

Electron Paramagnetic Resonance Investigation of Antimony Doped Tin(IV) Oxide

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The e.s.r. spectra from single crystals of tin(IV) oxide containing low concentrations of antimony and formed by vapour phase deposition provide no evidence for the presence of paramagnetic cations or superficially adsorbed paramagnetic oxygen species. Tin-antimony oxides of comparable composition but formed by precipitation techniques give broader signals which show no asymmetry. The signals are attributed to electrons trapped at anionic vacancies.

Introduction

Although a number of e.s.r. studies of rutile type hosts containing paramagnetic transition metal ions have been described [1] relatively little has been reported on antimony doped tin(IV) oxide. Tin(IV) oxide itself is a broad band *n*-type semiconductor in which the observed conductivity is attributable to donor levels [2, 3] which result from defects such as impurity cations and anion vacancies. Although the large forbidden energy gap [4, 5] of 3.5 eV prevents intrinsic conductivity at ordinary temperature, the introduction of antimony into the rutile lattice has been reported [6, 7] to produce a donor which is ionized at room temperature to give a marked increase in conductivity. An e.s.r. study of tin(IV) oxide has reported [8] that the material reduced *in vacuo* gives a signal ($g_{11c} = 1.905$, $g_{1c} = 1.876$) at 4K which may be assigned to either a Sn^{3+} ion or an electron trapped at an oxygen vacancy.

It is of additional interest that although tin(IV) oxide is a poor catalyst for the selective oxidation and ammoxidation of olefins the enhanced catalytic properties of antimony doped tin(IV) oxide have been known for many years [9]. The use of e.s.r. is a potentially powerful means by which the fundamental nature of tin-antimony oxide may be correlated with its catalytic character since the presence of spin

free species may reasonably be expected, to influence the nature of the material as an oxidation or ammoxidation catalyst.

Experimental

Single crystals of tin(IV) oxide containing 0.5% antimony were prepared by vapour phase deposition from antimony(V) chloride, tin(IV) chloride and water according to the method used [10] to prepare pure crystalline tin(IV) oxide. The dark blue needle shaped antimony doped crystals were formed between 1273 and 1373K.

A material of similar composition was also prepared by coprecipitation techniques by the simultaneous addition of tin(IV) chloride and an *aqua regia* solution of antimony metal to ammonium hydroxide solution. The alkalinity of the solution was maintained by the addition of more ammonia. The resulting white precipitate was filtered, washed, dried at 120 °C, ground to constant particle size and then heated at 873 K for 16 h to give a blue solid.

The e.s.r. data were obtained with a Decca X-band spectrometer operating at 9.8 GHz. The spectra were recorded at 298, 77 and 4 K and *g*-values were measured relative to DPPH (diphenylpicrylhydrazyl, $g = 2.0036$).

Results

The dark blue needles gave an e.s.r. absorption (Fig. 1) at 298K with $g_{(\text{average})} = 1.8733$. Similar signals of comparable linewidth and intensity were also recorded at lower temperature and upon evacuation of the sample to 10^{-5} Torr.

The material prepared by precipitation techniques gave a similar but broader signal than that recorded from the single crystals and gave a *g*-value of 1.890. Materials which had been thermally annealed at 773K for 12 h became light blue and failed to give an e.s.r.

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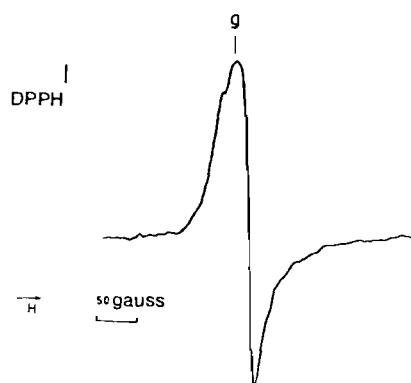


Fig. 1. E.s.r. spectrum of vapour phase deposited antimony doped tin(IV) oxide at 298K.

signal. Power saturation studies on the original oxides showed the signals to decrease in intensity without undergoing homogeneous line broadening when the microwave power was increased. No evidence for the presence of more than one paramagnetic species was observed.

Discussion

The room temperature e.s.r. spectrum recorded from the single crystals of antimony doped tin(IV) oxide may be attributed to either paramagnetic ions or electronic defects.

The tin(III) species has not been observed at room temperature although g -values of 2.014 and 2.090 have attributed [11] to Sn^{3+} in CaS and CaSe at 77K. Since Sn(III), as an S state ion, would not be expected to undergo rapid relaxation the e.s.r. spectrum of this species would show large hyperfine splittings. The signals reported here gave no evidence of magnetic hyperfine interactions with magnetic nuclei ^{117}Sn ($I = \frac{1}{2}$, 7.6% natural abundance) and ^{119}Sn ($I = \frac{1}{2}$, 8.6% natural abundance) within the regions 2000 G to low and high field of the main signal. Similarly the antimony(IV) signal [12] which would give a complex hyperfine pattern as a result of interactions with the magnetic nuclei ^{121}Sb ($I = \frac{5}{2}$, 57% natural abundance) and ^{123}Sb ($I = \frac{7}{2}$, 42% natural abundance) was not observed. It is clear therefore that the accommodation of antimony in the tin(IV) oxide lattice does not involve the reduction of the cations to a paramagnetic valence state. Furthermore the signals are dissimilar to those reported for adsorbed oxygen species on metal oxides [13, 14] and showed no diminution in linewidth when the sample was evacuated to 10^{-5} Torr.

The spectra are therefore best interpreted in terms of electronic defects. Given that ^{119}Sn and ^{121}Sb

Mössbauer spectroscopy [15, 16] have also shown that the accommodation of antimony within the tin(IV) oxide lattice does not involve reduction of either tin(IV) or antimony(V), charge balance in these materials appears to be achieved by the delocalization of electrons into low energy conduction bands formed by overlap of $5s$ orbitals [17]. Such a process would account for the increased conductivity in tin(IV) oxide when doped with antimony [6, 7]. In samples containing a low concentration of antimony these electrons would be equal in number to the dopant antimony atoms, and, since the high temperature preparation of tin-antimony oxides involves the loss of oxygen [18] would readily be trapped at the anionic vacancies and detected by e.s.r. measurements. The failure of the reheated samples to give an e.s.r. signal is consistent with the removal of the oxygen vacancies by thermal annealing in air. It is interesting that the g -values for the e.s.r. spectra from the tin-antimony oxides are lower than is normally expected for signals from trapped electrons in metal oxides [19–22]. Although g -values are known [23] to reflect the increasing atomic number of both cations and anions it is more reasonable that the values reported here are indicative of residual spin-orbit coupling between the trapped electrons and the neighbouring cationic species in the tin-antimony oxides.

The signals obtained from the coprecipitated materials are broader than those recorded from the single crystals and show no asymmetry. X-ray diffraction studies [18] have shown that tin-antimony oxides prepared by coprecipitation techniques and calcined at 873K are poorly crystalline materials. Presumably the precipitated solid contains a larger inhomogeneous distribution of antimony in the tin(IV) oxide rutile type lattice which gives rise to a greater interaction between the trapped electrons and consequent broadening in the e.s.r. signals.

The presence of trapped electrons in tin-antimony oxides may be related to the catalytic character of these materials for olefin oxidation. The enhanced activity which is achieved when tin(IV) oxide is doped with low concentrations of antimony has been related to the segregation of antimony to the surface [24–28] and associated with surface basicity [26] and active centres composed of acid-base pairs [28]. It is suggested here that the trapped electrons in tin-antimony oxides containing low concentrations of antimony may act as surface reducing or basic sites. The active centre for the partial oxidation of olefins may therefore be postulated as an acid-base pair containing tin(IV) as the acid site and a trapped electron as the basic site.

At high antimony concentrations the e.s.r. measurements show the materials to act as metallic conductors and thereby reflect the delocalization of electrons into the conduction band.

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