/I_1	d_{obs}	I/I_1	d_{obs}	I/I_1
4.770	–	–	9	4.771	3	4.755	2	4.755	2
4.529	–	–	10	4.528	6	4.529	6	4.528	8
4.270	–	–	30	4.270	6	4.270	11	4.270	12
4.040	–	–	63	4.041	17	4.040	20	4.040	29
3.838	3.835	001	100	3.835	100	3.833	90	3.833	100
3.769	3.762	020	84	3.769	81	3.750	86	3.750	52
3.648	2.642	200	90	3.648	86	3.648	100	3.648	61
3.376	3.411	011	84	3.388	17	3.388	17	3.381	19
3.343	–	–	30	3.351	17	3.351	16	3.351	17
3.087	3.109	111	36	3.087	21	3.087	25	3.087	24
2.928	–	–	51	2.928	21	2.927	15	2.926	55
2.746	–	–	56	2.751	15	2.751	21	2.751	24
2.708	2.684	021	34	2.708	35	2.690	22	2.693	25
2.667	2.661	207	32	2.667	26	2.668	46	2.667	20
2.621	2.617	201 220	65	2.624	62	2.629	45	2.629	40
2.526	2.528	–	23	2.526	13	2.508	13	2.508	23
2.298	–	–	22	2.298	5	2.298	8	2.307	10
2.264	–	–	13	2.264	4	2.264	5	2.264	6
2.178	2.172	221	13	2.178	12	2.178	5	2.178	5
2.156	2.149	221	21	2.156	17	2.156	23	2.151	12
2.082	2.098	031	12	2.082	5	–	–	–	–
2.016	2.038	131	13	2.016	6	2.016	5	2.016	7
1.973	1.966	311	20	1.973	3	1 973	9	1.973	8
1.921	1.917	002	24	1.923	2	1.923	17	1.923	18
1.882	1.879	040	20	1.880	3	1.880	20	1.880	12

*A few additional lines also appeared in the diffractogram, which were also observed when X-ray diffraction was taken of oxidized In_xWS_2 ($0 < x \leqslant 1$) compounds.

all compositions. Therefore, it appeared that indium intercalation in WS_2 did affect the disorder but to a lesser extent compared to MoS_2, an earlier observation already inferred from X-ray studies of these compounds, and may be explained by assuming that WS_2 permits easy entry to the incoming indium metal in between the layers without any hinderance, provided that the van der Waal gap for WS_2 is larger than MoS_2.

4. Conclusion

The indium intercalation compounds were character-

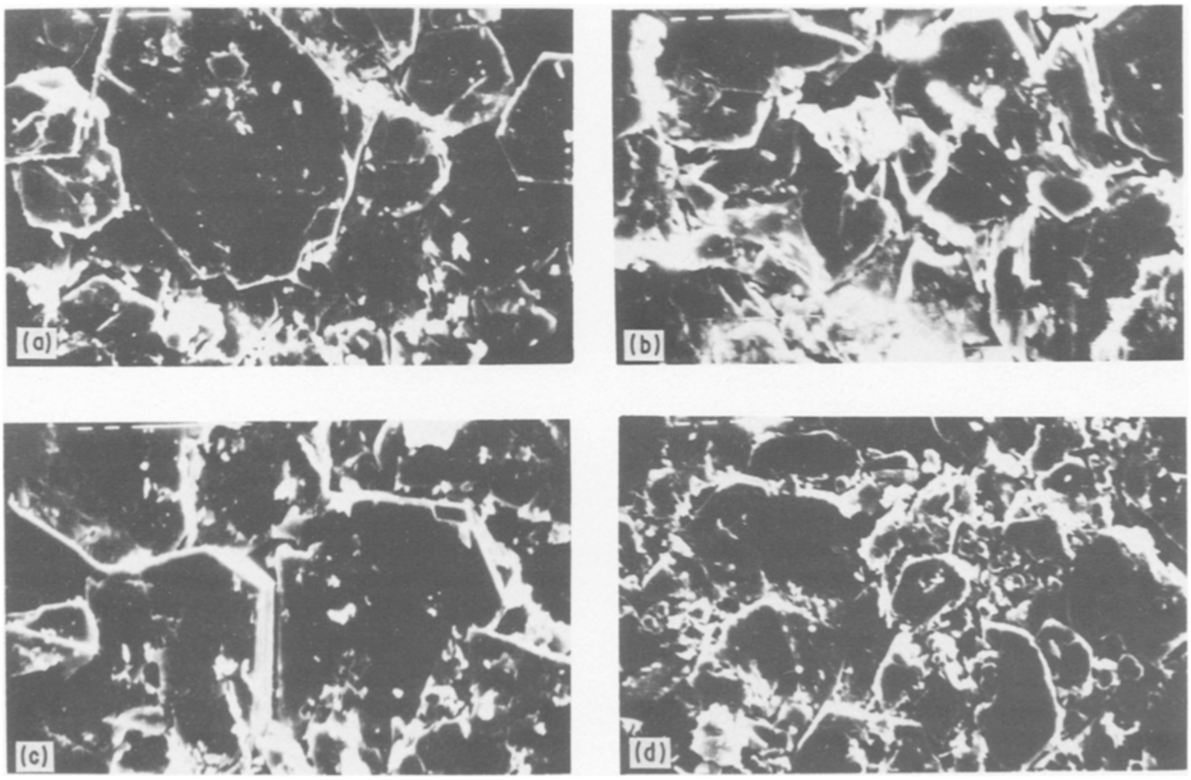

Figure 7 Scanning electron micrographs of In_xWS_2 ($0 \leqslant x \leqslant 1$) compounds. (a) WS_2, (b) $In_{1/3}WS_2$, (c) $In_{2/3}WS_2$, (d) $InWS_2$.

ized by X-ray diffraction, Seebeck coefficient, low-temperature (150 to 300 K) conductivity measurements, thermal analysis in air and argon atmosphere, and SEM studies, etc. All indium intercalated compounds of tungsten disulphide, In_xWS_2 ($0 \leqslant x \leqslant 1$) were found to yield single-phase materials with hexagonal structure and free of any binary phases. These compounds like host $2H-WS_2$, were p-type semiconductors, a behaviour contrary to its usual alkali and alkaline earth metal analogues [19–23] and can be explained on the basis of an existing band model of WS_2 [1]. The thermal stability behaviour of these compounds in air and argon atmosphere has also been studied and the formation of tungsten bronzes In_xWO_3 ($0 < x \leqslant 1$) from the oxidized product of In_xWS_2 ($0 < x \leqslant 1$) compounds has been proposed. SEM studies revealed the presence of hexagonal flakes in these compounds. Thus our work on In_xWS_2 ($0 < x \leqslant 1$) intercalation compounds like In_xMoS_2 [31] further supports Rouxel's [34] suggestion that there may be two or more classes of intercalation compounds with quite different behaviour of valency electrons.

Acknowledgement

The authors thank Professor G. V. Subba Rao, Head, Materials Science Centre, Indian Institute of Technology, Madras for stimulating discussion and suggestions on X-ray studies of these compounds, during his visit to I. I. T. Kharagpur.

References

1. J. A. WILSON and A. D. YOFFE, *Adv. Phys.* **19** (1969) 169.
2. F. JELLINEK, *Ark. Fur Kemi* **20** (1963) 447.
3. *Idem, MTP Int. Rev. Sci.* (*Inorg. Chem. Ser.*) **5** (1972) 533.
4. G. V. SUBBA RAO and C. S. SUNANDANA, in "Preparation and characterization of Materials", edited by J. M. Honing and C. N. R. Rao (Academic, London, 1981) p. 269.
5. A. D. YOFFE, in "Physics and Chemistry of Electrons and Ions in Condensed Matter", edited by J. A. Acrivos *et al.* (Reidel, Dordrecht, 1984) p. 437.
6. S. K. SRIVASTAVA, B. N. AVASTHI and S. BASU, *J. Sci. Ind. Res.* **41** (1982) 656.
7. S. K. SRIVASTAVA, B. N. AVASTHI, B. DAS and S. BASU, *Mater. Lett.* **1** (1983) 178.
8. S. K. SRIVASTAVA, B. N. AVASTHI and S. BASU, *J. Mater. Sci. Lett.* **3** (1984) 178.
9. S. K. SRIVASTAVA and B. N. AVASTHI, *J. Less-Common Metals* **124** (1986) 85.
10. *Idem,* Second Indo-Soviet Seminar on "Recent Advances in Catalysis and Catalytic Reaction Engineering", R.R.L., Hyderabad, 25 to 28 December (1986).
11. F. R. GAMBLE and T. H. GEMBALL, in "Treatise on Solid State Chemistry", Vol. 3, edited by N. B. Hannay (Pergamon, New York, 1976) p. 89.
12. G. V. SUBBA RAO and M. W. SCHAFER, in "Intercalated Layered Materials", edited by F. Levy (Reidel, Dordrecht, 1979) p. 99.
13. J. ROUXEL, *ibid.* p. 201.
14. R. SCHOLLOHORN, in "Inclusion Compounds", Vol. 1, edited by J. L. Atwood, J. E. D. Davies and D. D. MacNicol (Academic, London, 1984) p. 249.
15. O. WEISSER AND S. LANDA, "Sulphide Catalysts, their Properties and Applications" (Pergamon, Oxford, 1973).
16. M. S. WHITTINGHAM and A. J. JACOBSON, "Intercalation Chemistry" (Academic, New York, 1982).
17. H. TRIBUTSCH, *J. Electrochem. Soc.* **125** (1978) 1085.
18. J. E. ZIMMERMAN, *Cryogenics* **12** (1972) 19.
19. S. K. SRIVASTAVA and B. N. AVASTHI, *J. Mater. Sci.* **20** (1985) 3801.
20. W. RUDORFF and M. H. HICKS, *Angew Chem.* **71** (1959) 128.
21. W. RUDORFF, *Chimia* **19** (1965) 489.
22. E. BAYER and W. RUDORFF, *Z. Naturforsch,* **27b** (1972) 1136.
23. G. V. SUBBA RAO, M. W. SCHAFER and S. KAWARAZAKI, *J. Solid State Chem.* **9** (1974) 323.
24. S. K. SRIVASTAVA and B. N. AVASTHI, *Syn. Metals* **10** (1985) 213.
25. R. CHEVREL, M. SERGENT and J. PRIGENT, *J. Mater. Res. Bull.* **9** (1974) 1487.
26. J. M. JARASEON, F. J. DISALVO, D. W. MURPHY, G. HULL and J. V. WESZEZAK, *Phys. Rev.* **29** (1984) 172.
27. R. B. SOMOANO and J. A. WOOLAM, F. LERY (eds), "Intercalated Layered Materials" (Reidel, Dordrecht, 1979) p. 307.
28. A. E. VAN ARKEL and C. GREVECOCUR, *J. Less-Common Metals* **26** (1972) 399.
29. K. KOERTS, *Acta Crystallogr.* **16** (1963) 432.
30. J. M. VOORHOEVE-VANDER BERG, *J. Less-Common Metals* **26** (1972) 399.
31. F. J. DISALVO, G. W. HULL, L. H. SCHWARTZ, J. M. VOORHOEVE and J. V. WASZESAK, *J. Chem. Phys.* **59** (1973) 1922.
32. S. K. SRIVASTAVA and B. N. AVASTHI, *Syn. Metals* **11** (1985) 193.
33. J. F. FORD, G. MEYER and J. D. CORBETT, *Inorg. Chem.* **23** (1984) 2094.
34. J. ROUXEL, *Mater. Res. Bull.* **13** (1978) 1425.
35. B. G. YACOBI, F. W. BOSWELL and J. M. CARBETT, *J. Phys. C Solid State Phys.* **12** (1979) 218.
36. B. G. YACOBI, F. W. BOSWELL and J. M. CARBETT, *Mater. Res. Bull.* **14** (1979) 1033.
37. JCPDS, Powder Diffraction File, 5-363 (1976).
38. JCPDS, Powder Diffraction File, 6-416 21-326 (1976).
39. N. J. CLARK and L. P. MOST, *Mater. Res. Bull.* **18** (1983) 958.
40. P. G. DICKENS and M. S. WHITTINGHAM, *Q. Rev. Chem. Soc.* **22** (1968) 30.
41. G. HAGG and A. MAGNELI, *Rev. Pure Appl. Chem.* **4** (1954) 250.
42. S. K. SRIVASTAVA, unpublished work (1984).

Received 13 April
and accepted 29 June 1987