JOURNAL OF MATERIALS SCIENCE **24** (1989) 1919–1924

Synthesis and characterization of indium intercalation compounds of molybdenum diselenide, In$_x$MoSe$_2$ ($0 \leqslant x \leqslant 1$)

S. K. SRIVASTAVA, B. N. AVASTHI
Department of Chemistry, Indian Institute of Technology, Kharagpur-721302, India

The present work deals with the synthesis, structure and properties of indium intercalated compounds of molybdenum diselenide, In$_x$MoSe$_2$ ($0 \leqslant x \leqslant 1$). X-ray analysis shows that the intercalated compounds, In$_{1/3}$MoSe$_2$ like the host. 2H-MoSe$_2$ also possess a hexagonal symmetry with a small increase in *c* lattice parameter. However, a new phase appeared in In$_{2/3}$MoSe$_2$ and InMoSe$_2$ diffractogram due to In$_7$Se$_6$, In$_2$Se$_3$, In$_x$Mo$_6$Se$_8$ or In$_{3.33}$Mo$_{15}$Se$_{19}$. Room temperature magnetic susceptibility, thermoelectric power experiments and two probe conductivity measurements in the temperature range 25 to 300°C indicated that intercalated compounds also exhibit p-type diamagnetic semiconducting behaviour similar to the host MoSe$_2$ and results are explained on the basis of existing band models. Thermal stability behaviour of these compounds has also been studied and X-ray analysis of the oxidized product has also been made.

1. Introduction

During the past few years, there has been a great interest in layered compounds consisting of group IVB and VB and VIB transition metal dichalcogenide [1–13]. Recent applications includes intercalation compounds [14–16], high pressure–high temperature lubricant [15], long-life photo electrochemical solar cell [17], solid state electrolyte batteries [18] and in the field of catalysis [19].

Molybdenum diselenide, MoSe$_2$, is one such representative which possesses a characteristic layer type of structure and is a most promising material for modern use [5]. This layer type structure in MoSe$_2$ facilitates the process of insertion or intercalation by foreign metal atoms allowing the structure and electronic behaviour of the host to be changed. Earlier studies have shown that MoSe$_2$ could successfully be intercalated with alkali and alkaline earth metals [20–22]. Recently, we reported for the first time the synthesis of intercalation compounds of MoS$_2$, WS$_2$ and WSe$_2$ with the post transition metal indium. These results were found to be very interesting and encouraging and therefore we extended our studies on isostructural MoSe$_2$ compounds. In this paper, we report synthesis of indium intercalation compounds of molybdenum diselenide and its characterization by X-ray analysis for structure determination and particle size calculation, room temperature magnetic susceptibility and thermoelectric power experiments, conductivity measurements in the temperature range (25 to 300° C), thermal stability behaviour in the air atmosphere and X-ray analysis of the oxidized products etc.

2. Experimental details

2.1. Sample preparation

In the present study the In$_x$MoSe$_2$ ($0 < x \leqslant 1$) compounds were synthesized directly from the elements and the method of preparation was quite similar to that already reported for In$_x$WS$_2$ [9] and In$_x$MoS$_2$ [10] compounds. Appropriate amounts of the molybdenum metal powder (99.9% pure), selenium powder (99.9% pure) and semiconducting grade indium metal were weighed accurately to give the desired composition. The mixture was then placed inside a quartz tube and vacuum sealed. The initial reaction was carried out at 750° C for a period of 40 h. A loose powder product resulted, having a considerably greater volume than the reacting elements, and this was well mixed by mechanical shaking. Subsequently, a final reaction was carried out at 1000° C in the same sealed tube for 40 h followed by slow cooling to room temperature.

2.2. Characterization

Powder diffraction pattern of the samples were taken on a DRON-I USSR strip chart mV recorder (model COO No 1500) using MoKα radiation. Fast scan of $2° \text{min}^{-1}$ were recorded to examine the material for the possible presence of extra phases. The crystallite size was determined by Sherrer's method and a shape factor of 1.00 was applied.

Room temperature magnetic susceptibility was obtained using a Faraday balance with Caha RG electrobalance at 3×10^{-3} T field strength. The type of conductivity was determined by conventional thermoelectric power experiments. Conductivity measurements were made using a two-probe technique on a compressed circular pellet in the temperature range 300 to 600 K. Thermogravimetric analysis was made at atmospheric pressure up to 1000° C in MOM derivatograph (Hungary model, Paulik-Paulik). A linear heating rate of $10° \text{C min}^{-1}$, sensitivity of DTA $= \frac{1}{10}$ and TG = 200 mg, were maintained in all the samples. The oxidized products were also identified by X-ray analysis.

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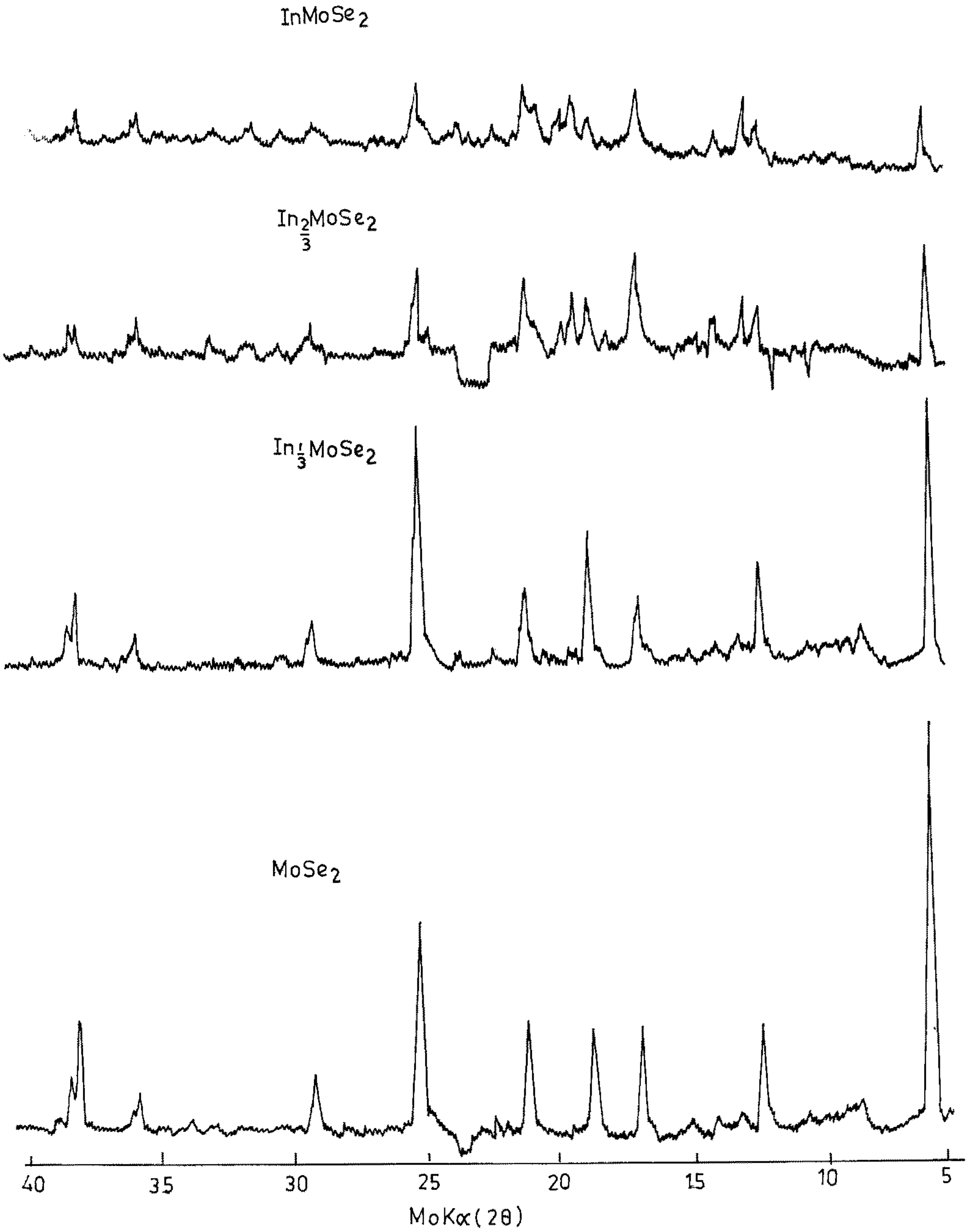

Figure 1 X-ray diffractograms of In_xMoSe_2 ($0 \leqslant x \leqslant 1$) compounds.

3. Results and discussion

Fig. 1 shows the X-ray diffractogram of In_xMoSe_2 ($0 \leqslant x \leqslant 1$) compounds. It appeared from the diffractograms that there exists quite a good resemblance between the host 2H-$MoSe_2$ and $In_{1/3}MoSe_2$ intercalation compound. This suggested that the arrangement of molybdenum and selenium remains almost the same even upon indium intercalation. Thus the $In_{1/3}MoSe_2$ compound may be regarded as possessing the space group $P6_3/mmc$ and a layer stacking sequence as given by BCB/AbA as in the host 2H-$MoSe_2$. The 001 reflections in $MoSe_2$ and $In_{1/3}MoSe_2$ are of very high intensity indicating thereby a strong orientation along the *c* axis. However, further intercalation of indium in $MoSe_2$ for example $In_{2/3}MoSe_2$ and $InMoSe_2$ produced a sharp decrease in the intensity of 001 reflections. Though intensity of 101 lines remained constant in $MoSe_2$ and $In_{1/2}MoSe_2$, it increased significantly for $In_{2/3}MoSe_2$ and $InMoSe_2$ compounds. The diffractograms of all these In_xMoSe_2 ($0 \leqslant x \leqslant 1$) compounds were also thoroughly scanned in order to ascertain the presence of any phases due to free indium, molybdenum or binary indium or molybdenum selenides e.g. InS, In_2Se_3, In_7Se_6, $MoSe_2$, $MoSe_4$, $Mo_{15}Se_{19}$ or ternary compounds e.g. $In_xMo_6Se_8$ and $In_{3.33}Mo_{15}Se_{19}$. Few new phases were seen to have appeared in the diffractograms of $In_{2/3}MoSe_2$ and $InMoSe_2$ compound. Thus the intensity of the peak with $d = 0.3085$ and 0.2840 nm in host $MoSe_2$ and $In_{1/3}MoSe_2$ is extremely low but it increases significantly in $In_{2/3}MoSe_2$ and $InMoSe_2$ compounds and may correspond to In_6Se_7 ($d = 0.3068$ nm) [23] in the former and to In_7Se_6 ($d = 0.2840$ nm) [23] and $In_{3.33}Mo_6Se_8$ ($d = 0.2836$ nm) [24] in the latter, respectively. In addition, three new lines at 0.2084, 0.2040 and 0.1710 nm also appeared in the diffractograms of $In_{2/3}MoSe_2$ and $InMoSe_2$ which were found to be absent in the host $MoSe_2$ and $In_{1/3}MoSe_2$ compounds. The line at 0.2084 nm may be due to $In_{3.33}Mo_{15}Se_{19}$ ($d = 0.2078$ nm) [24] or $In_xMo_6Se_8$ ($d = 0.2075$ nm) [25] whereas the other two lines may correspond to $In_xMo_6Se_8$ ($d = 0.2042$ nm)

TABLE I Indexing of diffraction pattern for In$_x$MoSe$_2$ ($0 \leqslant x \leqslant 1$) compounds

MoSe$_2$			In$_{1/3}$MoSe$_2$		In$_{2/3}$MoSe$_2$		InMoSe$_2$	
hkl	d (nm)	I/I_1	d (nm)	I/I_1	d (nm)	I/I_1	d (nm)	I/I_1
001								
002	0.6448	100	0.6451	100	0.6453	100	0.6453	100
004	0.3225	30	0.3230	47	0.3231	50	0.3231	40
006	0.2148	30	0.2153	55	0.2153	40	0.2153	40
008	0.1612	55	0.1615	85	0.1616	80	0.1616	80
hol								
103	0.2368	30	0.2364	30	0.2368	85	0.2367	80
105	0.1910	30	0.1908	30	0.1910	60	0.1911	90
101	0.1084	30	0.1085	20	0.1086	15	0.1087	40
203	0.1352	< 5	0.1350	5	0.1351	10	0.1352	30
205	0.1246	< 5	0.1244	< 5	0.1244	15	0.1244	25
h00								
100	0.2839	5	0.2839	10	0.2839	10	0.2839	30
200	0.1422	5	0.1422	15	0.1422	15	0.1422	30
hk0								
210	0.1073	15	0.1076	15	0.1074	25	0.1074	25
118	0.1150	10	0.1151	15	0.1151	20	0.1150	40
Other lines								
					0.3085	45	0.3085	65
					0.2840	25	0.2848	28
					0.2080	45	0.2083	65
					0.2043	20	0.2048	40
					0.17096	15	0.1709	25

[25] and In$_2$Se$_3$ ($d = 0.1712$ nm) [26] respectively. Therefore it may be concluded that In$_{1/3}$MoSe$_2$ retains the same hexagonal structure as MoSe$_2$, whereas new phases appeared in the case of In$_{2/3}$MoSe$_2$ and InMoSe$_2$ compounds. The d values for In$_x$MoSe$_2$ ($0 \leqslant x \leqslant 1$) compounds are calculated from the Fig. 1 and are recorded in Table I.

The unit cell parameters for hexagonal MoS$_2$ are given in Table II. The data compare well with those of Al-Hilli and Evan [27] ($a = 0.3299$ nm, $c = 2 \times 0.6489$ nm, $c/a = 1.9608$, $V = 0.121\,940$ nm^3). A small increase in c-lattice parameter in In$_{1/3}$MoSe$_2$ compound was produced unlike its alkali or alkaline earth metal analogue [20–22] where a relatively larger, increase in the c parameter was observed. However, the structural studies on some other layered transition metal dichalcogenides e.g. Al$_x$TaS$_2$, Al$_x$NbSe$_2$ [29], 2n$_x$TaS$_2$ [30], In$_x$WS$_2$ [9], In$_x$MoS$_2$ [10] and some other intercalation compounds e.g. Li$_x$YCl, Li$_x$GdCl [31] revealed that the process of intercalation does

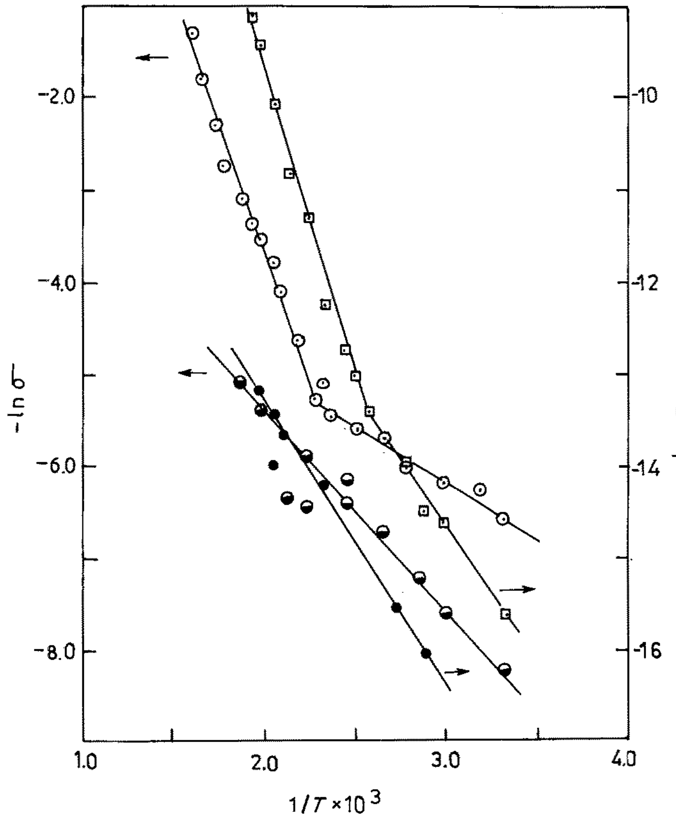

Figure 2 Temperature variation of conductivity for In$_x$MoSe$_2$ ($0 \leqslant x \leqslant 1$) compounds (⊙ In$_{2/3}$MoSe$_2$, ⊡ In$_{1/3}$MoSe$_2$, ● InMoSe$_2$, ◒ MoSe$_2$).

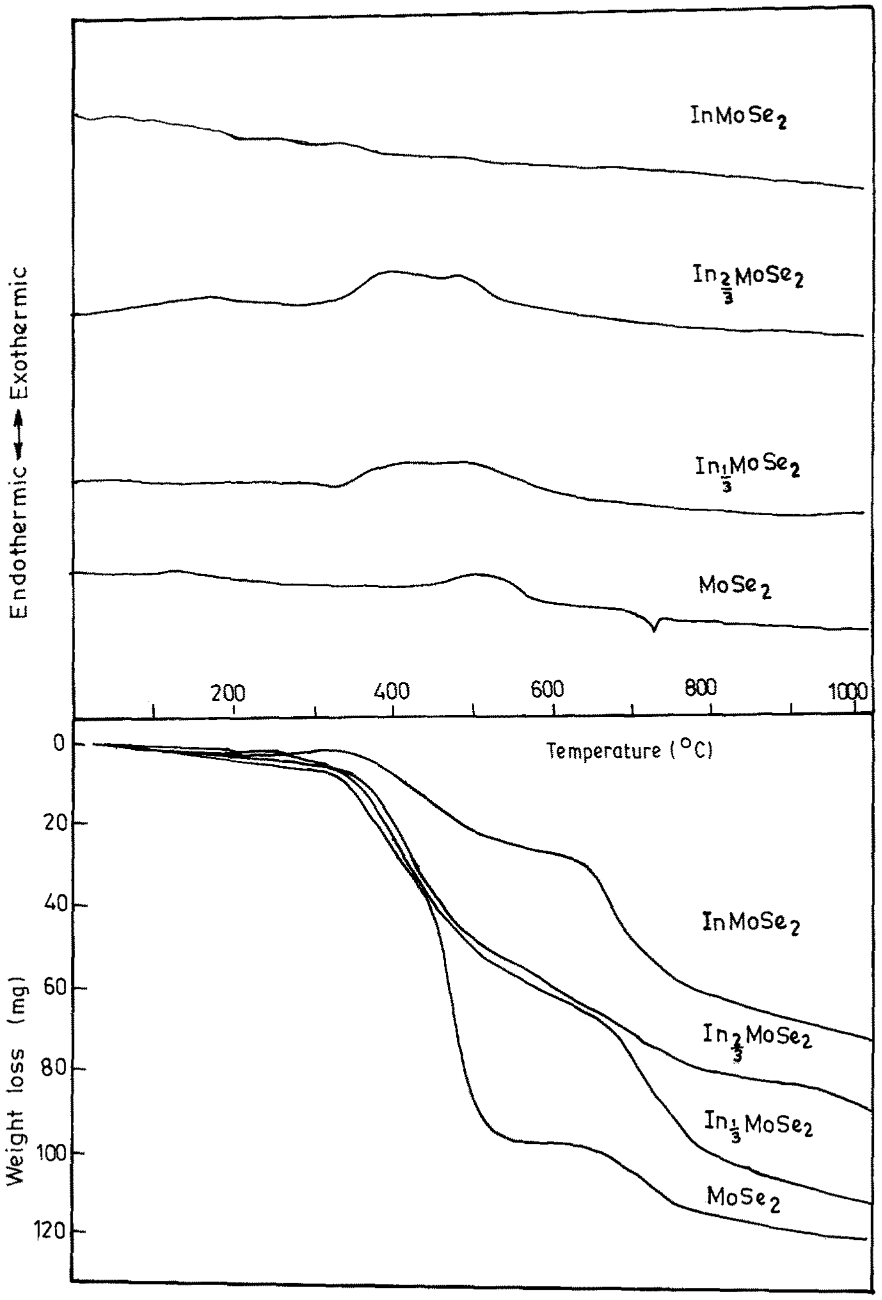

Figure 3 Thermograms of In_x-$MoSe_2$ $(0 \leqslant 1\ x \leqslant 1)$ compounds.

not necessarily produce a characteristic increase in c-parameter and is thought to be dependent on the size and concentration of the guest atom and the structure of the host crystal as well. The calculation of the crystallite size in $MoSe_2$ and $In_{1/3}MoSe_2$ compounds confirmed that there exists an isotropy towards the crystallite size (Table II).

Room temperature magnetic susceptibility and thermoelectric power experiments and conductivity measurements in the temperature range 25 to 300° C confirmed that all these In_xMoSe_2 $(0 < x \leqslant 1)$ compounds are n-type diagmagnetic semiconductors, Fig. 2 (Table II), a behaviour contrary to its metallic and paramagnetic nature for its alkali and alkaline earth metal analogues [20–22]. Therefore it may be concluded that a charge-transfer rigid-band model is not applicable in all the cases since it assumes that electrons transferred from the intercalate atoms are delocalized

TABLE II X-ray data and other characteristic features of In_xMoSe_2 $(0 \leqslant x \leqslant 1)$ compounds

	$MoSe_2$	$In_{1/3}MoSe_2$	$In_{2/3}MoSe_2$	$InMoSe_2$
Lattice Parameter				
a (nm)	0.3280	0.3280	–	–
c (nm)	2 × 0.6447	2 × 0.6570	–	–
$c/9$	0.196 55	0.196 85	–	–
V (nm)^3	0.120 13	0.122 92	–	–
Crystallite size (nm)	19.0	22.0	–	–
Magnetic susceptibility	Diamagnetic	Diamagnetic	Diamagnetic	Diamagnetic
Seebeck coefficient $S^0_{25°C}$ (V° C)$^{-1}$	+10.11	+0.544	+0.880	0.540
Conductivity 25° C (cm)$^{-1}$	2.7×10^{-4}	1.6×10^{-7}	1.35×10^{-3}	4.5×10^{-7}

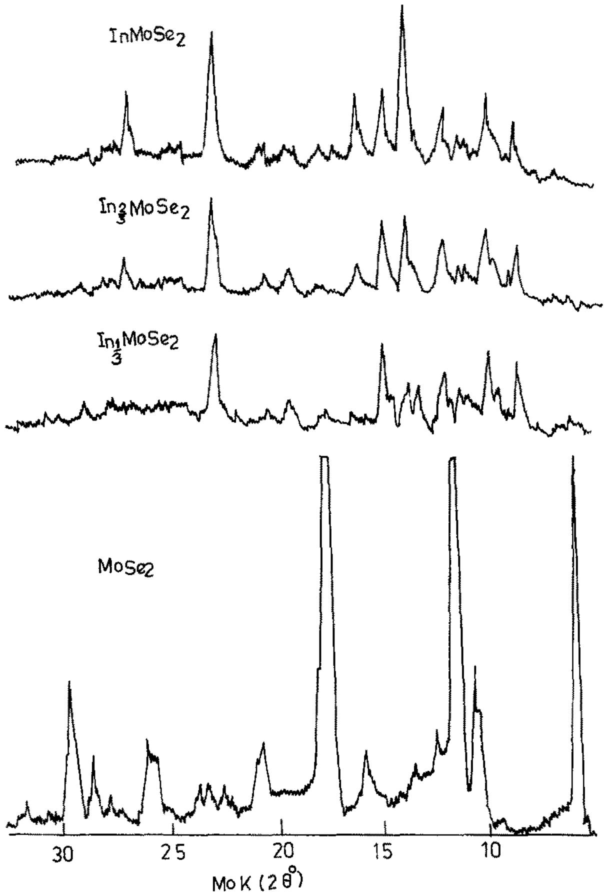

Figure 4 X-ray diffractograms for oxidized products of In_xMoSe_2 ($0 \leqslant x \leqslant 1$) compounds.

in the conduction band of the host crystal [1]. A behaviour similar to our case has also been observed by other workers on some other transition metal dichalcogenides, where the host crystal remained a semiconductor even upon intercalation. Thus Yacobi *et al.* [32, 33], on the basis of their studies on absorption edge measurement on $N^I_xZrS_2$ and $M^I_xHfS_2$ (M^I = Cu, Fe, $0.22 \leqslant x$), concluded that the intercalated atoms here might be regarded as analogous to deep level impurities leading thereby to an additional energy level near the top of the valency band or alternatively it may be due to the modification of the energy band structure of the host crystal due to interactions between the intercalate and sulphur atoms. According to Rouxel [34], in certain cases the electrons given up by the intercalate atoms may get trapped in certain sites rather than being delocalized in the conduction band of the host crystal. Trichet *et al.* [35], from their studies on M_xZrS_2 (M = Fe, Co, Ni), concluded that these compounds retain the semiconductor behaviour even upon intercalation. Thus it appears that there are two or more classes of intercalation compounds where the behaviour of intercalate valency electrons is quite different.

Fig. 3 shows the thermograms of In_xMoSe_2 ($0 \leqslant x \leqslant 1$) compounds in air. It is evident from the thermograms of $MoSe_2$ that there exist two distinct peaks. The first shallow exothermic peak at ≃ 525° C is due to its oxidation and a sharp weight loss in TG corresponding to the formation of MoO_3 was simultaneously observed, the presence of which was also confirmed from the X-ray analysis of the oxidation product [36] (Fig. 4). A second endothermic peak appeared at ≈ 760° C due to melting of MoO_3 and therefore a weight loss in TG was observed due to its evaporation. Thermograms in case of $In_{1/3}MoSe_2$ and $In_{2/3}MoSe_2$ showed the presence of only broad exothermic peak at 450 and 420° C respectively, whereas peaks became flatter in $InMoSe_2$. Though TG in all the cases showed a weight loss due to the oxidation and was found to decrease with increasing indium content in $MoSe_2$. It is, however, interesting to note here that the melting of these compounds did not take place even up to 1000° C. Such an observation has led to the conclusion that the pure In_xMoSe_2 ($0 \leqslant x \leqslant 1$)

TABLE III X-ray data for the oxidized products

$MoSe_2$		$In_{1/2}MoSe_2$		$In_{2/2}MoSe_2$		$InMoSe_2$	
d (nm)	I/I_1	*d* (nm)	I/I_1	*d* (nm)	I/I_1	*d* (nm)	I/I_1
0.6907	30	0.4769	72	0.4713	50	0.4713	23
0.3812	10	0.4078	88	0.4038	72	0.4038	29
0.3461	75	0.3577	43	0.3579	34	0.3577	15
0.3385	< 5	0.3363	64	0.3363	59	0.3363	15
0.3002	< 5	0.3069	45	0.3069	29	0.3069	15
0.2594	< 5	0.2937	47	0.2933	82	0.2927	100
0.2310	100	0.2729	40	0.2723	75	0.2559	45
0.1983	5	0.2297	24	0.2538	29	0.2523	39
0.1822	< 5	0.2109	28	0.2109	22	0.2109	13
0.1760	< 5	0.2007	24	0.2007	16	0.2007	13
0.1592	5	0.1794	100	0.1783	100	0.1790	79
0.1574	5	0.1424	24	0.1522	36	0.1528	40
0.1501	< 5						
0.1479	< 5						
0.1434	5						
0.1387	10						
0.1380	< 5						
0.1272	< 5						
0.1198	< 5						
0.1149	< 5						
0.1103	< 5						
0.0991	< 5						

intercalation compound does not contain any extra molybdenum selenide phases e.g. $MoSe_2$, Mo_3Se_4 etc., which upon oxidation must have formed MoO_3 and corresponding sharp endothermic peak due to its melting should have appeared in the thermograms.

Fig. 4 shows the X-ray diffractograms of the In_xMoSe_2 ($0 \leqslant x \leqslant 1$) oxidation products and the interplaner distance, *d*, along with their intensity are recorded in Table III. It may be noted here that the peaks initially present in $MoSe_2$ oxidation product i.e. MoO_3 almost disappeared and new *d*-lines were set in for In_xMoSe_2 ($0 \leqslant x \leqslant 1$) oxidized product. The *d* values in In_xMoSe_2 ($0 \leqslant x \leqslant 1$) oxidation products were also thoroughly scanned for all other possible phases e.g. InO, MoO_3, In_2MoO_6, $In_2(MoO_4)_3$ etc. and were found to be absent. An interesting feature in the diffractograms here is the remarkable resemblance excepting the peaks which appeared at 0.253 86, 0.152 28 nm and was due to the appearance of a new In_2O_3 phase (0.2529, 0.1525 nm) [37] or perhaps for $In_xMo_6Se_8$, $In_{333}Mo_{15}Se_{19}$ oxidized products. This further strengthens our conclusion, inferred from the X-ray studies of the pure In_xMoSe_2 ($0 \leqslant x \leqslant 1$) compounds, that a new phase appeared in the diffractograms of $In_{2/3}MoSe_2$ and $InMoSe_2$ due to In_7Se_6 or In_2Se_3.

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Received 16 February
and accepted 14 June 1988