

# Solid-state Reaction Study on Physically and Tribochemically Prepared $\text{BaC}_2\text{O}_4$ - $\text{SnC}_2\text{O}_4$ Mixtures

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The synthesis of barium metastannate,  $\text{BaSnO}_3$ , 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.  $\text{BaSnO}_3$ , though slightly contaminated by  $\text{BaCO}_3$ , 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  $\text{BaSnO}_3$ ,  $\text{SnO}_2$  and  $\text{Ba}_2\text{SnO}_4$ . The heat capacities of  $\text{BaSnO}_3$  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,  $\text{BaSnO}_3$ , is a member of the double oxides of the general formula  $\text{ABO}_3$  that are formed by reaction between the oxides of alkaline-earth metals ( $A = \text{Ca}, \text{Sr}, \text{Ba}$ ) 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 ( $\text{ASnO}_3$ , with  $A = \text{Ca}, \text{Sr}, \text{Ba}$  but not  $\text{Mg}$ ). 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  $\text{BaSnO}_3$ -based systems could be promising candidates for photocatalytic applications. Mizoguchi *et al.* [3] reported that  $\text{BaSnO}_3$  exhibits strong near-infrared luminescence at room temperature. Suggestions have also been made that, by combining  $\text{BaTiO}_3$  with  $\text{BaSnO}_3$  (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].

$\text{BaSnO}_3$  is usually prepared by the conventional solid-state synthesis (ceramic route) [5] starting from stoichiometric  $\text{BaCO}_3$ - $\text{SnO}_2$  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  $\text{Ba}(\text{OH})_2$  and  $\text{K}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$  were stirred vigorously, and after evaporation a xerogel of composition  $\text{BaSnO}_3 \cdot 2\text{H}_2\text{O}$  was obtained and finally calcined for 8 h at high temperature (1200–1400 °C). The hydrothermal synthesis of  $\text{BaSnO}_3$  was accomplished [9] by adding ammonia to  $\text{SnCl}_4$  hydrate to

obtain the gel  $\text{SnO}_2 \cdot x\text{H}_2\text{O}$  which was suspended in aqueous  $\text{Ba}(\text{OH})_2$  until a metal ratio  $\text{Ba}/\text{Sn} = 1.0$  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  $\text{BaSn}(\text{OH})_6$  was formed that easily decomposed to  $\text{BaSnO}_3$ . 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  $\text{Ba}(\text{NO}_3)_2$  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  $\text{BaSnO}_3$  and  $\text{Ba}_2\text{SnO}_4$ . A further calcination step (24 h at 1200 °C) was needed to obtain pure  $\text{BaSnO}_3$ .

In the present work the synthesis of  $\text{BaSnO}_3$  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  $\text{BaSnO}_3$  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 ( $10^\circ\text{C min}^{-1}$ , maximum temperature 1200 °C, air flow) on equimolar mixtures  $\text{BaC}_2\text{O}_4\text{-SnC}_2\text{O}_4$ . 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  $\approx 1100^\circ\text{C}$  ( $69.3 \pm 0.2\%$  vs. an expected value of 70.4%). This means that volatile impurities are contained in the mixture that

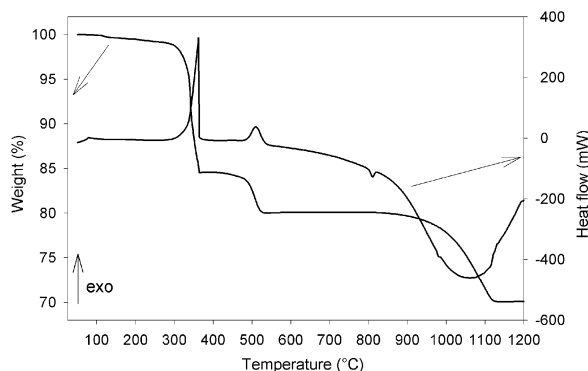


Fig. 1. TG/DSC curve of a physical mixture heated in air at  $10^\circ\text{C min}^{-1}$  up to 1200 °C.

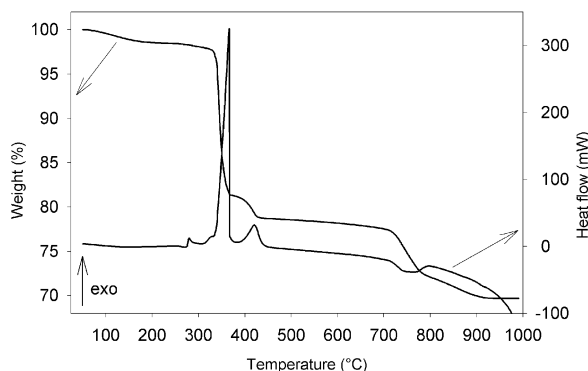


Fig. 2. TG/DSC curve of a mechanically activated mixture heated in air at  $10^\circ\text{C min}^{-1}$  up to 1000 °C.

account for an extra mass loss of  $-1.5 \pm 0.3\%$ . The first stage of mass loss (Stage I) ends at  $\approx 415^\circ\text{C}$  ( $M = 83.3 \pm 0.2\%$ ). From this value it results that, besides the release of the volatile impurities, the decomposition of  $\text{Sn}(\text{II})$  oxalate to  $\text{SnO}_2$  and a part of that of Ba oxalate to  $\text{BaCO}_3$  ( $0.38 \pm 0.05$  moles) also occurs. The second stage of mass loss (Stage II) ends within  $\approx 600^\circ\text{C}$ , and it corresponds to the remaining part of  $\text{BaC}_2\text{O}_4 \rightarrow \text{BaCO}_3$  decomposition: the mean final mass value is  $78.9 \pm 0.1\%$ , the expected value being 79.3%.

The exothermic enthalpy associated with stages I+II is quite reproducible ( $-460 \pm 8\text{ kJ}$ ) and can be expressed as  $-230 \pm 4\text{ kJ mol}^{-1}$  of decomposed oxalate. The following step Stage III) of mass loss starts at  $\approx 900^\circ\text{C}$  and refers to the  $\text{BaCO}_3 \rightarrow \text{BaO}$  decomposition. At  $\approx 800^\circ\text{C}$  a DSC endothermic peak is present that corresponds to the  $\text{BaCO}_3$  transition from the tetragonal to the cubic phase with an associated en-

thalpy of  $23.9 \pm 0.8 \text{ kJ mol}^{-1}$  BaCO<sub>3</sub> (in pure BaCO<sub>3</sub>  $\Delta H = +22.6 \text{ kJ mol}^{-1}$  BaCO<sub>3</sub>). Then the decomposition of BaCO<sub>3</sub> begins at  $\approx 800^\circ\text{C}$  and continues to occur very slowly with no detectable DSC peak up to  $\approx 1150^\circ\text{C}$ .

In the case of the milled mixture the constant mass value is attained at  $\approx 950^\circ\text{C}$  ( $68.8 \pm 0.7\%$  vs. an expected value of  $70.4\%$ ). This means that some volatile impurities were absorbed in the mixture, presumably during milling, that account for an extra mass loss of  $-2.2 \pm 0.9\%$ . 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  $380^\circ\text{C}$  and is constituted of a mass loss down to a mass value of  $80.4 \pm 0.7\%$ , and the accompanying exothermic peak has an enthalpy of  $-379 \pm 10 \text{ kJ}$ . Stage Ib is over (at  $\approx 450^\circ\text{C}$ ) at a mean mass value of  $77.7 \pm 0.8\%$ , and the accompanying exothermic peak has an enthalpy of  $-87 \pm 11 \text{ kJ}$ . The expected mass value for the formation of a mixture SnO<sub>2</sub>-BaCO<sub>3</sub> is  $78.8\%$ . By allowing for the relatively high standard deviation of the thermogravimetric datum ( $77.7 \pm 0.8\%$ ), it can be concluded that the mixture SnO<sub>2</sub>-BaCO<sub>3</sub> is formed at  $\approx 450^\circ\text{C}$  when starting from the milled mixture, while the same happens at  $\approx 600^\circ\text{C}$  when starting from the physical mixture. Therefore the SnO<sub>2</sub>-BaCO<sub>3</sub> mixture formation is complete some  $150^\circ\text{C}$  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<sub>2</sub>-BaCO<sub>3</sub> mixture: the total exothermic enthalpy associated with the peaks of stages I+II of the physical mixture is  $-460 \pm 8 \text{ kJ}$  and can be expressed as  $-230 \pm 4 \text{ kJ mol}^{-1}$  of decomposed oxalate. In the case of the milled mixture the total exothermic enthalpy associated with the peaks of stages Ia+Ib is  $-466 \pm 21 \text{ kJ}$  and can be expressed as  $-233 \pm 10 \text{ kJ mol}^{-1}$  of decomposed oxalate.

Stage II of the curve for the milled mixture begins at  $\approx 710^\circ\text{C}$  and ends at  $950^\circ\text{C}$ : it is constituted of a mass loss of  $-5.4 \pm 0.2\%$  that corresponds to the decomposition of  $\approx 54\%$  by mole of BaCO<sub>3</sub> present in the mixture, and it is accompanied by an endothermic peak whose mean enthalpy is  $+111 \pm 8 \text{ J g}^{-1}$  that corresponds to a value of  $+90 \pm 5 \text{ kJ mol}^{-1}$  BaCO<sub>3</sub>. The fact that the BaCO<sub>3</sub> decomposition begins some  $100^\circ\text{C}$  below the case with the physical mixture points

to the fact that such decomposition is modulated by the reaction with SnO<sub>2</sub> to give BaSnO<sub>3</sub>. No endothermic peak marking the tetragonal-cubic phase transition of BaCO<sub>3</sub> is observed as it is the case with pure BaCO<sub>3</sub> and the physical mixture. It is worth to note that the share of BaCO<sub>3</sub> decomposed before the end of the endothermic peak (*i. e.*  $T \approx 800^\circ\text{C}$ ) nearly corresponds to the moles of Ba carbonate that have been formed within  $\approx 380^\circ\text{C}$  *i. e.* under stage Ia. The remaining part ( $\approx 35\%$  by mole) of BaCO<sub>3</sub> undergoes decomposition in the range  $800$ – $950^\circ\text{C}$  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,  $10 \text{ K min}^{-1}$ ) to temperatures of  $750$ ,  $800$ ,  $850$ ,  $900$ ,  $950$ ,  $1000$ ,  $1100$ , and  $1200^\circ\text{C}$ . 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  $1200^\circ\text{C}$  in order to detect the extent of BaCO<sub>3</sub> decomposition that possibly did not occur within the performed thermal treatment.

Table 1 reports the mass values attained ( $M_{\text{fin}}$ , %) 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  $1200^\circ\text{C}$  are also reported in Table 1 ( $M_{\text{TG}}$ ).

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

$T$ ( $^\circ\text{C}$ )	AM- $M_{\text{fin}}$ (%)	AM- $M_{\text{TG}}$ (%)	PM- $M_{\text{fin}}$ (%)	PM- $M_{\text{TG}}$ (%)
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

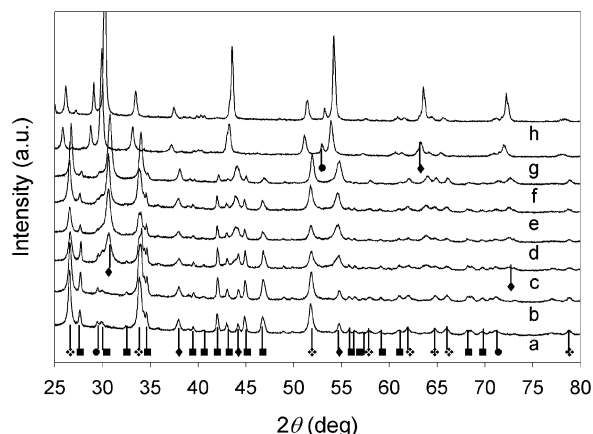


Fig. 3. Powder X-ray diffraction pattern of physical mixtures  $\text{BaC}_2\text{O}_4\text{-SnC}_2\text{O}_4$  heated in air to (a) 750 °C, (b) 800 °C, (c) 850 °C, (d) 900 °C, (e) 950 °C, (f) 1000 °C, (g) 1100 °C, and (h) 1200 °C.

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 ( $\text{SnO}_2$ ) and whiterite ( $\text{BaCO}_3$ ) are present. The peaks of  $\text{BaSnO}_3$  are showing up, besides those of  $\text{SnO}_2$  and  $\text{BaCO}_3$ , only when heating is extended up to 850–900 °C. The evidence for  $\text{BaSnO}_3$  increases when heating to 950 and 1000 °C, although  $\text{SnO}_2$  and  $\text{BaCO}_3$  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  $\text{BaSnO}_3$ , also those of unreacted  $\text{SnO}_2$  and  $\text{Ba}_2\text{SnO}_4$ . 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  $\text{BaSnO}_3$  but rather in a mixture of  $\text{BaSnO}_3$ ,  $\text{SnO}_2$  and  $\text{Ba}_2\text{SnO}_4$ .

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 forma-

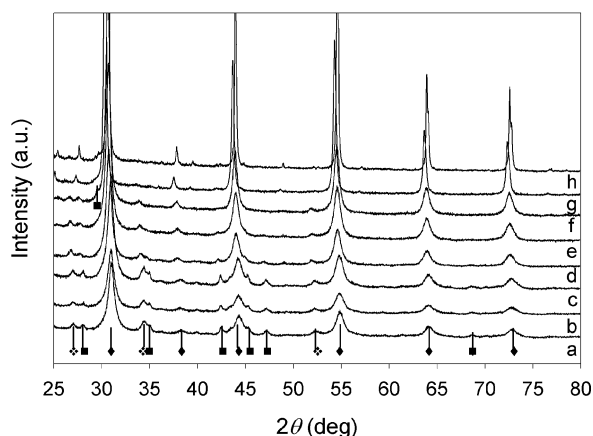


Fig. 4. Powder X-ray diffraction pattern of mechanically activated mixtures  $\text{BaC}_2\text{O}_4\text{-SnC}_2\text{O}_4$  heated in air to (a) 750 °C, (b) 800 °C, (c) 850 °C, (d) 900 °C, (e) 950 °C, (f) 1000 °C, (g) 1100 °C, and (h) 1200 °C.

tion of an equimolar mixture  $\text{SnO}_2\text{-BaCO}_3$  (77.3 %). The patterns indeed show quite broad peaks characteristic of  $\text{SnO}_2$  and  $\text{BaCO}_3$ , and rather broad peaks are also obtained that mark the presence of  $\text{BaSnO}_3$ .

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  $\text{BaSnO}_3$  (800 °C) although the peaks of  $\text{BaCO}_3$  and  $\text{SnO}_2$  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  $\text{BaSnO}_3$  are predominant.

The sample heated to 950 °C attains a final mass of 69.3 %, and the relevant diffraction pattern shows mainly the  $\text{BaSnO}_3$  peaks with only minor additions of both  $\text{BaCO}_3$  ( $2\theta \approx 28, 34, 42$ , and  $45^\circ$ ) and  $\text{SnO}_2$  ( $2\theta \approx 26.5, 33.8$  and  $53^\circ$ ). 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  $\text{BaCO}_3$  and  $\text{SnO}_2$ , while the diffraction patterns of the samples heated at 1100 and 1200 °C show only the peaks characteristic of  $\text{BaSnO}_3$ .

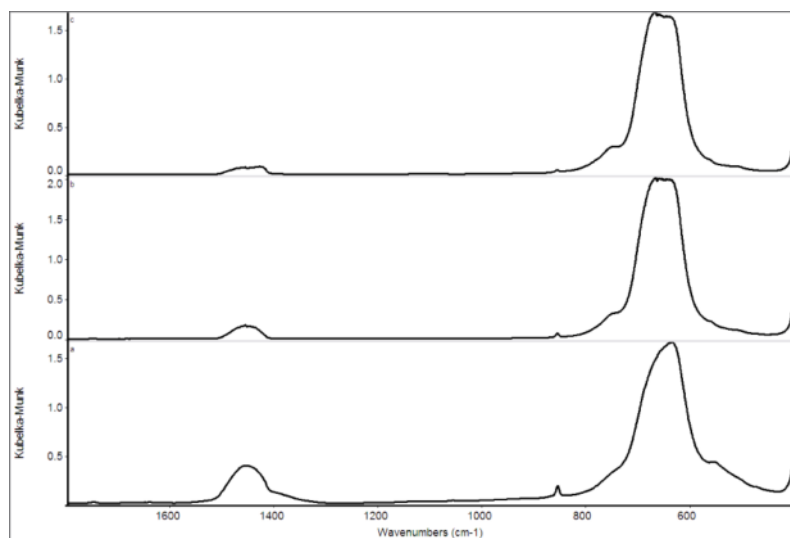


Fig. 5. Diffuse reflectance IR spectra of BaC<sub>2</sub>O<sub>4</sub>-SnC<sub>2</sub>O<sub>4</sub> mixtures subjected to mechanical activation and heated to 1000 °C (a), 1100 °C (b) and (c) 1200 °C.

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

$$1000\text{ °C: } C_p = 124.98 + 0.0507t - (1.1453 \times 10^4/t^2) \text{ J K}^{-1} \text{ mol}^{-1}$$

$$1050\text{ °C: } C_p = 130.41 + 0.0431t - (1.1593 \times 10^4/t^2) \text{ J K}^{-1} \text{ mol}^{-1}$$

$$1100\text{ °C: } C_p = 118.20 + 0.0508t - (9.5620 \times 10^3/t^2) \text{ J K}^{-1} \text{ mol}^{-1}$$

$$1150\text{ °C: } C_p = 122.00 + 0.0442t - (1.0020 \times 10^4/t^2) \text{ J K}^{-1} \text{ mol}^{-1}$$

$$1200\text{ °C: } C_p = 110.28 + 0.0562t - (9.052 \times 10^3/t^2) \text{ J K}^{-1} \text{ mol}^{-1}$$

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

However, it has to be considered that traces of BaCO<sub>3</sub> are still present in samples heated to 1200 °C. To try and assess the importance of the presence of BaCO<sub>3</sub> in the samples of BaSnO<sub>3</sub>, these very same samples have been subjected again to TG runs (maximum temperature 1000 °C; 10 °C min<sup>-1</sup>) that revealed a moderate mass loss due to the presence of BaCO<sub>3</sub> impurities formed by contact with air: samples heated at 1100 °C contain  $4.7 \pm 0.5\%$  by mass of BaCO<sub>3</sub> while the mass-% of BaCO<sub>3</sub> in the samples heated at 1150 and 1200 °C is, respectively, 2.8 and 1.2%. Such

a presence of BaCO<sub>3</sub> impurities has been confirmed by recording the IR spectra of these same samples (Fig. 5). The absorption bands at 856 and 1450 cm<sup>-1</sup> are characteristic of CO<sub>3</sub><sup>2-</sup>.

## Conclusions

The influence of mechanical activation of the mixtures BaC<sub>2</sub>O<sub>4</sub>-SnC<sub>2</sub>O<sub>4</sub> can be summarized as follows:

1. The total mass loss process is over at  $\approx 1150$  °C in the physical mixture while the same is true already at  $\approx 950$  °C in the case of the milled mixture.
2. The first stage of the thermal curves ends at  $\approx 450$  °C in the milled mixture and at  $\approx 600$  °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<sub>3</sub>-SnO<sub>2</sub>. Correspondingly, the enthalpy of the exothermic peak underlying the mass loss processes is nearly the same in both cases:  $\approx -230 \text{ kJ mol}^{-1}$  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<sub>2</sub> (secondary exothermic process;  $-283 \text{ kJ mol}^{-1}$ ) 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<sub>3</sub>. The difference between the physical and the milled mixture is seen



in the fact that the endothermic peak due to the tetragonal  $\rightarrow$  cubic transition of BaCO<sub>3</sub> is present in the DSC curve of the physical mixture at  $\approx 800^\circ\text{C}$ , while BaCO<sub>3</sub> decomposition is initiated in the milled mixture some  $100^\circ\text{C}$  below the transition point whose peak hence cannot be observed.

5. BaSnO<sub>3</sub>, though with variable content of BaCO<sub>3</sub> coming from the interaction with air, can be prepared by heating the milled mixture at  $T \geq 1000^\circ\text{C}$ . The product obtained by heating the physical mixture under the same experimental conditions is a mixture of BaSnO<sub>3</sub>, Ba<sub>2</sub>SnO<sub>4</sub> and SnO<sub>2</sub>.
6. The molar heat capacity of the samples obtained by heating the milled mixture to  $T \geq 1000^\circ\text{C}$  has been determined by MTDSC as a function of temperature in the  $50\text{--}380^\circ\text{C}$  range.

## Experimental Section

The starting chemicals SnC<sub>2</sub>O<sub>4</sub> (purity 98+ %) and BaC<sub>2</sub>O<sub>4</sub> (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  $50^\circ\text{C}$  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  $\approx 50\text{ mg}$  were placed into alumina cups and heated ( $10^\circ\text{C min}^{-1}$ , air flow  $100\text{ mL min}^{-1}$ ) from  $25^\circ\text{C}$  to  $1000^\circ\text{C}$ .

Samples of the mechanically activated mixture were heated in a tube furnace (static air,  $10^\circ\text{C min}^{-1}$ ) to temperatures of 750, 800, 850, 900, 950, 1000, 1100, and  $1200^\circ\text{C}$  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  $0.015^\circ$ , 2 s per step, 40 kV, 40 mA,  $2\theta = 25\text{--}80^\circ$ , radiation Cu K $\alpha$  radiation) with a powder X-ray diffractometer (Bruker D5005).

The molar heat capacity of the BaSnO<sub>3</sub> samples was determined by Modulated Temperature Differential Scanning Calorimetry (MTDSC, Q2000 DSC,  $T_{\text{zero}}$  technology, TA Instruments Inc. USA). The samples ( $\approx 20\text{ mg}$ ) were placed in a closed aluminum pan and heated under a nitrogen flow of  $50\text{ mL min}^{-1}$  in a quasi-isothermal mode, the sample being heated from 50 to  $380^\circ\text{C}$  in steps of  $10^\circ\text{C}$  and maintained at each of these steps for 10 min, while the temperature was oscillating with an amplitude of  $\pm 0.5^\circ\text{C}$  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  $1.0943 \pm 0.0075$  was obtained.

Diffuse reflectance FT-IR spectra of BaSnO<sub>3</sub> samples were recorded with a FT-IR spectrometer (iS10 by Nicolet, USA) on samples dispersed in KBr (5 mass %); 512 scans were used at  $4\text{ cm}^{-1}$  resolution and ratioed against 1024 scans collected on samples of pure KBr (99+ %, Sigma Aldrich, Italy).

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