Journal of Thermal Analysis and Calorimetry, Vol. 79 (2005) 411–414

SYNTHESIS AND CHARACTERIZATION OF $SrCo_xTi_{1-x}O_3$

M. A. F. de Souza[1], *A. G. Souza*[1*], *R. A. Candeia*[1], *D. M. A. Melo*[2], *L. E. B. Soledade*[1], *M. R. C. Santos*[1], *I. M. G. Santos*[1], *S. J. G. Lima*[3] *and E. Longo*[4]

[1]LTM, Departamento de Química, CCEN, Universidade Federal da Paraíba, CEP 58059-900 João Pessoa, PB, Brazil
[2]Departamento de Química, CCET, Universidade Federal Do Rio Grande do Norte, Natal, RN, Brazil
[3]LSR, Departamento de Tecnologia Mecânica, CT, Universidade Federal da Paraíba, CEP 58059-900 João PB, Paraíba, Brazil
[4]LIEC, Departamento de Química, Universidade Federal de São Carlos, São Carlos, SP, Brazil

The $SrTi_{1-x}Co_xO_3$ (x=0 to 0.2) system was prepared by the polymeric precursor method, also known as the Pechini method. The thermogravimetric curves of the powder precursors indicate that the mass loss below 200ºC is due to the loss of water and adsorbed gases, and, for higher temperatures, the mass loss corresponds to the decomposition of the organic substance. For this system, a decrease in mass loss and in the final decomposition temperature can be observed with increasing amount of Co. IR analyses show vibration bands corresponding to titanium oxide as well as bands ascribed to carbonates. By means of XRD analysis, a decrease in the lattice parameter was observed for the highest Co^{2+} substitution levels. This is probably due to the defect formation in the crystalline structure.

Keywords: *ceramics, polymeric precursor method, $SrTiO_3$, thermogravimetry*

Introduction

Strontium titanate-based ceramics have been widely used to produce some electronic components, such as grain boundary layer capacitors (GBLC), varistors, sensors, etc. [1]. $SrTiO_3$, a cubic perovskite-type crystal, has distinguished attention in its application in dielectrics for dynamic random access memories (DRAM), because of its high dielectric constant, lack of fatigue or aging problems in the working range, good thermal stability and high compatibility with device processes [2].

Strontium titanate is a promising compound, proving its usefulness in a wide range of applications. It can be used as a grain boundary barrier layer capacitor, oxygen-gas sensor, substrate for the epitaxial growth of a high temperature superconductor thin film and as a catalyst. $SrTiO_3$ also has superconductivity when a small amount of electron carriers are added by oxygen vacancies [3].

The general formula of the ideal perovskite structure is ABO_3 and has a face-centered cubic structure. The larger A cation is placed in a twelvefold-oxygen-coordinated site and the smaller B cation presents a sixfold-oxygen-coordination, occupying the center of an octahedron, in whose vertices are located six oxygen atoms [4]. In the present study, the Co^{2+} introduction leads to the replacement of sixfold-oxygen coordinated Ti^{4+} ions by Co^{2+} ions. An important point is the use of a network modifier (Co^{2+}) replacing Ti^{4+}, which is a network former.

Experimental

The polymeric precursor method was firstly described in 1967 by Pechini [5], and it has been successfully used to synthesize polycation oxides, either as powders [6] or as thin films [7]. This process is based on the polymerization of a metallic citrate with the use of a polyhydroxy alcohol, such as ethylene glycol. A hydrocarboxylic acid is used to chelate the cations in an aqueous solution. The addition of ethylene glycol leads to the organic ester formation. The polymerization, promoted upon the heating of the mixture, results a homogeneous resin, in which the metal ions are uniformly distributed throughout the organic matrix [8].

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

Titanium citrate was prepared as previously described. The scheme of powder synthesis is described in Fig. 1. $SrCo_xTi_{1-x}O_3$ (x=0 to 0.2) was obtained using a 3:1 citric acid:metal molar ratio, in order to guarantee the metal chelation. A 60:40 mass ratio of citric acid:ethylene glycol was used [9].

Powder precursors were analyzed by differential thermal analysis (DTA) and thermogravimetry (TG). After the final heat treatment between 500 to 1000ºC for different series of samples, the powders were evaluated using X-ray diffraction (XRD) and infrared spectroscopy (IR). DTA analysis (DTA-50 – Shimadzu) was performed with 5 mg samples and at a heating rate

---

[*] Author for correspondence: gouveia@quimica.ufpb.br

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

of 10 K min^{-1} up to 1000ºC, in air atmosphere. TG analysis was carried out at a heating rate of 10 K min^{-1} up to 950ºC. X-ray diffraction (D-500 – Siemens) was performed with the monochromatic K_αFe radiation (wavelength of 1.7393 Å). The data were obtained with 1.0 s step times and the step size was 0.020° (2θ) from 30–100°. The unit cell parameters were calculated using the Rede 93 program [10], developed at the Instituto de Química of Unesp, at Araraquara, SP, Brazil. Infrared analysis (MB series – Bomem) was done in the range of 400–2000 cm^{-1}, using KBr pellets.

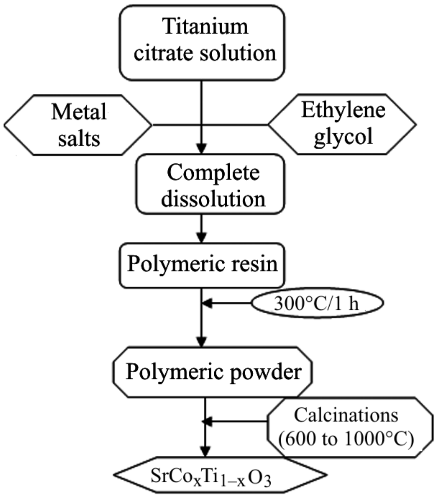

Fig. 1 Scheme of the synthesis of $SrCo_xTi_{1-x}O_3$ powders by the polymeric precursor method

Results and discussion

TG and DTG curves of the $SrCo_xTi_{1-x}O_3$ (x=0 to 0.2) powder precursors are shown in Figs 2a and b. The DTG peak temperatures are marked with T_p. The mass loss below 200ºC, is due to the loss of water and adsorbed gases (T_{p1}). Above this temperature, the mass loss corresponds to the decomposition of the organic substance (T_{p2}, T_{p5}). For the Co–Ti system, a decrease in mass loss and in the final decomposition temperature with increasing amount of Co can be seen.

DTA curves (Fig. 2c) indicate exothermic transitions, showing the liberation of a great amount of energy during the polymeric precursor method. The large

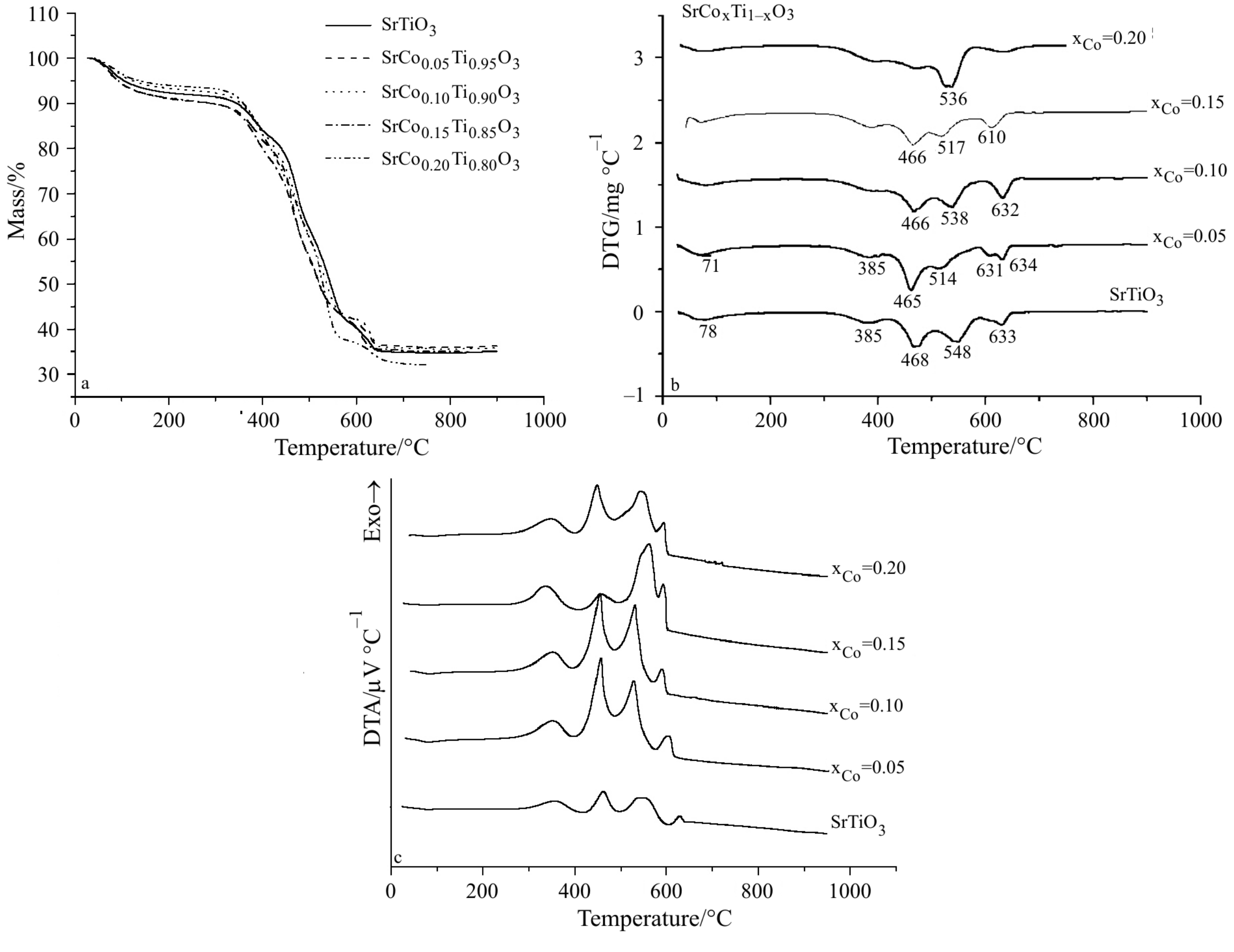

Fig. 2 a – TG, b – DTG and c – DTA curves of $SrCo_xTi_{1-x}O_3$ (x=0 to 0.2) samples

portion of organic matter used, undergoes an exothermic combustion reaction, associated to the oxidation of the carbonic chains. The consecutive decomposition steps are probably related to the combustion of different functional groups which are present in the polyester resin and decompose at different temperatures.

In the IR spectra (Figs 3a and b), three vibrations bands can be observed for strontium titanate (Fig. 3a). The first is a wide one, corresponding to the titanium oxide, located between 557 and 780 cm^{-1}. The bands at around 860, 1444 and 1652 cm^{-1} are related to carbonates [11]. As the temperature of heat treatment increases it is noticed that the carbonate vibrations decrease. On the contrary, the band representative to the metal–oxygen bond is much more pronounced as it is indicated by the vibration peak at 564 cm^{-1} (Fig. 3b). On the other hand, the $SrTiO_3$ sample does not present carbonate bands at 1000ºC, while these bands are present for samples with cobalt addition, indicating that cobalt carbonate is probably present in the material. This is probably due to the difficulty in replacing Ti^{4+}, which is a network former, by Co^{2+}, which is a network modifier. As the intensity of the carbonate band does not increase with cobalt addition, it seems that a part of Co^{2+} probably incorporates into the $SrTiO_3$ lattice, substituting Sr^{2+}.

Figures 4a and b show the X-ray diffraction patterns of the pure $SrTiO_3$ and of the $SrCo_xTi_{1-x}O_3$ (x_{Co}=0, 0.10, 0.15 and 0.20) systems, respectively. In Fig. 4a, the effect of the heat treatment on the structure of pure $SrTiO_3$ can be seen, whereas Fig. 4b illustrates the effect of increasing Co-substitution on the structure of $SrCo_xTi_{1-x}O_3$. Disregard of the temperature of heat treatment as well as the amount of Co^{2+} (x_{Co}) added, the samples exhibited a single phase.

Analyzing the data of the XRD diffraction patterns, the lattice parameters of $SrCo_xTi_{1-x}O_3$ could be calculated, by using of the Rede 93 program. Figure 5 presents those lattice parameters *vs*. Co-substitution (x_{Co}) and the temperature of the treatment. The volume of the unit cell, for the $SrTiO_3$ phase is of 59.55 Å^3, according to JCPDS 35-734 file. This is not substantially different from the unit cell volume of 59.547 Å^3, calculated from experimental data.

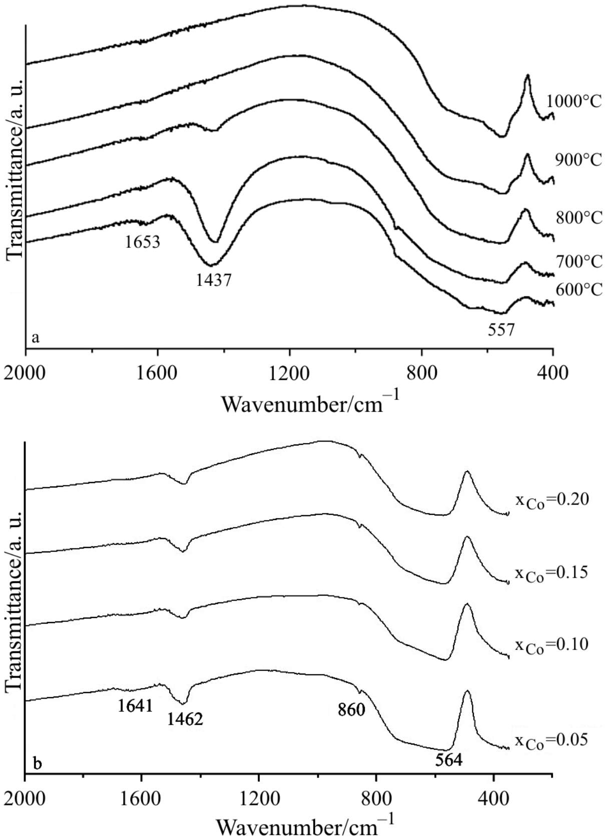

Fig. 3 a – Infrared spectra of $SrTiO_3$ powder precursor heat treated at different temperatures, b – infrared spectra of $SrCo_xTi_{1-x}O_3$ (x=0 to 0.2) systems after heat treatment at 1000ºC

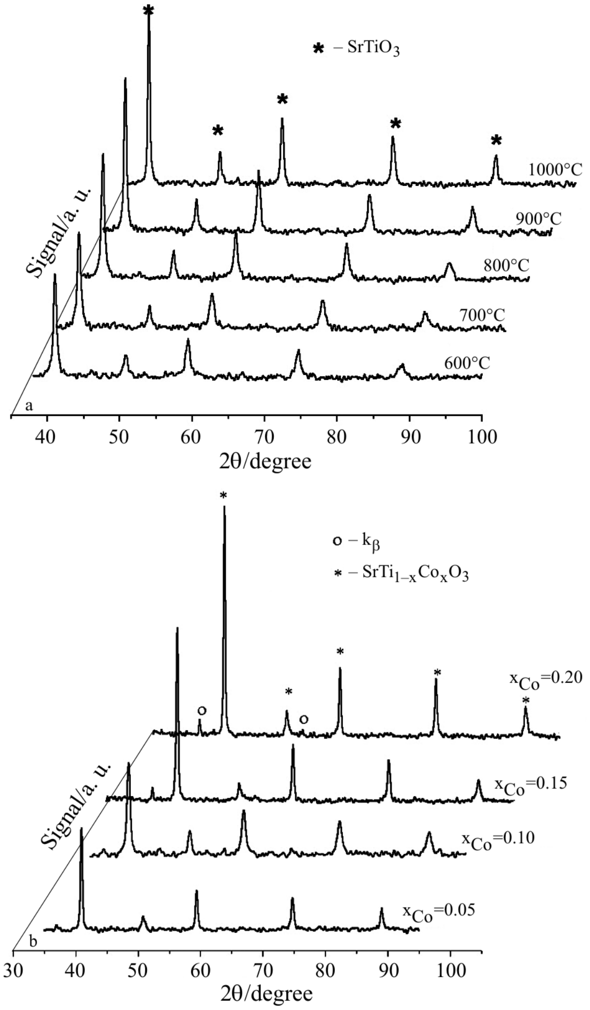

Fig. 4 a – XRD patterns of $SrTiO_3$ treated at different temperatures, b – XRD patterns of $SrCo_xTi_{1-x}O_3$ (x=0 to 0.2) heat treated at 1000°C

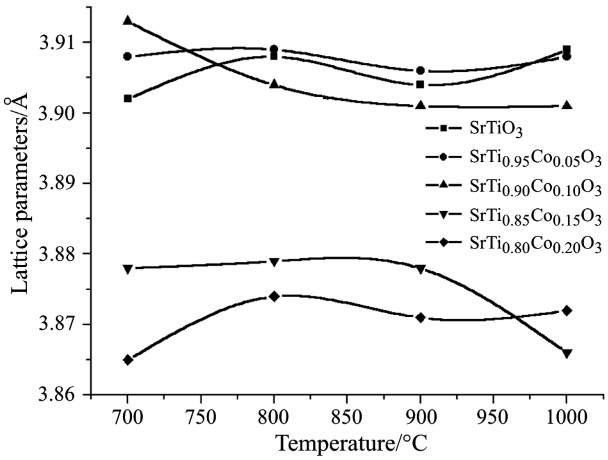

Fig. 5 Lattice parameters of the $SrCo_xTi_{1-x}O_3$ (x=0 to 0.2) system, heat treated at different temperatures

Lattice parameter results indicate that no meaningful change occurs when x_{Co} was 0.05 and 0.10. This indicates that cobalt is not introduced within the $SrTiO_3$ lattice, probably due to cobalt carbonate formation, as indicated by the infrared spectra. When x_{Co} was 0.15 and 0.20, the lattice parameter decreased. Since the intensity of the carbonate band does not increase with the cobalt concentration (Fig. 3b), it means that at the above mentioned concentrations cobalt replaces titanium in the lattice. As it was stated before, this is probably due to the difficulty of replacing Ti^{4+}, which is a network former, by Co^{2+}, which is a network modifier.

Since the ionic radius of Co^{2+} (0.74 Å) is larger than that of Ti^{4+} ion (0.61 Å) [12], the decrease of the lattice parameter is probably related to the ionic defects. It should be taken into account that the substitution of Ti^{4+} with Co^{2+} may lead to the formation of oxygen vacancies. Defect formation is described in Eq. (1), using Kröger–Vink notation [13].

$$CoO \xrightarrow{SrTiO_3} Co''_{Ti} + V_0^{\cdot\cdot} + O_0^{x} \qquad (1)$$

Conclusions

The aim of this work was the synthesis and characterization of $SrCo_xTi_{1-x}O_3$ (x=0 to 0.2) powders, prepared by the polymeric precursor method. The TG curves of the powder precursors indicate that the mass loss below 200ºC is due to the loss of water and over this temperature, the mass loss corresponds to the decomposition of the organic substance. When x_{Co} was higher than 0.1, a decrease in the decomposition temperature of the powder precursors was observed. It is related to the interaction of the metal with the polymeric chain and to the size of the polymeric chain in each sample. The IR analyses showed vibration bands corresponding to titanium oxide as well as bands assigned to carbonates. By means of XRD analyses, a decrease in the lattice parameter was observed in case of the highest substitution with Co^{2+}. This is probably due to the formation of defects in the crystalline structure. As the intensity of carbonate band does not increase together with the cobalt concentration, this indicates that cobalt replaces titanium in the lattice for higher substitution values (x_{Co}=0.10 and 0.20). For low substitution levels, Co^{2+} is probably present in the form of carbonates.

Acknowledgements

The authors acknowledge the Brazilian agencies CNPq and CAPES for their financial support.

References

1 L. Longtu, Z. Jingchang and G. Zhilun, Ceram. Int., 12 (2004) 27.
2 F. M. Pontes, E. R. Leite, E. J. H. Lee, E. Longo and J. A. Varela, J. Eur. Ceram. Soc., 21 (2001) 419.
3 Y. Marinova, J. M. Hohemberger, E. Cordoncillo, P. Escribano and J. B. Carda, J. Eur. Ceram. Soc., 23 (2003) 213.
4 A. Stashans and F. Vargas, Mater. Lett., 50 (2001) 145.
5 N. Pechini, U.S. Patent number 3,330,697 (1967).
6 A. L. Quinelato, E. Longo, E. R Leite, M. I. B. Bernardi and J. A. Varela, J. Mat. Sci., 36 (2001) 3825.
7 L. E. B. Soledade, E. Longo, E. R. Leite, F. M. Pontes, F. Lanciotti Jr., C. E. M. Campos, P. S. Pizani and J. A. Varela, Appl. Phys. A – Mater., 75 (2002) 629.
8 C. S. Xavier, C. E. F. Costa, S. C. L. Crispim, M. I. B. Bernardi, M. A. M. A. Maurera, M. M. Conceição, E. Longo and A. G. Souza, J. Therm. Anal. Cal., 76 (2004) 461.
9 F. M. Pontes, E. R. Leite, E. Longo, J. A. Varela, P. S. Pizani, C. E. M. Campos and F. Lanciotti, Adv. Mater. Opt. Electron., 10 (2000) 81.
10 C. O. Paiva-Santos, D. Garcia, Y. P. Mascarenhas and J. A. Eiras, Cerâmica, Assoc. Bras. Ceram., 35 (1989) 153.
11 P. Duran, D. Gutierrez, J. Tartag, M. A. Banares and C. Moure, J. Eur. Ceram. Soc., 22 (2002) 797.
12 W. D. Kingery, H. K. Bowen and D. R. Uhlmann, Introduction to Ceramics, 2nd Ed., John Wiley & Sons, New York, 3 (1976) 307.
13 F. A. Kröger and H. J. Vink, Solid State Phys., 3 (1956) 307.