Inorganica Chimica Acta, 63 (1982) 123–125

Mössbauer and X-ray Diffraction Investigations of the Tin–Europium–Oxygen System

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Received February 17, 1982

Tin–europium oxides prepared by calcination of tin(IV) oxide slurried with aqueous solutions of europium(III) chloride have been investigated by ^{119}*Sn and* ^{151}*Eu Mössbauer spectroscopy. The results, complemented by X-ray diffraction data, suggest that low concentrations of europium give the formation of a rutile-type phase containing europium(III) whilst preparations involving larger amounts of europium give biphasic products composed of the rutile-type material and the europium stannate,* $Eu_2Sn_2O_7$*, which is isostructural with pyrochlore.*

Introduction

The ability of both tin and europium to adopt different oxidation states in oxygen environments and their capacity to react with other metal oxides are well established aspects of the chemistry of these two elements. It is somewhat surprising therefore that the tin–europium–oxygen system appears to have been subjected to only limited examination. For example, although the solid state reaction at *ca.* 1500 °C between tin(IV) oxide and europium(III) oxide to give the europium stannate of composition $Eu_2Sn_2O_7$ [1] and the doping at 1250 °C of tin(IV) oxide single crystals by europium from evaporated aqueous solutions of europium(III) chloride [2, 3] have been reported, the preparation of tin–europium oxides from slurries or precipitates appears to have received little attention. In principle it might be expected that calcination of slurries or precipitates containing intimate mixtures of the cations in oxygen environments would readily lead to mixed oxide formation. In this respect it is relevant to note the recent use of Mössbauer spectroscopy [4–6] in investigations of cationic oxidation states and the phases formed in the tin–antimony–oxygen system by calcination of precipitates. Since tin and europium are both amenable to investigation by Mössbauer spectroscopy some materials formed by calcination of slurries of tin(IV) oxide with aqueous europium(III) chloride solution have been investigated by Mössbauer spectroscopy and X-ray diffraction in an attempt to identify the structural properties of the products and the nature of the cationic species.

Experimental

Tin–europium oxides were prepared from slurries of tin(IV) oxide with solutions of europium(III) chloride hexahydrate in water. The mixtures were dried at 120 °C (12 h), ground, and then slowly heated to 1250 °C in a stream of argon and maintained at this temperature for 24 hours. The europium content was determined by atomic absorption.

Tin-119 and Europium-151 Mössbauer spectra were recorded at 298 K and 77 K with a conventional constant acceleration spectrometer using $Ca^{119}SnO_3$ and $^{151}SmF_3$ sources. The Mössbauer spectra were computer fitted.

X-ray diffraction data were recorded with a Philips vertical goniometer (PW 1050/70) using Cu-K_α radiation.

Results and Discussions

The ^{119}Sn and ^{151}Eu Mössbauer parameters for the tin–europium oxides containing 6.4% and 12.9% europium are recorded in Table I.

The material containing 6.4% europium gave an X-ray diffraction pattern characteristic of a rutile-type solid with lattice parameters, $a = b = 0.4736 \pm 0.05$ nm, $c = 0.3185 \pm 0.04$ nm which are very similar to those reported [7] for pure tin(IV) oxide, $a = b = 0.47403 \pm 0.00002$ nm, $c = 0.31886 \pm 0.00002$ nm. Although the incorporation of europium into the tin(IV) oxide lattice might be expected to alter the lattice parameters it is significant, despite antimony(V) being more similar in size to tin(IV) and smaller

0020-1693/82/0000-0000/$02.75

TABLE I. Tin-119 and Europium-151 Mössbauer Parameters for Tin–Europium Oxides.

Europium Content %	Temperature K	^{119}Sn		^{151}Eu	
		$\delta^a \pm 0.03$ mm s^{-1}	$\Delta \pm 0.06$ mm s^{-1}	$\delta^b \pm 0.03$ mm s^{-1}	Γ mm s^{-1}
6.4	77			+0.25	2.59
	298	−0.02	0.65		
12.9	77			+0.66	3.04
	298	−0.02	0.69		

$^a\delta$ relative to SnO_2. $^b\delta$ relative to EuF_3.

than europium(III) [8], that the formation of tin–antimony oxide solid solutions is achieved without modification of the host lattice parameters [7]. Furthermore, whilst acknowledging that the presence of only tin(IV) oxide lines in the X-ray diffraction pattern does not constitute conclusive evidence for a monophasic product, no evidence was found for the existence of additional oxide phases which, given the concentration of each cation, might reasonably be expected to be detectable in a product which could be more accurately described as a mixture of tin and europium oxides. Moreover, the broader lines as compared with those recorded from pure tin(IV) oxide subjected to similar treatment are consistent with the influence of europium on the structural properties of the tin(IV) oxide lattice. In these respects it is significant that the ^{119}Sn Mössbauer quadrupole splitting is larger than that reported for pure tin(IV) oxide, Δ 0.56 mm s^{-1}, [9] and not significantly different from that observed in tin–antimony oxide solid solutions, Δ 0.61 mm s^{-1} [10]. Hence the larger size of europium as compared with antimony does not appear to cause any significant increase in the distortion of the tin(IV) oxide lattice and it would seem that the ^{119}Sn quadrupole splitting is mainly a reflection of the immediate oxygen environment about tin. The ^{151}Eu Mössbauer spectrum showed a single peak with a chemical isomer shift characteristic of europium(III) [11]. Hence the X-ray diffraction and Mössbauer data, although not unequivocal in their interpretation, are not inconsistent with the incorporation of low concentrations of europium(III) into the tin(IV) oxide rutile-type lattice. Furthermore, the results appear to complement those from cathodoluminescence studies of tin(IV) oxide single crystals doped with europium which were interpreted [3] in terms of the substitution of up to 8% europium(III) for tin(IV) in the tin(IV) oxide lattice with little distortion of the tin site symmetry.

The material containing 12.9% europium was shown by X-ray diffraction to be biphasic. The patterns were characteristic of the previously described rutile-type phase and the europium stannate, $Eu_2Sn_2O_7$, which adopts a pyrochlore structure [1]. The ^{119}Sn Mössbauer spectrum resembled that recorded from the monophasic rutile-type tin–europium oxide although the slightly larger quadrupole splitting corresponds to that recorded from biphasic products in the tin–antimony–oxygen system, Δ *ca,* 0.73 mm s^{-1} in which the rutile-type phase was formed in the presence of antimony tetroxide [10].

The ^{151}Eu Mössbauer spectrum was similar, albeit broader, to that recorded from the monophasic rutile-type material with a chemical isomer shift similar to that observed [12] in $Eu_2Sn_2O_7$. The domination of the spectrum by the pyrochlore phase also resembles the effects observed [5] in the ^{121}Sb Mössbauer spectra from tin-antimony oxides containing high concentrations of antimony which showed the predominance of Sb_6O_{13} or Sb_2O_4 phases. The biphasic nature of the products and the inherent difficulty associated with the measurement of europium quadrupole splittings [11] precluded further examination of the site symmetry and coordination of europium(III) in each of the two phases.

The detection of the biphasic product suggests that the limit of europium solubility in tin(IV) oxide is between 8% [3] and 13% The results reported here imply that the rutile-type phase is the most stable material at the reaction temperature and that the pyrochlore $Eu_2Sn_2O_7$ phase is formed when the europium content exceeds the limit of europium solubility in tin(IV) oxide.

It is interesting that the maintenance of electrical neutrality in tin(IV) oxide single crystals doped with europium(III) has been attributed [3] to the presence of interstitial tin(IV) and that the Mössbauer spectra from the materials investigated here gave no evidence for the reduction of either europium(III) or tin(IV). The results are consistent with the contention [13] that europium(II) fails to substitute into octahedral sites and in this respect it is pertinent to record that ^{121}Sb Mössbauer spectra

[6] are also indicative of the reluctance of antimony(III) with lone pair electrons to adopt octahedral sites in the rutile-type tin(IV) oxide lattice. It is also interesting that the electrically insulating nature of the europium stannates [3, 12] contrasts with the conductivity of tin–antimony oxides in which charge compensation is achieved by the delocalisation of electrons into conduction bands [5]. Furthermore it is relevant to note that the e.s.r. spectra from the tin–europium oxides gave no evidence for the presence of paramagnetic species or electrons trapped at anionic vacancies which could also be associated with charge balance [3], and in this respect the tin–europium oxides exhibit different properties from tin–antimony oxides [14].

Acknowledgement

The assistance of Dr. S. J. Lyle and Mr. W. A. Westall in recording the ^{151}Eu Mössbauer spectra is gratefully acknowledged.

References

1 C. G. Whinfrey, D. W. Eckart and A. Tauber, *J. Am. Chem. Soc., 82,* 2695 (1960).
2 D. F. Crabtree, *J. Phys., D: Appl. Phys., 7,* L17 (1974).
3 D. F. Crabtree, *J. Phys., D: Appl. Phys., 8,* 107 (1975).
4 F. J. Berry and A. G. Maddock, *Inorg. Chim. Acta, 31,* 181 (1978).
5 F. J. Berry, P. E. Holbourn and F. W. D. Woodhams, *J. Chem. Soc. (Dalton),* 2241 (1980).
6 F. J. Berry and B. J. Laundy, *J. Chem. Soc. (Dalton),* 1442 (1981).
7 D. R. Pyke, R. Reid and R. J. D. Tilley, *J. Chem. Soc. (Faraday 1), 76,* 1174 (1980).
8 R. D. Shannon, *Acta Cryst., A32,* 751 (1976).
9 F. J. Berry and A. G. Maddock, *Radiochim. Acta, 24,* 32 (1977).
10 F. J. Berry, *J. Catalysis, 37,* 349 (1982).
11 N. N. Greenwood and T. C. Gibb, 'Mössbauer Spectroscopy', Chapman and Hall, London, 1971, p. 548.
12 C. L. Chien and A. W. Sleight, *Phys. Rev. B, 18,* 2031 (1978).
13 M. Shafer, *J. Appl. Phys., 36,* 1145 (1965).
14 F. J. Berry and J. C. McAteer, *Inorg. Chim. Acta, 50,* 85 (1981).