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Ceramics International 30 (2004) 1939–1943

CERAMICS INTERNATIONAL

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Properties of PMN–PT fibres fabricated using powder of PMN–PT single crystals

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Received 26 November 2003; received in revised form 10 December 2003; accepted 22 December 2003

Available online 10 May 2004

Abstract

Lead magnesium niobate–lead titanate (PMN–PT) ceramic fibres with the nominal composition of $0.65Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.35PbTiO_3$ were synthesised using PMN–PT single crystal powder and poly(acrylic acid). The fibres were extruded directly by pressing the mixture through a spinneret. The fibres were well crystallised after sintering at 1250 °C and the final diameter was around 300 μm. The microstructural properties of the fibres were investigated using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The electrical characteristics of the fibre were determined by measuring the hysteresis *D–E* loop, relative permittivity and impedance spectrum. The measured results showed that this method can be used to fabricate PMN–PT fibres with good performance.

Keywords: PMN–PT; Ceramic fibre; Hysteresis

1. Introduction

Following the trend of developing tiny functional components using innovative materials design, the fabrication of piezoelectric ceramic fibres has attracted considerable interest. For example, piezoceramic fibres can be used as integrated compression and tension sensors [1]. Sol–gel processing [2], the relic process [3] and the viscous suspension spinning process (VSSP) [4] have been reported for fabricating ceramic fibres. The fibres of several popular piezoelectric materials have been fabricated successfully [5–9].

Among various piezoelectric materials, lead magnesium niobate–lead titanate (PMN–PT) becomes popular recently due to its ultrahigh piezoelectric properties [10]. It is the solid solution of a relaxor ferroelectrics PMN with a normal ferroelectrics PT. PMN–PT with 35 mol% $PbTiO_3$ is at its morphotropic phase boundary (MPB) region and it has anomalously high dielectric and piezoelectric properties within this region [11].

In this work, 0.65PMN–0.35PT (abbreviated as PMN–PT) fibres were fabricated by a powder mixing method. This method is simple and time-saving. In preparing the slurry for extrusion, the PMN–PT single crystals powder was mixed with an appropriate amount of binder. Using a slurry with suitable viscosity, the fibres can be extruded. The extruded fibres were dried at room temperature and then heat-treated to form the PMN–PT fibres. With this method, the organic content inside the as-prepared fibre is not as high as that in the sol–gel method, so the procedures of heat treatments of fibres can be simplified.

2. Experimental procedures

The starting material is 0.65PMN–0.35PT single crystal in powder form. The 0.65PMN–0.35PT single crystals were supplied by the Shanghai Institute of Ceramics. They were fabricated by the modified Bridgeman method [12] and the powder was obtained by crushing the off-cuts of the crystals. To minimize the particle size, the powder was ball-milled in ethanol for 2 h. The fibres can only be drawn using a slurry with appropriate viscosity, so the amount of binder

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0272-8842/$30.00
doi:10.1016/j.ceramint.2003.12.189

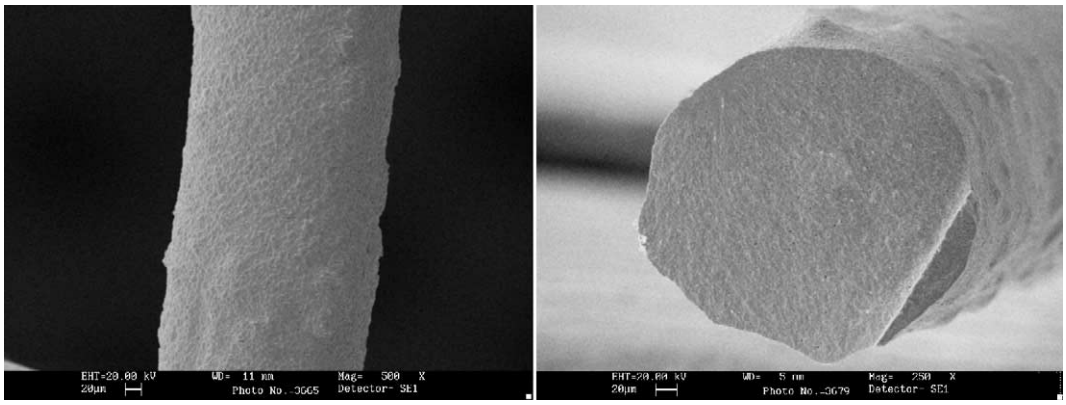

Fig. 1. The SEM micrographs of a PMN–PT fibre prepared by the powder mixing method (left: surface; right: cross-sectional view).

plays an important role in the fibre fabrication. The binder used was poly(acrylic acid) (PAA, 25% aqueous solution). After weighing the powder and binder with the appropriate weight ratio (1:0.5), the mixture was stirred until the slurry became homogenous. The slurry was then put into the mould of a fibre spinning machine (One Shot III from Alex James & Associate Inc., USA) for drawing the fibres. At around 45 °C, PMN–PT fibres were extruded through a mould containing a 500 mm diameter hole. The fibres were collected on a spindle. They were then kept at room temperature in air for a week for drying. PMN–PT fibres can then be obtained after a series of proper heat treatments.

With the powder mixing method, the amount of organic content inside the as-prepared fibres was minimised compared with the traditional sol–gel method. It is easy to burn out the organic content with the normal pyrolysis procedure and the pyrolysis temperature was ∼600 °C. After pyrolysis, the fibres were then calcinated and sintered. The calcination and sintering temperatures of the fibres were 850 and 1250 °C, respectively. To determine the fibre quality, scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used. The microstructure of the fibres was monitored by SEM (Leica, Steoreoscan 440). To find the crystallinity of the sintered fibres, the powders obtained from grinding the PMN–PT single crystals and the sintered fibres were examined using XRD (Philips, PW3710).

For the electrical characterization of the fibre, a single fibre was embedded in an epoxy matrix and chromium–gold electrode was coated only on the cross-sectional area of the fibre. The electric displacement–electric field hysteresis measurement (*D–E* loop) of the fibre was measured using a modified Sawyer–Tower circuit with the sample immersed in a silicone oil bath. After poling, the relative permittivity and the impedance of the fibre were measured using an impedance/gain phase analyser (Agilent 4294A).

3. Results and discussion

Figs. 1 and 2 show the microstructure of a sintered fibre. There is no pores and cracks on the surface as well as inside the fibre. Since the dimension of a fibre shrank during

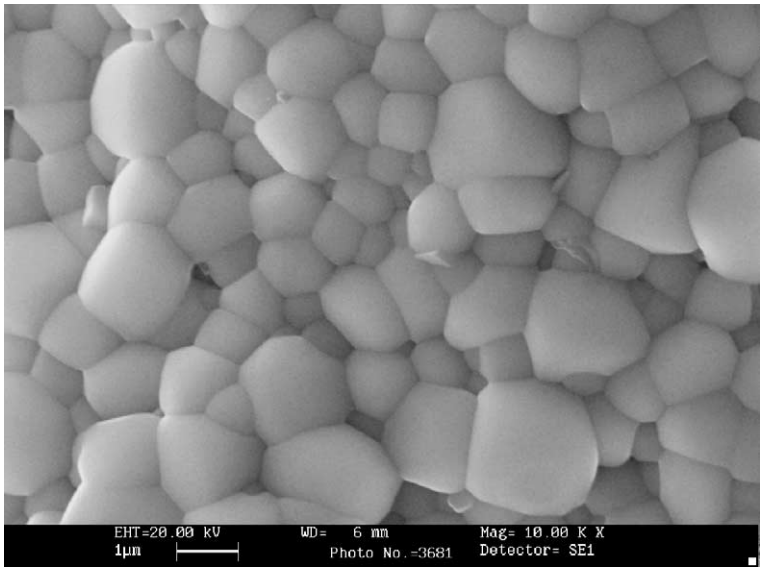

Fig. 2. The SEM micrograph of the cross-sectional area of a PMN–PT fibre.

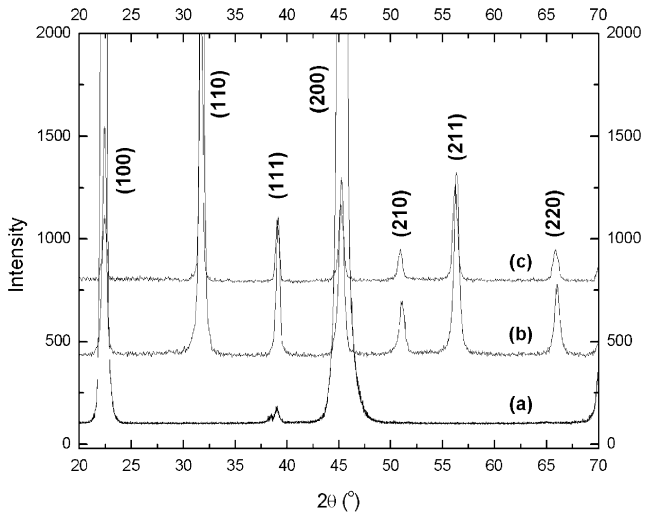

Fig. 3. XRD patterns of (a) the PMN–PT single crystal, (b) the ball-milled PMN–PT single crystal powder and (c) the PMN–PT fibre.

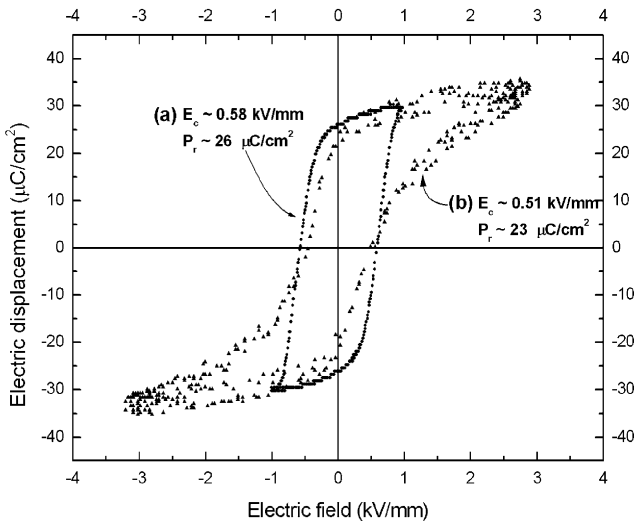

Fig. 4. The hysteresis loops of (a) the PMN–PT single crystal and (b) the single fibre prepared by the powder mixing method.

sintering, the final diameter of the fibre was ~300 μm. From Fig. 2, the cross-section of the fibre was magnified and the grains can be observed clearly. They were well grown and the grain size was ~1 μm. The crystalline structure of the PMN–PT fibre is similar to that of the ball-milled single crystal powder as shown in Fig. 3. It is seen that the single crystal powder becomes polycrystalline after ball milling. Nevertheless, the perovskite phase of the powder is still very pure.

The comparison of the hysteresis loop of a PMN–PT fibre and a single crystal of similar composition measured at room temperature is shown in Fig. 4. The remnant polarization, P_r, and coercive field, E_c, of the PMN–PT fibre show good agreement with that of a single crystal. The result shows that the ferroelectric properties have not changed significantly even though the sample is polycrystalline. Although the hysteresis behaviour of the fibre is similar to that of a single crystal, the field at which saturated polarization occurs is much higher in the fibre.

In this study, the PMN–PT fibre was poled under two different electric fields (1 and 2 kV/mm) at 130 °C. The poled samples were then short-circuit annealed at 40 °C for 8 h. The impedance/phase versus frequency spectra of the corresponding PMN–PT single fibre poled at 1 kV/mm are shown in Fig. 5. For the low poling electric field, the impedance signal of the fibre is very weak. When the PMN–PT fibre has been poled with a higher electric field, the resonance becomes much stronger and a pure strong thickness mode is

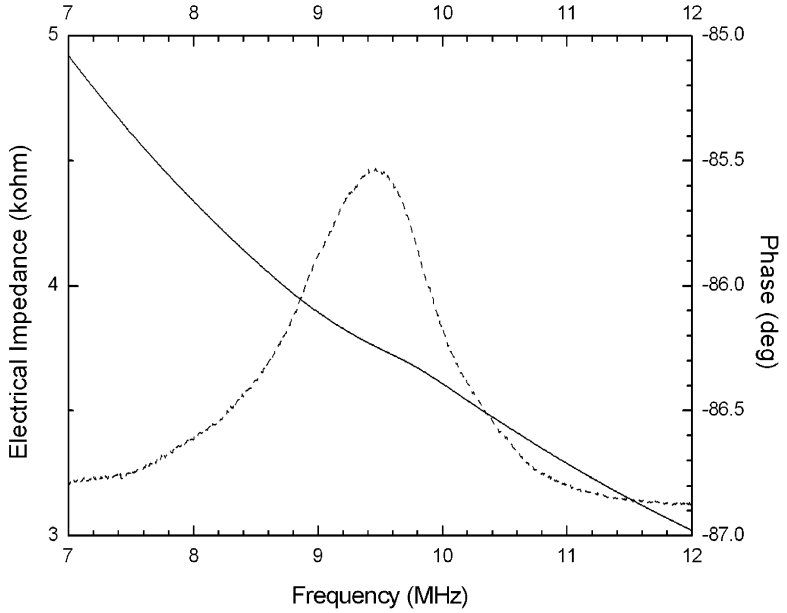

Fig. 5. The thickness mode of the PMN–PT single fibre poled with an electric field of 1.0 kV/mm.

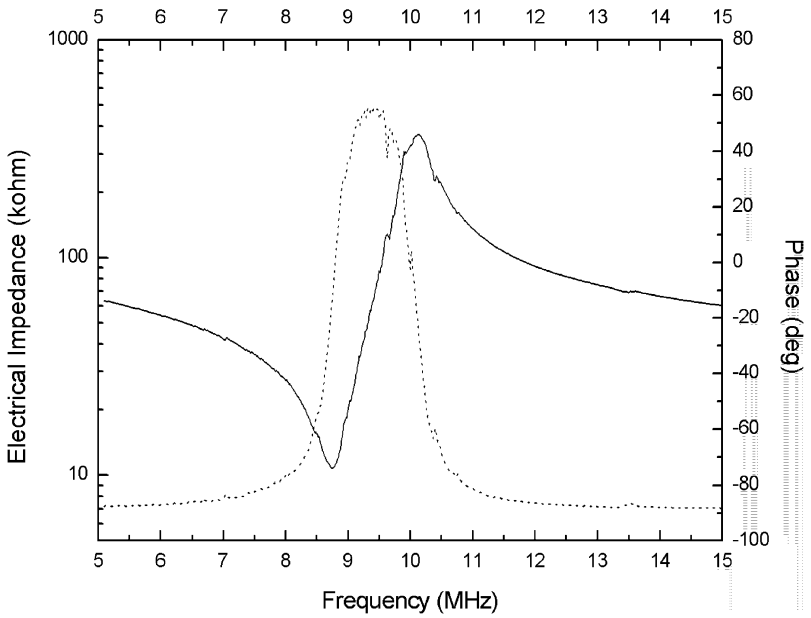

Fig. 6. The thickness mode of the PMN–PT single fibre poled with an electric field of 2.0 kV/mm.

Table 1
The experimental parameters of the PMN–PT single crystal, ceramic disc and fibre

Parameters	Single crystal	Ceramics	PMN–PT fibre	
Poling field (kV/mm)	1.0	2.0	1.0	2.0
k_t	0.65	0.43	0.41	0.54
K_{33}^{T} (poled)	6500	3000	2850	3050
N_t^{D} (Hz m)	2200	2000	1850	1930

Both ceramic samples were fabricated using the milled single crystal powder.

found as shown in Fig. 6. Based on the IEEE standard [13], the electrical properties of the PMN–PT fibres have been calculated and compared with that of a PMN–PT ceramic disc fabricated using the milled single crystal powder under similar conditions as shown in Table 1. The measured data of a PMN–PT single crystal disc are also listed for comparison. The dielectric permittivity and the frequency constant, N_t^{D}, of the fibres are comparable with that of the ceramic disc and they are lower than that of the single crystal. The electromechanical coupling coefficient, k_t, of the PMN–PT fibre (embedded in the epoxy), although lower than that of the single crystal, is reasonably high, which approaches the k_{33} value of the ceramics, after being poled under an electric field of 2 kV/mm. It is noted that the single crystal cracks easily if poled under high field at high temperature.

4. Conclusion

Crack-free PMN–PT fibres have been successfully fabricated by the powder mixing method. The final diameter and grain size of a well-crystallised fibre is ~300 and 1 μm, respectively. Various characterisations show that the PMN–PT fibres fabricated with the powder mixing method have reasonably good performance. In subsequent work, PMN–PT fibres prepared with this method will be used for fabricating PMN–PT/epoxy one to three composites and small-area hydrophones for medical ultrasonic applications.

Acknowledgements

This work was supported by the Hong Kong Research Grants Council (RGC PolyU 5193/00P) and the Centre for Smart Materials of the Hong Kong Polytechnic University.

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