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Rapid thermal processing of electrospun $PbZr_{0.52}Ti_{0.48}O_3$ nanofibers

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ABSTRACT

Electrospinning is potentially an effective way to prepare ceramic nanofibers using sol–gel precursors. However, the raw dried fibers require a sintering step that can lead to highly porous nanofibers or to a total loss of the fiber morphology. Generating dense sintered nanofibers via electrospinning is challenging, particularly in PZT fibers, where lead loss at high temperatures is amplified due to the large surface. This paper focuses on rapid thermal processing (RTP) of PZT nanofibers. The fibers thermal decomposition is studied in detail by TGA/DTA combined with mass spectroscopy and XRD. Pre-firing at 350 °C for 0.5 h is required for effective organics burnout. RTP for 30 s at 800 °C allows formation of the perovskite PZT phase, similar to conventional firing at 650 °C for 2 h. In summary, we demonstrated that a combination of pre-firing with RTP sintering can be used as an efficient and environmentally friendly process, leading to dense, smooth PZT nanofibers that are sensitive to deformation.

1. Introduction

Interest in piezoelectric materials in general and $PbZr_xTi_{(1-x)}O_3$ (PZT) in particular is increasing [1–5]. One of the promising ways to prepare PZT nanofibers is electrospinning [3–7]. However, unlike the preparation of polymer fibers where the size and structure are set during the spinning stage, ceramic fibers require a sintering step, where the organic components of the fibers are lost, and further shrinkage occurs due to sintering of the inorganic components. Based on Gaorong Han and co-workers [4,5] and on our experience, the high temperature conversion of the electrospun green fibers into coherent sintered ceramic fibers with required phase composition is challenging, especially when the diameter is on the order of 100 nm. The difficulties arise from the need to have a non-volatile polymer in the spinning solution to assure a proper rheology, and in addition from the use of various precursor metal organic or inorganic salts in the solution. The decomposition and conversion of all the above components into the respective oxides is associated with a significant weight loss (>50% in this work) during sintering leaving a highly porous structure before densification. Finally, local grain growth within the fiber coupled to the high initial porosity can easily result in the breakup of the fibrous morphology, giving rise to a powder as demonstrated below in the present paper. The above challenges explain why in spite of the extensive literature on electrospinning, and the commercial use of this promising technology in the production of polymeric nanofibers, it is utilized very rarely to make ceramic nanofibers products.

In light of the above, it is crucial to maintain the fiber morphology, mechanical stability and phase composition during the sintering stage of the PZT raw fibers. In this research, we compared a conventional sintering procedure (650 °C, 120 min) to a rapid thermal processing (500–800 °C, 0.5 min) of PZT ceramic nanofibers. This RTP technique is used in preparation of PZT thin films [8–10] but, to our best knowledge, the sintering of PZT nanofibers by this procedure was not published. In addition to the challenges discussed above in retaining the fibrous morphology during sintering, another issue with conventional sintering of PZT is the large lead losses at elevated temperatures, which create serious technological and environmental problems. These issues are amplified in the sintering of nanofibers, which have a higher surface to volume ratio than films or bulk bodies. In this paper, we demonstrate that these disadvantages can be avoided by a very short exposure to high temperature that gives rise to a smooth and dense fiber structure, prevents the formation of undesired pyrochlore phase [11,12] and yields the PZT perovskite phase. Finally, we demonstrate the qualitative performance of RTP sintered PZT nanofibers mats as displacement sensors.

2. Experimental

The main equipment for spinning included a high voltage power supply in the 0–40 kV range (SL40PN60/10003; Spellman, USA); a syringe pump and needle as spinneret electrode; an

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aluminum disk 20 cm in diameter, as a collecting electrode. The working distance and potential in all experiments were held at 20 cm and 15 kV, respectively.

The chemicals used to prepare precursor of PZT solutions were: titanium(IV) *iso*-propoxide (98%), zirconium(IV) *n*-propoxide (72–77%), lead 2-ethylhexanoate (41.7% Pb) from Strem, USA and polyvinylpyrrolidone (M_w = 1,300,000, Alfa Aesar).

Phase evolution was studied by XRD (MiniFlex, Rigaku, Japan). Thermal analysis was conducted by simultaneous TGA/DTG/DTA (SETSYS Setaram, France) coupled with evolved gas analysis by mass spectrometry (Thermostar GSD320, Pfeiffer, Switzerland). Heating rate was 5 °C/min up to 700 °C in flowing air of 30 cc/min. Morphology and elemental composition were investigated by HR-SEM/EDS (ULTRA plus, Zeiss, Zurich, Switzerland). The images were post processed with MS Office standard software by enhancing the contrast and sharpness to obtain higher features clarity.

The precursor sol preparation process is shown in Fig. 1. The procedure included mixing of initial metal–organic components in the following molar ratio: Pb:Zr:Ti = 1.1:0.52:0.48. Lead was added in excess to account for losses during sintering due to volatility of its oxides. Glacial acetic acid and 15 wt.% PVP in ethanol were added to obtain final sol. All components were mixed for at least 12 h in inert atmosphere. The sol was diluted with mixture of glacial acetic acid and ethanol at a ratio of 1:5, respectively. The sols were stirred for several hours before electrospinning. All operations with the sol prior to electrospinning are conducted under dry inert atmosphere.

Table 1
Weight composition of diluted sol used as precursor during electrospinning.

Material	(wt.%)
Lead 2-ethylhexanoate	12.7
Zirconium *n*-propoxide	5.0
Titanium *iso*-propoxide	3.1
Glacial acetic acid	12.5
Ethanol	62.9
PVP ($M_w \approx 1.3$ M)	3.8
Total	100.0

Final composition of the precursor sol is shown in Table 1.

All the electrospun green mats were pre-fired in air at 350 °C in a CM tube furnace (Bloomfield, NJ, USA). The fiber mats were sintered by two modes: conventional (slow) sintering in air using CM tube furnace and rapid thermal processing (RTP) in air using an IR furnace (MILA-5000-P-N, Japan).

Sensing measurements were made using an Instron universal testing machine (Instron, model 5568, USA) to create a constant amplitude cyclic loading on the sample in a 3-point bending geometry. The voltage changes in the PZT devices were measured

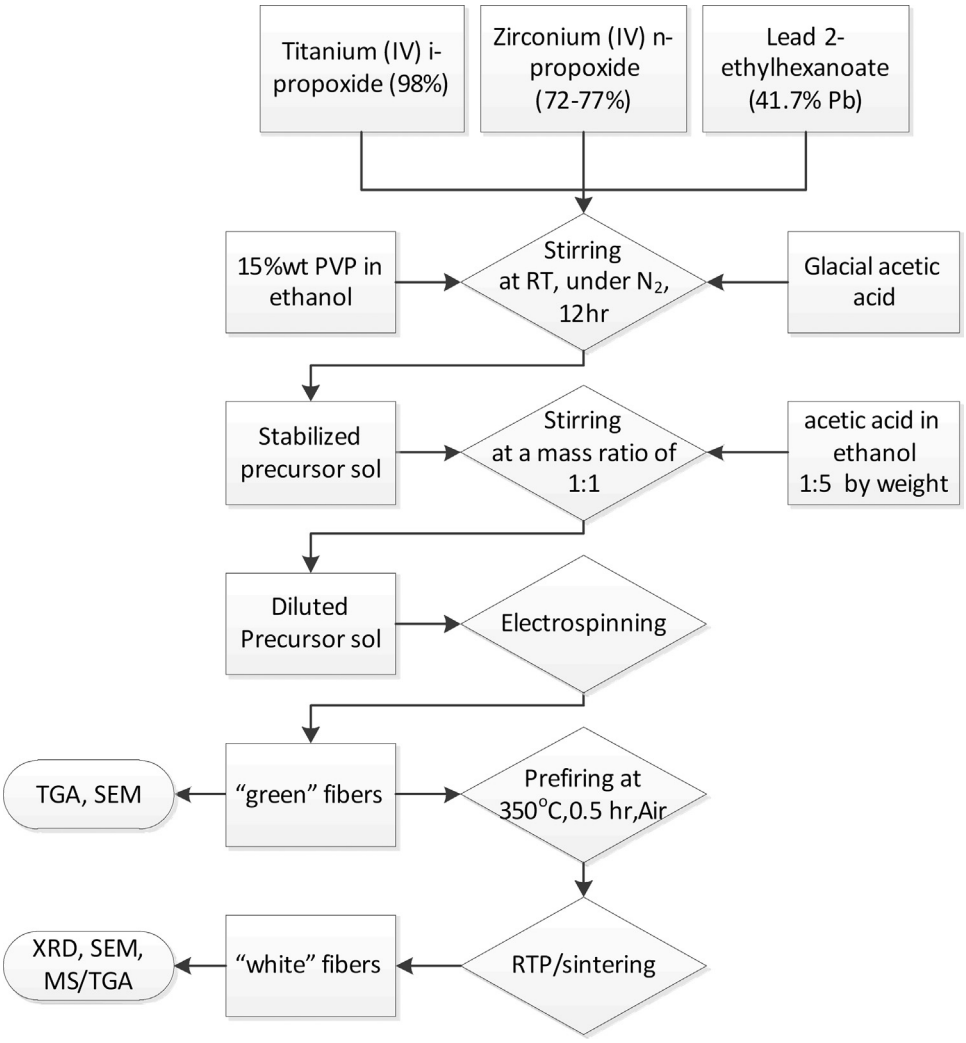

Fig. 1. Experimental flow chart of preparation and characterization of PZT fibers.