Solid-state Reaction Study on Physically and Tribochemically Prepared BaC_2O_4-SnC_2O_4 Mixtures

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The synthesis of barium metastannate, $BaSnO_3$, by heating mixtures of metal oxalates, either physically mixed or subjected to a phase of mechanical activation, up to temperatures in the range 750–1200 °C has been studied. Simultaneous thermogravimetric-differential scanning calorimetric (TG-DSC) analyses and powder X-ray diffractometry have been applied to check the advancement of the reactions. $BaSnO_3$, though slightly contaminated by $BaCO_3$, can be obtained by heating the activated mixture up to $T \geq 1000$ °C while heating a sample of a physical mixture at temperature as high as 1200 °C resulted in a mixture of $BaSnO_3$, SnO_2 and Ba_2SnO_4. The heat capacities of $BaSnO_3$ samples prepared at temperatures between 1000 and 1200 °C have been measured by modulated temperature differential scanning calorimetry (MTDSC) in the temperature range 50–400 °C.

Key words: Barium Metastannate, Mechanical Activation, Heat Capacity Measurements, Powder X-Ray Diffraction, Simultaneous TG-DSC

Introduction

Barium stannate, $BaSnO_3$, is a member of the double oxides of the general formula ABO_3 that are formed by reaction between the oxides of alkaline-earth metals (A = Ca, Sr, Ba) and those of some of the group IV elements. Such double oxides are of great industrial and technological importance. Barium stannate belongs to the family of alkaline-earth metastannates ($ASnO_3$, with A = Ca, Sr, Ba but not Mg). It is an n-type semiconductor with a band gap of 3.1 eV as desired for materials to be employed as gas sensors [1]. Borse *et al.* [2] were able to show that $BaSnO_3$-based systems could be promising candidates for photocatalytic applications. Mizoguchi *et al.* [3] reported that $BaSnO_3$ exhibits strong near-infrared luminescence at room temperature. Suggestions have also been made that, by combining $BaTiO_3$ with $BaSnO_3$ (BTS), multifunctional ceramic sensors which can measure temperature, relative humidity and gases such as propylene, acetylene and ethylene at ambient temperatures and pressures can be realized [4].

$BaSnO_3$ is usually prepared by the conventional solid-state synthesis (ceramic route) [5] starting from stoichiometric $BaCO_3$-SnO_2 mixtures ball-milled for 6 h under wet condition (acetone). After having been dried in an oven overnight, the powder samples are calcined in a Pt crucible for 8 h in air at 1250 °C.

The compound has also been prepared by alternative routes: G. Pfaff [6] prepared a peroxidic precursor by mixing the two metal chlorides with ammonia and hydrogen peroxide and treating the precursor thermally at 1200 °C. Song and Kim [7] proposed a coprecipitation process: they added excess oxalic acid to an equimolar solution of the two metal chlorides so forming a precipitate of mixed Ba-Sn oxalate. After filtering, washing and drying, the precipitate was calcined at 1050 °C for 3 h. Cerda *et al.* [8] prepared the compound by adopting a modified version of the sol-gel technique. The mixed solutions of $Ba(OH)_2$ and $K_2SnO_3 \cdot 3H_2O$ were stirred vigorously, and after evaporation a xerogel of composition $BaSnO_3 \cdot 2H_2O$ was obtained and finally calcined for 8 h at high temperature (1200–1400 °C). The hydrothermal synthesis of $BaSnO_3$ was accomplished [9] by adding ammonia to $SnCl_4$ hydrate to obtain the gel $SnO_2 \cdot xH_2O$ which was suspended in aqueous $Ba(OH)_2$ until a metal ratio $Ba/Sn = 1.0$ was attained. This suspension was placed in a sealed reaction vessel under different pressures (0.1 – 100 MPa) and temperatures (423 – 773 K) for 120 s: the intermediate phase $BaSn(OH)_6$ was formed that easily decomposed to $BaSnO_3$. An organic precursor has also been proposed [10], and a combustion method was reported [11] based on a SHS (Self Heat Sustained) reaction starting from pure metallic Sn and anhydrous $Ba(NO_3)_2$ in a stoichiometric ratio. After tin premelting at 250 °C (4 h), the temperature was raised to 800 °C (4 h) so that the reaction between liquid tin and Ba nitrate occurred. Finally the temperature was raised again to 1100 °C (12 h) to obtain a mixture of $BaSnO_3$ and Ba_2SnO_4. A further calcination step (24 h at 1200 °C) was needed to obtain pure $BaSnO_3$.

In the present work the synthesis of $BaSnO_3$ has been attempted by using a combination of mechanical (by high-energy milling) and thermal activation to obtain the desired product. The reaction has been studied by TG/DSC measurements and its progress was monitored by powder XRD patterns taken on samples of the mechanically activated mixture heated to temperatures between 750 and 1200 °C. The samples of $BaSnO_3$ obtained by heating the mechanically activated mixture at temperatures between 1000 and 1200 °C have been characterized by FT-IR spectroscopy, and the relevant molar heat capacity has been determined by modulated temperature differential scanning calorimetry (MTDSC).

Results and Discussion

TG-DSC results

Coupled TG-DSC runs were performed (10 °C min^{-1}, maximum temperature 1200 °C, air flow) on equimolar mixtures BaC_2O_4-SnC_2O_4. Figures 1 and 2 show runs with samples of physical (Fig. 1) and mechanically activated mixtures (Fig. 2). The examples are representative of all the thermal runs performed. The reported mass values have been obtained as the mean of six independent measurements.

In the case of samples of a physical mixture, a constant mass value is attained at ≈ 1100 °C (69.3 ± 0.2 % *vs.* an expected value of 70.4 %.). This means that volatile impurities are contained in the mixture that account for an extra mass loss of $-1.5 \pm 0.3\%$. The first stage of mass loss (Stage I) ends at ≈ 415 °C ($M = 83.3 \pm 0.2\%$). From this value it results that, besides the release of the volatile impurities, the decomposition of Sn(II) oxalate to SnO_2 and a part of that of Ba oxalate to $BaCO_3$ (0.38 ± 0.05 moles) also occurs. The second stage of mass loss (Stage II) ends within ≈ 600 °C, and it corresponds to the remaining part of $BaC_2O_4 \rightarrow BaCO_3$ decomposition: the mean final mass value is 78.9 ± 0.1 %, the expected value being 79.3 %.

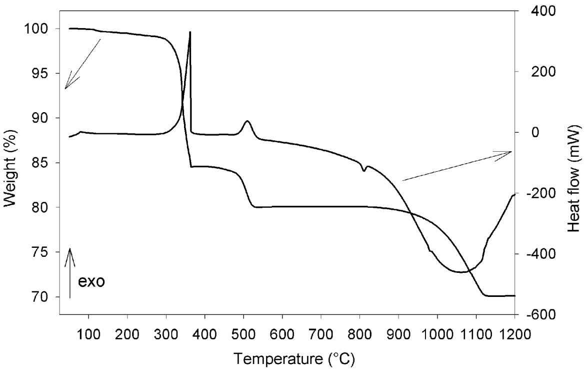

Fig. 1. TG/DSC curve of a physical mixture heated in air at 10 °C min^{-1} up to 1200 °C.

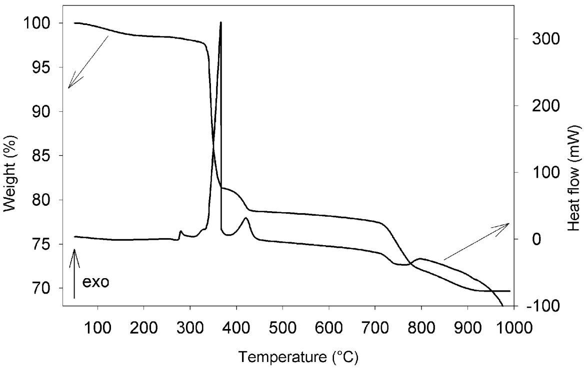

Fig. 2. TG/DSC curve of a mechanically activated mixture heated in air at 10 °C min^{-1} up to 1000 °C.

The exothermic enthalpy associated with stages I+II is quite reproducible (-460 ± 8 kJ) and can be expressed as -230 ± 4 kJ mol^{-1} of decomposed oxalate. The following step Stage III) of mass loss starts at ≈ 900 °C and refers to the $BaCO_3 \rightarrow BaO$ decomposition. At ≈ 800 °C a DSC endothermic peak is present that corresponds to the $BaCO_3$ transition from the tetragonal to the cubic phase with an associated enthalpy of 23.9 ± 0.8 kJ mol^{-1} $BaCO_3$ (in pure $BaCO_3$ $\Delta H = +22.6$ kJ mol^{-1} $BaCO_3$). Then the decomposition of $BaCO_3$ begins at ≈ 800 °C and continues to occurr very slowly with no detectable DSC peak up to ≈ 1150 °C.

In the case of the milled mixture the constant mass value is attained at ≈ 950 °C (68.8 ± 0.7% *vs.* an expected value of 70.4%). This means that some volatile impurities were absorbed in the mixture, presumedly during milling, that account for an extra mass loss of -2.2 ± 0.9%. It can be observed that, in the milled mixture, the reaction takes place in two main steps although the first of them can be subdivided into two sub-stages (Ia and Ib). Stage Ia takes place between 300 and 380 °C and is constituted of a mass loss down to a mass value of 80.4 ± 0.7%, and the accompanying exothermic peak has an enthalpy of -379 ± 10 kJ. Stage Ib is over (at ≈ 450 °C) at a mean mass value of 77.7 ± 0.8%, and the accompanying exothermic peak has an enthalpy of -87 ± 11 kJ. The expected mass value for the formation of a mixture SnO_2-$BaCO_3$ is 78.8%. By allowing for the relatively high standard deviation of the thermogravimetric datum (77.7 ± 0.8%), it can be concluded that the mixture SnO_2-$BaCO_3$ is formed at ≈ 450 °C when starting from the milled mixture, while the same happens at ≈ 600 °C when starting from the physical mixture. Therefore the SnO_2-$BaCO_3$ mixture formation is complete some 150 °C below the case with the physical mixture.

No influence of the mechanical activation seems to exist for what concerns the DSC part of the measurements that leads to the formation of the SnO_2-$BaCO_3$ mixture: the total exothermic enthalpy associated with the peaks of stages I+II of the physical mixture is -460 ± 8 kJ and can be expressed as -230 ± 4 kJ mol^{-1} of decomposed oxalate. In the case of the milled mixture the total exothermic enthalpy associated with the peaks of stages Ia+Ib is -466 ± 21 kJ and can be expressed as -233 ± 10 kJ mol^{-1} of decomposed oxalate.

Stage II of the curve for the milled mixture begins at ≈ 710 °C and ends at 950 °C: it is constituted of a mass loss of -5.4 ± 0.2% that corresponds to the decomposition of ≈ 54% by mole of $BaCO_3$ present in the mixture, and it is accompanied by an endothermic peak whose mean enthalpy is $+111 \pm 8$ J g^{-1} that corresponds to a value of $+90 \pm 5$ kJ mol^{-1} $BaCO_3$. The fact that the $BaCO_3$ decomposition begins some 100 °C below the case with the physical mixture points to the fact that such decomposition is modulated by the reaction with SnO_2 to give $BaSnO_3$. No endothermic peak marking the tetragonal-cubic phase transition of $BaCO_3$ is observed as it is the case with pure $BaCO_3$ and the physical mixture. It is worth to note that the share of $BaCO_3$ decomposed before the end of the endothermic peak (*i. e.* $T \approx 800$ °C) nearly corresponds to the moles of Ba carbonate that have been formed within ≈ 380 °C *i. e.* under stage Ia. The remaining part (≈ 35% by mole) of $BaCO_3$ undergoes decomposition in the range 800–950 °C with no relevant DSC peak.

Powder X-ray diffraction evidence

Samples of both physical and mechanically activated mixtures were heated in a tube furnace (static air, 10 K min^{-1}) to temperatures of 750, 800, 850, 900, 950, 1000, 1100, and 1200 °C. The samples were recovered and weighed in order to roughly check the progress of the reaction that had taken place during heating. Then powder X-ray diffraction patterns were taken to check which phases were formed during heating. Finally, TG runs of the samples were performed up to 1200 °C in order to detect the extent of $BaCO_3$ decomposition that possibly did not occurr within the performed thermal treatment.

Table 1 reports the mass values attained (M_{fin}, %) at the end of the heating ramp up to the temperatures (T) both in the case of physical (PM) and of activated mixtures (AM). The % mass value attained in the subsequent TG runs up to 1200 °C are also reported in Table 1 (M_{TG}).

Table 1. Mass values obtained at the end of heating ramps to temperatures (T) between 750 and 1200 °C (in step of 50 °C) for samples of physical mixtures (PM-M_{fin} %) and of activated mixtures (AM-M_{fin} %). M_{TG} (%) represents the mass value attained at the end of a TG run performed up to 1200 °C on samples (both PM and AM) previously subjected to the cited heating ramps.

T (°C)	AM-M_{fin} (%)	AM-M_{TG} (%)	PM-M_{fin} (%)	PM-M_{TG} (%)
750	76.2	94.4	79.9	87.7
800	71.5	94.6	80.3	86.2
850	71.2	94.9	76.4	90.3
900	70.1	96.0	74.0	92.3
950	69.3	96.0	76.3	90.6
1000	68.2	97.8	75.5	92.2
1100	68.8	99.1	70.5	98.1
1200	67.9	99.9	69.5	99.8

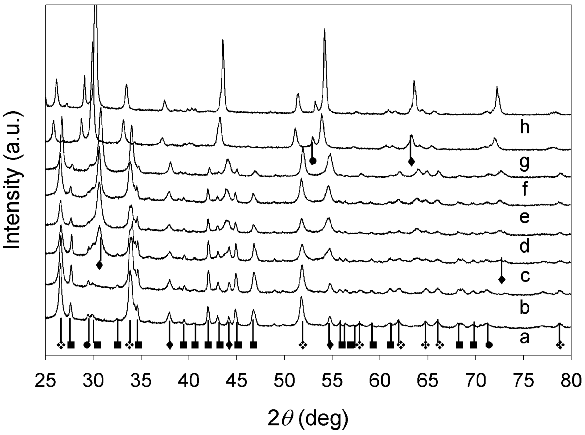

Fig. 3. Powder X-ray diffraction pattern of physical mixtures BaC_2O_4-SnC_2O_4 heated in air to (a) 750 °C, (b) 800 °C, (c) 850 °C, (d) 900 °C, (e) 950 °C, (f) 1000 °C, (g) 1100 °C, and (h) 1200 °C.

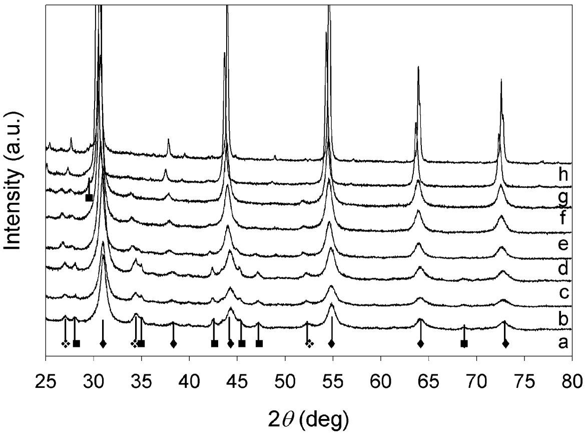

Fig. 4. Powder X-ray diffraction pattern of mechanically activated mixtures BaC_2O_4-SnC_2O_4 heated in air to (a) 750 °C, (b) 800 °C, (c) 850 °C, (d) 900 °C, (e) 950 °C, (f) 1000 °C, (g) 1100 °C, and (h) 1200 °C.

Fig. 3 shows the powder X-ray diffraction patterns recorded after heating of the samples of physical mixtures up to temperatures between 750 and 1200 °C (steps of 50 °C).

In the patterns of the physical mixtures heated to 800 °C only the peaks of cassiterite (SnO_2) and whiterite ($BaCO_3$) are present. The peaks of $BaSnO_3$ are showing up, besides those of SnO_2 and $BaCO_3$, only when heating is extended up to 850 – 900 °C. The evidence for $BaSnO_3$ increases when heating to 950 and 1000 °C, although SnO_2 and $BaCO_3$ peaks are still present. This is confirmed by the corresponding mass values which are in all cases higher than 75 %. The mass value attained becomes sensibly lower when heating is performed up to $T \geq 1100\,°C$ ($70 \pm 0.5\,\%$) coinciding with the value obtained in the TG/DSC runs ($69.3 \pm 0.2\,\%$). However, the diffraction patterns of these samples show, besides the peaks of $BaSnO_3$, also those of unreacted SnO_2 and Ba_2SnO_4. Thus, according to the powder X-ray diffraction evidence, heating a sample of a physical mixture to temperatures as high as 1200 °C does not result in complete formation of $BaSnO_3$ but rather in a mixture of $BaSnO_3$, SnO_2 and Ba_2SnO_4.

Fig. 4 shows the powder X-ray diffraction patterns recorded after heating of the samples of a mechanically activated mixture up to temperatures between 750 and 1200 °C (steps of 50 °C).

The sample heated at 750 °C has $M_{\text{fin}} = 76.2\,\%$, about 1 % lower than the value expected for the formation of an equimolar mixture SnO_2-$BaCO_3$ (77.3 %). The patterns indeed show quite broad peaks characteristic of SnO_2 and $BaCO_3$, and rather broad peaks are also obtained that mark the presence of $BaSnO_3$.

The samples treated at 800, 850 and 900 °C show quite similar values of final mass ($71.0 \pm 0.6\,\%$), in good agreement with the data ($71.3 \pm 0.8\,\%$ at $\approx 800\,°C$). The diffraction patterns show mainly peaks characteristic of $BaSnO_3$ (800 °C) although the peaks of $BaCO_3$ and SnO_2 are also present and have become sharper for the sample heated at 850 °C, thus showing a better crystallinity. On the contrary, their intensity is sensibly decreased in the patterns of the sample heated at 900 °C where the peaks characteristic of $BaSnO_3$ are predominant.

The sample heated to 950 °C attains a final mass of 69.3 %, and the relevant diffraction pattern shows mainly the $BaSnO_3$ peaks with only minor additions of both $BaCO_3$ ($2\vartheta \approx 28$, 34, 42, and 45°) and SnO_2 ($2\vartheta \approx 26.5$, 33.8 and 53°). The samples heated to 1000, 1100 and 1200 °C attain a mean mass value of $68.3 \pm 0.4\,\%$ that is indistinguishable, within the respective standard deviations, from the mean of the total mass variations of the activated mixtures determined in the thermoanalytical experiments ($68.8 \pm 0.7\,\%$). Only the diffraction patterns of the sample heated at 1000 °C show low-intensity peaks characteristic of $BaCO_3$ and SnO_2, while the diffraction patterns of the samples heated at 1100 and 1200 °C show only the peaks characteristic of $BaSnO_3$.

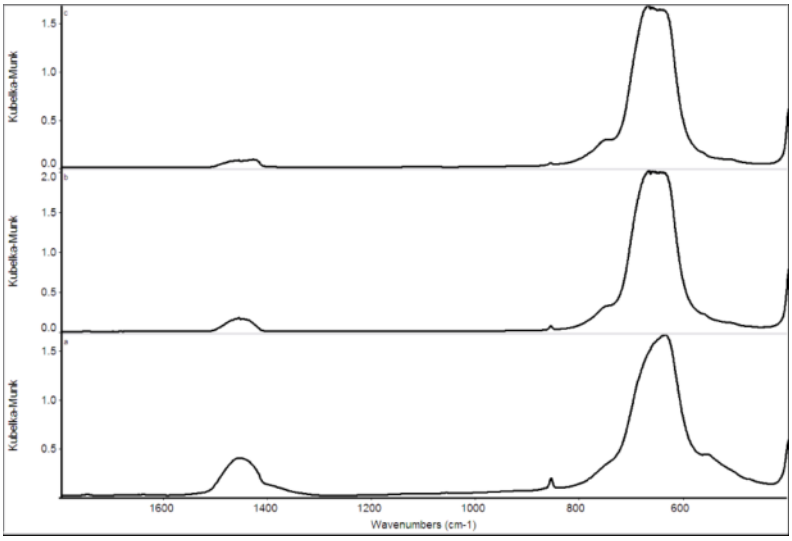

Fig. 5. Diffuse reflectance IR spectra of BaC_2O_4-SnC_2O_4 mixtures subjected to mechanical activation and heated to 1000 °C (a), 1100 °C (b) and (c) 1200 °C.

The molar heat capacity of the samples obtained by heating the milled mixtures up to $T \geq 1000\,^\circ\mathrm{C}$ has been determined by MTDSC. The relevant data have been fitted as a function of temperature by the second order polynomia:

1000 °C: $C_p = 124.98 + 0.0507\mathrm{t} - (1.1453 \times 10^4/\mathrm{t}^2)\,\mathrm{J\,K^{-1}\,mol^{-1}}$
1050 °C: $C_p = 130.41 + 0.0431\mathrm{t} - (1.1593 \times 10^4/\mathrm{t}^2)\,\mathrm{J\,K^{-1}\,mol^{-1}}$
1100 °C: $C_p = 118.20 + 0.0508\mathrm{t} - (9.5620 \times 10^3/\mathrm{t}^2)\,\mathrm{J\,K^{-1}\,mol^{-1}}$
1150 °C: $C_p = 122.00 + 0.0442\mathrm{t} - (1.0020 \times 10^4/\mathrm{t}^2)\,\mathrm{J\,K^{-1}\,mol^{-1}}$
1200 °C: $C_p = 110.28 + 0.0562\mathrm{t} - (9.052 \times 10^3/\mathrm{t}^2)\,\mathrm{J\,K^{-1}\,mol^{-1}}$

The coefficients of the polynomia are quite similar and the "mean polynomium" is: $C_p = (121.17 \pm 6.75) + (0.0490 \pm 0.005)\mathrm{t} - [(1.0336 \pm 0.1017) \times 10^4/\mathrm{t}^2]\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

However, it has to be considered that traces of $BaCO_3$ are still present in samples heated to 1200 °C. To try and asses the importance of the presence of $BaCO_3$ in the samples of $BaSnO_3$, these very same samples have been subjected again to TG runs (maximum temperature 1000 °C; 10 °C min^{-1}) that revealed a moderate mass loss due to the presence of $BaCO_3$ impurities formed by contact with air: samples heated at 1100 °C contain $4.7 \pm 0.5\,\%$ by mass of $BaCO_3$ while the mass-% of $BaCO_3$ in the samples heated at 1150 and 1200 °C is, respectively, 2.8 and 1.2 %. Such a presence of $BaCO_3$ impurities has been confirmed by recording the IR spectra of these same samples (Fig. 5). The absorption bands at 856 and 1450 cm^{-1} are characteristic of CO_3^{2-}.

Conclusions

The influence of mechanical activation of the mixtures BaC_2O_4-SnC_2O_4 can be summarized as follows:

1. The total mass loss process is over at ≈ 1150 °C in the physical mixture while the same is true already at ≈ 950 °C in the case of the milled mixture.
2. The first stage of the thermal curves ends at ≈ 450 °C in the milled mixture and at ≈ 600 °C in the physical mixture. The final mass corresponds in both cases to the value expected for the formation of a mixture constituted of $BaCO_3$-SnO_2. Correspondingly, the enthalpy of the exothermic peak underlying the mass loss processes is nearly the same in both cases: $\approx -230\,\mathrm{kJ\,mol^{-1}}$ for decomposed oxalates.
3. The fact that enthalpy is released during the decomposition of both oxalates is explained by hypothesizing that the oxidation of the released CO to CO_2 (secondary exothermic process; $-283\,\mathrm{kJ\,mol^{-1}}$) more than offsets the enthalpy absorption from the lattice demolition of both Sn(II) and Ba oxalates.
4. The second stage of the thermal curves corresponds to the decomposition of $BaCO_3$. The difference between the physical and the milled mixture is seen

in the fact that the endothermic peak due to the tetragonal → cubic transition of $BaCO_3$ is present in the DSC curve of the physical mixture at $\approx$ 800 °C, while $BaCO_3$ decomposition is initiated in the milled mixture some 100 °C below the transition point whose peak hence cannot be observed.

5. $BaSnO_3$, though with variable content of $BaCO_3$ coming from the interaction with air, can be prepared by heating the milled mixture at $T \geq 1000$ °C. The product obtained by heating the physical mixture under the same experimental conditions is a mixture of $BaSnO_3$, Ba_2SnO_4 and SnO_2.
6. The molar heat capacity of the samples obtained by heating the milled mixture to $T \geq 1000$ °C has been determined by MTDSC as a function of temperature in the 50 – 380 °C range.

Experimental Section

The starting chemicals SnC_2O_4 (purity 98+ %) and BaC_2O_4 (purity 99+ %) were purchased from Aldrich Chimica (Italy). Physical mixtures of molar ratio Ba/Sn = 1.0 were prepared by weighing the appropriate amounts of precursors and by suspending the powders in acetone under magnetic stirring for 6 h; the solvent was let to evaporate 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 four 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 h.

Simultaneous TG/DSC measurements were performed on pure samples and on mixtures with a TG-DSC Q600 (TA Instruments Inc. USA). Samples of $\approx$ 50 mg were placed into alumina cups and heated (10 °C min^{-1}, air flow 100 mL min^{-1}) from 25 °C to 1000 °C.

Samples of the mechanically activated mixture were heated in a tube furnace (static air, 10 °C min^{-1}) to temperatures of 750, 800, 850, 900, 950, 1000, 1100, and 1200 °C and the samples recovered and weighed in order to roughly check the progress of the reaction. Then powder X-ray diffraction patterns were taken. The relevant patterns were recorded in step scan mode (position-sensitive detector: step 0.015°, 2 s per step , 40 kV, 40 mA, $2\vartheta = 25 - 80°$, radiation Cu K_α radiation) with a powder X-ray diffractometer (Bruker D5005).

The molar heat capacity of the $BaSnO_3$ samples was determined by Modulated Temperature Differential Scanning Calorimetry (MTDSC, Q2000 DSC, T_{zero} technology, TA Instruments Inc. USA). The samples ($\approx$ 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, the sample being heated from 50 to 380 °C in steps of 10 °C 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. 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 1.0943 ± 0.0075 was obtained.

Diffuse reflectance FT-IR spectra of $BaSnO_3$ samples were recorded with a FT-IR spectrometer (iS10 by Nicolet, USA) on samples dispersed in KBr (5 mass %); 512 scans were used at 4 cm^{-1} resolution and ratioed against 1024 scans collected on samples of pure KBr (99+ %, Sigma Aldrich, Italy).

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