Surface segregation and phase separation in bismuth–tin pyrochlores

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The pyrochlore $Bi_2Sn_{2-x}Bi_xO_{7-x/2}$, which is a catalyst for the oxidative coupling of methane, has been studied in the range of composition $-0.2 \leqslant x \leqslant 1.0$. When heated in air in the range 200–1000 °C, the surface cation concentration is enriched in bismuth. Combining X-ray photoelectron spectroscopy (XPS) surface analysis and X-ray diffraction (XRD) phase analysis has allowed a distinction to be drawn between mechanisms contributing to the segregation process. Dependant upon the composition and temperature, an underlying thermodynamically driven surface enrichment in bismuth may be supplemented by the nucleation, separation and growth of a discrete bismuth oxide phase.

The potential for surface segregation to occur in multicomponent systems has been recognised for many years, but the phenomenon was only characterised when techniques for quantitative surface analysis became available. Metals and alloys were the first materials studied[1] and this was followed by work on mixed oxide systems relevant to catalysis. Pyke and co-workers[2,3] for example, systematically characterised the surface segregation of antimony in tin–antimony oxide catalysts which are selective in heterogeneous partial oxidation reactions. The observed composition and phase changes were related to features of the observed catalysis, particularly the selectivity. Since the early work, segregation in oxides has been much studied and the results related to the surface and bulk properties of catalysts, ceramics and glasses. The literature has been well reviewed[4] and it is apparent that the situation in multicomponent systems can be very complex, particularly if there is amorphous material present. For example, if a particular system is unstable to dissociation into two other phases, what is the role of surface segregation in the nucleation and growth of the new phase? Do discrete surface phases really exist in multicomponent catalysts and how does surface composition vary with the ambient atmosphere? Answering such questions is clearly of interest in its own right, but is also relevant to the development of selective catalysts and catalysts with good lifetime.

In a recent paper by Mims *et al.*,[5] the authors report a study of the catalytic properties of non-stoichiometric bismuth–tin pyrochlores used for the oxidative coupling of methane. Experimentally they observed that the intrinsic surface selectivity of the catalysts was independent of the bulk composition and they deduced that under reaction conditions, the surface of the catalysts was rich in bismuth oxide. XPS measurements on two compositions heat treated in vacuum showed evidence for the surface segregation of bismuth, supporting this deduction. However, the physical characteristics of the segregation process and the structural consequences were not explored. In this paper we report a systematic study of surface segregation in this system. Our aim is to add to the background knowledge of this catalyst and, perhaps more importantly, to use it as an example to explore some of the questions outlined above.

Experimental

The stoichiometric pyrochlore $Bi_2Sn_2O_7$ is chemically stable at high temperatures, but it may exhibit polymorphism dependant upon temperature or the presence of impurities.[6] If tin lattice sites are substituted by bismuth, the lattice is expanded and the system is unstable at high temperatures, tending to form free Bi_2O_3.[5] In the composition range $Bi_2Sn_{2-x}Bi_xO_{7-x/2}$, Mims *et al.* found a single phase exhibiting a linear increase in lattice parameter with x, for materials prepared at 400 °C and with values of x between 0 and 0.86. This phase was found to decompose, liberating bismuth oxide at a temperature dependant upon the value of x. At higher concentrations of bismuth, free bismuth oxide was found in addition to the expanded pyrochlore. We have prepared materials slightly rich and slightly deficient in bismuth ($x = +0.02$, -0.2), rich in bismuth in the single-phase region ($x = 0.6$) and with excess bismuth in the two-phase region ($x = 1.0$). Samples were prepared by coprecipitation from aqueous solution. The required amounts of hydrated bismuth nitrate and stannic chloride salts were added to deionised water containing sufficient nitric acid to ensure complete solution. This solution was added dropwise to a stoichiometric ammonia solution, ensuring that the pH remained above 12. The resulting white precipitate was allowed to settle, thoroughly washed, filtered and dried at 120 °C overnight. After grinding, aliquots from all compositions were heated in air for 16 h periods at temperatures in the range 200–1000 °C. Some samples were heated at specific temperatures for increasing time intervals in the range 5 min to 6 h. At 1000 °C the material was found to slowly lose mass, presumably as a result of volatilisation of bismuth oxide. The $x = 0.6$ material was therefore heated in a platinum crucible for 22 days at 1000 °C, recording the mass changes at intervals until equilibrium was achieved.

The surface composition of all samples was determined by XPS using a Kratos XSAM 800 spectrometer with a multichannel detector. Al-Kα radiation was the excitation source and spectra were collected at high resolution (1.2 eV) and in the fixed analyser transmission mode, which gives uniform resolution across the energy range. Samples were mechanically mounted to ensure good electrical contact and data analysis was achieved using the Kratos DS800 software. Examination of the spectra showed the materials to be free of any significant contamination other than a normal and small level of adventitious carbon at the surface. Spectra were therefore recorded for the C 1s, O 1s, Sn 3d and Bi 4f peaks. Since the experiments were concerned with the unmixing of mixed oxides, the bismuth/tin cation ratio was determined for all samples and expressed as a percentage in all the reported results. This ratio was determined simply from the peak areas, without correction for matrix efects. Although an approximation, the method is reasonable when comparing changes in series of materials of similar composition. A typical analysis for all four components is presented in Table 1, comparing the $x = 0.6$ sample at 600

Table 1 XPS analysis of the surface of $Bi_{2.6}Sn_{1.4}O_{6.7}$

element	calcination temp./°C	E_b/eV	atom%
Bi	600	163.9	10.82
Bi	850	159.1	10.62
Bi	600	169.3	7.15
Bi	850	164.3	8.02
Sn	600	491.4	4.66
Sn	850	486.5	3.74
Sn	600	499.9	2.91
Sn	850	495.0	2.15
O	600	528.4	7.09
O	600	531.3	8.65
O	850	530.5	44.13
O	600	535.4	34.5
O	850	532.7	8.5
C	600	282.7	4.28
C	850	282.1	1.74
C	600	285	10.95
C	850	285	10.67
C	600	289.0	9.00
C	850	286.5	10.43

and 850 °C. For the sample with $x=0.6$ fired to 700 °C the bismuth cation concentration was found to be reproducible within ±1%. The reported bulk compositions and stoichiometries are all determined from the preparation conditions. However, bulk composition was also determined by XPS on certain selected samples by argon ion etching for increased intervals until constant composition was achieved.

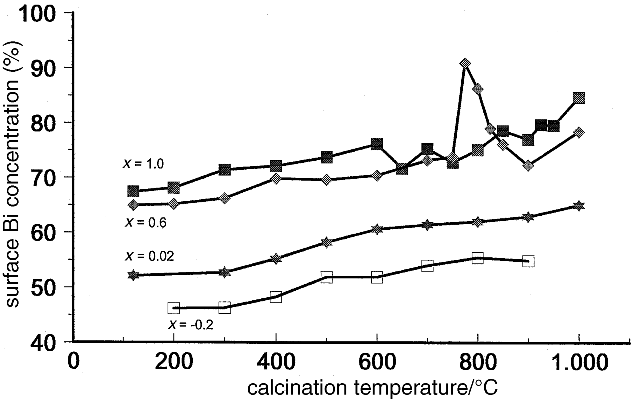

Fig. 1 Surface bismuth concentration of samples of $Bi_2Sn_{2-x}Bi_xO_{7-x/2}$ for various values of x as a function of calcination temperature

Phase composition was determined by powder X-ray diffraction, using a Philips diffractometer (Model PW 1710), Cu-Kα radiation and Philips APD 1700 software.

Results

The surface compositions of samples heated in air between 200 and 1000 °C are plotted in Fig. 1. Enrichment of the surface with bismuth is apparent, similar to that reported previously[5] after heating in vacuum. At 200 °C the surface concentration of bismuth was found to be close to the as-prepared bulk value for samples with the lower values of x. The sample with $x=1.0$ however was found to be deficient in bismuth (68% rather than 75%). With increasing temperature, all compositions showed progressive segregation of bismuth and this was regular except for the $x=0.6$ composition. The latter material showed a sudden increase in bismuth concentration at 775 °C to 91% bismuth, while at higher temperatures the composition gradually returned to the trend line at 1000 °C. This effect was found to be reproducible, all samples of this composition which had been heated to temperatures below 775 °C followed the reported curve when heated to higher temperatures and the critical temperature was located experimentally to within 25 °C. At 1000 °C, the degree of enrichment in bismuth was found to fall within the range 1.18–1.26 for all the compositions studied.

Kinetic experiments at 700 °C showed that the equilibrium surface composition was achieved within 10 min. Arrhenius plots of the degree of enrichment were found to be reasonably linear ignoring the excursion at 775 °C (Fig. 2). Values for the enthalpy of segregation are given in Table 2.

After equilibration at 1000 °C (Fig. 3) the $x=0.6$ sample was found to have lost 36% mass. This is close to the calculated value of 34% assuming that Bi_2O_3 is volatilised to leave stoichiometric $Bi_2Sn_2O_7$. Furthermore the surface cation com-

Table 2 Enthalpy of segregation of bismuth as a function of composition

composition	$x=-0.2$	$x=0.02$	$x=0.6$	$x=1.0$
enthalpy of segregation/ kJ mol^{-1}	0.58	0.76	0.46	0.40

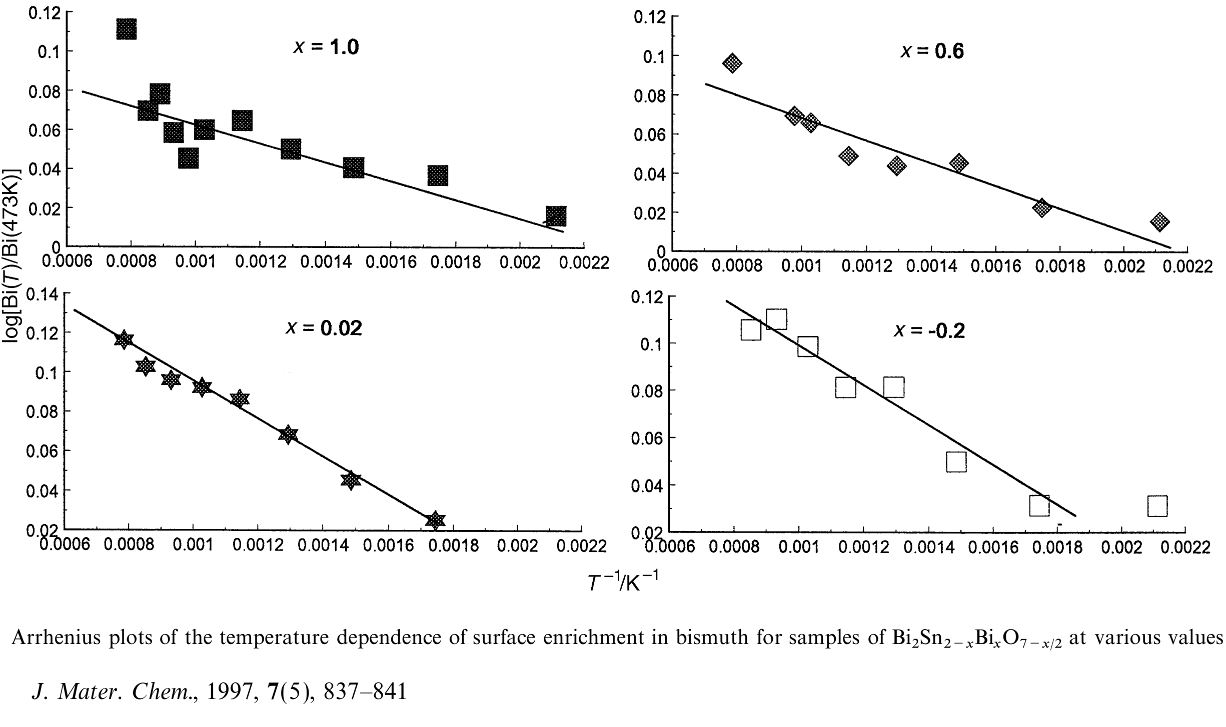

Fig. 2 Arrhenius plots of the temperature dependence of surface enrichment in bismuth for samples of $Bi_2Sn_{2-x}Bi_xO_{7-x/2}$ at various values of x

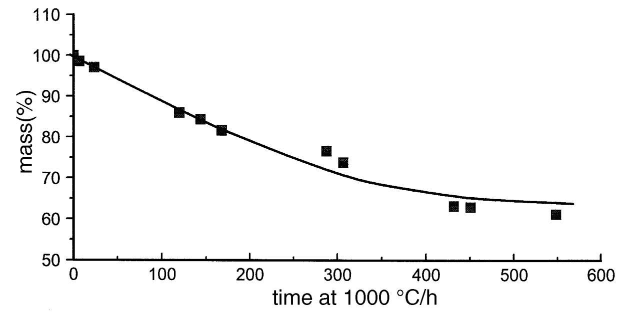

Fig. 3 Mass loss with time observed for $Bi_{2.6}Sn_{1.4}O_{6.7}$ heated in air at 1000 °C

position of 62.54% bismuth was found to be close to the surface composition of the near stoichiometric sample ($x=0.02$) heated to 1000 °C. Argon ion etching (Table 3) showed the equilibrated bulk ratio of bismuth to tin (45:55) to be close to the expected stoichiometry of the thermally equilibrated sample (1:1). It is well known that preferential sputtering can occur during ion etching and for this reason we have avoided using the method to determine bulk compositions. However the consistancy observed in the results suggests that the observed bismuth:tin ratio is little influenced by preferential etching effects.

Examination of the detail in the XPS spectra showed little difference in the peak shapes of the bismuth, tin, or oxygen peaks with calcination temperature, but there were differences with carbon. Referencing the binding energies to carbon at 285 eV, the $x=0.6$ series showed a significant change in binding energy of the bismuth and tin peaks. Below 750 °C values of 163.1 ± 0.9 and 490.6 ± 1 eV were obtained for the major bismuth and tin peaks and above 750 °C values of 159.4 ± 1.0 and 486.8 ± 1.2 eV, respectively.

Powder X-ray diffraction patterns of the 400 °C samples were rather broadened, but the materials heated to 600 °C corresponded to crystalline $Bi_2Sn_2O_7$ (JCPDS 34–1203) (Fig. 4). At the higher concentrations, four additional reflections were observed at 600 and 700 °C ($2\theta = 10.92$, 29.73, 30.31, 40.90). These reflections did not correspond to bismuth oxide. For $x=0.6$ (Fig. 4), the reflections were present at 700 °C but not at 800 °C, while at 800 °C free Bi_2O_3 was formed. At 900 °C, the separate bismuth oxide phase was still present, but heating overnight at 1000 °C reduced the proportion to the limit of detection. Prolonged heating at 1000 °C gave the pure $Bi_2Sn_2O_7$ phase. Upon indexing the bismuth–tin phase as the conventional body centred tetragonal form,[6] the lattice parameter data given in Table 3 were obtained.

For the composition $x=1.0$, the additional reflections were present at 700 °C, but disappeared at higher temperatures. Free Bi_2O_3 appeared at 800–900 °C, reached a maximum proportion at 950 °C and declined in proportion at 1000 °C.

Discussion

At compositions close to stoichiometric $Bi_2Sn_2O_7$, XPS analysis shows that the surface of samples heated in air is enriched in bismuth to a degree dependant on temperature. The method of preparation produces an amorphous coprecipitate with a surface cation composition close to the selected bulk value. When the material is heated, it crystallises and the surface cation ratio varies as the temperature is increased. The surface at equilibrium is enriched in bismuth which has diffused from the bulk. This component has the lower melting point and is the least refractory of the end-member oxides. In this respect the system is analogous to the tin–antimony mixed oxide system, where the surface is enriched in the altervalent antimony cation.[2] The kinetic experiments show that the diffusion processes involved in the segregation of bismuth are relatively rapid. The temperature dependence (Table 2) shows a maximum in the heat of segregation at the stoichiometric composition of the pure compound. Values found for the heat of segregation are rather low (<1 kJ mol^{-1}). This is perhaps to be expected since bismuth oxide has a rather low melting point (825 °C). In addition, the coprecipitation method of preparation is expected to produce a highly defective starting material which will contain paths for facile diffusion.

Table 3 Argon ion etching of $Bi_{2.6}Sn_{1.4}O_{6.7}$ heated to constant mass at 1000 °C. Cation concentration of bismuth as a function of etching time

etching time/min	0	30	60	90
atom% Bi	62.5	49.7	46.0	45.0

At higher concentrations of bismuth, there are similarities to the tin–antimony system, but some differences also become apparent. Excess bismuth can be accommodated by lattice expansion[5] and this is accompanied by the appearance of extra reflections in the powder XRD pattern. For the $x=0.6$ composition, surface enrichment in bismuth is again observed as the temperature is raised. At 750–775 °C a rapid increase in the bismuth concentration at the surface is apparent (Fig. 1). This corresponds to the appearance of free Bi_2O_3 in the XRD and the disappearance of the reported extra reflections as the concentration of bismuth in the bulk is necessarily reduced. The lattice parameter data (Table 4) also show a significant change. As the temperature is raised further to 1000 °C, the surface composition is observed to reduce gradually to the trend line and the free bismuth oxide phase detected by XRD also gradually disappears. Similarly, the lattice parameter values tend to return to the value at 700 °C. Since we have shown that the rate of volatilisation of bismuth oxide is very slow at 1000 °C but that the lattice diffusion of bismuth is fast, it is concluded that the two separate phases are reacting together as the temperature is raised to 1000 °C. This again gives an expanded structure, but possibly in a different polymorphic form since the extra X-ray reflections are no longer all present. Clearly the thermodynamics for nucleation, phase separation and re-reaction are finely balanced. Unfortunately the XPS spectra do not show any really significant changes in the peak shapes with the deduced phase changes, but the binding energies of both bismuth and tin do show a change at 750 °C in the $x=0.6$ series. Above this temperature, the binding energies are characteristic of Bi^{3+} and Sn^{4+} in stoichiometric oxides, while below this temperature the binding energies are some 3 eV higher, indicating unusual bonding. However, the XRD evidence describes the structural changes well. The important result to emphasise is that XPS is capable of characterising and distinguishing between the surface segregation and phase separation processes. Prolonged heating at 1000 °C induces the slow volatilisation of phase-separated oxide in both the bismuth–tin and antimony–tin systems. In the bismuth–tin case, volatile Bi_2O_3 is replaced at the surface by diffusing bismuth and the concentration in the bulk slowly falls. The ion etching experiment shows that, at equilibrium at

Table 4 Lattice parameter data for sample $Bi_{2.6}Sn_{1.4}O_{6.7}$ calcined for 16 h at various temperatures

calcination temperature/°C	a/nm	c/a
700	15.08	1.44
800	14.51	1.52
900	14.65	1.44
1000	15.17	1.40
1000[a]	15.13	1.41
single crystal[6]	15.08	1.43

[a] 22 days.

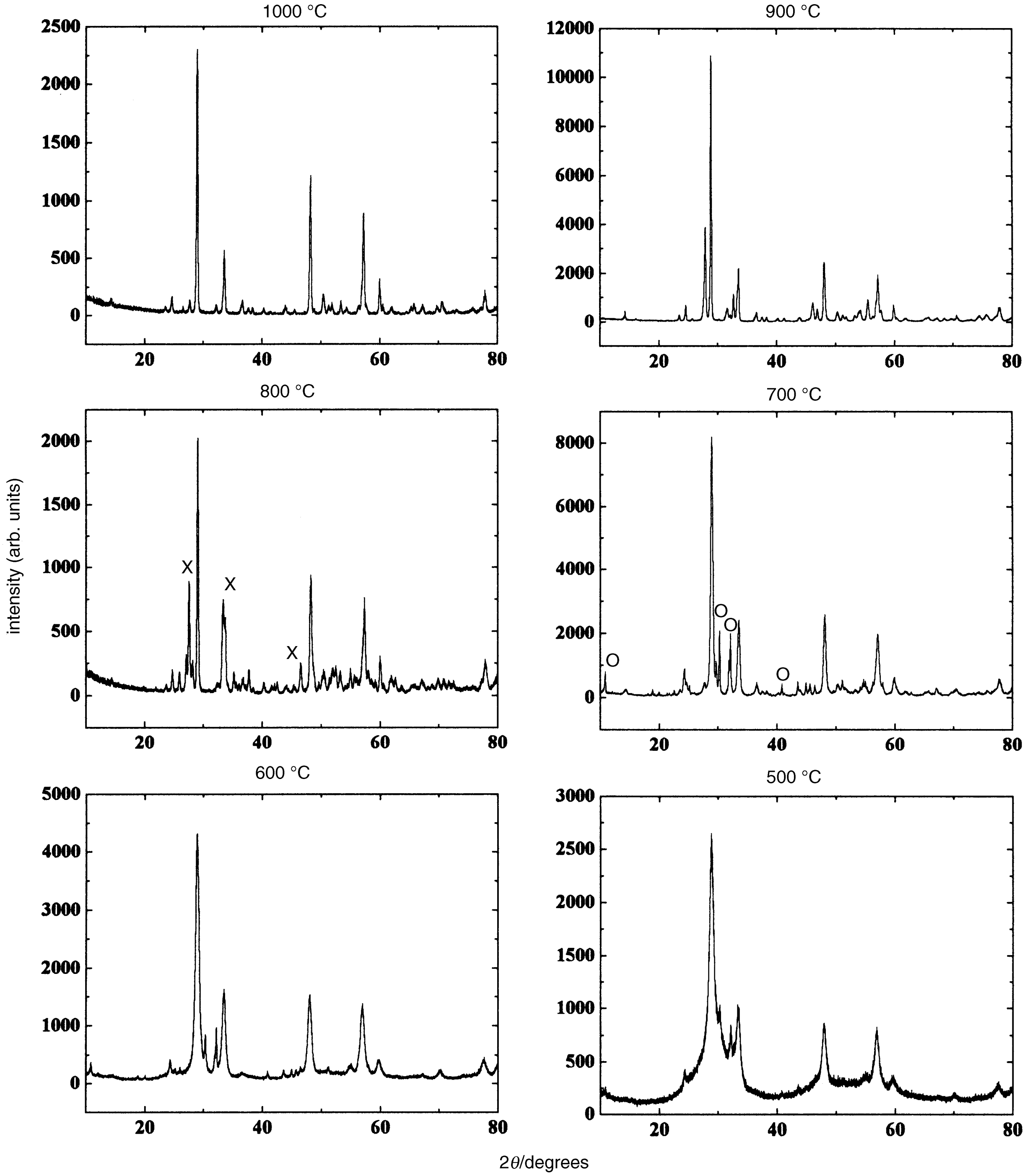

Fig. 4 XRD patterns of $Bi_{2.6}Sn_{1.4}O_{6.7}$ calcined for 16 h periods in the temperature range 500–1000 °C. Peaks labelled × are the major bismuth oxide peaks. Reflections labelled ○ are additional to stoichiometric $Bi_2Sn_2O_7$.

1000 °C, the bismuth/tin ratios at both the surface and in the bulk are reduced to values close to the stoichiometric compound. At equilibrium, the surface composition limit for the nucleation of free Bi_2O_3 is found to be about 63% bismuth. For antimony–tin the volatile oxide is Sb_2O_4 and volatilisation at 1000 °C continues until the bulk composition reduces to the solid solution limit of 4% antimony.[2] The corresponding nucleation limit was then found to be 25% antimony at the surface.

The sample studied in the region beyond the lattice expansion limit shows some further differences in behaviour. The $x=1.0$ composition exhibits the normal increase in surface bismuth composition with temperature, but the scatter of experimental points is found to be larger at the higher temperatures. However, a rapid increase in the surface bismuth concentration with the appearance of free bismuth oxide in the XRD is not observed as was the case for $x=0.6$; even though XRD shows that the free oxide increases in concentration to 950 °C and is then readsorbed at higher temperatures in a similar manner. We note, however, that the surface concentration of bismuth for the $x=1.0$ composition is found to be generally lower at all temperatures than that anticipated from the overall bulk composition. An explanation consistent with the experimental results is that when the bismuth concentration is beyond the single-phase limit, the preparation method produces small amounts of particulate bismuth oxide (at the limits of detection by XRD). The XPS analysis is averaged over the surface and derives a decreasing proportion of its signal from the near surface regions of the bulk with distance from the surface. Consequently, the method effectively determines a lower bismuth concentration because some of the exposed surface particles correspond to a composition at the limit of the expanded phase region. When a temperature is attained at which the latter phase dissociates and releases bismuth oxide, the pre-existing bismuth oxide particles grow, consuming the released bismuth. This leaves the surface of the expanded phase still exposed with a significant concentration of tin cations present. Therefore, there is little overall change in the experimentally averaged surface composition and the increased scatter in the experimental points may be associated with sintering effects. In contrast to this, when $x = 0.6$ and the dissociation temperature is reached, there are no pre-existing bismuth oxide nuclei. XRD shows that the released bismuth oxide is crystalline with a significant grain size. At 775 °C bismuth oxide must flood the exposed surface since the tin component is largely excluded from the analysis. The reduction in bismuth surface concentration at higher temperatures is clearly due to readsorption of the bismuth oxide phase, but some contribution from sintering of the bismuth oxide cannot be excluded.

Conclusions

A systematic study of the bismuth–tin mixed oxide system by a combination of quantitative surface analysis and bulk phase analysis has enabled us to characterise certain features of the surface segregation of bismuth. An underlying tendency for the surface of $Bi_2Sn_2O_7$ to be enriched with bismuth cations may be superimposed by phase separation, nucleation and growth effects when bismuth is present in values in excess of stoichiometry. These observations are relevant to any applications in heterogeneous catalysis at elevated temperatures, but the detail may depend on the exact composition of the ambient atmosphere at the operating conditions of the catalyst. Clearly the bismuth-rich materials are able to sustain a bismuth-rich surface over a wide range of conditions at elevated temperatures.

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