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Mechanical activation of calcium titanate formation from $CaCO_3$–TiO_2 mixtures

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Complete $CaTiO_3$ formation has been found to occur in $CaCO_3$—TiO_2 (anatase or rutile) mixtures subjected to mechanical activation by high energy milling. Such formation has been demonstrated to occur by rapid heating (20 K/min) up to 1250°C. The first stage of the reaction takes place as CaO forms, the reaction, then, proceeds at higher temperatures reaching its maximum rate at about 1000°C. Alternatively $CaTiO_3$ formation can be effected by 12-h annealing of the activated mixtures at temperatures between 750 and 850°C. Partial $CaTiO_3$ formation was realized when starting from physical mixtures neither by rapid heating to 1250°C nor by 12-h annealing at temperatures as high as 1000°C.

1. Introduction

Calcium titanate, $CaTiO_3$ (CT), is one of the important basic materials of ferroelectric ceramics. $CaTiO_3$ finds application also as a thermally—sensitive resistor element due to its negative temperature coefficient and as a refractory material with high corrosion resistance [1, 2]. It is mostly prepared by mixing the precursors thoroughly and firing. The resulting powder often shows a lack of homogeneity and excessive grain growth, which results in a material with low dielectric constant [3]. Alternative synthetic routes have also been applied (oxide coprecipitation from solution [4], sol-gel processing [5], thermal decomposition of peroxo–salts [6]). The mechanochemical route presents some advantages such as a more thorough mixing of the solid precursors which eventually leads to more uniform, small sized materials produced with lower time–temperature of the firing step. In this sense, Avvakumov [7] mechanochemically synthesized $CaTiO_3$ from milled mixtures of CaO [$Ca(OH)_2$]-TiO_2 (rutile). Mi [8] obtained crystalline $CaTiO_3$ by grinding CaO—TiO_2 mixtures (both rutile and anatase) and heating them up to about 950°C but he did not report any problem with CaO hydration though having performed the milling in air. Indeed Welham [9] succeeded in synthesizing $CaTiO_3$ by milling CaO—TiO_2 (rutile) mixtures under vacuum (to avoid CaO hydration-carbonation) for times up to 100 h and by annealing them at a temperature ($\approx$ 1000°C) below that generally adopted in solid state firing (1200–1400°C). Evans *et al.* [10] monitored with variable XRPD the reaction in $CaCO_3$—TiO_2 milled mixtures and showed that pure CT is obtained at 920°C.

The present work reports the results obtained in the study of the solid state synthesis of $CaTiO_3$ starting either from milled mixtures $CaCO_3$—TiO_2 (both rutile and anatase) or from the physical ones.

2. Experimental

The physical mixtures (molar composition 1:1; 2 lots of 3 g each) of $CaCO_3$ (99%, Aldrich, Italy) and TiO_2 (99.9%, Aldrich, Italy rutile or anatase) were prepared by suspending the powders in acetone under magnetic stirring (for 3 h) and by evaporating the solvent at 40°C. The mixtures were put into agate jars (3 agate balls ϕ12 mm, ball/sample mass ratio 5:3) with 8 ml of deionized water and milled for 100 h in a high energy planetary mill (Pulverisette 7, Fritsch, Germany) at 350 rpm. Then the slurries were dried and milled again for 70 h at 400 rpm.

The heating of the mixtures was monitored by TG Analysis [SDT 2960, simultaneous TG-DTA-DSC Analyser by TA Instruments Ltd., USA] performed on samples of about 50 mg heated at 5 K/min from room temperature (rt) up to different temperatures (between 750°C and 1000°C) under N_2 flow (100 ml/min). The XRPD patterns of the samples recovered from the thermal measurements, were obtained using a Bruker D5005 diffractometer ($2\vartheta = 20 \div 65°$, Cu K_α radiation, step scan mode, step width 0.02°, counting time 3 s, 40 kV, 40 mA). DSC experiments were performed at 20 K/min on all mixture samples up to 1200°C.

3. Results and discussion

3.1. TGA experiments

Fig. 1 shows the TG curves obtained on all types of mixture. It can be seen that milling results in a mass loss

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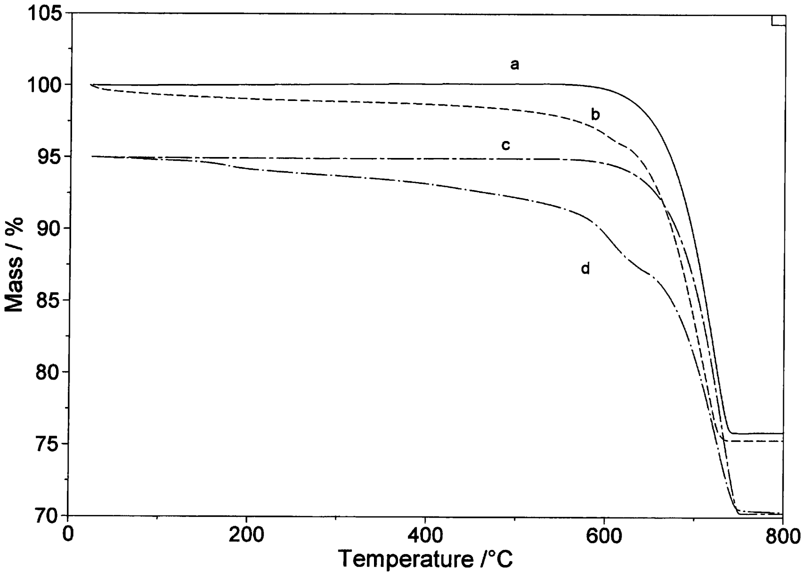

Figure 1 TG curves of physical and milled mixtures heated at 5 K/min up to 800°C: (a) rutile-based physical mixture, (b) rutile-based milled mixture, (c) anatase-based physical mixture, and (d) anatase-based milled mixture. Curves (c) and (d) have been shifted by 5% by mass downwards for clarity.

process (due to $CaCO_3$ decomposition) that, though taking place over a broader temperature range (200–750°C) than with the physical mixtures, is over at 750°C in all cases. Moreover in the milled mixtures the mass loss occurs in two stages (mostly evident in the case of the anatase-based mixture-trace d). This is likely to result from a small size fraction of $CaCO_3$ present in the mixture with the softer TiO_2 form (anatase). Table I reports the mean TG loss of the four types of mixture: it can be seen that the mass losses of the milled mixtures are only slightly larger than those of the physical ones. This is likely to be due to some moisture absorption during milling. Fig. 2 shows the XRD of the residues of the samples of Fig. 1. The samples of physical mixture (a,b) show, besides the peaks of the reacting oxides ($CaO—TiO_2$ rutile or anatase), some broad peaks (at $2\vartheta \approx 29°$, $34°$ and $51°$) that cannot be ascribed either to the reacting oxides nor to calcium titanate. Such peaks are more evident in the anatase-based physical mixture. In the case of the milled mixtures (c,d), the intensities of the reacting oxide peaks are much lower whereas the calcium titanate peaks are the more intense ones mostly in the case of the anatase-based mixture (d).

3.2. DSC experiments

Fig. 3 shows the DSC curves of all types of mixture. It can be seen that in the physical mixtures, after the endothermic peak corresponding to $CaCO_3$ decomposition, an exothermic peak is present at higher temperature in the case of the rutile-based sample. In the case of the milled mixtures an exothermic peak is showing up in the wake of the endothermic one so that, in these thermograms, neither the endothermic peak nor the exothermic one can be integrated and enthalpy data cannot be obtained. Therefore DSC runs were repeated on the milled mixtures by heating them up to 920°C, cooling down to 50°C and finally reheating to 1250°C. In the second heating the exothermic peaks are present in both mixtures. Table II resumes the enthalpies obtained from the DSC peaks of all the mixtures. The decomposition enthalpy of pure $CaCO_3$ was determined by DSC experiments performed under the same experimental conditions adopted for the mixtures: the mean of three independent runs was 1554.7 ± 23.5 J/g $CaCO_3$. The experimental endothermic enthalpies (Table II) are lower than the calculated ones for pure $CaCO_3$ decomposition. Such a difference can be attributed to the reaction between CaO and TiO_2 which is known to be exothermic (−81.02 kJ/mol CaO) [11]. By adding these differences to the enthalpies of the exothermic peak (ΔH_{exo} values in Table II), a value is obtained (ΔH_{res} values in Table II, expressed in kJ/mol $CaTiO_3$) that can be reasonably thought as being due to the reaction $CaO + TiO_2 \rightarrow CaTiO_3$. In the case of the milled mixtures (where the mass loss extent under the peak, α_{peak}, is <1) the rutile-containing sample shows an experimental endothermic enthalpy higher than the calculated one. The exothermic enthalpy is about 72% (rutile-based mixture) and about 58% (anatase-based mixture) of the expected one (−81 kJ/mol) for $CaTiO_3$ formation from the constituent oxides. However, although ΔH_{res} never attains the value of –81.0 kJ/mol, the XRD patterns of the residuals recovered after the DSC runs demonstrate that $CaTiO_3$ is the only compound obtained from both the milled mixtures whereas both CaO and TiO_2 (rutile) reflections are present, along with those of $CaTiO_3$, in the samples of the physical mixtures. Clearly a part of $CaTiO_3$ forms as CaO forms

TABLE I Mean mass loss of the four mixtures (the values are the mean of 6 independent measurements)

Mixture	ΔM (%)
$CaCO_3—TiO_2$ (R) PM	-24.18 ± 0.20
$CaCO_3—TiO_2$ (R) BM	-24.67 ± 0.65
$CaCO_3—TiO_2$ (A) PM	-24.07 ± 0.31
$CaCO_3—TiO_2$ (A) BM	-25.01 ± 0.37

(R) = rutile; (A) = anatase; PM = physical mixture; BM = milled mixture.

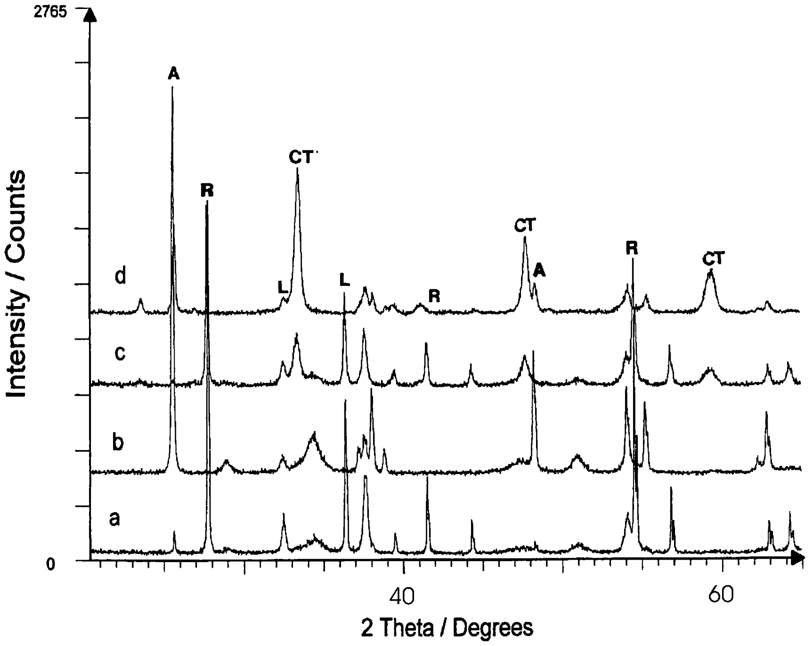

Figure 2 XRPD of the products of the TG runs of Fig. 1: (a) rutile-based physical mixture, (b) anatase-based physical mixture, (c) rutile-based ball milled mixture, (d) anatase-based ball milled mixture. A = anatase; R = rutile; L = CaO; CT = calcium titanate.

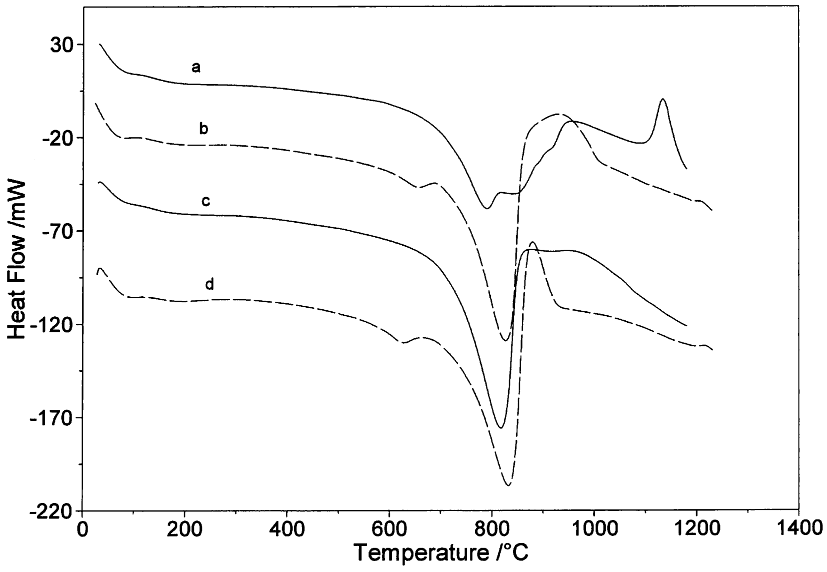

Figure 3 DSC curves of (a) rutile-based physical mixture, (b) rutile-based milled mixture, (c) anatase-based physical mixture, and (d) anatase-based milled mixture. The mixtures were heated at 20 K/min min up to 1200°C.

from $CaCO_3$ decomposition and another part at higher temperatures, namely under the exothermic peak. The situation of the rutile-containing mixture is an anomalous one: here the endothermic enthalpy is higher than the calculated one and this results from the different level of the baseline before and after the peak which, in turn, reveals an exothermic process ($CaO + TiO_2 \rightarrow CaTiO_3$) is hidden under the final stages of an endothermic one ($CaCO_3$ decomposition).

3.3. Annealing experiments

Samples of all mixtures were heated at 5 K/min up to increasing temperatures (from 750°C to 1000°C, steps

TABLE II DSC enthalpies (J/g mixture, mean of 2 independent runs) obtained from the endothermic and from the exothermic peaks (where present). See text for explanation

Mixture	α_{peak}	$\Delta H_{endo,exp}$	$\Delta H_{endo,calc}$	ΔH_{exo}	ΔH_{res}
$CaCO_3$—TiO_2(R) PM	≈1	738.9 ± 35.6	864.6	−132.7 ± 0.9	−46.5
$CaCO_3$—TiO_2 (R) BM	≈0.92	816.1 ± 80.0	793.1	−323.5 ± 2.1	−58.2
$CaCO_3$—TiO_2(A) PM	≈1	816.6 ± 26.9	864.6	–	−8.6
$CaCO_3$—TiO_2(A) BM	≈0.87	645.6 ± 10.2	754.8	−262.4 ± 1.7	−66.9

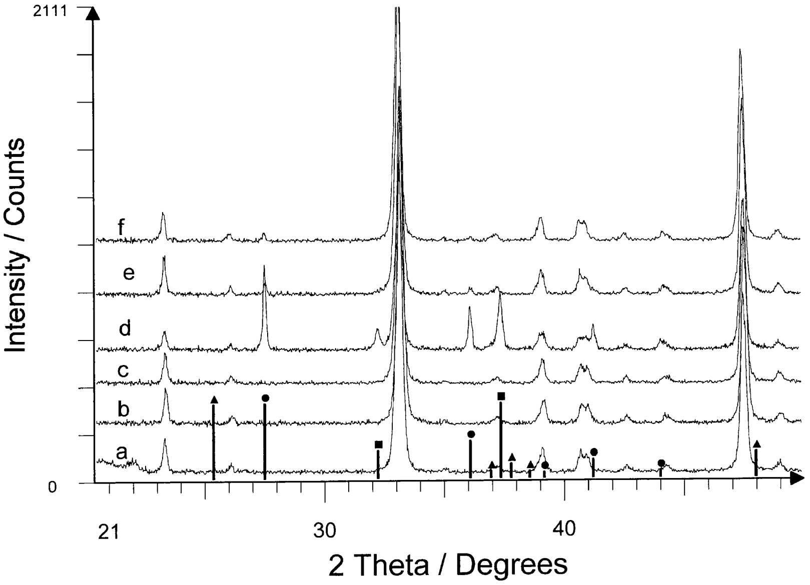

Figure 4 XRPD patterns of samples of anatase-based milled mixtures heated at 5 K/min up to 750°C (a), 800°C (b), 850°C (c) and kept at these temperatures for 12 h; XRPD patterns of samples of rutile-based milled mixtures heated at 5 K/min up to 750°C (d), 800°C (e), 850°C (f) and kept at these temperatures for 12 h. (▲) = anatase; (●) = rutile; (■) = CaO.

of 50°C) and annealed for 12 h. Fig. 4 shows some of the XRPD patterns of the samples of the mechanically activated mixtures after they were annealed. It can be seen that the anatase-based mixture, starting from that annealed at 800°C, only shows the peaks of $CaTiO_3$. The peaks of the reacting oxides are, on the contrary, present in the samples of the corresponding physical mixture subjected to the same thermal treatment. Furthermore, it has to be noted that anatase transforms into rutile by heating at 850°C (and at higher temperatures) and that only minor amounts of $CaTiO_3$ form when heating the physical mixtures. In the case of the rutile-based mixture, it can be seen that pure $CaTiO_3$ is not obtained from the milled mixture by annealing at temperature as high as 850°C. Only after 12-h annealing at 1000°C, pure $CaTiO_3$ is obtained. The reacting oxides are largely present in the samples of the physical mixture subjected to the same thermal treatment.

On the basis of the reported experimental observations, $CaTiO_3$ has been prepared by subjecting about 1 g of each milled mixture to thermal treatments of 16 h in a tubular furnace. The temperatures of treatment were 800°C for the anatase-based milled mixture and 950°C for the rutile-based milled mixture. The cell parameters (in Å) of the orthorhombic cell were $a = 5.4390 \pm 0.0015$, $b = 7.6430 \pm 0.0028$, $c = 5.3807 \pm 0.0024$ when starting from anatase and $a = 5.4380 \pm 0.0016$, $b = 7.6486 \pm 0.0028$, $c = 5.3876 \pm 0.0025$ when starting from rutile (JCPDS file number: 22-0153; $a = 5.4405$, $b = 7.6436$, $c = 5.38$).

4. Conclusions

- Complete $CaTiO_3$ formation has been found to occur in $CaCO_3$—TiO_2 (anatase or rutile) mixtures subjected to mechanical activation by high energy milling after thermal processing.
- Such a formation has been demonstrated to occur by rapid heating (20 K/min) up to 1250°C. A first stage of the reaction takes place as CaO forms and, then, the reaction proceeds at higher temperatures reaching its maximum rate at about 1000°C.
- Alternatively $CaTiO_3$ formation can be effected by a 12-h annealing of the activated mixtures at temperatures between 800°C (anatase-based sample) and 1000°C (rutile-based sample).
- $CaTiO_3$ formation was incomplete when annealing physical mixtures under identical conditions.

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