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Effect of mechanical milling on solid state formation of $BaTiO_3$ from $BaCO_3$–TiO_2 (rutile) mixtures

Vittorio Berbenni*, A. Marini, G. Bruni

CSGI, Dipartimento di Chimica Fisica dell'Università di Pavia, Viale Taramelli 16, 27100 Pavia, Italy

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Abstract

Barium metatitanate ($BaTiO_3$) is widely used because of its high dielectric constant, ferroelectric properties and positive temperature coefficient of electrical resistivity. The present work reports the results obtained in the set up of a preparation method of $BaTiO_3$ by milling and annealing mixtures of $BaCO_3$ and TiO_2 (rutile). High energy milling of a $BaCO_3$–TiO_2 (rutile) equimolecular mixture resulted in a noticeable temperature drop of the temperature where the reaction can occur. The formation of single phase $BaTiO_3$ was confirmed by thermogravimetric analysis (TGA) (both alone and coupled with Fourier transform infrared spectroscopy (FT-IR) evolved gas analysis), by differential scanning calorimetry (DSC) and X-ray powder diffractometry (XRPD). The formation of phases like Ba_2TiO_4 (orthotitanate), which are known to be detrimental for $BaTiO_3$ end performances, has only been revealed as an intermediate minor phase that disappears by annealing at temperatures as low as 750°C. At such temperatures the crystal size of the product is 400 Å. $BaTiO_3$ formation occurs either by a slow heating (2 K/min) of the milled mixture or by a rapid heating followed by an isothermal annealing of 12 h.

Keywords: High energy milling; Mechanical activation; Barium titanate; Solid state reaction; Thermogravimetric analysis

1. Introduction

Alkaline earth metal titanates are becoming increasingly important in the ceramics and electronic industries. In particular barium metatitanate ($BaTiO_3$) is widely used because of its high dielectric constant, ferroelectric properties and positive temperature coefficient of electrical resistivity [1]. Usually $BaTiO_3$ has been synthesized by the solid state reaction between $BaCO_3$ and TiO_2 at high temperature. However, this procedure can result in a ceramic with compositional inhomogeneities since phases like Ba_2TiO_4 (orthotitanate) and $BaTi_3O_7$ can form. Hence the intimate mixing of the starting powders is of paramount importance for $BaTiO_3$ preparation. Several possible preparation methods have been proposed that allow such an intimate mixing. These are, for example, oxide coprecipitation [2], sol-gel route [3] and thermal decomposition of oxo-salts [4]. However, all these methods imply additional process steps prior to the annealing phase.

A very effective way of mixing is represented by high energy mechanical milling. Indeed, by taking into account that in several applications of titanates some evenly distributed dopant element is added to

* Corresponding author. Tel.: +39-382-507211; fax: +39-382-507575.
E-mail address: berbenni@fisav.unipv.it (V. Berbenni).

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enhance the desired properties [5], the usefulness of the mechanical milling route cannot be overlooked. Gomez-Yanez et al. [6] studied the influence of long term milling a molar 1:1 $BaCO_3$–TiO_2 (anatase) mixture on the formation of barium titanate by high temperature annealing. According to their findings, both $BaTiO_3$ and orthotitanate (Ba_2TiO_4) form by calcining the milled mixtures up to 1200°C. Balaz and Plesingerova [7] brought into evidence that the apparent activation energy of $BaTiO_3$ formation from barium carbonate and titanium dioxide decreases with premilling the mixture before the high temperature treatment. Furthermore, their DTA traces showed an endothermic effect at 572 K which may be due, in the Author's opinion, to the decomposition of $Ba(OH)_2$ which is formed by hydration of BaO which in turn results from partial decomposition of $BaCO_3$ over 30 min milling. A direct, room temperature mechanochemical synthesis of $BaTiO_3$ has been performed by Welham [8] starting from the constituent oxides which have been milled under vacuum after a pre-annealing step of barium oxide (84 h at 1300°C) in order to decompose the hydroxide/carbonate layer which has been formed during storage. Recently, Xue et al. [9] reported a breakthrough in that they performed a room temperature synthesis by milling under nitrogen a mixture of Ba/Ti oxides.

However, as it has been said, the room temperature synthesis starting from the oxides has to overcome the problem of preventing barium oxide from hydration/carbonation by air moisture. On the other hand some indications [6] on the effect of milling on $BaTiO_3$ formation by annealing $BaCO_3$–TiO_2 mixtures seem quite contradictory and to some extent even discouraging. The present work reports the results obtained in the set up of a preparation method of $BaTiO_3$ by milling and annealing mixtures of $BaCO_3$ and TiO_2 (rutile).

2. Experimental

2.1. Starting chemicals and samples preparation

The starting chemicals were purchased by Aldrich Chimica (Italy): $BaCO_3$ (purity +99%) and TiO_2 (predominantly rutile as it has been demonstrated by taking the XRD patterns, purity 99.9%). A physical mixture (1:1 molar ratio by taking into account the different purities) was prepared by weighing the appropriate amounts of the two components and by mixing them in an agate mortar for about 10 min. Then the powders were suspended in acetone under magnetic stirring for 3 h and the solvent allowed to evaporate in an oven at 60°C overnight.

The physical mixtures were dry milled for different times (up to 159 h) in a high energy planetary mill (Pulverisette 7 by Fritsch, Germany) at 400 rpm rotation speed with 2 agate balls (12 mm diameter) in an agate jar. The ball/sample mass ratio was 10:1.

2.2. Experimental techniques

- Thermogravimetric analysis (TGA) measurements were performed by the 2950 thermogravimetric analyser (TA Instruments Inc., USA) connected to the TA5000 computer (also by TA Instruments Inc., USA). About 12 mg of the different samples were heated at 2 K/min and under a nitrogen flow of 100 ml/min from 25 up to 850°C where they have been maintained for 12 h.
- Another TGA measurement was carried out on the mixture milled for 159 h by connecting a thermobalance (TGA 951 Thermogravimetric Analyser by DuPont Inc., USA) to a Fourier transform infrared spectroscopy (FT-IR) Spectrometer (Model 730 FT-IR Spectrometer by Nicolet USA equipped with OMNIC™ proprietary software). This was done to analyse the gases evolved during the first part of the measurement. A sample was heated at 10 K/min up to 630°C. Nitrogen (65 ml/min) was used both as purging gas for the spectrometer and to sweep the gaseous products from the thermobalance into the FT-IR gas cell (kept at 200°C throughout the run). The spectra of the evolved gases were obtained by fast Fourier transform of 16 coadded interferograms collected at 8 cm^{-1} resolution. Specific absorbance chemigrams of the possible gaseous products (H_2O and CO_2) have been reconstructed at the end of the run by means of the Nicolet Series™ software.
- Differential scanning calorimetry (DSC) measurements were performed by a DSC 1500 (Stanton Redcroft, UK) connected to a data analysis system (by Polymer Laboratories, UK). About 20 mg of the sample were heated, under a nitrogen flow of

60 ml/min, at 2 K/min from room temperature to 900°C.

- Samples of both milled and unmilled mixtures were placed into the described thermoanalytical apparatuses so as to ensure they have been subjected to the same experimental conditions used in the thermoanalytical measurements. These samples were heated (2 K/min under nitrogen flow) up to increasing temperatures (from 550 up to 1000°C in steps of 50°C — Section 3.1). Furthermore, the same samples were rapidly heated (50 K/min) up to different temperatures (see details in the Section 3) where they were maintained for 12 h (Section 3.2). X-ray powder diffraction patterns were taken by putting the samples on a non diffracting silicon slide. Use was made of a X-ray powder diffractometer (Bruker D5005) equipped with a goniometer and a graphite bent crystal monochromator. X-ray powder diffractometry (XRPD) spectra were recorded (step scan mode: step 0.02°, 3s/step in the 2ϑ angular range 15–75°; 40 kV, 40 mA) in order to identify the compounds formed in the annealed mixtures.

3. Results and discussion

3.1. Dynamic annealing

Table 1 reports the results of the TGA runs performed on $BaCO_3$–TiO_2 mixtures milled for different times.

The mean value of the experimental mass losses reported in Table 1 is $-15.55 \pm 0.29\%$ while such a mean value, when calculated for the samples milled for 24 h or more, becomes $-15.69 \pm 0.19\%$ which nearly coincides with the expected one by taking into account the purity (99%) of the starting barium carbonate. Indeed the XRPD patterns of the longer milled sample (159 h), before its annealing, showed neither trace of barium titanium oxide(s) nor of barium oxide produced by carbonate decomposition. Fig. 1 reports the TGA curves of the physical mixture and of the longer milled sample (159 h). The following remarks are worth mention:

- The mass loss process initiates in the milled sample at room temperature and continues up to ca. 460°C where about 1.1% of the mass loss has taken place.

Table 1
Results of thermogravimetric scans on samples of $BaCO_3$–TiO_2 mixtures milled for different times (t_{bm}, h). ΔM_{850} represents the mass loss (%) at 850°C (maximum temperature). ΔM_{iso} is the mass variation (%) over the 12 h isothermal stage. $\Delta M_{tot} = \Delta M_{850} + \Delta M_{iso}$; $\Delta_{exp-calc}$ (μg) is the difference between the experimental mass loss (ΔM_{tot}) and the value calculated on the basis of the $BaCO_3$ decomposition

t_{bm} (h)	ΔM_{850} (%)	ΔM_{iso} (%)	ΔM_{tot} (%)	$\Delta_{exp-calc}$ (μg)
0	−14.18	−1.10	−15.28	39
12	−15.13	0.00	−15.13	52
24	−15.57	−0.13	−15.70	22
71	−15.63	−0.32	−15.95	−10
101	−15.56	−0.11	−15.67	22
114	−15.40	−0.32	−15.72	10
159	−15.11	−0.31	−15.42	41

On the contrary, no mass loss occurs in the physical mixture up to 670°C. It could well be that the high energy milling causes an increase in the surface area of the powders so that water intake by the sample during milling can result. If this were the case, an analysis of the gases evolved during this part of the run can help to establish the origin of the mass loss. As the gases which are likely to be released are water vapor and/or carbon dioxide, FT-IR spectroscopy has been used as gas detecting technique. Fig. 2 reports, as a function of time, the thermogravimetric curve (a) of a sample of the longer milled mixture. Also Fig. 2 reports the temperature (b), the integrated absorbance signal of water ((c); 3900–3400 cm^{-1}) and of carbon dioxide ((d); 2430–2250 cm^{-1}). It can be seen that up to 45 min into the run (corresponding to 455°C in the thermobalance) carbon dioxide is the main gas with only minor amounts of water being released.

- At about 550°C, an abrupt mass loss (ca. −1.40%) occurs in the milled samples. The coupled TG/FT-IR measurement shows that the gas released is carbon dioxide (Fig. 2d).
- The whole mass loss process is over, in the milled samples, at about 730°C while a 12 h isotherm at 850°C is needed for a complete mass loss in the unmilled mixture.

DSC measurements have been performed on samples of physical mixtures and of the longer milled sample (159 h). The DSC scan of the physical mixture (Fig. 3a) shows a double peak: a sharp endothermic

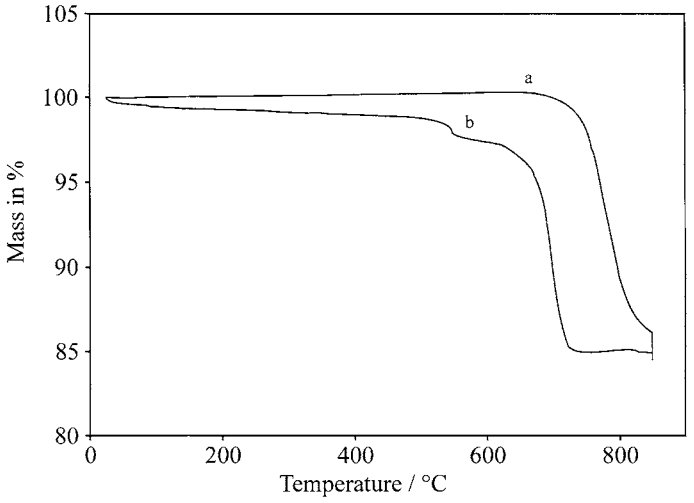

Fig. 1. TGA curves obtained on $BaCO_3$–TiO_2 (rutile) mixtures: (a) physical mixture; (b) mixture milled for 159 h.

one (with maximum at ca. 810°C) followed by a broad endothermic hump. The peak is over shortly below 900°C and from its total area an enthalpy value of 105.4 kJ/mol of $BaCO_3$ is obtained that nearly coincides with 104.6 which can be calculated from the thermodynamic data reported in the literature for the compounds involved in the reaction [10–12]. The DSC scan of the sample milled 159 h (Fig. 3b) shows

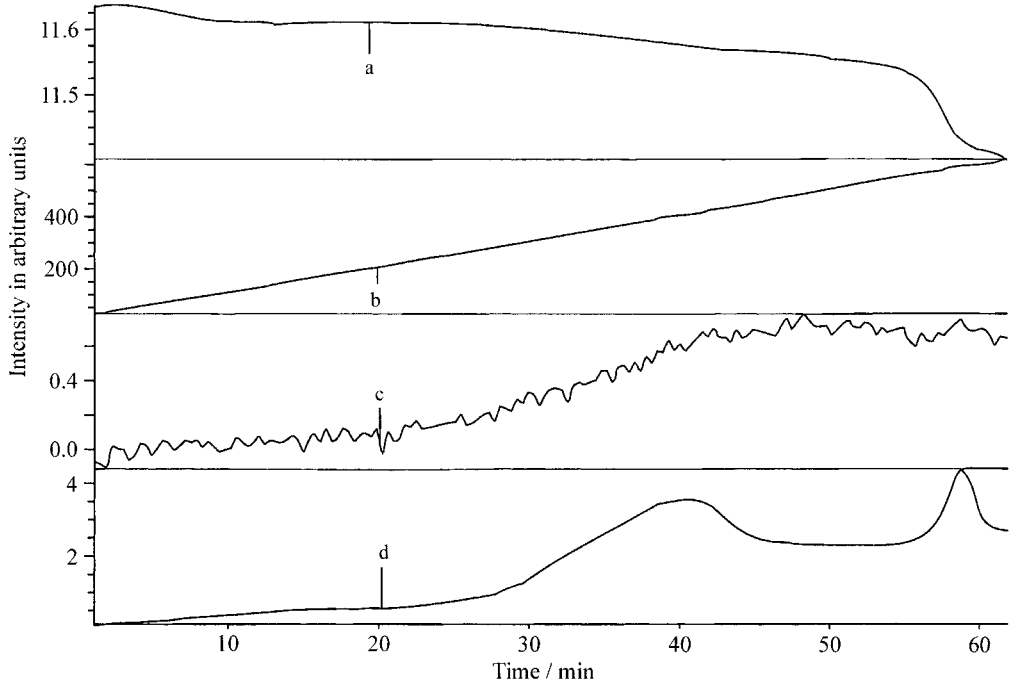

Fig. 2. TG/FT-IR measurement carried out on a 159 h milled sample. The following signals are reported as a function of time: (a) TGA curve (mg); (b) temperature (°C); (c) H_2O related integrated absorbance; (d) CO_2 related integrated absorbance.

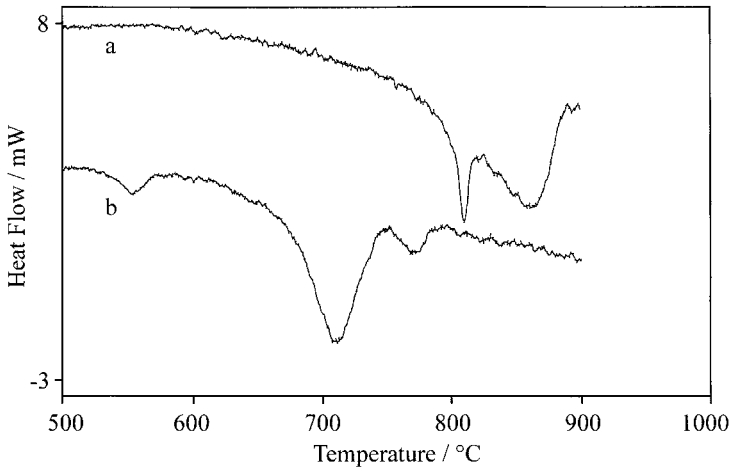

Fig. 3. DSC curves obtained on $BaCO_3$–TiO_2 (rutile) mixtures: (a) physical mixture; (b) mixture milled for 159 h.

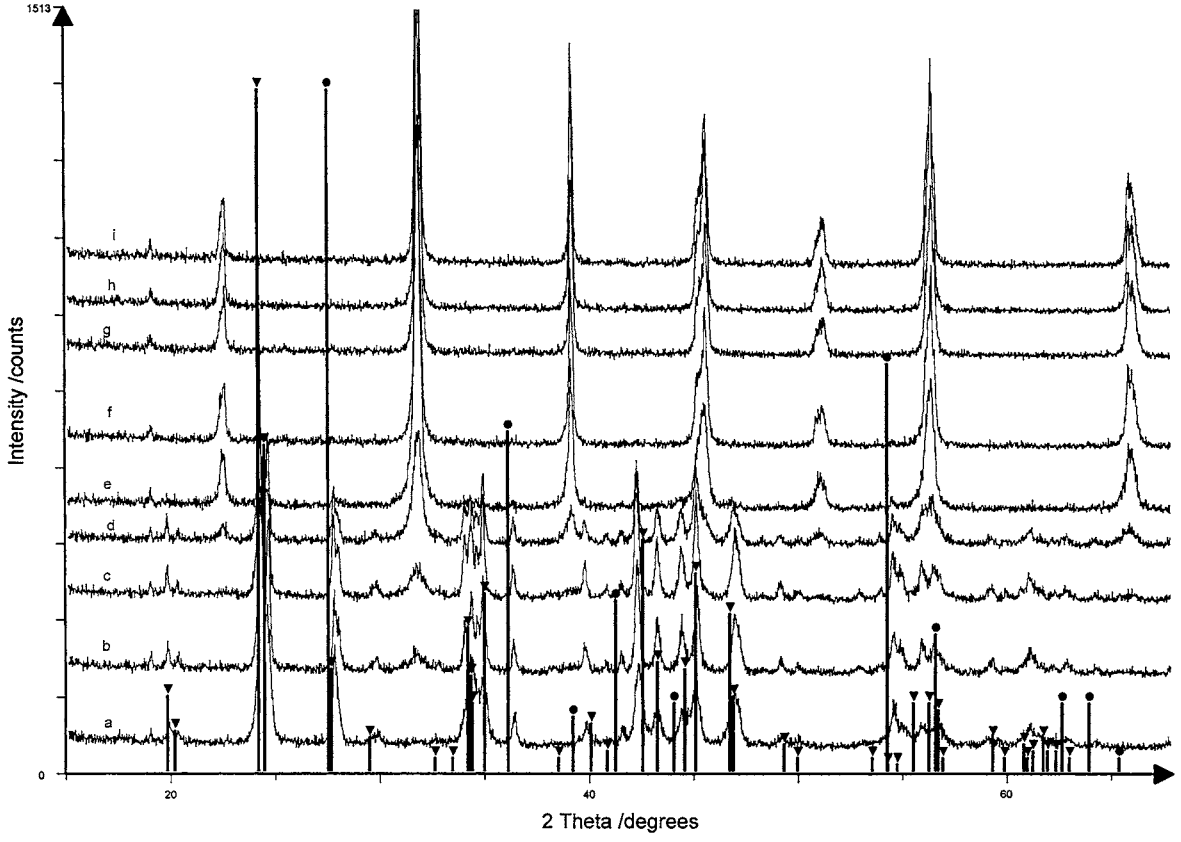

Fig. 4. XRD powder patterns obtained on samples of $BaCO_3$–TiO_2 (rutile) mixture milled for 159 h and annealed up to the following temperatures: (a) 550°C; (b) 600°C; (c) 650°C; (d) 700°C; (e) 750°C; (f) 800°C; (g) 850°C; (h) 900°C; (i) 1000°C. The markers refer to: $BaCO_3$ (triangles, JCPDS card no. 41-0373) and to TiO_2 (circles, JCPDS card no. 21-1276).

an endothermic peak starting at 525°C whose enthalpy value is 6.15 kJ/mol of $BaCO_3$. The main peak, which has an onset temperature of ca. 618°C, shows two effects (with maxima at ca. 700°C and ca. 760°C): a rather large and broad peak followed by a smaller one. The total area of the peak corresponds to 94 kJ/mol of $BaCO_3$. Therefore, the total enthalpy associated with the peaks recorded on the milled sample (ca. 100 kJ/mol of $BaCO_3$) is only slightly lower than that of the physical mixture. However, if the small peak at 525°C is referred to the mass loss (ca. 1.4%) taking place nearly at the same temperature, an enthalpy of 70 kJ/mol of $BaCO_3$ is obtained. Hence the enthalpy of the main peaks becomes close (103 kJ/mol of $BaCO_3$) to the value obtained with the unmilled mixture which, in turn, agrees with the enthalpy reported in the literature for $BaTiO_3$ formation.

Table 2
Mass loss values (ΔM_{iso}, %) recorded over 12 h isothermal stage performed at different temperatures (T_{iso}, °C). The parameter α represents the ratio between ΔM_{iso} and ΔM_{tot} (the total mass loss recorded in the thermogravimetric run)

T_{iso} (°C)	ΔM_{iso} (%)	α
575	−1.49	0.0984
587	−2.27	0.1484
600	−3.68	0.2393
610	−5.33	0.3432
625	−9.87	0.6368
635	−12.53	0.8042
645	−12.98	0.8305
690	−13.84	0.8661
720	−10.74	0.6713
750	−6.92	0.4325
780	−4.82	0.2649
810	−1.85	0.1147

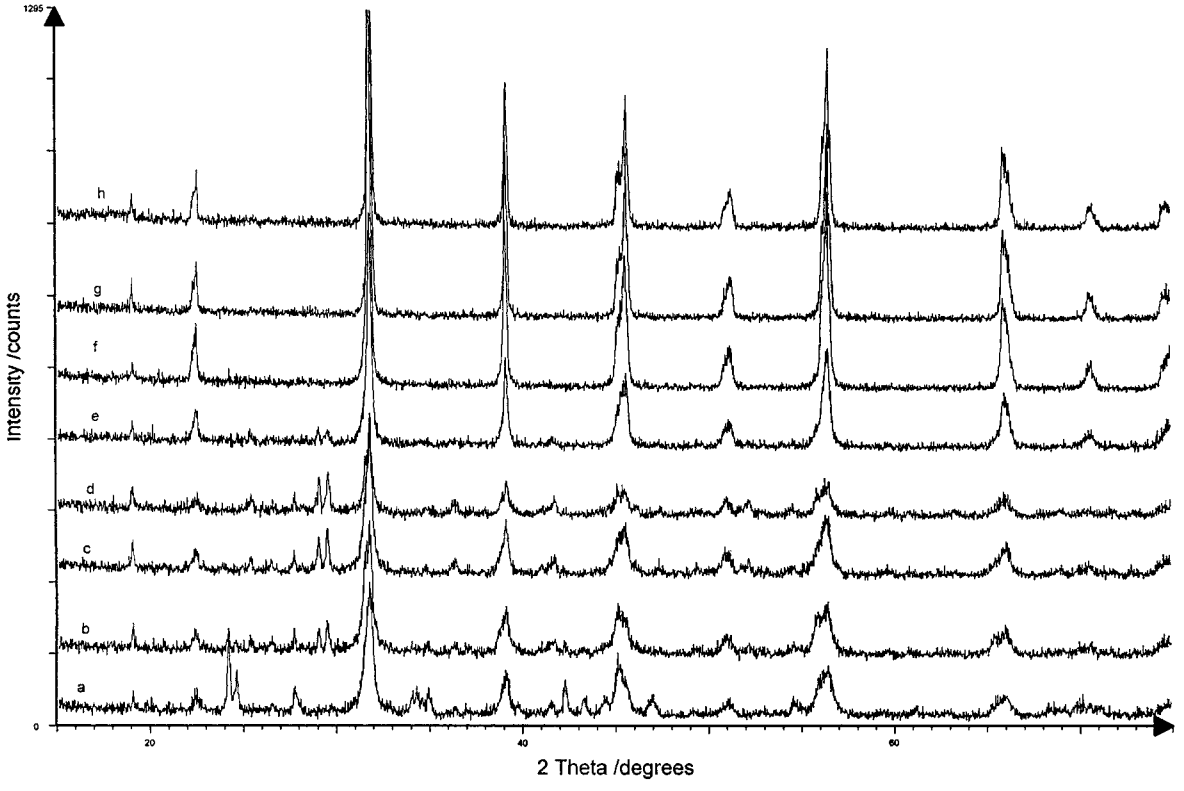

Fig. 5. XRD powder patterns obtained on $BaCO_3$–TiO_2 (rutile) mixture milled for 159 h. The samples have been rapidly heated up to increasing temperatures where they have been held for 12 h: (a) 635°C; (b) 650°C; (c) 670°C; (d) 690°C; (e) 720°C; (f) 750°C; (g) 780°C; (h) 810°C.

Samples of the mixture milled for 159 h which have been dynamically annealed into the TGA apparatus have been examined by XRPD. The relevant diffraction patterns are reported in Fig. 4. Only minor amounts of barium metatitanate seem to have been formed up to 650°C (see the $BaTiO_3$ 100% peak at $2\vartheta \approx 31.3°$) where the reflections pertaining to both $BaCO_3$ and TiO_2 are still the major ones that are present. Also up to 650°C the two most intense peaks (they are expected in the 2ϑ range $= 28.5-29.5°$) of the compound Ba_2TiO_4 (barium orthotitanate, see the JCPDS card no. 35-0813) are visible. However, this phase seems to have been formed only to a limited extent. Its formation could correspond to the small, endothermic DSC peak at 525°C. On the other hand barium metatitanate constitutes the only phase present at 750°C (see the JCPDS card no. 31-0174). From such a temperature, the situation does no longer change both as regards peak positions and intensities. Thus, the combined thermoanalytical (TGA, DSC) and diffractometric evidence suggests that barium metatitanate can be formed by heating at a moderate heating rate (2 K/min) an equimolecular, mechanically activated mixture of barium carbonate and rutile up to 750°C. The formation enthalpy of $BaTiO_3$ does not seem to be appreciably affected by milling the reacting mixture. On the other hand, milling strongly lowers the temperature of $BaTiO_3$ formation which takes place directly with only minor amounts of Ba_2TiO_4 which forms at intermediate temperatures

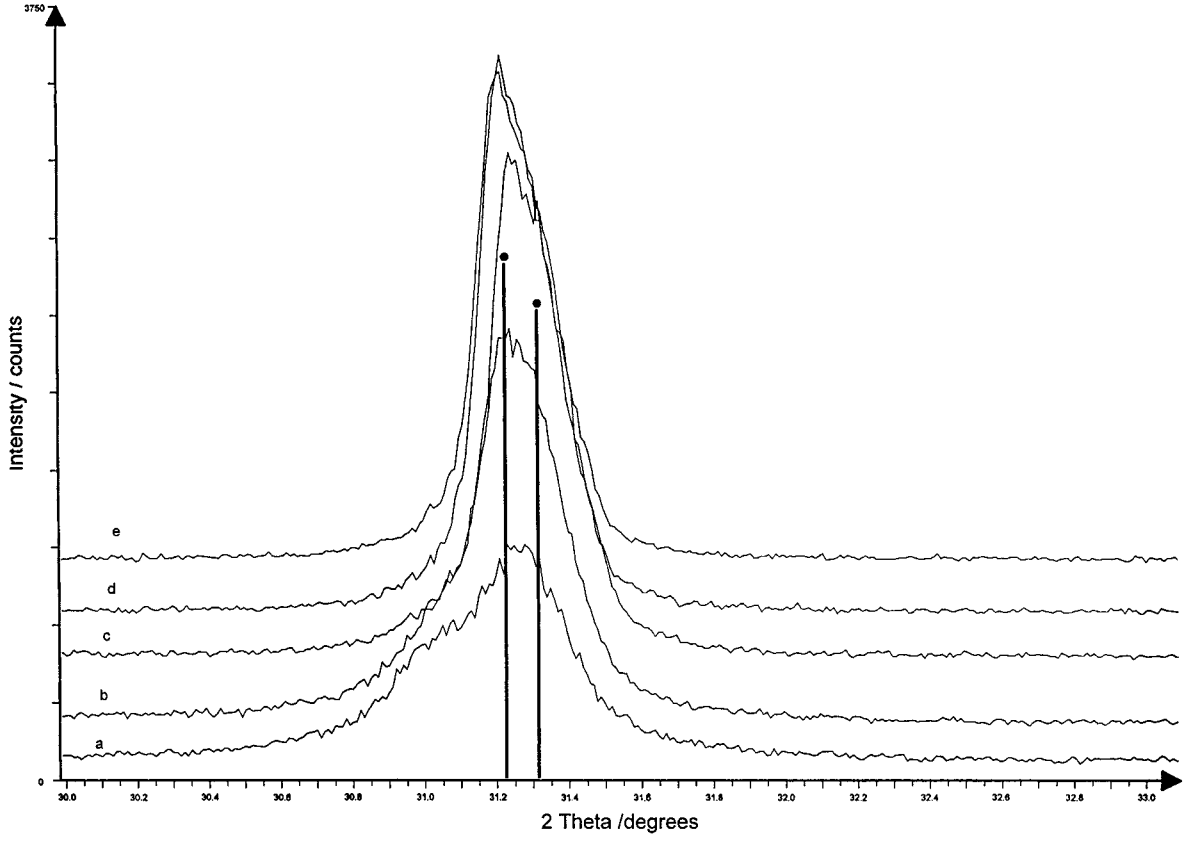

Fig. 6. XRD powder patterns obtained on $BaCO_3$–TiO_2 (rutile) mixture milled for 159 h. The samples have been rapidly heated up to increasing temperatures where they have been held for 12 h: (a) 670°C; (b) 720°C; (c) 750°C; (d) 780°C; (e) 810°C. The markers refer to $BaTiO_3$ (JCPDS card no. 31-0174).

(ca. 550–600°C) and disappears by reaction with TiO_2 at higher temperatures.

3.2. Isothermal annealing

Isothermal annealing experiments were performed on samples of the mixture milled 159 h by heating them rapidly (50 K/min) up to increasing temperatures (between 575 and 810°C). They were held isothermally for 12 h into the TGA apparatus under flowing nitrogen. In the cases ($T_{iso} < 720$°C) where no complete mass loss occurred within the isothermal stage, heating was resumed (2 K/min) up to 850°C after XRD analysis. Table 2 reports the mass loss values recorded over the mentioned isothermal stages along with the ratio (α) with respect to the total mass loss. It can be seen that this ratio increases for isothermal temperatures up to 690°C while it decreases at $T > 700$°C. Fig. 5 shows that, up to 690°C, besides the peaks related to $BaTiO_3$, also those of Ba_2TiO_4 and TiO_2 are present despite the most intense reflections of barium carbonate being absent after the isothermal treatment at 650°C. Some weak reflections of barium orthotitanate are still present after the annealing at 720°C, while barium metatitanate is the only phase present for $T_{iso} > 750$°C. Evidently, by rapidly heating the milled samples the carbonate decomposition proceeds faster than metatitanate formation so that orthotitanate, besides metatitanate, forms. However, at annealing temperatures above 700°C, the reaction between Ba_2TiO_4 and excess TiO_2 leads to the complete formation of $BaTiO_3$. From the full width at half maximum of the 100% intensity peak (see Fig. 6), the crystal size of barium metatitanate can be obtained at the different annealing temperatures by the Scherrer formula [13]. In the case of the sample annealed at 720°C a crystal size of 350 Å results while, at higher temperatures (up to 810°C), a common value of about 400 Å is obtained.

4. Conclusions

High energy milling of a $BaCO_3$–TiO_2 (rutile) equimolecular mixture resulted in a noticeable temperature drop of the temperature where the reaction can occur. The formation of single phase $BaTiO_3$ was confirmed by TGA (both alone and coupled with FT-IR evolved gas analysis), DSC and XRD powder diffractometry. The formation of Ba_2TiO_4 (orthotitanate), which is known to be detrimental for $BaTiO_3$ end performances, has only been revealed as an intermediate minor phase that disappears by annealing at temperatures as low as 750°C. At such temperatures the crystal size of barium metatitanate is about 400 Å.

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