



A Crystallization Study of Nanocrystalline PZT 53/47 Granular Arrays Using a Sol-Gel Based Precursor

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In this work, we intend to perform a detailed study on the crystallization process of PZT 53/47 nanostructured powders by starting out with an amorphous precursor synthesized by a sol-gel based solution. Our interests also lie in the feasibility for controlling the average grain size of the final structure in the submicron range on an *ab initio* basis. Purposely, Fourier transform infrared spectroscopy (FT-IR), Raman (Stokes and Anti-Stokes), X-ray diffraction (XRD) and scanning electron microscopy (SEM) are used to examine the microstructural characteristics based on previously reported differential thermal analysis/thermal gravimetric analysis (DTA/TGA) data. The results show a crystallization temperature of 800°C to attain pure perovskite phase with excellent morphological quality, average grain size $\langle D_G \rangle < 300$ nm and with average crystallite size $\langle D_C \rangle < 15$ nm.

KEY WORDS: Powders-chemical preparation; PZT synthesis; Sol-gel precursors; Microstructure-final; Vibrational spectroscopies; X-ray diffraction

1. Introduction

The lead zirconate titanate ceramic system ($\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$; PZT $(1-x)/x$) is one of the most well known ferroelectric materials, which features a very noticeable enhancement of its piezoelectric and dielectric responses when $x \sim 0.48$, in the vicinity of the morphotropic phase boundary (MPB). Due to this property, the compositions in this range have been exploited in sensors, actuators, accelerometers, imaging devices, microphones, microelectromechanical devices (MEMs), ferroelectric random access memories (FRAMs), ultrasound generation, *etc*^[1]. In the last decades, the sol-gel based synthesis of PZT has received special interest due to the well known limitations of the conventional powders routes when deal-

ing with molecular homogeneity^[2,3]; moreover, the interesting properties associated with size related effects exhibited by ferroelectric systems with average grain size well below $1 \mu\text{m}$ ^[4-8] and the potential use of these ceramics in a plethora of nanodevices have risen this interest in recent years^[9]. In addition, nanosized PZT particles are rather important in the fabrication of highly dense bulk ceramics which, even nowadays, comprise almost the entirety of the electroceramics market.

In this work, we studied the crystallization process of ultrafine PZT 53/47 ceramic powder synthesized by using a dried sol-gel amorphous precursor previously obtained according to a sol-gel route discussed and described in an earlier literature [10]. Our main interests are: (a) to get the most complete description of the crystallization process from the amorphous precursor to the desired crystalline material, and (b) to explore the formation of nanosized granular arrays as well as the feasibility for controlling the average grain size of the final structure in the submicron range on an *ab initio* basis.

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2. Experimental

2.1 Materials

The followed sol-gel based synthesis route has been clearly detailed in literature [10] and [11]; anyway, a brief description will be given here. Starting reagents for the sol-gel PZT solution were: (1) lead (II) acetate trihydrate ($\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$, Mallinckrodt Baker, Inc., 99.8% purity), (2) glacial acetic acid (HOAc , Mallinckrodt Baker, Inc., 99.7% purity), (3) zirconium (IV) propoxide ($\text{Zr}(\text{OPr})_4$, Sigma-Aldrich Co., 70 wt% in 1-propanol), (4) titanium (IV) propoxide ($\text{Ti}(\text{O}^i\text{Pr})_4$, Sigma-Aldrich Co., 97% purity), (5) acetylacetone (AcacOH , Sigma-Aldrich Co., 99% purity) and (6) 2-methoxyethanol (2-MOE, Mallinckrodt Baker, Inc., 100% purity).

2.2 Synthesis description

First, lead acetate was dissolved in acetic acid with a 1:3 molar ratio while stirred and refluxed at 115°C during 3 h for water removal and homogeneity purposes. After this step, a thick transparent solution was obtained, which was referred as solution A. On a separate process, stoichiometric amounts of zirconium and titanium alkoxides were mixed with acetylacetone on a 1:3.06 molar ratio in order to avoid fast hydrolysis of reactants. This mixture was stirred and refluxed at 90°C for 3 h to form a clear yellow solution referred as solution B. In this step, two different chelated metal complexes were formed along with the residual alcohol: $\text{Zr}(\text{Acac})_4$ and $\text{Ti}(\text{OPr})_2(\text{Acac})_2$. In both complexes the central atom attained its maximum coordination number and, therefore, these were the most stable configurations for each metal.

Afterwards, solutions A and B were then mixed together as appropriate amounts of solvent (2-MOE) were slowly added to attain the chosen working concentration ($C=0.35$ mol/l). After stirring for 24 h at room temperature, a light yellow solution was obtained. In this step, the dissolved lead acetate complex could react with 2-MOE forming a very stable acetate-methoxyethoxy lead complex^[12] that, also contributes to, turn this final solution into a very stable hydrophobic sol. A previous study regarding aging and stability of these precursor solutions has already been published^[11].

This final solution was dried at 100°C for several days and, after that, it was thermally treated in order to analyze the phase evolution from the amorphous PZT-precursor sol-gel network to the expected final perovskite structure.

2.3 Experimental techniques

Crystallization was monitored by means of vibrational spectroscopy (FT-IR and Raman), X-rays diffraction (XRD) and scanning electron microscopy

(SEM) techniques after treating the samples for 12 h at certain temperatures that were previously chosen. At this point, it is important to say that, for powders heated at 850 and 900°C, the treatment was carried out for just 2 h due to the high volatility of lead for 850°C and beyond.

The FT-IR analysis was carried out on a Thermo Nicolet Nexus 670 FT-IR in transmission mode with a resolution of 4 cm^{-1} in the 400–2000 cm^{-1} range. The excitation source was a Helium-Neon laser light incident on a KBr compact target containing 0.5% in weight of the sample under study.

Raman characterization (Stokes and Anti-Stokes) was made on an Almaga XR Dispersive Raman spectrometer equipped with an Olympus microscope (BX51). The Raman spectra were accumulated over 25 s with a resolution of ~ 4 cm^{-1} and using the 532 nm radiation from a Nd:YVO4 laser (frequency-doubled) as the excitation source.

SEM was carried out on fine ground powders in a Leica Cambridge Stereoscan 440 microscope and the XRD patterns were recorded over a 20–60 deg. 2θ range on a Bruker D8 Advance diffractometer with filtered $\text{CuK}\alpha$ radiation. In this technique, the identified phases were indexed by comparing the resulting diffraction patterns with those of similar compositions reported in the international union of crystallography (IUCr) JCPDS-ICDD database. Afterwards, the cell parameters for a rhombohedral unit cell (a , α) were determined by choosing the (020) and (121) diffraction lines and using the appropriate relationship between direct and inverse lattices^[13]:

$$\frac{1}{d_{hkl}^2} = [(h^2 + k^2 + l^2) \sin^2 \alpha + 2(hk + kl + hl) (\cos^2 \alpha - \cos \alpha)] / [a^2 (1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha)] \quad (1)$$

where d_{hkl} is the interplanar distance between parallel (hkl) planes and given by the Bragg's law:

$$2d_{hkl} \sin \theta = \lambda \quad (2)$$

In order to determine the average crystallite size from the XRD patterns, peaks profiles were fitted to a Lorentz function by the non-linear least squares fitting (NLLSF) method and the full width at half maximum parameter (FWHM or $\beta(2\theta)$) was calculated for every diffraction line. Then the average crystallite size ($\langle D_C \rangle$) could be determined by means of the Scherrer equation^[13]:

$$\langle D_C \rangle = \frac{\lambda}{\beta(2\theta) \cos \theta} \quad (3)$$

It must be stressed that the use of this formula implies that the reported value for $\langle D_C \rangle$ is just an average of all the crystallite sizes of every phase present in our samples^[13]. On the other hand, according to the metrological report by Uvarov and Popov^[14],

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