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Note

# DSC ANALYSIS OF DISPROPORTIONATION PRODUCTS OF SnO

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DSC has been used to determine the O/Sn ratio in the intermediate oxide (IO) $Sn_xO_{x+1}$ obtained as the disproportionation product of SnO ($250 \le T \le 400$ °C; $p_{O_2} \le 2$ mPa) together with metallic Sn. For this purpose the effect related to the melting of metallic Sn in the disproportionation products has been measured. The IO is characterised by an O/Sn ratio of 1.1 and exhibits non-stoichiometric features.

## INTRODUCTION

In recent years, close attention has been paid to the tin oxide films (SnO and $SnO_2$) used in many optical and electronic devices. It has been observed that vapour phase deposition gives rise to an oxide layer with an oxygen defect compared with $SnO_2$, because of a partial loss of oxygen during evaporation. The films thus obtained have an O/Sn ratio between 1.0 and 1.6, depending on evaporation conditions [1]. Films of an intermediate oxide, $SnO_y$ with $0.9 < y < 1.6$, have been obtained by radiofrequency reactive sputtering ($0.067 < p_{O_2} < 0.134$ Pa) with $SnO_2$ targets [2]. Also, the oxidation of an SnO film starts from a disproportionation reaction, followed by complete oxidation by means of the surrounding oxygen [3]. The O/Sn ratio in the IO depends on the temperature at which the amorphous film undergoes the transition to crystalline oxide; at 350 °C an O/Sn ratio of 1.37 has been observed [4]. An oxide with an oxygen content between SnO and $SnO_2$ has been determined by EELS (electron energy-loss spectroscopy) [5].

In the present paper, an O/Sn ratio of 1.1 has been obtained.

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## EXPERIMENTAL

Tests on several samples of disproportionated SnO were carried out on a differential scanning calorimeter (Perkin–Elmer, DSC-4). The scanning rate was 5 °C $\text{min}^{-1}$, which represents a good compromise between peak resolution and the consequent determination of the heat developed per unit mass, $q(x)$.

Table 1 lists the DSC data of the disproportionated SnO samples and reports both the temperature and time of disproportionation treatment, the value of the parameter $q(x)$ resulting from the thermograms and the value of the O/Sn ratio calculated from eqns. (2) and (5), below. X-ray diffraction showed that the control sample, SnO/1 h/630 °C, consisted of Sn and $SnO_2$; all of the other samples examined were found to be composed of metallic Sn and IO [6].

The obtained thermograms are shown in Fig. 1.

## DISCUSSION

The disproportionation reaction of $Sn^{II}$ may be written as follows [7]

$$2Sn^{II} \rightarrow Sn^{IV} + Sn^{0} \tag{1}$$

The disproportionation product of SnO at $T \leq 400\,°C$ is IO with a greater oxygen content than SnO

$$(x+1)SnO \rightarrow Sn_xO_{x+1} + Sn \tag{2}$$

If we use the notation: $q(x) = Q/m$, the heat effect due to the melting of metallic Sn ($Q$ = developed heat and $m$ = mass of the sample); $m_{Sn}$ = mass of Sn in samples disproportionating according to eqn. (2); $R_M = Sn/SnO$; and $L_f$ = melting latent heat of Sn, we obtain

$$\frac{m_{Sn}}{m} = \frac{Sn}{(x+1)SnO} = \frac{R_M}{x+1} \tag{3}$$

$$\frac{m_{Sn}}{m} = \frac{Q}{mL_f} = \frac{q(x)}{L_f} \tag{4}$$

TABLE 1

Disproportionated samples submitted to DSC analysis

| Disproportionation conditions [a] | Phases present | $q(x)$ ($\text{J g}^{-1}$) | O/Sn ratio |
|---|---|---|---|
| 10 h/350 °C | Sn + OI | 4.26 ± 0.02 | 1.1 |
| 100 h/350 °C | Sn + OI | 6.10 | 1.1 |
| 1 h/400 °C | Sn + OI | 5.48 | 1.1 |
| 10 h/400 °C | Sn + OI | 5.43 | 1.1 |
| 1 h/630 °C | $Sn + SnO_2$ | 25.29 | 2.0 |

[a] All disproportionation experiments were carried out at $p_{O_2} \leq 2$ mPa.

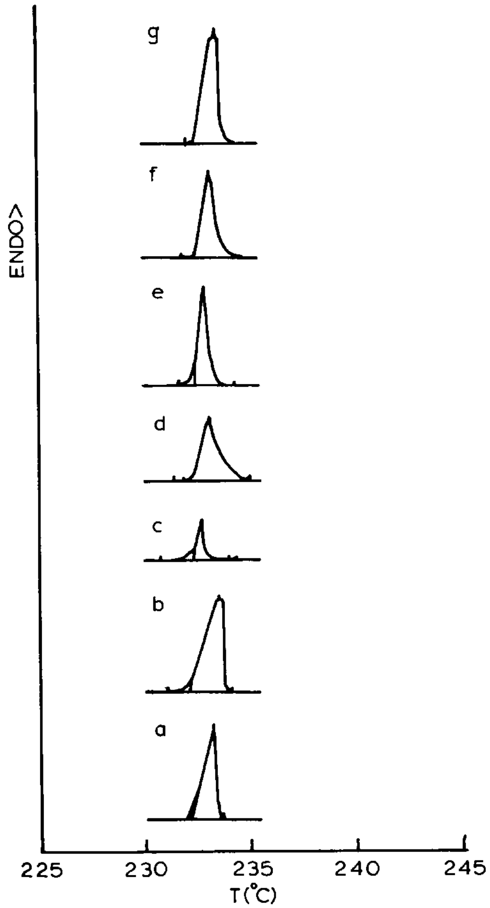

Fig. 1. Thermograms of metallic Sn and disproportionated SnO samples (scanning rate 0.5 °C $min^{-1}$): a, Sn bulk; b, Sn powder; c, SnO 10 h/350 °C; d, SnO 100 h/350 °C; e, SnO 1 h/400 °C; f, SnO 10 h/400 °C; and g, SnO 1 h/630 °C.

From eqns. (3) and (4) we obtain

$$q(x) = \frac{R_M L_f}{x+1} \qquad (5)$$

In order to take into account any instrumentation and impurity effects, the product $R_M L_f$ can be determined through a previous examination of a sample of SnO whose purity is accurately known (98.75% in this case), and disproportionated according to the relationship

$$2SnO \rightarrow SnO_2 + Sn \qquad (6)$$

corresponding to $x = 1$ in eqn. (2). Thus

$$q(1) = q_1 = \frac{R_M L_f}{2} \qquad (7)$$

From the thermogram of SnO/1 h/630 °C, we obtain $q_1 = 25.25$ J $g^{-1}$ and hence $L_f = 57.4$ J $g^{-1}$; the value reported in ref. 8 is $L_f = 59.5$ J $g^{-1}$.

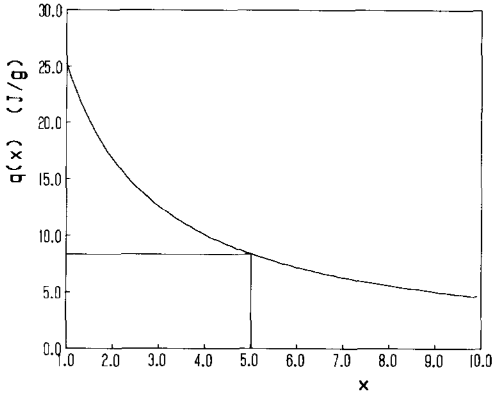

Fig. 2. Heat per unit mass $q(x)$ vs. $x$ for $Sn_xO_{x+1}$.

A plot of $q(x)$ versus $x$ is shown in Fig. 2.

In the literature, several formulae have been proposed for the intermediate oxide: $Sn_2O_3$, $Sn_3O_4$ and $Sn_5O_6$. From Fig. 2, if $1 \leq x \leq 5$, then $25.29 \geq q(x) \geq 8.43$ J $g^{-1}$. The choice among the possible formulae should be clear because of the rapid variation of $q(x)$ within the considered interval. The determination of $x$ becomes less accurate if $q(x) < 8$ J $g^{-1}$. All the experimental results, whenever the disproportionation product is IO, fall under this case. Therefore the SnO disproportionation ought to be considered from a different point of view: the IO should assume non-stoichiometric features and the disproportionations process could be interpreted as a redistribution of oxygen ions inside the SnO lattice.

The disproportionation temperature would be expected to play an important role in determining the oxygen content of IO. Nevertheless the DSC measurements of Sn latent melting heat are useful for the disproportionation temperature range (350–400 °C). Actually, only the samples which undergo disproportionation in this range consist of Sn and IO: for $T < 350\,^{\circ}$C the disproportionation is not complete, while at 0.5 h/450 °C it goes partially to $SnO_2$ [6].

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