Study of intermediate oxides in SnO thermal decomposition

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Abstract. Two series of room temperature x-ray and Mössbauer spectroscopy (MS) measurements were performed on powder SnO samples after 1 h annealing in air and Ar at temperatures between 473 and 1073 K in 100 K steps. Complementary measurements on one SnO sample treated in vacuum in this sequence were performed after the thermal treatment at 773 K. In the thermal evolution between SnO and SnO_2 the results show the presence of an intermediate oxide not only in the Ar and vacuum annealed samples but also in those annealed in air. The Mössbauer parameters of the 2^+ and 4^+ states for the intermediate oxide were determined. The results were consistent with a reaction rate dependent on the oxygen partial pressure.

1. Introduction

There are two well known tin oxides: SnO and SnO_2, both of them semiconductors with band gaps of about 2.5–3 and 3.6 eV, respectively. At standard pressure and temperature both crystallize in a tetragonal modification. While SnO_2 adopts the rutile-type form, the SnO presents a PbO-type structure.

From the two tin oxides the stannic one is, by far, the most used in technology, primarily in the form of thin films. Because of this, most efforts have been devoted to its understanding while the detailed mechanism for the transition SnO → SnO_2 has been scarcely investigated. It has been proposed [1] that it starts with a breakdown in the stoichiometric ratios. The reaction would start at $T > 573$ K and for this stage the formation of an intermediate metastable oxide coexisting with SnO_2 and metallic Sn, has been reported [1]. Its oxygen content should lie between those of SnO and SnO_2.

The intermediate oxide has been described as Sn_3O_4 [2] and subsequently as Sn_2O_3 [1]. To our knowledge just two indexations of the unit cell have been performed, ascribed to Sn_2O_3 and Sn_3O_4 respectively [1, 2]. In both cases different triclinic symmetries have been proposed. Yet the structure of the oxide is not known.

In recent years we have undertaken research to gain a better understanding of the parameters governing the thermal transformation of SnO. Thin Sn–O films were prepared by thermal evaporation and studied by perturbed angular correlations using both ^{111}In and ^{181}Hf [3–5].

Very recently we successfully applied conversion electron Mössbauer spectroscopy (MS) to similar films [6], to determine the hyperfine parameters of the 2^+ state in the

intermediate oxide. Here we present new results from MS experiments on the evolution of SnO under thermal annealing in different atmospheres.

2. Experimental procedure

Two series of room temperature MS measurements were performed on powder SnO (Baker) samples after cumulative 1 h annealing in air and Ar at temperatures between 473–873 and 473–1073 K respectively, in both cases in 100 K steps. After each annealing the sample capsule was opened to the air and the powder removed for the MS measurement.

Complementary measurements were carried out after the thermal treatment at 773 K on one SnO sample treated *in vacuo* following the previously mentioned sequence. This time the sample was not exposed to the open air after each annealing. In all cases the cooling of the sample took place in the furnace.

X-ray diffractograms (XRD) revealed the presence of SnO alone in the initial material. XRDs were taken on each sample after the annealing at 773 K. On the sample annealed in Ar, mentioned in the first paragraph, an XRD was also taken after annealing at 673 K.

Mössbauer spectra were recorded in a conventional constant acceleration apparatus with transmission geometry. The non-linearity was fitted to a second-degree polynomial. The 5-mCi $Ba^{119m}SnO_3$ source was kept at room temperature and driven in a triangular waveform. Isomer shifts were referred to a $CaSnO_3$ absorber. A non-linear least squares program with constraints was used to fit the spectra to Lorentzian line shapes.

3. Results

Figure 1 shows the Mössbauer spectra taken after each treatment in Ar and air. In addition to the 2^+ oxidation state corresponding to the doublet centred at about 2.5 mm s^{-1}, the emergence of the 4^+ state (the unresolved doublet centred at about 0.0 mm s^{-1}) can be observed after the annealing at 573 K. This is more evident in the Ar series. At higher temperatures (773 K) an unsplit line ($\simeq 2.5$ mm s^{-1}) belonging to Sn^0 also shows up. In both series a drastic change is apparent between 673 and 773 K.

The XRD taken on the sample treated in Ar at 673 K showed the lines corresponding to SnO. No evidence of SnO_2 was found although the Mössbauer spectrum showed the presence of the 4^+ state. The situation changes for the samples treated in Ar and vacuum after the annealing at 773 K since XRD showed the presence of β-tin, SnO_2 as well as the intermediate oxide but not of SnO. Comparatively we found more SnO_2 in the sample annealed in vacuum than in Ar. In addition to these phases the lines of SnO were also observed in coincidence with the MS results for the sample treated in air.

After annealing at 873 K in air, MS showed that both SnO and Sn^0 interactions disappeared while for the sample annealed in Ar even at this high temperature the presence of Sn is evident. It is observable that a small fraction of the intermediate oxide is still present in both cases.
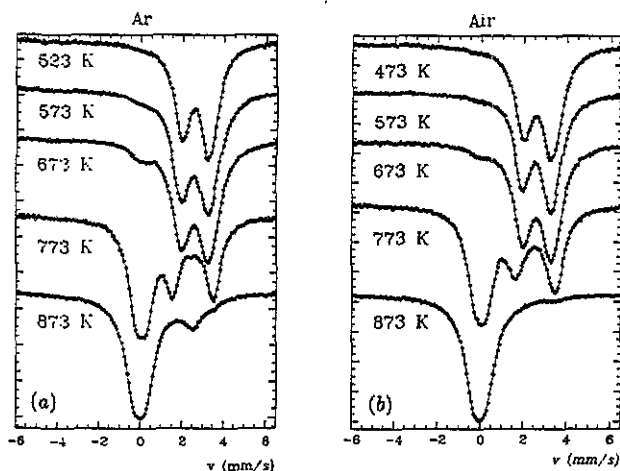
Figure 1. MS at room temperature taken on an SnO sample after annealing at the temperatures indicated for Ar (*a*) and air (*b*) atmospheres.
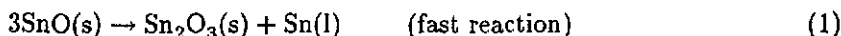
4. Discussion

The XRDs taken after the annealing at 773 K showed the intermediate oxide reported by Murken and Trömel to be Sn_2O_3 [1]. A Mössbauer spectrum of an SnO sample annealed at 723 K in vacuum, taken after the chemical removal of metallic Sn, is shown in [7]. It revealed two oxidation states: the 2^+ assigned to Sn_2O_3 and the 4^+ assigned to $SnO_2 + Sn_2O_3$. In a recent work [6] we characterized the 2^+ state unambiguously. Since the phases cannot be isolated, it was difficult to sort out the 4^+ interaction of the intermediate oxide, which is very close to SnO_2 in the Mössbauer spectra. However, since the XRD of the sample annealed at 673 K in Ar did not reveal the presence of SnO_2, and as at these temperatures the ratios are only just beginning to breakdown, we can tentatively assign the parameters found for the 4^+ state to the intermediate oxide. Besides, the 14% difference in the fitted ΔQs is indicative of the differing local environments of the Sn^{4+} in SnO_2 and in the sesqui-oxide. These arguments do not exclude the parameters being influenced by a small contribution of SnO_2, since it is well known that MS is notoriously more sensitive than XRD in the detection of small amounts of phases. But the fact that the fitted Γ is smaller than that corresponding to SnO_2 gives support to the assumption that SnO_2, if present, is not the majority phase.

On the other hand MS showed, after annealing at $T \geqslant 973$ K in Ar only, the signals belonging to the 4^+ state and to that of Sn. Since the Sn^{2+} state is not observed a decomposition seems already to have taken place. Therefore the Mössbauer spectra taken after annealing at 873 K in Ar should represent an intermediate stage in this decomposition.

Finally the rise in the contribution of the 4^+ state indicates that the reaction starts at $T \geqslant 573$ K, while in the range 673–773 K the higher rate of reaction takes place.

Our hyperfine results confirm the two-step reaction [1]:

$$3SnO(s) \rightarrow Sn_2O_3(s) + Sn(l) \qquad \text{(fast reaction)} \qquad (1)$$

$$2Sn_2O_3(s) \rightarrow 3SnO_2(s) + Sn(l) \qquad \text{(slow reaction)}. \qquad (2)$$

However, based on XRD, which shows that more SnO_2 is formed annealing in vacuum, the breakdown ratio of SnO seems to accelerate if the oxygen partial pressure is reduced (see figure 2 and table 1). Thus the temperature and oxygen partial pressure dependences of the rate of reaction suggested by our results would be consistent with an enhancement in the number of defects, favouring the nucleation of the new phase. Since the structure of the intermediate oxide is not known, it is difficult to correlate the observed hyperfine parameters to particular charge environments. However, in each series we can see the same height relation for the 2^+ site. As in SnO this could be assigned to a plate-like morphology for the intermediate oxide.
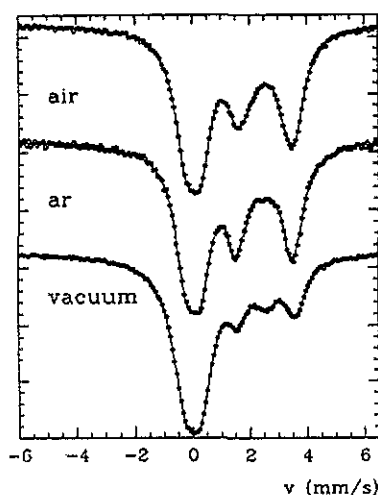

Figure 2. MS at room temperature taken on an SnO sample after the annealing programme described in section 2, up to 773 K, labelled according to the respective atmospheres.

Table 1. Hyperfine parameters corresponding to the spectra, shown in figure 1, taken after annealing in Ar. The parameters labelled a are those corresponding to crystalline SnO and SnO_2. Parameters labelled b correspond to the measurement taken after annealing *in vacuo*. IS refer to $CaSnO_3$ at 300 K. The solidus indicates that the parameter was kept fixed.

	Sn^{4+}				Sn^{2+}				Sn^0	
T_a(K)	ΔQ	IS	L_2/L_1	Γ	ΔQ	IS	L_2/L_1	Γ	IS	Γ
523					1.32_1	2.62_1	0.78_1	0.98_1		
573	$0.46_/$	$-0.02_/$	$1.00_/$	$0.90_/$	1.34_1	2.63_1	0.84_1	1.17_1		
673	0.43_3	-0.06_4	0.80_1	$0.80_/$	1.34_1	2.64_1	0.84_1	1.16_1		
773	0.53_1	0.05_1	1.00_3	0.91_1	1.96_1	2.52_1	0.82_1	0.84_1	2.54_3	$1.00_/$
873	0.56_1	-0.02_1	0.95_3	1.11_1	1.78_6	2.56_3	$0.83_/$	0.83_1	2.56_1	1.02_5
973	0.56_1	-0.01_1	$1.00_/$	1.21_1					2.56_1	1.02_2
1073	0.55_1	-0.02_1	$1.00_/$	1.24_1					2.55_1	0.94_2
a	0.50_1	0.00_1	1.00_1	0.97_2	1.36_1	2.68_1	0.87_1	0.92_1		
b	0.56_1	0.01_1	0.97_2	1.05_1	2.01_1	2.58_1	0.83_2	0.82_2	2.58_1	1.04_6

Finally, it is well known that PbO and PbO_2 are isostructurals for SnO and SnO_2 respectively. If the analogy could be extended to the sesqui-oxides the structure of

Sn_2O_3 should be that of a C-type oxide. This hypothesis agrees with the observed interactions, in particular the highly asymmetric environment of the 2^+ state in the intermediate oxide.

5. Conclusions

The thermal decomposition of SnO is shown by Mössbauer results. It begins slowly at $T \geqslant 573$ K and displays its fastest rate between 673 and 773 K. An intermediate oxide of assumed composition Sn_2O_3 [1] is formed.

The Mössbauer results at higher temperatures confirm the results reported in [1] with a final decomposition of Sn_2O_3 into SnO_2 and metallic tin. The hyperfine interaction of the Sn^{4+} environment of the intermediate oxide has been tentatively characterized by MS. It has been found to differ from SnO_2 suggesting quite different surroundings of the Sn^{4+} probes. The results reported in this work are consistent with a reaction rate dependent on the oxygen partial pressure and with the suggested two-step reaction.

Acknowledgments

References

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