Pb(Zr,Ti)O₃ [PZT] FIBERS—FORMATION AND PROPERTY MEASUREMENT METHODS

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Abstract Fine scale lead zirconate titanate (PZT) and niobium substituted PZT (Nb-PZT) piezoelectric fibers were fabricated from sol-gel processed viscous “sol” using the “spinning” methodology developed for the continuous production of glass fibers. Subsequent drying and firing at above 750°C gave pure perovskite PZT and Nb-PZT fibers of 30 μm in average diameter. Further densification and grain growth were evident for fibers fired at 1250°C. Experimental methods for the determination of dielectric and polarization properties were developed to overcome inherent electric field difficulty relevant to fine scale fibers. The dielectric constant and polarization hysteresis values of the fibers were comparable with that of bulk ceramics. Preliminary single fiber mechanical pull tests indicated that the tensile strength of 30 μm diameter PZT fibers were similar to that of bulk ceramics, being in the range of 35-55 MPa.

INTRODUCTION

Lead zirconate titanate (PZT) piezoelectric ceramics’ ability to efficiently convert electrical energy to mechanical and vice versa has made them attractive for both actuators and sensors in active control systems. This reversible transformation ability also makes piezoceramics viable candidates for passive vibration damping. For structural materials comprised of various fibers, i.e. glass and carbon, the incorporation of piezoelectric fibers is, therefore, inherently desired.

For fibers with diameters less than 100 μm, non-conventional methods have been employed, including the impregnation of host fibers with a precursor solution and hand drawing from a viscous sol. Single strand fibers fabricated thus far have been limited to lengths of a few centimeters, being for demonstration purposes only. Furthermore, little information regarding electrical and mechanical properties has yet to be reported.

It was the objective of this work to fabricate fine-scale PZT fibers using a "spinning" methodology developed for the continuous production of carbon and/or glass fibers. A further objective was to determine the electrical and mechanical properties of individual fibers prepared above.

EXPERIMENTAL PROCEDURE

PZT Fiber Fabrication

Detail processing of PZT sol-gel precursor for fiber formation was reported previously. Stoichiometric quantities of each chemical was weighed out in accordance with the PZT formulations Pb(Zr₀.₄₈Ti₀.₅₂)O₃ and Pb₀.₉₈₈(Ti₀.₄₈Zr₀.₅₂)₀.₉₇₆Nb₀.₀₂₄O₃, as reported in Jaffe, Cook, and Jaffe.

The precursor solution was transferred to a vessel consisting of a spinneret and a plunger. Fibers were extruded through the spinneret with twelve 100 μm diameter holes at ~7 kPa of pressure. The spun-drawn fibers were collected on a rotation drum with a variable speed control. Factors involved in controlling the diameter of the fibers are: (i) viscosity of the sol, i.e. control of hydrolysis and condensation reaction, (ii) spinneret diameter, and (iii) speed of the take-up drum.

Fibers with diameters ranging from 10 to 80 μm were fabricated. The fibers were dried at room temperature for approximately 12 hours, cut into lengths of ~10 cm and fired at temperatures from 750°C to 1250°C for 10 minutes. For samples fired at temperatures >1200°C, a lead atmosphere was created to minimize lead loss. The sintering condition of 750°C for 10 minutes
was chosen based on a previous study\textsuperscript{7} which was high enough to enable the formation of the desired perovskite structure, yet low enough to fire in open air without lead loss.

**Characterization**

Crystallinity and phase analysis of the fibers as a function of thermal treatment were determined using x-ray diffraction (XRD) analysis. The microstructure, i.e. grain size and degree of porosity, and diameter of the fibers were examined using scanning electron microscopy (SEM).

Dielectric constant and polarization of heat treated individual fibers were measured at room temperature using the holder described in Figure 1. A small amount of air-dried silver was applied to both ends of the fiber prior to both measurements. For the capacitance measurement, 1 to 2 cm length samples were used, whereas specimens ~3 mm in length were prepared for polarization measurement.

![Figure 1](image)

**FIGURE 1**. Fixture for fiber permittivity and polarization (a), and section view of electrode configuration (b).

The polarization hysteresis was measured with the fields of \( > 3 \text{ MV/m} \) at 10 Hz. In addition to chemical and electrical characterization, the mechanical integrity of the PZT fibers was also investigated. The tensile strength was determined for selected fibers at the Nagasaki University of Japan, using a technique described by Iwanaga et al.\textsuperscript{9} Specimens 1 to 2 mm in length, diameter range between 26 to 36 \( \mu \text{m} \), were glued to carbon fiber and the direct tensile strength was measured with a load range of 1 to 10g.

**RESULTS AND DISCUSSION**

**Microstructural Analysis**

As spun amorphous fibers corrected on the take-up drum were continuous and flexible with gold color. All of the XRD spectra of PZT and Nb-PZT fibers fired at 750°C and 1250°C revealed the presence of well-crystallized perovskite phase. Figure 3 presents SEM micrographs of PZT and Nb-PZT fibers after heat treatments. As presented, the diameter of the fibers were in the range of 20 to 50 \( \mu \text{m} \), showing little evidence of porosity on the surface of the fiber. SEM examination of the cross section of the PZT fibers fired at 750°C revealed 10 to 20% fine porosity uniformly distributed across the fibers, except near the dense surface, with grain sizes on the order of 0.2 - 0.3 \( \mu \text{m} \). Fibers processed at 1250°C possessed dense microstructures with grain sizes into the range of 2 to 8 \( \mu \text{m} \). A small amount of closed porosity (~0.3 \( \mu \text{m} \) in diameter), both in grains and at grain boundaries were evident in the cross sectional view of the fiber after the pull test. Fracture surface was intergranular. The fibers with Nb-PZT composition fired at 1250°C showed uniform and finer grain size, 1 to 3 \( \mu \text{m} \), and little porosity. The reason for the smaller grain size is due to the niobium substitution, which tends to inhibit grain growth of PZT in addition to many other characteristics governed by this "A-site vacancy additive".
Electrical Properties

The dielectric constant values of the various fibers processed are summarized in Table 1. Due to the small input signals, dielectric loss values for the PZT fibers were not measured. The PZT fibers showed comparable dielectric values to that of the bulk ceramics disk samples made from the same solution. The dielectric constant of the samples fired at 750°C gave lower values which were probably due to the combination of porosity and smaller grain size. Representative room temperature hysteresis polarization E-field behavior for Nb-PZT fired at 1250°C are shown in Figure 4. The ferroelectric nature of the single piezoelectric fiber has not been reported before. The polarization hysteresis provides direct evidence that these fibers can be polarized to induce the desired piezoelectric properties. The level of remanent polarization ($P_r$) of the fibers was 37 μC/cm² and coercive field ($E_r$) was 19 kV/cm.

FIGURE 2. SEM micrograph of:
(a) PZT fired at 750°C for 10 min.
(b) PZT fired at 1250°C for 10 min.
(c) Nb-PZT fired at 1250°C for 10 min.

FIGURE 4. Polarization hysteresis of Nb-PZT fiber (diameter 30 μm).
TABLE I. Dielectric Constant of Sol-Gel Derived PZT and Nb-PZT Fibers\(^a\)

<table>
<thead>
<tr>
<th>Ceramic</th>
<th>Heat Treatment Temp.[°C]/Time [min.]</th>
<th>Dielectric Constant (%) error</th>
</tr>
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<tbody>
<tr>
<td>PZT</td>
<td>750/10</td>
<td>670 (15)</td>
</tr>
<tr>
<td></td>
<td>1250/10</td>
<td>870 (10)</td>
</tr>
<tr>
<td>Nb-PZT</td>
<td>750/10</td>
<td>1100 (15)</td>
</tr>
<tr>
<td></td>
<td>1250/10</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Fiber : Average diameter of 30 μm.

**Mechanical Properties**

Preliminary data for the tensile strength of PZT fibers fired at 750°C and 1250°C determined using the pull test were 36 MPa and 40 MPa, respectively. Tensile strengths of ~55 MPa were found for Nb-PZT fibers. This higher value may be attributed to its smaller and more uniform grain size. Finer diameter fibers tended to give larger tensile strength values, though more data with different diameter samples is required to confirm this. Tensile strength values for bulk PZT ceramics reported in the literature is on the order of ~76 MPa\(^1\), with modulus of rupture using 3-point flexure is in the range of 10 to 40 MPa\(^1\). Therefore, the fiber tensile strength found for the fibers in this work is considered to be in a similar range as that of the bulk ceramic.

**ACKNOWLEDGEMENT**

The authors would like to acknowledge the contribution of Professor Hiroshi Iwanaga of Nagasaki University for fiber mechanical measurements. A special thanks to Professor Dan Edie and his group at Clemson University for letting us use their equipment and for their help. Also, the authors wish to thank Drs. L. Eric Cross and Keith Brooks for their help for this project. This project was supported by Office of Naval Research Grant No. N00014-92-1391.

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