

Available online at www.sciencedirect.com



Materials Research Bulletin 40 (2005) 1955-1967



www.elsevier.com/locate/matresbu

# Lead magnesium niobate-lead titanate fibres by a modified sol-gel method

Kwok-Ho Lam\*, Kun Li, Helen Lai-Wa Chan

Department of Applied Physics and Materials Research Centre, The Hong Kong Polytechnic University, Hunghom, Kowloon, Hong Kong, China

Received 5 August 2004; received in revised form 10 May 2005; accepted 27 May 2005 Available online 22 June 2005

# Abstract

Lead magnesium niobate–lead titanate (PMN–PT) ceramic fibres with the nominal composition of  $0.65Pb(Mg_{1/3}Nb_{2/3})O_3-0.35PbTiO_3$  have been fabricated by a modified sol–gel method. Due to the difficulty of dissolving the magnesium component, the mixed oxide method was used together with the traditional sol–gel method. To obtain crack-free fibres, pyrolysis was carried out at a very slow heating rate under specific atmosphere to control the organic burnout. The thermal and microstructural properties were investigated using thermogravimetric analysis, scanning electron microscopy and X-ray diffraction. The optimum sintering temperature is 1200 °C and yields a fibre with a final diameter of around 100  $\mu$ m. A single PMN–PT fibre has been poled and its electrical properties were measured. The properties of the fibre are found to be better than that of a ceramic disc. © 2005 Elsevier Ltd. All rights reserved.

Keywords: A. Ceramics; B. Sol-gel chemistry; D. Microstructure

# 1. Introduction

There are many piezoelectric materials used in ultrasonic transducer applications. The most common material is the lead zirconate titanate (Pb(Zr,Ti)O<sub>3</sub>, PZT) family which is well-known to have high piezoelectric strain constant, dielectric constant and electromechanical coupling [1]. In recent years, lead magnesium niobate–lead titanate (PMN–PT) single crystals have attracted extensive interest due to their

\* Corresponding author. Tel.: +852 2766 4162; fax: +852 2333 7629.

E-mail address: Kwok-HoLam\*02900857r@polyu.edu.hk (K.-H. Lam).

0025-5408/\$ – see front matter O 2005 Elsevier Ltd. All rights reserved. doi:10.1016/j.materresbull.2005.05.024

ultrahigh piezoelectric property compared with conventional piezoelectric ceramics [2]. It is a solid solution of relaxor ferroelectrics (PMN) with a normal ferroelectric (PT). Properties of PMN–PT are critically dependent on its composition and PMN–PT with 35 mol% PbTiO<sub>3</sub> is at its morphotrophic phase boundary (MPB) region [3,4]. At this composition, PMN–PT has anomalously high dielectric and piezoelectric properties as a result of the enhanced polarizability arising from the coupling between two equivalent energy states. It has found wide applications as transducers and actuators [5].

Piezoelectric ceramic/polymer 1–3 composites have found wide applications as transducers for medical ultrasound and underwater acoustics [6]. The dice and fill technique has been widely used to fabricate 1–3 composites in various laboratories and in commercial productions [6]. Due to the limitations of pillar geometry (~120  $\mu$ m), the operating frequency cannot be further increased. Incorporation of ceramic fine fibres into 1–3 composites is a promising way of scaling down the piezoelectric phase and reducing the interference of lateral resonance frequencies [7]. There are three major methods used to fabricate ceramic fibres including the sol–gel processing [8], the relic process [9] and the viscous suspension spinning process (VSSP) [10]. Among these methods, the sol–gel technique is useful in fabricating a large quantity of fibres and resulting in high purity and homogeneity. In the past, various types of fibres of Al<sub>2</sub>O<sub>3</sub> [11], SrZrO<sub>3</sub> [12], PbTiO<sub>3</sub> [13] and Pb(Zr<sub>x</sub>Ti<sub>1-x</sub>)O<sub>3</sub> [14–16] have been fabricated successfully by the sol–gel method. Recently, fine PZT fibres (<80  $\mu$ m diameter) have been fabricated by various methods [17,18]. However, there are few reports on fabrication of PMN–PT fibres.

In this work, the fabrication of 65PMN–35PT fibres was based on the sol-gel technique. The technology is based on solution chemistry in which the metal–oxygen–metal bonds are produced. It relies on the hydrolysis and condensation reactions of a metal alkoxide precursor solution. During this process, the gel network grows and so it is important to control the gel homogeneity. Addition of solvent facilitated the reactions. After the viscosity of the gel became higher, it was spun into fibres. The extruded fibres were dried at room temperature and then fired to induce a gel to ceramic conversion. Due to the difficulty of dissolving the magnesium solution, the traditional sol–gel method cannot be used to fabricate a crack-free PMN–PT fibre. A modified sol–gel method has been developed such that the magnesium solution is replaced by the oxide and the experimental details are given in the following sections. Besides studying the fabrication procedures, the properties of the fibres were also studied.

# 2. Experimental procedures

#### 2.1. Synthesis of the precursors

Two precursor systems were prepared to fabricate the PMN–PT fibre and the procedures for fabricating the fibres are illustrated in Fig. 1. In the traditional sol–gel method, the precursor system includes lead(II) acetate trihydrate [Pb( $O_2C_2H_3$ )<sub>2</sub>·3H<sub>2</sub>O; Acros, reagent ACS], magnesium nitrate salt [Mg(NO<sub>3</sub>)<sub>2</sub>], niobium(V) ethoxide [Nb(OC<sub>2</sub>H<sub>5</sub>)<sub>5</sub>; Strem, >99.9% Nb] and titanium(IV) *n*-butoxide [Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>; Acros, 99%]. Two solvents were used for this precursor system: *N*,*N*-dimethylformamide (DMF; Aldrich, 99%) as a common solvent and 2,4-pentanedione (Acros, >99%) as a solvent of magnesium nitrate. Before preparing the precursor solution, lead(II) acetate trihydrate was dried at 130 °C and magnesium nitrate was produced by drying the mixing solution of magnesium oxide and nitric acid. After mixing lead(II) acetate trihydrate and magnesium nitrate, niobium(V) ethoxide and titanium(IV) *n*-butoxide were added. The mixture was heated and stirred until it became a solution. The



Fig. 1. Schematic diagram of PMN-PT fibre fabrication.

solution was filtered and then refluxed with a rotary vacuum evaporator for at least 2 h. The sol to gel conversion occurred and a high viscosity gel was formed. The color of the precursors changed from pale yellow to dark orange during the concentrating process.

Another precursor system of modified sol-gel method is similar to the previous one except that the magnesium precursor and the solvent have been changed. This method is a sol-gel method with partially mixed oxide and is a new way for fabricating PMN–PT fibres. Magnesium oxide (Acros, reagent ACS) was used instead of magnesium nitrate. Since the magnesium precursor was changed, 2-methoxyethanol (MOE; Acros, >99%) can be used as a common solvent. During refluxing in a rotary vacuum evaporator, the oxide powders can be evenly distributed in the solution. The oxide powders in the solution will react with the precursors during subsequent heat treatments.

#### 2.2. Fibre drawing and heat treatments

Near the gel point of the solution, PMN–PT fibres were extruded through a mold containing 200  $\mu$ m diameter holes. The fibres were collected on a spindle. The gel fibres were then kept at room temperature in air for 2 weeks for drying. Ceramic fibres were obtained after a series of proper heat treatments.

Since the fibres contained a high amount of organic solvent, pyrolysis was carried out under a controlled atmosphere to regulate the organic burnout. A very slow heating rate of  $0.5 \,^{\circ}C/min$  was used and the pyrolysis temperature was up to 600  $^{\circ}C$ . The heating profile of pyrolysis was determined by a

thermogravimetric analysis (TGA). Various atmospheres were tried to reduce the organic burnout rate including air and carbon monoxide (CO). The optimum pyrolysis condition can be determined by the quality of fibres produced.

After pyrolysis, the fibres were then calcined and sintered. Since the calcination and sintering temperatures of fibres relate to that of the bulk ceramic samples, several temperatures were tried and the optimum temperature and dwell time were determined by the quality of the resulting fibres. For determining the burnout process and the fibre quality, thermogravimetric analysis, scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used. TGA (Netzsch, STA 449C) with the heating rate of 10 °C/min was used to show the effect of heat on the changing weight of the fibres in order to optimize the profile of pyrolysis. The microstructure of the fibres was monitored by SEM (Leica, Stereo 440). The crystallinity of ceramic fibres was investigated using XRD (Philips, PW3710). With the help of SEM and XRD, the optimal heating temperature was determined. For evaluating the quality of the fibres, the density was measured. Since the fibres are assumed having cracks and pores, density was measured based on the Archimedes' principle using an electronic balance. The density of sample can be determined using the following equation:

$$\rho = \frac{m_{\rm dry}}{m_{\rm dry} - m_{\rm water}} \times \rho_{\rm water} \tag{1}$$

where  $\rho$  is the density of the sample,  $m_{dry}$  the dry mass of the sample,  $m_{water}$  the mass of the sample suspended in water and  $\rho_{water}$  is the density of water which is assumed to be 1000 kg/m<sup>3</sup>.

#### 2.3. Electrical characterization

Because of the weak mechanical characteristics of a single ceramic fibre, the single fibre of around 0.25 mm long was embedded in an epoxy matrix with a diameter of around 2 mm to carry out electrical measurements. The chromium–gold electrode was only coated on the cross-sectional area of ceramic fibre. After poling under an electric field of 3 kV/mm at 60 °C for 0.5 h, the impedance and phase of the fibre was measured using the impedance gain phase analyzer (Agilent 4294A) with a test fixture (Agilent 16034E). With the resonant and anti-resonant frequencies in the impedance spectrum, the electromechanical coupling coefficient in the thickness direction ( $k_t$ ) and frequency constant in the thickness direction ( $N_t^D$ ) can be calculated based on the IEEE standard on piezoelectricity [19]. Besides, the capacitance of the fibre can also be measured and so the relative permittivity of the poled ceramic fibre can be obtained.

# 3. Results

#### 3.1. Thermal analysis of gel fibres

Long, continuous gel fibres with around 180  $\mu$ m diameter were drawn by controlling the drawing speed. The flexible gel fibres became brittle after drying.

The gel fibres contained high organic content and these organic substances were burned out during pyrolysis and the weight of fibres was reduced. From the TGA curves, the information on the stages of pyrolysis and on the temperature needed for each stage can also be extracted. It is useful for tailoring the



Fig. 2. Thermogravimetric analysis of PMN-PT gel fibres fabricated by both the sol-gel and modified sol-gel methods. Samples were heated at 10 °C/min.

heating profile to prevent fibre cracking during pyrolysis. Fig. 2 shows the TGA curves of fibres fabricated from both precursor systems. Comparing the two curves, it is seen that the fibre prepared by the modified sol–gel method is 5 wt.% higher in organic content. In the figure, many points with large changes in slopes can be observed. Those points indicate that there are rapid mass changes of the samples at the corresponding temperatures. Those rapid mass changes are the processes of chemical reactions, which are very important for the pyrolysis of fibres. According to the turning points of the TGA curves, the burnout process of fibres can be tailored and 1-h dwell time was kept at each stage.

### 3.2. Optimization of pyrolysis atmosphere

With information from the TGA curve, the organic burnout rate can be controlled and so the degree of fibre cracking can be reduced. In Fig. 3, the surface of a sol–gel fibre after pyrolysis is shown. The pyrolysis temperature is 600 °C for 1 h with a very slow heating rate of 0.5 °C/min. In Fig. 3(bottom), the pyrolysis profile was tailored using a TGA result, 1-h dwell time was kept at each turning point of a TGA curve. The cracking is greatly reduced after using the TGA result for pyrolysis. Nevertheless, cracks still existed because the oxygen pressure was high under an air ambient in the crucible, the organic components in the fibres were burnt out rapidly and produced lots of carbon monoxide and carbon dioxide (CO<sub>2</sub>). These gases produced many pores in the fibres or even blew off the surface layer of the fibre. In order to prevent the fibre from cracking, CO atmosphere was tried to reduce the oxygen content within the crucible. During pyrolysis, the black carbon powder was put inside the crucible to create CO atmosphere so that the organic burnout rate can be reduced. Fig. 4 shows the effect of CO atmosphere on the cross-section and surface of a sol–gel PMN–PT fibre that was heated using the TGA information. It



Fig. 3. SEM micrographs of a fibre using an air atmosphere (top) without the help of TGA and (bottom) with the help of TGA during pyrolysis.



Fig. 4. SEM micrograph of the sol-gel fibre using a CO atmosphere during pyrolysis.



Fig. 5. SEM micrograph of a fibre prepared by the modified sol-gel method using CO atmosphere during pyrolysis.

was found that the fibre is nearly crack-free using a CO atmosphere during pyrolysis. Subsequently, the modified sol-gel fibres also used a CO atmosphere during pyrolysis and the fibres were entirely crack-free as shown in Fig. 5.

#### 3.3. Gel to ceramic conversion

After pyrolysis, all the organic content inside the fibres was assumed to be burnt out. However, the fibres are still in an amorphous state. The gel fibres can be converted to ceramic fibres through calcination and sintering in lead atmosphere. In order to create the lead atmosphere, the fibres were covered with the PMN–PT powder during the high temperature heat treatment. The heating rate was increased from 0.5 °C/min to 3.0 °C/min. In order to determine the optimal sintering schedule, XRD analysis was used to determine the constituent phases in the calcined and sintered samples. From the XRD spectra, the amount of pyrochlore phase existed in the sample can be calculated by:

Pyrochlore phase (%) = 
$$\frac{I_{\text{pyro}}}{I_{\text{perov}} + I_{\text{pyro}}} \times 100$$
 (2)

where  $I_{pyro}$  refers to the (2 2 2) pyrochlore peak and  $I_{perov}$  refers to (1 1 0) perovskite peak [20]. As shown in Fig. 6, the pyrochlore phase decreases from 11.5% to 4.9% with an increase in the calcination temperature from 800 °C to 850 °C.

In order to find the optimal sintering temperature, XRD analysis and SEM are used to determine the phase change and monitor the microstructure of fibres, respectively. XRD spectra of sol–gel powder with different sintering temperatures are shown in Fig. 7. From the spectra, the perovskite phases are similar at different sintering temperatures and the difference in the resulting pyrochlore phase is only 1%.

To determine the optimal sintering temperature, the SEM technique is used. With different sintering temperatures, the microstructure of the fibres prepared by the modified sol–gel method changes as shown in Figs. 8–10. At 1150 °C, the grain is not well grown and the grain boundaries are not sharp. There are many pores within the fibre. As the temperature increases, the grain size increases. However, the grain growth became inhomogeneous at high sintering temperature (1250 °C). In comparison, the grains of



Fig. 6. Comparison of XRD spectra of modified sol-gel powders calcined at 800 °C and 850 °C for 2 h. The solid circle represents the perovskite phase and the open circle represents the pyrochlore phase.



Fig. 7. Comparison of XRD spectra of modified sol-gel powders sintered at 1150  $^{\circ}$ C, 1200  $^{\circ}$ C and 1250  $^{\circ}$ C for 2 h. The solid circle represents the perovskite phase and the open circle represents the pyrochlore phase.



Fig. 8. SEM micrograph of a fibre prepared by the modified sol-gel method sintered in a lead atmosphere at 1150 °C for 2 h.



Fig. 9. SEM micrograph of a fibre prepared by the modified sol-gel method sintered in a lead atmosphere at 1200 °C for 2 h.



Fig. 10. SEM micrograph of a fibre prepared by the modified sol-gel method sintered in a lead atmosphere at 1250 °C for 2 h.



Fig. 11. SEM micrograph of a sol-gel fibre sintered in a lead atmosphere at 1200 °C for 2 h.

fibres have grown homogeneously at 1200 °C and so the optimal sintering temperature should be 1200 °C. With a series of specific heat treatment, crack-free PMN–PT fibres can be fabricated successfully using a modified sol–gel method. From Fig. 9, the grain size of PMN–PT ceramic fibre sintered at 1200 °C for 2 h is around 1  $\mu$ m in diameter. Since the organic content was burnt out during pyrolysis, the dimension of fibres was reduced. The average final diameter of the fibres is around 100  $\mu$ m. However, the fibre prepared by the sol–gel method still has many cracks after sintering at any temperature as shown in Fig. 11.

#### 3.4. Performance of a single ceramic fibre

The measured impedance and phase versus frequency spectra of a single PMN–PT ceramic fibre is shown in Fig. 12. The calculated parameters are summarized in Table 1. The parameters of the ceramic fibre are compared with the parameters measured from the ceramic disc prepared by the sol–gel powder. The ceramic disc of 10 mm diameter and 1 mm thick was fabricated by the dry pressing method, which was sintered at 1200 °C and then poled under conditions similar to that of the fibre. The SEM micrograph of the cross-sectional of the ceramic disc in Fig. 13 shows that the microstructure and grain size of the ceramic disc are similar to that of the ceramic fibre (Fig. 9). In Table 1, it is found that the ceramics in both disc and fibre forms approach 95% theoretical density. Both the relative permittivity  $K_{33}^{T}$  and  $N_{t}^{D}$  of the fibre and disc are comparable. Because of the geometry, the  $k_{33}$  coefficient of the single fibre was obtained instead of the  $k_{t}$  coefficient. The result is reasonable that the calculated  $k_{33}$  coefficient of the single fibre is 0.50, which approaches the  $k_{33}$  value of the bulk ceramics.

# 4. Discussion

With the modified sol-gel method, crack-free PMN-PT fibres can be prepared after pyrolysis and sintering. With the sol-gel method, the fibres had small cracks after pyrolysis and they were cracked severely after sintering. Comparing the two methods, the main difference is the solvent. Due to the difficulty of dissolving the magnesium, during the preparation of sol-gel PMN-PT fibre, high boiling



Fig. 12. The thickness mode of a PMN-PT single ceramic fibre prepared by the modified sol-gel technique.

Table 1

Comparison between the piezoelectric coefficients of the PMN-PT ceramic fibre prepared by the modified sol-gel technique and that of the ceramic disc prepared by the modified sol-gel technique

Parameters	Ceramic disc	Ceramic fibre
Density (kg/m <sup>3</sup> )	7563	7583
k <sub>t</sub>	0.39	_
k <sub>33</sub>	-	0.50
$K_{33}^{\mathrm{T}}$ (poled)	2772	2991
$N_{\rm t}^{\rm D}$ (Hz m)	1878	1886

solvents (DMF; 2,4-pentanedione) were used. Since higher temperature will boil away the niobium(V) ethoxide (boiling point  $\sim$  140 °C), those high boiling solvents cannot be totally evaporated out during distillation and refluxing. Those organics will be liberated during further heat treatments and so cracks are formed easily. In the modified sol–gel method, low boiling solvent (MOE) was used. It was almost completely evaporated during refluxing, and so the resulted ceramic fibres can be crack-free.

# 5. Conclusion

Crack-free ceramic PMN–PT fibres have been successfully fabricated by a modified sol–gel method. To ensure that the organic content can be completely removed during pyrolysis, magnesium oxide and the low boiling solvent (MOE) were used. With the help of TGA information, a very slow heating rate and



Fig. 13. SEM micrograph of a disc prepared by the modified sol-gel method sintered in a lead atmosphere at 1200 °C for 2 h.

specific atmosphere were used to control the organic burnout rate. After calcination and sintering under optimized conditions, the fibres are well crystallized with nearly complete perovskite structure. The final diameter and grain size of ceramic fibres are around 100  $\mu$ m and 1  $\mu$ m, respectively. The electrical characterization of the single ceramic fibre reveals that the modified sol–gel method can be used to fabricate well-crystallized PMN–PT ceramic fibres with good properties especially the electromechanical coupling coefficient. In future work, the PMN–PT fibre will be used to fabricate PMN–PT fibre/ epoxy 1–3 composites for high-frequency ultrasonic transducer applications.

#### Acknowledgements

This work was supported by the Hong Kong Research Grants Council (RGC, project No. PolyU 5190/ 99P) and the Centre for Smart Materials of the Hong Kong Polytechnic University.

#### References

- [1] B. Jaffe, R.S. Roth, S. Marzullo, J. Res. Natl. Bur. Stand. 55 (1955) 239-254.
- [2] S.W. Choi, T.R. Shrout, S.J. Jang, A.S. Bhalla, Ferroelectrics 100 (1989) 29-38.
- [3] J. Kelly, M. Leonard, C. Tantiagte, A. Safari, J. Am. Ceram. Soc. 80 (4) (1997) 957–964.
- [4] T.R. Shrout, Z.P. Chang, N. Kim, S. Markgraf, Ferroelectr. Lett. 12 (1990) 63-69.
- [5] S.E. Park, T.R. Shrout, IEEE Trans. Ultrason. Ferroelectr. Freq. Control 44 (1997) 1140–1147.
- [6] H.P. Savakus, K.A. Klicker, R.E. Newnham, Mater. Res. Bull. 16 (1981) 677–680.
- [7] A. Safari, V. Janas, B. Jadidian, SPIE 2721 (1996) 240-250.
- [8] S.C. Choi, S.I. Aoki, M. Miyayama, D.A. Payne, H. Yanagida, The Fifth US Japan Seminar on Dielectric and Piezoelectric Ceramics, Internal Publication, 1990.
- [9] J.D. French, R.B. Cass, Am. Ceram. Soc. Bull. 77 (5) (1998) 61-65.
- [10] R.B. Cass, Am. Ceram. Soc. Bull. 70 (3) (1991) 424-429.
- [11] W. Glaubitt, W. Watzka, H. Scholz, D. Sporn, J. Sol-Gel Sci. Technol. 8 (1997) 29-33.
- [12] R.C. Pullar, M.D. Taylor, A.K. Bhattacharya, J. Mater. Sci. 33 (1998) 3229-3232.
- [13] M. Toyoda, Y. Hamaji, K. Tomono, J. Sol-Gel Sci. Technol. 9 (1997) 71-84.

- [14] O. Binkle, R. Nass, J. Sol-Gel Sci. Technol. 13 (1998) 1023-1026.
- [15] A. Towata, J.J. Hwang, M. Yasuoka, M. Sando, J. Mater. Sci. 35 (2000) 4009-4013.
- [16] Y. Hu, J. Sol-Gel Sci. Technol. 18 (2000) 235-247.
- [17] W. Watzka, S. Seifert, H. Scholz, D. Sporn, A. Schönecker, L. Seffner, Proc. Tenth IEEE Int. Symp. Appl. Ferroelectrics 2 (1996) 569–572.
- [18] D. Sporn, A. Schoenecker, Mater. Res. Innovations 2 (1999) 303–308.
- [19] IEEE Standard on Piezoelectricity, ANSI/IEEE Std. 176 (1987).
- [20] S.L. Swartz, T.R. Shrout, Mater. Res. Bull. 17 (1982) 1245-1250.