

Mechanochemical Synthesis of SrSnO₃

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The synthesis of strontium metastannate (SrSnO₃) has been performed by coupling mechanical activation with thermal activation of SnC₂O₄-SrCO₃ mixtures. The solid-state reaction has been studied by TG-DSC analysis and powder X-ray diffraction. By annealing experiments performed on physical mixtures (no mechanical activation) it has been assessed that the formation of SrSnO₃ occurs through the intermediate Sr₂SnO₄ and is complete only after annealing at 1400 °C. By performing the annealing experiments on activated mixtures it has been established that the formation of SrSnO₃ takes place directly at temperatures between 800 and 1000 °C. The SrSnO₃ samples obtained at 800 and 900 °C show, by TG analysis, mass loss processes that suggest that SrSnO₃ obtained at these temperatures absorbs H₂O and CO₂ from the air so that its use as gas sensor can be envisaged. This is no longer true for the sample obtained at 1000 °C or above.

Key words: Synthesis, SrSnO₃, Mechanical Activation, Heat Capacity, Powder X-Ray Diffraction

Introduction

Strontium stannate, SrSnO₃, is a member of the double oxides of the general formula ABO₃ that are formed by the reaction between the oxides of alkaline-earth metals (A = Ca, Sr, Ba) and those of some of the group IV elements. Strontium stannate crystallizes in the cubic perovskite structure and is a dielectric material of technological importance [1] that has also been investigated as a potential material for the detection and metering of gases (CO, CO₂, H₂, Cl₂, NO₂ and H₂O) [2, 3].

SrSnO₃ is usually prepared by a conventional solid-state synthesis (ceramic route) starting from mixtures Sr(NO₃)₂-SnO₂ or SrCO₃-SnO₂ subjected to thermal treatment at 1000–1200 °C [4], but it has also been prepared by different routes. Alves *et al.* [5] prepared SrSnO₃ by the polymeric precursor method starting from mixtures of tin chloride dihydrate, citric acid and ethylene glycol: the powder mixture was milled in an attrition mill in alcohol media and finally heated at temperatures from 250 to 700 °C. Wang *et al.* [6] proposed a co-precipitation process: they mixed Sr and Sn precursors in an alkaline solution so obtain-

ing SrSn(OH)₆ that was calcined for 1 h at 1000 °C. The same authors prepared SrSnO₃ by a combustion method: Sr nitrate and Sn(IV) chloride pentahydrate were dissolved in the minimum amount of distilled water, and the solution was added dropwise to an aqueous ammonia solution under magnetic stirring. The precipitate obtained was stirred in a solution of ammonium nitrate and urea and heated to 100 °C to minimize the amount of water. Finally the mixture was placed in an oven kept at 600 °C for 10 min to yield the target compound. Like other alkaline-earth stannates, SrSnO₃ can be prepared by the sol-gel technique [7], and it has also been obtained by the hydrothermal method [8] and by microwave-based synthesis [9].

In the present work the synthesis of SrSnO₃ has been attempted by using a combination of mechanical (by high-energy milling) and thermal activation. The reaction has been studied by TG/DSC measurements, and its progress was monitored by powder X-ray diffraction (PXRD) patterns taken on samples both of the physical mixture and the mechanically activated one subjected to 3 h thermal treatment at temperatures between 500 and 1400 °C. The thermally treated samples have been characterized by PXRD,

FT-IR spectroscopy, and TG analysis. The molar heat capacity of the synthesized SrSnO₃ has been determined by modulated-temperature differential scanning calorimetry (MTDSC).

Results and Discussion

Characterization of the mixtures

Fig. 1 compares the PXRD patterns of samples of a physical mixture (A) with those of a mixture mechanically activated for 6 h (B) and 15 h (C).

The physical mixture shows the peaks characteristic of SnC₂O₄ and SrCO₃. The peaks of SnC₂O₄ have disappeared in the 6 h- and 15 h-activated samples while only the most intense peaks characteristic of SrCO₃ appear though considerably broadened due to the extended amorphisation that occurs in these samples.

Fig. 2 shows the TG curves of samples of a physical mixture and of the mixtures mechanically activated for 6 h and 15 h. In the case of the physical mixture, two well separated steps of mass loss are observed. The mass value at the end of the first step ($84.2 \pm 0.3\%$) shows good agreement with the mass value expected for the formation of a SnO₂-SrCO₃ mixture (83.9%). The mean mass value at the end of the run (71.9 ± 0.2) shows good agreement with the value expected for the formation of a SrO-SnO₂ mixture (71.8%).

In the case of the milled mixtures four stages of mass loss are evident instead of two although the separations of the subsequent stages are less pronounced.

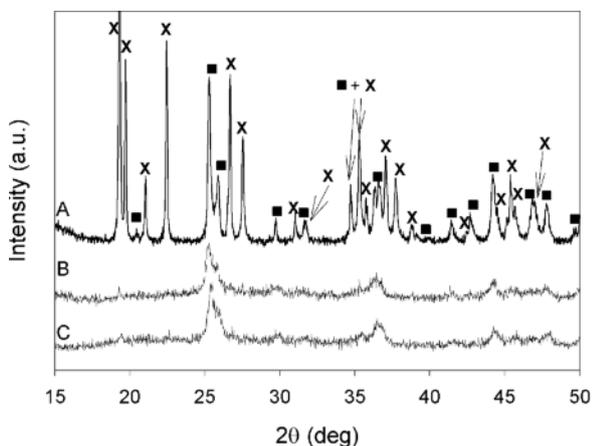


Fig. 1. PXRD patterns of (A) a physical mixture, (B) a mixture mechanically activated for 6 h and (C) a mixture mechanically activated for 15 h (■ SrCO₃; × SnC₂O₄).

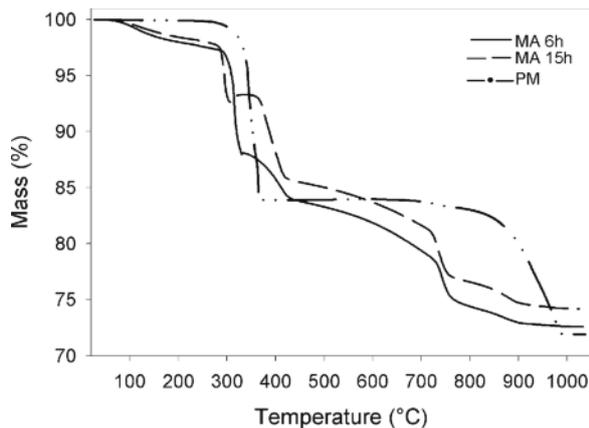
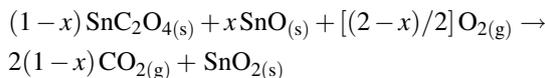


Fig. 2. Thermogram of SnC₂O₄-SrCO₃ mixtures [dash-dotted: physical mixture (PM); solid line: milled for 6 h (MA 6 h); dashed line: milled for 15 h (MA 15 h)].

However, the mass losing process of the milled mixtures ends at lower temperature as compared to the physical mixture. It can further be noted that the mass value attained at the end of the TG runs increases with increasing milling time. In a previous study performed on the solid-state system Li₂CO₃-SnC₂O₄ [10] it could be shown that during milling a share of SnC₂O₄ decomposes to SnO. In the case of the system under study an XRD evidence for SnO could only be obtained after longer milling times (60 h) with the mass value attained at the end of the TG run being much higher than expected. In our opinion, it is reasonable to assume that the higher than expected mass values obtained also after milling times of 6 and 15 h are due to the same phenomenon, although the extent of SnC₂O₄ decomposition to SnO induced mechanically is not large enough as to yield XRD peaks characteristic of SnO.

The reaction may take place during the thermal runs with the activated mixture:

- 1) stage 1 (up to ≈ 500 °C)



- 2) stage 2 (up to ≈ 1000 °C)



Fig. 3 shows the DSC curves of samples of the mixtures.

The DSC curve of the physical mixture presents an exothermic peak whose mean enthalpy is -355 ± 29 kJ

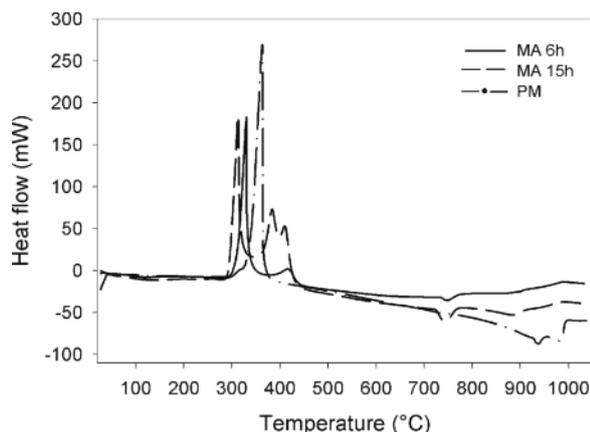


Fig. 3. DSC thermogram of SnC₂O₄-SrCO₃ mixtures [dash-dotted: physical mixture (PM); solid line (MA 6 h): milled for 6 h; dashed line (MA 15 h): milled for 15 h].

per mole of SnC₂O₄. It is proposed that the peak corresponds to the decomposition of SnC₂O₄ to SnO₂ and CO₂ because the exothermic peak ends with a mean mass value ($84.2 \pm 0.3\%$) in good agreement with the mass value expected for the formation of a SnO₂-SrCO₃ mixture (83.9%). The mean enthalpy is in fair agreement with the value obtained with pure SnC₂O₄ ($-350 \pm 7 \text{ kJ mol}^{-1}$). The mean enthalpy of the endothermic peak at higher temperatures ($232 \pm 35 \text{ kJ per mole of SrCO}_3$) is in fair agreement with the value obtained with pure SrCO₃ ($225 \pm 4 \text{ kJ mol}^{-1}$). Therefore it can be concluded that the thermal behavior of the physical mixture is the sum of those of the individual components.

The DSC curves of samples of mixtures milled respectively for 6 and 15 h are also shown in Fig. 3. Table 1 reports the mean mass values (M_{fin} , %) obtained at the end of the TG-DSC runs and the corresponding x values (moles of SnC₂O₄ decomposed during milling) obtained by comparing the mass values attained at the end of the runs with the expected values. Also reported are the mean enthalpies for the exothermic peak (kJ per mole of SnC₂O₄ for both experimental and expected values) and for the endothermic peaks (kJ per mole of SrCO₃).

The x value shows a trend to increase with milling time. The enthalpies of the exothermic processes reported in Table 1 ($\Delta H_{\text{exo,expm.}}$) can be compared with the values expected ($\Delta H_{\text{exo,expect.}}$) by taking into account all the processes associated with this peak: the oxidation of SnO formed from SnC₂O₄ during the mechanical activation (x moles, specific enthalpy value $-295 \text{ kJ per mole of SnO}$) and the decomposition of the remaining Sn(II) oxalate [$(1-x)$ moles; specific enthalpy value for SnC₂O₄ -350 kJ mol^{-1}]. The difference between the experimental and the expected exothermic enthalpies are within the standard deviation of the experimental data in the case of the samples activated for 6 h, while an excess of evolved heat is observed in the case of the mixtures activated for 15 h (batch B): $\approx -48 \text{ kJ per mole of SnC}_2\text{O}_4$, significantly higher than the standard deviation of the relevant enthalpy value (Table 1). The endothermic peak corresponds to the thermal decomposition of SrCO₃. The mean values of different batches of mixture (activated for 6 and 15 h) are reported in Table 1. The data are close to each other and also to the mean value obtained with the physical mixture ($+232 \pm 35 \text{ kJ per mole of SrCO}_3$). The mechanical activation therefore does not exert any marked influence on the enthalpy of the endothermic peak.

The DSC evidence obtained seems to be at variance with the PXRD evidence. Actually the patterns of the residuals recovered after the thermal runs performed on the physical mixture (Fig. 4, lower trace) show that the residuals of the unmilled sample are mixtures of SrCO₃, SrSnO₃, Sr₂SnO₄ and SnO₂. This suggests that at least a partial reaction between the formed oxides is taking place during the thermal runs. Such a conclusion could not be drawn from the DSC evidence alone that shows that the enthalpies of the two DSC peaks are very close to those obtained with the two pure components. On the other hand, the upper trace of Fig. 4 shows the PXRD patterns of the residuals obtained starting from the activated mixtures: such residuals only show peaks characteristic of SrSnO₃. Therefore, also in the case of the milled mixtures, the reaction between nascent oxides has been shown to be

Mixture	M_{fin}	x	$\Delta H_{\text{exo,expm.}}$	$\Delta H_{\text{exo,expect.}}$	ΔH_{endo}
6 h	72.0 ± 0.1	0.016 ± 0.005	-367 ± 17	-355	239 ± 17
15 h batch A	72.7 ± 0.1	0.064 ± 0.006	-388 ± 10	-371	240 ± 2
15 h batch B	73.7 ± 0.1	0.130 ± 0.007	-443 ± 4.0	-395	236 ± 1

Table 1. TG-DSC data of the runs performed on the activated mixtures.

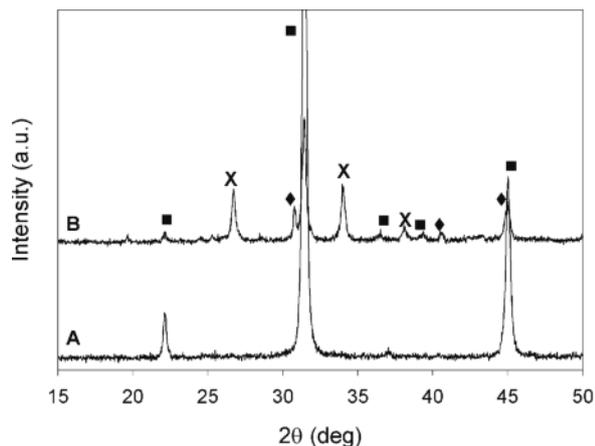


Fig. 4. PXRD patterns of the residuals recovered after TG/DSC runs performed with a physical mixture sample (lower curve) and with a milled mixture (upper curve) (■ SrSnO₃; ◆ Sr₂SnO₄; × SnO₂).

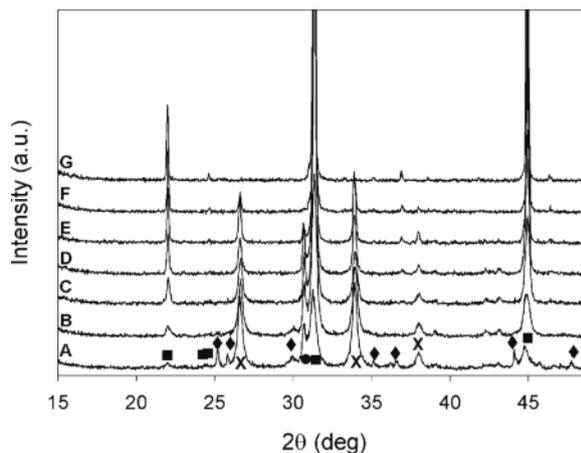


Fig. 5. PXRD diagrams of samples of physical mixtures annealed for 3 h at temperatures from 800 °C (A) up to 1400 °C (G) in steps of 100 °C (● Sr₂SnO₄; ◆ SrCO₃; ■ SrSnO₃; × SnO₂).

completed after the thermal runs although this experimental fact could not be deduced from the DSC data.

Thermal treatment of the mixture

Physical mixtures

Samples of a physical mixture were heated for 3 h in air at temperatures between 800 and 1400 °C (in steps of 100 °C). Table 2 reports the residual mass values (M_{res} , %) obtained after this treatment.

The mass values obtained at the end of the thermal treatment performed at 800 and 900 °C are significantly higher than the mass value expected for the total decomposition of both precursors (71.8%). On the contrary, the mean of the mass values ($71.3 \pm 0.7\%$) obtained at the end of the thermal treatments performed at $T \geq 1000$ °C is in fair agreement with the expected value. Fig. 5 shows the PXRD patterns of all the physical mixtures annealed for 3 h.

Table 2. Residual mass values (M_{res} , %) obtained after 3 h thermal treatment at different temperatures (T , °C) in air.

T (°C)	M_{res} (%)	T (°C)	M_{res} (%)
800	76.5	1200	72.0
900	73.5	1300	71.3
1000	70.7	1400	70.5
1100	72.1		

From the patterns shown in Fig. 5, it can be noted that the compounds formed after the annealing at 800 °C and 900 °C are SrCO₃, SnO₂, SrSnO₃, and Sr₂SnO₄. Therefore, the conclusion drawn from the residual mass values is confirmed by the PXRD patterns: complete decomposition of SrCO₃ has not occurred by thermal treatment performed up to $T < 1000$ °C.

The PXRD patterns of the mixtures annealed in the temperature range 1000–1300 °C do no longer show the peaks of SrCO₃. However, along with the peaks of SrSnO₃, the peaks of Sr₂SnO₄ and SnO₂ are also present. The intensity of the peaks of the two latter compounds decreases upon increasing the annealing temperature. This result shows that the reaction appears to take place in two stages:

- 1) $\text{SnC}_2\text{O}_4(\text{s}) + \text{SrCO}_3(\text{s}) + \text{O}_2(\text{g}) \rightarrow x\text{SrSnO}_3(\text{s}) + [(1-x)/2]\text{Sr}_2\text{SnO}_4(\text{s}) + [(1-x)/2]\text{SnO}_2(\text{s}) + 3\text{CO}_2(\text{g})$,
- 2) $[(1-x)/2]\text{SnO}_2(\text{s}) + [(1-x)/2]\text{Sr}_2\text{SnO}_4(\text{s}) \rightarrow (1-x)\text{SrSnO}_3(\text{s})$.

The second stage is proceeding slowly even at temperatures as high as 1300 °C, and it is only complete after a 3 h-annealing period at 1400 °C.

The samples obtained from the 3 h annealing of the physical mixture between 1000 and 1400 °C have been characterized both by TG analysis and FT-IR spectroscopy.

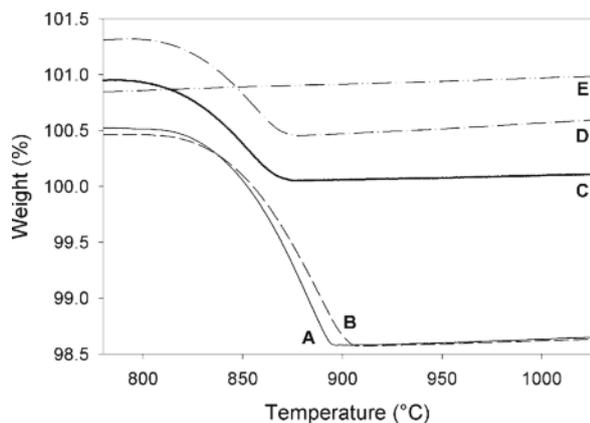


Fig. 6. TG runs performed on samples of physical mixtures heated for 3 h at temperatures of 1000 (A), 1100 (B), 1200 (C), 1300 (D) and 1400 °C (E).

Fig. 6 shows the TGA scans (10 K min^{-1}) obtained up to 1000 °C on these samples. The samples of the physical mixture annealed between 1000 and 1300 °C show a mass loss step at $T > 800$ °C that reflects

the decomposition of SrCO₃. The presence of SrCO₃ in the mixtures heated at $T \geq 1000$ °C is in contrast with the PXRD evidence (see Fig. 5) that did not show a trace of SrCO₃ in these mixtures. Such conflicting evidence can be explained by considering that the SrCO₃ that decomposes in these TG runs is not SrCO₃ that failed to decompose during the previous 3 h annealing period of the physical mixture between 1000 and 1300 °C, but it is rather SrCO₃ that has been formed by interaction of the annealed mixture with carbon dioxide present in the atmosphere [11]. In fact one of the envisaged applications of SrSnO₃ is as a gas sensor for carbon dioxide [2, 3]. Therefore, starting from the physical mixture, the formation of SrSnO₃ is complete only after an annealing for 3 h at temperatures as high as 1400 °C. However, the SrSnO₃ thus obtained is no more able to absorb carbon dioxide.

This result is confirmed by the IR spectra (Fig. 7) of the samples previously subjected to TG analysis.

The IR spectra of the samples annealed for 3 h up to 1300 °C show the band characteristic of the carbonate group ($\approx 1450 \text{ cm}^{-1}$) along with another band at

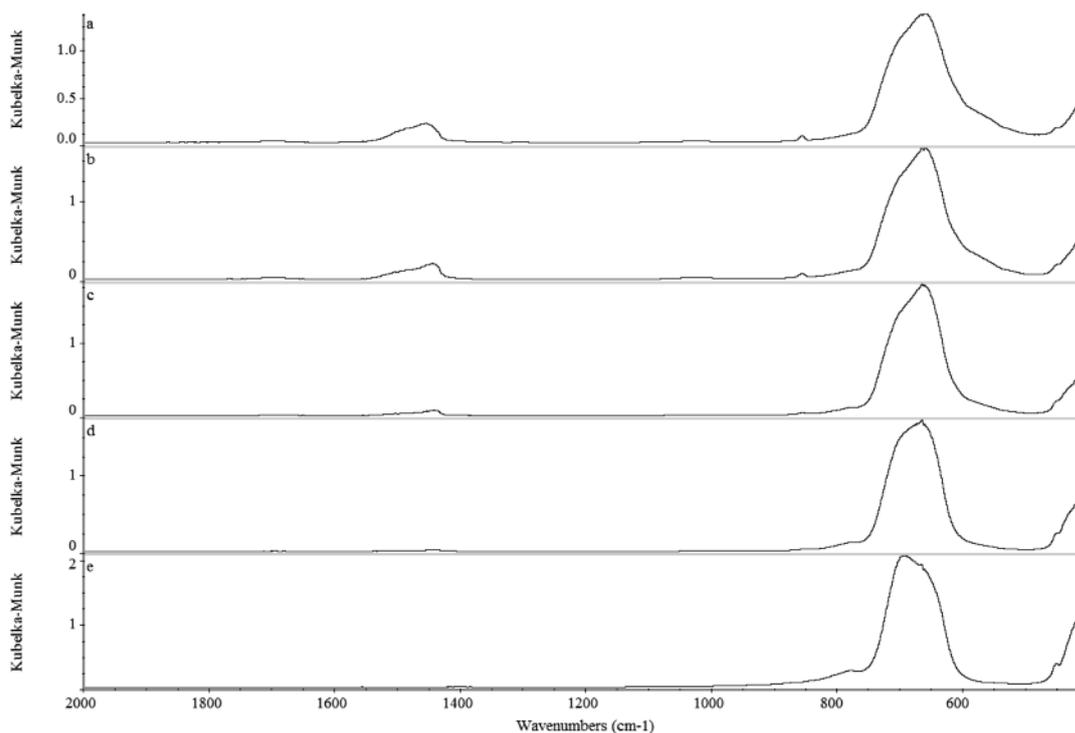


Fig. 7. Diffuse reflectance FT-IR spectra of samples of physical mixtures SrCO₃-SnC₂O₄ annealed for 3 h at temperatures of 1000 (a), 1100 (b), 1200 (c), 1300 (d), and 1400 °C (e).

$\approx 660 \text{ cm}^{-1}$ that is characteristic of the SnO_3^{2-} group. The band of the carbonate anion vanishes only in the IR spectrum of the sample annealed for 3 h at 1400 °C (e).

Mechanically activated mixtures

Mixtures milled for 6 h

Fig. 8 shows the PXRD patterns of the samples mechanically activated for 6 h and thermally treated for 3 h at temperatures between 500 and 1000 °C (in steps of 100 °C).

The mixtures annealed at 500 and 600 °C show the presence of unreacted SrCO₃ that is still present after the annealing at 700 °C even if, by annealing at such a temperature, the main peaks are those characteristic of SrSnO₃. Starting from the sample annealed at 800 °C, the only peaks present are those of SrSnO₃. There is no evidence for Sr₂SnO₄ (present in the patterns of the physical mixture annealed up to 1300 °C) for all temperatures of annealing.

Fig. 9 shows the PXRD patterns of the mixture activated for 15 h and annealed for 3 h at temperatures from 500 up to 1000 °C in steps of 100 °C.

The peaks characteristic of SrCO₃ are present in the patterns of the sample annealed up to 800 °C. Above 800 °C the peaks of the target phase (SrSnO₃) are also present but the intense peak of SnO₂ is still apparent. The peaks of SrCO₃ disappear by annealing at 900 °C. A thermal treatment for 3 h at 1000 °C has

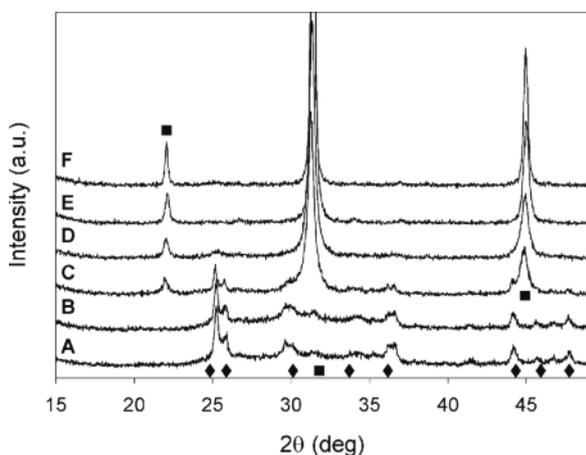


Fig. 8. PXRD patterns of samples mechanically activated for 6 h and annealed for 3 h from 500 (A) up to 1000 °C (F) in steps of 100 °C (♦ SrCO₃; ■ SrSnO₃).

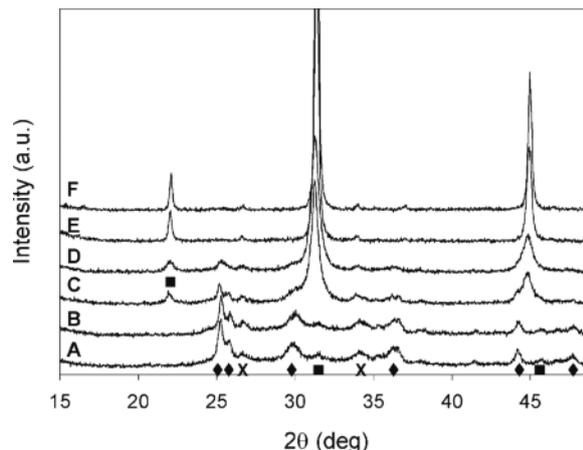


Fig. 9. PXRD patterns of mixtures activated for 15 h from 500 (A) up to 1000 °C (F) in steps of 100 °C (♦ SrCO₃; ■ SrSnO₃; × SnO₂).

to be performed in order to obtain patterns where the only peaks present are those characteristic of SrSnO₃. Therefore, it appears that SrSnO₃ can be prepared from mechanically activated equimolar mixtures of SrCO₃ and SnC₂O₄ annealed at temperatures between 800 and 1000 °C which are much lower than the 1400 °C needed to obtain the complete formation of SrSnO₃ when starting from a physical mixture. It has, however, been established that the annealing temperature needed to obtain pure SrSnO₃ is dependent on the milling time as it increases from 800 °C (milling time: 6 h) up to 1000 °C (milling time: 15 h).

TGA measurements have been performed on samples of SrSnO₃ prepared by 3 h thermal annealing of the activated mixtures at temperatures in the range 800–1000 °C. Three stages of mass loss appear as is shown in Table 3.

The first step (ΔM_1 , %) up to ≈ 300 °C is associated with mass losses increasing with the annealing temperature. It is well known that SrSnO₃ is hygroscopic, and this stage of mass loss is likely related with water adsorbed on the annealed samples. In the second step

Table 3. Mass loss data of samples of SrSnO₃ prepared by 3 h annealing of the milled mixtures at 800, 900 and 1000 °C.

T (°C)	ΔM_1 (%)	ΔM_2 (%)	ΔM_3 (%)
800	-2.1 ± 0.5	-3.0 ± 0.5	-1.2 ± 0.4
900	-1.0 ± 0.1	-1.4 ± 0.3	–
1000	–	–	–

Sample	<i>a</i>	<i>b</i>	<i>c</i>
Physical mixt. 3 h at 1400 °C	124.76	0.0383	−37 519
Milled mixt. 6 h + 3 h at 1000 °C (A)	120.52	0.0392	−48 961
Milled mixt. 6 h + 3 h at 1000 °C (B)	127.86	0.0344	−40 062
Milled mixt. 15 h + 3 h at 1000 °C (A)	121.85	0.0334	−40 621
Milled mixt. 15 h + 3 h at 1000 °C (B)	119.47	0.0318	−37 348
Mean	122.9 ± 3.4	0.031 ± 0.007	−40 902 ± 4738

Table 4. Coefficients of the polynomials ($C_p = a + bT + cT^{-2}$) interpolating the C_p data as a function of temperature (T , °C).

the mass loss (ΔM_2 , %) between ≈ 300 and ≈ 650 °C also decreases with increasing annealing temperature. The nature of this step of mass loss is not clear as the temperature range where it occurs seems to be too high if water release would be its origin, but it seems to be too low if the process would be SrCO₃ decomposition. Clearly, an analysis of the evolved gas will be of help to make this point clear. The last step of mass loss (ΔM_3 , %) between 700 and 950 °C is likely due to the decomposition of SrCO₃ formed on the surface of SrSnO₃ by the reaction with carbon dioxide present in the atmosphere [11]. The milled mixture annealed at a temperature of 800 °C shows considerable mass loss over all three temperature ranges. That annealed at 900 °C only shows minor mass losses over the first two temperature ranges. Only the sample annealed at 1000 °C does not show significant mass losses in the entire temperature range. This means that SrSnO₃ prepared at temperatures of 800–900 °C can be considered for application as gas sensor, but that this is no longer true for the sample prepared at 1000 °C.

Heat capacity of SrSnO₃ as a function of temperature

The C_p values have been determined by MTDSC in the temperature range 50–380 °C for mechanically activated samples (6 h and 15 h) annealed for 3 h at 1000 °C and from samples of a physical mixture annealed for 3 h at 1400 °C. Table 4 reports the coefficients (a , b , c) of the polynomials $C_p = a + bT + cT^{-2}$ that interpolate the C_p data as a function of temperature (T , °C). The values are very similar for all the samples examined.

Conclusion

TG measurements have shown that the reaction between SnC₂O₄ and SrCO₃ in a physical mixture occurs in two separate steps, namely the decomposition of SnC₂O₄ to SnO₂ and the decomposition of SrCO₃ to SrO. In the case of the mechanically activated mixture the number of TG steps doubles, but

the mass value attained at the end of the TG run increases with increasing milling time. This has been tentatively ascribed to SnC₂O₄ → SnO decomposition that occurs during milling as it is the case of the mechanically activated mixtures Li₂CO₃-SnC₂O₄ reported previously [10]. On the contrary, the DSC evidence shows that no differences seem to exist between the course of the reaction in the physical and in the milled mixtures. There is X-ray evidence that a mixture of Sr₂SnO₄, SrSnO₃ and SnO₂ is obtained at the end of the thermal run performed on the physical mixture, while SrSnO₃ is the only product formed at the end of the same run performed on milled samples.

Annealing of the physical mixture (3 h) leads to the complete formation of SrSnO₃, through the intermediate Sr₂SnO₄, only at temperatures as high as 1400 °C. SrSnO₃ obtained in this way does not absorb gas (CO₂, H₂O) from moist air, and its application as gas sensor cannot be envisaged.

SrSnO₃ is obtained directly from mixtures mechanically activated by high-energy milling (for 6 and 15 h) by annealing for 3 h at temperatures of 800, 900 and 1000 °C. SrSnO₃ generated in this way shows water absorption at room temperature only in the case of samples prepared at 800 °C. SrSnO₃ prepared at 900 °C shows water absorption to a lesser extent, while no water absorption occurs with the product prepared at 1000 °C.

The thermal capacity of SrSnO₃ prepared by annealing the milled mixture for 3 h at 1000 °C shows a temperature dependence that is indistinguishable from that of SrSnO₃ prepared by annealing of the physical mixture for 3 h at 1400 °C.

Experimental Section

The starting chemicals [SnC₂O₄ (purity 98+ %) and SrCO₃ (purity 99+ %)] were purchased from Aldrich Chimica, Italy. Physical mixtures of molar ratio of Sr to Sn = 1 : 1 were prepared by weighing the appropriate amounts of precursors and by suspending the powders in acetone

under magnetic stirring for 6 h whereupon the solvent was evaporated in an oven at 50 °C overnight. The mechanically activated mixtures were prepared by dry milling lots of 1 g of physical mixtures: the powders were put into zirconia jars (12.5 mL) of a planetary mill (Pulverisette 7 by Fritsch, Germany) with 4 zirconia balls (12 mm diameter; the mass ratio between the milling balls and the sample powder was 7 : 1). The mill was operated at 600 rpm (rotation speed) for 6 and 15 h. Several batches of each milled sample were prepared. TG/DSC measurements were performed on pure samples and on mixtures (both physically and mechanically activated) with a Q600 simultaneous TG/DSC analyzer (TA Instruments Inc., USA). Samples of ≈ 50 mg of the mixtures were placed into alumina cups and heated (heating rate 10 K min⁻¹, air flow 100 mL min⁻¹) from 25 up to 1000 °C. Samples of physical mixtures were heated in a tube furnace (static air, 10 K min⁻¹) up to 800, 900, 1000, 1100, 1200, 1300, and 1400 °C with isothermal stage of 3 h at the end of each heating ramp. Samples of the mechanically activated mixtures were heated in a tube furnace (static air, 10 K min⁻¹) up to 500, 600, 700, 800, 900, and 1000 °C with an isothermal stage of 3 h at the end of each heating ramp. Then powder X-ray diffraction (PXRD) patterns were recorded in step scan mode (CuK α radiation, step width 0.015°, 2 s per step, 40 kV, 40 mA, $2\theta = 15-50^\circ$) with a Bruker D5005 powder X-ray diffractometer.

The molar heat capacity of the SrSnO₃ samples was determined by modulated temperature differential scanning

calorimetry (MTDSC, Q2000 DSC, T_{zero} technology, TA Instruments Inc., USA). The samples (≈ 20 mg) were placed in a closed aluminum pan and heated under a nitrogen flow of 50 mL min⁻¹ in a quasi-isothermal mode, *i. e.* the sample was heated at temperatures between 50 and 380 °C in steps of 10 K and maintained at each of these steps for 10 min while the temperature was oscillating with an amplitude of ± 0.5 °C and with a period of 70 s. In this way the true reversing heat capacity could be measured. Before the measurements the instrument was calibrated under the same experimental conditions with a sapphire disk according to the manufacturer's instructions: a calibration constant of 1.094 ± 0.008 has been obtained.

Diffuse reflectance FT-IR spectra of SrSnO₃ samples were recorded with a FT-IR spectrometer (iS10 by Nicolet, USA) on samples dispersed in KBr (5% mass): 512 scans were co-added at 4 cm⁻¹ resolution and ratioed against 1024 scans collected on samples of pure KBr (99+ %, Sigma Aldrich, Italy).

The thermal stability of the prepared samples of SrSnO₃ has been tested by performing TG runs on samples prepared from the physical mixture (annealing for 3 h at 1000 up to 1400 °C in steps of 100 °C) and from the mechanically activated mixture (annealing for 3 h at 800, 900 and 1000 °C). The TG runs were conducted under dry nitrogen flow (50 mL min⁻¹) and with a heating rate of 10 K min⁻¹ up to 1000 °C on a Q5000 thermobalance (TA Instruments Inc., USA).

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