

Synthesis and characterization of PbTiO_3 and Ca and Mn modified PbTiO_3 fibres produced by extrusion of diol based gels

S. CHEWASATN, S. J. MILNE*

Division of Ceramics, School of Materials, The University, Leeds, LS2 9JT, UK

Lead titanate precursor gels were prepared using a diol sol–gel system. Water and nitric acid were added to the sols and their effect on the extrusion characteristics of the gels established. After examining the microstructure of the fired fibres obtained from sols containing different water and acid ratios, the merits of incorporating excess lead and/or adding manganese or calcium salts to the sols were also considered. It proved possible to produce unmodified PbTiO_3 fibres that were crack-free having a diameter of ca. 250 μm and grain size of ca. 0.3 μm with a density of ca. 7.1 g cm^{-3} . However, the best fibres were achieved from gels containing 2 mol % of added calcium nitrate. These fibres had a density ca. 7.4 g cm^{-3} and a grain size of ca. 0.3 μm .

1. Introduction

Several types of piezoceramic–polymer composites have been developed for potential applications such as sonar and medical diagnostics. The properties of the composite depend not only on the type and volume fraction of the component phases but also on the manner in which the components are interconnected. A variety of different connectivities are possible. For example, the piezoceramic may exist as discrete particles evenly distributed in the polymer matrix or in the form of rods or fibres which can be aligned to produce anisotropic properties. The latter structures are referred to as 1–3 composites [1], the numbers signifying that the ceramic phase extends in one dimension and the polymer in three dimensions. In practice the ceramic will clearly have some two-dimensional character but the aim is to fabricate a structure in which the ceramic is continuous in the direction perpendicular to the electroded faces and is surrounded by a continuous layer of polymer.

Unfortunately, the geometry of 1–3 composites leads to a number of manufacturing difficulties. 1–3 composites were originally made by combining large PZT particles several mm in size with a polymer [2]. Because the particle size was approximately equal to the thickness of the resulting composite sample, the composites approached the connectivity of a 1–3 structure. Subsequently, ceramic rods with diameters of 0.25 mm or more were used. They were fabricated by extruding a mixture of PZT particles, polyvinyl alcohol and water [3]. The extruded rods were furnace fired at 1300 °C for 30 min and then re-fired in a hot isostatic press at 1300 °C under a pressure of 20 MPa. The minimum diameter of the rods was ca. 0.25 mm and composites of up to 50 vol % of PZT rods

0.44–0.84 mm in diameter could be prepared by mechanically aligning the fibres and embedding them in an epoxy polymer.

More recently the benefits of adding a sintering flux to the PZT paste prior to extrusion have been demonstrated. It is thus possible to lower the sintering temperature to ≤ 1000 °C leading to reduced problems of lead loss by volatilization. The diameter of the fired fibres was ca. 0.4 mm and they were used to produce composites containing up to 50 vol % PZT [4].

Although these relatively thick fibres are easy to handle and to fabricate into aligned composites, a more homogeneous piezoelectric response across the surface of the composite would be achieved by using smaller diameter fibres and smaller distances between the fibres. There is also evidence that the hydrostatic piezoelectric coefficient (d_h) and the voltage coefficient (g_h) increase with decreasing fibre diameter [4].

Extrusion or drawing of filaments from a polymeric gel, rather than a paste, is a promising means of producing smaller diameter fibres. In the past this research group has demonstrated the merits of extruding lead titanate (PT) precursor gels produced by a methoxyethanol based sol–gel route [5]. However, Phillips and Milne [6] have subsequently demonstrated an improved sol–gel route for PT and PZT gel synthesis that, in the field of thin film manufacture, has led to major processing improvements [7, 8]. The route is also attractive for fibre production [9]. The new route uses diols as the gel forming solvent. Presented here is a detailed account of the properties of PT and modified PT fibres produced by the new route, and the merits of using the fibres in 1–3 composite manufacture are discussed.

* Author to whom all correspondence should be directed.

2. Experimental procedure

The processing scheme for preparing PbTiO_3 fibres is presented in Fig. 1. Lead acetate trihydrate, $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$, titanium diisopropoxide bisacetylacetonate, $\text{Ti}(\text{OC}_3\text{H}_7)_2(\text{CH}_3\text{COCHCOCH}_3)_2$, abbreviated TIAA, and propanediol, $\text{HO}(\text{CH}_2)_3\text{OH}$, obtained from Aldrich Chemical Co., were used to prepare precursor solutions according to the procedure originally reported by Philips *et al.* [7, 8]. The assayed $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ reagent was dissolved in propanediol in 1:5 molar ratio of Pb to diol and refluxed for 1 h. This solution was then cooled to 80°C prior to adding TIAA in an equimolar ratio of Pb to Ti. The second reflux was carried out for 4 h with one distillation at ca. $80\text{--}85^\circ\text{C}$. The resulting solution, which was the PT stock solution, was yellow with a density of ca. 1.2 g cm^{-3} and a concentration of ca. 1.0 M.

Other solutions were prepared by mixing the stock solution with water, 2-propanol, $(\text{CH}_3)_2\text{CHOH}$ and nitric acid in various ratios as listed in Table I. One series of sols had a constant molar ratio of Pb, Ti/ $\text{C}_3\text{H}_7\text{OH}/\text{HNO}_3$ of 1/0.5/0.01 but various ratios of added water were used. Sols containing added

water, Table I, are labelled W sols. One sol was further modified with increasing additions of nitric acid, taking care to maintain a constant water ratio, Table I. This series is labelled C.

Where appropriate, additives, such as manganese acetate, excess lead acetate and/or calcium nitrate, were dissolved in the sols to allow the preparation of chemically modified PT fibres, Table II.

The sols were concentrated at 80°C with continuous stirring to form viscous liquids and then heat treated (aged) at 80°C in an oven to form gels for fibre extrusion experiments. The gels were piston extruded through a 0.5 mm diameter orifice; a floor standing Instron instrument was used to control the extrusion rate.

The thermal decomposition characteristics of the gel fibres were identified using differential thermal analysis (DTA) and thermogravimetric analysis (TGA). The gel fibres, of which three samples, S0, W1 and C20 were studied, were pre-dried at 120°C for 3 days and then analysed using a heating rate of 5°C min^{-1} . To determine crystallization behaviour, the dried gel fibres were heat treated for 1 h at temperatures from 300 to 750°C , applying a heating rate of 5°C min^{-1} and a cooling rate of 3°C min^{-1} . X-ray diffraction patterns were recorded using a Phillips APD 1700 diffractometer. The microstructures of fired

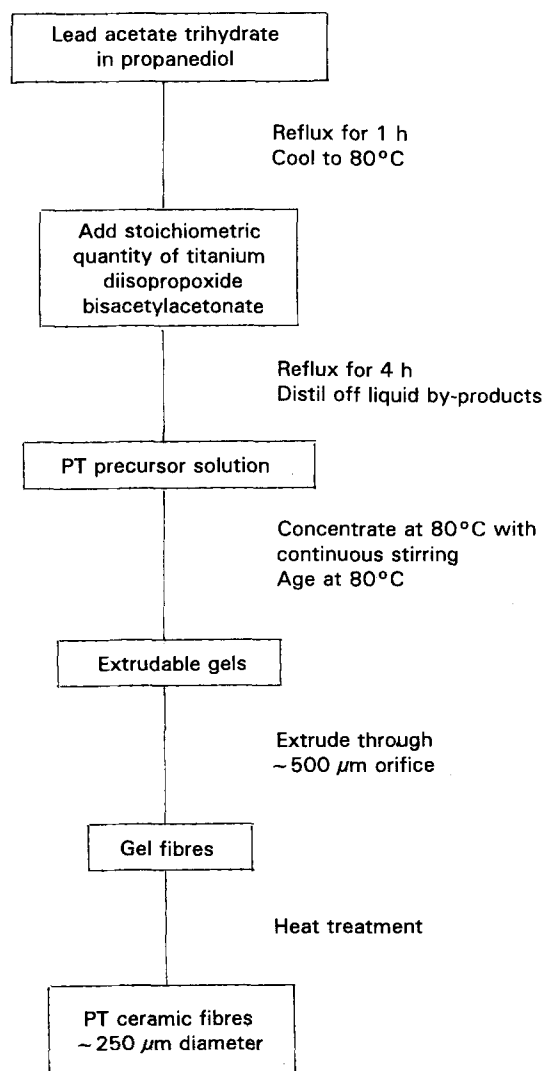


Figure 1 Flow diagram for the preparation of PbTiO_3 fibres by the diol gel extrusion process.

TABLE I Compositions of precursor solutions and ageing conditions for fibre formation.

Sample	Reagent molar ratio $\text{H}_2\text{O}:\text{C}_3\text{H}_7\text{OH}:\text{HNO}_3$ (per mol of Pb, Ti)	Ageing temperature ($^\circ\text{C}$)	Minimum ageing time for forming gel fibres, t_e (days)
Stock	—	80	21
W1	1:0.5:0.01	80	19
W2	2:0.5:0.01	80	31
W4	4:0.5:0.01	80	55
W20	20:0.5:0.01	80	76
CO1	1:0.5:0.01	80	19
CO2	1:0.5:0.02	80	15
CO3	1:0.5:0.03	80	11
C20	1:0.5:0.20	80	4

TABLE II Compositions of precursor solutions and ageing conditions for modified PT fibre formation.

Sample	Reagent molar ratio $\text{H}_2\text{O}:\text{C}_3\text{H}_7\text{OH}:\text{HNO}_3$ (per mol of Pb, Ti)	Ageing temperature ($^\circ\text{C}$)	Minimum ageing time for forming gel fibres, t_e (days)
PT + 3 mol % Pb	1:0.75:0.01	80	17
PT + 4 mol % Mn	1:0.75:0.01	80	15
$\text{Pb}_{1-x}\text{Ca}_x\text{TiO}_3$ ($x = 0.02$)	—	80	19
PT + 2 mol % Ca	1:2:2	80	26

($\text{H}_2\text{O}:\text{C}_3\text{H}_7\text{OH}:\text{CH}_3\text{COOH}$)

fibres were studied using scanning electron microscopy (Hitachi S-700).

The optimum ageing and firing schedule for converting gel fibres to PbTiO_3 fibres of maximum density was determined for W1 fibres. Various dwell temperatures, between 600 and 800 °C, were studied for heating rates of 3, 5 or 10 °C min^{-1} . Samples were held at the set temperature for 30 min. For practical purposes, the dried extruded fibres were broken into ca. 10 cm lengths prior to firing. Fibre densities were then determined using water displacement pycnometry.

Composites were prepared by manually aligning the fibres in a glass tube and then impregnating them with an epoxy resin (Dow Chemicals product D.E.R. 353).

3. Results

All sol compositions listed in Table I increased in viscosity with time and eventually transformed to gels. It was found that further ageing at 80 °C was required in order to improve the extrusion characteristics of the gels. When gels were extruded without this ageing step a liquid phase separated from the gel during extrusion and it was not possible to produce coherent fibres. The minimum ageing time for the production of continuous extruded gel fibres is referred to as t_e . In sols to which water had been added to the base mixture the value of t_e increased with increasing water ratio, from 19 days for W1 to 76 days for W20, Table I. In contrast, adding increased levels of nitric acid led to a sharp reduction in t_e , Table I. For the highest HNO_3 concentration studied, sample C20, t_e was equal to 4 days.

As would be expected, raising the ageing temperature from 80 to 100 °C accelerated the ageing process. For example, t_e for W2 was reduced from 31 days to 6 days by using this higher ageing temperature.

It was subsequently found that ageing the gels for 2–3 weeks beyond t_e at room temperature enabled longer fibres, ≥ 30 cm, to be produced, Fig. 2. Without this step extruded fibres were 5–10 cm long. Fibres were pliable and easy to handle but melted if fired directly after extrusion. However, this thermoplastic

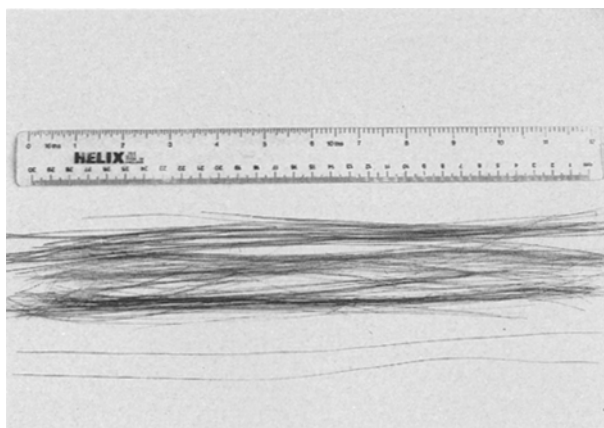


Figure 2 Extruded gel fibres (unmodified) dried at room temperature.

behaviour disappeared after the extruded fibres were further aged at room temperature for ca. 3 days. This procedure was subsequently adopted for all gel types.

The thermal decomposition characteristics of examples of S0, W1 and C20 extruded gel fibres that had been pre-dried at 120 °C are shown in Figs 3 and 4. In general, two broad weight loss steps were observed in all gels as they were heated to ca. 475 °C, at which point a smaller but sharp weight loss occurred (Fig. 3). The latter was completed by 520 °C, signifying final conversion to ceramic PbTiO_3 . The fractional weight loss of the S0 stock gels below 450 °C was significantly greater than for W1 and C20, whilst between 475–520 °C the percentage weight loss in the S0 sample was around half of that occurring in each of the other two samples, Fig. 3. The overall total weight loss in S0 samples was ca. 26% as opposed to ca. 21% for W1 and C20.

The corresponding DTA traces of each of the three sample types, again pre-dried at 120 °C, each displayed two distinct exotherms at ca. 490 °C and 520 °C in addition to broad low temperature effects, Fig. 4. However, the relative intensity of the former two peaks in the S0 gels was the reverse of those in the W1 and C20 samples. The ca. 490 °C peak in each sample actually had an onset temperature of ca. 470 °C, correlating to the onset temperature for the final TGA

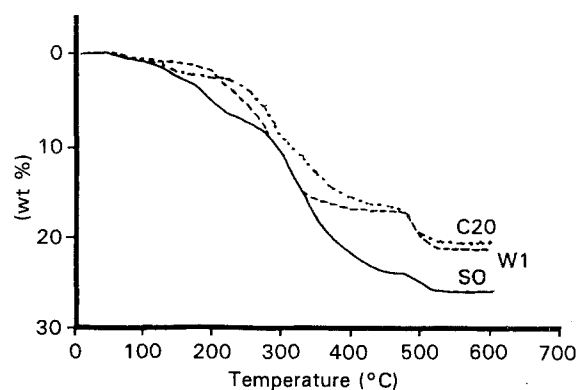


Figure 3 TGA data for SO, W1 and C20 samples.

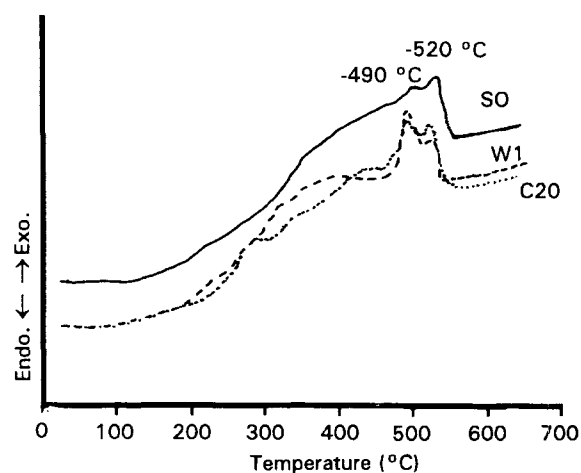


Figure 4 DTA data for SO, W1 and C20 samples.

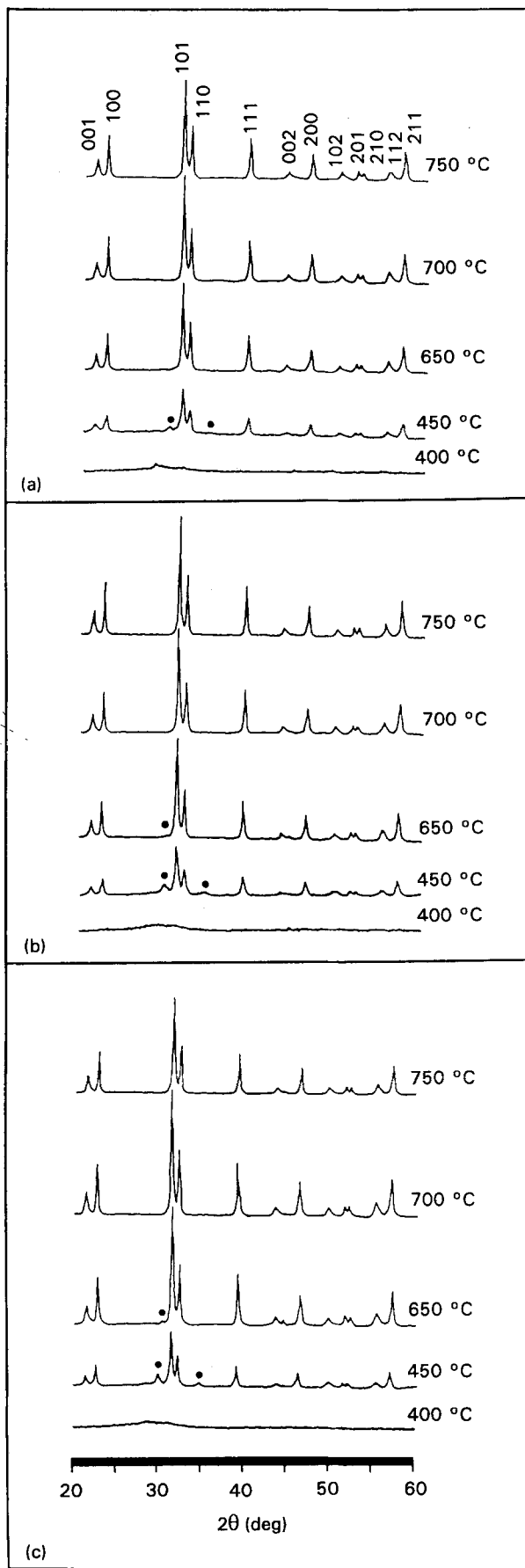


Figure 5 X-ray diffraction results as a function of firing temperatures for: (a) SO gels; (b) W1 gels; (c) C20 gels (* = pyrochlore phase).

weight loss that signified final elimination/combustion of organics. The lower intensity of this DTA exotherm in S0 compared to that of W1 and C20

traces is consistent with the smaller final weight loss in TGA data, Fig. 3. The final DTA peak at ca. 520 °C in each sample is attributed to crystallization to PbTiO_3 .

X-ray diffraction patterns of the S0, W1 and C20 gels that had been heat-treated at temperatures from 300 to 750 °C for 1 h were mutually similar, as shown in Fig. 5. The onset of crystallization to tetragonal PbTiO_3 and a small proportion of a pyrochlore phase was first detected in gels fired at 450 °C. The pyrochlore phase persisted in samples heat treated up to 650 °C, although it had almost disappeared at this temperature in the S0 sample, Fig. 5a. Heating all samples at 700 °C resulted in tetragonal single phase materials and sharply defined X-ray patterns, Fig. 5.

As stated earlier, W1 fibres were subjected to various heat treatments in order to evaluate a satisfactory firing schedule for the conversion of the gel fibres to coherent ceramic fibres. It was found that these criteria were best satisfied using a heating rate of 5°C min^{-1} and holding the fibres at 750 °C for 30 min followed by cooling at 3°C min^{-1} . Higher firing temperatures and/or longer firing times were not pursued because of likely PbO volatilization. Thereafter this schedule was adopted for all gel types. After firing, the fibres visually retained the physical integrity of the extruded gels, but stresses during firing caused the fibres to buckle, Fig. 6.

Fired fibres prepared from the stock, S0, sols exhibited severe surface cracking and disruption to the fibre structure, Fig. 7a. There was also a high incidence of surface porosity and microcracks in an otherwise dense surface skin, Fig. 7b. The as-fired surface and transverse sections both revealed a reasonably dense microstructure with a grain size of ca. $0.3\ \mu\text{m}$, Fig. 7c and d. Various additions of water, acid and isopropanol were studied with the aim of improving the structure of the fibres. However, none of the W series of sols, Table I, led to any reduction in fibre cracking; in fact there was a noticeable incidence of internal cracking that disclosed a ripple-like structure in transverse sections, Fig. 8. The degree of cracking intensified with increasing water additions. The grain size was similar to that of fibres derived from S0 gels, ca. $0.3\ \mu\text{m}$, again with no difference between the sur-

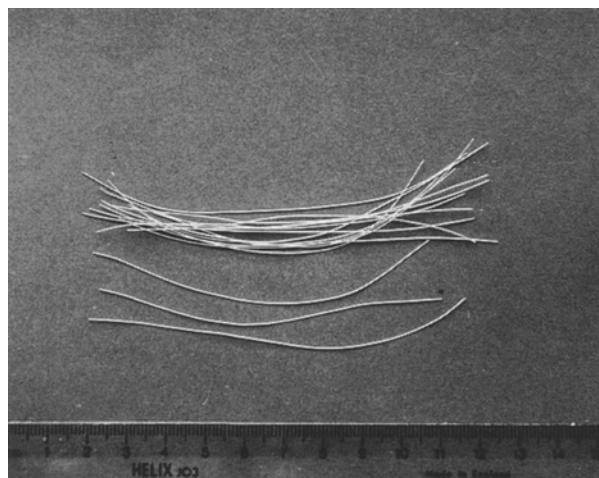


Figure 6 PbTiO_3 fibres heat treated to 750 °C for 30 min.

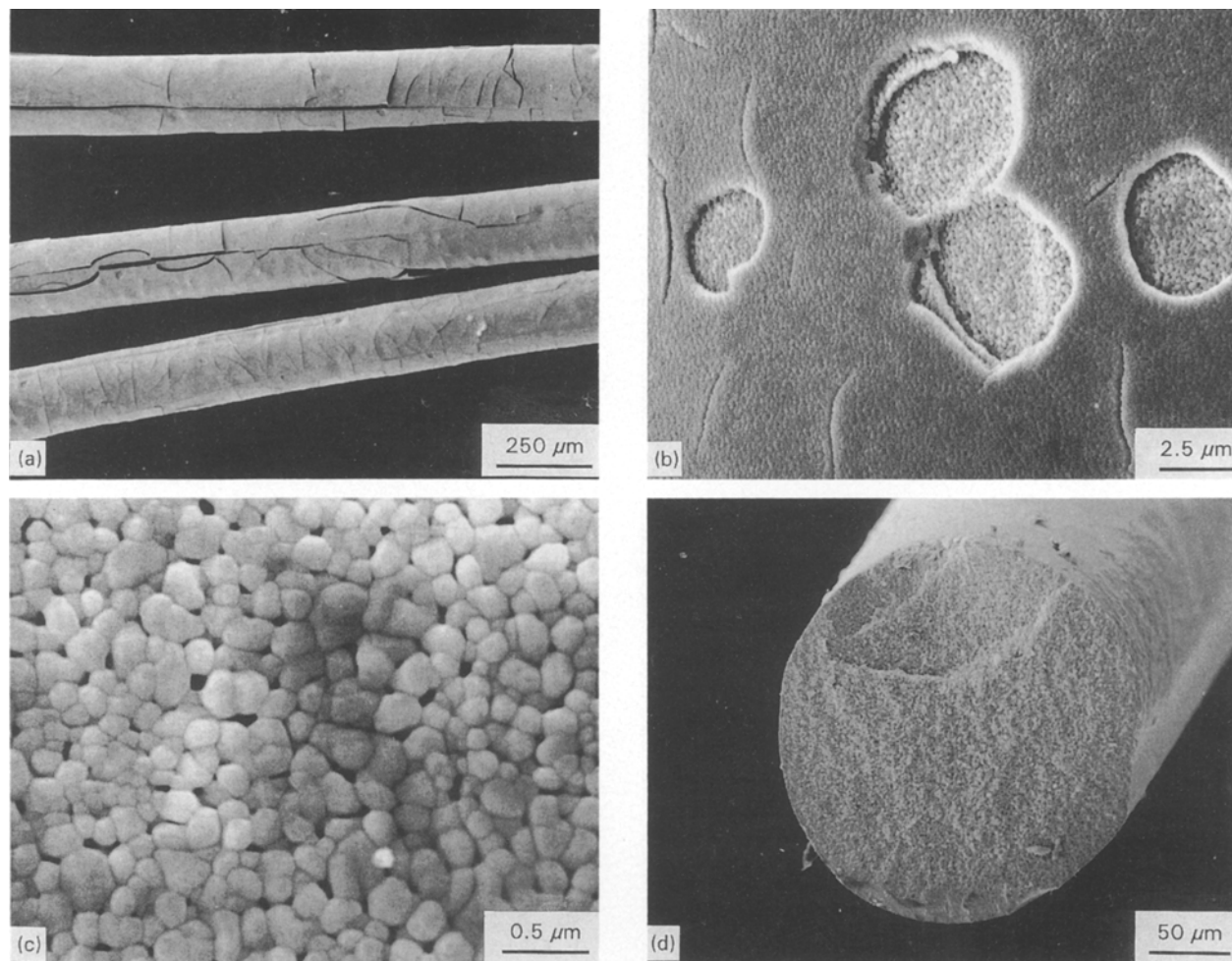


Figure 7 SEM micrographs of PbTiO_3 fibres prepared from SO stock gels showing: (a) extent of fibre cracking; (b) surface pitting and microcracking; (c) microstructure; (d) transverse section.

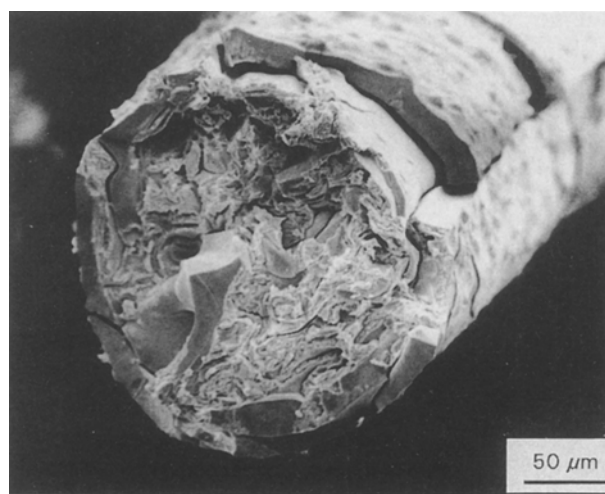


Figure 8 Transverse section of PbTiO_3 fibres made from W1 gels.

face and internal grain size. Except where stated, all subsequent gel types studied also led to this grain size.

Increasing the amount of acid in the gel-precursors gradually reduced the incidence of surface cracking in the ceramic fibres. Of the various C sols studied, C20 with the highest acid concentration, Table I, resulted in predominantly crack-free PbTiO_3 fibres, Fig. 9. These were ca. $250 \mu\text{m}$ in diameter with a measured

density of ca. 7.1 g cm^{-3} . Transverse sections (in Fig. 9c) were similar to Fig. 7d.

In a separate series of experiments the merits, or otherwise, of adding manganese, calcium and excess lead, either singly or in combination, to the sols were examined, Table II.

The structure of fired fibres extruded from W1 gels containing 3 mol % of excess Pb is shown in Fig. 10. Surface cracking was apparent, but on a much finer scale than in equivalent unmodified W1 samples, Fig. 10a. There was also a rather different surface topography in the excess lead fibres, possibly resulting from lead migration to the surface. Cross-sections appeared to be dense and of reasonably uniform microstructure, Fig. 10b.

Additions of 4 mol % manganese acetate produced fibres with a similar surface appearance to those of the Pb modified fibres, Fig. 11a. Perhaps this is not surprising since no compensating reduction in the Pb content was undertaken, and because manganese is known to substitute on Pb lattice sites, "excess" lead would be expected to be liberated during firing. Interestingly, the internal structure of the manganese modified fibres, Fig. 11b, was rippled in a similar manner to that of the unmodified W1 sols.

When fibres were made from 2 mol % calcium modified gels in which there was a compensating

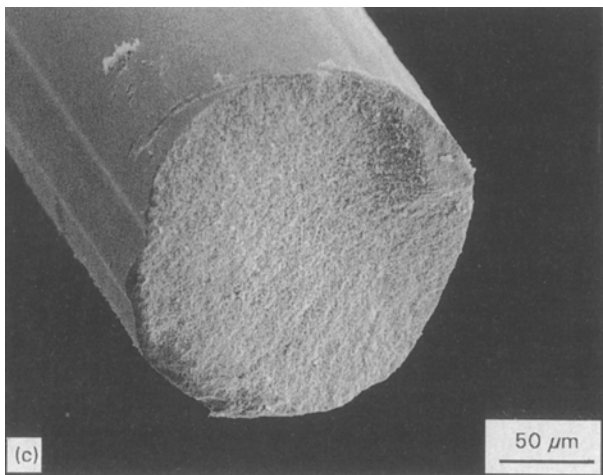
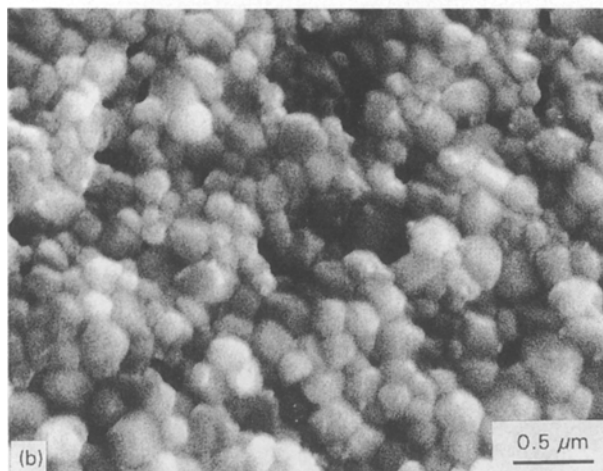
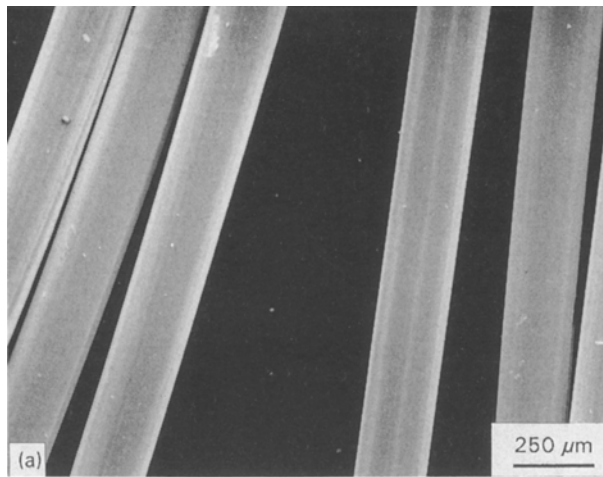


Figure 9 SEM micrographs of the surface structure of PbTiO_3 fibres prepared from C20 gels: (a) surface sections; (b) microstructure; (c) transverse section.

deficit of Pb in the starting sols, severe fibre cracking resulted, Fig. 12. Cross-sections and surfaces were of quite different appearance to any of the other fibre types studied. No water, propanol or acid were added to these sols. In cross-section, a dense outer collar some $40\ \mu\text{m}$ in thickness was observed surrounding a rippled and cracked internal core, Fig. 12b. The surface microstructure was also distinctive, being composed mainly of ca. $0.5\ \mu\text{m}$ dense grains interspersed with "islands" of smaller $0.1\ \mu\text{m}$ grains, Fig. 12c. The

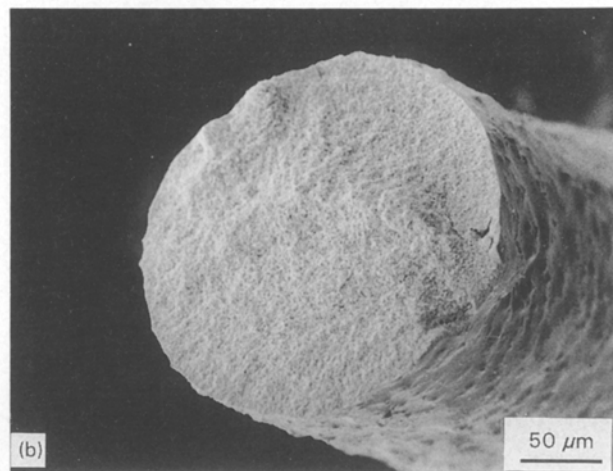
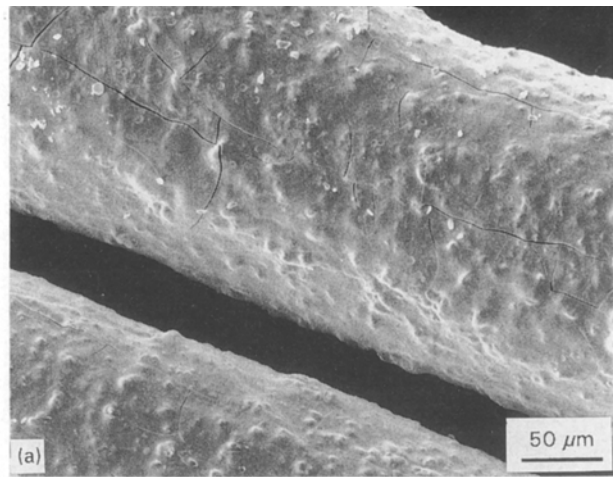


Figure 10 SEM micrographs of $\text{PbTiO}_3 + 3\ \text{mol}\ \%$ Pb modified fibres: (a) surface and (b) transverse sections.

reasons for these distinctive structures in Ca-PT gels are not yet understood.

Finally, when 2 mol % of added calcium was introduced (with no Pb compensation) fibres of the highest quality of all gel formulations used in this study were produced. There was no surface or internal cracking, the surfaces were smooth and free from large scale porosity, Fig. 13. Fibres were ca. $250\ \mu\text{m}$ in diameter and had a density of ca. $7.4\ \text{g cm}^{-3}$ theoretical with a grain size of ca. $0.3\ \mu\text{m}$. It should be noted that these sols also contained added acetic acid.

Fibres prepared from C20 gels were used to demonstrate the production of 1–3 piezoceramic–polymer composite structures. These small diameter ($0.25\ \text{mm}$) fibres were rather fragile and this led to difficulties in assembling them into composite structures. A maximum packing density of ca. 35 vol % fibres could be achieved by packing the buckled fibres together in a cylindrical container and impregnating them with an epoxy resin. The resulting composite structure is shown in Fig. 14.

4. Discussion and conclusions

All the gels studied could be extruded to produce continuous fibres after an appropriate ageing period. The mechanisms of changes in gel structure during this period are not yet understood. Likewise, the

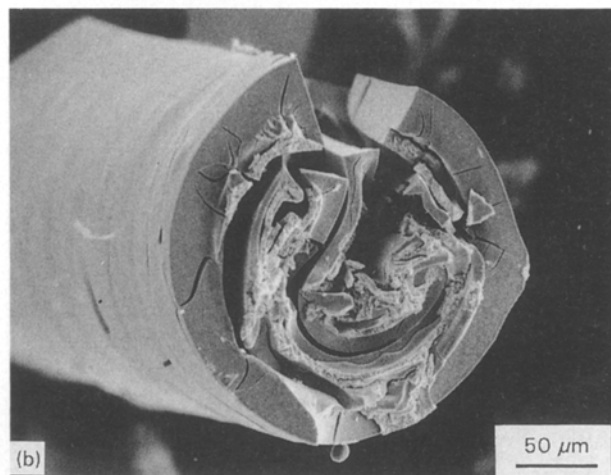
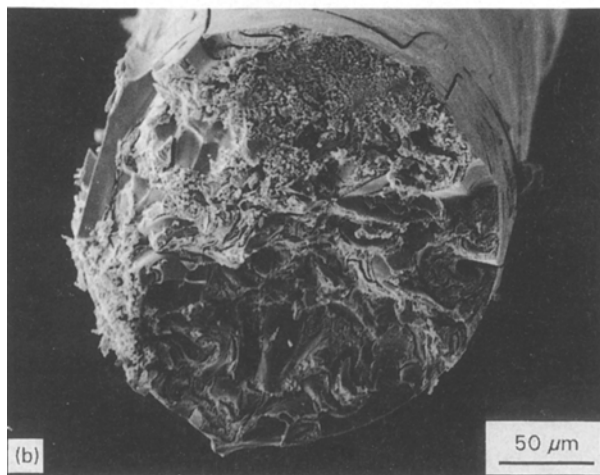
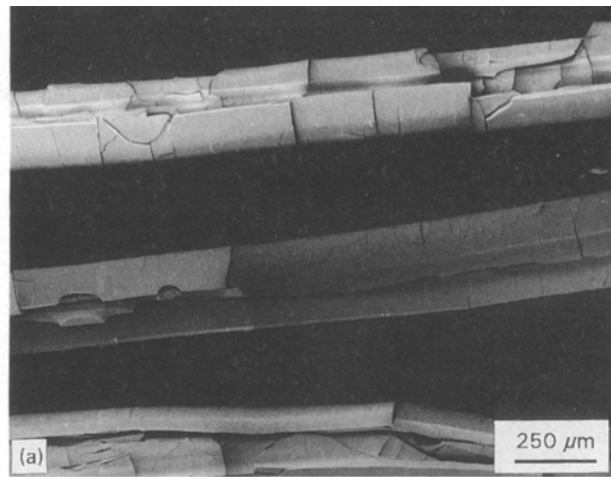
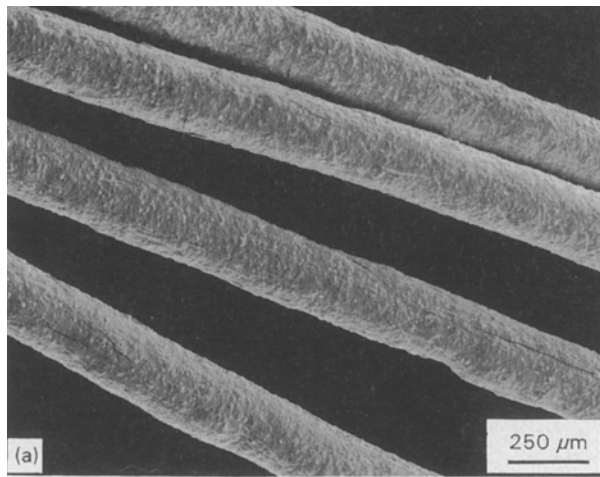


Figure 11 SEM micrographs of $\text{PbTiO}_3 + 4 \text{ mol \% Mn}$ modified fibres: (a) surface and (b) transverse sections.

variation in the response of the fibres to heating after ageing at room temperature requires further analysis.

The greater weight loss in stock gel fibres during TGA heating experiments compared to systems to which water, acid and propanol had been added implies that the added reagents led to an increased production of volatile organic by-products in the latter. These were presumably lost by evaporation during the various heat treatment and ageing steps prior to TGA runs.

The effect of added water on gel times and t_e values indicates that water acted mainly as a diluent. Increases in the water ratio merely led to a progressive decrease in gelation rates. The effect of water on diol sols is thus in contrast to the behaviour of PbTiO_3 precursor sols made by the popular methoxyethanol based sol-gel route [10, 11], and implies that hydrolysis reactions do not play an important role in polymer and gel formation in the new diol sol-gel process.

Under acid-catalysed conditions there was a marked increase in the rates of gelation relative to those of stock sols.

Preliminary NMR studies (unpublished) on a more simple titanium-propanediol sol-gel system indicate that gelation proceeds by exchange of the isopropoxy ligands of titanium diisopropoxide bisacetyl acetonate by diol groups, eventually leading to a repeating

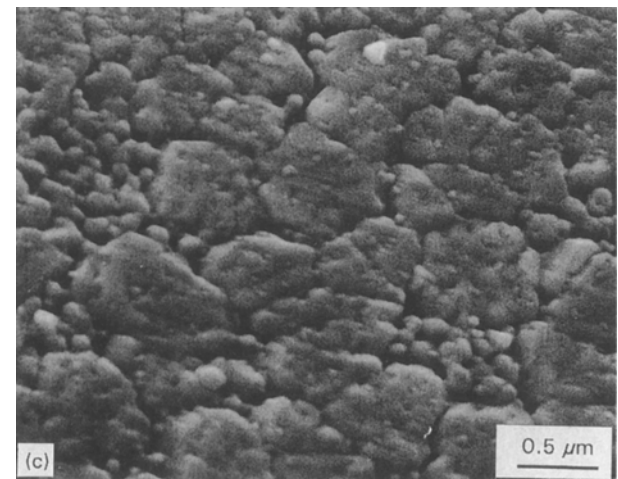


Figure 12 SEM micrographs of fibres produced from $\text{Pb}_{0.98}\text{Ca}_{0.02}\text{TiO}_3$ starting sols; (a) surface sections; (b) transverse section; (c) microstructure.

$[-\text{Ti}-\text{O}(\text{CH}_2)_3-\text{Ti}-]$ structure. The present results for C sols suggest that protonation may play an important role in this type of exchange and gelation mechanism(s), although at this stage the possibility that hydrolysis also occurs in acid catalysed diol sols cannot be excluded.

Certainly, acid modification results in a gel network that is better suited for resisting shrinkage stresses during the gel to ceramic conversion. The incidence of

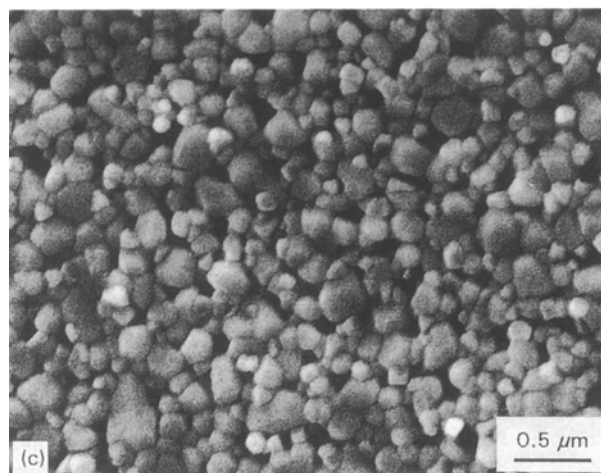
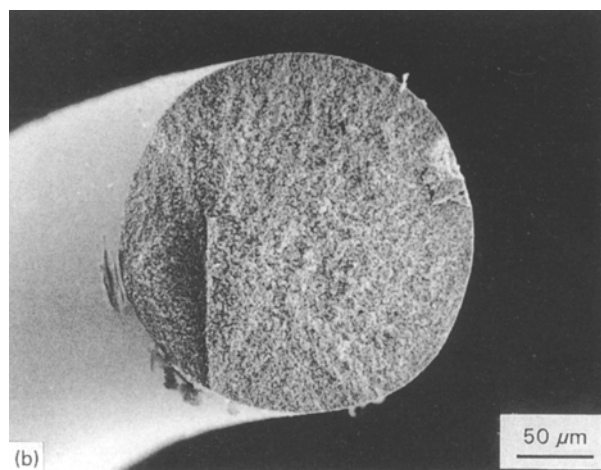
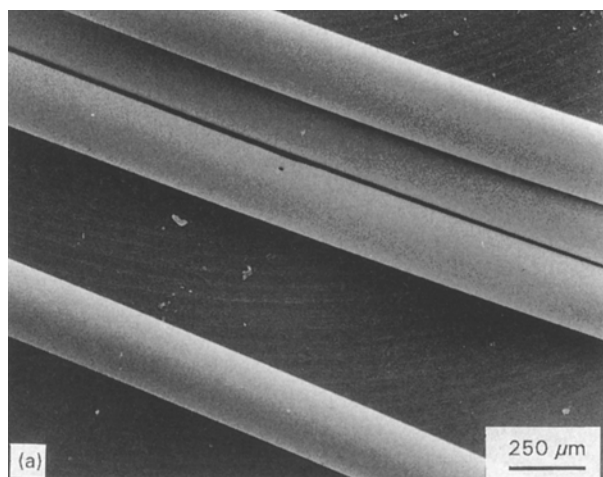


Figure 13 SEM micrographs of $\text{PbTiO}_3 + 2 \text{ mol } \% \text{ Ca}$ modified fibres: (a) surface sections; (b) transverse section; (c) microstructure.

fibre cracking decreased with increasing levels of nitric acid, the C20 gel producing the highest quality unmodified PbTiO_3 fibres.

It was thought that excess lead would assist in sintering by forming a liquid phase during firing, whereas manganese and calcium substitutions for Pb on the PbTiO_3 crystal lattice would reduce the tetragonal c/a ratio and may thus inhibit cracking when

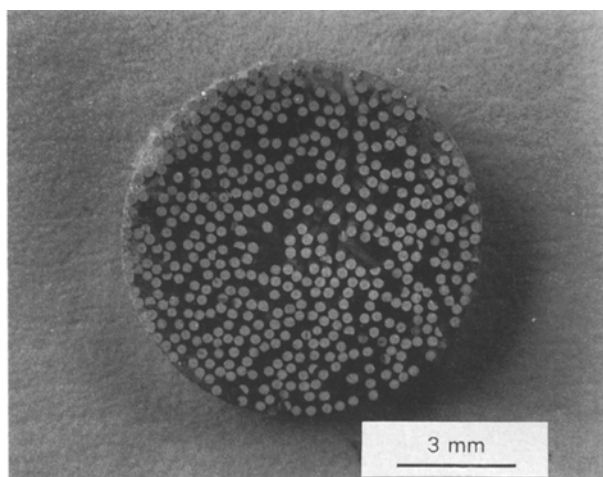


Figure 14 1–3 piezoceramic–polymer composite structure fabricated from PbTiO_3 fibres (made from C20 gels) and an epoxy resin polymer phase. The section shown was ca. 2 mm thick.

cooling the fibres through the cubic-tetragonal phase transition.

The results indicate that a combination of the two effects, i.e. simple addition of calcium with no compensating reduction in the Pb ratio, produced the best results. A further contribution to the favourable fibre properties found in this system may result from the choice of calcium nitrate as the starting reagent. Any nitric acid, if formed as a by-product during sol ageing, would act in an analogous manner to that described above for the C series of sols; the acetic acid added may also have influenced fibre properties.

In conclusion, it has been possible to manufacture crack-free ca. 250 μm diameter PbTiO_3 fibres by extrusion of gels which had been produced from specific acid catalysed sols or sols to which 2 mol % of calcium nitrate had been added.

Acknowledgements

We wish to thank J. Tontrakoon for useful discussions. S. Chewasatn thanks the Royal Thai Government for financial support.

References

1. R. E. NEWNHAM, D. P. SKINNER and L. E. CROSS, *Mater. Res. Bull.* **13** (1978) 525.
2. W. B. HARRISON, in Proceedings of the Workshop on Sonar Transducer Materials, Naval Res. Lab. (1976) p. 257.
3. K. A. KLICKER, J. V. BIGGERS and R. E. NEWNHAM, *J. Amer. Ceram. Soc.* **64** (1981) 5.
4. J. TONTRAKOON, PhD thesis, The University of Leeds, Leeds (1993).
5. H. JANUSSON, C. E. MILLAR and S. J. MILNE, *Mat. Res. Soc. Symp. Proc.* **180** (1990) 421.
6. N. J. PHILLIPS and S. J. MILNE, *J. Mater. Chem.* **1** (1991) 893.
7. N. J. PHILLIPS, M. L. CALZADA and S. J. MILNE, *J. Non-Cryst. Solids.* **147** and **148** (1992) 285.

8. N. J. PHILLIPS, M. L. CALZADA and S. J. MILNE, British Patent Application 9114476.6 July (1991).
9. S. CHEWASATN and S. J. MILNE, in *Third Euro-Ceramics Proc.*, Vol. 1., edited by P. Duran and J. F. Fernandez (Faenza Editrice Iberica, Spain, 1993) p. 335.
10. K. D. BUDD, S. K. DEY and D. A. PAYNE, *Proc. Brit. Ceram. Soc.* **36** (1985) 107.
11. K. D. BUDD, S. K. DEY and D. A. PAYNE, *Mater. Res. Soc. Symp. Proc.* **73** (1986) 711.

*Received 15 December 1993
and accepted 10 January 1994*