

## An Investigation of Phases in the Titanium–Antimony–Oxygen System

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### Abstract

The nature of solid phases formed in the titanium–antimony–oxygen system by the calcination of precipitates in air has been investigated by powder X-ray diffraction, electron microscopy, Mössbauer spectroscopy, thermal analysis, and temperature programmed reduction techniques. The amorphous solids formed by mild temperature dehydration are converted to crystalline, and frequently multiphasic, materials when calcined at temperatures exceeding *ca.* 500 °C. The nature of the crystalline materials depends on the relative concentrations of the titanium and antimony cations in the initial precipitates and the calcination temperature. Antimony(V) in monophasic low-antimony content solids induces the structural transformation of the anatase form of titanium dioxide to the rutile modification at a lower temperature than is normally expected. Materials containing an excess of *ca.* 30% antimony and heated at temperatures exceeding *ca.* 500 °C are usually multiphasic and contain an antimony-containing rutile related phase. Evidence has been found for the occurrence of the mixed oxide of composition  $Sb_3Ti_2O_{10}$  in some multiphasic materials. Titanium–antimony oxides calcined at high temperatures in air may be described as solid solutions of low concentrations of antimony(V) in rutile titanium(IV) oxide. The tolerance of rutile titanium dioxide for the incorporation of antimony depends on the temperature and duration of thermal treatment.

### Introduction

The significant attention which has been given to the fundamental properties of antimony-containing mixed oxides with a rutile-type structure has recently been reviewed [1] and has focused attention on the sparsity of data which has been accumulated on titanium–antimony oxides, especially antimony-doped archetypal rutile titanium(IV) oxide. Indeed,

despite the known catalytic properties of titanium–antimony oxides for hydrocarbon oxidation and ammoxidation [2], there is little unanimity about the nature of phases which can exist in the titanium–antimony–oxygen system [3–6]. It is especially pertinent to note that the phase compositions of materials formed over a range of antimony concentrations has not been investigated and the conditions under which solid solutions of antimony in rutile titanium dioxide are formed are currently unclear.

We have therefore prepared some titanium–antimony oxides by the calcination of precipitates and we report here on our investigations of the materials by powder X-ray diffraction, electron microscopy,  $^{121}Sb$  Mössbauer spectroscopy, thermal analysis and temperature programmed reduction techniques.

### Experimental

Titanium–antimony oxides were prepared by methods similar to those described in the patent literature [2] but involving the calcination of precipitates with antimony concentrations ranging from 0–100 mol% antimony. Titanium tetrachloride (10 g) in concentrated hydrochloric acid (37 ml) was mixed with water (51 g). Appropriate amounts of antimony(V) chloride were added to stirred aliquots of titanium tetrachloride which had been diluted with water (500 ml). Ammonia was slowly added until the mixture attained a pH of *ca.* 8. The resulting precipitates were filtered, washed with water, dried at 150 °C (12 h) and sequentially calcined in air at temperatures between 380 and 1200 °C for 12 h.

Powder X-ray diffraction data were recorded with a Philips vertical goniometer (PW 1050/70) using  $Cu K\alpha$  radiation.

Antimony-121 Mössbauer spectra were recorded with a Cryophysics MS-121 microprocessor controlled Mössbauer spectrometer using a 0.45 mCi  $Ca^{121m}SnO_3$  source and absorbers containing *ca.* 15 mg of  $^{121}Sb$  per  $cm^2$ . The data were recorded with both the source and the absorber at 77 K. The drive velocity was calibrated with a cobalt-57/rhodium source and a natural iron foil. All spectra were computer fitted.

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Temperature programmed reduction (tpr) experiments using *ca.* 50 mg of sample and a 10% hydrogen–90% nitrogen reducing gas flow rate of *ca.* 20 ml per minute were performed with either a Carbolite temperature programmer, a katherometer, and a Johnson Matthey hinged furnace, or with a Pye Unicam series 104 gas chromatograph furnace and programmer. Preparative scale experiments were performed with *ca.* 1 g samples and a reducing gas flow rate of 120 ml per minute.

Simultaneous thermal analyses were performed in air with a Stanton Redcroft TG780 apparatus using platinum boats and an alumina reference. Samples (*ca.* 50 mg) were heated from 25 to 1500 °C at a rate of 10 °C per minute.

Electron micrographs were obtained with a Philips EM400T electron microscope. Chemical analyses were determined with an EDAX energy dispersive X-ray analysis system interfaced with the Philips EM400T electron microscope operating in the STEM mode.

## Results and Discussion

The phases identified by powder X-ray diffraction in the titanium–antimony–oxygen system when the precipitates were calcined for 12 hour periods at various temperatures up to 1000 °C are summarized in Fig. 1.

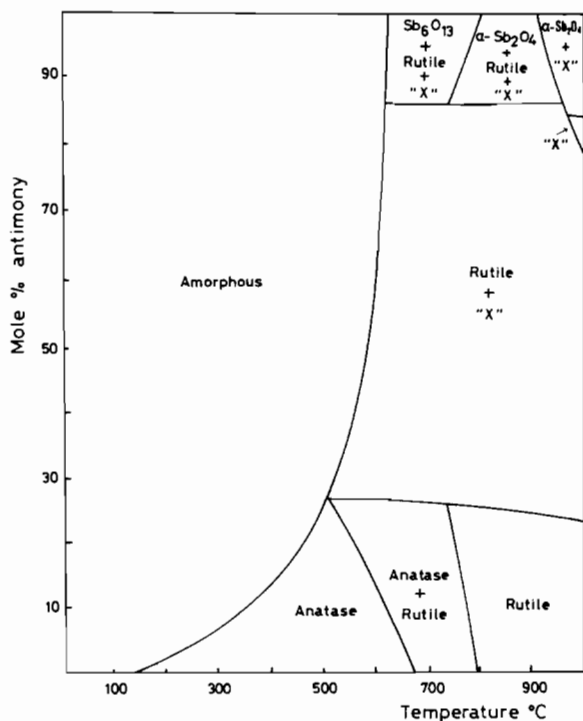


Fig. 1. Schematic representation of phases formed in the titanium–antimony–oxygen system following the calcination of precipitates for 12 h.

Materials calcined at low temperatures were found to be amorphous to X-rays. The onset of crystallization, as determined by the acquisition of well defined narrow and interpretable X-ray diffraction patterns, depended on the antimony content and calcination temperature. It is important to note that the boundaries in Fig. 1 were not generally easy to define and must be interpreted with appropriate caution. Samples with low antimony concentrations, *i.e.* *ca.* 1–30% antimony, and heated to moderate temperatures, *i.e.* temperatures exceeding *ca.* 200–500 °C depending on the antimony content, gave X-ray diffraction patterns which, although broad lined, were characteristic of pure titanium dioxide. For example, the X-ray diffraction data recorded from materials with low antimony concentrations and calcined at temperatures below *ca.* 650 °C were characteristic of the anatase modification of titanium(IV) oxide. Calcination of these samples at higher temperatures produced materials which X-ray diffraction showed to be mixtures of anatase and rutile titanium dioxide. Subsequent heating at temperatures exceeding *ca.* 800 °C gave the exclusive formation of the rutile modification of titanium(IV) oxide. The results from these materials therefore showed that the conversion of anatase to rutile titanium dioxide occurs at lower temperatures than the transition temperature of *ca.* 1000 °C which has been reported in the literature [4, 7, 8]. Antimony-121 Mössbauer spectroscopy revealed the presence of antimony(V) in these solids and the results suggest that the main group element antimony is able to induce this structural transformation of anatase to rutile titanium(IV) oxide at lower temperatures than expected. The observations are therefore similar to those recorded from studies of vanadium doped titanium dioxide [9, 10], which also reported a lower than expected temperature for the conversion of anatase to rutile titanium(IV) oxide.

An interesting development in the phase diagram occurred when the titanium–antimony oxide containing *ca.* 30% antimony was calcined at temperatures of *ca.* 1000 °C. The X-ray diffraction patterns showed the products to contain a rutile-type phase and another material, characterized by twenty nine peaks in the X-ray diffraction pattern, which we refer to here as material 'X'. The intensity of the contribution of material X to the X-ray diffraction patterns increased with increasing antimony concentration and, in the higher antimony content samples, was found to coexist with the rutile phase at temperatures as low as *ca.* 500 °C. It is interesting to note that these biphasic materials formed from solids with initial antimony concentrations in the region 35–85% and heated at temperatures between *ca.* 600 and 800 °C gave broad lined X-ray diffraction patterns indicative of poorly crystalline materials which, on subsequent heating to temperatures exceeding *ca.*

800 °C, showed a decrease in the intensity of the contribution of the rutile phase and a concomitant increase in the intensity of the contribution from material X.

The material X was obtained in the absence of any other phases when samples containing *ca.* 80% antimony were calcined at temperatures between *ca.* 950 and 1000 °C. Twenty of the twenty nine peaks in the X-ray diffraction pattern characterizing phase X corresponded to the X-ray diffraction pattern recorded from the material previously described [4, 5] as  $4\text{TiO}_2 \cdot 3\text{Sb}_2\text{O}_4$  or  $\text{Sb}_3\text{Ti}_2\text{O}_{10}$  (Table I). However, the nine unassigned peaks in the X-ray diffraction pattern recorded from X precluded the unequivocal description of X as  $4\text{TiO}_2 \cdot 3\text{Sb}_2\text{O}_4$  or  $\text{Sb}_3\text{Ti}_2\text{O}_{10}$ . In this respect it is pertinent to note that an uncharacterized titanium–antimony oxide has been reported [3] to give three strong X-ray diffraction peaks corresponding to *d*-spacings of 2.99, 3.03 and 2.76 Å. One of these peaks (2.99 Å) corresponded to one of the unassigned peaks of material X whilst the other two were also common to

$\text{Sb}_3\text{Ti}_2\text{O}_{10}$ . Hence the X-ray diffraction data alone were insensitive to the characterization of material X as either a mixture of phases or a new monophasic material.

Simultaneous thermal analysis showed material X to decompose at *ca.* 1150 °C, as reported [4] for  $\text{Sb}_3\text{Ti}_2\text{O}_{10}$ , and to subsequently crystallize into a solid which was shown by X-ray diffraction and  $^{121}\text{Sb}$  Mössbauer spectroscopy to be an antimony(V)-containing rutile-type phase. The simultaneous thermal analysis results gave no evidence for the presence of more than one phase.

Antimony-121 Mössbauer spectroscopy and temperature programmed reduction techniques showed that material X contained both antimony(V) and antimony(III) and was reduced in hydrogen in a single step to antimony(0). The results did not provide any information on whether material X is single or multiphasic in nature.

Electron microscopy and energy dispersive X-ray analysis showed material X to consist of large crystalline particles of various shapes and in which the antimony content ranged from *ca.* 22% in some spherical and oblong particles to *ca.* 73% in some flat platelet crystals. In this respect it is relevant to note that the antimony content of the flat platelet crystals was similar to the 77% which would be expected in a phase of composition  $\text{Sb}_3\text{Ti}_2\text{O}_{10}$  and that the electron diffraction patterns recorded from the platelets were different from those recorded from the other crystalline particles in material X. Hence we conclude that there is insufficient evidence to show that X is a new monophasic material and we would suggest that the results of our investigations reported here be tentatively associated with a material containing more than one phase of which one may be the mixed oxide  $\text{Sb}_3\text{Ti}_2\text{O}_{10}$ .

Titanium–antimony oxides prepared from reactant mixtures with antimony concentrations exceeding *ca.* 85% gave powder X-ray diffraction patterns showing the presence of the rutile-type phase, material X, and either the antimony oxide  $\text{Sb}_6\text{O}_{13}$  at temperatures between *ca.* 600 and 800 °C, or the  $\alpha$ -antimony tetraoxide,  $\alpha\text{-Sb}_2\text{O}_4$ , at temperatures between 800 and 1000 °C. Although the conversion of  $\alpha$ - to  $\beta\text{-Sb}_2\text{O}_4$  normally occurs [11] at *ca.* 1100 °C it is relevant to note recent work [12, 13] which has shown that vanadium induces the transformation of  $\alpha$ - to  $\beta\text{-Sb}_2\text{O}_4$  at temperatures as low as *ca.* 800 °C. The absence of any evidence for the formation of  $\beta\text{-Sb}_2\text{O}_4$  in the materials investigated here suggests that titanium does not influence the low temperature  $\alpha$ - to  $\beta\text{-Sb}_2\text{O}_4$  transformation temperature.

All the titanium–antimony oxides calcined at 1000 °C gave, following further calcination at 1200 °C, powder X-ray diffraction patterns and  $^{121}\text{Sb}$  Mössbauer spectra characteristic of crystalline

TABLE I. Powder X-ray Diffraction Data Recorded from Material X

$2\theta$	Intensity	$d_{\text{obs}}$ (Å)	$d_{\text{calc}}$ (Å) $\text{Sb}_3\text{Ti}_2\text{O}_{10}$	Assignment
19.50	9	4.56		b
24.78	10	3.60		b
25.42	38	3.50	3.52	a
29.68	98	3.01	3.01	a
30.02	100	2.98		b
32.60	37	2.75	2.75	a
33.12	10	2.70		b
35.10	12	2.56	2.56	a
37.28	4	2.41		b
37.75	14	2.38	2.39	a
39.49	10	2.28	2.29	a
41.38	3	2.18	2.18	a
42.00	4	2.15		b
42.83	4	2.11	2.11	a
45.80	6	1.98	1.98	a
46.54	3	1.95		b
46.90	4	1.94	1.94	a
47.50	6	1.91	1.91	a
50.60	6	1.80	1.80	a
50.95	4	1.79		b
52.35	7	1.75	1.75	a
54.41	8	1.68	1.68	a
55.70	12	1.65		b
56.10	10	1.64	1.64	a
56.65	15	1.62	1.62	a
62.15	8	1.49	1.49	a
63.20	6	1.47	1.47	a
65.60	5	1.42	1.42	a
67.55	4	1.39	1.38	a

a,  $\text{Sb}_3\text{Ti}_2\text{O}_{10}$ . b, Unassigned.

antimony(V)-containing titanium(IV) oxide. Although this observation may not be surprising for low-antimony-content materials it is interesting to note that material X, which was present in many of the samples formed at 1000 °C, decomposed at *ca.* 1150 °C into a solid rutile-type phase and volatile antimony oxides. Furthermore, and despite previous reports [3, 4] that up to *ca.* 15% antimony may be accommodated in the rutile structure, our results are more consistent with a significantly lower upper limit, *e.g.* <*ca.* 5% following calcination at 1000 °C for 10 days, which decreases with subsequent higher temperature calcination. Indeed, the tolerance of the bulk rutile lattice for the accommodation of antimony appears to be critically dependent on the temperature and duration of thermal treatment and the conditions under which bulk equilibrium in these materials may be achieved is difficult to define and will be the subject of further investigation.

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