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THERMAL AND STRUCTURAL CHARACTERIZATION OF $Sr_{1-x}Co_xTiO_3$ OBTAINED BY POLYMERIC PRECURSOR METHOD

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In the recent years, the interest concerning to the synthesis of complex oxides, to be applied as electronic ceramics is continuously increasing. One good example is strontium titanate, displaying a perovskite structure, which favors the occurrence of important electronic properties. In the present study, $Sr_xCo_{1-x}TiO_3$ powders, in which $0 \leq x \leq 0.3$, were synthesized by the polymeric precursor method, achieving good a stoichiometric control and presented a crystalline structure at temperatures as low as 600°C. These systems were thermally and structurally characterized using thermogravimetric analysis (TG/DTA), X-ray diffraction (XRD) and infrared spectroscopy (IR). The TG results of the powder precursors show that the mass loss process observed for the undoped and Co-doped $SrTiO_3$ takes place in four well-defined stages. These stages are related to the evaporation of water and to the combustion of the organic matter present in the powder precursors (pyrolysis process). The addition of cobalt to the $SrTiO_3$ promotes a decrease in the mass loss and also decreases the final decomposition temperature of the organic matter. The XRD analysis showed a single phase when 10% of Sr^{2+} was replaced by Co^{2+}. When the extent of cobalt substitution was higher than 10 mol% and the substance was heat treated over 900°C, a $CoTiO_3$ secondary phase appeared. By means of IR, it was possible to observe the vibration bands related to the Ti–O bonds and to carbonates.

Keywords: *cobalt, Pechini method, $SrTiO_3$*

Introduction

The stoichiometry of a perovskite structure is ABX_3, characterized by structural flexibility - its structure varies slightly depending on the temperature and composition [1]. This group of materials has been widely studied in materials science due to their technological application and many times with regard to the transition phases [2, 3]. These applications can be done with the material processed as powder or film and their properties are also influenced by the type of defect formed in the structure.

$SrTiO_3$ is a compound with perovskite structure and cubic symmetry, whose dodecahedral sites are occupied by Sr^{2+} and octahedral sites are occupied by Ti^{4+}. Its electric and magnetic properties have been studied, specially when it is processed as a thin film. During a solid-state synthesis, some problems are observed as low stoichiometric control, leading to the formation of undesirable phases. Several reaction routes have been suggested for synthesis of this titanate. However, the distinct chemical behavior of Ti^{4+} and Sr^{2+} in solution can lead to some problems such as cation segregation and stoichiometry deviation.

One of the most popular chemical synthesis is the sol–gel procedure, which has three possibilities: colloidal gel solution, polymeric inorganic gel from organometallic compounds and polymeric precursor method. The last one, based on Pechini method [4], has been widely used to obtain ceramic powders and thin films [5, 6]. It has important advantages as chemical homogeneity of components in molecular scale, precise and direct control of stoichiometry in complex systems, synthesis at low temperatures, possibility of obtaining nanometric particles and process simplicity.

In this work, $Sr_{1-x}Co_xTiO_3$ (x=0 to 0.3) was synthesized using Pechini method [3–5]. Thermal properties and structural evolutions were evaluated as a function of the amount of Co and calcination temperature.

Experimental

The polymeric precursor solution was prepared by Pechini process, which is used to synthesize mixed-cation oxide ceramics. This process is based on metallic citrate polymerization with the use of ethylene glycol. A hydrocarboxylic acid is used to form chelated cations in an aqueous solution. The addition of a glycol, such as ethylene glycol, leads to organic ester formation. Polymerization, promoted by heating, leads

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to a homogeneous resin in which metal ions are uniformly distributed throughout the organic matrix [7].

In the synthesis, the following reagents were used: citric acid (Vetec), ethylene glycol (Synth), cobalt nitrate (Aldrich Chemical Company), strontium acetate (Riedel), titanium isopropoxide (Hulls-Ag).

Titanium citrate was prepared as described in [7]. Powder synthesis is described in Fig. 1. $Co_xSr_{1-x}TiO_3$ (x=0 to 0.3) was obtained using a 3:1 molar ratio of citric acid:metal, in order to provide metal chelation. A 60:40 mass ratio of ethylene glycol:citric acid was used.

The powder precursor was analyzed by DTA and TG. After calcination between 600 and 1000°C, powders were evaluated by X-ray diffraction (XRD) and infrared spectroscopy (IR).

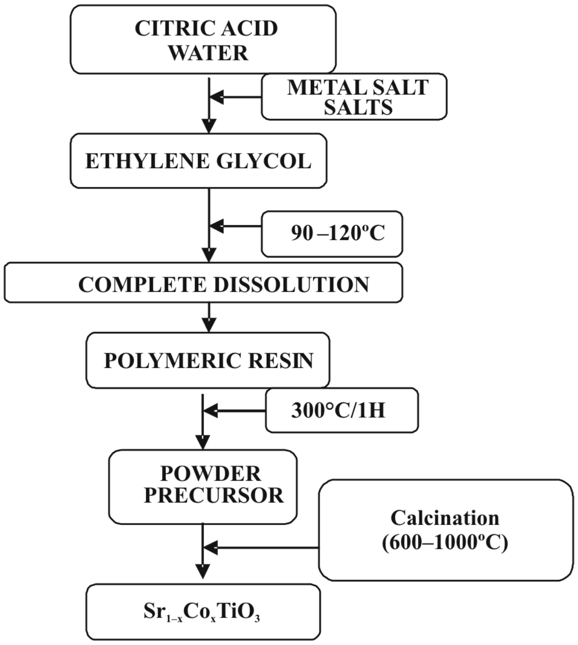

Fig. 1 Illustrative flowchart of $Sr_{1-x}Co_xTiO_3$ synthesis using the polymeric precursor method

DTA analysis (DTA-50 – Shimadzu) was carried out with 5 mg of material, at a heating rate of 10°C min^{-1} up to 1000°C, in air atmosphere. TG analysis (TG-50 – Shimadzu) was carried out at a heating rate of 10°C min^{-1} up to 950°C.

X-ray diffraction (D-5000–Siemens) was carried out applying Fe monochromatic radiation (K_α=1.7393 Å). Lattice parameters were calculated using Rede 93 Program, developed in the Chemistry Institute of Unesp in Araraquara-Brazil. Relative crystallinity was calculated using the peak intensities and Eq. (1).

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

where I=intensity of the (110) plane peak; I_0=intensity of the (110) plane peak of the least crystalline sample; I_{100}=intensity of (110) plane peak of the sample with the highest crystallinity.

Crystallite size was calculated using Scherrer Eq. (2). [8]

$$t = \frac{0.9\lambda}{\beta cos\theta} \qquad (2)$$

where t=crystallite size; λ=wavelength of the electromagnetic radiation; θ=Bragg angle; β=corrected half-width of the diffraction peak, corrected according to Eq. (3)

$$\beta^2 = B^2 - b^2 \qquad (3)$$

where B=full width to half maximum of the (110) plane peak of the sample; b=full width to half maximum of the peak of the standard material. In the present case, quartz was used as external standard.

Infrared analysis (MB series–Bomem) was done using KBr pellets in the range of 400–2000 cm^{-1}.

Results and discussion

TG and DTG curves (Figs 2a and 2b) showed two decomposition steps for $SrTiO_3$, with and without cobalt addition. The first step is related to water evaporation and the second is representative for the polymer decomposition. According to Table 1, it can be observed when the added amount of cobalt is less than 20 mol%, carbon chains are decomposed at higher temperatures. This may be due to an increase in carbonic chain. When 30% Co^{2+} was added to the material, the decomposition temperature decreased.

Figure 2c illustrates the DTA curves for all powder precursors. Samples present four exothermic peaks, due to carbon combustion. When the amount of cobalt increases, the peak at about 530°C disappears and the peak at 630°C decreases.

According to the infrared spectra (Fig. 3), three vibrational bands can be observed – the first one is a broad band in the range of 550–780 cm^{-1}, related to Ti–O stretching, while bands at 860 cm^{-1} and 1446 cm^{-1} are related to carbonate [9]. With the increase of temperature and amount of cobalt, the intensity of carbonate vibration bands decrease, while the bands related to the metal–oxygen bond are better developed. An important point is the decrease in carbonate band intensity as the amount of cobalt increases. This result is in agreement with the thermoanalytical results, which indicate the disappearance of the peak at 630°C, in the precursor where the cobalt:strontium ratio is 30:70.

Figures 4a and 4b show the XRD patterns of $Sr_{1-x}Co_xTiO_3$ (x=0, 0.1, 0.2 and 0.3), after calcination.

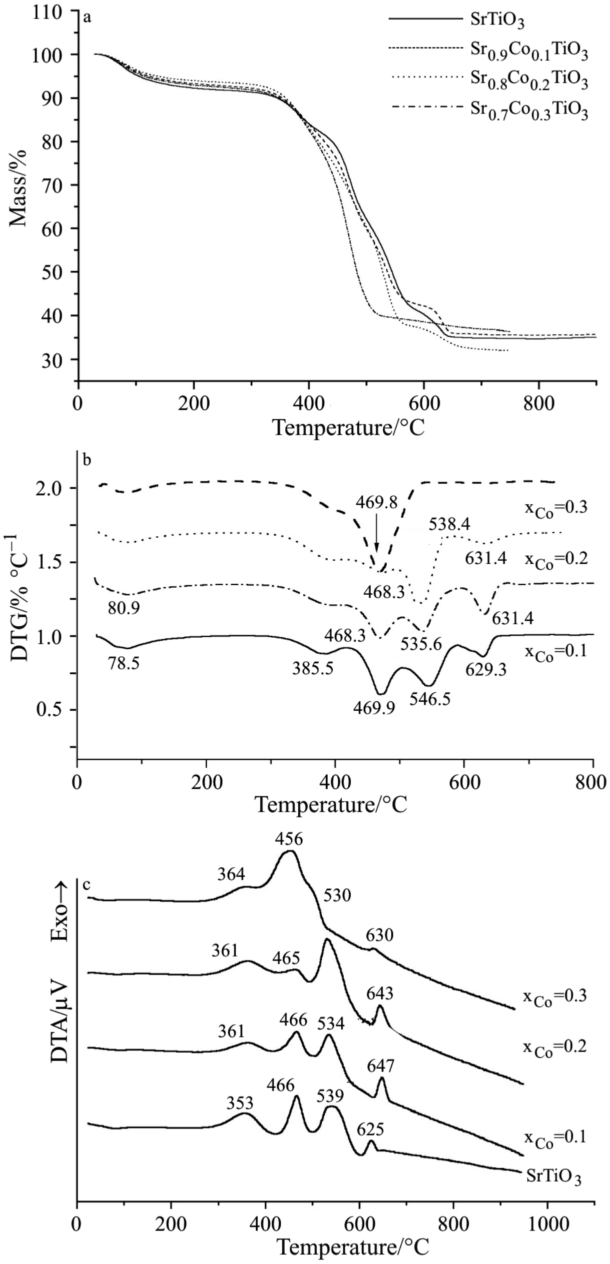

Fig. 2 Thermoanalytical curves of the powder precursor of $Sr_{1-X}Co_XTiO_3$ (x=0 to 0.3).
a – TG curves, b – DTG curves, c – DTA curves

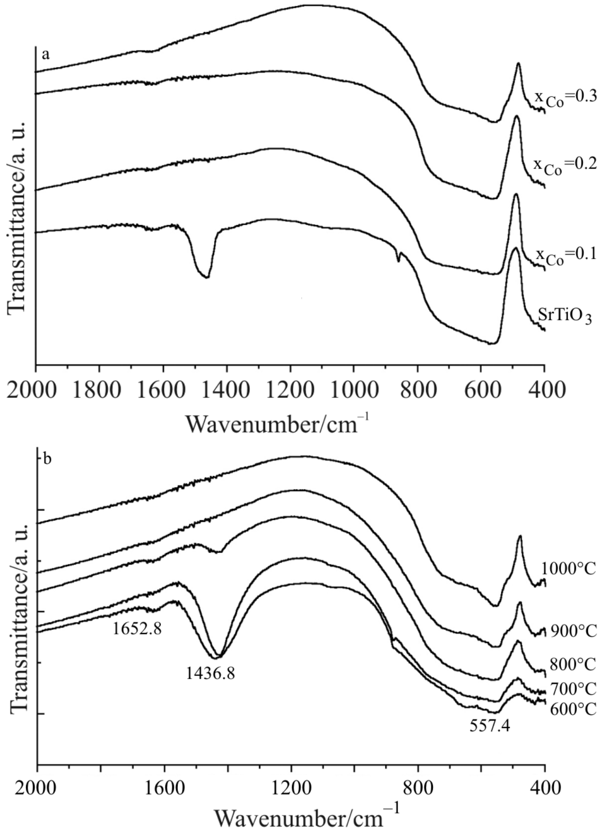

Fig. 3 Infrared spectra of the $Sr_{1-X}Co_XTiO_3$ (x=0–0.3). a – after calcination at 1000°C, b – sample $Sr_{0.7}Co_{0.3}TiO_3$, calcined at different temperatures

Single phase $SrTiO_3$ is obtained after calcination at all temperatures, as well as in $Sr_{0.9}Co_{0.1}TiO_3$. Samples $Sr_{1-x}Co_xTiO_3$, where x=0.2 and 0.3, exhibit a secondary phase, that was identified as $CoTiO_3$, after calcination above 800°C. This is probably due to the high amount of cobalt, that leads to a lattice distortion, due to the difference in cobalt and strontium ion radii.

The variation of lattice parameter as a function of temperature is presented in Fig. 5. The theoretical unit cell volume (JCPDS de nº 35-734) of $SrTiO_3$ is 59.55 nm^3, while the experimental one is 59.55 nm^3, indicating the good agreement of the results.

When the amount of cobalt and the temperature increase, lattice parameters tend to decrease, as it can be observed in Fig. 5. This is probably due to the difference in Co^{2+} and Sr^{2+} ion radii (in octahedral sites, Co^{2+} and Sr^{2+} radii are 0.075 and 0.118 nm, respectively) [10]. $Sr_{0.7}Co_{0.3}TiO_3$ presents a higher lattice parameter than samples with lower cobalt content. This is probably due to a lower cobalt content in the unit cell, as it is indicated by $CoTiO_3$ segregation.

Crystallite size results are presented in Fig. 6. Above 700°C, the samples with cobalt addition present similar crystallite size values, which are higher than the samples without cobalt. This is probably due to the smaller ion radius of Co^{2+}, compared to Sr^{2+}, making the process of diffusion easier, leading to an increase in crystallite size.

With increasing temperature, an increase in the crystallite size is observed. It can be explained by the thermally activated nucleation and growing process which affects the crystallite formation.

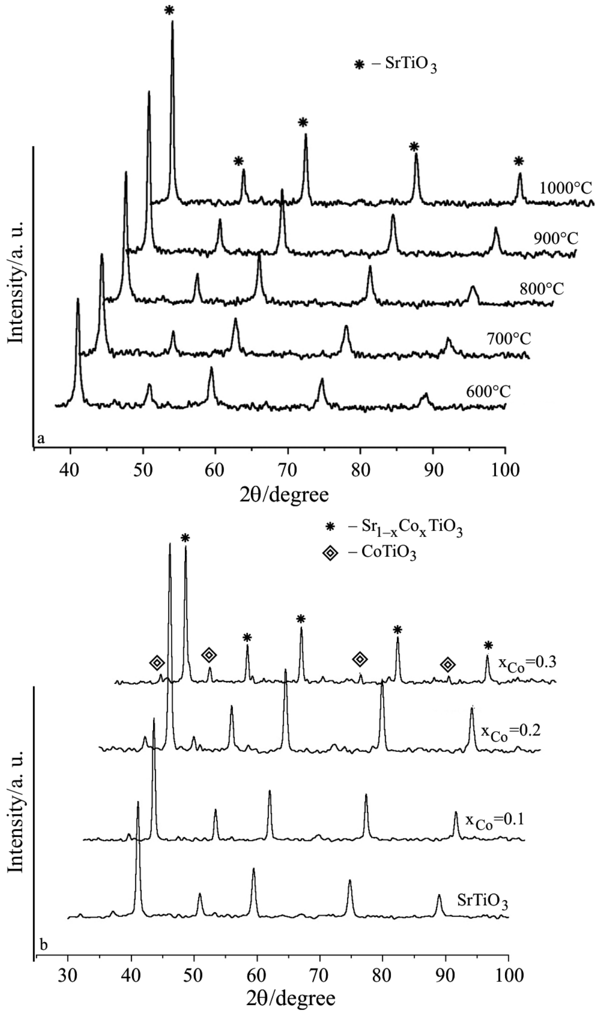

Fig. 4 a – XRD patterns of $SrTiO_3$, calcined at different temperatures; b – XRD patterns of $Sr_{1-x}Co_xTiO_3$ (x=0–0.3) calcined at 1000°C

Conclusions

$SrTiO_3$ was obtained by Pechini method, without the formation of secondary phases. DTA curves indicate exothermic peaks, due to organic material decomposition. Infrared spectra show titanium oxide bands, as well as carbonates, a decrease in this intermediate phase is observed, as the amount of cobalt increases. XRD patterns indicate single phase materials, up x_{Co}=0.2. Lattice parameters decrease when the amount of cobalt increases, due to its smaller ionic radius. This fact also leads to an increase in the crystallite size.

Acknowledgements

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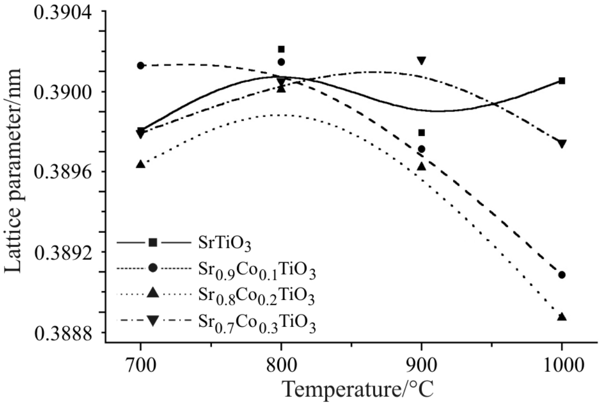

Fig. 5 Lattice parameters of $Sr_{1-x}Co_xTiO_3$ (x=0–0.3), calcined at different temperatures

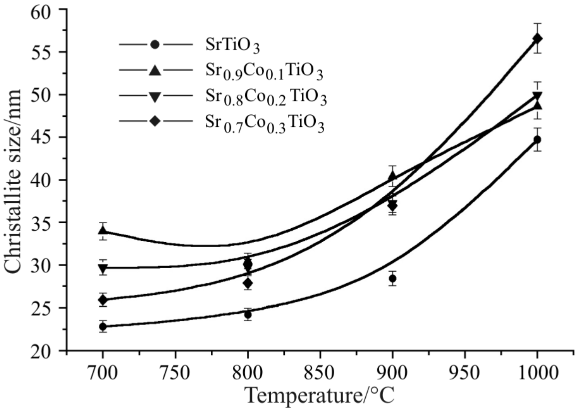

Fig. 6 Crystallite size of $Sr_{1-x}Co_xTiO_3$ (x=0–0.3), calcined at different temperatures

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