Synthesis and characterization of Sr$_{1-x}$Mg$_x$TiO$_3$ obtained by the polymeric precursor method

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Abstract

Strontium titanate (SrTiO$_3$; STO), a semiconductor displaying the perovskite structure, has been extensively studied, both as thin films and as powders, due to its high dielectric constant, good capacitance, and other properties. In the present work, the synthesis of Mg-substituted SrTiO$_3$ powders was studied using the polymeric precursor method. This method, also known as the Pechini method, has many advantages such as chemical homogeneity of multicomponents at the molecular scale and a direct and precise control of stoichiometry in complex systems at relatively low temperatures. The powders were characterized by thermogravimetry (TG)/differential thermal analysis (DTA). After the heat treatment between 600 and 1000 °C, the powders were characterized by X-ray diffraction (XRD) and infrared spectroscopy (IR). Thermal analysis results indicate successive exothermic and endothermic steps. After crystallization, a single-phase material was obtained for samples containing less than 20 % of Mg. The crystallite size was nanometric and a high crystallinity was obtained. Infrared spectroscopy indicated vibration bands characteristic of carbonates and metallic oxides.

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1. Introduction

Strontium titanate (SrTiO$_3$; STO) is a compound with perovskite structure, with a face-centered cubic symmetry, where Ti is located in octahedral sites and Sr is located in cubic sites [1].

Recently, materials with distorted perovskite structure (ABX$_3$) have attracted the attention of the researchers due to a wide variety of physical phenomena presented by them. Many of these phenomena are strictly related to distortions in the ideal cubic structure. An important point is the study of electric and magnetic properties—some materials present colossal magnetoresistance (MRC) near the point of spin ferromagnetic ordering, at Curie temperature [2,3].

SrTiO$_3$ (STO) has been one of the most popular materials since the discovery of its incipient ferroelectricity and first polar soft mode behavior. Owing to its high dielectric permittivity that increases on cooling, and its low microwave (MW) losses, it is the most attractive material for many high frequency and MW applications, particularly at low temperatures [4]. STO modified with Mg may be used as an oxygen sensor, with great efficiency between 600 and 750 °C, while pure STO acts above 800 °C [5].

In the present work, the technique used in the synthesis was the sol–gel, which comprises three types: colloidal gel solution, inorganic polymeric gel using organometallic compounds, and the polymeric precursor method.

The polymeric precursor method, developed by Pechini [6], has been widely used to obtain ceramic powders and...
films [7–11]. It has many advantages such as: chemical homogeneity of multicomponents in molecular scale; direct and precise control of stoichiometry in complex systems at relatively low temperatures; and possibility of obtaining nanometric particles and processing simplicity. Moreover, the polymeric precursor method is very flexible, being used to obtain different systems, with different structures.

In this work, Mg was added to strontium titanate in the amounts of 10, 20, 30, and 40 mol%, according to the stoichiometry \( \text{Sr}_{1-x}\text{Mg}_x\text{TiO}_3 \). The syntheses were carried out by the polymeric precursor method. After the heat treatment, the samples were characterized in terms of structure and crystallite morphology.

2. Experimental procedure

2.1. Samples

The following reagents were used in the synthesis: citric acid (Vetec), ethylene glycol (Synth), magnesium acetate (Aldrich), strontium acetate (Riedel), and titanium isopropoxide (Hulls-Ag).

Titanium citrate was prepared as described in the literature [5]. The synthesis of the powders is described in Fig. 1. \( \text{Sr}_{1-x}\text{Mg}_x\text{TiO}_3 \) \((x=0 \text{ to } 0.4)\) was obtained using a citric acid: metal molar ratio of 3:1, in order to guarantee the metal chelation. A 60:40 mass ratio of citric acid/ethylene glycol was used.

2.2. Thermal measurements

After the primary heat treatment, at 300 °C for 1 h, the powders were analyzed by differential thermal analysis (DTA) and thermogravimetry (TG). After the final heat treatment at a temperature ranging from 600 to 1000 °C, the powders were evaluated by X-ray diffraction (XRD) and infrared spectroscopy (IR).

The DTA analyses (DTA-50, Shimadzu) were carried out with 5 mg samples with a heating rate of 10 °C min\(^{-1}\) up to 1000 °C, in air atmosphere. The TG analyses (TG-50, Shimadzu) were performed with a heating rate of 10 °C min\(^{-1}\) up to 950 °C.

2.3. X-ray diffraction

X-ray diffraction (D-500, Siemens) was performed with the Fe monochromatic radiation \((K\alpha=1.7393 \text{ Å})\), with a scan rate of 0.03 °C s\(^{-1}\) and a step of 1 s. The lattice parameters were calculated using the Rede 93 Program [12], developed at the Chemistry Institute of Unesp in Araraquara, SP, Brazil.

The relative crystallinity was evaluated in order to compare the behavior of the different samples in relation to the crystallization. The calculations used the peak intensities, according to Eq. (1).

\[
CR(\%) = \frac{I - I_0}{I_{100} - I_0} \times 100
\]

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 \(I_{1000}\)=intensity of 100% peak of the most crystalline sample.

The crystallite sizes were calculated using Scherrer’s equation [13].

\[
t = \frac{0.9\lambda}{B\cos\theta}
\]

where: \(t\)=crystallite size, \(\lambda\)=wavelength of the electromagnetic radiation applied, \(\theta\)=Bragg angle, and \(B\)=full-width at half maximum of the most intense peak, corrected according to Eq. (3):

\[
B^2 = B^2 - b^2
\]

where: \(B\)=full width at half maximum of the 100% peak of the sample and \(b\)=full-width at half maximum of the 100% peak of the external standard (quartz in the present case).

2.4. Infrared spectroscopy

The infrared analyses (MB series, Bomem) were carried out using KBr pellets at the 400–4000 cm\(^{-1}\) range.

3. Results and discussion

TG curves (Fig. 2a) indicate two decomposition steps in the \(\text{Sr}_{1-x}\text{Mg}_x\text{TiO}_3\) powder precursors, for \(x=0, 0.1, 0.2, 0.3\) and 0.4. The first step starts at around 100 °C, being.
ascribed to water elimination and to the desorption of gases. The second step starts at around 250 °C, being attributed to thermal decomposition of the organic material. The thermogravimetric data are listed in Table 1.

Endothermic peaks at higher temperatures are also observed, indicating the crystallization process. An increase in crystallization temperature with magnesium addition is observed. Samples with \( x \geq 0.2 \) present two peaks, probably due to the magnesium segregation.

Fig. 2b illustrates the DTA curves for all powder precursors. The curves present exothermic peaks above 200 °C due to the decomposition of the organic material. Magnesium addition changes this profile, decreasing the number of exothermic peaks. This is probably due to a change in the polymerization process or in the pyrolysis process, which may be altered by the catalytic effect of inorganic ions [14,15]. Moreover, Arya et al. [11] relate the decomposition temperature to the heat of formation of the bonds between the metal ions and the carboxylate groups of citric acid. The DTA data are listed in Table 1.

Fig. 3a and b present the XRD patterns for \( \text{Sr}_{1-x}\text{Mg}_x\text{TiO}_3 \) (\( x = 0 \) to 0.4) powder precursors after the heat treatment between 600 and 1000 °C for 1 h. Samples containing 0% to 20% of magnesium are single phase, maintaining the perovskite structure (JCPDS: 35-734) of undoped strontium titanate, even for low heat treatment temperatures (600 °C). No intermediate phases are observed, indicating the high homogeneity of the polymeric resin. Strontium titanate synthesis, without secondary phases or intermediate phases, was also reported by Leite et al. [9]. On the other hand, Arya et al. [11] found a small amount of \( \text{Sr}_4\text{Ti}_3\text{O}_{10} \) as a secondary phase.

Samples with higher concentrations of magnesium present \( \text{MgTiO}_3 \) as a secondary phase (Fig. 3b). The perovskite structure cannot be maintained with such a high magnesium content. It should be stressed that pure \( \text{MgTiO}_3 \) presents the hexagonal ilmenite structure [16]. According to Arya et al. [11], barium-doped \( \text{SrTiO}_3 \) does not present secondary phases. The different behavior of magnesium may be due to the higher difference in ionic radius, as \( \text{Mg}^{2+} \) is much smaller than \( \text{Sr}^{2+} \). Based on the obtained lattice parameters, the experimental unit cell volume was calculated for the undoped \( \text{SrTiO}_3 \) heat-treated

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**Table 1**

**TG/DTA results of the powder precursors**

<table>
<thead>
<tr>
<th>TG (2nd step)</th>
<th>Sample</th>
<th>Ti (°C)</th>
<th>Tp (°C)</th>
<th>Tf (°C)</th>
<th>Mass loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{SrTiO}_3 )</td>
<td>246</td>
<td>496</td>
<td>654</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>( \text{Sr}<em>{0.9}\text{Mg}</em>{0.1}\text{TiO}_3 )</td>
<td>155</td>
<td>489</td>
<td>726</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>( \text{Sr}<em>{0.8}\text{Mg}</em>{0.2}\text{TiO}_3 )</td>
<td>195</td>
<td>497</td>
<td>741</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>( \text{Sr}<em>{0.7}\text{Mg}</em>{0.3}\text{TiO}_3 )</td>
<td>186</td>
<td>496</td>
<td>741</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>( \text{Sr}<em>{0.6}\text{Mg}</em>{0.4}\text{TiO}_3 )</td>
<td>214</td>
<td>500</td>
<td>753</td>
<td>60</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>DTA Sample</th>
<th>Exothermic peaks</th>
<th>Endothermic peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1st peak (°C)</td>
<td>2nd peak (°C)</td>
</tr>
<tr>
<td>( \text{SrTiO}_3 )</td>
<td>357</td>
<td>450</td>
</tr>
<tr>
<td>( \text{Sr}<em>{0.9}\text{Mg}</em>{0.1}\text{TiO}_3 )</td>
<td>357</td>
<td>466</td>
</tr>
<tr>
<td>( \text{Sr}<em>{0.8}\text{Mg}</em>{0.2}\text{TiO}_3 )</td>
<td>357</td>
<td>480</td>
</tr>
<tr>
<td>( \text{Sr}<em>{0.7}\text{Mg}</em>{0.3}\text{TiO}_3 )</td>
<td>367</td>
<td>478</td>
</tr>
<tr>
<td>( \text{Sr}<em>{0.6}\text{Mg}</em>{0.4}\text{TiO}_3 )</td>
<td>363</td>
<td>484</td>
</tr>
</tbody>
</table>
at 900 °C as 59.55 nm³. The theoretical value, JCPDS file 35-734, was 59.547 nm³.

The values of the lattice parameter, as a function of magnesium amount, at different temperatures is presented in Fig. 4. For all the temperatures studied, a decrease in the lattice parameter of up to \( x = 0.3 \) can be noticed. At about such substitution level, the perovskite structure can still accommodate the smaller Mg\(^{2+}\) ion, which also presents a higher covalent character than Sr\(^{2+}\). For higher magnesium substitution levels, the segregation of magnesium occurs, leading to the ilmenite segregation. Thus, the content of the low ionic radius magnesium in the perovskite phase diminishes, leading to the upward tendency in the lattice parameter.

Relative crystallinity results are presented in Fig. 5. Below 800 °C, random results were obtained. At 900 °C, an increase in relative crystallinity is observed up to \( x = 0.20 \), followed by a decrease. This may due to MgTiO\(_3\) segregation. At 1000 °C, the energy available to the crystallization is higher, leading to a higher crystallinity. An increase in the crystallinity is observed with the magnesium addition.

In relation to crystallite size (Fig. 6), its increase with temperature is observed, being more remarkable at 1000
A change in mass transport mechanism may be present. At this temperature, an increase of crystallite size with magnesium addition is also observed, being different from the results at other temperatures.

According to DTA results, magnesium addition enhances the nucleation process at higher temperatures (indicated by endothermic peaks). On the other hand, the relative crystallinity and crystallite size are increased. This may be associated to an easier diffusion process due to the addition of a smaller ion into the crystal lattice.

Two bands are observed in infrared spectra (Fig. 7). The first one is noticed at about 1500 cm\(^{-1}\), being related to the presence of carbonate. The second is located between 800 and 500 cm\(^{-1}\), being related to the metal–oxygen bond (Mg–O, Ti–O, and Sr–O). The carbonate band is only observed for the sample without magnesium, indicating that an intermediate amorphous phase may be formed in the SrTiO\(_3\) synthesis. The presence of carbonate bands in SrTiO\(_3\) synthesis, using the polymeric precursor method, was also reported by Leite et al. [9] and Arya et al. [11].

4. Conclusions

The results obtained suggested that the magnesium addition changes the precursor powder. As a consequence, no carbonate is observed, while the thermal decomposition is modified. In relation to crystallization process, a different behavior is also observed not only in the crystallite nucleation (as observed in DTA) but also in its growth (as observed in crystallite size and relative crystallinity results). An important point is the segregation of MgTiO\(_3\), displaying a hexagonal ilmenite structure at higher magnesium amounts. The results obtained in the present work suggest that the limit of magnesium substitution might be around 20–30%, although only one figure cannot be stated for such limit, as X ray diffraction cannot detect small amounts of crystalline phases. Moreover, this limit may vary with temperature, as indicated by the results of the lattice parameter.

Acknowledgments

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