

Mechanism of high-temperature oxidation of tin selenide

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High-temperature oxidation of SnSe in the temperature interval 25 to 650°C has been studied by X-ray photoelectron spectroscopy, X-ray diffraction and thermal analysis techniques. Exposure to dry oxygen (760 torr pressure) at up to 200°C leads to the formation of SnO₂ on the surface. The high-temperature bulk oxidation between 250 and 650°C goes through distinct steps of formation of intermediate tin oxoselenides, presumably SnOSe or SnSeO₂ and its subsequent conversion to SnO₂.

1. Introduction

During recent years, the study of the interaction of oxygen with semiconductor surfaces has become very important, since this information has a bearing on the understanding of many practical and fundamental problems associated with device fabrication and also with degradation of the device characteristics.

In contrast to other semiconducting materials, the narrow-gap IV-VI compounds have received very little attention, especially in the area of surface research. As an integral part of our study on the nature of chemical bonding and oxidation/chemisorption of monochalcogenides, we have investigated the SnSe-O₂ system using X-ray photoelectron spectroscopy, differential thermal analysis and X-ray diffraction techniques.

2. Experimental procedures

2.1. Materials

Tin selenide was prepared from spectroscopically pure tin and selenium obtained from Johnson Matthey and Koch Light (UK), respectively, by mixing them in stoichiometric proportion and vacuum sealing in a silica tube. This mixture was heated to 400°C and maintained at that temperature for 4 h. The temperature was further raised to 900°C and the sample was maintained at this temperature for 20 h after which it was furnace-cooled to 300°C. The sample was then quenched in ice-cold water. The X-ray diffraction pattern of the powder sample was recorded on a Philips 1730 X-ray diffractometer to confirm the formation of a single-phase compound of SnSe. X-ray results as shown in Fig. 1 are in good agreement with those of Agnihotri [1].

2.2. Photoelectron spectroscopy

2.2.1. Spectrometer parameters

Photoelectron spectra (PES) were recorded on a VG Scientific (UK) ESCA-3-MK-II Electron Spectrometer fitted with a preparation chamber. MgK α (1253.6 eV) radiation was used to excite the photoelectrons. A description of the instrument and the calibra-

tion of the binding energy (BE) scale have been reported in our earlier publications [2-5]. All the spectra were recorded with the same spectrometer parameters such as 4 mm entry slit and 20 eV pass energy, which gave a resolution of 1.2 eV (full width at half maximum, FWHM) for the Au4f_{7/2} (84 eV) energy level.

2.2.2. Treatments

Photoelectron spectra were recorded after various treatments as listed below. In all cases the Sn 3d, O 1s and Se 3p levels were recorded.

(A) The surface of SnSe was argon ion-etched until no signal arising from oxygen 1s and carbon 1s were observed. The parameters for sputtering were 10⁻⁶ torr argon pressure, beam energy 5 kV and beam current 50 μ A focused on to 1.0 cm² of the sample. The ratio of Sn/Se, the BE of Sn 3d_{5/2} and Se 3p_{3/2} levels were checked between etching. They were found to remain unchanged, indicating no preferential sputtering of tin or selenium within the time interval used to remove surface contaminants.

(B) A clean surface at 25°C was exposed to oxygen.

(C) A clean surface was heated to 100°C and exposed to oxygen.

(D) A clean surface was heated to 200°C and exposed to oxygen.

(E) A clean surface was heated to 250°C in air for 2 h.

(F) A clean surface was heated to 450°C in air for 2 h.

(G) A clean surface was heated to 650°C in air for 2 h.

(H) SnSe was heated to 1000°C in air (thermal analysis studies) and the PES were recorded.

(I) SnSe was heated in a vacuum-sealed silica tube (vacuum better than 10⁻⁶ torr for 100 h at 550°C).

For Treatments B, C and D, an oxygen pressure of 760 torr was used and the samples were exposed to oxygen for 15 min. Treatments A to G were carried out in the preparation chamber of the spectrometer.

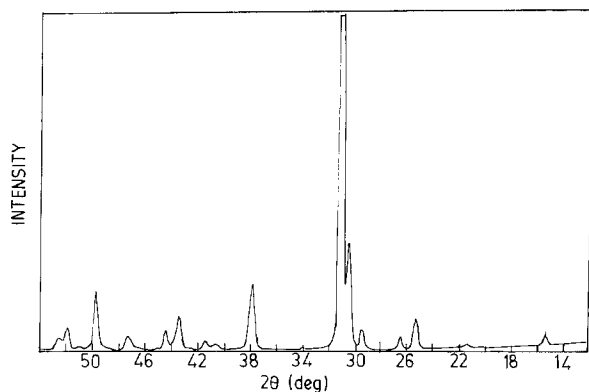


Figure 1 X-ray diffraction pattern of SnSe.

2.3. X-ray diffraction

With a view to identifying the new species observed, fresh SnSe was heated to 600°C in air for 4 h and powder X-ray diffraction patterns were recorded after each hour of heating. The X-ray diffraction (XRD) patterns were recorded using a Philips 1730 X-ray diffractometer with CuK α radiation.

2.4. Thermal analysis

Thermal decomposition studies were performed on a Netzsch (West Germany) ST 409 differential thermal analyser which has the facility to record simultaneously the results of differential thermal analysis (DTA), thermogravimetric analysis (TG), derivative thermogravimetric analysis (DTG) and the sample temperature (T). The temperature of the sample was recorded using a precalibrated Pt(10%) Rh–Pt thermocouple. An appropriate amount of SnSe was loaded on a suitable crucible and was mounted on the alumina rods of the sample carrier. The decomposition studies were carried out in nitrogen, oxygen and dynamic air atmospheres.

3. Results and discussion

3.1. Photoelectron spectra

3.1.1. Argon ion-etched SnSe

The BE of Sn 3d_{5/2} and Se 3p_{3/2} levels obtained from an argon ion-cleaned surface (Treatment A) are shown in Fig. 2a (Curve I) and Fig. 3 (Curve I), respectively, and the corresponding BE values are 485.6 eV (Sn 3d_{5/2}) and 159.6 eV (Se 3p_{3/2}), (Table I). The Sn 3d_{5/2} level in SnSe was found to be shifted to the high BE side by 1.0 eV with respect to the corresponding level in pure metallic tin. The Se 3p_{3/2} level was shifted to the low BE side by 2.1 eV as compared to the corresponding level in pure selenium [3].

3.1.2. Oxygen treatment

On Treatments B, C and D no change was observed in the BE values of the Se 3p_{3/2} level. However, the Sn 3d_{5/2} level developed an asymmetry and this asymmetry became more pronounced at higher temperatures. Using a non-linear least-squares Gaussian computer fit, the experimental curves were resolved into two components (shown by dotted lines in Fig. 2b). The BE values of the resolved components are 485.6 and 486.7 eV. The 485.6 eV level was attributed to the unreacted SnSe surface and that of 486.7 eV to the formation of SnO₂ on the surface. Two types of oxygen with BE values 530.6 and 531.4 eV were observed (Fig. 2c). The ratio of peak area O 1s_{530.6}/O 1s_{531.4} was found to increase after oxygen treatment. With increasing oxygen exposure, the O 1s level corresponding to BE 530.6 eV became more pronounced and the intensity of O 1s_{531.4} started decreasing.

3.1.3. Air heating

On Treatments E and F (Fig. 4a, Curves I and II) the Sn 3d_{5/2} peak developed asymmetry on the high BE side. The resolved Gaussian component corresponded to unreacted SnSe (485.6 eV) and SnO₂ (486.7 eV). On

TABLE I Binding energy values of SnSe after various treatments

Treatment	Temperature (°C)	Binding energy (eV)					
		Se 3p _{3/2}	Sn 3d _{5/2}	O 1s	ΔE_{Se}	ΔE_{Sn}	τ_{Se}
Tin metal (argon-cleaned)	—	—	484.6	—	—	—	—
Selenium (argon-cleaned)	—	161.70	—	—	—	—	—
SnSe (argon-cleaned)	—	159.60	485.6	—	2.1	1.0	2.1
Tin metal heated in air	—	—	486.7	—	—	—	—
SnSe heated in oxygen for 15 min at 760 torr pressure	25	159.6	485.6	—	2.1	1.0	—
			486.7	—	—	2.1	—
	100	159.6	485.6	530.6	2.1	1.0	—
			486.7	531.4	2.1	2.1	—
SnSe heated in air for 2 h	200	159.6	485.6	530.6	2.1	1.0	—
			486.7	531.4	2.1	2.1	—
	250	160.0	485.6	530.6	1.7	2.4	2.4
			486.7	532.6	—	—	—
	450	160.3	485.6	530.6	1.4	—	2.7
			486.7	532.6	—	—	—
	650	159.4	485.6	530.6	2.1	—	3.1
		160.9	486.7	532.6	0.8	—	—
	1000	161.8	—	530.6	—	—	—
		165.5	486.7	—	3.8	—	—

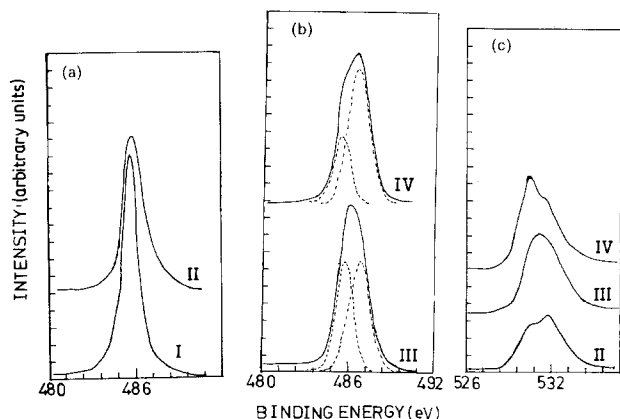


Figure 2 PES of SnSe heated in oxygen atmosphere for 15 min at 760 torr pressure: (a, b) Sn $3d_{5/2}$ level, (c) O 1s level. Curves I, SnSe unreacted; II, 25°C; III, 100°C; IV, 200°C.

the other hand, the Se $3p_{3/2}$ level started shifting to the high BE side (Fig. 4c). The line-width (FWHM) also showed an increase from its initial value of 2.1 eV. Treatment G gave only one Sn $3d_{5/2}$ level at 486.7 eV (Fig. 4a), indicating a complete oxidation. On the other hand the Se $3p_{3/2}$ level which was originally at 159.6 eV shifted to 160.9 eV. The shift in BE (ΔE) decreased to 0.8 from 2.1 eV on heating the sample in air over the temperature interval 250 to 650°C, and the line-width (FWHM) increased from 2.1 to 3.1 eV. The Se $3p_{3/2}$ level with 3.1 eV line-width was resolved into two components with BE values of 159.4 and 160.9 eV. Two types of oxygen with BE values 530.6 and 532.6 eV were also observed (Fig. 4b).

After Treatment H, the PES showed three peaks in the BE region 155 to 172 eV (Fig. 3, Curve III) corresponding to Se 3p levels and only a single peak corresponding to the Sn $3d_{5/2}$ level (486.7 eV). The Se 3p level was resolved into two pairs. The BE values of the resolved components of Se $3p_{3/2}$ levels are 161.8 and 165.5 eV. From the available literature data, the 161.8 eV level was assigned to selenium and that at 165.5 eV to SeO_2 [6].

3.1.4. Vacuum heating

The PES of SnSe heated in a vacuum for 100 h at 550°C (Treatment I) was identical to that obtained from SnSe, indicating that the compound is stable under vacuum heating.

3.1.5. PES analysis

The shift in the energy levels of tin and selenium in the compound SnSe indicates a decrease in the positive

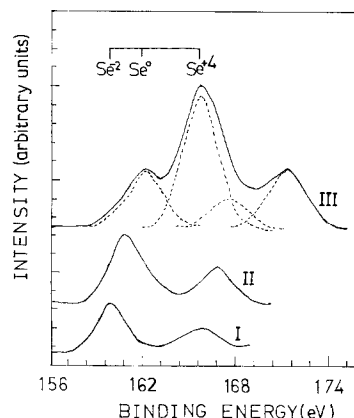


Figure 3 PES of Se 3p levels: Curve I, SnSe; Curve II, (SnO + Se) heated in vacuum; Curve III, SnSe heated to 1000°C (end-product of DTA analysis).

charge density around the tin nucleus and also an electron transfer from tin to selenium. From the available data [4, 5, 7, 8] the 486.7 eV is assigned to SnO_2 and the 485.6 eV level to unreacted SnSe surface. The O 1s level at 530.6 eV is assigned to lattice oxygen in SnO_2 because of its high negative shift (O^{2-}) and the correspondence between the systematic rise in its intensity with that of the tin peak from SnO_2 . The oxygen at 531.4 eV is assigned to chemisorbed oxygen [9] and the O 1s at 532.6 eV to surface hydroxide groups [9]. The large line-width exhibited by the Se $3p_{3/2}$ level in SnSe heated at 650°C is attributed to the formation of a new compound. SnSe is very stable under vacuum heating.

So far no XPS studies of the oxidation of SnSe have been reported in the literature. However, Vasilev *et al.* [10] have studied the oxidation and thermal decomposition of tin chalcogenides by Mossbauer (MB) spectroscopy. The results are (a) SnSe on prolonged heating in vacuum gives rise to $SnSe_2$ and β -Sn, (b) appreciable oxidation of SnSe in air begins at 400°C, (c) the MB spectra of specimens heated in air exhibit not only the spectrum of the initial compound but also that of Sn(IV), and (d) the reaction of oxygen with monochalcogenides is apparently associated with the formation of an intermediate compound. The new compound has been identified as $Sn_5O_6Se_4$. The MB spectrum of this compound consists of two lines of different width which corresponds to the presence of Sn(II) in this compound. Some of the tin atoms are surrounded by selenium and some by oxygen atoms. Heating SnSe above 600°C reduces the intensity of the oxochalcogenides. The formation of $SnSe_2$ and β -Sn

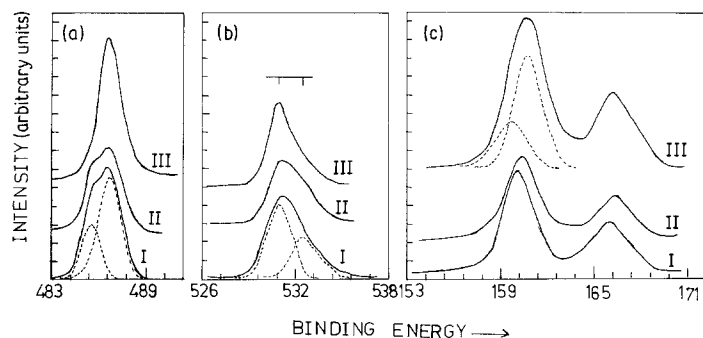


Figure 4 PES recorded after heating SnSe in air for 2 h: (a) Sn $3d_{5/2}$, (b) O 1s, (c) Se 3p. Curves I, 250°C; Curves II, 450°C; Curves III, 650°C.

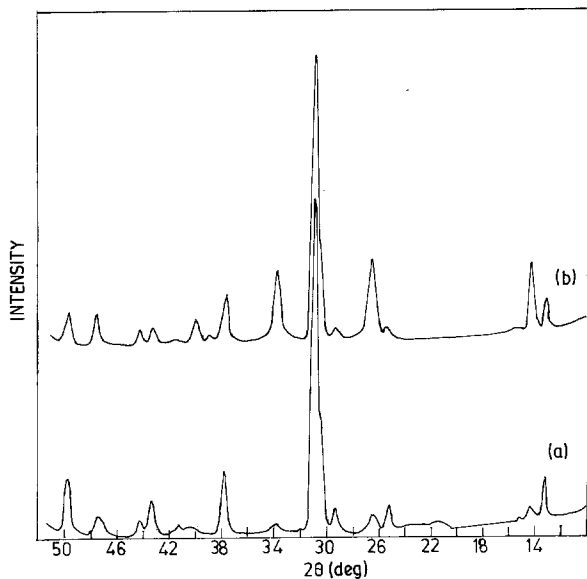
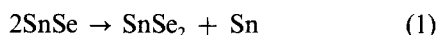


Figure 5 X-ray diffraction pattern of SnSe after heating in air for (a) 1 h, (b) 2 h.

according to the equation



is ruled out in the present case because SnSe heated for 100 h at 10^{-7} torr vacuum did not show any difference in PES as compared to SnSe.

3.2. X-ray analysis

With a view of identifying the new species observed in our XPS studies, fresh SnSe was heated at 600°C for 4 h in air and X-ray powder diffraction patterns were recorded after each hour of heatings (Figs 5a and b, Figs 6a and b and Fig. 7a). The appearance of two prominent new lines with d values 0.610 and 0.662 nm in addition to other lines corresponding to SnO_2 , SnSe and selenium was observed. As the heating was continued, the intensity of the 0.662 nm line started decreasing and the 0.610 nm line intensity started increasing. After 4 h of heating, the 0.662 nm line completely disappeared. When SnSe was heated to 900°C , only lines corresponding to SnO_2 were present. Though it is very difficult to identify the new com-

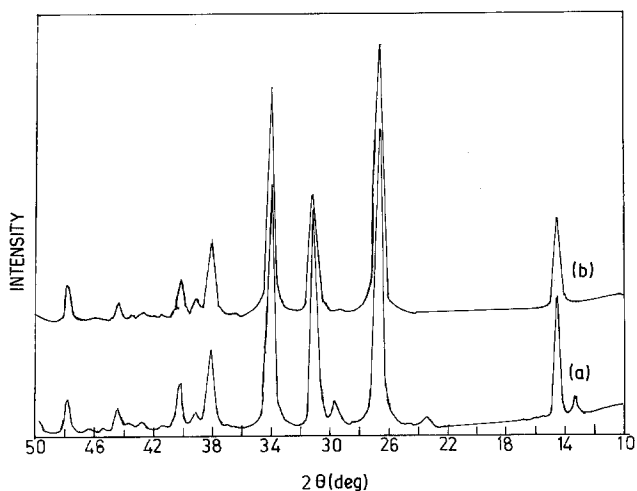


Figure 6 X-ray diffraction patterns of SnSe after heating in air for (a) 3 h, (b) 4 h.

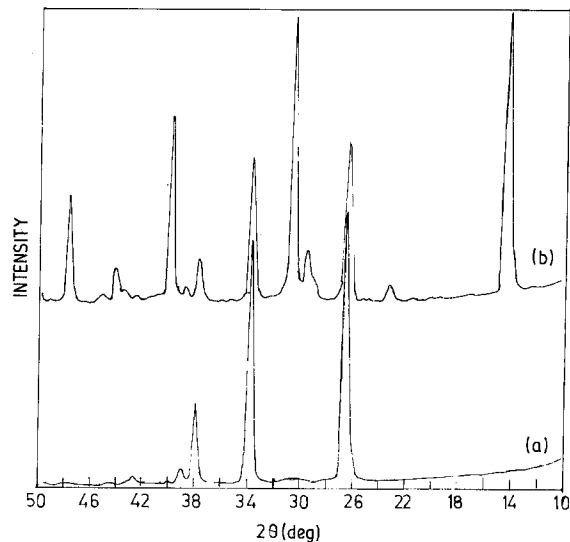


Figure 7 X-ray diffraction patterns of (a) SnSe after heating in air for 6 h; (b) $(\text{SnO} + \text{Se})$ heated in a vacuum (10^{-7} torr) for 2 h.

pound which is formed, it is evident from the X-ray pattern that when SnSe is heated in air at 600°C , two new compounds are formed and gradual conversion of SnSe to SnO_2 takes place with the release of free selenium.

3.3. Thermal analysis

The DTA curve obtained from a sample of SnSe heated in a nitrogen atmosphere showed a small exothermic peak around 400°C and an endothermic peak at 852.6°C . Since no changes in the TG and DTG were observed, the exothermic peak at 400°C was attributed to a phase change. The endothermic peak at 852.6°C is due to the melting of the compound. At temperatures above 852.6°C a gradual weight loss was observed which has been attributed to the sublimation of selenium.

Fig. 8 shows the DTA analysis of the sample carried in oxygen atmosphere at a heating rate of 5°C min^{-1} . Four exothermic peaks at 400, 620, 666 and 733°C were observed. The first one was assigned to a phase change due to reasons explained earlier. The sample gains weight in the temperature interval 600 to 680°C covered by two endothermic steps at 620 and 660°C . The total weight gain is $\sim 8\%$. This corresponds to an addition of one oxygen atom per mole of SnSe. Further there is a weight loss in the range 660 to 750°C

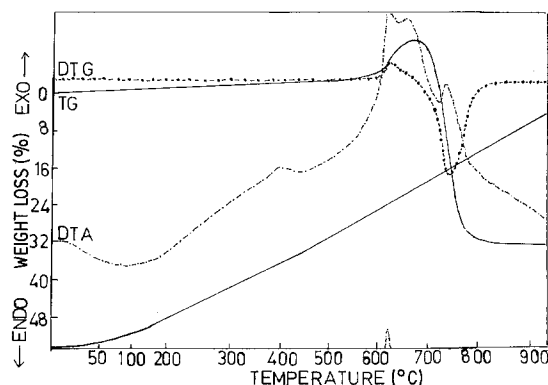
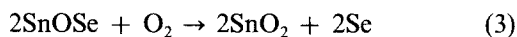


Figure 8 TG, DTG and DTA curves of SnSe heated in oxygen.

covered by the endothermic peak at 733°C. The net weight loss from the initial to the final weight is 23.9% and corresponds to the total oxidation of SnSe to SnO₂. These observations can be explained on the basis of the following reactions taking place in the sequence shown below:

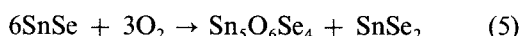


In the temperature range 666 to 733°C there is a gradual drop in TG which indicates simultaneous oxidation of SnO₂ and slow sublimation of selenium. At 744°C there is a sharp drop in TG which is an indication of the completion of the loss of selenium.

A variety of oxoselenide compounds can be formed when SnSe is heated in air/oxygen such as SnSeO₄, Sn₅O₆Se₄, SnOSe etc. The formation of SnSeO₄ can be ruled out because this reaction leaves 75% of the compound unreacted, according to the chemical equation



The formation of Sn₅O₆Se₄ can also be eliminated since it involves the formation of SnSe₂.



The melting point of SnSe₂ is 580°C and as the DTG did not show any endothermic peak at 580°C, corresponding to the melting of this compound, it is reasonable to rule out the formation of Sn₅O₆Se₄.

The mechanism of oxidation of SnSe to SnO₂ in dynamic air is observed to be more significant. Fig. 9 gives the DTA analysis of SnSe in a dynamic air atmosphere. Again four exothermic peaks were observed at temperatures 409, 625, 750 and 785°C. Table II gives in detail the temperature, the percentage of weight loss and the possible mechanism of reaction. The first step (labelled (a) in Fig. 9) is a weight gain of 11.6% (due to absorption of oxygen) which resulted in the formation of SnOSe and possibly some SnSeO₂. X-ray diffraction studies of SnSe heated at 600°C for different intervals of time gave a complex diffraction pattern indicative of the formation of more than one compound. Compared to SnOSe, SnSeO₂ is extremely unstable; it therefore disintegrates instantaneously into SnO₂ and knocks out free selenium gradually in the form of vapour. This cycle continues till all SnSe is converted to SnO₂ as end-product. The second step (b) is a weight loss of 13.4% (1.8% from the original SnSe weight). The third step (c) is a weight gain of ~3.7% and the fourth and the fifth steps are weight losses of 11.5% and 5.6%, respectively. The most

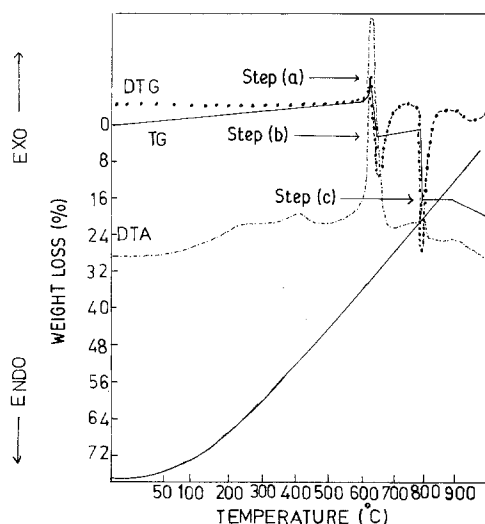
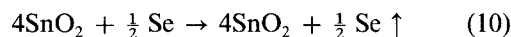
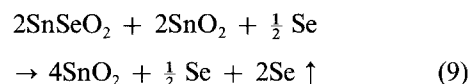
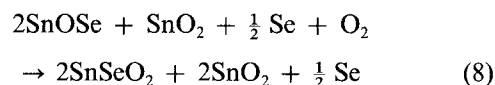
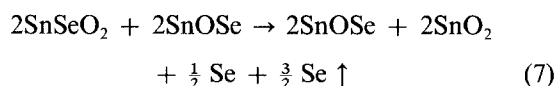


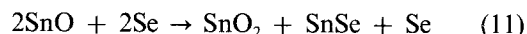
Figure 9 TG, DTG and DTA curves of SnSe heated in air.

likely thermal decomposition mechanism for SnSe in air could be written as follows:



3.4. Oxoselenides

We have attempted to prepare oxoselenide compounds by heating SnO and selenium in stoichiometric proportions at a temperature of 450°C for 2 h in vacuum and quenching in ice-cold water. The X-ray diffraction pattern of this sample was found to have lines corresponding to SnO₂, selenium and SnSe. The formation of SnO₂ is attributed to a disproportionation reaction of the type given



In addition, we have also observed a line with a *d* value of 0.6145 nm which matches with the X-ray diffraction line obtained after heating SnSe in air. However, single-phase SnOSe could not be obtained.

4. Conclusions

On the basis of the XPS, XRD and DTA analyses, we

TABLE II Thermal decomposition of SnSe in air

Stage of decomposition	Temperature range (°C)	Maximum temperature (°C)	Weight gain (%)		Possible chemical reactions
			Experimental	Theoretical	
I	25 to 624	624	+11.6	+12.2	$4\text{SnSe} + 3\text{O}_2 \rightarrow 2\text{SnOSe} + 2\text{SnSeO}_2$
II	624 to 650	624	-13.1	-13.4	$2\text{SnOSe} + 2\text{SnSeO}_2 \rightarrow 2\text{SnOSe} + 2\text{SnO}_2 + \frac{1}{2}\text{Se} + \frac{3}{2}\text{Se} \uparrow$
III	650 to 835	835	+3.7	+4.2	$2\text{SnOSe} + 2\text{SnO}_2 + \frac{1}{2}\text{Se} + \text{O}_2 \rightarrow 2\text{SnSeO}_2 + 2\text{SnO}_2 + \frac{1}{2}\text{Se}$
IV	—	835	-19.5	-19.8	$2\text{SnSeO}_2 + 2\text{SnO}_2 + \frac{1}{2}\text{Se} \rightarrow 4\text{SnO}_2 + \frac{1}{2}\text{Se} + 2\text{Se} \uparrow$
V	875 to 960	960	-5.6	-6.2	$4\text{SnO}_2 + \frac{1}{2}\text{Se} \rightarrow 4\text{SnO}_2 + \frac{1}{2}\text{Se} \uparrow$

draw the following conclusions on the oxidation of SnSe.

1. At lower temperatures (below 200° C) the interaction of oxygen with SnSe leads to surface oxidation with the formation of SnO₂.

2. There is an indication of phase change of SnSe at 410° C.

3. When SnSe is heated in air or oxygen, the formation of new intermediate compounds is indicated by XPS and XRD and they are identified from DTA.

4. The high-temperature bulk oxidation of SnSe to SnO₂ takes place in two distinct steps. First an intermediate oxoselenide is formed, which subsequently reacts with additional O₂ to give SnO₂. Selenium is vaporized as free selenium or SeO₂ during the second step.

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