Note

Antimony-121 Mössbauer Study of the Effects of Calcination on the Structure of Tin–Antimony Oxides

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The formation of tin–antimony oxides by the calcination of gels produced by alkaline precipitation of tin(IV) and antimony(V) chlorides has been investigated by ^{121}Sb Mössbauer spectroscopy. Calcination at 300 °C produces partially dehydrated solids in which some Sb^V is reduced to Sb^{III}. The subsequent transformation to blue poorly crystalline materials at 600 °C in which the cations occupy oxygen environments is associated with further dehydration and the initiation of thermally induced structural changes. Prolonged heating at 600 °C or short period calcination at high temperature is accompanied by the segregation of a separate Sb_2O_4 phase. The high concentration of Sb^{III} which accompanies calcination at 1 000 °C is associated with the formation of a monophasic solid solution of antimony in tin(IV) oxide in which the surface is enriched in antimony.

A PREVIOUS ^{121}Sb Mössbauer investigation of tin–antimony oxides [1] examined materials calcined at 600 °C according to methods which have been used to prepare catalysts for the selective oxidation and ammoxidation of hydrocarbons. However, two separate groups [2,3] have subsequently reported structural investigations of tin–antimony oxides calcined over a range of temperatures. Although both groups report thermally induced phase changes there is a general lack of agreement on the precise interpretation of the data. Figueras and co-workers [3] described materials containing up to 30% antimony and calcined between 500 and 850 °C as solid solutions which give the separation of an additional Sb_2O_4 phase when calcined at higher temperatures. In contradiction, Pyke *et al.*[2] proposed that the limit of antimony solubility in tin(IV) oxide is very low and only achieved at high temperatures when any Sb_2O_4 formed at *ca.* 600 °C is volatilised. There is a further lack of unanimity concerning the changes in oxidation state and chemical environment of antimony which accompanies the thermal treatment. Since ^{121}Sb Mössbauer spectroscopy is a sensitive means of monitoring the thermally induced structural and chemical changes around antimony and characterising the nature of the antimony bearing phases, a further study has been conducted on materials calcined between 300 and 1 000 °C.

EXPERIMENTAL

Tin–antimony oxides were prepared by the simultaneous addition of appropriate quantities of tin(IV) and antimony(V) chloride to ammonium hydroxide solution. The white precipitates were removed by filtration, washed, dried at 120 °C, and heated in air at 300, 800, or 1 000 °C for either 16 h or 14 d. The ^{121}Sb Mössbauer spectra were recorded with a conventional constant acceleration spectrometer with both the $Ba^{121m}SnO_3$ source and absorber at 4.2 K. The data were computer-fitted according to procedures previously described.[1]

RESULTS AND DISCUSSION

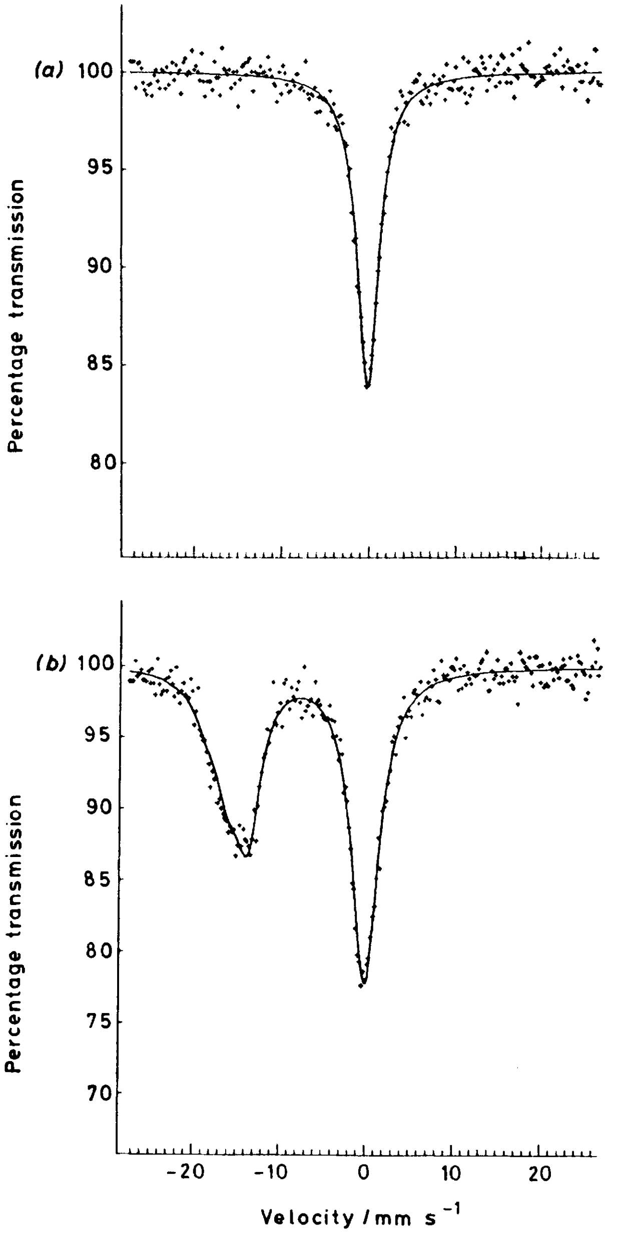
The ^{121}Sb Mössbauer data are recorded in the Table. The chemical isomer shifts are reported relative to InSb as a reference standard. Typical spectra are depicted in the Figure.

The ^{121}Sb Mössbauer spectrum of the white tin–antimony oxide calcined at 300 °C containing 4% antimony showed a single peak characteristic of Sb^V whilst the material containing 20% antimony gave a two-peaked spectrum consistent with the additional presence of Sb^{III}. Since calcination at 300 °C would be expected to involve further dehydration of the precipitate dried at 120 °C the appearance of Sb^{III} may be associated with the reduction of Sb^V as occurs during the dehydration of an antimony(V) hydroxide gel.[4] The Mössbauer spectra are therefore consistent with a partially dehydrated amorphous solid [2] and suggest that units composed of antimony cations in approximately octahedral oxygen–hydroxyl environments could readily coexist in random arrays with similarly co-ordinated tin(IV) species.[5]

Antimony-121 Mössbauer parameters for tin–antimony oxides

		Sb^{III}			Sb^V		
% Sb in sample	Calcination treatment	$\delta^* \pm 0.1$/ mm s^{-1}	$e^2qQ \pm 0.5$/ mm s^{-1}	$\Gamma \pm 0.8$/ mm s^{-1}	$\delta^* \pm 0.1$/ mm s^{-1}	$\Gamma \pm 0.4$/ mm s^{-1}	Area ratio Sb^{III} : Sb^V
4	300 °C/16 h				8.66	3.02	
4	800 °C/16 h	−7.04		4.77	8.16	3.07	0.04
10	800 °C/16 h	−5.38		5.40	8.41	3.60	0.16
20	300 °C/16 h	−4.58		4.65	8.65	3.96	0.13
20	1 000 °C/14 d	−6.41	17.80	3.48	8.68	3.75	0.82
40	1 000 °C/14 d	−6.48	18.11	4.34	8.84	4.64	1.17
50	800 °C/16 h	−6.04	16.84	4.13	8.74	4.72	0.86
$Ba^{121m}SnO_3$					8.76	3.45	

* Relative to InSb.



Antimony-121 Mössbauer spectra (relative to barium stannate) of tin–antimony oxide containing: (*a*) 4% antimony and calcined at 300 °C for 16 h; (*b*) 20% antimony and calcined at 1 000 °C for 14 d

The Mössbauer parameters of the blue tin–antimony oxides calcined for 16 h at 600 °C have been related [1,5] to the occupation by Sb^{III}, Sb^{V}, and Sn^{IV} of oxygen environments with the data for Sb^{V} and Sn^{IV} being characteristic of such species octahedrally co-ordinated to oxygen in a rutile type structure.[4,6-9] The broad line widths are consistent with the occupation by the cations of a heterogeneity of sites as a result of dehydration and thermally induced lattice reconstruction. One of the *X*-ray diffraction investigations [3] described these tin–antimony oxides as solid solutions accommodating up to 30% antimony within the tin(IV) oxide lattice. However, the Mössbauer data for these materials may more readily be associated with a material which, according to the more comprehensive investigation by both *X*-ray diffraction and electron microscopy,[2] consists of a dehydrated poorly crystalline solid containing random arrays of cations in oxygen environments. Indeed, Pyke *et al.*[2] report that the presence of only SnO$_2$ lines in the *X*-ray diffraction pattern does not constitute unambiguous evidence for the formation of a solid solution. Hence the description [3] of a material containing 5 atom % antimony and calcined at 500 °C as a solid solution of Sb^{V} in tin(IV) oxide is without contemporary confirmation. Furthermore, the detection of only an Sb^{V} contribution in the Mössbauer spectrum of this material need not justify interpretation [3] in terms of a charge compensation mechanism involving the delocalisation of electrons into conduction bands. The similar spectrum reported here [Figure (*a*)] for the material containing 4% Sb calcined at 300 °C shows that the Sb^{V} resonance may quite reasonably be attributed to the species within an octahedral array of oxygen atoms in a disordered matrix. Similarly, the presence of Sb^{III} in materials containing >10% antimony need not, as has been reported,[3] reflect an alternative charge balancing process. The observation of both Sb^{III} and Sb^{V} in similar materials calcined at 300 °C or 600 °C for 16 h [1] is more consistent with dehydration and concomitant reduction of Sb^{V} as occurs during the pyrolysis of antimonic acid.[4] In such systems charge balancing processes are not required.

It is of further interest that Figueras and co-workers [3] only detected biphasic systems when the tin–antimony oxides had been calcined at 950 °C, whereas similar materials containing a rutile and an antimony oxide phase were detected by Mössbauer spectroscopy [1] and *X*-ray diffraction [2] in solids containing >10% antimony when calcined at 600 °C. The appearance of an antimony oxide phase at this lower temperature is quite reasonable given the aggregation of the SnO$_2$ octahedra and counter-migration of antimony which [2,10] accompanies the change in colour from white to blue at 400 °C. Furthermore, the ^{121}Sb Mössbauer spectra of materials with a high antimony content calcined at 800 °C or 900 °C display peak area ratios which endorse evidence from *X*-ray photoelectron spectroscopy for the segregation of an Sb$_2$O$_4$ phase under similar conditions.[10,11] The detection of both Sb^{V} and Sb^{III} in the Mössbauer spectrum of the material containing 4% antimony calcined at 800 °C illustrates the high sensitivity of the technique to small quantities of Sb^{III}.

Pyke *et al.*[2,10] have shown that prolonged calcination at 1 000 °C in air of precipitates with initially high antimony concentrations causes volatilisation of any Sb$_2$O$_4$ and the formation of an equilibrated material containing the limit of antimony solubility within tin(IV) oxide of *ca.* 4 atom % but with a surface composition close to 25% antimony. The Mössbauer spectra from these materials exhibit high Sb^{III} : Sb^{V} ratios [Figure (*b*)]. Given the reluctance of Sb^{III} to adopt octahedral co-ordination [12] it is significant that the lattice parameters [2] for these tin–antimony oxides are similar to those of pure SnO$_2$ and therefore inconsistent with the accommodation of Sb^{III} with a lone pair of electrons within the lattice. It seems therefore that the increase in Sb^{III} content with increasing temperature may be associated with the high-temperature loss of oxygen [2] and enrichment of the surface in antimony. In this respect it is interesting that the antimony(III) resonances were amenable to fitting according to a quadrupole split model and gave large values of e^2qQ which suggest the occupation by Sb^{III} of more asymmetric sites than those in Sb_2O_4 [4,6] and tin–antimony oxides calcined at lower temperatures. The data may be associated with the presence of Sb^{III} in a surface site in which the neighbouring tin(IV) species [10] contribute to the electric field gradient.

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