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Microstructural characterization using the Rietveld method in lead lanthanum titanate ceramics system produced by combustion synthesis

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Abstract

The (Pb,La)TiO_3–PLT ferroelectric ceramic system was synthesized through the combustion reaction method using a mixture of urea and glycine in different ratios as fuel. Also, it was studied the effect of the lead oxide amount in the initial batch. X-ray diffraction analysis has been used to follow the evolution of the processes that occurs during the preparation of the material and to determine the size and shape of the average crystallite and its microdeformation. A single perovskite phase with small and homogeneous particles was obtained. The overall results, combined with those from the structural refinement using de Rielveld method, showed that the cell parameter and the size and shape of the particles are influenced by the fuel ratio used.

Keyword: Combustion synthesis

1. Introduction

The ferroelectric ceramic system $PbTiO_3$, or PT, is a well known ferroelectric system with high Curie temperature ($T_c = 490\,^\circ C$), high tetragonality factor ($c/a = 1.064$) and relatively low dielectric permittivity ($\varepsilon'_r = 200$). To avoid cracks and high porosity due to the thermal expansion anisotropy during the cooling down through T_c in the PT ceramic bodies, doping is commonly used to process this material. For instances, La modified lead titanate (PLT) ceramics are an interesting material for a large variety of applications that include ferroelectric memories, pyroelectric sensors and piezoelectric devices. Moreover, the structural characteristics and the physical and chemical properties of the PLT depend strongly on the methodology employed in its preparation. Various preparation methods such as coprecipitation,[1–4] hydrothermal synthesis[5,6] and sol–gel,[7–9] have been used to produce PLT. Among the various existing methods of chemical synthesis, combustion reaction is an alternative and promising technique for preparing PLT, leading to highly pure and chemically homogeneous particles.[10–14]

The combustion reaction method is simple, involving a very fast chemical and exothermic reaction to form the material. The key characteristic of the process is that the heat required to trigger the reaction is supplied by the reaction itself instead of coming from an external source.[12] Metallic nitrates, which are the source of cations for the formation of metallic oxide, react with the fuel reducer, resulting in the formation of a fine, dry and usually crystalline powder oxide.[12] Apart from the before mentioned advantages, the combustion reaction method also has interesting characteristics such as its simplicity (since it does not require multiple stages), its relatively low cost, and the fact that it usually results in products with the desired structure and composition.[12,13] This paper reports the microstructural characterization using the Rietveld refinement method in lead lanthanum titanate ceramics system produced by combustion synthesis.

2. Experimental

Ceramic powders of the ferroelectric perovskite-type (Pb,La)TiO_3 from different batch formula (equivalent to a different amounts of lead oxide excess in the final product) were prepared by combustion synthesis. The raw materials were $Pb(NO_3)_2{\cdot}9H_2O$ (Merck), $La(NO_3)_2{\cdot}6H_2O$ (Merck) and tetraethyl orthotitanate $Ti(OC_2H_5)_4$ (Merck). Different amounts

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Table 1
Sample nomenclature as function of the glycine/urea concentration ratio and batch formula, for $x = 0.20$

Fuel	Batch formula: $(Pb_{1-y},La_x)TiO_3$		
	$y = x$	$y = 1.250x$	$y = 1.375x$
100% urea	A201	B201	C201
50% urea + 50% glycine	A203	B203	C203
100% glycine	A205	B205	C205

The total fuel amount corresponds to a fuel-to-oxidizers ratio = 1.

of urea H_4CN_2O (Merck) and glycine $H_5C_2NO_2$ (Aldrich), correspondent to a total fuel-to-oxidizers ratio = 1, were added to the crucibles containing the metallic precursors. Samples were labeled according to the batch formula and the fuel ratio as displayed in the Table 1. The system was placed in a pre-heated hot-plate (Cole-Palmer Instrument) at a constant temperature in the range of 300–600 °C. The temperature profile in the crucible was monitored with an optical pyrometer, Raytec, model MA2SC. The mixture frothed and swelled, until a fast explosive reaction take-off, with a large amount of evolved gas. After the ignition, the crucibles were placed in a muffle pre-heated at 500 °C for the ending of the reaction, and then at 700 °C/30 min for a further thermal treatment.

The X-ray powder diffraction (XRD) patterns were collected with a Rigaku Rota Flex on a rotating anode source, using a flat-plate Bragg–Brentano geometry, operating with Cu Kα radiation, 50 kV, 100 mA and equipped with a graphite monochromator. The powder diffraction pattern was recorded in the range of $2\theta = 3$–$80°$, with a step of 0.02°, and at rate of 5 s/step. The structural refinement was performed using the Rietveld technique as implemented in the computer program package Fullprof.[15] In this method the overall diffraction profile is calculated as the sum of overlapping peaks, which position, function shape and intensity are defined by the unit cell parameters, zero-point correction, and half-width parameters. All these parameters are refined by the least-squares method to achieve the best agreement between the measured and the calculated profile. Thompson–Cox–Hastings pseudo-Voigt peak profile functions[16] were used to the profile fitting. The XRD diffraction patterns of the 700 °C/30 min thermal treated samples were used for the structural refinement analysis by the Rieltveld method. The initial crystalline cell parameters adopted were those from ICSD 68975 file.

3. Results and discussions

Table 2 and Fig. 1 shows up the R_{Brogg} factor values and the cell parameters based on the tetragonal symmetry for the perovskite structure, respectively, obtained for the PLT powders through the Rietveld method. It was found that the powders present 95–98% of the crystalline perovskite phase. The results reveal that the *C* is the cell parameter that presents effective changes respect to the synthesis conditions (Fig. 1). It is clear that the *c* parameter, as well as the volume cell, is smaller for the powder synthesized with the mixture of the fuels (urea and glycine) when samples from the same batch formula are compared.

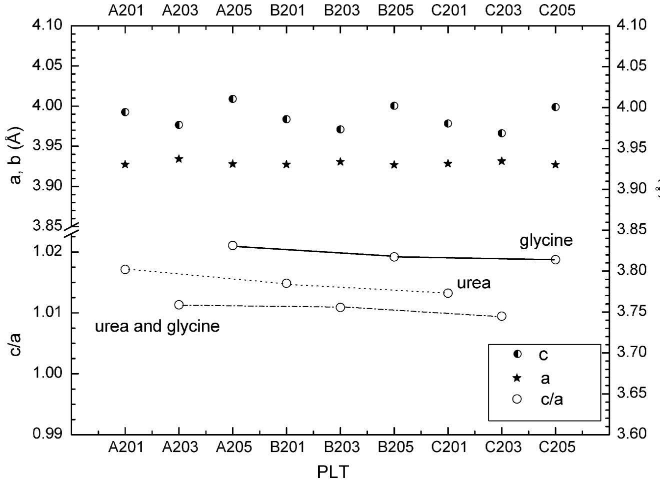

Fig. 1. Unit cell parameters calculated from the Rietveld refinement analysis for the PLT samples named as indicated at Table 1, and tetragonality factor (*c*/*a*) calculated. The lines are only a guide for the eyes to show the differences on the results as a function of the fuel type used during the combustion synthesis of the PLT powder.

The calculated tetragonality factor values are compared as a function of the sample type in the Fig. 1. The values observed for the PLT samples, which fuel was glycine and urea, are close to those found for the ceramic bodies with similar composition prepared by the conventional solid state reaction method at higher temperatures ($c/a = 1.013$), for instances, calcined at 800 °C and sintered at 1200 °C,[7] and calcined at 900 °C and sintered at 1200 °C.[17] This fact confirms that the fuel mixture of urea and glycine in the combustion synthesis of PLT is very efficient to guarantee the incorporation of the La^{3+} cation into the crystalline structure, expected to be in the Pb^{2+} sites, generating distortions in the unity cell not only due to the ionic radius size mismatch but also due to the cationic vacancy formation for the electroneutrality maintenance. These samples also showed smaller values for the crystalline average maximum strain among the compositions prepared with the same batch formula, as can be seen from the Fig. 2. Moreover, for the same kind of fuel used during the synthesis, the tetragonality factor *c*/*a* was smaller how less PbO amount was considered in the batch formula (see Fig. 1 and Table 1).

Table 2
Agreement factors for each PLT sample analyzed by the Rietveld method

Sample	A201	A203	A205	B201	B203	B205	C201	C203	C205
R_{Brogg}	4.18	5.42	4.86	4.50	4.86	5.67	4.44	4.86	4.20
R_{wp}	13.0	15.4	13.6	14.1	14.4	15.2	10.6	14.0	13.0
R_{factor}	2.83	3.34	2.97	2.83	3.18	3.28	2.72	3.48	2.70

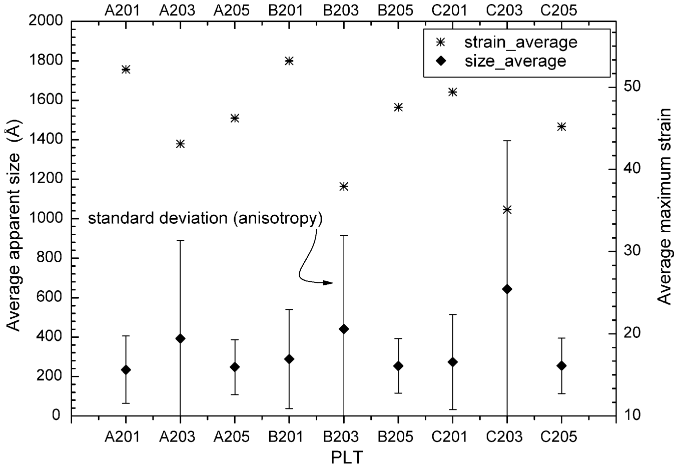

Fig. 2. Crystallite average size and average maximum strain calculated by the Rietveld refinement method for the PLT powders. The bar indicates the standard deviation (the anisotropy) for the crystallite average size referred to one crystallographic axis.

Another important result involving the crystallite characterization through the structural Rietveld refinement method of the PLT powders is the size anisotropy, as represented in the Fig. 2. The crystallite size anisotropy is markedly higher for the samples synthesized with the urea/glycine fuel mixture, especially for the composition with less PbO amount in the batch formula (or C composition, see Table 2). This fact reveals that the particle growing habit can be strongly influenced by the synthesis experimental conditions on the combustion method as the case of the chemical composition of the fuel.

From the data analysis refinement, powders with the particles of smaller *c* parameter or *c*/*a* (or those prepared with the mixture of urea and glycine) besides showing the highest crystallite average sizes (Fig. 2) also presented particles with plate shape (not shown here). Although this particle morphology was not found for the other samples prepared with each individual fuel. The particle average shape encountered for the samples obtained using glycine as fuel is more closed to the spherical since the model suggested the growing of plates in opposite sites from the center of the particle, resulting in a reduction of the size anisotropy. In the case of the urea as a fuel, the XRD refinement results showed particles with an anisotropy intermediary to those found for the samples prepared with glycine and the mixture of fuels. This particle average morphology behavior was confirmed by the scanning electronic microscopy of the powders (not shown here).

4. Conclusions

(Pb,La)TiO_3 powders, with 20 mol% of lanthanum, successfully prepared by combustion synthesis process, were fully analysed using the Rietveld refinement method through the X-ray diffraction data. The compounds, indexed in the tetragonal symmetry of the perovskite phase, presented sensible changes of the lattice parameters, the tetragonality factor (*c*/*a*), the particle average size and strain, and the particle morphology depending on the kind of fuel, used during the synthesis process and the PbO amount considered in the batch formula.

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