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The use of sols in tape casting for PZT ceramics

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Abstract

Lead zirconate titanate (PZT) precursor sols were prepared by a diol and triol sol-gel route and used as an additive for tape casting of PZT layers. The powders, of composition $Pb(Zr_{0.52}Ti_{0.48})O_3$, were prepared by a two step mixed oxide route using lead carbonate, zirconia and titania starting powders. Various amount of sols i.e. 0, 15, 35 and 45 vol% sol were applied to the slurry. Viscosity of the slurry and flexibility of green tapes were critical factors. After binder burnout, the tapes were examined by SEM . An interesting tape with a high sol-gel content, of 45 vol% sol had distinguishable features from other tapes, with the sol clearly occupying pore space and linking particle together which could assist densification.

Keywords : PZT, lead zirconate titanate, PZT diol sol, PZT triol sol, tape casting, single layer tape

Introduction

Lead zirconate titanate, PZT, is a ferroelectric ceramic which is used in electromechanical device applications such as transducers, actuators and capacitors. Most of these devices are produced as multilayer materials . By means of the tape-casting method, sheet ceramics of large area and small thickness can be prepared quickly and reliably (Neito, *et al.* 1996). Normally the casting slip consists of an inorganic powder, solvent, deflocculant, binder and plasticiser. However in some works, a sol is applied to the slip system for extrusion or casting. For example Kumar, *et al.* (1997) used monohydroxide alumina oxide (Boehmite, AlOOH) as a reactive binder for extrusion of alumina ceramics. The boehmite-γ-alumina mixture appeared to result in a dense alumina ceramic. Petroff, *et al.* (1994) was interested in zirconia hydrogels which aided the dispersion and stabilisation of ceramic powder in water and also behaved as a binder in casting.

Because similar work was done successfully in using a sol as a binder for assisting the uniaxial die pressing of PZT powder

(Tangwiwat and Milne, *et al.* 1999). Using sol in another systems such as slip casting might be possible. The objective of this research is to study effects of sol on single layer tape. There are two parts to this work-tape casting of the slip prepared by dispersing PZT powder in a sol and tape casting of the slip prepared by adding PZT sol as an additional component.

Experimental procedure

PZT Powder

Raw materials used were: $PbCO_3$ (Aldrich, purity > 99.9%); TiO_2 (Aldrich, purity >99.9%); and ZrO_2 (Aldrich, purity > 99%). The PZT powder was prepared in a two step procedure : initially zirconium titanate (ZT) powder was prepared from ZrO_2 and TiO_2 in a molar ratio of 52 : 48. The ZT mixture was ball milled in isopropanol with zirconia grinding media for 24 h; the suspension was dried under a heat lamp and passed through a 300 μm mesh size polyester sieve before calcination at 1500°C for 2 h. The calcined ZT powder was ball milled for 24 h to break down agglomerates following the same procedure as above. The milled ZT powder was mixed with $PbCO_3$, in a 1:1 molar ratio, ball milled and calcined for 2 h at 750°C.

PZT Sols

The diol sols were prepared from propanediol solutions of lead acetate, and zirconium and titanium alkoxides modified with equimolar ratios of pentanedione. Details of the PZT sol preparation procedure were reported elsewhere (Phillip, *et al.* 1992; and Tu, *et al.* 1996).

For triol sol preparation in a dry nitrogen glove box, zirconium n-propoxide and acetylacetone were weighed out with a molar ratio of 2 to 1. The mixture was refluxed in an oil bath at 80°C to 90°C for 2 h. After the reaction was completed, a golden solution was obtained. Then the solution was left to cool down before titanium isopropoxide bisacetylacetonate (Alfa Co., 73wt% in 2-propanol) abbreviated TIAA, lead acetate trihydrate and 1,1,1-tris (hydroxymethyl) ethane (Aldrich Co.), abbreviated THOME, were added to the solution. Finally, the mixture was heated at 60°C to 70°C for 4 h. The final product was a viscous golden solution; of a concentration of ca. 1.18 mol dm^{-3} (expressed in terms of PZT equivalent).

TAPE – Casting Slip

An organic binder / solvent based tape-casting system was chosen. The components of the slip consisted of powder, solvent, binder, plasticiser and dipersant i.e. synthesized PZT powder n-propanol (Aldrich), Hypermer KD-2 (ICI supplier), polyvinyl butyral (Cairn Chemical), dibutyl phthalate (Aldrich). Furthermore the extra constituent, PZT sol, was added to the slip to study its effects.

Firstly, the dispersant was dissolved in the solvent in a plastic jar. Secondly the PZT powder was added and the mixture was shaken by a shaker-mixer (Spex^{TM}) for 30 min before binder, plasticiser and sol were added. Finally, the mixture was shaken again for 30 min. The slip formulation is given in Table 1.

Table 1 Slip formulation for tape-casting.

Components	Slip 1 (% vol)	Slip 2 (% vol)	Slip 3 (% vol)	Slip 4 (% vol)
PZT	38.5	28	22	17
n-propanol	52	47	31	23.5
Hypermer KD-2	3	3.5	3.5	3.5
PVB	4.5	4.5	6	8
DBP	2	2	2.5	3
Sol	0	15	35	45

The slip was cast on carrier paper (Steralease 46^{TM}) from Sterling Coated Materials Limited in a system with a moving doctor blade on a fixed table. The blade speed was 25 mm min^{-1}. After casting, the tapes were left overnight to let solvents evaporate. The dried tapes were carefully peeled off from the carrier paper.

The organic substances in the tapes were removed slowly at a heating rate of 30°C h^{-1} and held at 500°C for 1 h. Afterwards, the single layer tapes were examined by SEM.

Results and Discussion

Tape casting of the slip prepared by dispersing PZT powder in sol

During the initial investigation into the use of sols for tape-casting PZT, sol and powder were mixed, with no other ingredients added. The PZT powder and sol were mixed in a ratio of 5 g PZT powder to 2 cm^3 of sol. This ratio enabled slurries to be prepared which were not too thick or too thin to cast. The powder for this experiment was PZT-2 (milled); the sol concentration was 1.1 mol dm^{-3}. After casting on silicone coated carrier film (Steralease 46^{TM}), the tape was left to dry at room temperature. The details of casting conditions were shown above.

It was found that the tape of PZT powder with triol sol, dried within a few hours at room temperature, whereas the tape of PZT powder with diol sol did not dry at room temperature within this timescale. It had to be dried in an oven at 100°C for 2 hours. The difference in duration of drying can be attributed to the shorter gelation time of the triol sols.

Unfortunately, after drying in the oven, the tape made with the diol sol broke into small pieces. In the case of the tape with triol sol, the tape-cast layer remained intact, but was very brittle. This illustrated that the PZT sol, when used without any of the additives normally employed to formulate traditional slurries, could in the case of triol sols, be used to deposit coherent PZT layers but was unable to provide sufficient plasticity to produce layers of sufficient flexibility for tape-casting. Tape flexibility is important to comply with of the handling procedures used in large scale fabrication.

Usually, a range of organic additives is used to produce suitable slips or slurries. PZT slips are usually prepared using n-propanol as a solvent, Hypermer KD-2 as a dispersant, polyvinyl butyral as a binder and dibutyl phathalate as a plasticiser. In fact the organic binders in the slip promote various other effects such as improved wetting, delayed sedimentation, and increased viscosity. Requirements of a binder for use in a tape casting slip are: (I)compatibility with the system; (II)ability to function as a stabilization aid; (III)ability to produce a lubricant effect between particles; (IV)no interference either with solvent evaporation or with trapped air; (V)easy burnout without leaving residues; (VI)effective at low concentration, and (VII)a high molecular weight (Moremo, R. 1992).

Interesting work using zirconium hydrogel as a binder to fabricate PZT by slip casting was carried out by Petroff, *et al.* (1994). They found that green bodies were robust enough to allow some green-state sanding and grinding. From this point of view, sol-gel binders have been shown to be suitable for certain applications. In the present work PZT sol by diol and triol routes were shown to be beneficial for die pressing fabrication since they produced strong green pellets. However the sols on their own are not suitable for tape casting because the dried sol cannot function as a combined dispersant, plasticiser and binder so as to produce a green tape which can be easily handled and stored.

However others have shown that simply dispersing PZT powder in a PZT sol is a promising system for spin coating thick films on a solid substrate. For example Barrow, *et al.* (1997) were successful in preparing PZT films, 60 μm in thickness, by spin coating a mixture of PZT dispersed in a sol made by the acetic acid route (Yi and Sayer, 1991).

Tape casting of the slip prepared by adding PZT sol as an additional component.

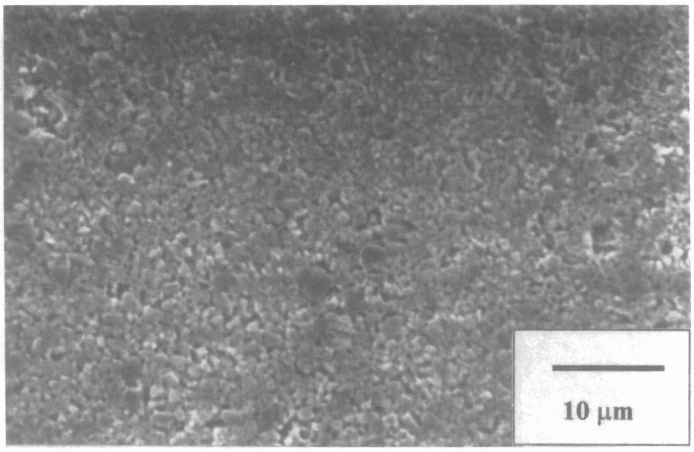
For tape-casting applications, it was decided to examine if there were any benefits in adding PZT sol as an additional component to slips made using a conventional recipe based on a solvent, dispersant, binder and plasticiser. The PZT triol sol was selected for this experiment since it gave a reasonable drying time.

The four formulas of slip, shown in Table were prepared with a triol sol content of 0 (sample 1), 15 (sample 2), 35 (sample 3), and 45 % by volume (0, 1.9, 5.3 and 8.5 wt% respectively) were prepared to study the effect of sol additions. The composition of each slip is shown in Table 2.

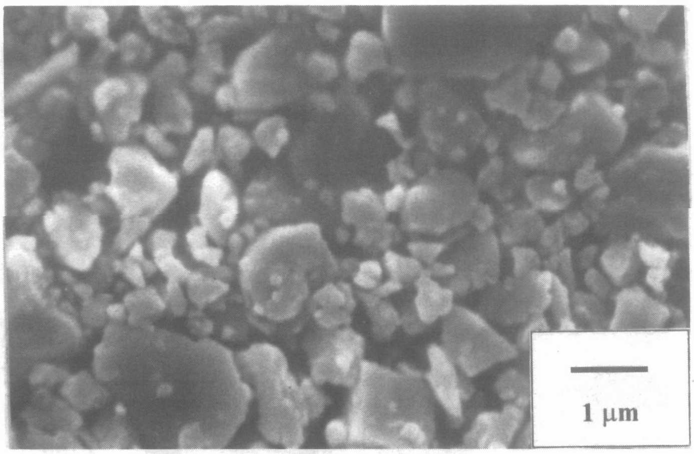
Table 2 Composition of slip for tape casting.

Components	% by volume			
	Sample 1	**Sample 2**	**Sample 3**	**Sample 4**
PZT content	83.4	72.7	69.3	62.2
PZT from sol	0	1.9	5.3	8.5
Solid content	83.4	74.6	74.6	70.7
Organic content	16.6	25.4	25.4	29.3

SEM micrographs of the single tape-cast layers after burnout at a heating rate of 30°C h^{-1} and holding at 500°C for 1 h, are shown in Figures 1-4.



(a)

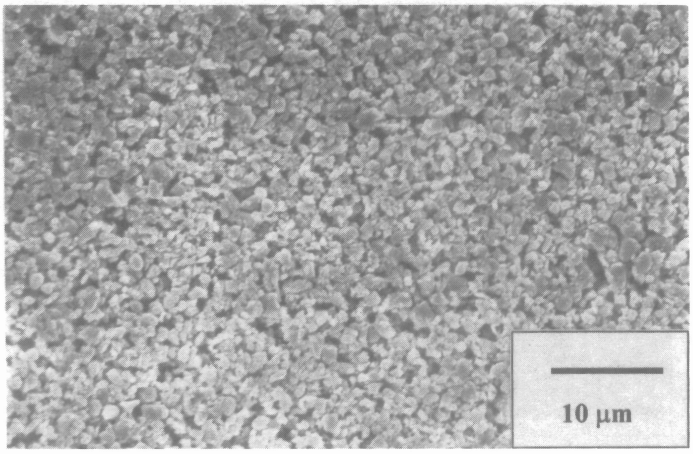


(b)

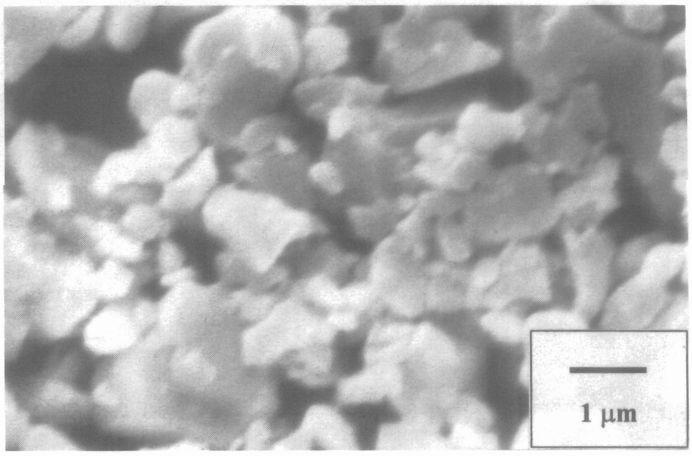
Figure 1 SEM micrograph of tape after binder burnout with 0 % sol.

(a) Magnification x 1,450.

(b) Magnification x 10,000.



(a)

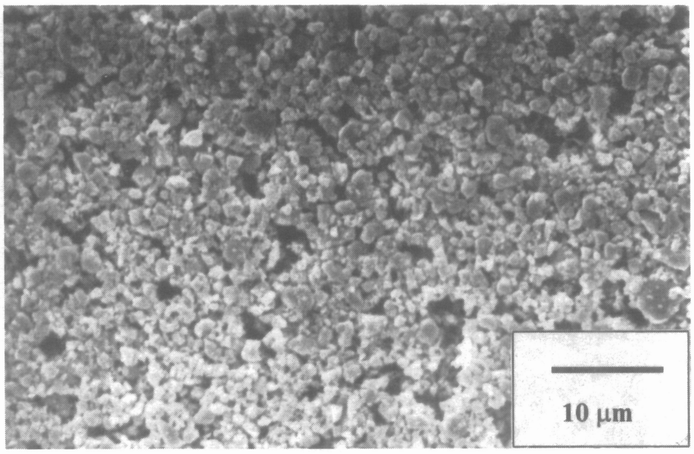


(b)

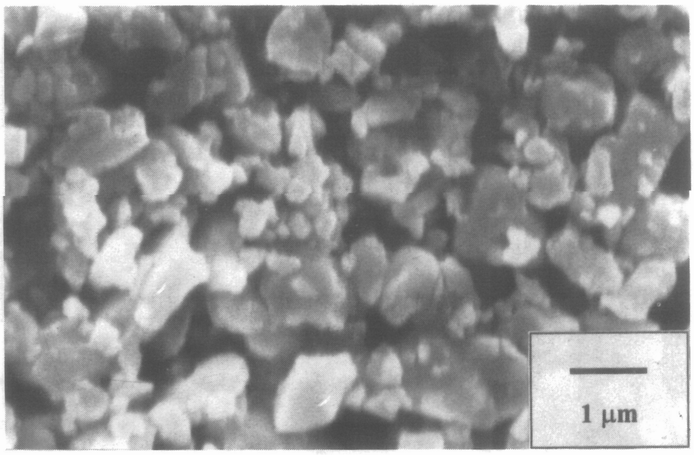
Figure 2 SEM micrograph of tape after binder burnout with 15 vol% sol.

(a) Magnification x 1,450.

(b) Magnification x 10,000.



(a)

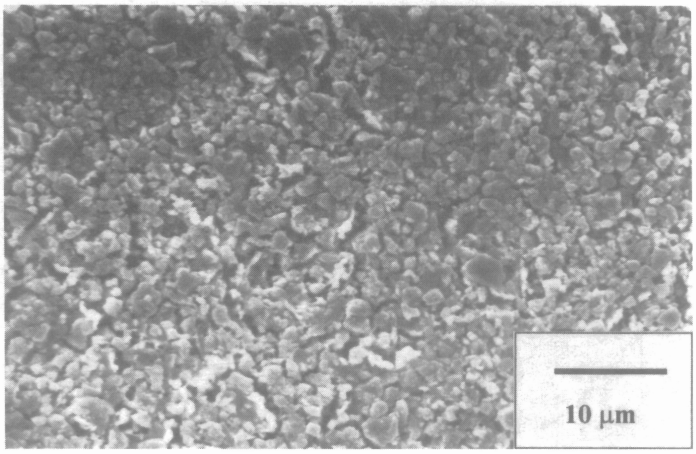


(b)

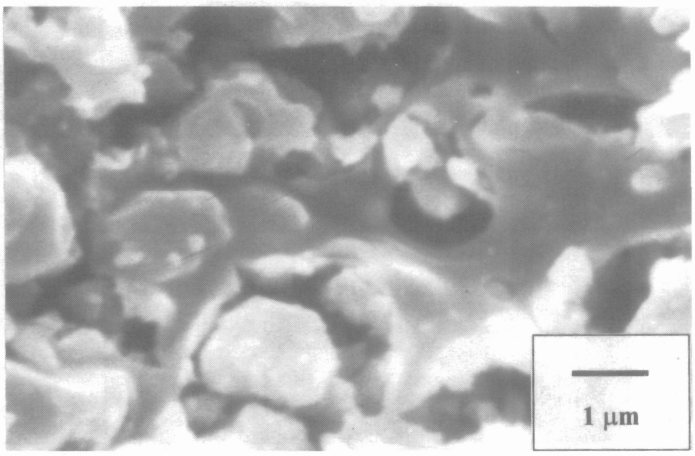
Figure 3 SEM micrograph of tape after binder burnout with 35 vol% sol.

(a) Magnification x 1,450.

(b) Magnification x 10,000.



(a)



(b)

Figure 4 SEM micrograph of tape after binder burnout with 45 vol% sol.

(a) Magnification x 1,450.

(b) Magnification x 10,000.

It is difficult to detect any significant differences in SEM micrographs of tapes with 0, 15, and 35 vol% sol, although there is a suggestion that there may be a more porous microstructure in the sol samples. The tape made without any sol sample 1 had a higher solids content than the other two tapes. For example in the formulation used for the 15 vol% sol mixture (sample 2), the solid content of PZT powder was decreased by about 10 vol% because the amount of organic components was increased; after burnout this substantial increase in organic content would be expected to produce a more porous structure.

In the case of tapes with 45 vol% sol, Figure 4(a), different features from the other samples were apparent. It had a larger particle size and showed less porosity. At higher magnification, Figure 4(b) some particles were clearly joined together by a film which is presumably a consequence of the sol-gel binder. Perhaps in the samples with lower sol content this phenomena occurred in more restricted regions and was not observed in the areas of the sample examined by SEM.

Conclusions

A slip of the mixture between PZT powder and PZT sol could be cast to form a tape on a carrier film, but after drying the tape was too fragile to handle. Therefore PZT sol on its own was not a useful binder for tape casting. However it could be used as an additive to a conventional slip, together with other organic components such as dispersant, plasticiser and organic binder.

After binder burnout, a tape with a high sol-gel content, 45 vol% sol, had distinguishable features from other tapes, with the sol clearly occupying pore space and linking particles together. This may have benefits in subsequent densification but the tapes were less flexible than those made conventionally. The 45 vol% sol content corresponded to a wt% equivalent PZT from the sol of 8.5 %, similar to that used for the bulk ceramic investigations.

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