J MATER SCI **41** (2006) 1739–1744

Effect of mechanical activation on the formation of lead titanates from $PbCO_3$ – TiO_2 mixtures

V. BERBENNI*, C. MILANESE, A. MARINI
CSGI – IENI CNR - Dipartimento di Chimica Fisica dell'Università di Pavia, Viale Taramelli 16, 27100 Pavia, Italy
E-mail: berbenni@matsci.unipv.it

N. J. WELHAM
Extractive Metallurgy, Murdoch University, South Street, Murdoch, WA 6150, Australia

$PbTiO_3$ powders have been prepared by mild annealing (2 h at 600°C) of $PbCO_3$:TiO_2 mixtures previously subjected to mechanical activation, while a thermal treatment of about 12 h at $T >$ 850°C is needed to obtain $PbTiO_3$ from a physical mixture. Although the temperature and enthalpy of the DSC peak corresponding to $PbCO_3$ decomposition are not affected by mechanical energy, in the case of the mechanically activated mixtures an exothermic event due to the reaction $PbO + TiO_2 \rightarrow PbTiO_3$ shows up. Furthermore, SEM micrographs and the XRD line broadening allow to conclude that $PbTiO_3$ powders obtained from activated mixtures are of nanometer size. $PbTi_3O_7$ has been prepared starting from mechanically activated $PbCO_3$:$3TiO_2$ mixtures by 1 h annealing at 850°C while 100 h at 800°C were required to yield this compound from unmilled mixtures. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

Lead Titanate, $PbTiO_3$, is a perovskite-type ferroelectric material with noticeable dielectric, pyroelectric and piezoelectric properties [1]. It is stable at room temperature as tetragonal phase (see JCPDS file no. 06-0452) that transforms to a cubic phase (see JCPDS file no. 40-0099) at $T \approx 490°C$, known as temperature of ferroelectric anomaly [2]. Synthesis of $PbTiO_3$ both as powder or as thin film has been accomplished by different routes such as sol-gel [3] and hydrothermal synthesis [4]. Lead titanate powders with mean particle size of 150 nm have also been obtained by calcinating (1 h at 600°C) a polymeric precursor prepared by the Pechini process [5]. Fine powders of $PbTiO_3$ have been prepared by a sol-precipitation process starting from organometallic solution of Ti/Pb and from Pb/Ti mixed acetate – hydroxide [6]. A precipitate forms by NaOH addition and its thermal treatment at 500–600°C yielded pure tetragonal $PbTiO_3$ with a c/a ratio of 1.054 and an average crystallite diameter of 50 nm. Fang and coworkers [7] performed a comparative study on phase development of $PbTiO_3$ powders prepared either by conventional coprecipitation and by microemulsion-refined coprecipitation. They found that the latter route leads to $PbTiO_3$ at lower temperature (≈500°C) without intermediate formation of pyrochlore phase ($Pb_2Ti_2O_6$). Besides, the $PbTiO_3$ powders obtained by conventional coprecipitation consisted of particles in the μm size whereas discrete particles of about 100 nm have been obtained with the microemulsion method. An amorphous Pb–Ti–O hydroxide precursor [8] has been prepared by coprecipitation from mixed Pb/Ti nitrate solution treated with ammonia with subsequent mechanical activation of the precursor by high energy milling for times up to 30 h before the final calcination of 20 h at 650°C. It is shown that the mechanical activation prior to the calcination results in $PbTiO_3$ powders with much more uniform particle size (300–500 nm) with respect to those obtained without mechanical activation (≈500 nm, with some more coarsened particles of 4–5 μm). Finally nanosized lead titanate powders have been successfully prepared via mechanochemical route starting from PbO and TiO_2 [9].

In the present work we studied the influence exerted by mechanical activation on the solid state reactions occurring between $PbCO_3$ and TiO_2 with the final aim to synthesize lead titanates ($PbTiO_3$ and $PbTi_3O_7$). It has been shown that solid state reaction between milled precursors occurs at temperatures lower than it is the case

---

*Author to whom all correspondence should be addressed.

0022-2461 © *2006 Springer Science + Business Media, Inc.*
DOI: 10.1007/s10853-006-3949-0

with physical mixtures. This is a particularly important factor as concerns this system as high temperature is likely to imply loss of volatile PbO and to result in particle coarsening. Namely, in the case of $PbTiO_3$, nanosized powders could be obtained at moderate temperature (650°C).

2. Experimental

2.1. Starting chemicals and samples preparation

The starting chemicals were purchased by Aldrich Chimica (Italy): $PbCO_3$ (purity 99.99%) and TiO_2 (purity 99.9%). Physical mixtures of molar ratio Pb:Ti respectively 1:1 and 1:3 were prepared by weighing the appropriate amounts of the two components and by mixing them in an agate mortar for about 10 min. To ease the mechanical mixing the powders were suspended in acetone under magnetic stirring for 3 h and the solvent was allowed to evaporate slowly in oven at 60°C. The mechanically activated mixtures were prepared by dry milling the physical mixtures for 170 h in a planetary mill (Pulverisette 7 by Fritsch, Germany) operating at 350 rpm (rotation speed) with 4 agate balls (12 mm diameter) in an agate jar (ball/sample mass ratio 5:1).

$PbTiO_3$ samples have been prepared by solid state reaction either from the physical mixture (thermal schedule: heating at 5 K/min up to 850°C + isothermal stage of 24 h) and from the milled mixture (heating at 5 K/min up to 650°C + isothermal stage of 2 h).

2.2. Experimental techniques and conditions

2.2.1. Thermoanalysis experiments

TGA Measurements were performed by a 2950 thermogravimetric analyser (TA Instruments Inc., USA) connected to a TA 5000 computer (also by TA Instruments Inc., USA). The samples (about 50 mg) were heated at 5 K/min (100 ml/min nitrogen flow) from 25°C up to different temperatures ranging between 600°C and 950°C and held in isothermal condition for 12 h (unless otherwise stated).

Simultaneous DSC/TGA measurements were performed with a SDT 2960 apparatus (TA Instruments Inc., USA) connected to the TA 5000 computer. The samples ($\approx$50 mg) were placed in an alumina pan and heated (120 ml/min nitrogen flow) at 5 K/min from 25°C up to 850°C. The enthalpy values were determined from the area of the DSC peaks. DSC calibration was performed using sapphire (heat capacity calibration) and zinc (enthalpy calibration).

2.2.2. X-ray powder diffraction experiments

X-ray powder diffraction patterns were recorded in step scan mode (step 0.02°, 3 s/step, 40 kV, 40 mA) by a X-ray powder diffractometer (Bruker D5005) equipped with a goniometer and a graphite bent crystal monochromator. XRPD patterns have been taken on different samples:

(1) samples recovered after the TG runs were put on a non diffracting silicon slide and analysed in order to identify the compounds formed during the heating of the mixtures;

(2) samples of both milled and unmilled mixtures have been heated at 5 K/min under nitrogen flow up to 850°C in a high-temperature chamber (Anton Paar HTK1200) fitted into the X-ray powder diffractometer in order to evaluate the extent of the solid state reaction. Three subsequent XRD patterns were recorded respectively at 600–650–700–750–800 and 850°C. The samples remained about 2.5 h at each temperature;

(3) $PbTiO_3$ samples prepared by solid state reaction from the milled mixture (2 h at 650°C) were put on a non diffracting silicon slide and analysed in order to calculate the crystal size from XRD line broadening by the Debye–Scherrer equation. The instrumental line broadening was determined using as reference the patterns of $PbTiO_3$ sample prepared from the physical mixture (24 h at 850 °C).

2.2.3. Scanning electron microscopy experiments

Samples prepared by solid state reaction either from the milled mixture (2 h at 650°C) and from the physical one (24 h at 850°C) have been examined by scanning electron microscopy (SEM, Model Stereoscan 200 by Cambridge, UK). Before analysis the samples have been sputtered under vacuum with gold metal.

3. Results and discussion

3.1. $PbCO_3 – TiO_2$ Mixtures

3.1.1. Thermoanalytical measurements

Fig. 1a shows the TG scans performed under nitrogen flow at 5 K/min up to 900°C on $PbCO_3 – TiO_2$ physical (full lines) and milled (dashed lines) mixtures. It can be seen that no considerable lowering of the temperature of the mass loss process results by milling the mixtures. Clearly the temperature range where the decomposition of $PbCO_3$ occurs is not sensibly affected by mechanical activation.

To verify the progress of $PbTiO_3$ formation, TG runs have been performed by heating samples of both mixtures at 5 K/min up to temperatures between 600°C and 950°C (in steps of 50°C) with an isothermal stage (12 h) appended to the ramp. For the physical mixtures, the mean value of the final mass at the end of these runs is 87.54% ± 0.84 (expected 87.32%) that shows rather a high standard deviation. The XRD powder patterns of the thermally treated samples always show, besides the presence of $PbTiO_3$, peaks that refer to PbO (high temperature, orthorhombic phase) and/or to TiO_2 so meaning that the reaction between PbO and TiO_2 is not completed at temperatures as high as 850°C.

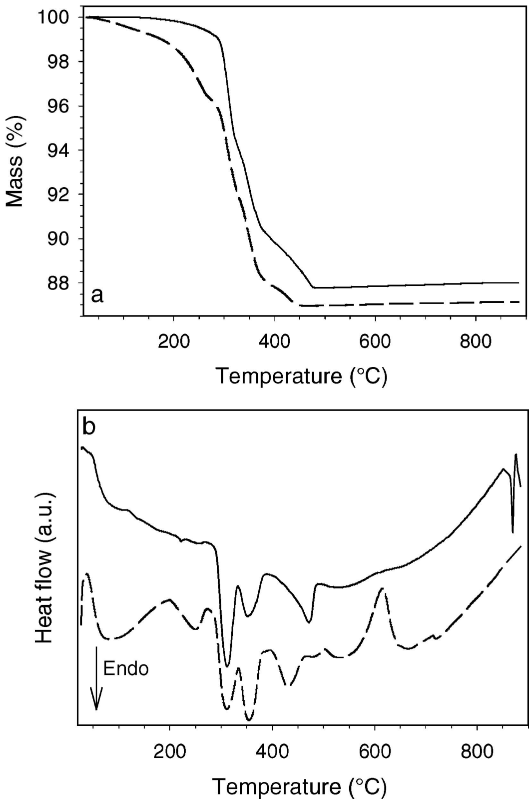

Figure 1 (a) TG curves obtained under nitrogen at 5 K/min on $PbCO_3$:TiO_2 mixtures: physical mixtures (full line); milled mixtures (dashed line). (b) DSC curves obtained under nitrogen at 5 K/min on $PbCO_3$:TiO_2 mixtures: physical mixtures (full line); milled mixtures (dashed line).

For the milled mixtures, the mean value of the final mass is 87.28% ± 0.09, in very good agreement with the expected one (87.32%). In this case the XRD powder patterns of the samples thermally treated at $T \geq 600°C$ show only the reflections of $PbTiO_3$ so meaning that in the milled mixtures the reaction between nascent PbO and TiO_2 is completed at temperatures as low as 600°C.

Therefore from combined TG/XRPD evidences it can be argued that mechanical activation does not affect the process of lead carbonate decomposition but rather it acts to ease the reaction of titanium dioxide with nascent lead (II) oxide.

As concerns the DSC traces (Fig. 1b), it can be seen that in the case of the physical mixture four endothermic peaks are present. By referring to the mass variations recorded under the peaks, it can be deduced that the first two correspond to the formation of Pb_3O_4 while the third one refers to the PbO formation. The endothermic melting of PbO appears at ≈868°C. In the case of the milled mixture the DSC traces differ with respect to those of the physical mixtures for the presence of a further endothermic peak at ≈250°C (that likely corresponds to the release of moisture intaken during milling) and of a broad exothermic peak at ≈600°C without associated mass change. Furthermore no PbO melting peak is present.

Table I summarizes the enthalpy values of the endothermic DSC peaks of pure $PbCO_3$ (unmilled and milled) and of the mixtures (physical and milled) as deduced from the total area under the signal. It appears that mechanical activation does not affect the decomposition enthalpy (ΔH_1) of pure $PbCO_3$ whereas the enthalpy of the corresponding peak is lower in the mixtures and this is more evident in the case of the milled mixture. These differences can be explained by some extent of the exothermic reaction (hidden under the endothermic peak) between TiO_2 and nascent PbO to form $PbTiO_3$. Hence mechanical activation results in an increased extent of such an "hidden" reaction and an exothermic enthalpic contribution of −14.6 kJ/mol $PbTiO_3$ results from the difference between the experimental enthalpy of $PbCO_3$ decomposition in the milled mixture and in the pure milled $PbCO_3$. The exothermic peak present in the DSC curve of the milled mixture at ≈600°C corresponds to a further share of the reaction as suggested from the fact that the XRD powder patterns of a milled sample heated just above the exothermic DSC peak (750°C) only show the reflections of $PbTiO_3$. Furthermore no PbO melting peak is present in the DSC trace of the milled mixture. By referring the enthalpy of such an exothermic thermal effect to the $PbTiO_3$ that forms under the peak, the value of −11.5 kJ/mol $PbTiO_3$ is calculated. Therefore an exothermic enthalpic contribution (−26.1 kJ/ mol $PbTiO_3$) is determined in the case of the milled mixture :it is doubtful if such an enthalpy can be assumed to correspond to the reaction $PbO + TiO_2 \rightarrow PbTiO_3$. It seems more realistic to ascribe such an excess exothermic term to the release of mechanical energy stored during milling and released in the wake of the reaction $PbO + TiO_2 \rightarrow PbTiO_3$ that takes place.

3.1.2. XRPD-HT measurements

Fig. 2 shows the XRPD patterns of a physical mixture heated up to 850°C (with XRD patterns taken every 50°C between 600 and 850°C) : it can be seen that up to 800°C excess of both reacting oxides is present. The patterns taken at 850°C show the reflections of cubic $PbTiO_3$ (high temperature phase) only. However the XRPD pattern

TABLE I DSC results on $PbCO_3 – TiO_2$ samples (physical and milled mixtures)

Sample	ΔH_1 (J/g)	$T_{max,1}$ (°C)	ΔH_1(kJ/mol $PbCO_3$)	ΔH_{exo}
$PbCO_3$ (as received)	270.5	314.9	72.3	–
$PbCO_3$ (milled)	271.5	351.6	72.6	–
$PbCO_3$-TiO_2 (physical)	186.6	311.1	66.5	–
$PbCO_3$-TiO_2 (milled)	171.3	337.9	58.0	−33.0 J/g (−11.8 kJ/mol) $PbTiO_3$

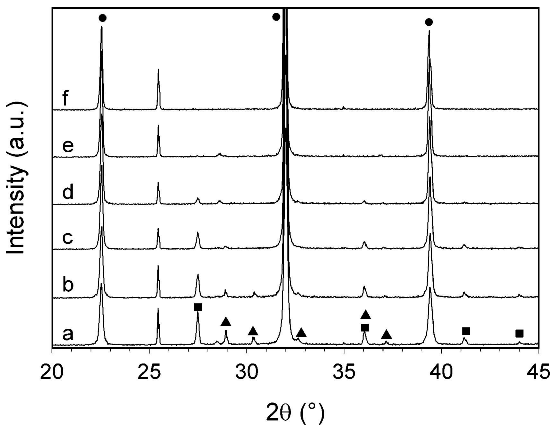

Figure 2 XRPD patterns of a $PbCO_3$:TiO_2 physical mixture taken into an environmental chamber heated at 5 K/min up to (a) 600°C (b) 650°C (c) 700°C (d) 750°C (e) 800°C (f) 850°C. The sample was kept $\approx$ 2.5 h at each temperature. Squares: TiO_2 JCPDS file no. 21-1276. Triangles: PbO JCPDS file no. 38-1477. The peaks located at $2\vartheta \approx 25°$ originate from alumina sample holder.

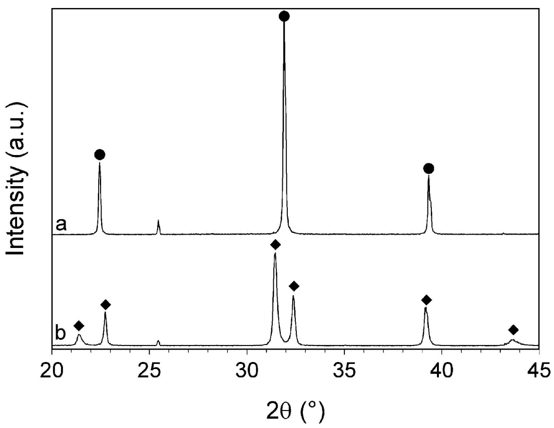

Figure 3 XRPD patterns of a $PbCO_3$: TiO_2 milled mixture taken into an environmental chamber heated at 5 K/min up to 600°C (Pattern a). Pattern (b) is of the same sample after it has been cooled down to room temperature. Lozenges: $PbTiO_3$ tetragonal (JCPDS file no. 06-0452); Circles: $PbTiO_3$ cubic (JCPDS file no.40-0099). The peaks located at $2\vartheta \approx 25°$ originate from alumina sample holder.

taken on the same sample after it was cooled down to room temperature shows also the presence of PbO and TiO_2 so indicating that the product obtained from the physical mixture at 850°C (where the sample has been kept for 2.5 h) is not stable. It could be that $PbTiO_3$ obtained in these conditions contains small amounts of pyrochlore phase ($Pb_2Ti_2O_6$) which, upon cooling, decomposes to tetragonal $PbTiO_3$ (low temperature phase) and $PbO+TiO_2$.

On the contrary, the XRPD patterns collected on a sample of mechanically activated mixture heated up to 600°C show that cubic $PbTiO_3$ (high temperature phase) is the only phase present (see Fig. 3, pattern a). The lattice parameter of cubic $PbTiO_3$ is 3.9703 ± 0.0083 Å that fairly agrees with the value of 3.9610 Å reported in JCPDS file n. 40-0099). This very same sample cooled down to room temperature shows that tetragonal $PbTiO_3$ (low temperature phase) is the stable product formed from milled mixture (see Fig. 3, pattern b). The lattice constants of this sample have been determined and the relevant values ($a = b = 3.8984 \pm 0.0017$ Å, $c = 4.1543 \pm 0.0032$ Å) show a fair agreement with those reported in the JCPDS file no. 06-0452 ($a = b = 3.8993$ Å, $c = 4.1532$ Å).

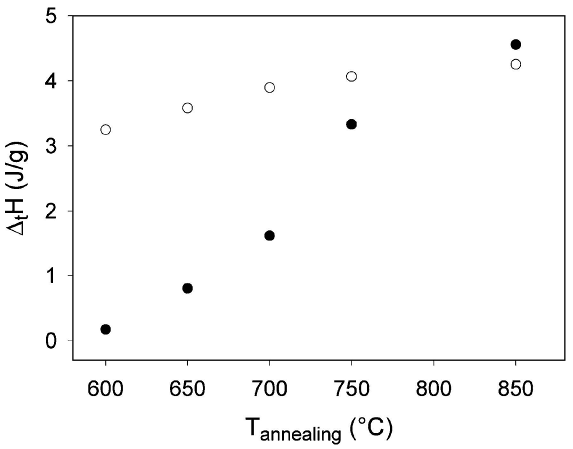

Figure 4 Enthalpy of the tetragonal – cubic transition of $PbTiO_3$ (ferroelectric anomaly) as a function of the temperature of 12 h-annealing ($T_{annealing}$). Filled circles: $PbCO_3$:TiO_2 physical mixture. Empty circles: $PbCO_3$:TiO_2 milled mixture.

The difference in the extent of $PbTiO_3$ formation has been monitored by analyzing the values of the tetragonal-cubic transition enthalpy that occurs at $\approx$490°C: Fig. 4 shows the enthalpy values determined by DSC on samples of both physical and milled mixtures previously annealed for 12 h at temperatures increasing between 600° and 850°C. The values measured for the milled mixture show only a slight increasing drift with temperature while those of the physical mixture clearly increase until, for $T_{annealing} = 850°C$, they it nearly superimpose to those of the milled mixture. This trend confirms the results obtained by XRPD experiments.

Fig. 5 shows SEM micrographs of the samples obtained from the physical mixture (annealed 24 h at 850°C under nitrogen) and from the milled one (annealed 2 h at 650°C under nitrogen). It can be observed that the particle size is strongly affected by the milling process: indeed the physical mixture contains particles as large as $\approx 5\ \mu m$ while the particles of the milled sample are of submicrometric size.

The crystal size of $PbTiO_3$ obtained from the milled mixture has been evaluated by using the Debye–Scherrer equation: a crystal size of 22.4 ± 3.8 nm has been obtained by determining the instrumental line broadening from the XRPD of a sample prepared from the physical mixture annealed 24 h at 850°C. It is reported [10] that the Curie temperature decreases by decreasing crystal size: this is confirmed in this work as the mean onset temperature of the transition peak is $480.4 \pm 0.8°C$ for $PbTiO_3$ obtained from the milled mixtures whereas it is $487.4 \pm 2.1°C$ for $PbTiO_3$ obtained from the physical mixtures.

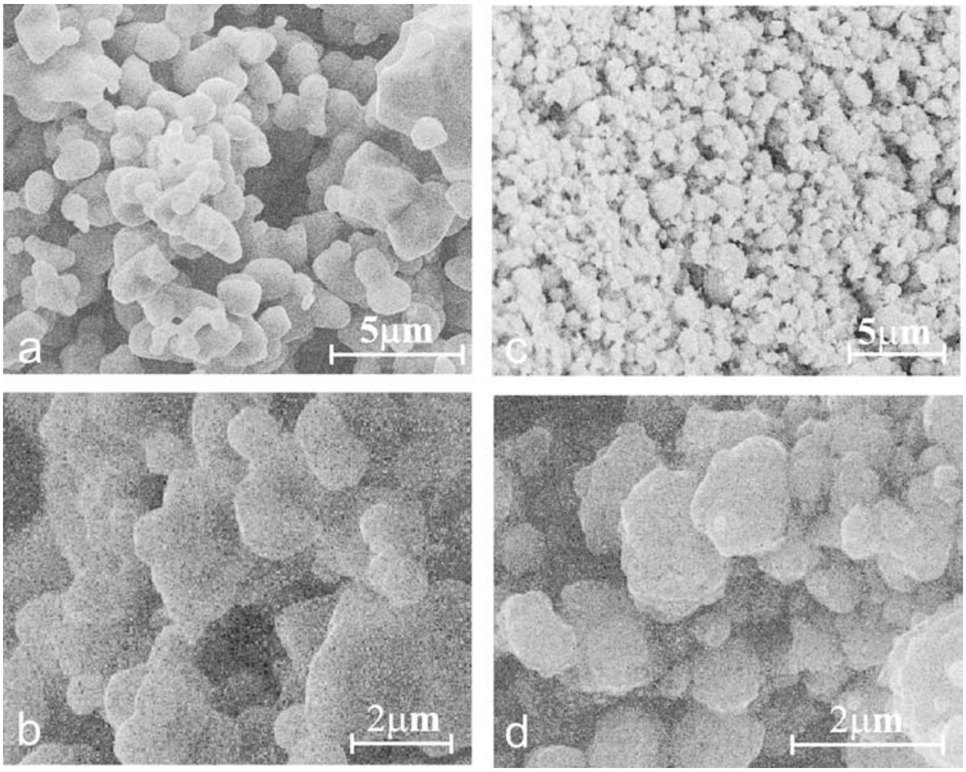

Figure 5 SEM Micrographs of (a, b) Physical mixture heated 24 h at 850°C (c, d) Mechanically activated mixture heated 2 h at 650°C.

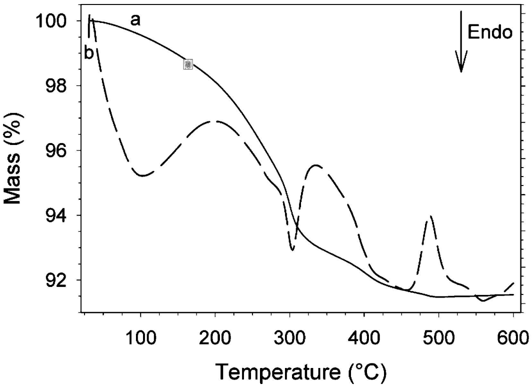

Figure 6 TG/DSC scans performed under nitrogen at 5 K/min on $PbCO_3$:$3TiO_2$ milled mixture. TG signal: full line, a; DSC signal: dashed line, b.

3.2. $PbCO_3 - 3TiO_2$ mixtures

Fig. 6 shows a TG/DSC run performed on a sample of milled $PbCO_3$-$3TiO_2$ mixture. The total mass loss value fairly agrees with the expected value (−8.68%). As concerns the DSC curve (b, dashed line), a single endothermic peak is present (instead of 3 as it was the case with the 1:1 mixture) for $PbCO_3$ decomposition and the corresponding enthalpic change, namely 50.2 kJ/mol $PbCO_3$, is lower than the corresponding value obtained in the case of pure $PbCO_3$ decomposition (72.6 kJ/mol $PbCO_3$). This difference (−22.4 kJ) can be accounted for by some exothermic process hidden under the endothermic peak. It is reasonable that such a value is connected with the formation of $PbTiO_3$ formation since it is close to the value of −26.1 kJ/mol $PbTiO_3$ obtained as the excess exothermic enthalpy when starting from the milled mixture of 1:1 composition. At higher temperatures (≈500°C) an exothermic peak is found whose enthalpy (−18.6 kJ/mol $PbTiO_3$) can be ascribed to the further reaction between $PbTiO_3$ and TiO_2 to yield $PbTi_3O_7$.

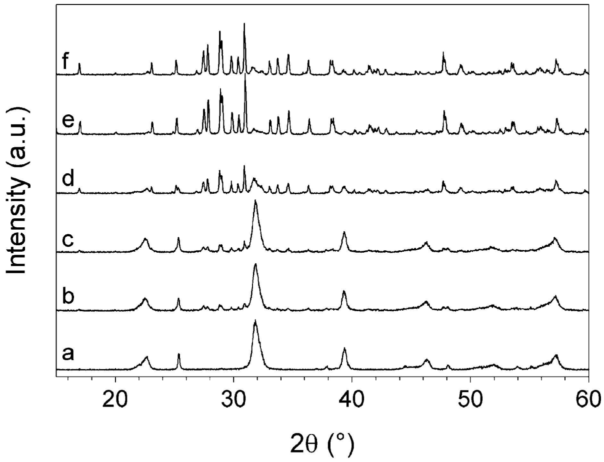

Figure 7 XRPD patterns of $PbCO_3$:$3TiO_2$ Mechanically activated mixtures annealed: (a) 12 h 700°C (b) 24 h 700°C (c) 36 h 700°C (d) 12 h 750°C (e) 20 h 800°C (f) 1 h 850°C.

Fig. 7 shows the XRD powder patterns of the milled mixtures recovered after annealing performed for different times at temperatures between 700 and 850°C. In the case of annealing at 700°C (for 12 h, pattern a) the reflections of excess TiO_2 are showing, besides other broad ones falling at angular positions between those of tetragonal (low temperature) $PbTiO_3$ and cubic (high temperature) $PbTiO_3$. By longer annealing at 700°C (24 h, pattern b - 36 h, pattern c), some reflections attributable to $PbTi_3O_7$ [11] are present. No $PbTi_3O_7$ reflections have been found in the physical mixtures treated under the same experimental conditions. By annealing at 750°C for 12 h (pattern d) the reflections of $PbTi_3O_7$ are the main ones present. The reflections pertaining to $PbTiO_3$ nearly disappear by annealing for 20 h at 800°C (pattern e) and, finally, 1 h annealing at 850°C results in nearly complete $PbTi_3O_7$ formation (pattern f). It has to be noted that again the XRPD patterns of the physical mixture (annealed under the same time/temperature of annealing) only show the reflections of $PbTiO_3$ and TiO_2. Indeed, according to [11], more than 100 h at 800°C were needed to obtain $PbTi_3O_7$ (with some impurity of $PbTiO_3$ and TiO_2). The lattice parameters of the milled sample annealed for 20 h at 800°C are: $a = 10.7241 \pm 0.0043$ Å, $b = 3.8066 \pm 0.0013$ Å, $c = 6.5762 \pm 0.0021$ Å, $\alpha = \gamma = 90$, $\beta = 98.256°$. They are in fair agreement with those reported in [11]. Further thermal experiments have been conducted by heating the milled mixtures at $T > 900°C$: it has been shown that $PbTi_3O_7$ thermal decomposition occurs that yields $PbTiO_3$ and TiO_2. However a DSC run up to 1200°C performed on the $PbTi_3O_7$ sample (prepared at 800°C) to try and evaluate the decomposition enthalpy only showed a shallow endothermic region between 1000 and 1100°C instead of a proper peak.

4. Conclusions

(i) TG measurements performed on both milled and unmilled $PbCO_3 – TiO_2$ mixtures show that the temperature range of lead carbonate decomposition is not sensibly affected by mechanical activation while DSC measurements show that the energetics of $PbTiO_3$ formation depends on the mechanical activation: indeed the milled mixtures show an exothermic peak that is related to the formation of lead titanate;

(ii) Variable temperature XRPD shows that a 2 h annealing at 600°C starting from milled mixtures leads to a complete formation of $PbTiO_3$ while temperatures higher than 800°C are needed to obtain the same result when starting from physical mixtures. This point is confirmed by the trend of the enthalpy of ferroelectric anomaly of $PbTiO_3$ as a function of the annealing temperature;

(iii) XRD line profile analysis performed by using the Debye – Scherrer equation allowed to conclude that the crystal size of lead titanate prepared from the milled mixtures is about 25 nm;

(iv) The annealing of a mechanically activated $PbCO_3$-$3TiO_2$ mixture (20 h at 800°C or 1 h at 850°C) results in nearly complete $PbTi_3O_7$ formation while the XRPD patterns of the physical mixture annealed under the same conditions only show the reflections of $PbTiO_3$ and TiO_2. The DSC analysis of the milled mixture suggests that the reaction proceeds in two steps: formation of $PbTiO_3$ and reaction of this compound with excess TiO_2 to yield $PbTi_3O_7$.

References

1. A. J. MOULSEN and J. M. HERBERT, Electroceramics (Chapman and Hall, New York, 1990).
2. K. ISHIKAWA, K. YOSHIKAWA and N. OKADA, *Phys. Rev. B* **37** (1988) 5852.
3. A. AHMAD, P. BEDARD, T. A. WHEAT, A. K. KURIAKOSE and A. G. MC DONALD, *J. Solid State Chem.* **93** (1991) 220.
4. C. E. MILLAR, L. PEDERSEN and W. W. WOLNY, *Ferroelectrics* **133** (1992) 271.
5. E. C. PARIS, E. R. LEITE, E. LONGO and J. A. VARELA, *Mat. Lett.* **37** (1998) 1.
6. K. J. STANLY, I. PACKIA SELVAM and V. KUMAR, *ibid* **40** (1999) 118.
7. J. FANG, J. WANG, L. M. GAN and S. C. NG, *ibid* **50** (2002) 304.
8. T. YU, Z. X. SHEN, J. M. XUE and J. WANG, *Mat. Chem. Phys.* **75** (2002) 216.
9. J. XUE, D. WAN and J. WANG, *Mater. Lett.* **39** (1999) 364.
10. S. G. LU, H. LIU, Y. HAN, L. ZHANG and X. YAO, *Ferroelectr. Lett.* **18** (1994) 115.
11. K. AYKAN, *J. Am. Cer. Soc.* **51** (1968) 577.

Received 2 March
and accepted 6 June 2005