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To cite this article: Manfang Mai et al 2009 J. Phys.: Conf. Ser. 152 012077

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Preparation and Characterization of Lead Zirconate Titanate Ceramic Fibers with Alkoxide-Based Sol–Gel Route

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Abstract. Lead zirconate titanate (PZT) fibers with diameters from 10μm to 40μm were prepared via a sol-gel route. Several kinds of chemicals were used, including lead acetate trihydrate, zirconium n-butoxide and titanium n-butoxide, in addition to butanol as a solvent. As a water source for hydrolysis reaction, Pb(CH₃COO)₂·3H₂O was directly used without further adding of water or catalyst conventionally. Acetylacetonate and acetate were added as stabilization agents to obtain stable sols for fiber drawing. The gel-to-ceramic conversion was characterized with thermal analysis, infrared spectroscopy and X-ray diffraction. A pure perovskite phase was obtained after heat treatment at 650ºC for 1h. By using scanning electron microscope (SEM), it was observed that a lower rate of heat treatment resulted in a denser microstructure of the fibers. The relative permittivity and the P-E hysteresis loop of the crystalline PZT fibers were also measured and discussed in the paper.

1. Introduction

Lead zirconate titanate (PZT) materials have been widely used in electric-mechanical applications such as transducers and motors for their excellent ferroelectric and piezoelectric properties. However, PZT bulk material has high density, low hydrostatic piezoelectric coefficients of charge and voltage, along with high stiffness, which limit its performance in certain applications including hydrophones and ultrasonic devices. Therefore, it has been focused on composite fabrication of PZT-based piezoelectric materials for sensing and actuating. PZT fiber is a good candidate for 1-3 piezoelectric composite, which has been prepared by extrusion[1], impregnation[2], viscous suspension-spinning process (VSSP)[3] and sol-gel[4-7]. Meanwhile, sol-gel technique offers the advantages of homogenous chemistry in multicomponent system and easy adjustment of composition. Moreover, it produces fibers with less crack in fine-scale diameter less than 100μm. Methoxythanol (MOE) is the most commonly used solvent, which was introduced in 1985 by Budd et al.[8]. Methoxythanol route provides high-quality precursor, but toxic and unfriendly for use. Recently, carboxylic acid route[9] and diol route[10] have been reported for the preparation of PZT based systems. However, no report has been brought out on directly drawing PZT fibers using butanol as solvent by sol-gel method.

In this study, several kinds of raw chemicals were used, especially butanol as solvent, acetylacetonate and acetate ligands as stabilizers to control the processing of hydrolysis and condensation. Emphasis was paid on the preparation process of the fibers.
2. Experimental Procedure

2.1. Preparation of gel fibers

Starting reagents were used to prepare the precursor sol for fiber drawing with lead acetate trihydrate (Pb(CH₃COO)₂·3H₂O, 99.5% purity), titanium n-butoxide (Ti(O·n-C₄H₉), 97% in butanol), zirconium n-butoxide (Zr(O·n-C₄H₉), 80% in butanol), and n-butanol (C₄H₉OH, AR reagent grade) as the solvent. A flow-chart is present in figure 1, showing the processing for PZT precursor sol. The atomic ratio in the starting solution was Pb:Zr:Ti = 1:0.52:0.48, no excess lead ion was introduced. Acetylacetonate was firstly added to the Zr-Ti mixtures as a chelating agent to reduce alkoxide hydrolysis with molar ratio between 1:1 and 2:1 for acetylacetonate to (Ti+Zr) alkoxide. Acetic acid was then added to the mixture of lead acetate and butanol to increase the solubility of lead acetate. As hydration resource, Pb(OAc)₂·3H₂O was directly used without any distillation or addition of water. The precursor solutions remained stable for a year.

![Flow-chart for PZT precursor sol](image_url)

**Figure 1.** Flow-chart for PZT precursor sol

It was conducted that the solvent was evaporated and the solution was concentrated at various curing temperatures from 25°C to 80°C, the time to gelation was significantly reduced from 60 hours at 25°C to 4 hours at 80°C. Therefore, all of the precursor solutions were efficiently cured at 80°C in this paper.

When the solution achieved the desired viscosity, it was poured into a spinnerette with a 100µm pinhole at the bottom. Fiber extrusion was carried out at ambient temperature. The gel fibers were collected on a take-up wheel, and then they were dried for 2 days at ambient temperature.

2.2. Heat treatment of gel fibers

Different samples of the fibers were sintered between 850°C and 1050°C for 1h at 50°C increments, each at a heating rate of 5°C/min. By using of crucible with PbO, lead atmosphere was conducted during the pyrolysis and sintering to compensate the lead volatilization.
2.3. Characterization of fibers
Thermal gravimetric analysis (TGA) and differential temperature analysis (DTA) were employed to monitor the organic burn-out temperature of the PZT fibers and the chemical reactions at a heating rate of 5°C/min in air. The transitions of the molecular and phase structure of the gel fibers were investigated by FTIR (AVATAR360, Nicolet Ltd.) in the wave number ranging from 4000 cm\(^{-1}\) to 400 cm\(^{-1}\) using KBr disk method. Crystallographic evolution was identified with X-ray diffraction (XRD) using CuK\(_{\alpha}\) radiation (X’pert PRO, Panalytical Ltd.). The morphology of the fibers was observed by a scanning electron microscope (SEM, Philips Ltd.).

For the electrical characterization of PZT fibers, bundles of twenty fibers cut for a length of 3mm were used to amplify the signals, as the output signal of a single fiber was quite low. Electrodes were applied by air-dried silver paste painted on both ends of the fibers. The cross sections of the fibers were observed by SEM. The dielectric constant and loss were measured using an Agilent 6500B precision impedance analyzer at 10kHz. The P-E hysteresis loop of the fibers was obtained using a ferroelectric precision tester (RT6000HVS, Radiant Ltd.) in a silicon oil bath at room temperature.

3. Results and Discussions

3.1. Characteristics of gel fibers
Continuous gel fibers were successfully produced, as shown in figure 2. As-drawn gel fibers were yellowish transparent and homogeneous. The diameter of the gel fibers was affected by the precursor viscosity and the drawing speed\(^[4]\). Gel fibers with 40-100µm diameter were easily obtained by carefully controlling these two factors. The gel fibers were very flexible just as drawn, and became brittle after aging for several days.

![Figure 2.](image)

3.2. Thermal Behavior of PZT Gels
TGA/DTA curves of the PZT gel powders were displayed in figure 3. Three main stages in the decomposition reactions were shown in the TGA curve. The first stage of weight loss below 180°C resulted from the removal of molecular water and butanol with boiling point at 117°C. The second drastic one of weight loss between 180°C and 370°C corresponded to the decomposition of acetate groups. After that, there was a slight weight loss due to the residual organic groups and carbon compositions. The gel powders consisted of about 70% solid components.

Exothermic and endothermic reactions which related to solvent removal and crystallization of PZT were shown in DTA curve. At temperature 100°C, there was an endothermic peak corresponding to the removal of solvent. The broad exothermic event at temperature 360°C was responsible for the acetate burn-out and the removal of residual carbon and decomposed organics, as well as the primary crystallization. The exothermic peak in 450-550°C region was due to phase transformation, which was also observed in the XRD patterns.
3.3. Molecular and phase evolution of PZT Gels

The FTIR transmittant spectra of the PZT gel powders heat-treated at a rate of 5°C/min to various temperatures was shown in figure 4. The spectrum of PZT gels had characteristic doublets at 1553 and 1413cm⁻¹, which were assigned to the asymmetric and symmetric COO vibration, respectively; the 1337cm⁻¹ band, was attributed to the deformation vibration of CH₂ groups; the peaks at 1050 and 1018cm⁻¹ were corresponded to the stretching of the C-O bond of butanol. 3400cm⁻¹ band was ascribed to O-H groups and the shoulder at 2900cm⁻¹ was related to the stretching vibration of C-H bonds[11]. These bands decreased in intensity as the heat treatment temperature increased and disappeared at 600°C. The band at 460-600cm⁻¹ was corresponded to Ti-O and Zr-O stretching vibration[12], which shifted to higher wave-numbers and became sharp as the heat treatment temperature increased.

Sol-gel powders were heat-treated in the temperature range of 400°C-700°C for 1h to observe the development of the phase structure of PZT, which was displayed in figure 5. Diffraction peaks attributed to metallic lead and pyrochlore phase were observed at 400°C. When the heat treatment temperature was up to 650°C, pyrochlore phase disappeared and only the perovskite phase was obtained.
3.4. Morphology of PZT fibers
The cross section of the fiber and longitudinal surface were shown in figure 6, with heat treatment temperature ranges from 650°C to 1050°C. It can be seen that the surface of the fibers was very smooth; the interior of the fiber was dense, free from large pores or other defects. The grain size of the fibers sintered at 900°C and 950°C was 0.2-0.5µm. When the sintering temperature was higher than 1000°C, grain size was up to 1µm, which was also in accordance with Meyer’s report [7].

![Figure 6. SEM micrographs of ceramic PZT fibers heat-treated at (a) 650°C for 1h; (b) 850°C for 1h; (c) 900°C for 1h; (d) 950°C for 1h; (e) 1000°C for 1h; (f) 1050°C for 1h](image)

3.5. Dielectric and ferroelectric properties measurement
Ferroelectric hysteresis loop of the fibers heat-treated at 1000°C for 1h were measured as shown in figure 7. A typical ferroelectric hysteresis loop was observed using 20Hz triangular waves. The hysteresis loop was square with the remnant polarization ($P_r$) of 25µC/cm² and coercive field ($E_c$) of 9kV/cm. However, well saturated hysteresis loop could not be obtained even when large electric field was applied. This may due to: (1) organic content remained in the fibers by insufficient burnout that may retard densification of the fiber resulting in the large leakage current density; (2) non switching linear response ascribed to space charge polarization which is originated from pores in the fibers[13]. The permittivity and dielectric loss angle of the PZT fibers heat-treated at 1000°C for 1h measured at 10kHz were 581 and 0.01, respectively. The value of dielectric constant here is lower than those of R. Steinhausen[14] and Yong-II Park[13], but similar to that of Meyer[5]. Such a low permittivity was attributed to the presence of pores left inside the fibers during the removal of organics in the heat treatment process.

![Figure 7. Hysteresis loop of PZT fibers heat-treated at 1000°C for 1h](image)
4. Conclusions
The PZT ceramic fibers were successfully prepared by the sol-gel technique from the solutions of lead acetate tribhxyde, zirconium n-butoxide and titanium n-butoxide, using butanol as solvent. As a water source for hydrolysis reaction, Pb(OAc)\(_2\)·3H\(_2\)O was directly used. Acetylacetonate and acetate were added as stabilization agents to obtain stable sols. The suitable viscosity of the sols was achieved for fiber drawing.

Single perovskite phase was obtained after the fibers were heat-treated at 650°C for 1h. The diameter of the PZT ceramic fibers was from 10µm to 40µm. Lower heating rates were employed to avoid cracking with dense and smooth surface. The grain size of the fibers increased with the heat treatment temperature, which was up to 1µm when heat-treated at 1000°C.

It was confirmed that the PZT fibers heat treated at 1000°C had ferroelectric property. The fibers showed square-shaped hysteresis loop with the remnant polarization (P\(_r\)) of 25µC/cm\(^2\) and coercive field (E\(_c\)) of 9kV/cm. The permittivity and dielectric loss angle of the PZT fibers heat-treated at 1000°C were 581 and 0.01 at 10kHz, respectively.

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