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Organotin sulfides as precursors for nanometric γ-Sn_2S_3 powders: a study by ^{119}Sn Mössbauer spectroscopy and X-ray powder diffraction

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Organotinsulfides $Sn_4S_4R_6$ (R = methyl, *n*-butyl and phenyl) were employed as single-source precursors for nanometric tin sulfides. The residues obtained after pyrolysis in hydrogen, nitrogen and oxygen were characterized by X-ray diffraction, ^{119}Sn Mössbauer spectroscopy, scanning electron microscopy and X-ray electron probe microanalysis. The results clearly showed the formation of tetragonal SnO_2 (rutile-type structure) in oxygen and pure phase orthorhombic γ-Sn_2S_3 in nitrogen when $Sn_4Bu_4S_6$ (2) was employed as precursor. The ^{119}Sn Mössbauer spectroscopic results were very important in the elucidation of the decomposition process. Compound 2 is the best starting material for the process. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: Mössbauer spectroscopy; tin sulfide; organotin compounds

INTRODUCTION

The synthesis and characterization of narrow-bandgap semiconductors, especially SnS_2 and SnS, have received much attention in the last few years, owing to their optical and electronic properties.[1] Tin sulfides have three main phases: SnS_2 and SnS, which exhibit layer structures, and Sn_2S_3, which forms a ribbon-like structure.[2] The structure of SnS_2 is similar to CdI_2, where each tin atom lies in the centre of an octahedron bonded to six sulfur atoms.[3,4] Tin(II) sulfide displays a distorted rock-salt structure that is isostructural to GeS (orthorhombic, *Pbnm* group); six sulfur atoms surround each tin centre with three short Sn–S bonds within the layer and three long bonds formed to sulfur in the next layer.[5] The Sn_2S_3 is a mixed valence tin(II)/tin(IV) compound with the same local order as the other tin sulfides but it exhibits a ribbon-like structure.[6] All tin sulfides present semiconducting properties. The bandgap of SnS_2 (n-type) is situated at 2.07–2.18 eV[7] and for SnS (n-type or p-type) it is located between silicon and GaAs, at 1.08 to 1.51 eV.[8] Sn_2S_3 is a direct forbidden semiconductor with a bandgap of 0.95 eV and has a highly anisotropic conduction.[9]

All preparation methods of bulk tin sulfides require either high reaction temperatures (more than 300 °C) or special reactors. Those methods are: solid-state reactions,[10] solid-state methathesis[11] and mechanochemistry.[12] The solvothermal synthesis has attracted more attention, as the metal chalcogenides can be prepared in milder conditions.[13]

In order to prepare pure tin sulfides in mild and simpler conditions we have studied single-source precursors such as $Sn_4S_4R_6$ (R = methyl (Me, **1**), *n*-butyl (*n*-Bu, **2**) or phenyl (Ph, **3**)). We have published a very preliminary study dealing with the use of such a precursor for the preparation of SnS at 350 °C.[14] In that study we observed that another product was obtained in going further with the decomposition process up to 500 °C, which we attributed to SnO_2. However, in the present study we obtained Sn_2S_3 as the final product on heating the precursors to 500 °C. The residues were studied by X-ray diffraction (XRD), scanning electron microscopy

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(SEM) and ^{119}Sn Mössbauer spectroscopy, which has been extensively employed by our group.[15] The latter technique is an efficient tool for identifying mixtures of tin with different oxidation states (even in small amounts) not detectable by powder XRD.

EXPERIMENTAL

Synthesis and characterization of the organotin complexes

The synthesis and characterization of the precursors and the preparation of tin sulfides has been published previously by our group.[14] The chemical structure of $Sn_4R_4S_6$ (R = methyl (Me; **1**), *n*-butyl (*n*-Bu, **2**) or phenyl (Ph, **3**)) is shown in Fig. 1.

Thermal decomposition of precursors

Thermal decomposition of **1**–**3** was carried out in a tube furnace in H_2, O_2 and N_2 atmospheres until 500 °C using a heating rate of $5\,^\circ C\ min^{-1}$ and gas flux of $100\ ml\ min^{-1}$.

XRD patterns were collected with Rigaku Geigerflex equipment using nickel-filtered Cu Kα radiation ($\lambda = 1.5418$ Å) and a graphite monochromator in the diffracted beam. A scan rate of $4^\circ\ min^{-1}$ was applied to record a pattern in the 2θ range of 4–80°.

^{119}Sn Mössbauer measurements were performed on a conventional apparatus, with the samples at liquid nitrogen temperature and a $CaSnO_3$ source kept at room temperature, in the residue obtained after pyrolysis in order to identify the tin oxidation state and number of different sites.

The SEM images were taken using JEOL JSM-840A equipment and the samples were previously covered with a thin gold layer; the X-ray electron probe microanalysis (EPMA) was carried out using a JXA 89000 RL wavelength/energy-dispersive combined microanalyser with samples covered with a thin film of carbon deposited by sputtering.

RESULTS AND DISCUSSION

The diffraction patterns of the residues of **1**–**3** obtained in O_2 (Fig. 2A) indicate the formation of pure tetragonal

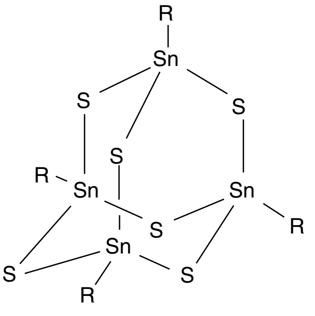

Figure 1. Chemical structure of $Sn_4S_6R_4$ (R = methyl, *n*-butyl or phenyl).

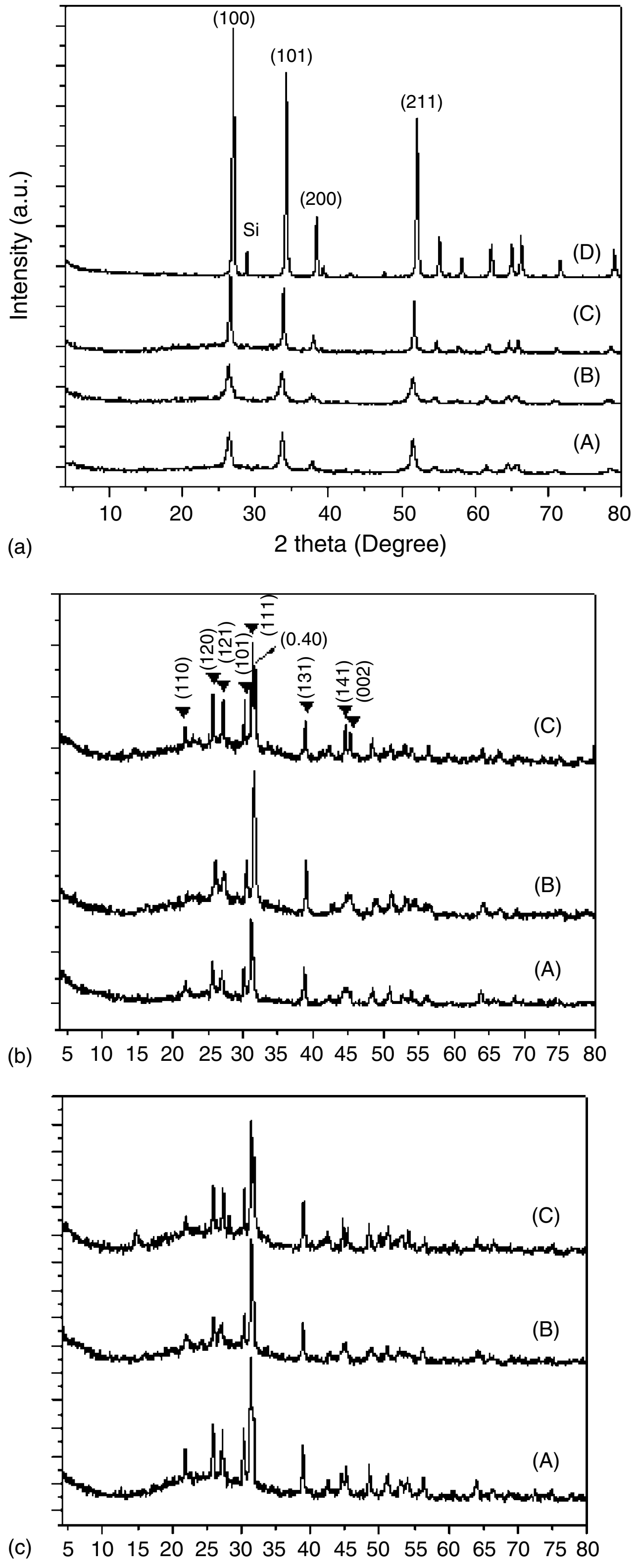

Figure 2. Diffractograms of the residue of $Sn_4Me_4S_6$ (a), $Sn_4Bu_4S_6$ (b), $Sn_4Ph_4S_6$ (c) decomposed in (A) oxygen, (B) nitrogen and (C) hydrogen; (D) standard SnO_2.

(rutile-type) SnO_2 with lattice parameters $a = b = 4.738$ Å and $c = 3.188$ Å (JCPDS-ICCD 1996, card no. 41–1445), which has been successfully obtained by us employing the same strategy.[15,16]

The XRD results of those products decomposed in N_2 and H_2 (Fig. 2B and C) showed diffraction lines at $2\theta/° = 21.97$, 26.05, 27.35, 30.46, 31.52, 32.18, 39.01, 43.09, 44.69, 45.42, 48.71, 48.57, 53.16 and 56.06; this matches with both orthorhombic SnS-Herzenbergite (JCPDS-ICCD 1996, card no. 41-1445) and the orthorhombic γ-Sn_2S_3 phase (JCPDS-ICCD 1996, card no. 30–13790).

X-ray EPMA revealed the presence of tin and oxygen in all samples decomposed in oxygen; no trace of sulfur was observed. On the contrary tin and sulfur were detected in the other materials obtained in inert or reducing atmospheres; this was important evidence that the sites detected by ^{119}Sn Mössbauer spectroscopy corresponded to tin sulfides, since from the parameters it is not possible to distinguish tin(II) or tin(IV) oxides from the respective sulfides.

Table 1. ^{119}Sn Mössbauer parameters[a] (isomer shift (IS), quadrupole splitting (QS), area and width) obtained at liquid nitrogen temperature for the pyrolysis residue of $Sn_4Me_4S_6$ (**1**), $Sn_4Bu_4S_6$ (**2**) and $Sn_4Ph_4S_6$ (**3**) obtained in O_2, N_2 and H_2

Residue	Tin site	IS/ mm s^{-1}	QS/ mm s^{-1}	Area/ %	Width/ mm s^{-1}
(**1**)/O_2	Sn(II)	3.39	0.80	8	0.90
	Sn(IV)	0.30	0.50	92	0.90
(**1**)/N_2	Sn(II)	3.33	0.92	89	0.90
	Sn(IV)	1.00	0.60	11	0.90
(**1**)/H_2	Sn(II)	3.31	0.85	52	0.94
	Sn(IV)	0.06	0.58	48	0.90
		0.08	1.62		
(**2**)/O_2	Sn(IV)	0.08	0.24	100	0.90
(**2**)/N_2	Sn(II)	3.28	0.96	57	0.90
	Sn(IV)	0.09	0.52	43	0.90
(**2**)/H_2	Sn(II)	3.38	1.05	58	0.94
	Sn(IV)	0.42	0.40	42	0.90
		0.70	2.25		
(**3**)/O_2	Sn(II)	3.07	0.89	2	0.90
	Sn(IV)	0.03	1.14	98	0.90
(**3**)/N_2	Sn(II)	3.38	0.80	64	0.90
	Sn(IV)	0.90	0.60	36	0.90
(**3**)/H_2	Sn(II)	3.33	0.95	52	0.94
	Sn(IV)	0.62	0.43	48	0.90
		0.53	1.45		
Sn_2S_3[b]	Sn(II)	3.35	0.97	41	0.90
	Sn(IV)	0.46	0.88	59	0.90
SnS_2[b]	Sn(IV)	0.85	0.76	100	0.90

[a] The errors associated with IS, QS, and width are ±0.05 mm s^{-1} and 2% for the area.
[b] Those are standards compounds.

The ^{119}Sn Mössbauer spectra clearly confirmed the XRD and EPMA results obtained for the residue prepared in O_2, which revealed a single signal of tin(IV) corresponding to the formation of SnO_2 as major product and a small amount of tin(II) not detected in the XRD experiment. The parameters IS and QS (Table 1) match perfectly with our previous results.[15]

The spectra of the other residues obtained in N_2 and H_2 displayed two sets of signals, corresponding to a mixture of tin(II) and tin(IV) sulphides, as supported by EPMA. On performing the experiment with a standard of Sn_2S_3, the same pattern of two sets of signals with IS = 3.35 mm s^{-1}, QS = 0.97 mm s^{-1} for tin(II) and IS = 0.46 mm s^{-1}, QS = 0.88 mm s^{-1} for tin(IV) were encountered. The residue of $Sn_4Bu_4S_6$ (**2**) decomposed in N_2 yielded the best phase of Sn_2S_3 in view of its Mössbauer spectrum line shape,

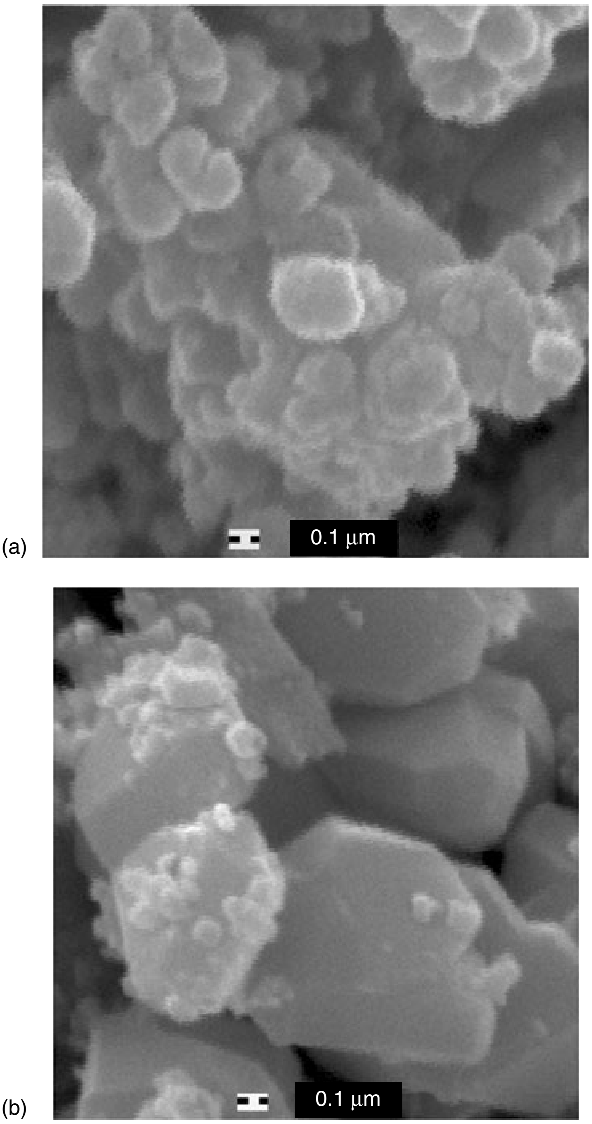

Figure 3. SEM images of the residue of $Sn_4Bu_4S_6$ (**2**) in oxygen (a), nitrogen (b) and hydrogen (c).

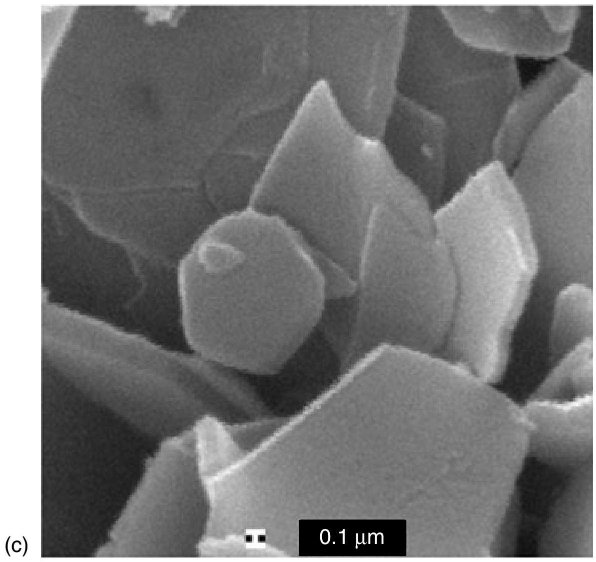

Figure 3. (*Continued*).

which resembles perfectly the corresponding spectrum of the standard.

The SEM images for the residues of **2** (Fig. 3) revealed a particle size of 10 nm for all residues. The SnO_2 obtained in oxygen presents the same morphology as for the material obtained previously.[15] Well-formed crystals of Sn_2S_3 were prepared in N_2, whereas in H_2 it crystallizes in the form of plates and seems less crystalline than the other material.

CONCLUSIONS

The results reported here have shown that the organotin sulfides $Sn_4R_4S_6$ ($R = Me$, *n*-Bu, Ph) decompose, in oxygen, into nanosized grains of the rutile-type tetragonal snO_2 in high yield. On the other hand, pure phase orthorhombic γ-Sn_2S_3 was obtained in nitrogen when $Sn_4Bu_4S_6$ (**2**) was employed as a precursor.

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