ELSEVIER

Ceramics International 31 (2005) 281–286

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Preparation and ferroelectric properties of PZT fibers

M. Zhang[a,*], X.D. Wang[a], F.M. Wang[a], I.M. Miranda Salvado[b], P.M. Vilarinho[b], W.C. Li[a]

[a]*Department of Physical Chemistry, University of Science and Technology Beijing, Beijing 100083, PR China*
[b]*Department of Ceramics and Glass Engineering, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal*

Received 18 November 2003; received in revised form 22 March 2004; accepted 3 May 2004
Available online 25 August 2004

Abstract

Lead zirconate titanate (PZT) fibers have been prepared via sol–gel route using acetic acid to acidify the precursors. The molecular structure of precursors is investigated by FTIR, liquid and solid ^{13}C-NMR. The crystallization behavior and the microstructure of PZT fibers are analyzed and discussed. The dielectric properties are also measured by piezoAFM. A pure perovskite phase was obtained after heat treatment at 973 K. The domain structure was observed, which showed that PZT fibers have ferroelectric properties. The permittivity of the PZT fiber was 544.

Keywords: PZT fiber; Domain structure; Acetic acid

1. Introduction

Owing to increased anisotropy, excellent flexibility and improved strength over monolithic lead zirconate titanate (PZT) ceramics, PZT fibers have recently been paid more attention by researchers [1]. Moreover, fine-scale fiber-shaped piezoelectric 1–3 composite have been studied for the development of high-frequency (25–70 MHz) ultrasonic transducers for medical applications [2,3]. A 40 MHz transducer of fine scale fiber 1–3 piezo-composites has been constructed, which showed a bandwidth of 54% and −47 dB insertion loss at center frequency [3].

Ceramic fibers have ever been fabricated using the viscous suspension spinning process (VSSP) [4], but the instrument is too big to be used in laboratory. David [5] has tried to prepare PZT fibers by the replication process, the diameter of the fibers being about 200–250 μm.

Sol–gel processing has been used to prepare synthetic materials of high chemical reactivity [6]. This method makes possible to prepare ceramics and thin films that are difficult to be obtained by conventional methods, and also to control their geometry and microstructure at the same time. Several research works have been done to prepare PZT fibers by the sol–gel method [6–10].

Because of brittleness and micrometer range in diameter of the fibers, the electrode is difficult to be pasted on both sides of the fiber. Only a few works have focused on the dielectric properties of fibers. Steinhausen et al. [7,11] calculated the properties of the fibers by comparing the properties of 1–3 composites prepared with these fibers with the results obtained by finite element method (FEM) modeling. The dielectric properties of single fiber have not been obtained yet. However, a modified atomic force microscope (AFM) made possible to detect the piezoelectric response of thin films [12]. In this piezoelectric atomic force microscope (PiezoAFM) mode the AFM tip effectively becomes the top electrode of the system. The surface of a fiber is big enough to hold an AFM tip whose typical radius is about 12–15 nm. At the bottom the fibers are fixed by the conductive silver paste. It is then possible to determine the piezoelectric response of the fiber, so that the dielectric properties can be obtained. The relative reports on PZT fiber have seldom been seen yet.

In this study, PZT fibers are prepared via sol–gel route using acetic acid to acidify the precursors. The

* Corresponding author. Fax: +86 10 62322845.
E-mail address: zhangmei@metall.ustb.edu.cn (M. Zhang).

0272-8842/$30.00
doi:10.1016/j.ceramint.2004.05.016

crystallization behavior and the microstructure of PZT fibers have been analyzed and discussed. The dielectric properties are also measured by piezoAFM.

2. Experimental procedure

Lead acetic acid trihydrate ($Pb(COO)_2\ 3H_2O$, Panreac), titanium isopropoxide ($Ti(O–C_3H_7)_4$, Fluka), zirconium propoxide ($Zr(O–C_3H_7)_4$, Fluka) were used as the starting materials, and isopropanol was used as solvent. The atomic ratio of the Pb:Zr:Ti of the solution was 1:0.53:0.47 and no excess lead was introduced. After PZT precursor sol was obtained, the mixture of acetic acid and pure distilled water was added into the precursor. After hydrolyzed and condensed at 373 K, the gel fibers were drawn out, by dipping a glass stick into the PZT viscous sol and pulling up the fibers by hand. The pulling rate was about 10∼15 cm/s as estimated. Then the gel PZT fibers were aged at room temperature for 3 days and dried at 333–373 K. After completely dried, the fibers were heat treated at a heating rate of 1 K/min. In order to burn out completely the organic compounds, heat treatment was hold 60 min at 623 K. The detailed processing scheme for PZT fibers preparation is presented in Fig. 1.

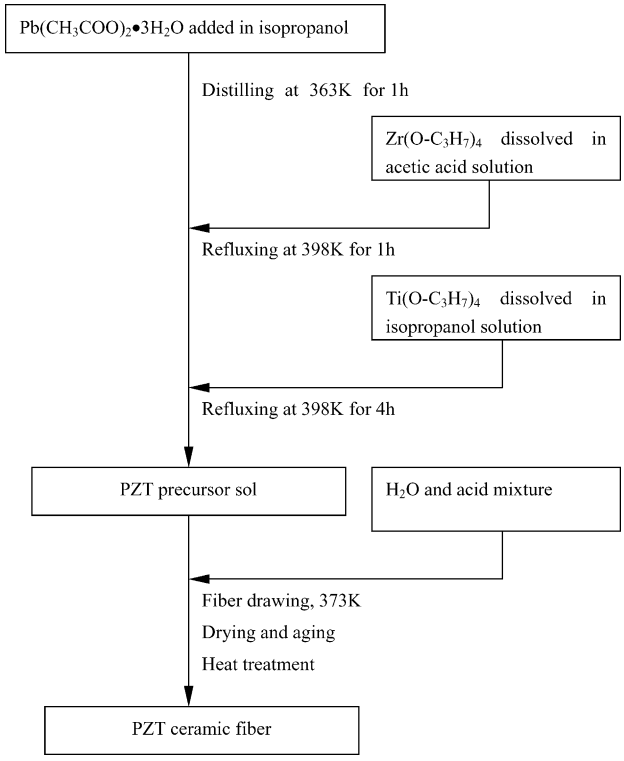

Fig. 1. Scheme for the preparation of PZT fibers.

The crystalline phase of the PZT fibers was identified by X-ray powder diffraction (XRD), the thermal decomposition characteristics of the gel powders were identified by differential thermal analysis (DTA) and thermogravimetric analysis (TGA) at a heating rate of 10 K/min in the air. The transitions of the molecular structures of the precursor and solid phase were investigated by Fourier transform infrared (FTIR) in the wave number region 4000–400 cm^{-1}. The microstructure of PZT fibers was observed by scanning electron microscopy (SEM) and the PZT grains were investigated by AFM.

The dielectric properties of PZT fibers were investigated by piezoAFM. PiezoAFM was carried at 16 V peak-to-peak AC signal on a number of regions of the PZT surface. The AC signal induces a converse piezoelectric response in the PZT fiber. This oscillation is detected by the AFM photodiodes and the resulting signal is detected by a lock-in amplifier.

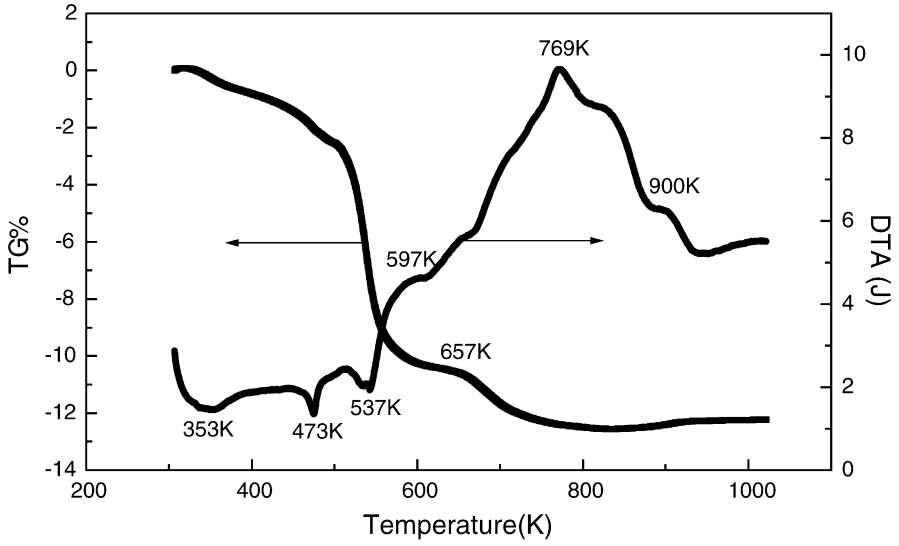

Fig. 2. TGA and DTA curves of aged PZT gel fibers.

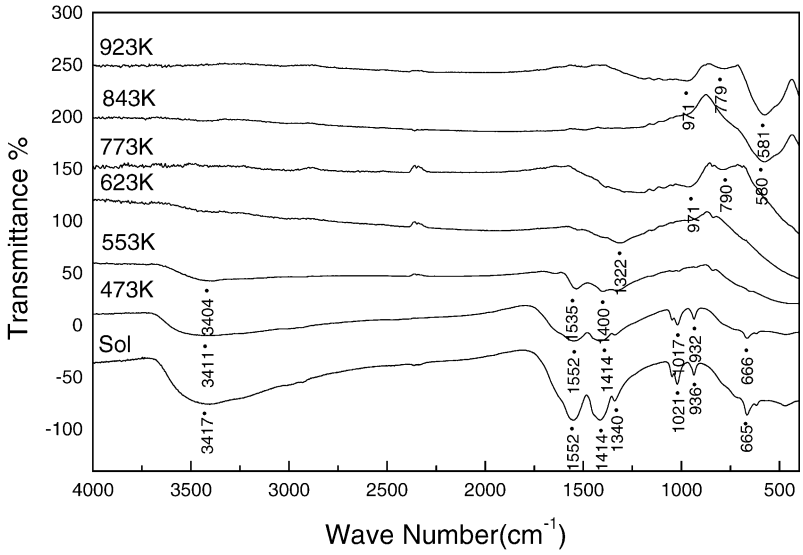

Fig. 3. FTIR spectra of the PZT sol and fibers heat-treated at different temperatures.

3. Results and discussions

3.1. Thermal evolution of gel fiber and FTIR analysis

TGA and DTA curves of PZT gel are shown in Fig. 2. A total weight loss of about 10 wt.% for the gel fibers treated from 473 to 573 K was observed from TGA curve. In accordance, DTA curve exhibited two endothermic peaks in this temperature range, which indicated that the organics were decomposed and released. No significant weight loss was observed for temperatures higher than 673 K. In DTA curve there was a broad exothermic peak at about 597 K, which was attributed to acetate burnout and the removal out of residual carbon and decomposed organics [2]. At 769 K a strong exothermic peak occurred which corresponded to the formation of the perovskite phase as observed in XRD patterns of 773 K samples. The other exothermic peak, observed at 900 K, was attributed to the crystalline PZT phase growth from the residual amorphous phase.

The evolution of the molecular structure of PZT fibers was investigated by FTIR, as shown in Fig. 3. The absorption at about 3600–3000cm^{-1} was associated to O–H vibration. The 1550 cm^{-1} and 1400 cm^{-1} bands, were ascribed to the symmetric and asymmetric C–O vibration of −COO groups [7,10]. The 1322 cm^{-1} band, was attributed to the deformation vibration of CH_3 groups. The peak at 932 cm^{-1}, was attributed to the vibration of C–C bonds [13]. The peak at about 1020 cm^{-1} was ascribed to vibration of CH_3 groups. All these absorption bands, which were related to the acetic acid, isopropanol and propoxide group, greatly decreased in intensity as the heat treatment temperature increased up to 623 K, which confirmed that the organic was decomposed before 623 K.

Along with the increasing heat treatment temperature up to 773 K, the peak at 790 cm^{-1} and 580 cm^{-1}, which were attributed to Ti–O bond and perovskite phase [7], emerged and became stronger. This result indicated that the perovskite phase was formed at 773 K and increased for higher heat treatment temperature. These results are in agreement with DTA results.

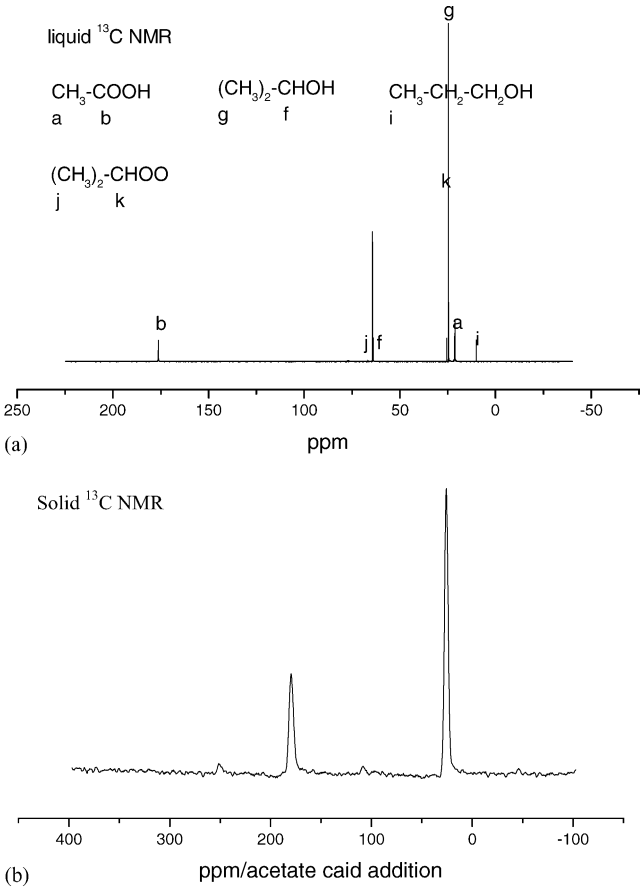

Fig. 4. ^{13}C-NMR spectra of (a) liquid ^{13}C-NMR spectrum and (b) solid ^{13}C-NMR spectrum.

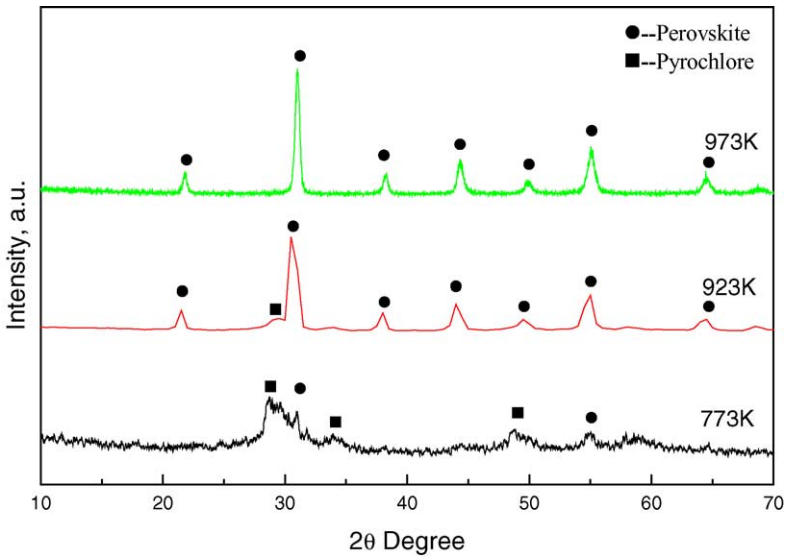

Fig. 5. XRD results of the fibers after heat treatment.

3.2. Liquid and solid ^{13}C-NMR analysis

The liquid and solid ^{13}C-NMR spectra of the samples are shown in Fig. 4. It is observed that the major resonances are assigned to isopropanol and propanol [14,15], Comparing the solid ^{13}C-NMR result with liquid ^{13}C-NMR results, obvious changes can be observed. The resonances assigned to isopropanol, propanol and acetic acid disappeared, which showed that they decomposed during the heat treatment of the PZT precursor. Two primary peaks, at 180 and 26 ppm, were assigned to acetate ligands [14–16]. It seemed that alkoxy groups were completely replaced by the acetate groups. Assink et al.[15] reported the same replacement in the PZT system. Doeuff et al. [13] also presented the complete replacement of alkoxy group in a titanium system. According to refs. [14,17], the broadness of the peaks indicated that the acetate ligand bond to different metals and possibly bond to the chemical structure with uni- and bidentate bond. Hence, the primary polymeric species formed in the sample is oxo acetate.

3.3. Crystallization behavior

XRD (Fig. 5) showed that after heat-treatment at 773 K the PZT fibers were mainly composed of two phases, PZT and pyrochlore, this last being the main phase. But the PZT phase became the main phase at 923 K. Monophasic PZT perovskite phase was observed at 973 K. Together with

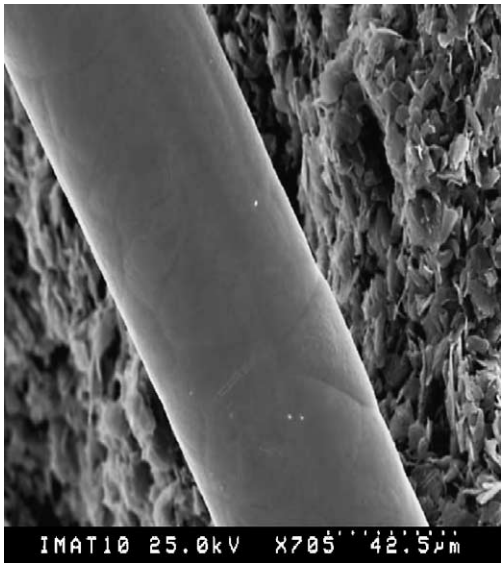

Fig. 6. Topograph of PZT fiber.

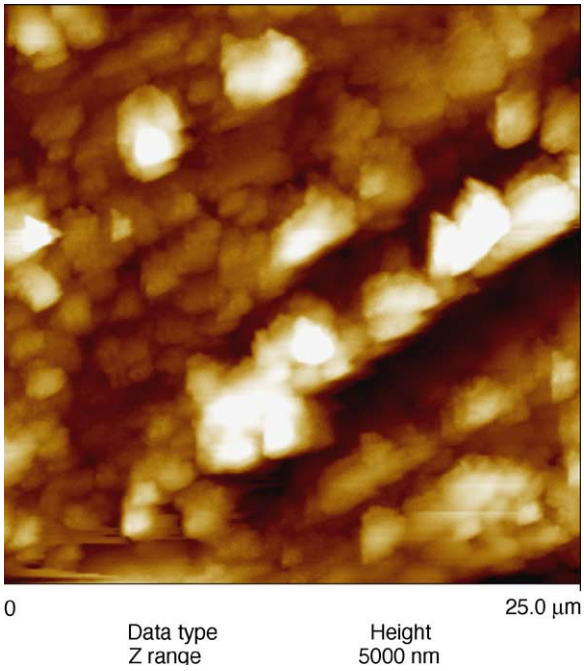

Fig. 7. AFM observation on the surface of PZT fiber.

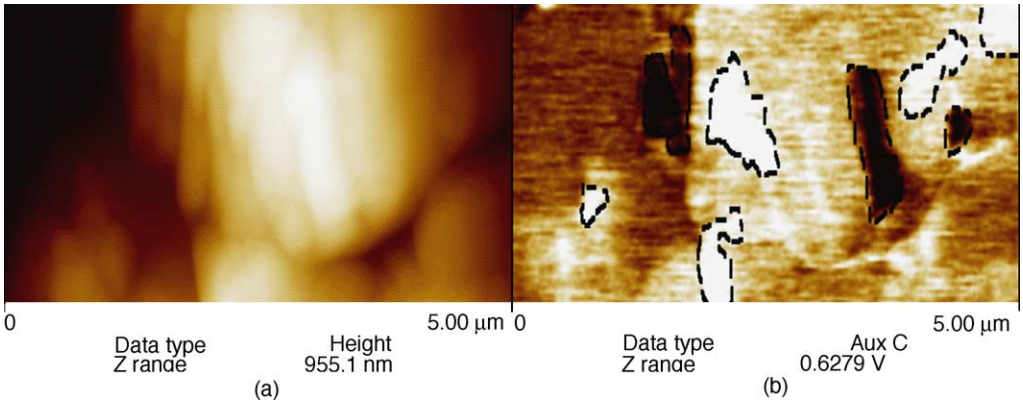

Fig. 8. Domain structure observation in the PZT fiber of (a) before polarized and (b) after polarized.

DTA and FTIR results, these results indicated that the formation of the PZT phase in the fibers started before 773 K and was completed at 973 K.

3.4. Microstructure of PZT fiber

The microstructure of PZT fiber was examined by SEM and AFM as shown in Fig. 6 and Fig. 7. It can be observed from Fig. 6 that the PZT fibers are homogeneous, with smooth surface, and about 40 μm in diameter. AFM photo also shows that the PZT grains are closely compacted with each other. However, there are some pores in the surface. The PZT grains have a typical vermicular structure and the grain size was calculated to be about 1.76 μm wide and 2.49 μm long.

3.5. Dielectric properties measurement

Using PiezoAFM instrument the charged image of the PZT fiber was observed (Fig. 8). As shown in Fig. 8(b), after the fiber is electrified, the particles, marked in the dashed circle, changed into dark color while the other appeared as white color. Because those grains have been polarized under a positive or negative voltage, so that domain structures appeared as white or dark color, respectively. At the same time, the unpolarized area, containing as-grown domain structure, showed only slight variation of the contrast. This image proved that PZT fibers have ferroelectric properties. By comparing the crystallite structure with the piezoresponse image, it resulted that domains were limited by the grain boundaries [18] and crystallite size [19].

The permittivity of a PZT fiber heat-treated at 1273 K for 30 min was measured to be 544 at 10 kHz. R.Steinhausen et al.[7] have detected the effective permittivity, to be equal to 550, in 65 vol% PZT fibers composites. He reported that broken fibers may affect the properties of the composites. In this study, the PZT fibers presented a low permittivity, which was attributed to the presence of pores left inside the fiber (as observed in Fig. 7) due to the loss of organics during the fibers heat treatment.

4. Conclusion

Dense, homogenous PZT fibers about 40 μm in diameter have been prepared using acetic acid to acidify the precursor. According to FTIR, liquid and solid ^{13}C-NMR analysis, an oxo acetate molecular structure was formed in the PZT precursors. As indicated by DTA, FTIR and XRD analyses, the formation of the PZT phase in the fibers started before 773 K and was completed at 973 K. Using a PiezoAFM instrument, the domain structure was observed, which showed that PZT fibers have ferroelectric properties. The permittivity of a PZT fiber was measured to be 544. Such a low permittivity was attributed to the presence of pores inside the fiber.

Acknowledgement

The work was supported by the Foundation for Science and Technology of Portugal (FCT) under Grant no. SFRH/BPD/3589/2000.

Reference

[1] A. Towata, H.J. Hwang, M. Yasuoka, M. Sando, Seeding effects on crystallization and microstructure of sol–gel derived PZT fibers, J. Mater. Sci. 35 (2000) 4009–4013.
[2] R.J. Meyer, T.R. Shrout, S. Yoshikawa, Lead zirconate titanate fine fibers derived from alkoxide-based sol–gel technology, J. Am. Ceram. Soc. 81 (4) (1998) 861–868.
[3] R.J. Meyer, J. Lopath, P.S. Yoshikawa, T.R. Shrout, High-frequency 1–3 composite transducers fabricated from alkoxide-derived PZT fibers, IEEE Ultrason. Symp. (1997) 915–918.
[4] R.B. Cass, Fabrication of continuous ceramic fiber by the viscous suspension spinning process, Ceram. Bull. 70 (3) (1991) 424–429.
[5] D.J. Waller, A. Safari, R.J. Card, M.P. O'Toole, Lead zirconate titanate fiber/polymer composites prepared by a replication process, J. Am. Ceram. Soc. 73 (11) (1990) 3503–3506.
[6] Y. Hu, Preparation of lead zirconate titanate ceramic fibers by sol–gel method, J. Sol–Gel Sci. Tech. 18 (2000) 235–247.
[7] R. Steinhausen, T. Hauke, W. Seifert, H. Beige, W. Watzka, S. Seifert, Finescaled piezoelectric 1–3 composites: properties and modeling, J. Eur. Ceram. Soc. 19 (1999) 1289–1293.

[8] W. Glaubitt, W. Watzka, H. Scholz, D. Sporn, Sol–gel processing of functional and structural ceramic oxide fibers, J. Sol–Gel Sci. Tech. 8 (1997) 29–33.
[9] Y. Park, M. Miyayama, Electrical properties of $Pb(Zr_{0.53}{\cdot}T_{0.47})O_3$ (PZT) fibers fabricated by sol–gel technique, Key Eng. Mater. 157-158 (1999) 33–40.
[10] S. Yoshikawa, U. Selvaraj, P. Moses, Q. Jiang, T.R. Shrout, $Pb(Zr{\cdot}Ti)O_3$(PZT) fibers-fabrication and properties, Ferroelectrics 154 (1–4) (1994) 325–330.
[11] R. Steinhausen, T. Hauke, H. Beige, W. Watzka, Properties of fine scale piezoelectric PZT fibers with different Zr content, J. Eur. Ceram. Soc. 21 (2001) 1459–1462.
[12] S. Dunn, S.P. De Kroon, R.W. Whatmore, An examination of thin film lead scandium tantalum oxide (PST) using piezoAFM, J. Mater. Sci. Lett. 20 (2001) 179–181.
[13] S. Doeuff, M. Henry, C. Sanchez, J. Livage, Hydrolysis of titanate alkoxides: modification of the molecular precusors by acetic acid, J. Non-Cryst. Solids 89 (1987) 206–216.
[14] R.A. Assink, R.W. Schwartz, ^{1}H and ^{13}C-NMR investigations of $Pb(Zr\ Ti)O_3$ thin-film precursor solutions, Chem. Mater. 5 (1993) 511–517.
[15] D.P. Birnie III, N.J. Bendzko, ^{1}H and ^{13}C-NMR observation of the reaction of acetic acid with titanium isopropoxide, Mater. Chem. Phys. 59 (1999) 26–35.
[16] H.O. Kalinowski, S. Berger, S. Braun, Carbon ^{13}NMR Spectroscopy, Wiley, New York, 1988.
[17] N. Sriprang, D. Kaewchinda, J.D. Kennedy, S.J. Milne, Processing and sol chemistry of a triol-based sol–gel route for preparing lead zirconate titanate thin film, J. Am. Ceram. Soc. 83 (8) (2000) 1914–1920.
[18] A. Gruverman, O. Auciello, H. Tokumoto, Image and control of domain structures in the ferroelectric thin films via scanning force microscopy, Annu. Rev. Mater. Sci. 28 (1998) 101–123.
[19] W. Cao, C.A. Randall, Grain size and domain size relations in bulk ceramic ferroelectric materials, J Phys. Chem. Solids 57 (10) (1996) 1499–1505.