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Formation of cadmium stannates studied by electron spectroscopy

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The formation of $CdSnO_3$ and Cd_2SnO_4 from cadmium and tin oxides in closed vessels was studied over a range of temperature by thermal analysis, X-ray powder diffraction and electron spectroscopy. The results, presented in diagrammatic form, enable suitable reaction conditions to be chosen for the formation of either stannate in the monophase form. ESCA and SIMS examination of the reactants and products indicates that the commercial CdO starting material contains small amounts of carbonate and suboxide impurities, which however have no effect on the formation of the final product. Electron spectroscopy also indicates that the cadmium stannates, once formed, are significantly more resistant to atmospheric carbonation or hydration than is the parent CdO.

1. Introduction

Conducting oxide materials are of special interest for a number of solar energy conversion applications. One promising system recently under investigation is CdO/SnO_2. Two distinct compounds, Cd_2SnO_4 and $CdSnO_3$ exist within the CdO/SnO_2 system [1, 2]. Dicadmium stannate is reported to have high optical transmission over the visible range as well as high conductivity [3, 4]. Potential usefulness of this compound in transparent electrode and heat mirror applications has been indicated by many authors [5–12]. Monocadmium stannate is reported to have promising photoelectrochemical properties [3,13].

During the preparation of either of the cadmium stannates as monophase by solid state reaction, the desired product may be contaminated both by the reactant oxides and the other stannate [14, 15], which contamination can influence the optical, electrical and photoelectrochemical properties of the product. In order to prepare either Cd_2SnO_4 or $CdSnO_3$ in monophase form by solid state reaction, precise knowledge of the formation and thermal stability of these compounds is essential. To gain this information, a detailed study was made of the reactions by X-ray diffractometry and thermal analysis. More detailed structural information concerning the cadmium stannates can be gained from recently-developed analytical techniques such as ESCA (or X-ray photoelectron spectroscopy) and SIMS (secondary ion mass spectrometry). ESCA has been extensively used in studies of inorganic compounds [16, 17], and although the literature data on ternary compounds [18] are still sparse, it is clear that this powerful technique can provide useful structural information as well as surface analysis of ternary oxides.

Some data on the binding energies in CdO and SnO_2 are reported in the literature [17–24]; because of its relatively greater importance, CdO has received more attention, but nonconcordant data have been reported [20, 22, 24]. No ESCA data for cadmium stannates are available in the literature. The present paper reports some of the results of an investigation of the CdO/SnO_2 system which forms part of a joint research programme between the Materials and Energy Research Centre and Brunel University.

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2. Experimental details

The staring materials were reagent grade CdO and SnO_2 powders (Merck). Intimate mixtures of the oxides were prepared, containing mole ratios of CdO to SnO_2 of 1:1 and 2:1. Semiquantitative DC arc analysis of the unreacted 2:1 mixture indicated the following elemental impurity levels:- Fe $\leqslant$ 0.02%, Cu $<$ 0.02%, Al = 0.01%, Ti = 0.01%, Ni $<$ 0.003%, Pb = 0.01 to 0.02%. No other impurity elements were detected.

Samples of about 10 g were heated for 6 h in closed alumina crucibles at 700 to 1150° C. The products were ground to $< 100\,\mu m$, and 10 wt% high purity silicon powder was added as an internal standard for semiquantitative X-ray powder diffraction.

The X-ray photoelectron spectra of both reactants and products were recorded on a Kratos ES350 ESCA spectrometer using Al–$K\alpha$ X-rays as the excitation source. The working pressure in the chamber was better than 10^{-8} torr. In order to calibrate the binding energy scale of the spectra, the carbon 1s level arising from oil contamination was taken as 285 eV. In some samples, an extremely thin layer of gold was evaporated on non-conductive samples, the gold $4f_{7/2}$ line being taken as 83.8 eV.

SIMS spectra were obtained using a Physical Electronics Auger/ESCA/SIMS system equipped with a quadrupole mass spectrometer. The working pressure in the chamber was 2×10^{-10} torr and sputtering was carried out at a pressure of 5×10^{-6} torr of argon or oxygen.

Small samples (6 to 8 mg) were heated in a Stanton Redcroft 781 simultaneous TG and DTA thermal analyser at a heating rate of $5^\circ\,min^{-1}$ in a dynamic air atmosphere with a flow rate of $50\,ml\,min^{-1}$.

Evolved gas analysis (EGA) was carried out in a Stanton Redcroft TG770 thermobalance connected to an Extranuclear quadrupole mass spectrometer using helium as the carrier gas. A heating rate of $10^\circ\,min^{-1}$ was used in these experiments.

3. Results and discussion

3.1. Formation conditions for the two stannates

Fig. 1 shows the XRD phase distribution diagram for 1:1 mixtures heated to different temperatures. Although the X-ray sample preparation was carefully controlled, the difficulties inherent in quantitative X-ray powder diffraction are such that the results of Fig. 1 can only be considered as semiquantitative. However, it is clear from Fig. 1 that at about 700° C, Cd_2SnO_4 slowly begins to form. The reaction rate increases with temperature, up to 900° C, at which temperature the formation of Cd_2SnO_4 is almost complete, and the CdO fully consumed.

Above 900° C, a second reaction takes place, in

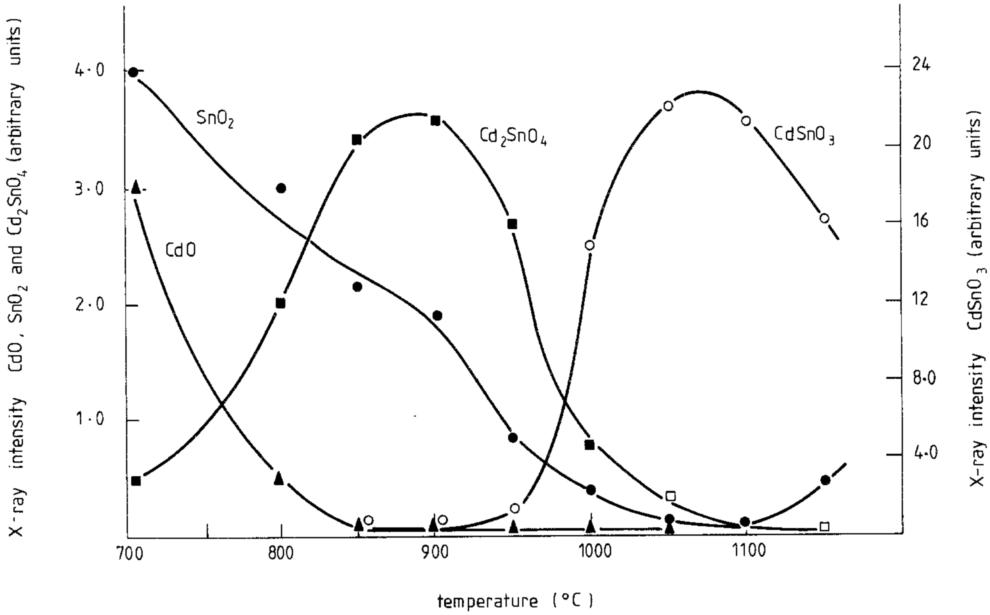

Figure 1 Semiquantitative phase distribution for 1:1 mixtures of CdO and SnO_2, heated at each temperature for 6 h in a closed vessel.

which $CdSnO_3$ is formed:

$$Cd_2SnO_4 + SnO_2 \rightleftarrows 2CdSnO_3 \qquad (1)$$

The rate of this reaction also increases with temperature, reaching completion at 1060 to 1070° C under the present experimental conditions. At higher temperatures, the $CdSnO_3$ decomposes to CdO and SnO_2.

Fig. 2 shows the course of the reactions occurring in $2CdO{:}SnO_2$ mixtures. In this diagram, the X-ray intensities of CdO, SnO_2 and $CdSnO_3$ are plotted as a ratio of the intensity of Cd_2SnO_4. Fig. 2 shows that Cd_2SnO_4 formation reaches completion in 2:1 mixtures at about 1050° C, at which temperature no X-ray lines due to CdO, SnO_2 or $CdSnO_3$ can be detected. Above this temperature, Cd_2SnO_4 decomposes to $CdSnO_3$ and CdO.

3.2. Thermal analysis of the CdO/SnO_2 system

The thermobalance curves of the starting oxides CdO and SnO_2 are shown in Fig. 3 (curves A and B). No significant weight change occurs in SnO_2 up to about 1050° C, above which temperature volatilization begins. By contrast, the commercial grade CdO used here undergoes at least two lower-temperature weight losses in air; the first is complete by about 200° C, the second (of about 0.9%) being complete by about 380° C. Analogous weight losses found for mixtures of the two oxides (curve F) originate in the CdO component, and are associated with two DTA endotherms, of which the lower-temperature endotherm is split (curve G). Independent DTA experiments on reagent grade $CdCO_3$ and freshly precipitated $Cd(OH)_2$ show that the endothermic decomposition temperatures of these two compounds correspond well with the CdO endotherms at 363 and about 200° C respectively (curve G). However, dehydroxylation of $Cd(OH)_2$ gives rise to a single unsplit endotherm, by contrast with curve G.

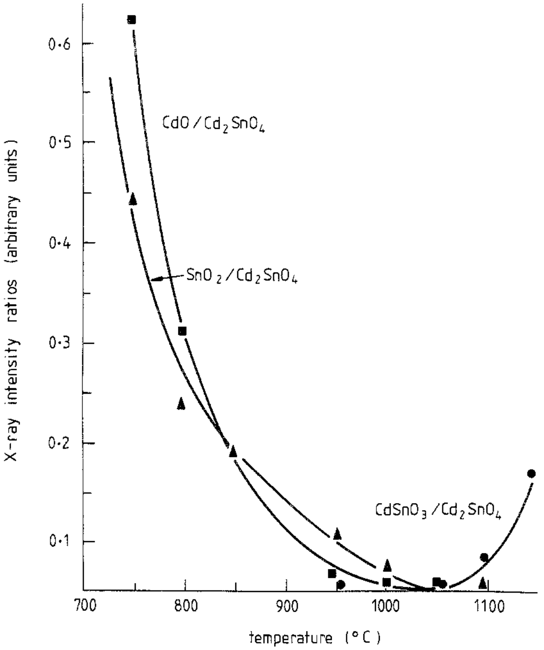

Figure 2 Semiquantitative phase ratios for 2:1 CdO/SnO_2 mixtures heated at each temperature for 6 h in a closed vessel.

Further information about the origin of these low-temperature reactions in the CdO reactant was sought by evolved gas analysis (EGA); unfortunately, for instrumental reasons, these experiments had to be conducted in a dynamic helium atmosphere, and therefore may not exactly reflect the situation in flowing air under which the other thermal analyses were carried out. EGA of CdO alone confirmed that the weight loss at about 350° C is due to carbonate decomposition (curve C), but unexpectedly the lower-temperature weight losses are also accompanied by the evolution of smaller amounts of CO_2. No evidence was found for any significant evolution of water (curve D), oxygen (curve E) or any other volatile species over this temperature range, although in some other commercial cadmium oxides also examined, a water peak was found at about 200° C, indicating $Cd(OH)_2$ impurity, in addition to the carbonate which was found in all samples examined.

Mixtures of Merck CdO with SnO_2 behaved similarly to the Merck CdO alone, evolving CO_2 in at least two stages (curve H) but showing no evidence of any other gaseous evolved species. Thus, the DTA endotherm at about 200° C in these samples appears not to be due to hydroxide decomposition, but rather, may be due to some reaction which either is inhibited by the oxygen-deficient conditions of the EGA experiment, or produces a condensible species. Such a reaction could involve the suboxide Cd_2O, which is shown by SIMS (next section) to be present in the surface layers of commercial CdO. Thermal disproportionation of this compound by the reaction

$$Cd_2O \rightarrow CdO + Cd \qquad (2)$$

would give a weight loss but no evolved species which would be detectable by the mass spectrometer, since the Cd/CdO products would be expec-

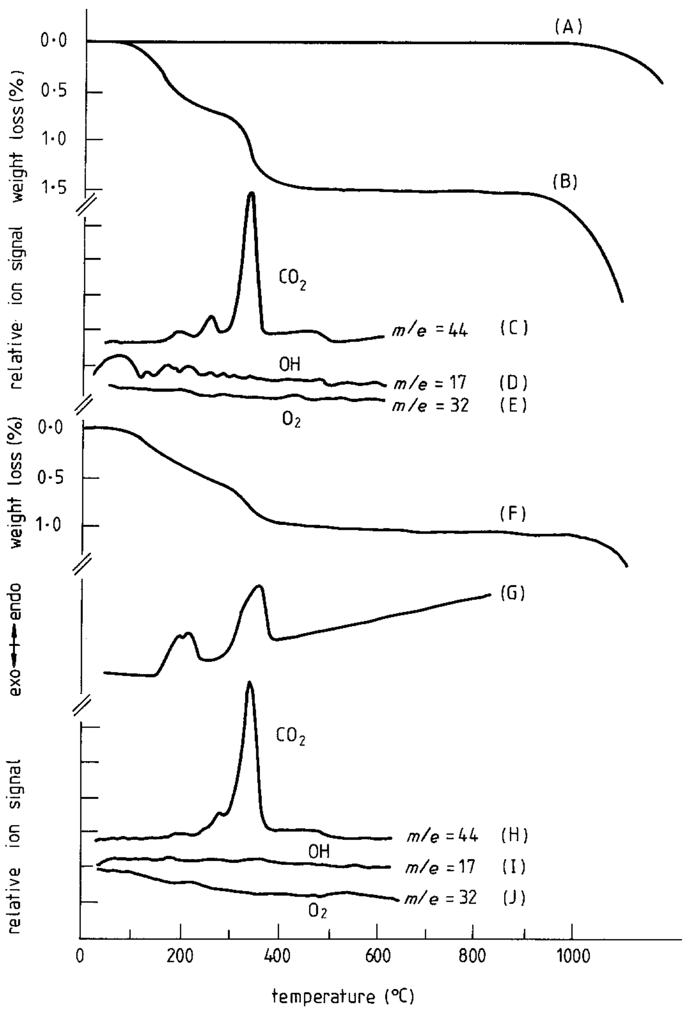

Figure 3 Thermal analysis of cadmium and tin oxides and their mixtures. Curves A, B, F, G in dynamic air (50 ml min^{-1}), heating rate 5° min^{-1}. Curves C to E, H to J in dynamic helium (30 ml min^{-1}), heating rate 10° min^{-1}. A–TG curve for SnO_2, B–TG curve for CdO, C–mass 44 evolution from CdO, D–mass 17 evolution from CdO, E–mass 32 evolution from CdO, F–TG curve for CdO/SnO_2 mixture, G–DTA curve for CdO/SnO_2 mixture, H–mass 44 evolution from CdO/SnO_2 mixture, I–mass 17 evolution from CdO/SnO_2 mixture, J–mass 32 cadmium evolution from CdO/SnO_2 mixture.

ted to condense on the cooler parts of the furnace assembly (orange-yellow films were in fact observed in the cooler zones of the apparatus after these experiments).

To further investigate the possibility that small amounts of cadmium are thermally evolved in such a reaction, small samples of Merck CdO were heated at a constant linear rate in a tantalum boat placed in a microfurnace of such geometry that any evolved vapour would immediately be swept by a stream of nitrogen carrier gas into the heated sampling beam of an atomic absorption spectrophotometer equipped with a cadmium lamp. The whole apparatus therefore constitutes an extremely sensitive evolved gas thermal analyser, specific for cadmium. Experiments with Merck CdO showed a rather abrupt appearance of cadmium in the atmosphere above the sample at about 210° C, corresponding well with the first significant weight loss and DTA peak. Identical results were obtained from mixtures of CdO and SnO_2. The sensitivity of the detection method in this experiment is such that very small amounts of evolved cadmium can be detected; the results should not be taken to indicate the onset of gross sublimation at about 200° C. Curve B in Fig. 3 shows that such sublimation becomes appreciable only at about 900° C under the dynamic air atmosphere of these TG experiments. Although this sublimation might appear to interfere with cadmium stannate formation which becomes significant at about 1050° C, under the static atmosphere conditions of the present stannate syntheses, the onset of CdO sublimation is delayed to still higher temperatures, possibly due to the absorption of the CdO vapour on the surface of the SnO_2 particles and its consequent retention in the reaction system.

Three main conclusions arise from the thermal analyses.

1. The common major impurity in commercial CdO is $CdCO_3$, which endothermically decomposes at about 360° C.

2. A lower-temperature reaction at 190 to 220° C could be due to decomposition of $Cd(OH)_2$ in some commercial CdO samples, but in the present CdO is due to the disproportionation of Cd_2O.

3. Since all these impurities decompose to CdO well below the temperature of its reactions with SnO_2, their presence does not interfere with the thermal synthesis of the cadmium stannates.

3.3. Spectroscopic characterization of the reactants and products

More detailed information about the cadmium stannate products was sought by comparing their ESCA and SIMS spectra with those of the reactant oxides. Curve A in Fig. 4 shows the ESCA spectrum of the cadmium $3d_{5/2}$ peak of the CdO starting material used here.

The pronounced shoulder on this peak has previously been reported [22], and suggests the presence of two overlapping peaks due to cadmium in different environments. Assuming the binding energy of the carbon 1s peak to be 285 eV, the binding energies of the two cadmium $3d_{5/2}$ peaks of CdO are 404.8 and 406 eV. The peak at 404.8 eV corresponds reasonably well with the literature value for pure CdO. Three possibilites have previously been considered by Hammond *et al.* [22] for the assignment of higher-energy cadmium $3d_{5/2}$ peaks; these are $Cd(OH)_2$, $CdCO_3$ and CdO_2.

The presence of a small amount of carbonate was confirmed both by thermal analysis and also by the small carbon 1s peak at about 289 eV (Fig. 5a). This carbonate peak is, however, of low intensity compared to the other carbon 1s peak arising from oil contamination, and appears unlikely to account solely for the large cadmium $3d_{5/2}$ peak at 406 eV.

Although the presence of $Cd(OH)_2$ was confirmed by some CdO samples, thermal analysis showed its concentration not to be significant in the present Merck CdO. However, the oxygen 1s peak in this CdO also has two components, at 529 eV (the oxide peak), and 532.4 eV (curve B in Fig. 4). The presence of the second component suggests that another Cd–O species may also be present, in addition to $CdCO_3$, which has its oxygen 1s peak at 531.2 eV [22]. Such a species could not be CdO_2, in which the reported cadmium $3d_{5/2}$ binding energy is 0.6 eV *less* than in CdO, which in turn has a cadmium binding energy 0.8 eV less than metallic cadmium [22]. On this basis, the cadmium $3d_{5/2}$ peak of CdO_2 should occur on the lower binding energy side of the CdO peak.

Another Cd–O species not considered by Hammond *et al.* [22] is Cd_2O, for which some thermal analysis evidence was presented in Section 3.2. Further evidence for the presence of Cd_2O in the surface layers of the CdO comes from the SIMS spectrum of Merck CdO (Fig. 6), which shows two sets of peaks due to cadmium and CdO,

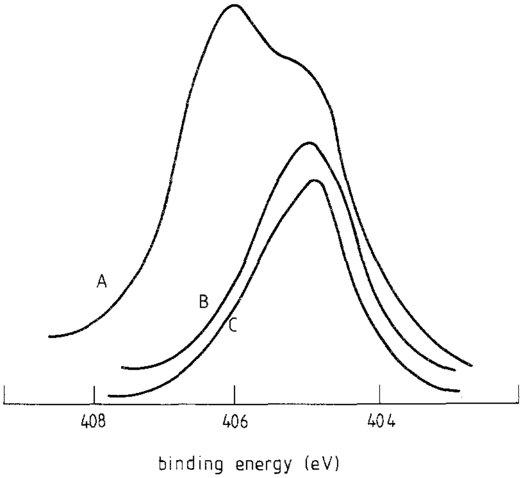

Figure 4 Typical cadmium $3d_{5/2}$ ESCA spectra. A–Reagent grade CdO, B–Cd_2SnO_4, C–$CdSnO_3$.

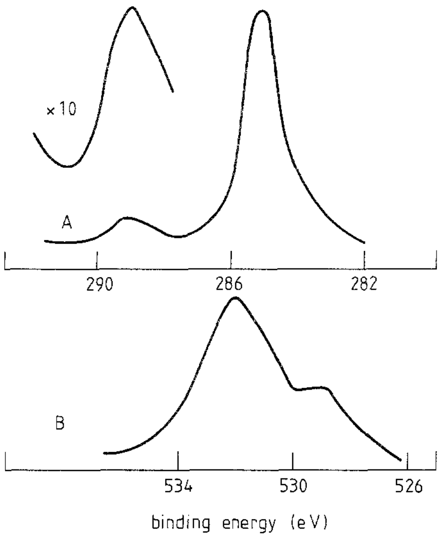

Figure 5 Typical ESCA spectra of reagent grade CdO. A–carbon 1s spectrum, B–oxygen 1s spectrum.

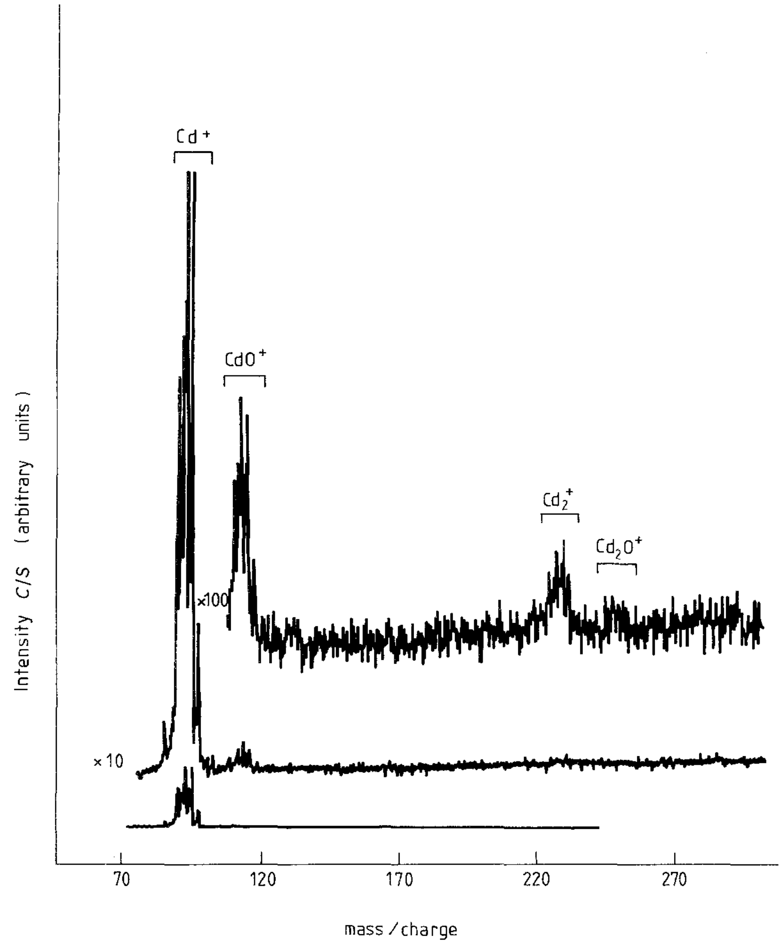

Figure 6 Positive SIMS spectrum of reagent grade CdO.

and two other sets due to Cd_2 and Cd_2O. Prolonged sputtering of the sample with argon ions results in the almost complete removal of the peaks due to Cd_2 and Cd_2O, suggesting that these species reside in the surface layers, and are not simply an artefact of the sputtering process.

SIMS examination of metallic cadmium and several other cadmium compounds, including $CdSnO_3$ and Cd_2SnO_4 showed no sign of the lines due to Cd_2 and Cd_2O, suggesting that the presence of these species may be a unique feature of commercial CdO. It must be emphasized, however, that the concentrations of contaminants which can be detected in the surface layers by ESCA and SIMS can be extremely small, and even the more gross contaminant $CdCO_3$ is below the detection level of XRD (its concentration in Merck CdO appears from the TG experiments to be about 3.5 wt %).

A further experimental observation which must be taken into account when considering possible reasons for the double ESCA peaks of CdO is that coating the sample with a very thin layer of gold removes the higher-energy component of the cadmium $3d_{5/2}$ peak, leaving the single CdO peak at about 405 eV. This could indicate the presence of a charging effect in the sample, or it may simply be due to the modification of the surface layers during the coating process.

The ESCA spectra of the cadmium stannate product phases (curves B and C in Fig. 4) show single cadmium $3d_{5/2}$ peaks with binding energies very close to that of pure CdO. No double cadmium $3d_{5/2}$ peak was found in any of the cadmium stannates examined, not even in samples exposed to air for several weeks. The tin $3d_{5/2}$ peaks recorded for the stannates showed binding energies close to that of pure SnO_2 (Table I).

The removal of both gross and surface impurities from commercial CdO during thermal synthesis of the stannates and the non-reappearance of the contaminants even after exposure of the products to the atmosphere indicates that the stannates should be more chemically stable than CdO,

TABLE I X-ray photoelectron binding energies for cadmium and tin oxides, and their compounds

	Cd $3d_{5/2}$ (eV)	Sn $3d_{5/2}$ (eV)
CdO	404.8	–
SnO_2	–	486.4
$CdSnO_3$	404.8	486.3
Cd_2SnO_4	404.7	486.2

a property which could render them superior for applications such as transparent electrode materials, in which the chemical instablity of CdO has proved to be a drawback [14].

4. Conclusions

1. The impurities present in comercial CdO are shown by thermal analysis and surface analysis techniques to be $CdCO_3$ and Cd_2O, the latter probably occurring only in the surface layers. Some commercial cadmium oxides also contain $Cd(OH)_2$ impurities. All these impurities are destroyed during thermal synthesis of cadmium stannates, and in no way interfere with the high-temperature reactions.

2. Below about 900° C, Cd_2SnO_4 is the stable product formed in 1:1 mixtures of cadmium and tin oxides in static air. Above about 1070° C, $CdSnO_3$ becomes the dominant phase. In 2:1 mixtures (cadmium-rich), Cd_2SnO_4 is dominant up to about 1050° C. By careful selection of the reaction conditions with reference to Figs. 1 and 2, it is possible to synthesize either Cd_2SnO_4 or $CdSnO_3$ in the monophase form.

3. Electron spectroscopy suggests that once formed, the cadmium stannates have superior stability to CdO, showing no tendency to carbonate, hydrate or form surface suboxides on exposure to ambient air. These compounds should therefore be suitable in many applications for which CdO is too unstable to air.

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