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INFLUENCE OF PROCESSING CONDITIONS ON THE THERMAL DECOMPOSITION OF $SrTiO_3$ PRECURSORS

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The present work investigates the influence of milling and calcination atmosphere on the thermal decomposition of $SrTiO_3$ powder precursors. Both pure and neodymium-modified $SrTiO_3$ samples were studied. Milling did not significantly influence numerical mass loss value, but reduced the number of decomposition steps, modifying the profiles of the TG and DTA curves. On the other hand, milling increases the amount of energy liberated by the system upon combustion of organic matter. It was also observed that the milling process, associated to the calcination in an oxygen atmosphere, considerably decreases the amount of organic matter and increases the final mass loss temperature.

Keywords: *atmosphere, milling, Pechini method, $SrTiO_3$, thermal decomposition*

Introduction

$SrTiO_3$ is a compound displaying a perovskite structure with the Pm3m space group at room temperature. Below –173°C, a transformation into a tetragonal structure occurs, with the I4/mmc space group [1, 2]. Perovskites consist in face-centered cubic structures, in which titanium displays a six-fold coordination and strontium a twelve-fold oxygen coordination [3, 4].

Single crystal strontium titanate, $SrTiO_3$, presents an important technological interest in the microelectronics industry due to its high dielectric constant, good magnetic, ferroelectric and insulating properties, wear resistance, high resistance against oxidation, and high chemical and thermal stabilities [5].

$SrTiO_3$ powders have been widely studied due to their luminescent and optical properties. The ferroelectric and dielectric properties of metal oxides with the perovskite structure are of great importance in the electronic industry [6, 7].

Intense visible photoluminescence at room temperature has recently been reported for structurally disordered perovskite titanates, $ATiO_3$, where A=Pb, Ca, Sr and Ba [8]. On the other hand, the study of luminescent properties of rare earth elements has been increasing because of their applications in optoelectronics devices and flat panel displays. These cations may be located in several crystalline matrices, such as metal oxides, metal–organic complexes and a variety of semiconductor materials [9].

Doped $SrTiO_3$ powders synthesized by the polymeric precursor method have been recently studied. The effect of magnesium or cobalt addition in the structural and thermal properties was evaluated [3, 4, 10]. This method has been successfully used for the synthesis of complex oxides, leading to powders with good stoichiometric and morphologic control. Comparing to other chemical synthesis methods, the polymeric precursor one presents the advantage of low cost, once the reagents used in larger amounts are relatively cheap and relatively low temperatures are employed [11].

The polymeric precursor method consists in the formation of a chelate between metallic cations and a hydroxycarboxylic acid such as citric acid. Later, chelate is polymerized with a polyhydroxy alcohol such as ethylene glycol, forming a precursor resin, within which cations are randomly distributed [11].

In this work, both pure and neodymium doped strontium titanate was synthesized by the polymeric precursor method. The influence of the milling of the precursor and calcination atmosphere on the thermal decomposition was evaluated.

Experimental

Titanium citrate was prepared according to procedure described in literature [12], using titanium isopropoxide (Huss HG) as precursor. For the formation

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of the resin, a certain amount of citric acid was added to the titanium citrate solution, at 90°C. 3:1 citric acid:metal ratio was used. After solubilization, neodymium oxide, Nd_2O_3 (Merck) and strontium nitrate (Vetec) were added to the solution, followed by ethylene glycol (Vetec). In this procedure 60:40 citric acid:ethylene glycol mass ratio was used.

The polymeric resin was calcined at 300°C for 1 h. After this first calcination, some powder precursor samples were submitted to a milling process in an alcoholic medium for 4 h in an attritor type mill. In some samples, a second calcination was performed in an oxygen atmosphere with a flow of 2 mL min^{-1}, at 330°C for 12 h. The precursor was de-agglomerated and calcined in oxygen again, as previously module. In each step, the powders were tested using a TA 2960 Simultaneous DTA-TGA unit, (TA Instruments, Newcastle, Delaware, USA). The experiments have been carried out from room temperature to 1000°C in air atmosphere at a flow rate of 10 mL min^{-1}, and a heating rate of 10°C min^{-1}. About 10 mg of sample were weighed in alumina crucibles.

The powder precursors were heat treated in air between 400 and 700°C for 2 h. The structural transformation was evaluated by X-ray diffraction (D-5000 Siemens). The analyses were obtained with a 0.03° step and a step time of 1.0 s, using the CuK_α radiation. Using the XRD data, the FWHM values of the (110) peak of perovskite were calculated. The lattice parameters of the unit cells were calculated using Rede 93 program, developed by Paiva Santos, based on the least square method [13]. The relative crystallinity (CR) was evaluated in order to compare the behavior of the different samples in relation to the crystallization. For the calculations the peak intensities were used, according to Eq. (1).

$$CR(\%) = \frac{I - I_0}{I_{100} - I_0} \cdot 100 \qquad (1)$$

where I=intensity of the 100% peak of the X-ray diffraction pattern, I_0=intensity of the 100% peak of the least crystalline sample, and I_{100}=intensity of 100% peak of the most crystalline sample.

Infrared spectroscopy analyses were performed in a BOMEM model MB-102 spectrophotometer. The spectra, using KBr tablets, were determined in the range of 2000–400 cm^{-1}.

Results and discussion

TG curves as well as the corresponding mass loss table of the unmilled precursors are given in Fig. 1a and Table 1. They indicate four thermal decomposition steps. In the first step, the precursors loose water and of some surface adsorbed gases. Most of the organic matter is eliminated in the second and third steps. The fourth step is ascribed to the carbonate elimination. The increase of the amount of Nd^{3+} slightly reduces the extent of mass loss.

The DTA curves for these same samples before milling are in Fig. 1b. There is one endotherm peak between 69 and 83°C, related to the loss of water and adsorbed gases. Another one is between 600 and 605°C, attributed to the elimination of carbonates. Among them two exothermic peaks are noticed, the first is between 345 and 356°C and the second is between 443 and 500°C (Table 1). These two peaks are ascribed to the combustion of organic material, which are characteristic to the synthesis process.

Table 1 TG results related to carbon decomposition in powder precursors before milling

Sample	2nd step		3rd step		4th step	
	T_{max}*/°C	Δm/%	T_{max}/°C	Δm/%	T_{max}/°C	Δm/%
undoped	356	17.7	472	42.4	568	3.7
1% Nd	342	24.0	453	39.3	599	3.4
4% Nd	349	20.7	454	39.7	592	4.0
8% Nd	359	10.4	457	42.1	588	5.6

*T_{max} values correspond to DTG peak temperature

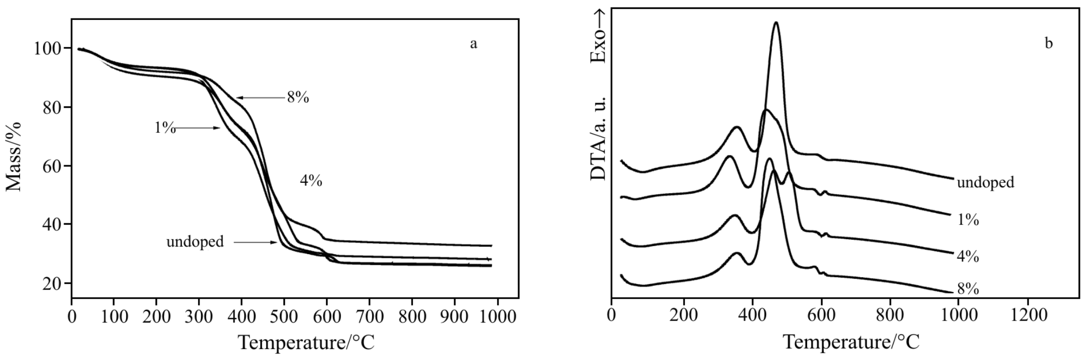

Fig. 1 a – TG and b – DTA curves of the powder precursors of pure and Nd doped $SrTiO_3$ before milling

Table 2 TG results related to carbon decomposition in powder precursors after milling

Sample	2nd step		3rd step	
	T_{max}*/°C	Δm/%	T_{max}/°C	Δm/%
undoped	340	56.0	623	4.9
1% Nd	314	24.0	610	3.9
4% Nd	320	53.0	599	5.0
8% Nd	315	54.1	626	4.8

Table 3 DTA peak temperatures for the powder precursor, before (BM) and after milling (M)

Sample	2nd peak/°C		3rd peak/°C		4th peak/°C	
	BM	M	BM	M	BM	M
undoped	351	338	469	N.O.	604	631
1% Nd	350	346	454	446	608	604
4% Nd	347	338	483	432	603	616
8% Nd	355	341	454	432	598	604

N.O.=not observed

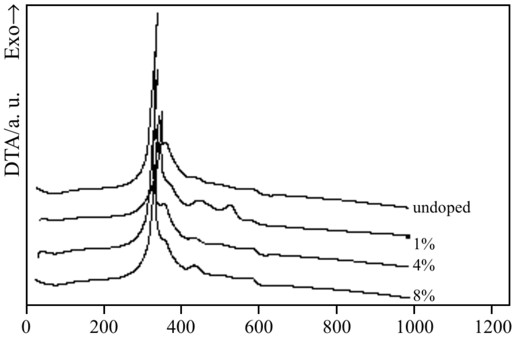

Fig. 2 DTA curves of the powder precursors of pure and doped SrTiO$_3$, after milling

Feitosa *et al*. synthesized SrTiO$_3$, in which Sr was partially substituted by Mg [3] or Co [4]. The authors reported that two thermal decomposition steps were observed in the TG curves, as well as exothermic and endothermic peaks in the DTA curves. In another work, Ti was substituted by Co and five decomposition steps were noticed in the TG curves. The DTA curves showed four exothermic peaks [10].

Milling does not influence meaningfully the mass loss values, but decreases the number of decomposition steps from four to three. Similarly to the precursor before milling, the first step is related to the elimination of water and adsorbed gases; the second one is related to organic material combustion; and the third one to carbonate elimination, Table 2.

It should be stressed the behavior observed in the TG/DTA profiles of the milled precursors (Figs 2 and 3a). The high amount of energy eliminated during combustion process leads to a loop in DTA curves. As a consequence, TG curves become discontinuous, with a small temperature decrease at the same temperature interval.

It may also be observed that DTA peaks are sharper and appear at lower peak temperatures than in case of precursors before milling (Table 3). These results indicate that milling leads to a more homogeneous particle size distribution and to a smaller particle size. This way, a higher specific surface area is in contact with oxygen, increasing the amount of energy evolved during the combustion. The smaller temperatures observed may also be ascribed to the higher reactivity toward oxygen, after milling. Two exothermic peaks at around 500 and 580°C are not presented in Table 3. They are also related to the combustion of the organic matter. The peak regarding the carbonate elimination is observed at higher temperatures.

After milling and calcination in oxygen atmosphere, a smaller mass loss (11%), and less decomposition steps are observed (Fig. 3a). Conversely, the final mass loss temperature increases, indicating the presence of refractory carbonates (endothermic reaction). The TG curves indicate that about 6% of carbonate is still present after calcination in oxygen. This amount is similar to the milled and unmilled samples. As it is displayed in Fig. 3b, the DTA peak temperature agrees with the mass loss in the TG curve. Similar results were obtained for doped samples.

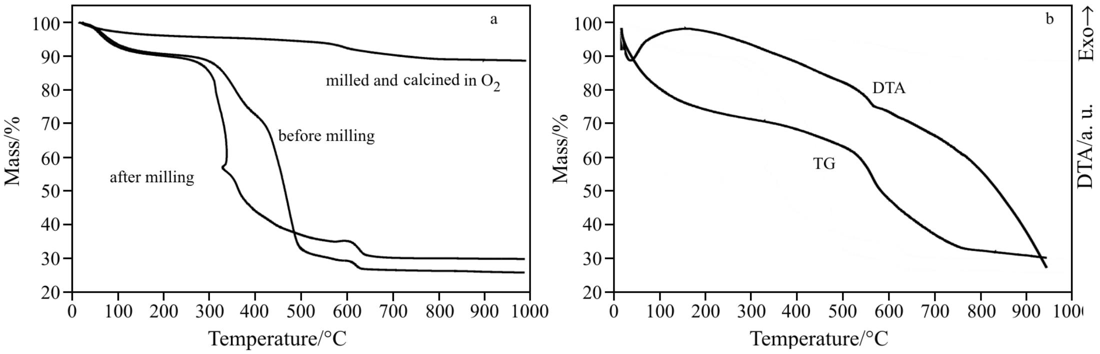

Fig. 3 a – TG curves of the powder precursors for pure SrTiO$_3$; b – TG and DTA curves of the powder precursors of SrTiO$_3$ with milling and calcination in oxygen atmosphere

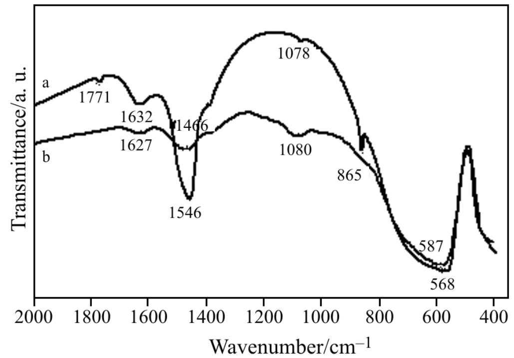

Fig. 4 Infrared spectra of the $SrTiO_3$ powder, after milling; a – after calcination in an oxygen atmosphere at 330°C for 24 h, followed by b – calcination at 700°C for 2 h

The infrared spectrum (Fig. 4) of the heat treated precursor in oxygen presents one band at 1770 cm^{-1}, that can be assigned to C=O stretching of the ester. The band at 1630 cm^{-1} can be assigned to the COO stretching mode for a unidentate complex. The bands at about 1460, 1080 and 860 cm^{-1} can be assigned to carbonate [14]. This result is in agreement with the TG/DTA findings, indicating that carbonates are present even when the sample is calcined in oxygen. Ester band disappears upon calcination at 700°C, while the other bands remarkably reduce their intensities. On the other hand, a band at 1080 cm^{-1} is observed, indicating that hydroxyls are present on the surface of the material. The wide band between 800 and 500 cm^{-1} indicates the organization of the system, being related to the metal–oxygen bond (Nd–O, Ti–O and Sr–O).

The X-ray diffraction patterns show that the system contains strontium carbonate, $SrCO_3$, and anatase, TiO_2, as secondary phases at 330°C temperature (Fig. 5a). However, the intensities of these $SrCO_3$ and TiO_2 peaks decrease with the increase of the calcination temperature (Fig. 5b). The high crystallinity observed at 330°C is attributed to the easy cation organization in the structure, since the sample is almost free of organic matter.

The relative crystallinity meaningfully increases between 500 and 600°C, indicating the decrease in the amount of amorphous material (Fig. 6a). On the other hand, the FWHM values decrease at this temperature range, indicating a much longer range of periodicity. The unit cell is smaller than the theoretical one, with small changes as calcination temperature increases (Fig. 6b).

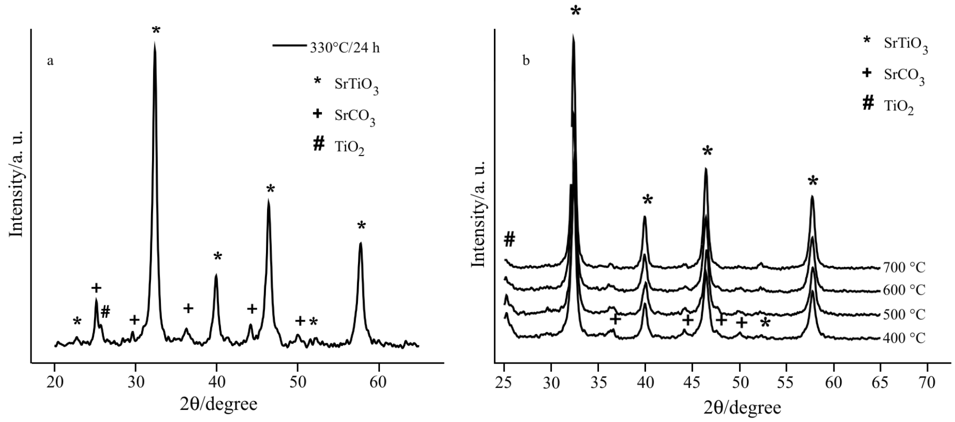

Fig. 5 XRD patterns of the $SrTiO_3$ powder, after a – milling and calcination in oxygen atmosphere at 330°C, followed by b – calcination between 400 and 700°C

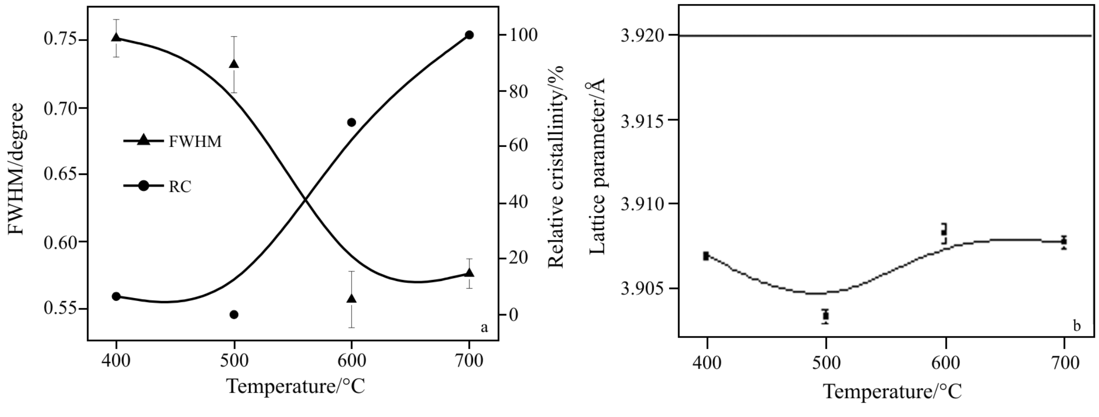

Fig. 6 a – Relative crystallinity and FWHM; b – lattice parameter of the $SrTiO_3$ as a function of temperature

Conclusions

The present work investigated the influence of milling and calcination atmosphere on the thermal decomposition of $SrTiO_3$ powder precursors. Both pure and neodymium-doped $SrTiO_3$ samples were studied.

The mass losses of the powder precursors are due to the elimination of (*i*) water and of some gases adsorbed on the surface of the material, (*ii*) organic matter and (*iii*) CO_2 from strontium carbonate decomposition. The high energy milling reduces the number of mass loss steps and increases the amount of energy liberated from the system upon the elimination of organic substance, which takes place at a lower temperature, as evidenced by the DTA curves.

The high energy milling, associated to the previous calcination of the precursor powders in oxygen atmosphere, reduces considerably the amount of mass loss, indicating that the oxygen atmosphere accelerates the decomposition of the organic matter. Conversely, it increases the final mass loss temperature, indicating a higher difficulty for the elimination of carbonates.

With regard to the presence of carbonate the TG, XRD and FTIR experiments are in agreement that milling and heat treatment in oxygen the removal of carbonate did not succeed completely. Based on TG curves the presence of about 6% of carbonate is estimated at 700°C.

The high crystallinity of the compound as low temperature as 330°C is due to the easy cation organization in the structure, since the sample is almost free of organic matter. As it is expected the increase of the calcination temperature favors the crystallization of the material.

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