

## Perovskite nanostructures obtained by a hydrothermal electrochemical process

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### Abstract

Increasing the miniaturisation is a key factor in the manufacturing process of the new, high-performances electronic devices. Thin/thick films represent a solution for the miniaturisation and the films can be obtained by different techniques such as RF sputtering, vacuum evaporation, laser ablation, CVD, sol–gel processing, hydrothermal electrochemical procedures. The aim of the paper is to investigate the hydrothermal electrochemical synthesis of perovskite nanostructured thin films. The influence of the synthesis parameters (pH, substrate, current density, temperature) on the composition, morphology and microstructure of the films was studied.

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### 1. Introduction

Nanotechnology is based upon the living nature, with systems' working at a defined nanoscale. The applications of nanotechnology are based on the fact that at the nanoscale materials properties are different to those of conventional bulk materials, with some being controlled by the surface of the material. Nanotechnology is based on previous investigations of materials chemistry and seeks to understand the origin of their properties, and provide a basis for designing new materials.<sup>1</sup> Some selection criteria have to be taken into account when a new material is proposed, namely the properties and the manufacturing methods. The manufacturing methods have to be selected carefully to obtain a material with a defined morphology and enhanced properties of the nanostructured materials in comparison to predetermined theoretical properties.<sup>2</sup> Some techniques such as high-energy ball milling, electrodeposition, gas phases, vacuum, sol–gel, hydrothermal and aerosol are used to obtain nanoparticles, and nanostructured functional and structural materials.<sup>2</sup> Chemical vapour deposition (CVD), plasma spraying and sol–gel techniques used for obtaining thin films, multilayer nanocomposites and functionally graded materials are expensive and involve long synthesis times. However, the

usage of nanostructured materials is limited due to the difficulty of producing these materials in large quantities, economically and efficiently.<sup>3</sup> Electrochemical and electrophoresis processes represent a cheap alternative, easy accessible for obtaining thin films and multilayer materials. Hydrothermal electrochemical procedures combine hydrothermal methods with electrochemical treatment and imply the deposition of oxide polycrystalline films on a reactive metallic electrode. In 1989, Yoshimura<sup>4</sup> applied for the first time this procedure to synthesise barium titanate based films. Hydrothermal electrochemical methods represent one solution to obtain ceramic films coatings. The major advantages of this method are low working temperature, the possibility of coating the substrates with different shapes, in situ film growth, the possibility of the selective growth (only on metallic active substrates), and preparation of nanostructured polycrystalline films.

Up to now the thin films have been studied mainly from the point of view of the relationship between their nanostructure and properties.<sup>5</sup> In the literature there are few data regarding the correlation between hydrothermal electrochemical conditions (pH, temperature, current density, time, working electrode surface) and the morphology and microstructure of the thin films. The aim of this paper is to investigate hydrothermal electrochemical synthesis of lead zirconate titanate (PZT) thin films starting from soluble salts of Ti(IV), Zr(IV) and Pb(II) with different Zr:Ti molar ratios. The results obtained for the Zr:Ti molar ratio = 52:48 are presented.

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## 2. Experimental procedure

Zr(IV), Ti(IV), Pb(II) aqueous solutions were used as starting materials for PZT-based films. The precursor was prepared by mixing these solutions with an appropriate amount of mineraliser reagent (KOH). The precursor was introduced in the Teflon vessel of a digitally controlled autoclave (Cortest, USA) endowed with three electrodes (working, reference and counter electrode). The PZT film formation was characterised by cyclic voltametry, chronoamperometry and cronopotentiometry using a Radiometer apparatus (Voltalab PGZ 100) with Voltmaster 4 software. Microstructure and phase investigations were performed to characterise PZT thin films synthesised under hydrothermal electrochemical conditions. Phase analysis (XRD) employed a computer-controlled DRON 2 instrument, using Cu K $\alpha$  radiation between 10 and 80° of 2 $\theta$ . Microstructures were examined using HITACHI S 4100 Scanning Electron Microscope (SEM/EDS).

The aim of the experimental work was to study the nucleation and growth of the electrodeposited films from a complex electrolyte containing lead, zirconium and titanium; a very difficult system with many solution equilibrium and electrode reactions. The hydrothermal electrochemical deposition method for the synthesis of PZT films was compared with the electrochemical one for the same system. Table 1 summarises typical samples experimental deposition conditions.

## 3. Results and discussions

### 3.1. Phase analysis of the PZT films by X-ray diffraction

XRD spectra of PZT films were collected and indexed. The summary of findings (Fig. 1) revealed the following:

(a) amorphous films with a very small amount of lead dioxide were obtained by electrochemical deposition on titanium substrates with submicron roughness of about 450 nm (sample S 5);

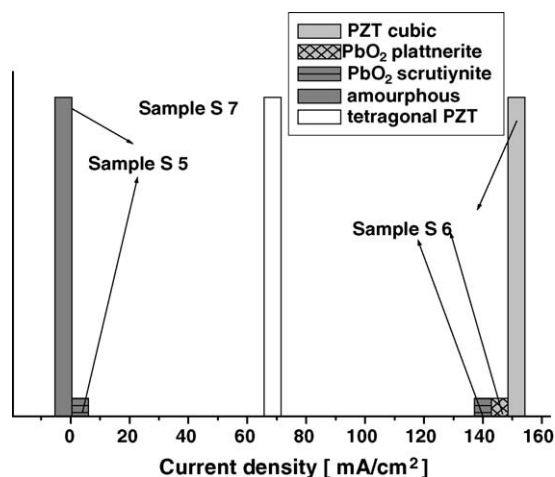


Fig. 1. Phase analysis for the PZT films deposited by electrochemical and hydrothermal electrochemical methods as a function of the current density.

Table 1  
PZT-based films samples

Sample	Deposition parameters	Substrate
S 1	Electrochemical procedure Acid medium Time 5 min Thermal treatment after deposition	Polycrystalline Pt Micron roughness
S 2	Electrochemical procedure Acid medium Time 25 min Thermal treatment after deposition	Polycrystalline Pt Submicron roughness
S 3	Electrochemical procedure High alkaline medium Time 5 min Thermal treatment after deposition	Polycrystalline Ti Micron roughness
S 4	Electrochemical procedure High alkaline medium Time 25 min Thermal treatment after deposition	Polycrystalline Ti Micron roughness
S 5	Electrochemical procedure High alkaline medium  Time 10 min Thermal treatment after deposition	Polycrystalline Ti Submicron roughness of about 450 nm
S 6	Hydrothermal electrochemical procedure High alkaline medium  Time 5 min Temperature 150 °C	Polycrystalline Ti Submicron roughness of about 450 nm
S 7	Hydrothermal electrochemical procedure High alkaline medium  Time 10 min Temperature 150 °C	Polycrystalline Ti Roughness of about 100 nm
S 8	Hydrothermal electrochemical procedure High alkaline medium Time 5 min Temperature 150 °C	Polycrystalline Ti Roughness 10 nm

(b) hydrothermal electrochemical deposition processes on a titanium substrate with submicron roughness of about 450 nm led to crystallised films containing cubic PZT as major phase and a very small quantity of lead dioxide (sample S 6);

(c) hydrothermal electrochemical deposition processes on titanium substrates with the roughness of about 100 nm led to the crystallisation of tetragonal PZT films (sample S 7).

### 3.2. Chemical composition of the deposited layers deposited by electrochemical and hydrothermal electrochemical methods

In Fig. 2 the evolution of lead, zirconium, titanium and oxygen content as a function of current density, pH and substrate surface is presented. The following conclusions may be drawn from then data. The electrochemical deposition process lead to a layer in which there are weak interactions between the components (lead, zirconium, titanium) and the deposition

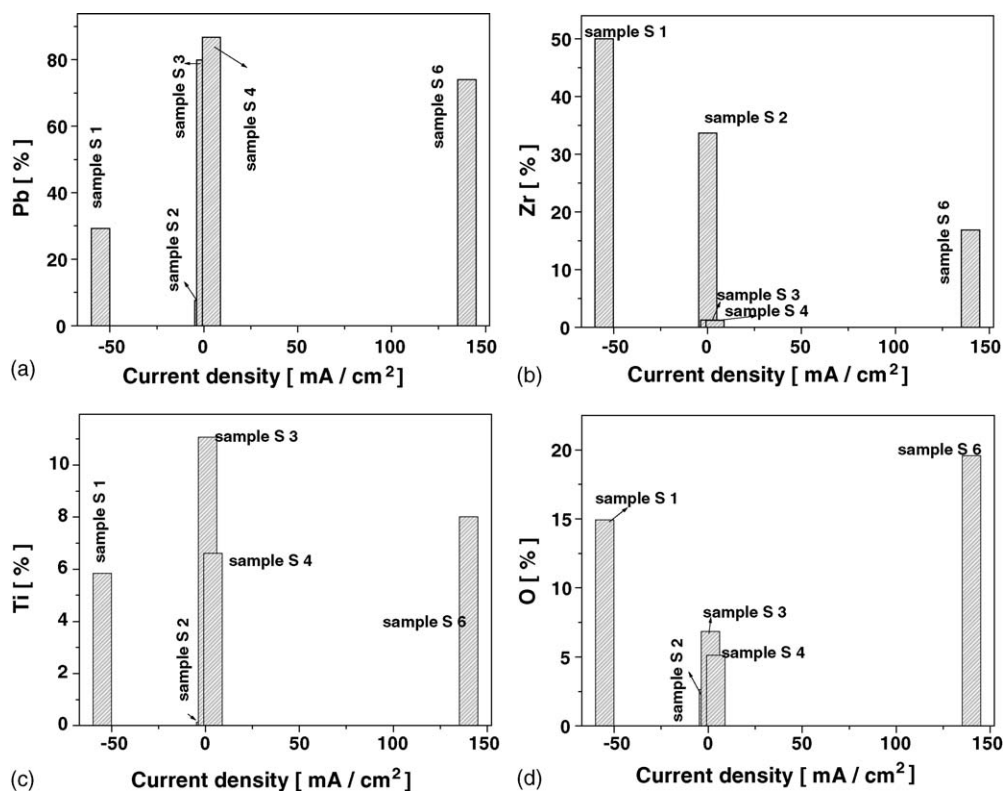


Fig. 2. Composition of PZT films deposited by electrochemical and hydrothermal electrochemical methods as a function of the current density, pH and substrate: (a) Pb; (b) Zr; (c) Ti; and (d) O.

potential of the components is negative in an acid medium and positive in an alkaline medium. A possible explanation could be that in acid the number of active centres (growth sites) increased and the concentration of particles increased (sample S 1). As a consequence the concentration gradients increased and surface diffusion ceased to be the slowest step. In an acid medium the concentration of zirconium in the deposited layer is higher due to the high positive charge of zirconium. In an alkaline medium the deposition process took place at a

higher positive potentials compared to the deposition potential of lead (samples S 2, S 3 and S 4). Zirconium and titanium required a higher activation energy than that for lead. As a consequence the molar ratio Pb:Ti:Zr in the deposited films is different from the theoretical one. For example in the case of sample S 1 the molar ratio Pb:Ti:Zr is 1:1.71:0.2 compared to the theoretical value of 1:0.23:0.11. Such a phase composition is undesirable due to its unfavourable electronic properties.<sup>5</sup>

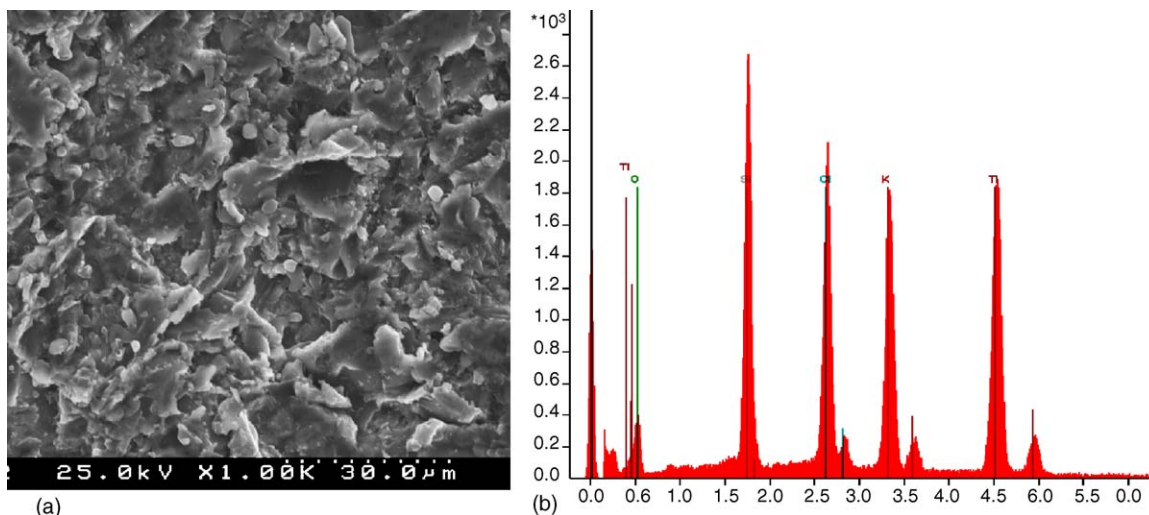


Fig. 3. SEM micrograph (a) and EDS analysis (b) of PZT-based films synthesised by electrochemical procedure from soluble salts of lead, titanium and zirconium (sample S 1).

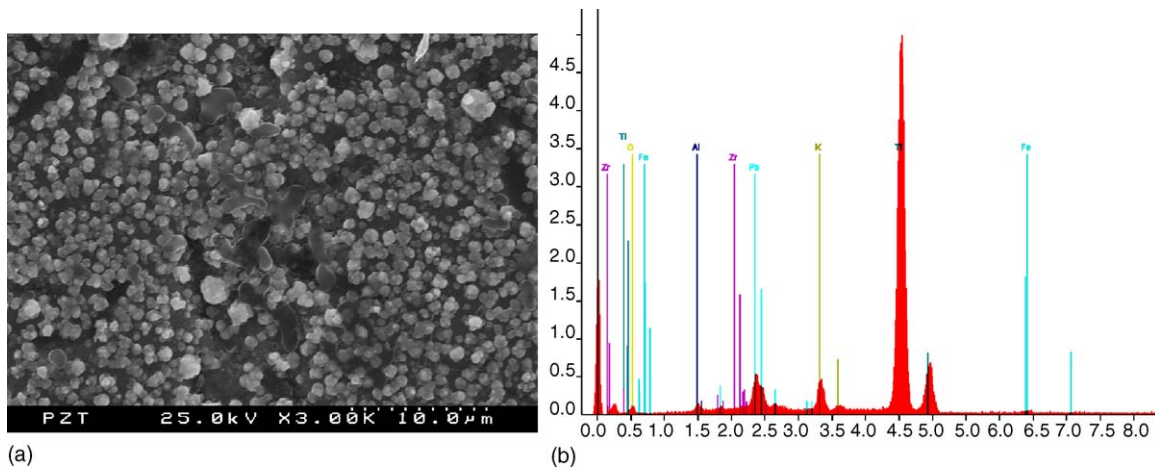


Fig. 4. SEM micrograph (a) and EDS analysis (b) of PZT-based films synthesised by hydrothermal electrochemical procedure from soluble salts of lead, titanium and zirconium (sample S 8).

According to XRD analysis, the hydrothermal electrochemical processes lead to uniform layer formation from a homogeneous solid solution of lead titanate and lead zirconate. The hydrothermal electrochemical process took place in two steps: first a solid solution PZ-PT is formed in situ; secondly the solid solution is deposited on the substrate. The deposition potentials of lead, zirconium and titanium are displaced to more positive values during co-deposition.<sup>6</sup> The stoichiometry is maintained (sample S 6 and S 8). For example in the case of the sample S 6 the molar ratio Pb:Ti:Zr is 1:0.186:0.104 compared to the theoretical value of 1:0.23:0.11.

### 3.3. Scanning electron microscopy of PZT films deposited by electrochemical and hydrothermal electrochemical procedures

Thin films of PZT were characterized by scanning electron microscopy. Typical micrographs are presented in Figs. 3–5. Micrograph corresponding to the sample S 1 synthesised by electrochemical deposition process (Fig. 3), the film showed high

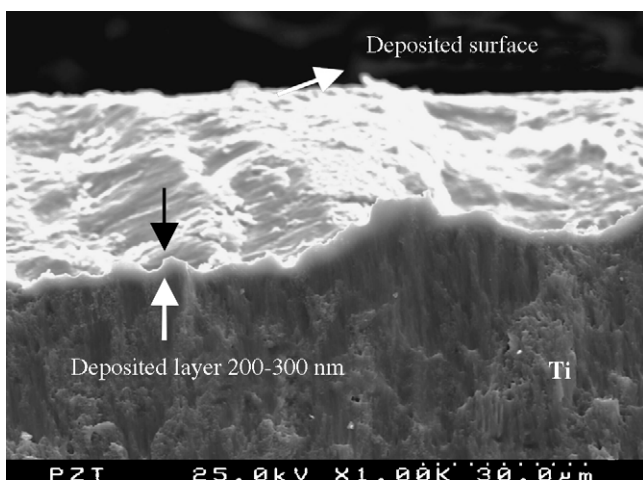


Fig. 5. SEM micrograph (cross-section) of PZT-based films synthesised by hydrothermal electrochemical procedure from soluble salts of lead, titanium and zirconium (sample S 8).

structural inhomogeneity (spherical and elongated grains). The deposited layer exhibits high porosity. EDS analysis revealed the presence of Ti, Zr, Pb, K (from KOH used as the mineralizing agent in the synthesis process) and Si from the metallic substrate. Micrograph of sample S 8 synthesised in hydrothermal electrochemical conditions (Fig. 4) exhibit low porosity with clear defined grains and polyhedral particles, which grew in the pores. EDS analysis confirmed the presence of Pb, Zr and Ti elements as the main elements in the film. The thickness of the films deposited under hydrothermal electrochemical conditions is in the range 200–300 nm (Fig. 5).

## 4. Conclusions

PZT-based films were synthesised by electrochemical and hydrothermal electrochemical procedures starting from soluble salts of lead, titanium and zirconium. The influence of pH, time and substrate surface on the deposited films was studied. Electrochemical deposition processes, both in acid medium on polycrystalline Pt substrate and in alkaline medium on polycrystalline Ti substrate, initially lead to amorphous films. After thermal treatment the crystalline films thus obtained are non-stoichiometric with respect to Pb/Zr/Ti contents. The hydrothermal electrochemical procedure in an alkaline medium on polycrystalline Ti substrate leads directly to crystalline films with the stoichiometric compositions. No thermal treatment was necessary after the deposition process. The substrate roughness influenced the morphology and the microstructure of the film in both electrodeposition procedures, while the substrate type and pH influenced only the deposition potential and the electrochemical reactions.

Additional studies are required to establish the mechanism of the hydrothermal electrochemical deposition process in the complex system Pb(II)–Ti(IV)–Zr(IV).

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