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Hydrothermal synthesis of ultradisperse PZT powders for polar ceramics

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Abstract

Polar ceramics with high homogeneity, high sinterability and nanocrystalline structure can be obtained by hydrothermal procedures. The aim of this paper is to study the influence of the hydrothermal reaction conditions on the properties of a PZT powder synthesized from soluble salts of Pb (II), Ti (IV) and Zr (IV). Therefore carefully chemical quantitative analysis (ICP, DCP, AAS) and microstructural investigations (XRD, SEM/EDX, DSC and RAMAN) have been performed. Based on these results a mechanism for hydrothermal synthesis of PZT was proposed. The fundamental research represents a work in progress in the PZT thick films synthesis by hydrothermal/electrochemical procedures.

Keywords: Microstructure prefiring; Perovskites; Powders–chemical preparation

1. Introduction

The lead based perovskite ceramic is widely used in several applications in different forms as bulk, thin and thick layers.[1] Its preparation generally involves two steps: the obtaining of the ceramic powder and the sintering of the shaped structures. The usual method is the oxide-mixing technique in which a desired chemical composition is made by firing raw oxides (calcinations), then crushing them into fine powder. More recently, in order to achieve microscopic compositional uniformity, wet chemical methods (as co-precipitation, alkoxide, hydrothermal) have been employed. By using such methods enhanced homogeneity and finer grained and very high purity powders have been obtained. Among these, hydrothermal synthesis is a useful method for preparing ceramic materials (ferroelectrics, relaxor) from a variety of precursor feedstock (oxides, nitrates, alkoxides). The hydrothermal procedure combined the effects of solvent, temperature and pressure on ionic reactions equilibrium, can stabilize the desirable products and inhibits the formation of undesirable products.[2,3] Different lead zirconate titanate composition were synthesized by hydrothermal procedure.[4–6] Parameters such as: medium alkalinity, reagents, concentration, hydrothermal treatment temperatures and proceeding times, nature of precursors and mineraliser influence the synthesis. In the open literature there are few data about the way in which these parameters influence the powders characteristics and sintering behaviour. The aim of the paper is to investigate hydrothermal synthesis of undoped PZT 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 = 57:43 are presented.

2. Experimental procedure

The feedstock Zr (IV), Ti (IV) and Pb (II) solutions have been prepared by dissolution of pure $ZrCl_4$, $TiCl_4$ and Pb $(NO_3)_2$ in distilled water. An appropriate amount of H_2O_2 was added during the preparation of $TiCl_4$ solution. The precursor was then prepared by mixing these solutions with an appropriate amount of mineraliser reagent (KOH). PZT powders were then precipitated in Teflon autoclaves (temperature 200 °C, pressure 4.5 bar, time from 15 min to 12 h, at different pH values). The precipitates were filtered, washed with distilled water to remove the soluble chlorides and nitrates and dried for several hours in air at 110 °C.

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Table 1
Results of DSC analysis and DTA measurements

DSC analysis (20–700 °C)		DTA measurements (20–1000 °C)
Sample P 24 Low pH, 3 h	Sample P 26 Low pH, 12 h	Sample P 24 Low pH, 3 h
• 115.48 °C endothermic peak (adsorbed water elimination) • 308.58 °C exothermic peak a crystallisation process of some amorphous oxides) • 506.47 °C small exothermic peak (starting the formation of PZT phase) • 579.95 °C exothermic peak (PZT phase is formed)	• 108.18 °C endothermic peak (adsorbed water elimination) • 300.81 °C exothermic peak (a crystallisation process of some amorphous oxides) • 420.99 °C small exothermic peak (starting the formation of PZT phase) • 509.24 °C exothermic peak (PZT phase is formed)	• 120 °C endothermic peak (adsorbed water elimination, 3.68% weight loss) • 350 °C small exothermic peak (a crystallisation process of some amorphous oxides, 1.96% weight loss) • 510 °C small exothermic peak (starting the formation of PZT phase, 0.76% weight loss) • 580 °C small exothermic peak (PZT phase is formed, 0.76% weight loss) • > 650 °C endothermic peak (lead oxides looses, 15.61% weight loss)

The powders composition was determined by chemical quantitative analysis (ICP and DCP). Powders phase composition was investigated by XR diffraction (Cu K_α radiation, modernised DRON 2 difractometer) and RAMAN spectroscopy (RAMAN system R 2001, operating range 200–2800cm^{-1}). Complex thermal analyses of the dried powders were performed by DSC (detector type Du Pont, DSC V4) and DTA (derivatograph C-MOM computer controlled). The analyses were performed in air at a heating rate in the range 5–10 °C/min. Dried powders morphology was determined by SEM(XL-30-ESEM TMP electron microscope with EDAX analyser).

3. Results and discussions

DSC and DTA curves of the dried samples synthesised in hydrothermal conditions at low pH values, 3 and 12 h respectively are presented in Fig. 1a–c. In Table 1 the main phase transformations occurring in the system are summarised.

DTA measurements for the dried powders synthesised in hydrothermal conditions at high pH values, 6 h, show only an endothermic peak at 117.3 °C, weight loss 3.65% (adsorbed and chemically bonded water elimination) without any other peak up to 1000 °C.The evolution of the ignition losses with the hydrothermal synthesis conditions is shown in Fig. 2. Dried powders synthesised at low pH values exhibit high ignition losses independent of the hydrothermal treatment time. It was observed that for the dried samples synthesised at high pH values the ignition losses decreased with the hydrothermal treatment time due to the increasing of the crystallisation degree.

XRD spectra of the dried PZT powder hydrothermaly synthesized at high pH values and different treatment times have been performed. The measurements have been done using a CuK_α radiation in a scattering angle range between 20 and 70°. The XRD analysis performed on samples treated between 2 and 6 h showed the evolution from an amorphous phase to a crystalline one in correlation with the duration of the treatment (Fig. 3). The indexing procedure showed the presence of a major tetragonal crystalline phase. The elementary cell parameters from Table 2 give a lattice distortion ratio between 1.02 and 1.03.

RAMAN spectra of the dried PZT samples synthesised in hydrothermal conditions at different times and pH values are presented in Fig. 4. It can be observed that in the samples synthesised at low pH values the lead oxide and titanium dioxide characteristic peaks are present, while the samples synthesised at high pH values reveal tetragonal PZT characteristics peaks.

SEM photographs of the samples synthesised in hydrothermal conditions at different times and pH

values are presented in Fig. 5. The SEM photograph (Fig. 5a) of the powder synthesised at low pH value, 12 h, 200 °C revealed amorphous agglomerated material on which micro crystals are deposited (sizes in the range 1.09–10.75 μm). After 3 h of hydrothermal treatment at high pH value, 200 °C, the PZT powder presents a mixture of amorphous material and crystals (sizes in the range 0.95–6.7 μm) (Fig. 5b). After 6 h of hydrothermal treatment at high pH value and 200 °C, the morphology of PZT powder particle is completely changed (Fig. 5c): individual crystals having dimensions between 1.4 and 3.5 μm can be observed.

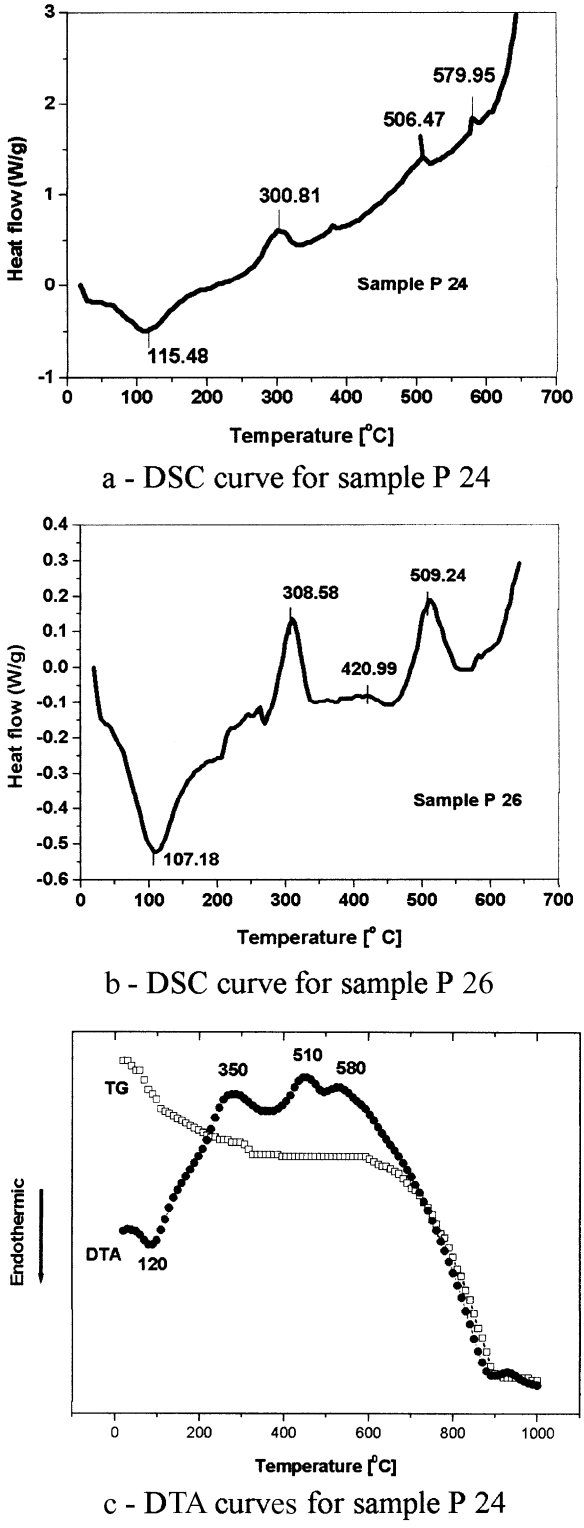

Fig. 1. DSC and DTA curves for dried samples hydrothermally synthesized at low pH values: (a) DSC curve for sample P24; (b) DSC curve for sample P26; (c) DTA curves.

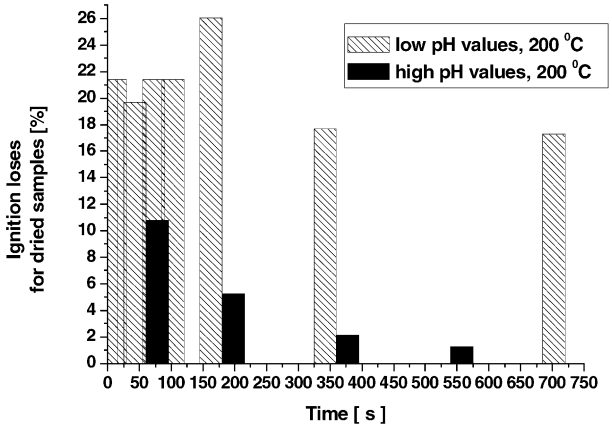

Fig. 2. Evolution of the ignition loses with the hydrothermal synthesis conditions.

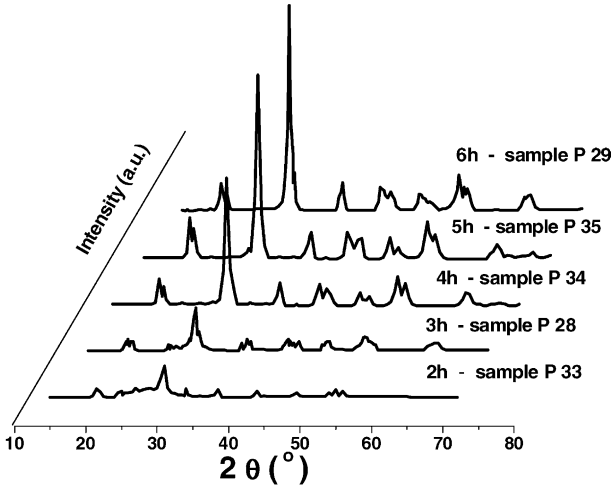

Fig. 3. XRD patterns of dried PZT powders obtained from soluble Ti (IV), Zr (IV) and Pb (II) precursors at high pH values, 200 °C, 2–6 h.

Table 2
The elementary cell parameters obtained through XRD

Sample	Treatment time (h)	a (Å)	b (Å)	c/a
P 33	2	Amorphous		
P 28	3	4.04_4	4.18_9	1.03_6
P 34	4	4.03_4	4.10_2	1.01_7
P 35	5	4.04_1	4.12_6	1.02_1
P29	6	4.01_1	4.13_6	1.03_1

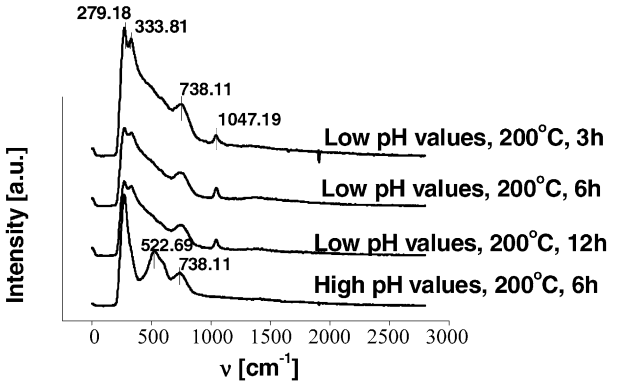

Fig. 4. RAMAN spectra of dried PZT powders obtained from soluble Ti (IV), Zr (IV) and Pb (II) precursors at different pH values, 200 °C, 3–12 h.

4. Modelling the hydrothermal synthesis of PZT powders

Experiments taking into account pH, temperature, time, concentration were performed to model the hydrothermal synthesis. The equilibrium reactions in the complex systems Pb–Ti–Zr–H_2O taking into account the presence of KOH as mineraliser, NO_3^- and Cl^- from the raw materials were studied. Actual equilibrium concentrations of the reactants and products for the real working conditions were calculated. For high alkaline solutions Pb (II), Ti (IV), Zr (IV) completely transform to the correspondent hydrous oxides. The conversion degree of lead hydrous oxide to $PbO*TiO_2$ it was ~0.4, while for $PbO*ZrO_2$ it was ~1 independent of the hydrothermal temperature. This results are different from classical synthesis route were $PbO*TiO_2$ was the first compound observed in the system. In low alkaline solutions lower conversion degrees were observed in accordance to experimental data.

5. Conclusions

Crystalline PZT powders with controlled stoechiometry could be prepared by hydrothermal reaction of hydrous oxides. In accordance with thermodynamic models, it appears that initially lead zirconate forms. It can be assumed that lead zirconate forms the nuclei for further crystallisation of PZT. Kinetics factors strongly affect crystallization process, and detailed studies are further required. Individual crystals with tetragonal/rhombohedral crystalline structures were formed in high alkaline solutions, crystallization degree increasing with hydrothermal treatment time. At lower pH and treatment times amorphous and agglomerated powders precipitated.

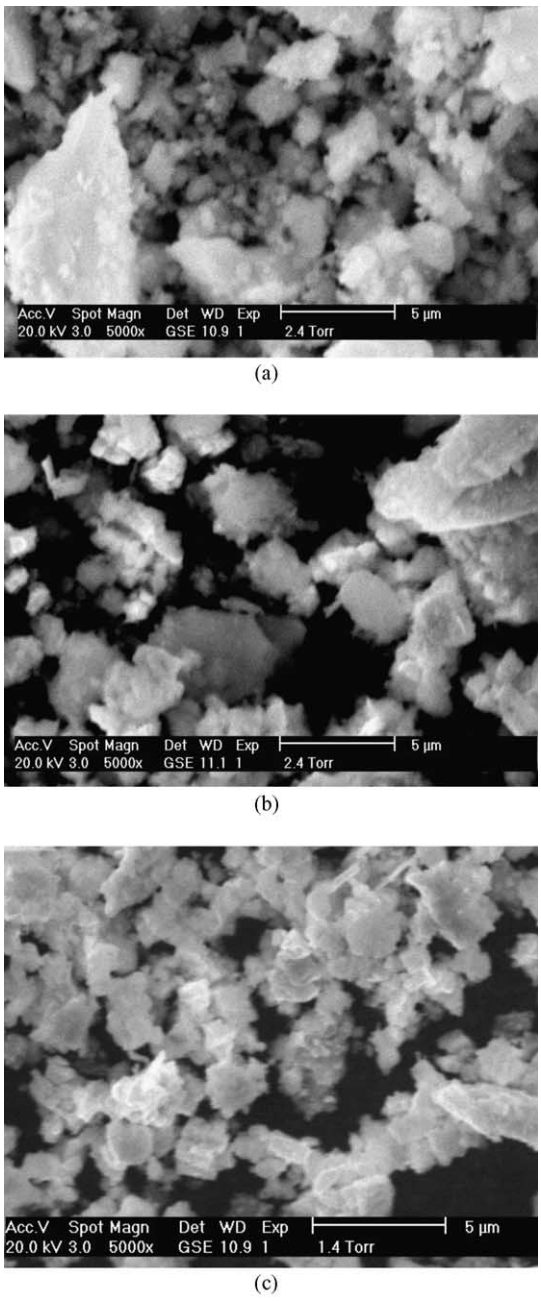

Fig. 5. SEM micrographs of dried PZT powder obtained from soluble Ti (IV), Zr (IV) and Pb (II) precursors: (a) low pH value, 200 °C, 12 h; (b) high pH value, 200 °C, 3; (c) high pH value, 200 °C, 6 h.

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