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Influence of Polymerization on the Synthesis of $SrTiO_3$: Part I. Characteristics of the Polymeric Precursors and their Thermal Decomposition

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Abstract: The influence of polymerization on the thermal decomposition of polymeric precursors and phase formation was investigated during synthesis of $SrTiO_3$. The precipitation of polymeric precursor in acetone produced a more thermal stable precursor with lower weight loss during decomposition. This more stable precursor retarded the formation of the $SrTiO_3$ phase. From thermal analysis, XRD and FT-IR the presence of an intermediate phase during decomposition of the precursors was observed. This is a mixed (Sr,Ti) carbonate phase with the proposed composition of $Sr_2Ti_2O_5.CO_3$.

1 INTRODUCTION

In the past few years a growing interest was observed in ceramics based on mixed-cation oxide, mainly for the electronic ceramic industry. The processing of homogeneous polycation ceramics required the development of chemical methods such as sol-gel,[1,2] citrates and oxalates precipitation,[3,4] polymeric precursors,[5,6] etc. These methods allow the synthesis of ceramic powders with strict control of stoichiometry, good sinterability, as well as good control of particles and agglomerates morphologies.

The conventional method of mechanical mixing of TiO_2 and $SrCO_3$ for $SrTiO_3$ synthesis and other titanates requires high calcination temperatures (1000–1100°C) leading to powders with low sinterability. Moreover the method has other inconveniences such as low control of stoichiometry and phase formation. Several chemical routes have been suggested for synthesis of this titanate. However the distinct chemical behavior of Ti and Sr in solution can lead to some problems such as cation segregation[8] and stoichiometry deviation.[7] Hydroxide coprecipitation is not an indicated technique for $SrTiO_3$ and $BaTiO_3$ synthesis since the Ti^{4+} and Sr^{2+} show hydrolysis in different pHs. Moreover the condensation reaction of Ti–OH groups is fast in basic medium (which is the precipitation condition for $Sr(OH)_2$) leading to formation of $TiO_2.xH_2O$ agglomerates.[8] To avoid the formation of Ti–O–Ti type bonds the Ti cations should be complexed with organic groups. Then chemical methods indicated for synthesis of titanates are those based on the complexation of citrates, oxalates, sol–gel and polymeric precursors.

The chemical synthesis based on polyesters obtained from citrates was developed by Pechini[9] and is intensively used for synthesis of several polycations oxides,[5,6] including $SrTiO_3$.[10,11] This method is based on chelation or complexation of cations by hydroxycarboxylic acid such as citric acid. The source of cations can be diverse. The chelation process occurs during the mix of cations and citric acid in aqueous solution. This solution,

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with no particle in suspension, is mixed with a glycol such as ethylene glycol and heated up to 90–100°C until complete water elimination. The polymerization occurs at 130–140°C through the polyesterification reaction among citrate salt and ethylene glycol. Thus the formation of transparent solid polyester resin with no phase segregation is observed in this condition. The general idea of this method is to obtain a random distribution of cations at atomic level in a solid resin. After this stage the polyester is decomposed to eliminate the excess of organic material and the cation is oxidized to form the desirable stoichiometric phase.

The disadvantages of polymeric precursor-based methods are the large amount of weight loss and the formation of strong agglomerates during calcination. The decomposition of organic material during calcination can provide additional combustion heat leading to formation of partially sintered agglomerates. Then the reduction of weight loss as well as the control of the precursors thermal decomposition is fundamental for the improvement of this method.

Two mechanisms have been proposed to explain the decomposition of polymeric precursors or mixed citrates during the synthesis of barium or strontium titanates. Hennings and Mayr[12] studied the decomposition of Ba and Ti citrates and concluded that the compound $BaTi(C_5H_6O_7)_3.6H_2O$ is decomposed in several stages until $BaCO_3$ and TiO_2 is formed at a temperature range of 360–500°C. In this way the process does not lead to cations mixing at atomic level but produces extremely fine particles of $BaCO_3$ and TiO_2 that react to form $BaTiO_3$ at temperatures around 800°C.

Kumar *et al.*[13] studied the decomposition of Ba and Ti polymeric precursors, obtained by the Pechini process, and concluded that there is an intermediate phase during the decomposition of the precursor. This phase is highly disordered. On the basis of thermal analysis, X-ray diffraction and Raman spectroscopy it is concluded that the compound is barium and titanium oxycarbonate with a stoichiometry close to $Ba_2Ti_2O_5CO_3$. The $BaTiO_3$ is directly obtained by endothermic decomposition of this compound. Since these authors did not find evidence of $BaCO_3$ or TiO_2, the mixing of cations in the atomic level was still present during the thermal decomposition.

Similar results were obtained by Cho *et al.*[14] for thermal decomposition of Sr and Ti polymeric precursors obtained by the Pechini method. On the basis of X-ray diffraction and infrared spectroscopy these authors identified a carbonate phase at 530°C. They did not find evidence of crystalline phases of $SrCO_3$ and TiO_2. The composition of carbonate phase was suggested to be $Sr_2Ti_2O_5.CO_3$. The $SrTiO_3$ is obtained from the decomposition of this mixed carbonate.

The objective of the present study is to analyze the influence of the precursor polymerization during the synthesis of $SrTiO_3$. In Part I the influence of the precursor preparation route on thermal decomposition and phase formation is reported. In Part II the influence of the precursor preparation route on the morphology of $SrTiO_3$ particles will be analyzed.

2 EXPERIMENTAL PROCEDURES

2.1 Chemical synthesis

The materials used for $SrTiO_3$ synthesis as well as the sources are described in Table 1. The synthesis was based on the Pechini method. From titanium isopropoxide the titanium citrate solution was prepared with a concentration of 0·0510 ± 0·0005 grams of TiO_2 per gram of solution. This solution has a ratio of citric acid to TiO_2 of 2·12 (by mol) and a ratio of citric acid to ethylene glycol of 60/40 (ratio in mass). $SrCO_3$ was dissolved in this solution until the ratio of Sr/Ti reached 1·0 (ratio in mol). This new (Sr,Ti) solution has a citric acid to ($SrO + TiO_2$) ratio of 1·24 (by mol), keeping the citric acid to ethylene glycol ratio of the titanium citrate starting solution.

From this (Sr,Ti) solution two different preparation routes for the polymeric precursors were considered as shown in the flow chart of Fig. 1.

Route 1 (R1) is the traditional Pechini method[9] with polymerization and formation of rigid and porous foam at 250°C, followed by milling of this foam and calcination for different temperatures and times. Route 2 (R2) is a newly developed route in which powder precursor is obtained after the precipitation of water polymer solution in acetone. The volume ratio of polymer water solution and acetone was 2/1. The acetone was chosen for precipitation because its low polarity related to water. After precipitation a white particle solid was obtained. This powder precursor was treated at 250°C for 3 h, followed by milling and calcining at different temperatures and times. To under-

Table 1. Raw materials used in the $SrTiO_3$ synthesis

Raw material	Source
Titanium isopropoxide	Aldrich Chemical Co., Wisconsin, USA
$SrCO_3$	Riedel de Haen A. G.
Citric acid	Merck
Ethylene glycol	Merck

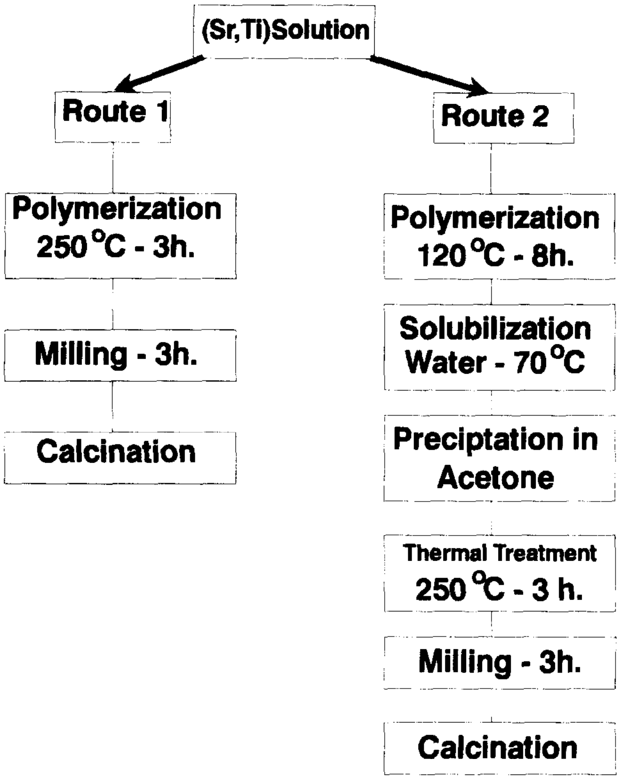

Fig. 1. Flow chart used for polymeric precursors preparation.

stand the phase formation during the thermal decomposition a titanium solution was prepared and polymerized at 250°C, followed by milling and calcining at several temperatures.

2.2 Characterization methods

To analyze the phase formation from the (Sr,Ti) precursor decomposition the following were used: X-ray diffraction (XRD) (with Cu Kα radiation), infrared spectroscopy (FT-IR) (using KBr pellets), and thermal gravimetric analysis (TGA) in air atmosphere. To characterize the polymeric precursors obtained by routes R1 and R2 infrared spectroscopy (FT-IR) (using KBr pellets), differential scanning calorimetry (DSC) (in nitrogen atmosphere with 10 ml/min flux), and nuclear magnetic resonance with spin magic angle (MAS-NMR) of carbon C_{13} (with a spectrometer of 300 MHz) were used. To help the TGA and MAS-NMR analysis polyester resin samples were prepared by reacting citric acid and ethylene glycol (mass ratio 60/40) at 120°C, named in this study pure polymer. A Ti solution was also polymerized at 120°C for 8 h.

To verify the possible cations segregation in the synthesized precursors by routes R1 and R2 scanning electron microscopy (SEM) with X-ray microanalysis by dispersive energy (EDS) was used. The precursors obtained from routes R1 and R2 were covered with a thin layer of carbon to avoid static charge. A line scan analysis was used to verify the concentration of Ti and Sr.

3 RESULTS AND DISCUSSION

3.1 Characterization of polymeric precursors

Figure 2 shows the infrared spectrum of the precursor processed by route R2 (precipitated). The vibrations of OH groups bonded to the polymer (3430 cm^{-1}) and vibrations of CH–CH_2 groups (2954 cm^{-1}) are observed in this figure. Vibrations at 1730 and at 1210 cm^{-1} related to C=O stretching mode for the ester (R-COO-R) are also observed. The complexation of Ti and Sr metallic cations can be analyzed by vibrations at 1640 cm^{-1}, 1560 cm^{-1} and 1400 cm^{-1}. The vibration at 1640 cm^{-1} is characteristic of a COO^- stretching

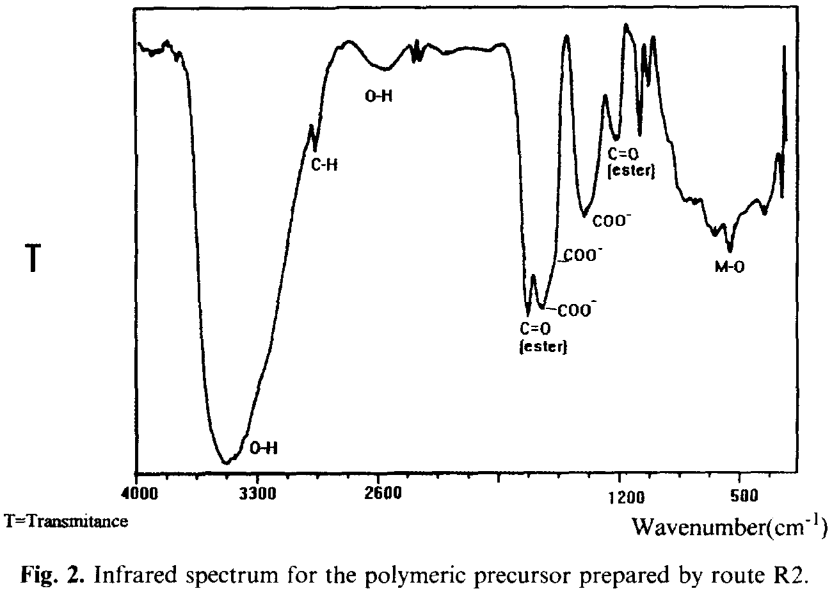

Fig. 2. Infrared spectrum for the polymeric precursor prepared by route R2.

mode for a unidentate complex and the vibrations at 1560 cm^{-1} and at 1400 cm^{-1} are related to a COO^- stretching mode for a bidentate complex.[15] Below 650 cm^{-1} vibrations associated with metal oxygen stretching are observed. The polymer prepared by route R1 showed an infrared spectrum similar to that shown in Fig. 2.

The C_{13} MAS-NMR spectrum of the precursors containing Ti(a) and those obtained by routes R1(b) and R2(c) are shown in Fig. 3. The spectrum of Fig. 3(a) shows an intensive signal related to CH_2–CH_2 carbon groups (chemical shift in the range of 64 ppm), quaternary carbons at 74 ppm and a COO^- group in the range of 170 to 190 ppm. The shoulders indicated by A and B suggest the existence of more than one CH_2–CH_2 and COO^- group. The spectrum of Fig. 3(b) shows essentially the same signals as Fig. 3(a). However the signal due to quaternary carbon is divided into two signals, one at 75 ppm and the other at 88 ppm. The signal of carbon for the COO^- group is divided into three different signals: one at 171 ppm, another at 174 ppm and the third at 184 ppm. For the group CH_2–CH_2 it is defined by two signals, one at 61 ppm and the other at 64 ppm and a shoulder indicated by the letter C. The analysis of this spectrum indicates the existence of two quaternary carbons, one associated to the Ti citrate (75 ppm) and the other associated to Sr citrate (89 ppm) and three different COO^- groups, indicating carboxylic groups bonded to Sr and Ti (174 and 171 ppm) and to an ester group (R–COO–R) formed during polymerization of ethylene glycol (185 ppm).

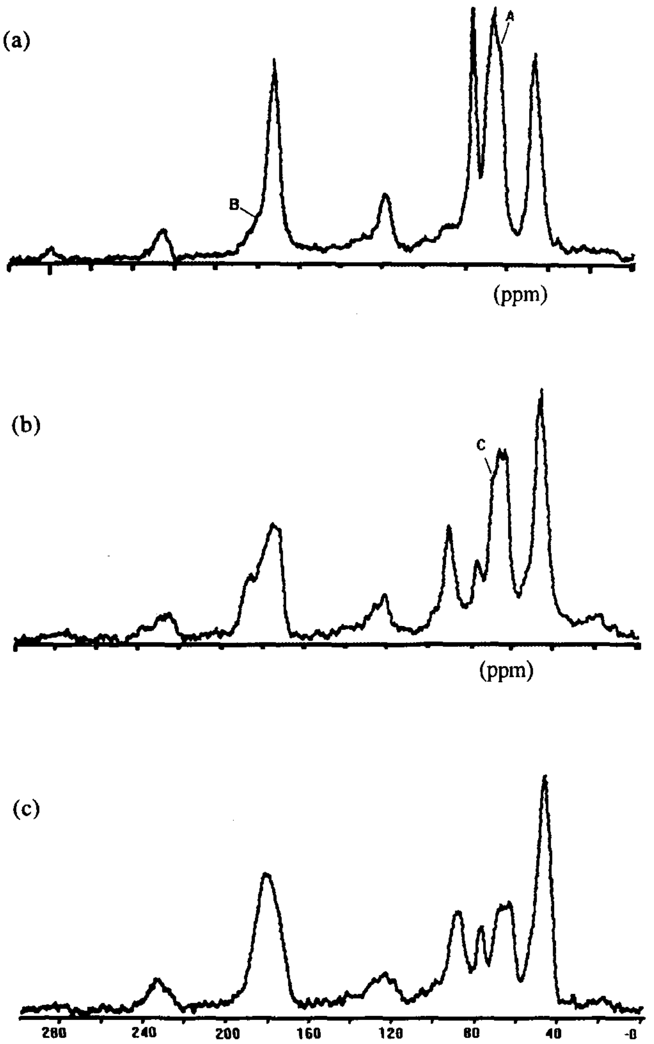

Fig. 3. MAS-NMR spectrum of C_{13}: (a) Ti-polymeric precursor; (b) polymeric precursor from route R1; and (c) polymeric precursor from route R2.

Figure 3(c) shows the spectrum of the precursor prepared by route R2 and a difference between this spectrum and the spectrum of the precursor prepared by route R1 (Fig. 3(b)) can be observed. In this spectrum the same quaternary carbon with no chemical shift and only one signal for the COO^- group at 180 ppm is observed. Another difference in these spectra is the intensity decrease of the signal for the CH_2–CH_2 group of the precursor obtained by route R2. This signal comes from the ethylene glycol.

The results of the MAS-NMR showed differences between the precursors processed by the two routes with a strong difference in the signal intensity of the CH_2–CH_2 group. The higher intensity of this signal in the precursor processed by route R1 can be related to the excess of ethylene glycol.

For a complete reaction among ethylene glycol and citric acid it is necessary to have the same amount of equivalent mass for both reagents. Defining equivalent mass (*EM*) as:

$$EM = m/f \qquad (1)$$

where m and f are respectively mol and functionality of each reagent. Then for citric acid EM is equal to 49·3 (functionality 4) and for ethylene glycol EM is equal 31 (functionality 2). Considering 100 parts of ethylene glycol (P_{EG}), the amount of parts of citric acid (P_{CA}) for an equimolar reaction is given by:

$$P_{CA} = P_{EG} \cdot EM_{CA} \qquad (2)$$

where EM_{CA} is the equivalent mass of the citric acid. Then it is necessary for 158·9 parts of citric acid to react with 100 parts of ethylene glycol. This is equivalent to the relation in mass of 61·4% to 38·6% close to the relation 60/40 used in this work. However with complexation of cations by citric acid there is a decrease in the functionality of citrate increasing the value of EM. This implies that less amount of ethylene glycol is necessary for an equimolar reaction. However the relation 60/40 of citric acid to ethylene glycol was kept during all

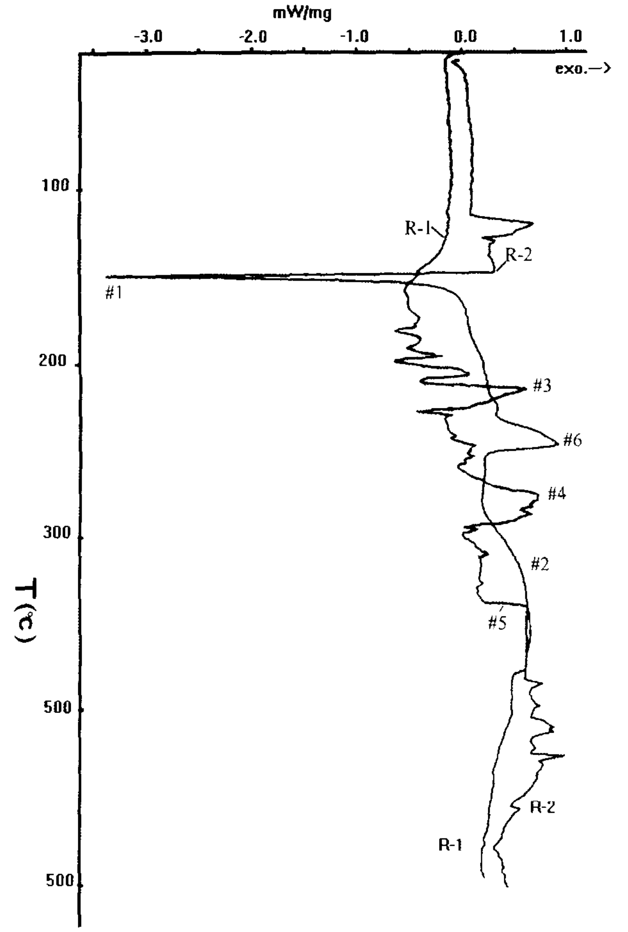

Fig. 4. DSC thermogram of the polymeric precursors obtained by routes R1 and R2. Heating rate of 10°C/min in nitrogen atmosphere.

syntheses and as a consequence an excess of ethylene glycol remained.

The SEM-EDS analysis of the precursors processed by both routes R1 and R2 showed a homogeneous distribution of Sr and Ti, indicating that during the synthesis no cation segregation occurred.

Figure 4 shows the thermal behavior of the precursors processed by routes R1 and R2 analyzed by DSC at a heating rate of 10°C/min. In this figure different behavior for both precursors that would be expected due to differences observed in NMR is observed. Several exothermic transformations in the precursor R1 for temperatures higher than 200°C are observed. The difference in energy for the transformation (#3) at 212°C is 44·1 J/g. The exothermic transformation (#4) at 275°C releases 86·2 J/g and the transformation (#5) at 340°C releases 190 J/g. For the precursor processed by route R2 an endothermic transformation (#1) at 148°C with energy variation of 81·3 J/g is observed, and two exothermic transformations at 247°C (#6) with release of 57·5 J/g and at 280°C (#1) with a release of 39·6 J/g. The endothermic transition #1 related to the precursor R2 was not observed during cooling and further heating, indicating that this reaction is not reversible. This is probably a reticulation reaction among the chain macromolecules. This reaction was not observed in the precursor processed by the route R1. The exothermic transformations #4 and #5 of the precursor R1 and #2 of the precursor R2 should be associated to the thermal degradation of the precursors. The exothermic transformations #3 of precursor R1 and #6 of the precursor R2 should be associated to the coordination change of the Sr and Ti cations by the carboxylic groups.

3.2 Phase formation

Polymeric precursors R1 and R2 were heat treated at 250°C for 3 h and calcined in air at different temperature and time. Figure 5 shows XRD patterns of precursors R1 and R2 after calcining at 350°C for 3 h. The amorphous nature of these precursors after calcination is observed. The infrared spectrum of these precursors is shown in Fig. 6. Spectrum (a) refers to precursor R1 and spectrum (b) refers to precursor R2. The vibrations at 1567 cm^{-1} and 1406 cm^{-1} are related to cation coordination by carboxylic groups in the form of a bidentate complex. Vibrations in the region 1360–1070 cm^{-1} and a strong band in the

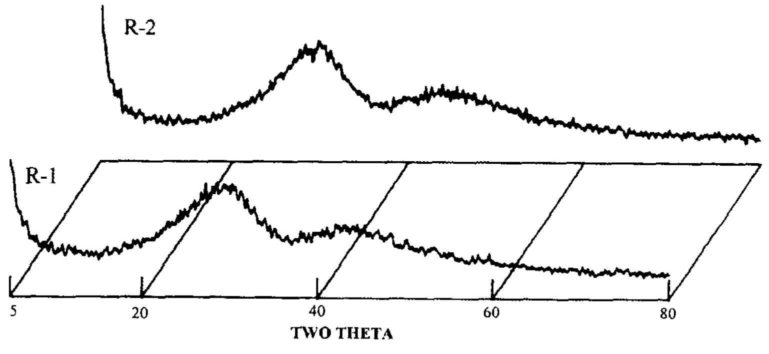

Fig. 5. XRD patterns of the polymeric precursors processed by routes R1 and R2 after calcination at 350°C for 3 h.

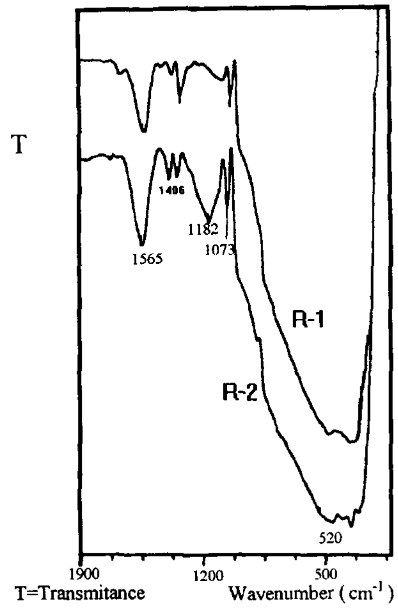

Fig. 6. FT-IR spectra of the polymeric precursors processed by routes R1 and R2 after calcination at 350°C for 3 h.

region of 500 cm^{-1} related to metal–oxygen stretching are also observed. The stretching at 1730 cm^{-1}, related to ester groups, and at 1640 cm^{-1} related to COO$^-$ stretching of unidentate complex were not observed. This demonstrates that at this temperature the polyester was decomposed and the monodentate bonds were broken.

Figure 7 shows the infrared spectrum of precursors R1 and R2 after calcination at 450°C for 3 h. Similar vibrations between the precursors are observed, with an intense band at 1450 cm^{-1} and bands less intense at 1770 cm^{-1}, 1073 cm^{-1}, and at 850 cm^{-1}. These vibrations are characteristic of CO_3^{-2} carbonate groups.[15] In the region of M–O stretching the definition of two bands are observed, one in the region of 560 cm^{-1}, which is typical of Ti–O stretching where Ti^{4+} cations are octahedrally coordinated.[16] The vibrations at 560 cm^{-1} and 370 cm^{-1} are typical of metal–oxygen stretching in titanates.[16,17] These spectra indicate the presence of $SrTiO_3$ phase and the change of the cations coordination from carboxylic groups to carbonate groups. The phase $SrTiO_3$ is confirmed in the XRD patterns of Fig. 8. In these patterns the evolution of the phase formation for precursors R1 and R2, calcined at 450°C for 1, 3 and 9 h is observed. In these diffractograms the presence of $SrTiO_3$ and an unknown phase (C) in precursor R1 after 1 h of calcination is observed. For the precursor R2 only the unknown phase (C) for the same calcination period was observed. The infrared spectrum of the precursor R2 after calcination at 450°C for 1 h shows only vibrations related to carbonate groups and a single strong band in the region of metal–oxygen stretching.

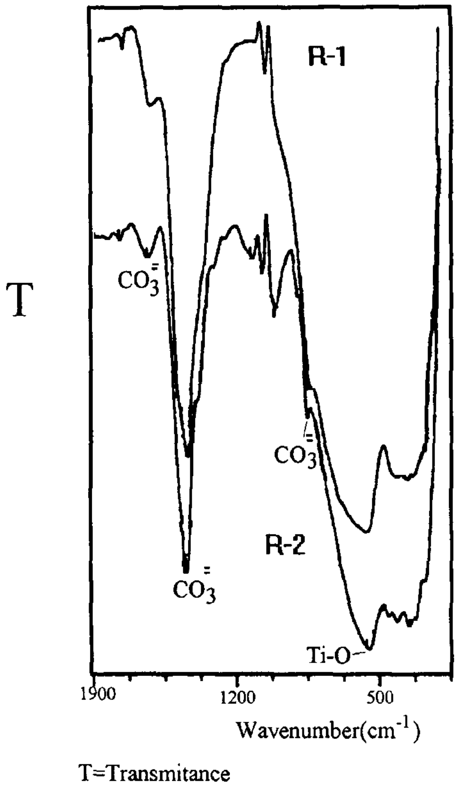

Fig. 7. FT-IR spectra of the polymeric precursors processed by routes R1 and R2 after calcination at 450°C for 3 h.

The vibration characteristic of the titanate phase is not well defined during this calcination period. Increasing the calcination time to 3 and 9 h the increase in the intensity of the $SrTiO_3$ phase and the intensity of the phase C for both precursors R1 and R2 (Fig. 8) is observed.

The analysis of the above results indicates that the decomposition of precursor R1 starts before precursor R2. Moreover the $SrTiO_3$ phase comes from the decomposition of the C phase. Considering the results of the infrared spectra for both precursors it is possible to conclude that the C phase must be a carbonate phase.

XRD results of phase C were indexed and Table 2 shows main values for this phase as well as XRD results of TiO_2 (anathase) and $SrCO_3$ phases. From this table it is possible to conclude that the C phase is not TiO_2 or $SrCO_3$. Other arguments that support this conclusion were given by the following experiment. A Ti citrate solution with ethylene glycol was polymerized and decomposed in the same way as in the route R1. Figure 9 shows the XRD pattern after calcination at 350°C and 450°C for 3 h. It is observed that only the anathase phase exists at 350°C while anathase and rutile coexist after calcination at 450°C. Only the amorphous phase in the XRD pattern for the decomposition of both precursors R1 and R2 at 350°C is observed. Thus the phase C is not related to any TiO_2 crystalline phase.

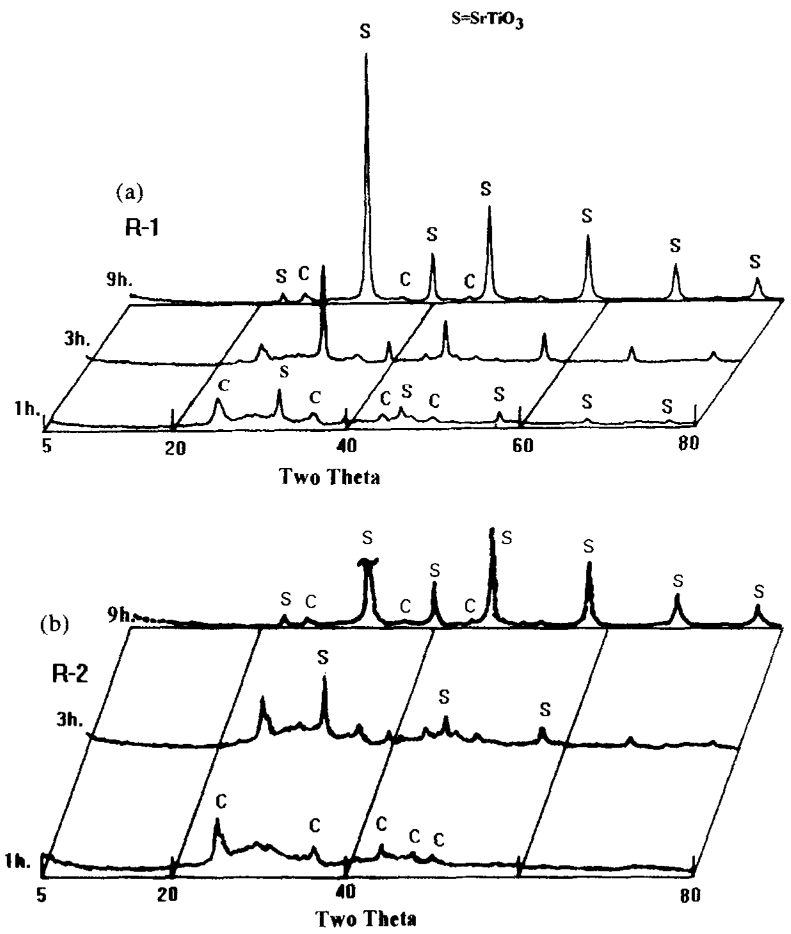

Fig. 8. XRD patterns of the polymeric precursors after calcination at 450°C for different times: (a) obtained by route R1; and (b) obtained by route R2.

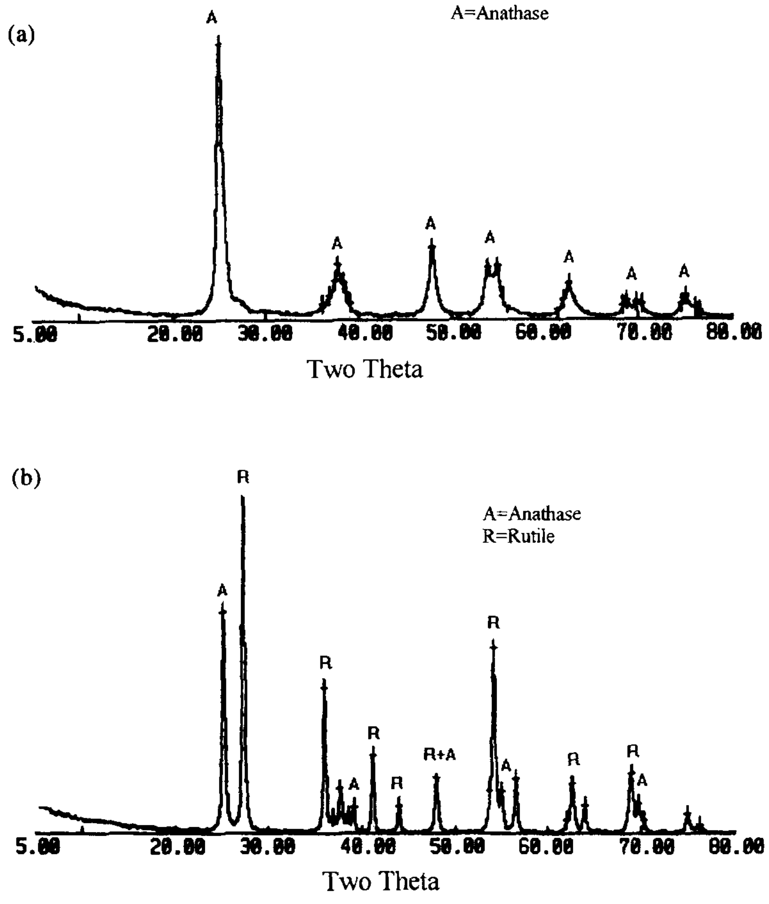

Fig. 9. XRD patterns of the Ti solution polymerized at 250°C and calcined for 3 h: (a) at 350°C; and (b) at 450°C.

Table 2. XRD results for intermediate phase C, TiO_2 (anathase), and $SrCO_3$

Phase C		TiO_2 (anathase)		$SrCO_3$	
d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
3·531	100	3·523	100	3·464	100
3·458	69	2·376	20	3·388	46
2·998	60	1·895	26	2·970	13
2·957	52	1·696	18	2·801	11
2·886	55	1·668	19	2·513	13
2·841	52	1·481	13	2·418	32
2·473	52	1·346	6	2·030	39
2·052	54	1·271	6	1·967	16
1·906	42	—	—	1·918	14
1·823	39	—	—	1·887	25

3.3 Thermogravimetric analysis (TG)

Figure 10 shows the thermogravimetric analyses of the pure polymer (with no cation) (a), of the precursor R1 (b), and of the precursor R2 (c). These thermograms show that the polymer without cations decomposes in one step (Fig. 10(a)), with maximum decomposition rate at 332°C for a heating rate of 10°/min. The precursor R1 (Fig. 10(b)) shows three decomposition stages, one at 280°C, another at 425°C and the third stage is a gradual decomposition in the temperature range of 600 to 700°C. For the precursor R2 (Fig. 10(c)) four steps for decomposition are observed. Two steps are observed at 290°C and 362°C. In the region of 400°C a third weight loss occurs, followed by a well-defined weight loss at 660°C. Two points should be analyzed. The first is that the decomposition of precursor R1 starts first compared with precursor R2 which is in agreement with DSC and XRD results. The second is that the precursor R2 shows weight loss 10% smaller than the weight loss of precursor R1, which agrees with results of MAS-NMR.

Considering that the reaction rate for the precursors R1 and R2 are controlled by thermal decomposition and that it occurs from the surface following linear kinetics, the reaction rate is thus given by:[18]

$$d(\Delta m/m_0)/dt = A\exp(-\Delta H/RT) \qquad (3)$$

where $\Delta m/m_0$ is the mass variation, t is the time, R is universal gas constant, T is the absolute temperature, A is a pre-exponential factor and ΔH is the reaction enthalpy. Considering constant heating rate (α) during thermal decomposition, we get:

$$dt = dT/\alpha \qquad (4)$$

Considering A weakly dependent on T and making a substitution of eqn (4) into eqn (3),

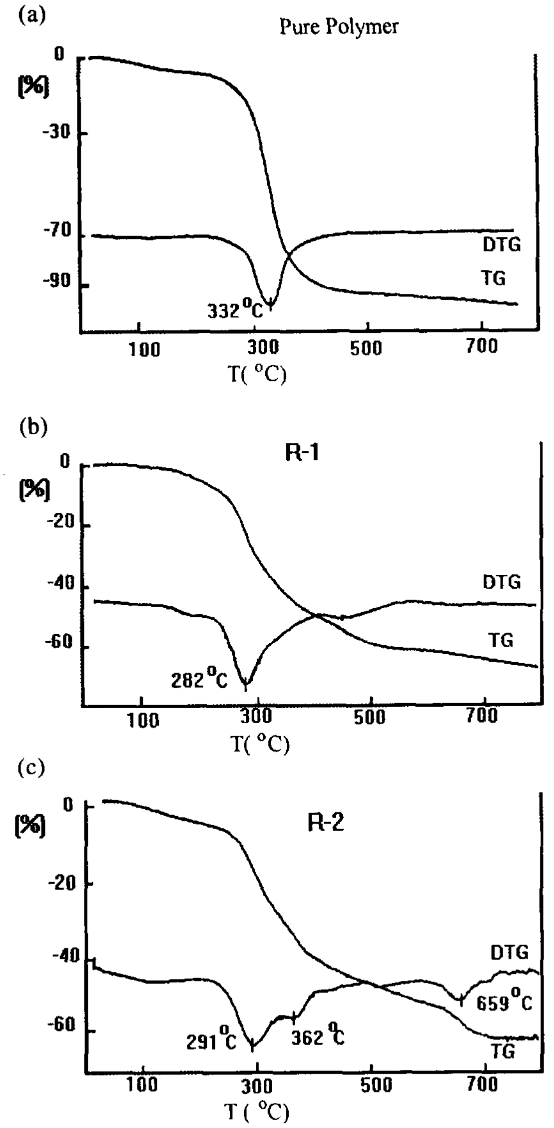

Fig. 10. Thermal gravimetric analysis in air atmosphere with heating rate of 10°C/min: (a) pure polymer; (b) precursor processed by route R1; and (c) precursor processed by route R2.

$$\Delta m/m_0 = (ART^2/\alpha\Delta H)\cdot\exp(-\Delta H/RT) \qquad (5)$$

The slope of the plot of log $\Delta m/m_0$ as function of $1/T$ should be $-\Delta H/R$. This non-isothermal method of analysis was applied to decomposition studies of the pure polymer, precursors R1 and R2, and $SrCO_3$, using TG data. Linear regression was used to calculate ΔH, which was considered constant in the temperature range analyzed. Table 3 shows the results of the non-isothermal decomposition. It is observed in this table that the enthalpy (ΔH) for decomposition of $SrCO_3$ is 73·1 kJ/mol in the temperature range of 970 to 1140°C and 83·4 kJ/mol in the temperature range of 1240 to 1320°C, that is, typical energies for breaking strong ionic bonds as bidentate carbonates. For the decomposition of the R1 and R2 precursors in the temperature range of 250 to 350°C enthalpies of 15·8 kJ/mol and 14·3 kJ/mol, respectively, were observed. In the same way the decomposition of

Table 3. Enthalpies (ΔH) obtained from non isothermal decomposition reaction

Sample	Temperature range (°C)	ΔH (kJ/mol)	Correlation factor
$SrCO_3$	970–1140	73·1	0·998
	1240–1320	83·1	0·999
R1	250–350	15·8	0·996
R2	250–350	14·3	0·983
Pure polymer	250–350	15·8	0·992

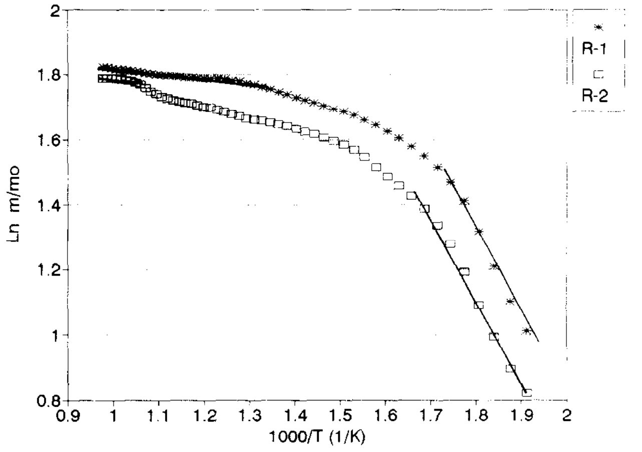

Fig. 11. Log ($\Delta m/m_0$) as function of T^{-1} for the precursors obtained by routes R1 and R2. Heating rate of 10°C/min.

the pure polymer at this temperature range was observed to be 15·8 kJ/mol. It is evident that there is a decomposition of the polymeric matrix in this temperature range. In the temperature range of 600–700°C this corresponds to the final weight loss of precursors R1 and R2, the enthalpy of reaction is low as indicated by the low slope of the curves of Fig. 11.

Thus the enthalpy involved during thermal decomposition of precursors R1 and R2 is not higher than 20 kJ/mol and no weight loss was observed for temperatures above 700°C. The above results indicate that there is low probability for formation of ultra fine $SrCO_3$ during decomposition of the precursors R1 and R2 since this carbonate decomposes at high temperatures with an enthalpy of 80 kJ/mol. These results are also in agreement with the XRD analysis.

3.4 General discussion

The analyses of the results show that the change of the synthesis route has a strong influence on the polymer structure. The preparation route by precipitation (R2) led to formation of a compound with polymeric characteristics containing Sr and Ti cations without excess of ethylene glycol as shown by the MAS-NMR data. The precipitation after further washing removes the excess ethylene glycol, forming a precursor with less weight loss during calcination.

Another difference between the precursors R1 and R2 is that in the precursor R2 a reticulation reaction among the chain macromolecules is observed. Thus the compound R2 is more thermally stable, retarding its decomposition for temperatures above 290°C while the decomposition of the precursor R1 starts at 260°C. The thermal stability of the precursor R2 should retard the formation of the $SrTiO_3$ phase.

The XRD, FT-IR, DSC and TG results suggest the following stages for the decomposition of precursors R1 and R2. The first stage consists of the bond rupture of unidentate carboxylic groups around 250°C. The second stage consists of the degradation of the polyester matrix at 300°C, followed by a change in coordination of the Sr and Ti cations from groups COO^- to groups CO_3^{2-}, forming a mixed carbonate at 450°C. Above this temperature the decomposition of this carbonate occurs forming $SrTiO_3$. This carbonate decomposes in the range of 600–700°C with a weight loss of 8% (Fig. 10(c)) which represents 16% of the remaining mass (49%). This value is near to the theoretical value of 13% for the weight loss for the mixed carbonate of type $Sr_2Ti_2O_5.CO_3$ proposed by Cho *et al.*[14]. Then the last stage of the decomposition is the formation of $SrTiO_3$ from the mixed carbonate, as indicated by the reaction below:

$$Sr_2Ti_2O_5 \cdot CO_3 \xrightarrow{\Delta} 2SrTiO_3 + CO_2\uparrow \qquad (6)$$

The hypothesis of formation of $SrTiO_3$ from the reaction of $SrCO_3$ with TiO_2[12] is not supported by the experimental results of this study. This means that the mix of Sr and Ti cations at the atomic scale is kept during all synthesis process.

4 CONCLUSIONS

The preparation route (R2) leads to precursors in powder form with Sr and Ti cations homogeneously distributed in the solid macromolecule matrix with no excess of reagents. The more stable structure of this precursor, compared with precursor prepared by traditional Pechini route (R1), favors its decomposition at higher temperatures that retards the formation of $SrTiO_3$. Both syntheses route R1 and R2 lead to formation of an intermediate mixed carbonate with stoichiometry close to $Sr_2Ti_2O_5.CO_3$.

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