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Tin sphene micron-sized powders

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Abstract

A new sol–gel route is used to prepare tin sphene micron-sized powders. An aqueous solution of silicic acid is used as the silicon precursor. The influence of the calcium salt as well as the solvent used to dissolve the tin salt is discussed. Three methods have been employed to prepare the xerogel: a rapid evaporation of the solution, a refluxing of the solution and an hydrothermal preparation. The coupling of X-ray diffraction and ^{119}Sn Mössbauer spectroscopy allows to identify the different phases and to optimise the synthesis parameters. In addition, the Mössbauer spectra allowed to identify the various sites of tin and their evolution with annealing temperature. An almost pure (95%) tin sphene can be prepared as monodisperse spherical powders. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: $CaSnSiO_5$; Mössbauer spectroscopy; Powders-chemical preparation; Sol–gel processes; X-ray methods

1. Introduction

Tin sphene, malayaite, is a tin calcium silicate, the formula of which is: $CaSnSiO_5$. This silicate is isomorphous with the sphene $CaTiSiO_5$; it crystallises in the monoclinic system (space group $P2_1/a$, cell parameters: $a = 7.146$ Å, $b = 8.887$ Å, $c = 6.668$ Å, $\beta = 113.35°$). The structure has been described by Higgins et al.[1]; it is built from infinite chains of corner-sharing SnO_6 octahedra, these chains being connected through isolated SiO_4 tetrahedra to form a 3D "$SnSiO_4$" network. The calcium ions are situated inside this network with a very irregular heptacoordination. Substitutional solid solutions of foreign cations are possible on the tin and calcium sites and allow to prepare industrial pigments.[2–4]

Tin sphene has already been prepared using several methods. The solid state route consists in mixing stoichiometric amounts of the oxides and heating at 1400°C during 6 h.[5] The as-prepared product is pure but the grain size cannot be controlled. Ferrer et al.[4] used a sol–gel route to prepare tin sphene starting from silicon alkoxide $Si(OC_2H_5)_4$. This preparation leads to 50 to 80% in tin sphene with a large size distribution. This is not really surprising as the alkoxide route is often difficult to control in the case of trimetallic oxides. In the case of silicate compounds, an alternative could be a water soluble precursor in place of the alkoxide. Recently, we developed a new route based on $KHSi_2O_5$. This product can easily be prepared by reacting silicon powder with alcoholic potassium hydroxide.[6,7] It is very soluble in water ($s > 31 g.l^{-1}$) and the potassium ion can be exchanged on a cation-exchange resin. Evaporation at room temperature of the $H_2Si_2O_5$ solution leads to transparent, stable gels.

In this paper, we use this method to prepare tin sphene powders. We study the influence of the synthesis parameters, calcium salt–solvent–heating method, on the purity and size distribution of the tin sphene.

2. Experimental

Aqueous $H_2Si_2O_5$ solutions ($[Si] = 0.2$ mol/l) are used as silicon precursor. They are prepared either from $KHSi_2O_5$ or $Na_2SiO_3,5H_2O$ (Fluka product) by exchanging the alkali-metal ion for H^+ on an Amberlite resin.[8] The tin salt $SnCl_2,2H_2O$ is dissolved either in

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alcohol (ethanol or methanol) or in water acidified with HCl or HNO_3 (pH = 1). Three calcium salts have been used: $CaCl_2$, $Ca(NO_3)_3,4H_2O$, $CaCl_2,2H_2O$. In each preparation, boric acid (2%) is added as mineraliser.

Equimolar amounts of tin and calcium salts are mixed at room temperature. The $H_2Si_2O_5$ solution is then added. Three different procedures were investigated to prepare the gel: heating to reflux at 100°C under atmospheric pressure during 3 days (samples labelled R), reaction in a PTFE-lined steel bomb under autogenous pressure at 200°C during 3 days (samples labelled B), drying on a hot plate at 120°C during 30 min (samples labelled P). The so-obtained gels are dried at 120°C in an oven. Table 1 summarises the conditions of preparation. The xerogels are then calcined at different temperatures (between 1000 and 1400°C) during 4 h.

X-ray diffraction patterns were taken on a Seifert/XRD3000 diffractometer using Cu-K_α radiation over the range $5 < \theta/°/25$ with a scan rate of $1°\ \mathrm{min}^{-1}$ and were compared to the JCPDS files. ^{119}Sn Mössbauer spectra were recorded at room temperature on an Elscint AME 40 (EG and G) spectrometer. The γ-rays source is constituted by ^{119m}Sn in a $CaSnO_3$ matrix. The velocity scale was calibrated using a standard spectrum of an iron absorber obtained with a ^{57}Co(Rh) source. The velocity origin was defined with the absorption spectrum of $BaSnO_3$ recorded at room temperature. Absorbers were prepared from powders mixed with Apiezon grease. Concentrations are equal to 1 mg/cm^2 in ^{119}Sn in order to avoid spectrum enlargement. Spectra have been analysed with the program IZOFIT[10] with refinements based on a least-square method. Scanning electron microscopy (SEM) pictures were taken on a Cambridge-type scanning electron microscope.

3. Results and discussion

3.1. Xerogel synthesis

Xerogels are white when the solvent is acid and yellow if an alcohol is used due to organic residuals. X-ray characterisation confirms the differences in the chemical behaviour (Fig. 1). The first conclusion is that the preparation method has no influence on the crystallinity of the solid. For example, sample B8 prepared in hydrothermal conditions is amorphous as is sample R1 prepared in refluxing conditions. In contrast, the calcium salt is important. The nitrate leads to a poorly crystallised solid containing SnO_2 crystallites (samples B2 and R2 for example). But tin dioxide is also observed in xerogels prepared without nitrate: for example, in sample R8 prepared with calcium chloride dihydrate and ethanol. Thus, the partial oxidation of Sn(II) may have different origins, the effect of nitrate or the oxygen during the reactions or the drying. Indeed, the following reaction mentioned in the literature[9] may occur:

$$2SnCl_2 + O_2 \rightarrow SnO_2 + SnCl_4$$

Even in the case of amorphous xerogel (sample B8 for example), Mössbauer spectroscopy shows the presence of tin dioxide. Indeed, the spectrum in Fig. 3d presents a singlet around $\delta_1 = 2.57$ mm/s characteristic of Sn(II) in a regular surrounding[10] and this peak can be attributed to a Sn–O bond. But the weak absorption observed around $\delta_2 = 0.04$ mm/s and $\Delta_2 = 0.47$ mm/s corresponds to a Sn(IV) atom in an irregular environment and can be attributed to the dioxide.[10] The percentage of dioxide is estimated from the spectrum to be approximately 23%.

Another poorly crystallised phase has been identified in the xerogels. $CaCl_2,2H_2O$ crystallises in the gels prepared from alcohol and calcium chloride (for example, samples B7, P7, R7). Thus, calcium separates in the gel but we will see that this fact has no influence on the final product.

3.2. Thermal behaviour of the xerogels

After drying, xerogels are finely ground and calcined at 1000, 1200 and 1400°C during 4 h. At each stage, samples are characterised by X-ray diffraction. In order to estimate the percentage of tin sphene formed, we used the following formula:

$$(\%)\text{Sphène} = \frac{I_{200}(CaSnSiO_5)}{I_{110}(SnO_2) + I_{121}(CaSnO_3) + I_{200}(CaSnSiO_5)}$$

where I_{hkl} (X) is the intensity of the main peak of the phase X. This calculation allows a comparison between the samples.

Table 1
Preparation conditions of the xerogels

Solvent	HCl		HNO_3		MeOH		EtOH	
Ca salt	Chloride	Nitrate	Chloride	Nitrate	Chloride	Chloride dihydrate	Chloride	Chloride dihydrate
Bomb 200°C/3 days	B1	B2	B3	B4	B5	B6	B7	B8
Hotplate 120°C/30 min	P1	P2	P3	P4	P5	P6	P7	P8
Refluxing 100°C/3 days	R1	R2	R3	R4	R5	R6	R7	R8

Whatever the preparation conditions, the formation of tin sphene does not begin below 1000°C. At this temperature, the composition of the solid is rather complicated. Fig. 2, taken on sample B8, shows the presence of $CaSnO_3$ (labelled o), α-$CaSiO_3$ and ω-$CaSiO_3$ (labelled α and ω) and, finally, the rather well crystallised dioxide (labelled D). The presence of $CaSnO_3$ is surprising as B_2O_3, formed from the boric acid, is thought to inhibit the formation of this phase.[5,11] At this temperature, the percentage of tin sphene is only 10%. At 1200°C, the phases ω and o has disappeared but not the phase α. The percentage of dioxide is still important and equal to 49%. Thus it is necessary to heat at 1400°C to get the tin sphene almost pure, only soiled by a small amount of dioxide. This impurity cannot be removed by a longer heating and the percentage of tin sphene in the all cases is limited to 97% as reported in some anterior works.[11]

Mössbauer spectra taken on sample B8 calcined at different temperatures are presented in Fig. 3. Mössbauer parameters are gathered in Table 2. All the spectra are situated, in terms of isomere shift, in a domain characteristic of Sn(IV).[12] The spectrum corresponding to the gel calcined at 1000°C (Fig. 3c) is treated with three components. The first one ($\delta = -0.04$ and $\Delta = 0$) corresponds to the calcium stannate $CaSnO_3$. This is in agreement with the X-ray indexation. The parameters obtained for the two other components are attributed to SnO_2[13] and the tin sphene. After calcination at 1200°C, only two components can be identified with contribution equal to 50% : the dioxide and the tin sphene (Fig. 3b). Finally, Fig. 3a shows the spectrum of the gel calcined at 1400°C. The contribution of dioxide is around 5%.

Table 3 summarises the main results obtained from X-ray diffraction. It confirms that the preparation method, bomb–hot plate–refluxing, is not the major parameter. The second remark is that nitric acid acts as an inhibitor of the tin sphene formation. When it is used, the maximum percentage is equal to 65% and, moreover, $CaSnO_3$ is still present at high temperature with a noticeable percentage. The use of chlorhydric acid allows better results. However, it is difficult to get more than 90% of tin sphene soiled with tin dioxide and traces of calcium silicates. Thus, the best results are obtained with ethanol as solvent. In each case, the tin sphene percentage is around 93–95%. The results obtained with methanol are not so good. It is not easy to explain the differences observed between the two

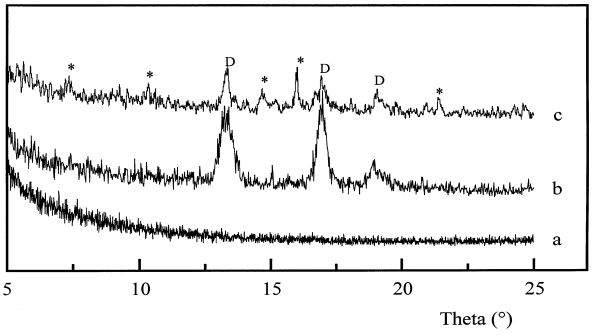

Fig. 1. Influence of the synthesis conditions on the xerogel structure. (a) sample B8, (b) sample B2, (c) sample B7.* $CaCl_2,2H_2O$; D, SnO_2.

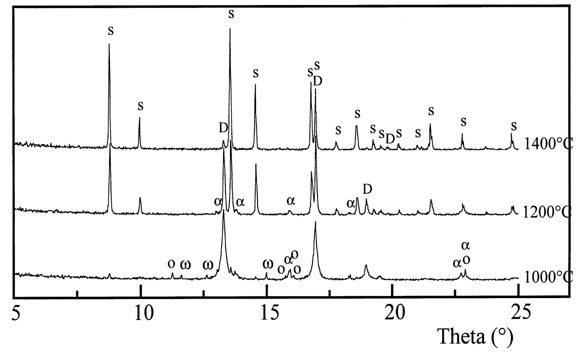

Fig. 2. Thermal evolution of the sample B8: S, $CaSnSiO_5$; D, SnO_2; α, α-$CaSiO_3$; ω, ω-$CaSiO_3$; o, $CaSnO_3$.

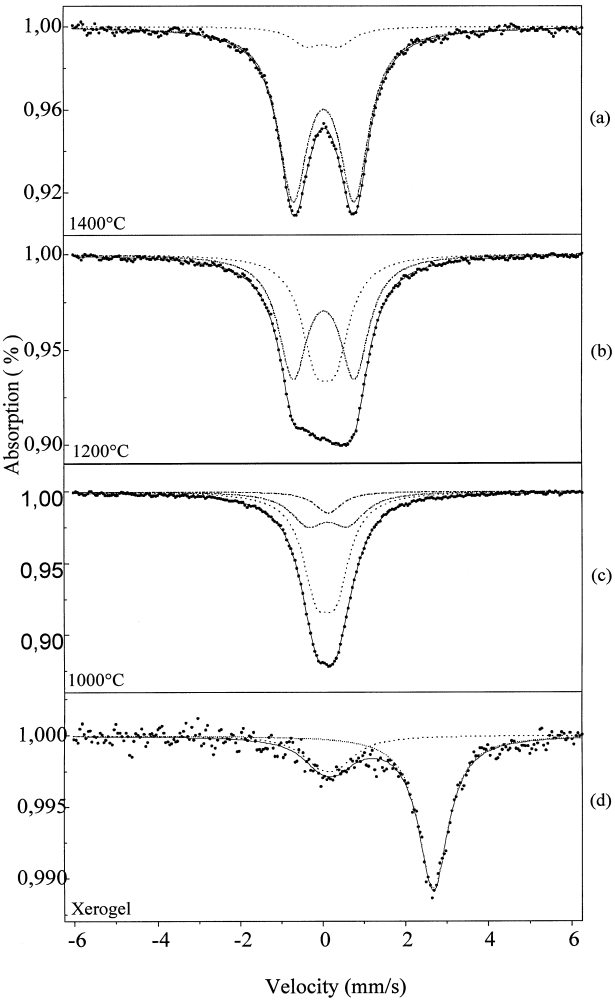

Fig. 3. ^{119}Sn Mössbauer spectra of sample B8: (a) 1400°C, (b) 1200°C, (c) 1000°C, (d) xerogel.

Table 2
Mössbauer parameters for sample B8 calcined at different temperatures[a][b]

Sample B8	xerogel	1000°C	1200°C	1400°C
δ_1	2.573 (7)	–	–	–
Δ_1	–	–	–	–
Γ_1	0.88 (2)	–	–	–
C_1	77	–	–	–
δ_2	–	0.04 (7)	–	–
Δ_2	–	–	–	–
Γ_2	–	0.78 (4)	–	–
C_2	–	8	–	–
δ_3	0.04 (5)	−0.01 (3)	−0.01 (1)	−0.08 (1)
Δ_3	0.47 (8)	0.48 (5)	0.52 (2)	0.6 (3)
Γ_3	0.8 (2)	0.7 (1)	0.94 (4)	0.6 (4)
C_3	23	63	50	5
δ_4	–	0.03 (3)	−0.062 (6)	−0.05 (1)
Δ_4	–	0.96 (5)	1.51 (1)	1.46 (2)
Γ_4	–	1.00 (5)	0.79 (2)	0.8 (1)
C_4	–	29	50	95
χ^2	0.488	0.454	0.365	0.512

[a] Isomere shifts are expressed in reference to $BaSnO_3$ (errors in parentheses).

[b] δ, isomere shift; Δ, quadrupole splitting; Γ, width at mid-height; C, Contribution; χ^2, control parameter for the refinements.

Table 3
X-ray diffraction analysis of the xerogels calcined at 1400°C[a]

	Ca nitrate	Ca chloride	Ca chloride dihydrate
HCl	B2: s = 90; d = 10;α	B1: s = 88; d = 12; α;ω	
	R2: s = 91; d = 9;α;ω		
	P2: s = 88; d = 12; α	P1: s = 81; d = 19;α;ω	
HNO_3		B3: s = 60; d = 40	
	P4: s = 65; d = 20 o = 15; ω	P3: s = 64; d = 30 o = 6; ω	
		B5: s = 86; d = 14	B6: s = 70; d = 30
MeOH			R6: s = 82; d = 18; o
		P5: s = 92; d = 8; α	P6:s = 91; d = 9; α
EtOH		B7: s = 89; d = 11; α	B8: s = 93; d = 7
		R7: s = 94; d = 6; α	R8: s = 94; d = 6; α
		P7: s = 93; d = 7; α	P8: s = 95; d = 5

[a] s, $CaSnSiO_5$; d, SnO_2; α, α-$CaSiO_3$; o, $CaSnO_3$; ω, ω-$CaSiO_3$.

alcohols. However, it is well known in sol–gel science that the structural arrangement in sols and gels are remarkably sensitive to the choice of the reactants.[14]

The tin sphene powders have been observed by SEM (Fig. 4). When the product is almost pure (samples B8 and P8), the morphology of the powder is regular showing quasi spherical grains with a mean size around 1.5 μm. In contrast, the sample B4 prepared with nitric acid shows an heterogeneous distribution of grains. It is likely that this difference depends on the presence of nitrate ions in solution as already noticed in other works.[7,15]

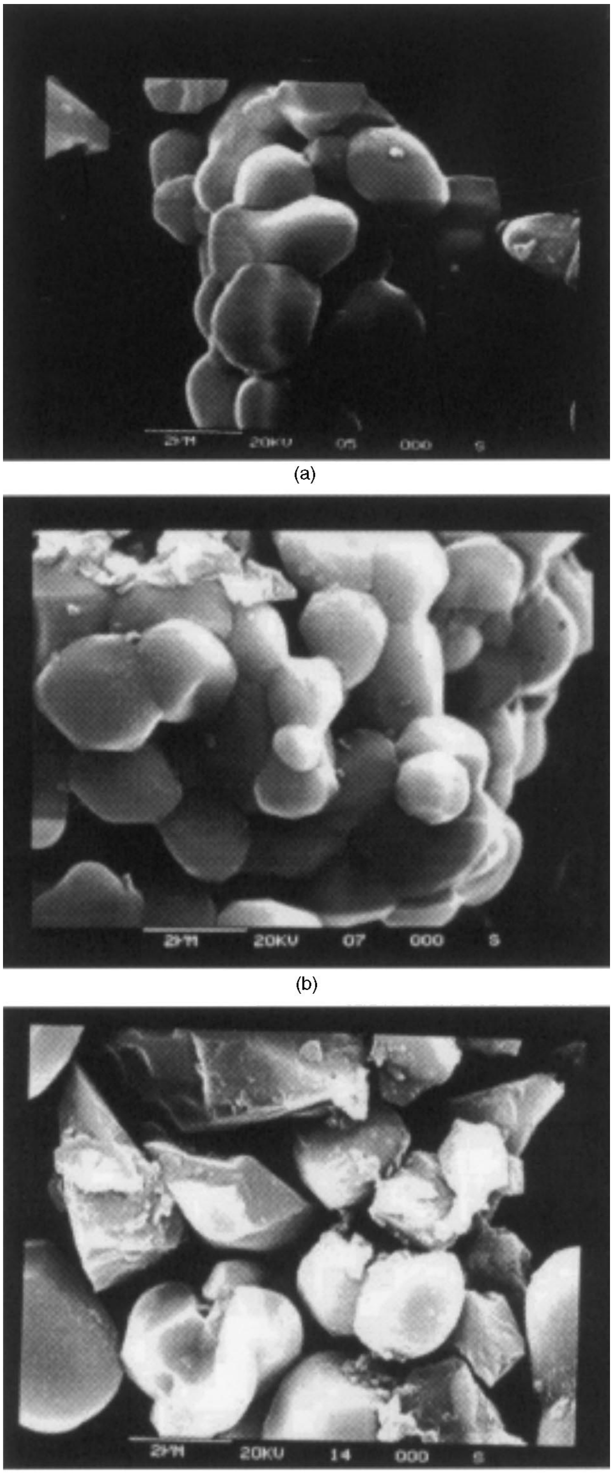

Fig. 4. SEM pictures of samples calcined at 1400°C: (a) sample B8, (b) sample P8, (c) sample B4.

4. Conclusion

We report a new aqueous sol–gel process for the preparation of micron sized tin sphene powders. Starting from a water soluble silicate, tin chloride and different calcium salts, a series of xerogels has been prepared and calcined. Their structural characterisation shows that the most important parameters for the preparation of pure tin sphene is the calcium salt and the solvent used to dissolve tin chloride. When calcium chloride and ethanol are used, a homogeneous spherical powder is obtained.

The aim of this work is the preparation of colored industrial pigments. It is well known that the hue and the color purity depend on the particle size.[16] Thus the preparation of monodisperse micron sized powders is a key point in the obtention of such pigments. Preparations of colored tin sphene powders, by partial substitution on the calcium site, are in progress.

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