Nanometric 'Pb IND.1-x"La IND.x'Ti'O IND.3'(x=0, 0.13 and 0.27) powders obtained by the polymeric precursor method

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Nanometric $\text{Pb}_{1-x}\text{La}_x\text{TiO}_3$ ($x = 0, 0.13$ and $0.27$) powders obtained by the polymeric precursor method


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Abstract

PLT ($\text{Pb}_{1-x}\text{La}_x\text{TiO}_3$, in which $x = 0, 0.13$ and $0.27$) powders were successfully synthesized using the polymeric precursor method, based on the Pechini method. The polymeric precursors were calcined at temperatures ranging from 350 to 500 °C for 4 h. X-ray diffraction (XRD) showed the evolution of the crystalline phase starting from the amorphous precursor. Thermogravimetric analyses (TG) and differential thermal analyses (DTA) of the powder precursors showed the influence of the pH on the elimination of organic material. PLT powders have a tendency to form agglomerates, what can be verified by comparing the values of the average particle sizes obtained by Brunauer–Emmett–Teller method, BET ($D_{\text{BET}}$) with the values of the average crystallite sizes obtained by XRD ($D_{\text{XRD}}$).

1. Introduction

The dielectric, pyroelectric and piezoelectric properties of lead titanate (PT), a ferroelectric material, are extremely important from the technological and scientific standpoints. PbTiO$_3$ presents a high pyroelectric coefficient, a high dielectric constant and a Curie temperature ($T_c$) of 490 °C. Up to the late 1960s, PT was considered of little technological interest, due to processing problems, resulting in highly distorted crystalline lattices in the phase transition from paraelectric to ferroelectric or from cubic to tetragonal.

The isomorphic substitution of lead by lanthanum has been found to induce intriguing changes in the physical properties of PbTiO$_3$ material. As a consequence, the properties of lanthanum-doped lead titanate materials mostly depend on the lanthanum concentration. Thus the adjustment of the Pb/La molar ratio can be used to optimize important technological characteristics. As a consequence, PLT may be used in a wide range of different applications, such as pyroelectric, piezoelectric or electro-optic materials, optical waveguides, infrared sensors, dynamic random access memories and non-volatile memories [1–4].

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Ferroelectric materials had been used in the bulk form in a variety of fields. Today, these materials are deposited in the form of thin film, allowing for the development of many applications, such as FRAM and DRAM memories, capacitors, transistors, etc. Thus, considerable attention has been recently focused on the development of technologies for their growing use as thin films.

PbTiO$_3$ is normally prepared by solid-state reaction of PbO and TiO$_2$, at high temperatures. However, due to certain limitations inherent to the process, particularly those involving particle size and contamination during processing, this method is slowly giving way to various chemical methods of powder preparation [5–9] that require relatively low calcination and sintering temperatures. These processes allow for a close control of the chemical compositions, providing good homogeneity, due to the thorough mixing of the liquid components, and narrow particle size distribution of the products. Among the existing chemical routes, the sol–gel and co-precipitation techniques are the most widely investigated for the preparation of ceramic powders [7–9].

Moon et al. [10] synthesized lead titanate powders by the hydrothermal method. By reacting titanium isopropoxide with acetylacetone during the mixing of the solution, a pure lead titanate phase with a perovskite structure was synthesized at temperatures as low as 150 °C. It was determined that the pH of the hydrothermal reaction medium and the initial Pb/Ti ratio are the most critical factors in the formation of stoichiometric PbTiO$_3$.

In the polymeric precursor method [11,12], an α-hydroxycarboxylic acid, preferably citric acid, is used to chelate various cations. In the presence of a polyhydroxy alcohol, normally ethylene glycol, these chelates react with the alcohol to form a polyester. Paris et al. [12] used the polymeric precursor method to produce PT powders, later heat treated at 600 °C for 1 and 2 h, obtaining particle sizes of 0.13 and 0.15 μm, respectively. Leite et al. [13] demonstrated the phase evolution of lead titanate processed by the polymeric precursor method. Their results indicated that the cubic perovskite PbTiO$_3$ (PT) phase is formed from an inorganic amorphous precursor at the temperature of 444 °C.

The purpose of the present work was to synthesize homogeneous Pb$_{1-x}$La$_x$TiO$_3$ powders with $x = 0$, 0.13 and 0.27.

2. Experimental procedures

The precursor solution containing metallic cations was prepared with a Pb(II)/Ti(IV) molar ratio 1:1. Titanium isopropoxide was dissolved in an aqueous citric acid solution at 90 °C by stirring, using a 3:1 citric acid/Ti(IV) molar ratio. The amount of Ti(IV) in the solution (in mass) was determined by gravimetry. In the case of pH 8 resins, the pH of the precursor resins was adjusted by the addition of NH$_4$OH.

Proper amounts of lead acetate trihydrate and lanthanum oxide were later dissolved in the titanium citrate solution in order to obtain the undoped and La$^{3+}$-doped PbTiO$_3$ powders, with the stoichiometry Pb$_{1-x}$La$_x$TiO$_3$, $x = 0$, 13 and 27 mol%. Ethylene glycol was added at a 60:40 citric acid/ethylene glycol mass proportion. The solution was polymerized at 250 °C for 3 h, followed by calcination at 300 °C for 4 h. **Fig. 1** describes the flow chart for the preparation of the stoichiometric Pb$_{1-x}$La$_x$TiO$_3$ powders, in which $x = 0$, 13 and 27 mol%. These powders will be hereinafter named 0-PLT, 13-PLT and 27-PLT, respectively.

The powders calcined at different temperatures were characterized by X-ray diffraction (XRD) (Model D – 5000, Siemens) coupled to a graphite monochromator and using the Cu Kα radiation. The lattice parameters were calculated by the minimum least square method, using silicon in the powder form (at the proportion of 30 wt%) as an internal standard and employing the program Rede 93, developed by Paiva-Santos et al. [14]. The average crystallite size was estimated by the Scherrer equation:

$$D_{XRD} = \frac{0.9\lambda}{[(B_{\text{obs}})^2 - (b)^2]^{1/2}} \cos \theta \tag{1}$$

where $D_{XRD}$ is the average crystallite size, $\lambda$ the wavelength (1.5456 Å), $B_{\text{obs}}$ the FWHM that is related to the (2 0 0) peak of the sample and $b$ is the FWHM of the Si internal standard. Thermogravimetric (TG) and differential thermal analyses (DTA) (Model STA 409, NETZSCH) were conducted in an air atmosphere, at different temperatures, using a heating rate of 5 °C/min to detect thermal variations and weight changes during the heating process. Ten to 15 mg of the treated powders were used in each test.
Isothermal nitrogen adsorption/desorption analyses (Model ASAP 2000, Micromeritics Instrument Corp., Norcross, GA) were carried out to determine the surface area, hysteresis curve, and pore-size distribution of the powders. The Brunauer–Emmett–Teller (BET) method was used to determine the surface area, whereas the Barrett–Joyner–Halenda (BJH) method was used to determine the pore size. Assuming spherical particles, the average particle size ($D_{\text{BET}}$) was calculated from measured specific surface area ($S_{\text{BET}}$) and particle density ($\rho$), using the following equation [15]:

$$D_{\text{BET}} = \frac{6}{\rho S_{\text{BET}}}$$ (2)

Fig. 1. Flow chart for the preparation procedure of the X-PLT powders.
Fig. 2. TG and DTA curves of pH 1 resins (a) 0-PLT, (b) 13-PLT and (c) 27-PLT.
Fig. 3. TG and DTA curves of pH 8 resins (a) 0-PLT, (b) 13-PLT and (c) 27-PLT.
Fig. 4. XRD patterns of the powders prepared in pH 1, calcined for 4 h at the 350–500 °C temperature range, corresponding to (a) 0-PLT, (b) 13-PLT and (c) 27-PLT.
Fig. 5. XRD patterns of the powders prepared in pH 8, calcined for 4 h at the 350–500 °C temperature range, corresponding to (a) 0-PLT, (b) 13-PLT and (c) 27-PLT.
Scanning electronic microscopy (SEM) was used to examine the microstructural evolution and particle size of the specimens.

3. Results and discussion

The thermal analyses for the pH 1 resins are displayed in Fig. 2a–c. A similar thermal decomposition behavior was noticed for all the La concentrations, as shown in the TG and DTG curves. The total mass losses are in the 65–80% range for all the La concentrations, and the complete burn-off of the organic matter takes place at about 600 °C. The resins obtained with pH 8, Fig. 3a–c, exhibit a total weight loss of 75–85% and the complete burn-off of the organic matter occurs at a higher temperature, in the range from 570 to 650 °C. The DTA curves for resins 0, 13 and 27-PLT, prepared at pH 1 and illustrated in Fig. 2, show a well-defined peak between 400 and 550 °C. The DTA curves, displayed in Fig. 3 for resins 0, 13 and 27-PLT prepared at pH 8, reveal the presence of a broad peak beginning at 300 °C and ending at 650 °C. The peaks, in both cases, correspond to the combustion of organic material.

The DTA curves for all the resins revealed an intense peak close to the temperature of crystalline phase formation. However, an analysis of the DTG curves attributed these peaks to the combustion of the organic material. The TG results indicate that the resins prepared at pH 1 present a higher oxygen reactivity when compared to the resins prepared at pH 8. Since at the temperature of about 500 °C diffusion is the rate controlling step of the combustion of the carbonaceous materials, one might expect that the resins prepared at pH 1 present a more opened structure than the ones prepared at pH 8.

A theoretical study is being undertaken at our laboratories and its partial results seem to indicate that the average distance between adjacent citrate groups is smaller in the case of pH 8 than in the case of pH 1.

Fig. 4a–c shows the evolution of the crystalline phase formation in the 0, 13 and 27-PLT powders obtained from precursors synthesized with pH 1, at temperatures ranging from 350 to 500 °C. At low temperatures, an amorphous phase is obtained, which crystallizes with no intermediate phase, at a higher heat treatment temperature. Similar behavior was observed in the powders obtained in the case of pH 8, as shown in Fig. 5a–c, respectively. It was observed that the formation of the crystalline phase in the precursors prepared with pH 8 occurred at temperatures higher than the ones observed for the precursors obtained with pH 1. This fact is related to the lower final combustion temperatures for the case of pH 1 resins (Figs. 2 and 3). The presence of La was also found to favor the crystalline phase formation at a lower temperature, particularly in the case of the precursor prepared at pH 8. The phase formation study revealed that the cubic perovskite phase (space group $Pm\bar{3}m$) is formed for La = 13 and 27 mol%, while the tetragonal perovskite phase (space group $P4mm$) is observed for the undoped samples. The cubic phase usually was only observed at a La concentration of approximately 27 mol% [16].

<table>
<thead>
<tr>
<th>Powder</th>
<th>Temperature (°C)</th>
<th>Parameter $a$ (Å), $\Delta = \pm 0.003$</th>
<th>Parameter $c$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-PLT (pH 1)</td>
<td>450</td>
<td>3.904</td>
<td>4.122</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>3.892</td>
<td>4.143</td>
</tr>
<tr>
<td>13-PLT (pH 1)</td>
<td>450</td>
<td>3.948</td>
<td>3.948</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>3.946</td>
<td>3.946</td>
</tr>
<tr>
<td>27-PLT (pH 1)</td>
<td>450</td>
<td>3.943</td>
<td>3.943</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>3.941</td>
<td>3.941</td>
</tr>
<tr>
<td>0-PLT (pH 8)</td>
<td>450</td>
<td>3.896</td>
<td>4.146</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>3.895</td>
<td>4.142</td>
</tr>
<tr>
<td>13-PLT (pH 8)</td>
<td>450</td>
<td>3.946</td>
<td>3.946</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>3.948</td>
<td>3.948</td>
</tr>
<tr>
<td>27-PLT (pH 8)</td>
<td>450</td>
<td>3.944</td>
<td>3.944</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>3.937</td>
<td>3.937</td>
</tr>
</tbody>
</table>
Table 1 presents the lattice parameters of all the powders, calculated as previously explained by the least square method, using the Rede 93 program [14]. As indicated, the experimental values of the powders are very close to those reported in the literature [17]. The calculated results of the lattice parameters for the samples prepared at pH 1 and pH 8 showed similar values. These results suggest that homogeneous PLT powders can be synthesized by this process, even at a relatively low temperature. The theoretical values of the parameters are: $a = 3.961\,\text{Å}$ and $a = 3.899\,\text{Å}$ and $c = 4.153\,\text{Å}$ for the cubic and tetragonal PLT, respectively.

PLT powders tend to form agglomerates, what is confirmed by a comparison of the average particle size values obtained by BET ($D_{\text{BET}}$) with the average crystallite sizes obtained by XRD ($D_{\text{XRD}}$), as shown in Table 2. This tendency decreases as the amount of La increases (Fig. 6). These findings suggest that the presence of larger amounts of La favors the formation of single crystal particles. Since an intermediate amorphous phase is reported, this behavior may derive from the influence of La on the nucleation and growth rates of the crystalline phase. The addition of La is believed to decrease the nucleation rate and increase the growth rate. On the other hand, a smaller particle size was obtained, indicating the lower sintering degree. As a consequence, increasing the La concentration should result in powders with larger crystallites and smaller particles, as compared with lower La concentration powders.

The formation of agglomerates, shown by SEM in Fig. 7, does not allow to accurately measuring the particle sizes, which, consequently were measured by BET mean values. On the other hand, the micrographs confirm the BET results, showing a smaller sintering between the particles with a higher La content, indicated by the presence of fewer necks.

Table 2

<table>
<thead>
<tr>
<th>Powder</th>
<th>pH 1</th>
<th>pH 8</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D_{\text{BET}}$ (nm)</td>
<td>$D_{\text{XRD}}$ (nm)</td>
</tr>
<tr>
<td>0-PLT</td>
<td>75.20</td>
<td>18.5</td>
</tr>
<tr>
<td>13-PLT</td>
<td>40.36</td>
<td>17.8</td>
</tr>
<tr>
<td>27-PLT</td>
<td>24.91</td>
<td>24.1</td>
</tr>
</tbody>
</table>

Fig. 6. $D_{\text{XRD}}/D_{\text{BET}}$ vs. La percentage for the powders calcined at 500 °C for 4 h.
Fig. 7. SEM micrographs of the powders prepared in pH 8 and calcined at 500 °C for 4 h, corresponding to (a) 0-PLT, (b) 13-PLT and (c) 27-PLT.
4. Conclusions

The final combustion temperature of the polymeric precursors prepared at pH 1 is lower than the one related to the precursors prepared at pH 8. Similarly, the powders obtained from the former precursors form a crystalline phase also at comparatively lower temperatures, as revealed by XRD.

It was shown by X-ray diffraction that the powders prepared in the present work display experimental lattice parameters, whose values are very similar to the ones reported in the literature. The results of this study demonstrate that the polymeric precursor method is appropriate to produce homogeneous PLT powders at a relatively low temperature.

Increasing the La doping level increases the average crystallite size and decreases the particle size, which is confirmed by the nitrogen adsorption/desorption, XRD and SEM analyses. The presence of larger amounts of La leads to the formation of single crystal particles.

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References