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The Oxidation State of Antimony in Antimony-Doped Rutile

FRANK J. BERRY* AND PATRICIA M. GOGARTY

Department of Chemistry, University of Birmingham, P.O. Box 363,
Birmingham B15 2TT, England

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Antimony-121 Mössbauer spectroscopy, powder X-ray diffraction, and energy dispersive X-ray analysis show that solid solutions of <4% antimony in titanium(IV) oxide contain only antimony(V) in the rutile structure with lattice parameters similar to those of pure titanium dioxide. The results are in distinct contrast to those recently reported (N. Morita, T. Endo, T. Sato, and M. Shimada, *J. Solid State Chem.* **68**, 106 (1987)) from a study of the same system by powder X-ray diffraction, atomic absorption spectrophotometry, and X-ray photoelectron spectroscopy. © 1988 Academic Press, Inc.

Introduction

The titanium–antimony–oxygen system has recently been identified (*1*) as having received a sparsity of attention. We have therefore initiated a comprehensive investigation of the solid-state properties of antimony-doped rutile titanium(IV) oxide by a range of techniques and will subsequently report on the results in detail. However, a recent paper (*2*) has described results which are in sharp contrast to those currently being obtained by ourselves; thus, in this preliminary communication, we report some of the essential findings of our work.

Experimental

Titanium–antimony oxides were prepared by the calcination of precipitates nominally containing various concentrations of 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 the titanium tetrachloride solution which had been diluted with water (500 ml). Ammonia was slowly added until the mixtures attained a pH of ca. 8. The resulting precipitates were filtered, washed with water, dried at 150°C (12 hr) and calcined in air at temperatures up to 1200°C.

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

Antimony-121 Mössbauer spectra were recorded with a microprocessor controlled Mössbauer spectrometer using a 0.45-mCi Ca $^{121m}SnO_3$ source and samples containing ca. 30 mg ^{121}Sb cm^2. The data were collected with both the source and the absorber at 77 K. The drive velocity was cali-

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* To whom all correspondence should be addressed.

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brated with a cobalt-57/rhodium source and a natural iron–foil absorber. All the spectra were computer fitted using the MOSFIT program and those found to give the most acceptable fits to the data and satisfactory χ^2 values were used for interpretation. The chemical isomer shift data are quoted relative to indium antimonide.

Chemical analysis of the titanium–antimony oxides was achieved by use of a 9100/60 EDAX energy dispersive X-ray analysis system interfaced with a Philips EM400T electron microscope which was operated in the STEM and in the microprobe mode.

X-ray photoelectron spectra were recorded with a Vacuum Generator ESCA III Mark 1 instrument using Al$K\alpha$ radiation. The samples were investigated as fine powders mounted on double-sided adhesive tape and examined at room temperature. The binding energies were measured relative to the carbon 1*s* signal at 284.6 eV arising from carbon impurity on the sample surface.

Results and Discussion

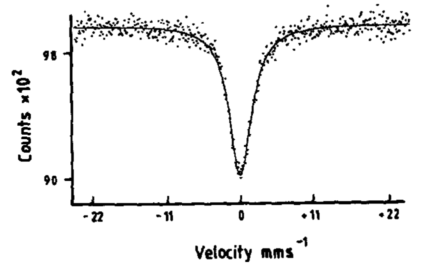

FIG. 1. Antimony-121 Mössbauer spectrum recorded from a titanium–antimony oxide formed at 1000°C.

Four precipitates containing 5, 20, 30, and 80% antimony gave, following calcination at 1000°C for 24 hr, powder X-ray diffraction patterns characteristic of rutile titanium(IV) oxide. The lattice parameters of the mixed oxides, as derived from the powder X-ray diffraction data, $a = b = 4.598 \pm 0.003$ Å, $c = 2.968 \pm 0.003$ Å, were essentially similar within the errors and independent of the antimony content in the initial precipitates. The lattice parameters are smaller than those recently reported (*2*) for rutile when containing antimony in a concentration up to 7 mole% in an Sb_2O_4 equivalent and which had been prepared from the calcination of titanium(IV) oxide and antimony tetraoxide at 1000°C for 24 hr. Further heating of our samples, for example at 1100°C for 10 days, produced a decrease in lattice parameters to values, $a = b = 4.594 \pm 0.003$ Å, $c = 2.962 \pm 0.003$ Å, which were similar to those recorded from pure titanium dioxide $a = b = 4.593 \pm 0.003$ Å, $c = 2.959 \pm 0.003$ Å. Energy dispersive X-ray analysis showed the antimony concentration in the calcined oxides to decrease from ca. 4% in materials heated at 1000°C to ca. 1.5% in samples further calcined at 1100°C. Simultaneous thermal analysis of the precipitates dried at 150°C showed large weight losses from the high antimony content materials at elevated temperatures which can be associated with the volatilization of large quantities of antimony oxide.

The antimony-121 Mössbauer spectra recorded from the titanium–antimony oxides calcined at 1000°C showed single absorptions, δ 8.54 ± 0.05 mm sec^{-1}, Γ 2.41 mm sec^{-1}, characteristic of antimony(V) (Fig. 1). The results contrast with the recent report (*2*) based on X-ray photoelectron spectroscopy that antimony substitutes as antimony(III) for titanium(IV) in the rutile structure. The X-ray photoelectron spectra recorded from our samples were, as in some other antimony-containing mixed oxides with a rutile-type structure (*3*, *4*), not amenable to interpretation in terms of the oxidation state of antimony. Given the sensitivity and large differences between the ^{121}Sb Mössbauer chemical isomer shifts for antimony(V) and antimony(III) (*5*), we contend that the titanium–antimony oxides formed by the calcination of precipitates at

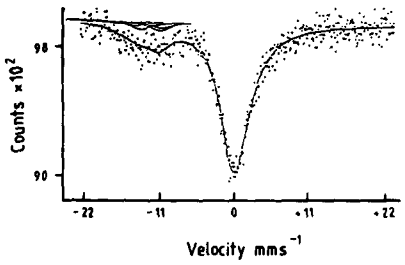

FIG. 2. Antimony-121 Mössbauer spectrum recorded from a titanium–antimony oxide formed at 150°C.

high temperatures are best described as materials in which small concentrations of antimony(V) are accommodated within the titanium(IV) oxide lattice. Indeed, given the preference of antimony(V) for sixfold octahedral coordination (*6*) and the greater stability of antimony(III) in fourfold coordination (*6*) it would seem more reasonable to expect the accommodation of antimony(V) within the rutile structure.

Therefore the results reported here suggest that the titanium–antimony oxides formed at high temperatures derive from the thermally induced dehydration and crystallization of an initially amorphous titanium–antimony hydroxide precipitate. We envisage that the antimony which cannot be accommodated within the octahedral sites in the rutile lattice, such as antimony (III) which was identified by the additional absorption, δ -5.01 ± 0.05 mm sec^{-1}, e^2qQ 20.49 mm sec^{-1}, Γ 3.81 mm sec^{-1}, in the ^{121}Sb Mössbauer spectra recorded from materials heated at moderate temperatures (Fig. 2) and which is formed (*7*) by the partial thermal reduction of antimony(V), migrates to the surface of the rutile-type phase to form α-antimony tetraoxide which volatilizes at elevated temperatures. This model is similar to that previously proposed for the formation of solid solutions of low concentrations of antimony(V) in rutile-related tin(IV) oxides (*8*, *9*).

Finally we report that our preliminary investigations of titanium–antimony oxides prepared by solid-state reactions between titanium dioxide and antimony tetraoxide indicate that they are similar to those prepared by the calcination of precipitates.

Acknowledgments

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