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Effect of urea on lead zirconate titanate—$Pb(Zr_{0.52}Ti_{0.48})O_3$—nanopowders synthesized by the Pechini method

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Abstract

PZT powders were synthesized by a chemical method using the conventional Pechini method and a urea-modified Pechini method, where the smooth pH increase, by the decomposition of urea, allows a better control of the pH. The FTIR spectra revealed that the precursor gel in conventional Pechini method is formed by a mixture of unidentade- and bridged-bonded complexes between the metallic cations and the citric acid. On the other hand, the precursor gel in the modified Pechini method is formed essentially by unidentade complexes. The modified Pechini method leads to homogeneous sub-micrometric spherical particles of 0.1 μm and a 7.4 m^2 g^{-1}surface area.

Keywords: Sol–gel processes; Microstructure pre-firing; Pb(Zr,Ti)O_3; Powders—chemical preparation

1. Introduction

Lead zirconate titanate $Pb(Zr_xTi_{1-x})O_3$ (PZT) is technologically important in electronics and microelectronics due to its unique piezoelectric and ferroelectric properties. PZT ceramics have been extensively used as electromechanical transducer materials,[1] temperature sensors,[2] and ferroelectric memories,[3] among others. The electromechanical response of these ceramics is maximized when x is close to 0.5, which corresponds to the limit between the tetragonal and rhombohedral regions of the phase diagram, denominated morphotropic phase boundary (MPB).

PZT powders have traditionally been prepared by the conventional solid-state reaction between the oxide reagents (PbO, ZrO_2, and TiO_2).[4] This method requires long thermal treatments followed by intermediate milling, besides relatively high temperatures to complete the diffusion reaction leading to compositional fluctuations which strongly influence the electrical properties of the ceramics.[5]

Alternatively, many chemical methods have been employed to achieve highly reactive powders with low compositional fluctuations and narrow MPB. Among them are the hydrothermal synthesis,[6] co-precipitation[7,8] and sol–gel[9] techniques, and the Pechini-based methods.[10]

The Pechini method is based on the formation of metallic complexes with carboxylic acid, normally citric acid, followed by a polymerization reaction with a polyalcohol, normally ethylene glycol, generating polyester. In order to avoid differential precipitation and to obtain a homogeneous Pb, Ti and Zr chemical solution it is important to control the pH and NH_4OH is normally used for that.

Tas[11] and Gajbhiye et al.[12] prepared nanosized PZT powders from water-soluble chlorides by the homogeneous precipitation via urea decomposition. The decomposition of urea in aqueous solution is accompanied by the controlled supply of ammonia and CO_2 into the solution.[12]

In the present paper, PZT powders were synthesized by a chemical method using the conventional Pechini method and a urea-modified Pechini method, where the smooth pH increase, by the decomposition of urea, allows a better control of the pH. The role of urea in the gel phase and its

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influence on the morphologic characteristics of the obtained PZT powder are evaluated.

2. Experimental

2.1. The conventional Pechini method

Lead acetate ($Pb(CH_3COO)_2 \cdot 3H_2O$, 99.9%, Reagen), zirconium isopropoxide isopropanol complex ($Zr[OCH(CH3)_2]4 \cdot (CH_3)_2CHOH$, 99.9%, Aldrich) and titanium isopropoxide ($Ti[OCH(CH_3)_2]_4$, 97%, Aldrich) were used as metallic cation sources. Aqueous solutions of zirconium and titanium citrates were prepared separately by dissolution of the proper alkoxide in a citric acid (CA) solution heated at 60 °C under constant stirring. After total dissolution, ethylene glycol (EG) was added to each solution and the temperature was kept at 120 °C for 3 h. Stoichiometric amounts of each citrate were mixed and kept at 90 °C. Lead acetate dissolved in distilled water was added to this mixture, followed by the addition of NH_4OH 30 vol.% to adjust the pH to 6.5. After pH stabilization, the solution was kept at 120 °C for gelation.The formed gel was heated at a 5 °C min^{-1} heating rate, to 250 °C and kept at this temperature for 1 h. The heating process continued to 400 °C, at a 5 °C min^{-1} heating rate, and the temperature was kept for 1 h. This heating treatment was done to eliminate the organic material. The powders obtained by this method, named PZT–NH_4OH, were treated at 400, 500, 600, 700 and 800 °C for 2 h.

2.2. The urea-modified Pechini method

In this preparation, after adding lead acetate, the temperature was kept constant at 90 °C. Urea (NH_2CONH_2, 98%, Sigma) was added until the pH reached 6.5 by homogeneous decomposition of urea. Since this step took about 2 h, the urea amount added was, probably, in large excess. Fig. 1 displays the flowchart for the conventional and urea-modified Pechini preparation.

The gels were characterized by thermal analysis (TGA) (DUPONT 2100) in synthetic air from room temperature to 600 °C at a heating rate of 10 °C min^{-1}.

The role of urea in the gel phases was investigated by infrared absorption analysis (FTIR) (Perkin-Elmer FTIR, spectrum 2000) in the 4000–400 cm^{-1} range (resolution: 4 cm^{-1}). For this, liquid films of the gels were prepared over Irtran crystal. KBr pellets for the powder samples treated at 400 °C and 800 °C were also prepared and used in this investigation.

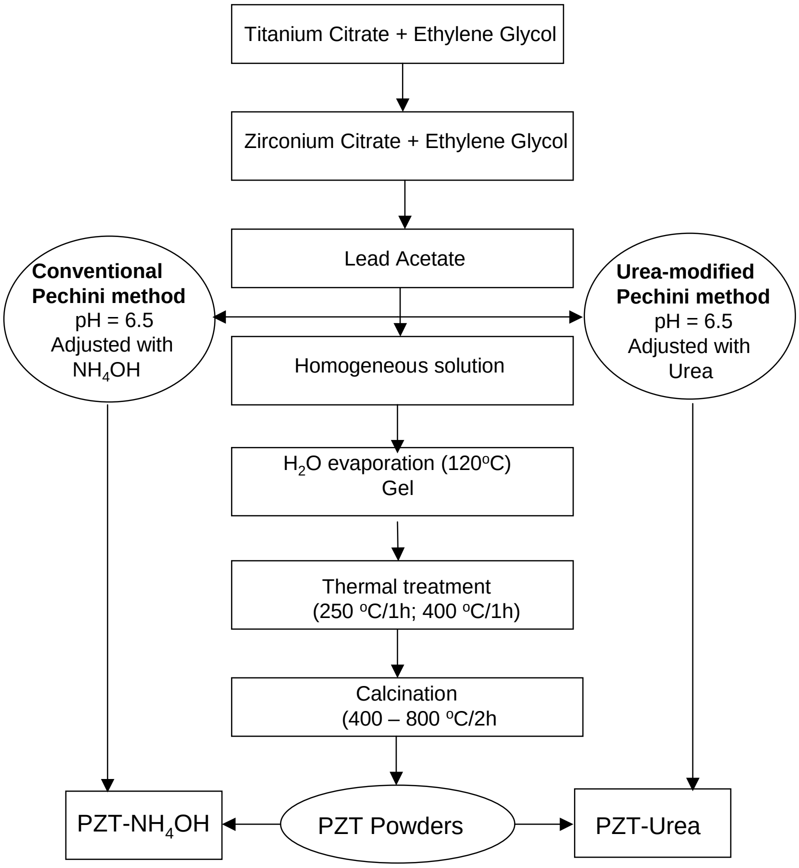

Fig. 1. Flowchart for the synthesis of PZT powders by the gel-citrate method.

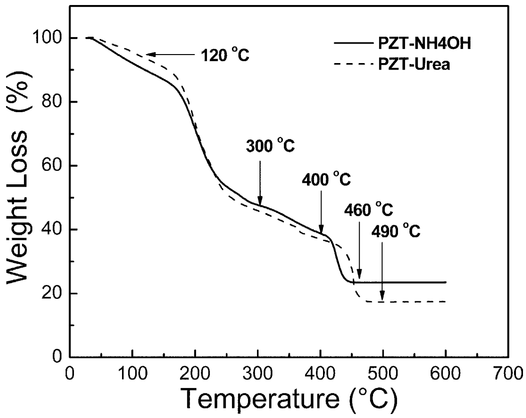

Fig. 2. TGA analysis for PZT–NH_4OH and PZT–urea gels in synthetic air atmosphere and heating rate of 10 °C min^{-1}.

The crystalline phases were identified by X-ray diffraction (SIEMENS D5000) using radiation Cu Kα, from 10 to 80° 2θ. The surface area was measured from N_2 adsorption curves by the BET method (MICROMERITCS FLOW SORB II 2300). The particle size was calculated from the values of surface area, by the equation:

$$D_{\mathrm{BET}} = \frac{6}{dS_{\mathrm{BET}}},$$

where, D_{BET} is the mean particle size, S_{BET} is the surface area and d is the PZT theoretical density (8.147 g cm^{-3}). Scanning electron microscopy (SEM) (LEO, 435 VPi) was used to observe the morphology of the powders treated at different temperatures.

3. Results

The thermal analysis results of PZT–NH_4OH and PZT–urea gels are shown in Fig. 2. It can be observed that the thermal decomposition of each gel occurs with different mechanisms. From room temperature to 100 °C, the weight loss can be attributed to free water. From 120 to 300 °C the thermal events can be attributed to the elimination of water resultant from the ester formed between the citric acid and ethylene glycol, urea decompositions and free citrate. It is possible to verify that the rates of some events are different, indicating that the presence of residual urea modifies the molecular arrangement in the gel, what alters its thermal behavior. The probable change in the gel molecular arrangement may result in changes in the PZT crystallization kinetics with alteration in the morphology of the material.[13]

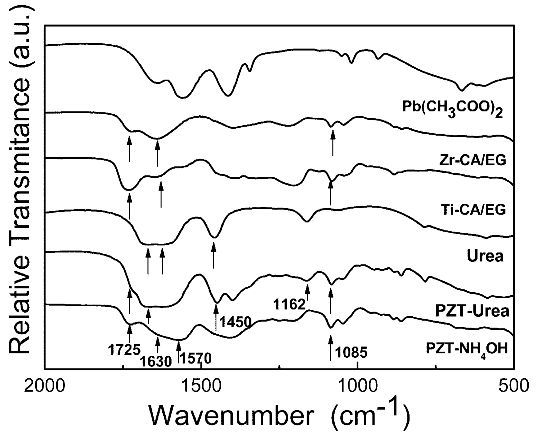

Fig. 3. FTIR spectra of lead acetate, zirconium citrate solution, titanium citrate solution, urea, PZT–urea gel, and PZT–NH_4OH gel.

Fig. 3 shows the FTIR spectra of the gel precursors, PZT–urea and PZT–NH_4OH gels. In this figure, Ti-CA/EG, Zr-CA/EG represents, respectively, the initial solution for Ti and Zr ions, prepared as described in Fig. 1, and $Pb(CH_3COO)_2$ is lead acetate solid.

Table 1
Principal bands referent to the FTIR PZT–NH_4OH and PZT–urea spectra

$CO(NH_2)_2$ (urea)		PZT–NH_4OH		PZT–urea	
cm^{-1}	Assigned	cm^{-1}	Assigned	cm^{-1}	Assigned
1667 s	ν (CO)	1724 w	$\nu\ (CO)_{ester}$	1725 sh	$\nu\ (CO)_{ester}$
1625 s	$\delta_s\ (NH_2)$	1630 sh	$\nu\ (COO^-)_{monod}$	1666 s	$\nu\ (CO)_{urea}$
1457 s	ν_{as} (CN)	1570 s	$\nu_{as}\ (COO^-)_{bridge}$	1623 s	$\delta_s\ (NH2)_{urea}\ \nu_s\ (COO-)_{monod}$
1162 m	ν (NH)	1408 s	$\nu_s\ (COO^-)_{acetate}$	1400 s	$\nu_s\ (COO^-)_{acetate}$
–	–	1207 vw	–	1448 w	$\nu_{as}\ (CN)_{urea}$
–	–	1085 m	EG	1269 vw	
–	–	1047 m	EG	1162 w	$\nu\ (NH)_{urea}$
–	–	884 w	EG	1083 w	EG
–	–	860 w	EG	1051 w	EG
–	–	640 vw	–	881 w	EG
–	–	–	–	859 w	EG
–	–	–	–	783 vw	
–	–	–	–	584 vw	
–	–	–	–	528 vw	

w: weak, vw: very weak, s: strong, vs: very strong, m: middle, b: broad, sh: shoulder, ν: stretching, ν_s: symmetric stretching, ν_{as}: asymmetric stretching, δ: deformation, δ_s: symmetric deformation.

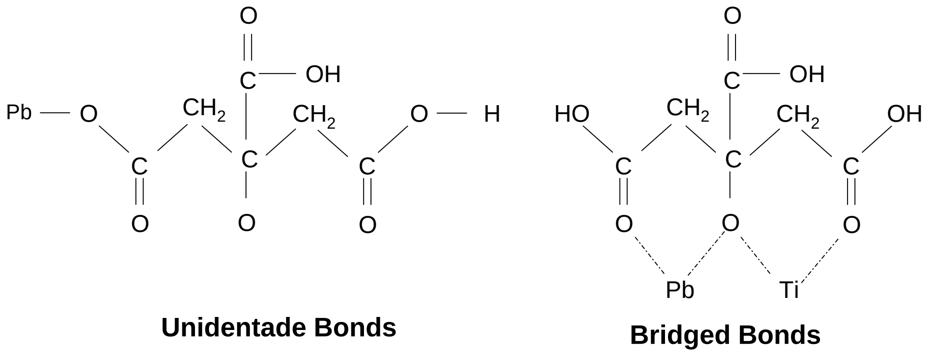

Fig. 4. Schematic model for the unidentade and bridged bonds formed between citric acid and the metallic cations.

By comparing the urea and PZT–urea FTIR spectra it is possible to observe that the bands at 1667, 1625, 1457, and 1162 cm^{-1} related to the urea are present in both spectra. Probably due to the large urea excess during the pH adjustment step, it is possible to suggest that urea was partially decomposed, remaining in PZT–urea gel.

The band at 1725 cm^{-1} is observed in both the Ti and Zr initial solution, as well as in the PZT–urea and PZT–NH_4OH precursor gels. This band is attributed to the ester C=O stretching mode (ν $(CO)_{ester}$), formed by the polymerization between CA and EG.[14,15] The band around 1630 cm^{-1}, observed in Ti-CA/EG (1648 cm^{-1}), Zr-CA/EG (1639 cm^{-1}), PZT–NH_4OH (1630 cm^{-1}) and PZT–urea (1623 cm^{-1}), is attributed to the carboxylate stretching in unidentade metallic complex formed between CA and Ti and Zr ions.[14] On the other hand, the band at 1570 cm^{-1} is not observed in the individual precursor's (Ti-CA/EG, Zr-CA/EG, $Pb(CH_3COO)_2$ and PZT–urea spectra, but it is observed only in the PZT–NH_4OH spectrum. This band can be caused by the asymmetric COO^- stretching (ν_{as} $(COO^-)_{brid}$) in bridged bonds formed between the metallic cations and CA, which involves two terminal carboxyl groups and the alkoxyl group in CA.[14] These observations suggest that the PZT–NH_4OH gel is formed by a mixture of bridged unidentade complexes[15] while the PZT–urea is essentially formed by cations unidentade complex with the CA.

The presence of urea obstructs the formation of bridges with AC which influences the morphologic characteristics of PZT obtained by these two methods. Table 1 shows

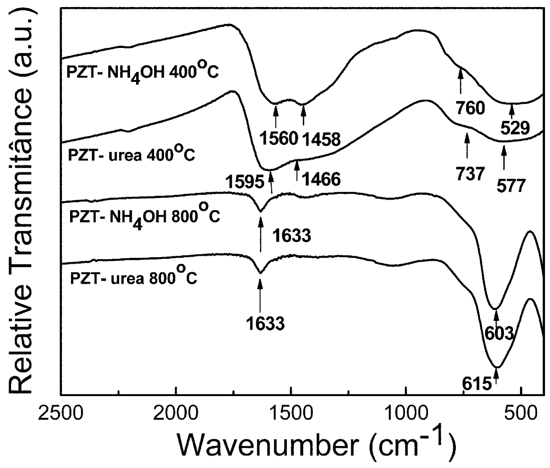

Fig. 5. FTIR spectra of PZT–NH_4OH and PZT–urea samples treated at 400 and 800 °C for 2 h.

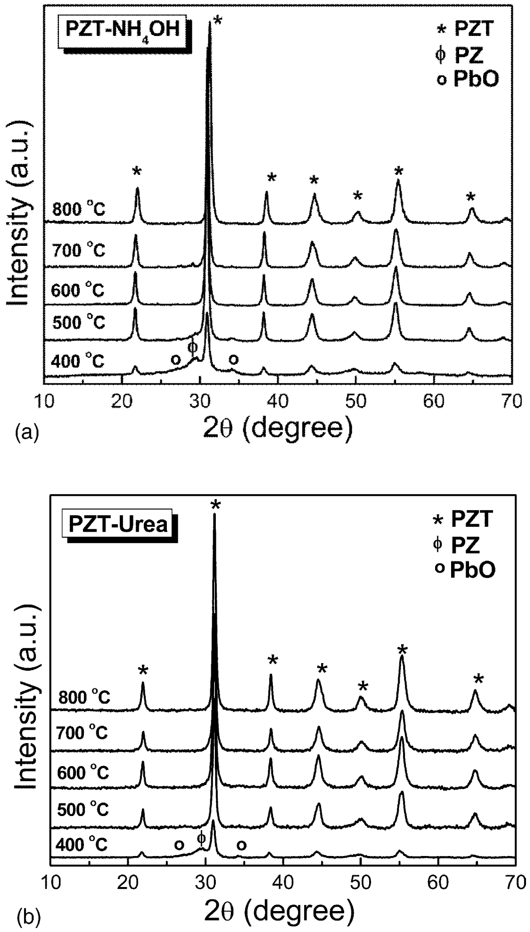

Fig. 6. X-ray patterns for the PZT samples synthesized by the conventional and urea-modified Pechini method, treated at different temperatures for 2 h.

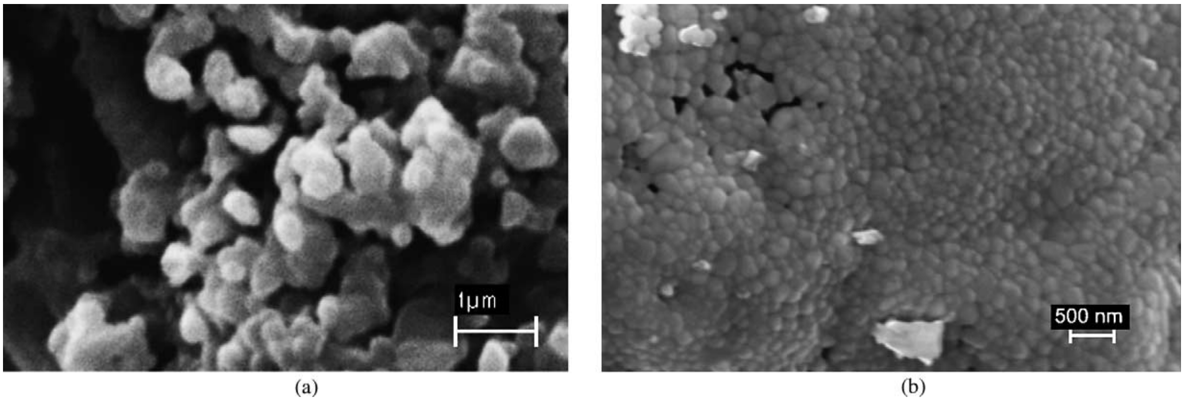

Fig. 7. SEM micrographs for the PZT powders treated at 600 °C for 2 h: (a) PZT–NH_4OH and (b) PZT–urea.

the principal bands referent to the FTIR PZT–NH_4OH and PZT–urea spectra.

Fig. 4 represents the schematic model for the unidentade and bridged bounds formed between the citric acid and the metallic cations.[14,15]

Fig. 5 shows the FTIR spectra of the PZT–NH_4OH and PZT–urea gels treated at 400 °C for 2 h and 800 °C for 2 h. The bands observed at 1560 and 1458 cm^{-1} in the FTIR spectra of PZT–NH_4OH gels treated at 400 °C for 2 h, as well as those bands observed at 1595 and 1466 cm^{-1} in the FTIR spectra of PZT–urea treated at 400 °C for 2 h, are attributed to carbonate ions,[16–18] while the broad bands around 550–800 cm^{-1} in these spectra are assigned to the M–O (M = metal) bonds. It is observed that the bands referent to the carbonate disappear and practically only the bands attributed to M–O bonds (slight shifted to lower wavenumber) are observed in the FTIR spectra of samples treated at 800 °C for 2 h.

The X-ray patterns for different powders treated from 400 to 800 °C for 2 h are shown in Fig. 6. It can be observed that the PZT crystallization process is similar in both methods. The secondary $PbZrO_3$ (PZ) (JCPDS 20–0608 and 35–0739) and PbO phases are formed during the treatment at 400 °C. These phases disappear with the treatment at 600 °C and a pure phase PZT is obtained. These results show that PZT powder can be prepared at relatively low temperatures (500–600 °C) for both methods.

The SEM image in Fig. 7 shows the PZT–NH_4OH and PZT–urea powders treated at 600 for 2 h. The PZT–NH_4OH powder presents spherical particles with an average diameter around 0.25 µm (Fig. 7a), while PZT–urea powder presents spherical uniform-sized particles of 0.1 µm, approximately (Fig. 7b).

The BET analysis for PZT–NH_4OH and PZT–urea samples treated at 600 °C for 2 h, revealed a 2.8 and 7.4 $m^2\,g^{-1}$ surface areas, respectively. The mean particle size, calculated from the surface area, is 0.26 µm, for PZT–NH_4OH and 0.1 µm for PZT–urea, which is in agreement with the SEM results. The powder characteristics are summarized in Table 2.

Table 2
Characteristics of the PZT–NH_4OH and PZT–urea powders treated at 600 °C for 2 h

	PZT–NH_4OH	PZT–urea
Particle morphology	Almost spherical	Spherical
Particle size (MeV) μm^{-1}	0.25	0.10
Surface area (BET) $m^2\,g^{-1}$	2.8	7.4
Equivalent spherical diameter (µm)	0.26	0.10

4. Conclusions

These results allowed concluding that the precursor gel in conventional Pechini method is formed by a mixture of unidentade- and bridged-bonded complexes between the metallic cations and the citric acid. On the other hand, the precursor gel in the modified Pechini method is formed essentially by unidentade complexes. The presence of urea obstructs the formation of bridged bonds with the citric acid, which is reflected in the morphologic characteristics of the powders. The modified Pechini method leads to homogeneous sub-micrometric spherical particles of 0.1 µm and a 7.4 $m^2\,g^{-1}$surface area.

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