

Mechanically assisted solid state synthesis of Mg_2SnO_4

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Abstract Simultaneous TG–DSC measurements have been used to study the solid state reaction in the system $\text{SnC}_2\text{O}_4\text{--}4\text{MgCO}_3\cdot\text{Mg}(\text{OH})_2\cdot x\text{H}_2\text{O}$ ($\text{Sn}:\text{Mg} = 0.5$). The results obtained with physically prepared mixture and with mixture mechanically activated by high-energy milling are compared. Synthesis of the compound Mg_2SnO_4 has been attempted starting from both type of mixture: Mg_2SnO_4 forms by annealing the activated mixture at temperatures between 850 and 1,000 °C while it can hardly be obtained from physical mixtures even by thermal treatment at temperature as high as 1,300–1,350 °C. Mg_2SnO_4 prepared by annealing the activated mixture has been characterized by diffuse reflectance FT-IR spectroscopy, modulated temperature differential scanning calorimetry, scanning electron microscopy, and specific surface area measurements (B.E.T. method).

Keywords Mg_2SnO_4 · High-energy milling · Solid state synthesis · Mechano-thermal synthesis · Molar heat capacity

Introduction

In the system MgO--SnO_2 the existence of two compounds has been assessed: Mg_2SnO_4 is a stable phase while the compound MgSnO_3 that has also been reported [1] is deemed to be stable at temperature not exceeding 700 °C [2]. The spinel compound Mg_2SnO_4 has been recently proposed for

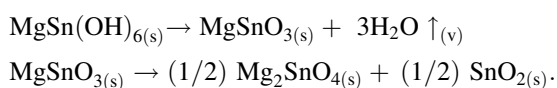
applications in electronic ceramics: an example of such applications is the use of this material in manufacturing dielectric plates for cellular phones and high speed computing devices. As a matter of fact it is a material suitable for capacitors that have been shown to offer stable performance, low permittivity, and small loss tangent [3–6]. Tin oxides are considered the most promising anode materials for lithium-ion batteries. However, the alloying/de-alloying of Li with Sn causes a drastic volume change leading to cracking of the electrode and rapid capacity decay. To overcome this problem, compounds of the type M_2SnO_4 ($\text{M} = \text{Mg}, \text{Mn}, \text{Co}$) have been tested as inert matrices in which tin oxide can be dispersed to prepare tin oxides spinel-based anodes for Li-ion batteries [7]. The presence of other inactive materials acting as matrices could buffer the volume expansion and contraction during cycling of the cell. In this sense, Mg/Sn composite oxides are considered an alternative anode material for use in Li-batteries [8]. Mg_2SnO_4 has also found application as inert matrix to dispose of radioactive material mainly nuclear waste from spent nuclear fuel [9].

Mg_2SnO_4 has been prepared by conventional solid state synthesis. $\text{MgO}, \text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}, 4\text{MgCO}_3\cdot\text{Mg}(\text{OH})_2\cdot 5\text{H}_2\text{O}$ have been used as Mg-precursors while SnO_2 was chosen as tin precursor [6, 7, 9]. The mixtures had to be thermally treated at temperatures between 900 and 1,400 °C to obtain Mg_2SnO_4 .

Mg_2SnO_4 has also been prepared by alternative routes. Silva et al. [10] mixed two solutions: the first one was composed of citric acid and magnesium nitrate while the second one contained tin citrate and citric acid. The mixture was heated at 90 °C. Finally, ethylene glycol was added to the solution. The obtained viscous solution has been calcined at 300 °C to obtain the powder precursor that had to be annealed for 1 h at 700 °C to obtain Mg_2SnO_4 . Azad [11] prepared Mg_2SnO_4 from a stoichiometric

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metallic mixture Mg/Sn that was heated (under argon) at 250 °C to melt Sn. Then the temperature was raised and maintained for 2 h at 775 °C: a mixture of Mg₂Sn, Sn, and Mg₂SnO₄ has formed and thermal treatments at temperatures as high as 1,200 °C were needed to obtain Mg₂SnO₄ free from SnO₂. Again Xiao et al. [8] proposed an alternative synthesis method starting from a slurry of SnCl₄·5H₂O (1.7 g) and PVP (0.1 g; molar mass ≈ 30,000) in v/v = 1:1 water–ethanol. Aqueous NaOH (500 g/L; 10 mL) is added to the slurry that in turn is poured into a solution of Mg(NO₃)₂ (10 g/L; 30 mL) under a vigorous stirring. A solution is obtained that is placed into an autoclave and heated 24 h at 180 °C: the product is MgSn(OH)₆ that, after being filtered and repeatedly washed, is calcined at 850 °C for 5 h in a nitrogen atmosphere. The reaction that takes place in two steps is:



In this study, the synthesis of Mg₂SnO₄ has been attempted starting from stoichiometric mixtures of 4MgCO₃·Mg(OH)₂·xH₂O and SnC₂O₄ by using a combination of mechanical energy (conveyed to the system by high-energy milling) and of thermal energy to get the desired product. The reaction has been studied by simultaneous thermogravimetry/differential scanning calorimetry (TG/DSC) measurements and its progress has also been monitored by recording X-ray powder diffraction (XRPD) patterns of samples of the milled mixture calcined for 8 h at temperatures as high as 1,000 °C. The same study has been performed on samples of physical mixture calcined for times up to 175 h at temperatures as high as 1,350 °C. The samples of Mg₂SnO₄ obtained by calcining the mechanically activated mixture at 850, 900, 950, and 1000 °C have been characterized by diffuse reflectance Fourier transform infrared spectroscopy (DR/FT-IR), by modulated temperature differential scanning calorimetry (MTDSC) and by specific surface area measurements.

Experimental section

The starting chemicals [SnC₂O₄ (purity 98+ %) and 4MgCO₃·Mg(OH)₂·xH₂O (purity 99+ %)] were purchased from Aldrich Chimica (Italy). Physical mixtures of molar ratio Mg/Sn = 2.0 were prepared by weighing the appropriate amounts of precursors and by magnetically stirring the powders for 6 h. Then the solvent was let to evaporate in 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 550 rpm (rotation speed) for 5 h.

Simultaneous TG/DSC measurements were performed on pure samples and on mixture samples (both physical and mechanically activated) with a TG-DSC Q600 simultaneous TG/DSC analyser (TA Instruments Inc. USA). Samples of ≈ 50 mg of the mixtures were placed into alumina cups and heated (10 K/min, air flow 100 mL/min) from 25 °C up to 800 °C. Residuals recovered after the simultaneous TG/DSC runs performed both on physical and milled mixture samples have been examined by XRPD.

Samples of physical mixture have been put into alumina boats and heated, in air, at 10 K/min up to temperatures of 800, 900, 950, 1000, 1050, 1100, 1150, 1250, 1300, and 1350 °C for times from 8 to 175 h. Samples of milled mixture have also been put into alumina boats and heated, in air, at 10 K/min up to temperatures of 750, 800, 850, 900, 950, and 1000 °C for 8 h. All these samples have been examined, after the thermal treatment, by XRPD. The relevant patterns were recorded in step scan mode (Position sensitive detector: step 0.015°, 2 s/step, 40 kV, 40 mA, 2θ = 15–65, radiation Cu Kα) with an X-ray powder diffractometer (Bruker D5005).

The molar heat capacity of the Mg₂SnO₄ 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, in a quasi-isothermal mode i.e., the sample has been 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. The instrument, before the measurements, was calibrated under the same experimental conditions with a sapphire disk according to the manufacturer's instructions: a calibration constant of 1.0943 ± 0.0075 has been obtained.

Diffuse reflectance FT-IR spectra of Mg₂SnO₄ samples have been recorded with a FT-IR spectrometer (iS10 by Nicolet USA). The spectra have been collected on samples dispersed in KBr (5% mass): 512 scans have been co-added at 4 cm⁻¹ resolution and ratioed against 1,024 scans collected on samples of pure KBr (99+ %, Sigma Aldrich, Italy).

The specific surface area of Mg₂SnO₄ was determined by N₂ adsorption (BET method). The nitrogen adsorption curve was recorded by a Sorptomatic 1990 (Thermo Electron Corporation) operating with the static volumetric principle. The correction for the volume of the sample was introduced by measuring the He adsorption.

SEM microphotographs were collected on gold-sputtered samples with a Zeiss (EVO MA 10) scanning electron microscope.

Results and discussion

Combined thermal/XRPD evidence

Simultaneous TG/DSC measurements have been performed on samples of tin(II) oxalate and basic Mg carbonate hydrate [4MgCO₃·Mg(OH)₂·xH₂O] heated up to 800 °C.

The decomposition of SnC₂O₄ (Fig. 1) occurs in a single step with a mass loss of $-26.78 \pm 0.21\%$ (mean of four independent measurements; expected mass loss -27.10%). The accompanying exothermic peak has an enthalpy of -383 ± 7 kJ (mol oxalate)⁻¹.

The mass loss process of basic Mg carbonate hydrate [4MgCO₃·Mg(OH)₂·xH₂O] takes places in four stages (Fig. 2) although, the first, below 100 °C, is barely detectable. However, the first two of them are reasonably due to the dehydration process. The dehydration enthalpy of 43.7 ± 2.1 kJ(mol H₂O)⁻¹ is obtained as the mean of five independent measurements. The following two stages (decomposition of Mg carbonate and Mg hydroxide) are only partially separated. The mean mass value attained at the end of the measurement is $42.42 \pm 0.41\%$ (mean of five independent measurements). On the basis of this final mass value, the extent of hydration of basic Mg carbonate has been established as $x = 4.5$. To verify this result a sample of Mg basic carbonate has been annealed for 12 h at 250 °C that represents the temperature where the dehydration attains its maximum in the dynamic run. At the end of the isothermal period the mass is 83.12% (expected, for $x = 4.5$, 83.10%). The combined mass loss of stages 3 and 4 is accompanied by a double endothermic peak with a total enthalpy of $+277 \pm 10$ kJ (mol Mg basic carbonate)⁻¹.

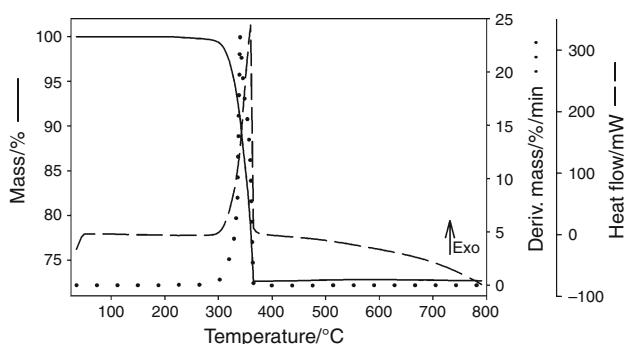


Fig. 1 TG (full line), DSC (long dashed line), and DTG (dotted line) of a sample of SnC₂O₄ (heating rate 10 K/min, air flow)

Figure 3 shows the TG/DSC curves obtained on a sample of physical mixture. It can be seen that four stages are present in the TG curve while the separation between these stages is less evident as regards the DSC curve. The combination of the mass loss and of the peak enthalpy of the first stage yields a mean dehydration enthalpy of 42.7 ± 2.6 kJ(mol H₂O)⁻¹ that is in good agreement with the dehydration enthalpy of pure Mg basic carbonate. Stage 2 shows an exothermic peak with an associated enthalpy of -918.1 ± 38.9 J g⁻¹ corresponding to -365 ± 15 kJ (mol Sn oxalate)⁻¹ that is in good agreement with the exothermic enthalpy obtained with pure tin(II) oxalate [-383 ± 7 kJ(mol Sn oxalate)⁻¹]. Indeed the mass value attained at the end of the exothermic peak ($77.61 \pm 0.59\%$) is in good agreement with the mass value expected if both the dehydration process and the decomposition of Sn oxalate to Sn(IV) oxide would have been occurred (77.74%). Stages 3 and 4 show a mass loss process that attains a constant mass value ($58.42 \pm 0.38\%$; 800 °C) in good agreement with the mass value expected for the formation of a mixture 2MgO–SnO₂ (58.20%). The associated endothermic peak has an enthalpy of $+179.5 \pm 6.0$ J (g mixture)⁻¹ that referred to Mg precursor results

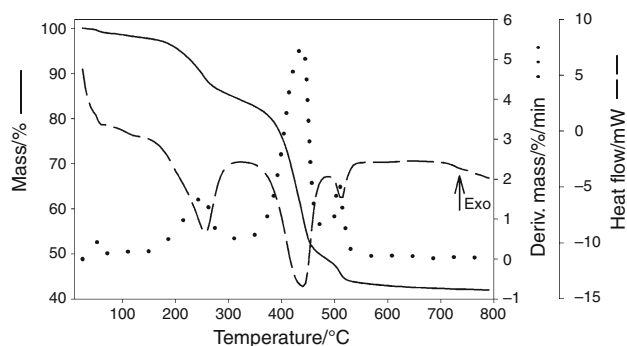


Fig. 2 TG (full line), DSC (long dashed line), and DTG (dotted line) of a sample of 4MgCO₃·Mg(OH)₂·xH₂O (heating rate 10 K/min, air flow)

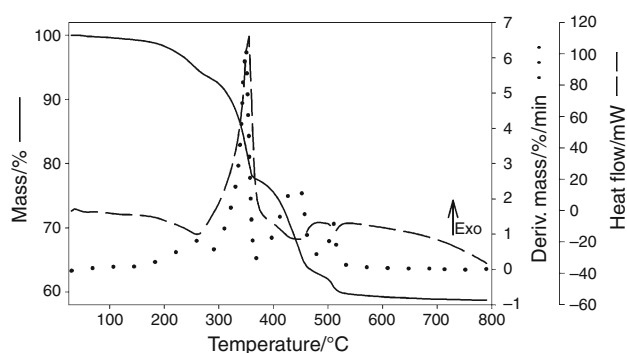


Fig. 3 TG (full line), DSC (long dashed line), and DTG (dotted line) of a sample of physical mixture (2/5) 4MgCO₃·Mg(OH)₂·xH₂O–SnC₂O₄ (heating rate 10 K/min, air flow)

+178 ± 6 kJ(mol Mg basic carbonate)⁻¹. Such a value is well lower than the mean enthalpy value [+277 ± 10 kJ(mol Mg basic carbonate)⁻¹] obtained with pure Mg precursor. The difference between the enthalpy of this peak in the case of pure Mg basic carbonate and of the physical mixture is ≈ -100 kJ and this suggests that something, beyond Mg hydroxide and carbonate decomposition, seems to be going on during stages 3 and 4 of the thermal run on the physical mixture. On the other hand, Fig. 4 shows that the main XRPD peaks observed on the residual of the physical mixture recovered at the end of the simultaneous TG/DSC run are those characteristic of MgO and SnO₂ although two minor peaks (≈ 24° and ≈ 30°) can be seen in the pattern that are probably due to MgSnO₃ (≈ 24°) and SnO (≈ 30°). At this point, the difference observed between the enthalpy of the DSC peak associated with stage (3 + 4) for pure Mg basic carbonate and for the physical mixture could be due to the formation of minor amounts of MgSnO₃ or could simply be an artifact due to the poor separation of stages 2 and (3 + 4) in the DSC curve.

The TG/DSC curve of the milled mixture (Fig. 5) shows that the separation between the stages has become sensibly worse than that obtained with physical mixture as concerns both DSC and TG signal. Indeed the dehydration peak is not distinguishable in the DSC trace so that the dehydration enthalpy cannot be calculated. The well evident exothermic peak of stage 2 shows an enthalpy of -573.3 ± 58.4 J g⁻¹ that corresponds to -228 ± 23 kJ that, if referred to Sn precursor, is lower than the exothermic enthalpy obtained with pure Sn oxalate (-383 ± 7 kJ) and with physical mixture (-365 ± 15 kJ). Indeed the mass value attained at the end of the exothermic peak (70.31 ± 0.48%) is well lower than the mass value expected for the formation of a mixture 4MgCO₃·Mg(OH)₂-SnO₂ (77.74%) and this indicates that the process under the exothermic peak involves the SnC₂O₄ → SnO₂ decomposition (exothermic) but also

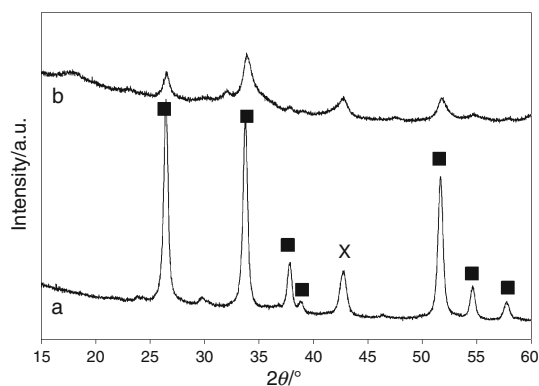


Fig. 4 XRPD patterns of the residuals recovered after heating (air) at 10 K/min up to 850 °C (Q 600) Pattern a: physical mixture; pattern b: milled mixture (filled square SnO₂-JCPDS 01-077-0452; times symbol MgO-JCPDS 01-077-2364)

part of decomposition of MgCO₃/Mg(OH)₂ (endothermic). Stage 3 consists only of a small endothermic peak with a very scattered enthalpy value +61.1 ± 23.5 J(g mixture)⁻¹ corresponding to +24 ± 9 kJ that is well lower than the mean enthalpy value [+178 ± 6 kJ(mol Mg basic carbonate)⁻¹] obtained in stage (3 + 4) of the curve of physical mixture. If we add the heat absorbed under stage 3 (≈ +24 kJ) to the extra-heat absorbed under stage 2 (-228 kJ = -383 kJ + x kJ i.e., x ≈ +155 kJ) we obtain an amount of heat (≈ +180 kJ) that referred to the decomposition of the Mg precursor [≈ +390 kJ(mol Mg basic carbonate)⁻¹] is well higher than the mean enthalpy value [276 ± 10 kJ(mol Mg basic carbonate)⁻¹] obtained with pure Mg precursor. Such an excess of heat absorbed could be due to the reaction between the formed oxides (MgO and SnO₂) to give Mg₂SnO₄. In an attempt to further investigate this point, XRPD patterns have been recorded on samples of the residual of the mechanically activated mixture recovered at the end of the simultaneous TG/DSC (Fig. 4). The patterns show rather broad peaks. However, some of them could be tentatively ascribed to Mg₂SnO₄ such as the broad peak at 2θ ≈ 17°. Furthermore, a very broad peak is present at 2θ ≈ 32 ÷ 38°: in this angular range the 100% peak of Mg₂SnO₄ is present along with another minor peak characteristic of the same compound. However, in this region the second most intense peak of SnO₂ is also expected. Another diffuse peak is present in the angular range 2θ ≈ 41 ÷ 44° where two peaks characteristic of Mg₂SnO₄ are present (a major at 2θ ≈ 42° and a minor at 2θ ≈ 46°). However, in this region the 100% peak of MgO is also expected. The peak at 2θ ≈ 52° is reasonably that characteristic of SnO₂. Again a small intensity, broad peak at 2θ ≈ 55° can be due either to SnO₂ or to Mg₂SnO₄.

The XRPD evidence of the residual recovered at the end of the TG/DSC runs performed on the milled mixture is clearly different from that coming from the residual of the physical mixture. However, no evidence of complete

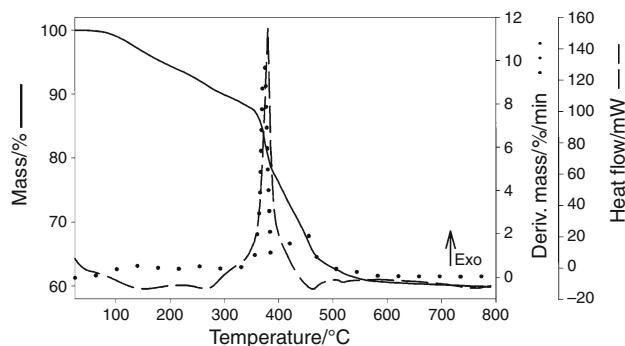


Fig. 5 TG (full line), DSC (long dashed line), and DTG (dotted line) of a sample of mechanically activated mixture (2/5) 4MgCO₃·Mg(OH)₂·xH₂O-SnC₂O₄ (heating rate 10 K/min, air flow)

conversion of MgO and SnO₂ to Mg₂SnO₄ is obtained at the end of the TG/DSC run performed on both types of mixture.

Study of the solid state reaction

Figure 6a shows the XRPD patterns of samples of physical mixtures annealed in air 8 h at temperatures between 700 and 1,000 °C. It can be seen that all the samples show the peaks characteristic of SnO₂ and MgO (patterns a–f). However, it has to be noted that Mg₂SnO₄ partially forms. Indeed it can be observed that the peak at $2\theta \approx 34^\circ$ is more intense than the peak at $2\theta \approx 26.7^\circ$ that is the 100% peak of SnO₂ for the samples thermally treated at the highest temperatures. This stems from the fact that at the highest temperatures some Mg₂SnO₄ forms that has its 100% peak at $2\theta \approx 34^\circ$. Moreover, the peaks at $2\theta \approx 23^\circ$ (MgSnO₃) and $2\theta \approx 30^\circ$ (SnO) are also present. Figure 6b shows the XRPD patterns of samples of physical mixtures annealed in air for 8 h at temperatures between 1,050 and 1,350 °C. The XRPD patterns of the sample mixture heated at 1,050 °C (patterns a)

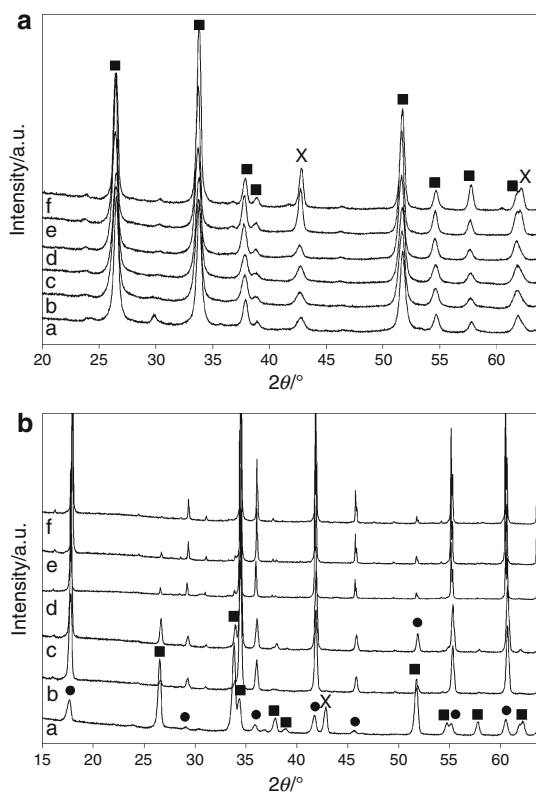


Fig. 6 **a** XRPD patterns of samples of physical mixtures annealed for 8 h at 700 °C (a), 800 °C (b), 850 °C (c), 900 °C (d), 950 °C (e), and 1000 °C (f) (filled square SnO₂-JCPDS 01-077-0452; times symbol MgO-JCPDS 01-077-2364). **b** XRPD patterns of samples of physical mixtures annealed for 8 h at a 1050 °C, b 1100 °C, c 1150 °C, d 1250 °C, e 1300 °C, and f 1350 °C (filled square SnO₂-JCPDS 01-077-0452; times symbol MgO-JCPDS 01-077-2364; filled circle Mg₂SnO₄-JCPDS 01-074-2152)

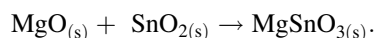
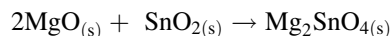
show both the peaks characteristic of the component oxides and those of Mg₂SnO₄. Samples annealed at temperatures of 1100 (b), 1150 (c), 1250 (d), and 1300 °C (f) show the peaks characteristic of Mg₂SnO₄ and, besides, also those of the component oxides mainly SnO₂ (see the peaks at $2\theta \approx 26.7$ and 38°). Furthermore a peak at $2\theta \approx 31^\circ$ is present whose origin is presently not known. Therefore, thermal treatments of physical mixtures at temperatures as high 1,350 °C proved not to be able to form XRPD phase pure Mg₂SnO₄ starting from physical mixture.

The samples of the mechanically activated mixture have been annealed for 8 h at temperatures between 750 and 1,000 °C. Figure 7 shows the XRPD patterns of these samples.

The following observations apply:

- The XRPD patterns of samples obtained by thermal treatments at 750 and 800 °C show broad peaks characteristic of Mg₂SnO₄ but the 100% peak of SnO₂ is also present along with other broad peaks (at $2\theta \approx 23.5, 32.5, 48^\circ$) characteristic of MgSnO₃. This demonstrates that the reaction is not yet over by thermal treatments at temperatures up to 800 °C;
- by performing an 8 h annealing at 850 °C, the most intense reflexion of SnO₂ disappears while the peaks of MgSnO₃, although rather weak, are still present. Annealing of 8 h at 900, 950, and 1000 °C results in the presence of the diffraction peaks characteristic of Mg₂SnO₄ only.

At temperatures up to 800 °C two reactions occur between the forming oxides:



Above 800 °C, MgSnO₃ decomposes according to the reaction:

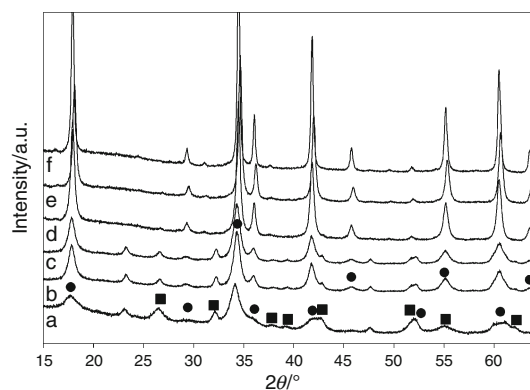
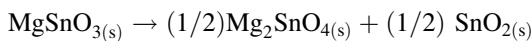


Fig. 7 XRPD patterns of samples of activated mixtures annealed for 8 h at: a 750 °C, b 800 °C, c 850 °C, d 900 °C, e 950 °C, and f 1000 °C (filled square SnO₂-JCPDS 01-077-0452; filled circle Mg₂SnO₄-JCPDS 01-074-2152)



And the excess SnO_2 reacts with remaining MgO to give $\text{Mg}_2\text{SnO}_4(s)$.

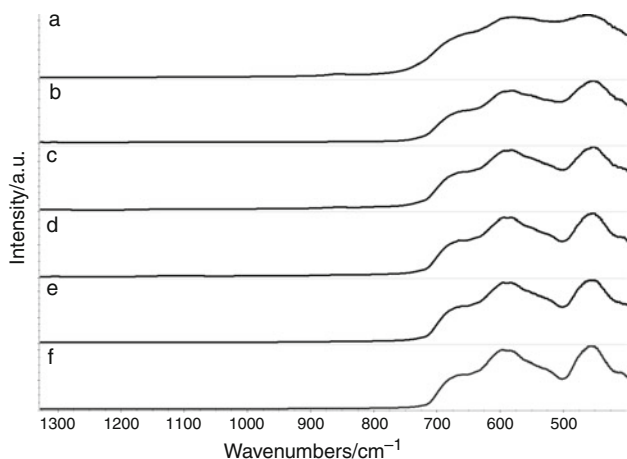
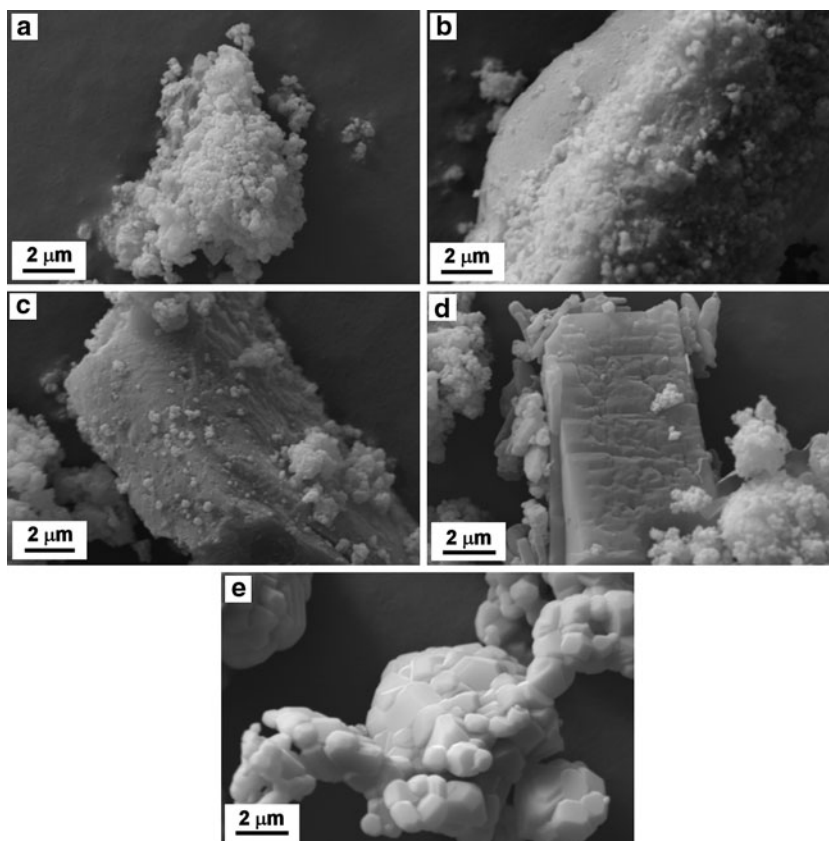


Fig. 8 Diffuse reflectance FT-IR spectra of samples of activated mixtures annealed for 8 h at, 750 °C (a), 800 °C (b), 850 °C (c), 900 °C (d), 950 °C (e), and 1000 °C (f). The ordinate is in arbitrary units

Fig. 9 SEM micrographs of samples of mechanically activated mixture annealed 8 h at 850 °C (a), 900 °C (b), 950 °C (c), 1000 °C (d) and of physical mixture annealed 8 h at 1350 °C (e)



Characterization of Mg_2SnO_4

Figure 8 shows the diffuse reflectance FT-IR spectra of the Mg_2SnO_4 samples obtained from 8 h annealing of the activated mixture at different temperatures. The main feature of the spectra is the double peak due to the symmetrical and antisymmetrical stretching of the Sn–O bonds with maxima, respectively, at $\nu_2 = 587 \pm 6$ and $456 \pm 1 \text{ cm}^{-1}$. It is to note that the separation between the two peaks is sensibly diminished in the case of the spectra obtained by annealing the mixture at 750 °C (a) and at 800 °C (b).

The molar heat capacity of the samples obtained from annealing the milled mixtures has been determined by MTDSC. It has been assessed that the data of the samples prepared by annealing the activated mixture at temperatures between 850 and 1,000 °C are in good agreement between them. The relevant data have been fitted as a function of temperature by the second order polynomial listed in the following:

$$850 \text{ °C}: C_p = 112.7 + 0.2758T - 0.0004T^2$$

$$900 \text{ °C}: C_p = 113.6 + 0.2507T - 0.0004T^2$$

$$950 \text{ °C}: C_p = 113.9 + 0.2924T - 0.0004T^2$$

$$1000 \text{ °C}: C_p = 118.64 + 0.2804T - 0.0004T^2$$

It can be concluded that the heat capacity data of Mg_2SnO_4 samples prepared by annealing the milled

mixture at temperatures between 850 and 1,000 °C can be represented, as a function of temperature, by the relationship:

$$C_p = (114.7 \pm 2.3) + (0.2748 \pm 0.0152)T - 0.0004T^2$$

The microstructure of the samples has been monitored by microscopic observation (Fig. 9) and these very same samples specific surface area of the samples has been determined. It can be seen that the microstructure of Mg₂SnO₄ prepared at 850 °C (a) is constituted by a very irregular surface that explains the high surface area (24.42 m² g⁻¹). The situation changes as concerns the sample prepared by annealing at 900 °C (b): here part of the surface appears to be more flat and regular and, accordingly, the specific surface area is diminished (18.72 m² g⁻¹). The sample surface becomes even more regular for the sample obtained at 950 °C (c) and the specific surface area continues to decrease (15.73 m² g⁻¹). Such a trend of the surface microstructure and specific area is also verified at 1,000 °C (d): a wider part of the surface has become flat and the surface area plunges to 9.68 m² g⁻¹. Figure 9e shows, for sake of comparison, the microstructure of the Mg₂SnO₄ prepared by annealing the physical mixture at 1,350 °C: the surface has now become totally flat and no small grains are visible on the surface. Accordingly, the surface area has become only 0.51 m² g⁻¹.

Conclusions

The reaction taking place between Sn(II) oxalate (SnC₂O₄) and basic Mg carbonate [4MgCO₃·Mg(OH)₂·4.5H₂O] has been studied by simultaneous TG–DSC measurements performed both on physically prepared mixture and on mixture mechanically activated. It has been shown that, in the case of the physical mixture, the reaction occurs in three steps: dehydration of the Mg basic carbonate, decomposition of SnC₂O₄ to SnO₂ and decomposition of the MgCO₃–Mg(OH)₂ mixture to MgO. The enthalpy of the first two processes is close to that obtained with both Mg precursor (dehydration) and Sn precursor (decomposition of tin precursor). On the contrary, the heat absorbed during the third process (decomposition of Mg precursor) is ≈ 100 kJ lower in the physical mixture. However, the XRPD patterns of the residual recovered after the TG/DSC run on the physical mixture mainly show the peaks of the decomposition products (MgO + SnO₂). The TG/DSC run of the activated mixture shows a completely different

situation: the evaluation of dehydration enthalpy is not possible while the decomposition of the tin precursor and the Mg precursor are partially superimposed as concerns both the TG and the DSC run. The XRD patterns of the residual recovered after the TG/DSC run shows weak, diffused, and broad peaks that can hardly be assigned to single phases but rather reveal the presence of a mixture of the constituent oxides (mainly SnO₂) and of the product (Mg₂SnO₄).

The solid state reaction has been studied by annealing samples of both type of mixture at different temperatures: it has been shown that Mg₂SnO₄ forms by annealing the activated mixture at temperatures between 850 and 1,000 °C while the same compound cannot be obtained as pure XRPD phase from physically prepared mixtures annealed at temperatures as high as 1,300–1,350 °C.

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