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# Powders of $Pb(Zr_xTi_{1-x})O_3$ by sol–gel coating of PbO

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Powders of lead zirconate titanate (PZT) are prepared by coating a PbO powder with very fine particles containing titanium and zirconium derived from an alkoxide sol. The size of the particles in the coating increases from 10 nm to 100 nm with the increase in the pH during preparation from 3 to 10.5. The powders calcine at low temperature ($\simeq 600\,^{\circ}C$) to single-phase PZT without the formation of any intermediate phase. The tetragonal and rhombohedral phases are found to coexist between $x = 0.535$ and 0.545. Careful calcination of the powders is needed to ensure removal of residual organics; otherwise the residual carbon reduces PbO to metallic lead leading to high currents during poling. Loss of lead on sintering is significantly lower (1.4 wt%) as compared to samples from conventional powders (6.4 wt%). Successful poling of the sintered samples is achieved when the powders are prepared without using sol stabilizers and are calcined without pelletizing. Washing of the powders is not helpful, perhaps because it leads to change in stoichiometry due to loss of material. A dielectric constant of 950 and $d_{33} > 190$ pC $N^{-1}$ are easily achieved.

## 1. Introduction

The performance of piezoelectric materials such as lead zirconate titanate (PZT) is determined, to a large extent, by their compositional homogeneity, microstructure and purity. Conventionally these materials are prepared by the mixed oxide route, which requires high calcination and sintering temperatures and leads to compositional fluctuations. Several chemical processing routes aiming at ultra-fine and ultra-pure powders with well-controlled chemical composition have been reported in the literature [1–11]. Many of these methods employ a sol–gel process using alkoxides [6–11]. These methods usually produce powders which are compositionally quite homogeneous as indicated by a narrow width of the morphotropic phase boundary (MPB). The calcination and sintering of these powders can also be done at much lower temperatures. However, severe problems are often encountered when poling of the sintered pellets is attempted, presumably because of the effect of the residual organics. Because of this, the data on the piezoelectric properties of the sintered material prepared from these powders is very meagre.

In the present work, we have investigated the influence of the processing conditions on the properties (especially the piezoelectric and dielectric properties) of the sol–gel-prepared PZT powders.

The compositional fluctuations in the PZT powders result because of the low diffusivity of zirconium and titanium cations; the lead ions diffuse at a faster rate and readily achieve a uniform distribution. We have therefore used a hybrid sol–gel process in which only the zirconium and titanium ions are provided from liquid alkoxide precursors, while lead comes from PbO powder. Furthermore, to promote homogeneity, a mixing schedule has been used which results in a coating of Ti–Zr on PbO particles.

Alkoxides of titanium (titanium tetrabutoxide, ttb) and zirconium (zirconium *n*-propoxide, zr*n*p) hydrolyse rapidly if exposed to atmospheric moisture. The hydrolysis can be slowed down by using stabilizing agents such as diethanolamine (DEA) and acetic acid in small amounts. In the present work, the PZT powder was prepared from the stabilized sols, as well as without any stabilization. In the latter case, the processing was carried out in a controlled-atmosphere glove box.

## 2. Experimental procedure

### 2.1. Preparation of powders using stabilized sols

Zrnp, ttb (both from Alfa products, MA, USA), DEA (AR Grade, Ranbaxy, New Delhi, India, distilled in the laboratory for further purification) and propanol (AR Grade, S.D. Fine Chemicals, Boisar, Gujrat, India) were mixed in a 200 ml flask for about 30 min. PbO powder (99.9%, Aldrich, Gillingham, UK) was then added slowly into this solution to give a composition $x = 0.535$ in $Pb(Zr_xTi_{1-x})O_3$ which is near MPB. To this a mixture of acetic acid and triply distilled water was added gradually while stirring. The molar composition of the reagents taken was as follows:

| PbO | Zrnp | Ttb | DEA | Propanol | $H_2O$ | acetic acid |
|---|---|---|---|---|---|---|
| 1 | 0.69 | 0.47 | 0.76 | 20 | 4 | 0.2 |

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The contents of the flask were then dried into a cake-like mass under vacuum at 70 °C in a rotary evaporator. This was further dried in an air oven at 70 °C for 8 h. It was then ground in a mortar and pestle. This is called powder "S".

## 2.2. Preparation of powders using unstabilized sols

Here the preparation of the powder was carried out in a glove box containing dry air. Lead oxide was first rapidly blended with ttb and zr*n*p for about 30 min in 200 ml of propanol. Triply distilled water (320 ml) of pH ranging from 3–10.5 (adjusted by using either nitric acid or ammonium hydroxide solution) was then added, resulting in a thick slurry which was stirred for 12 h. The slurry thus obtained was treated in two ways.

(a) The powder in the slurry was repeatedly washed with triply distilled water followed by decanting and drying in an air oven at 70 °C. Here the composition of the powder was kept fixed at $x = 0.535$, but the pH of the water used during preparation was varied between 3 and 10.5. These powders are termed US-1.

(b) The slurry was directly dried while stirring at 90 °C. Here the pH was fixed at 10.5 but the compositions were varied to give $x = 0.525$, 0.535, 0.538, 0.540 and 0.545 (powder US-2).

## 2.3. Calcination and sintering

Calcination of the powders is a critical step in the alkoxide-derived powders. The aims of the calcination treatment are to form a uniform PZT powder and to drive away the residual organics completely. The powders were calcined with or without pelletizing at 400–800 °C for times ranging from 1–3 h (powders S and US-1). Powder US-2 was calcined at 750 °C for 24 h without pelletizing.

For sintering, the calcined powders were granulated through a 80 mesh sieve after the addition of 2 wt % PVA as binder, and compacted at 210 MPa into pellets of 12 mm diameter × 50 mm high. The binder was removed by holding the pellets at 600 °C for 5 h and the sintering was then carried out at 1200 °C/4 h. The PbO loss during sintering was limited to $<0.3$ wt % using $PbZrO_3$ + 5 wt % PbO as packing powder. The samples were sliced into 1 mm thick discs and electroded by applying a silver paint.

The powders were subjected to differential thermal analysis (DTA) and thermogravimetric analysis (TGA). They were heated to 400, 500, 600, 700 and 800 °C and held for 1 h and their X-ray diffraction patterns were taken using a diffractometer (Rich Seifert Iso Debyeflex 2002). The morphology of the coatings made at different pH values was observed in a scanning electron microscope (Jeol JSM 840 A). The phases present in the sintered samples were identified. Dielectric measurements were carried out on electroded samples at 100 kHz using an impedance analyser (HP 4194 A). The sintered samples were poled at 110 °C for 20 min by applying an electric field of 3.5 kV mm$^{-1}$ in transformer oil and cooling to 40 °C with field. Strain coefficient was measured after 24 h using a $d_{33}$ meter (model CADT, Channel Products). Electromechanical coupling coefficients were calculated from the resonant and antiresonant frequencies. The density of the samples was found by measuring their weight in air and while suspended in water. Fracture surfaces of the sintered pellets were examined in the SEM.

# 3. Results

The different methods of preparing powder led to no apparent changes in the characteristics of the powders. It was only in their response to poling and in their piezoelectric properties that the different powders produced different results. Thus the results described below are common to all the powders, unless otherwise stated.

## 3.1. Powder characteristics

### *3.1.1. Change in colour of powders*

The colour of the PbO powder changed from yellow to white after the coating process in all cases. A yellowish colour, characteristic of PZT is restored upon heating the powder to a temperature above 600 °C due to reaction of the coating and PbO. This indicates that the PbO particles become coated completely with an adherent coating which does not separate even during repeated washing.

### *3.1.2. Coating morphology*

Fig. 1a–c show coated PbO powders made at pH 3, 7 and 10.5, respectively. The size of the particles in the coating varies with pH being about 10 nm for pH 3 and pH 5, 30–50 nm for pH 7 and 100 nm for pH 10.5.

### *3.1.3. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA)*

DTA and TGA were performed on powder US-1 prepared at pH 10.5 and pH 7, respectively. Rapid weight loss occurs up to 400 °C as shown in Fig. 2. This is due to removal of water which is complete at 120 °C and the decomposition of organics at around 310 °C. These two events are seen as endothermic and exothermic peaks, respectively, in the DTA plot shown in Fig. 3. An exothermic peak is also observed at 520–530 °C, corresponding to the formation of PZT phase. Removal of organic groups continues to occur even beyond 600 °C at a slow rate.

### *3.1.4. Crystallization on heating*

Fig. 4 shows the evolution of the X-ray diffraction pattern of the coated powders ($x = 0.535$, powder US-1) on heating. The as-coated powder produces a broad peak centred at $2\theta = 30°$. This shows the coating is amorphous. After heating at 400 °C for 1 h, no significant change in X-ray pattern is observed

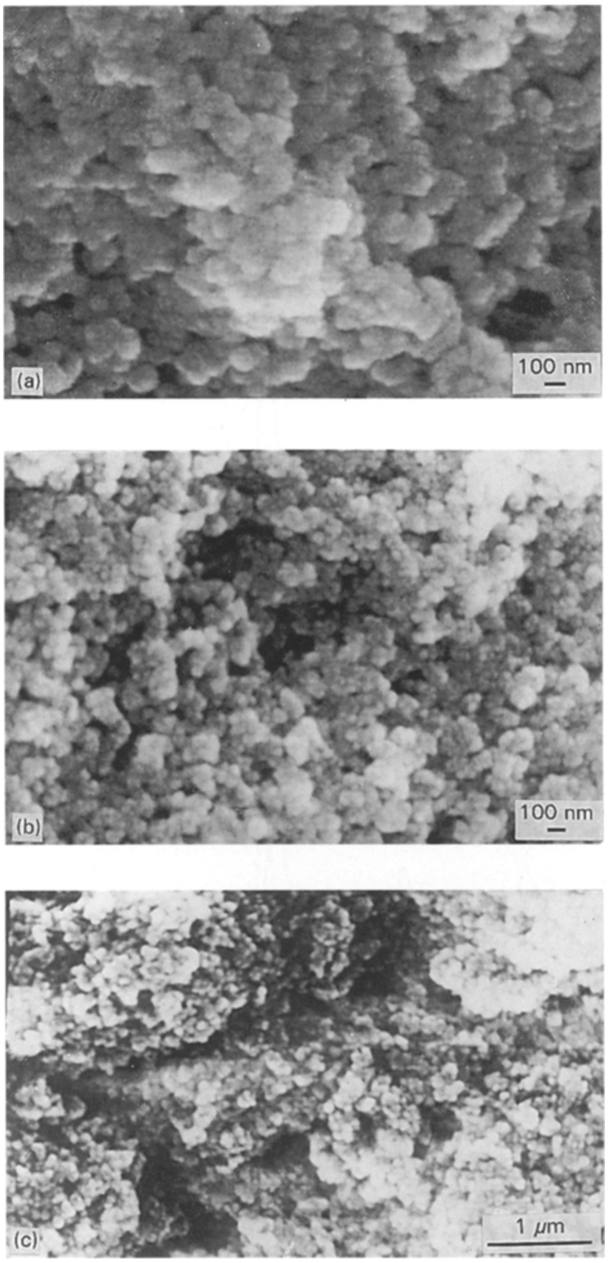

*Figure 1* Micrographs of coated PbO powders (US-1) prepared at different pH comparing the size *d*, of the particles in the coating: (a) pH = 3, $d \simeq 10$ nm; (b) pH = 7, $d \simeq 30$–$50$ nm; (c) pH = 10.5, $d \simeq 100$ nm.

except that the broad peak becomes sharper indicating that the crystallization has already set in. At 500 °C/1 h, additional crystalline peaks begin to appear corresponding to PZT peaks (some peaks of free PbO also briefly appear as discussed later). The PZT peaks become increasingly distinct and sharper as the temperature of the heat treatment is increased. At 600 °C all the peaks can be identified as those corresponding to the tetragonal phase of PZT. Heating at higher temperatures makes the peaks sharper.

## 3.2. Properties of the sintered samples

### 3.2.1. Lead loss

The loss of lead on sintering is significantly lower (1.4 wt %) in the samples made using the hybrid sol–gel route compared to those made from conventional mixed oxide route (6.4 wt %) when no atmosphere powder is used. The lead loss can be further restricted to <0.3 wt % by using a $PbZrO_3$ + 5 wt % PbO powder.

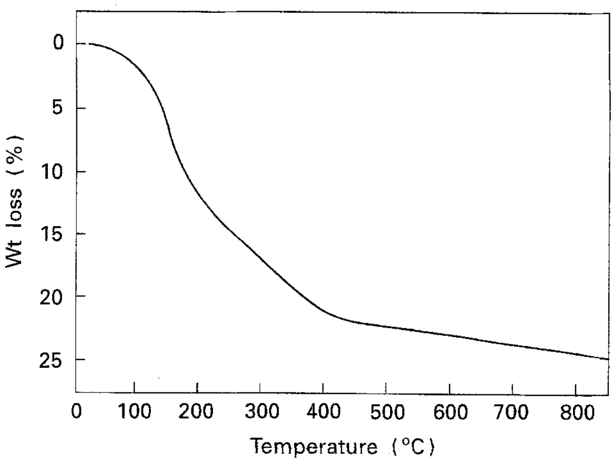

*Figure 2* TGA plot of coated powders (US-1) prepared at pH 7.

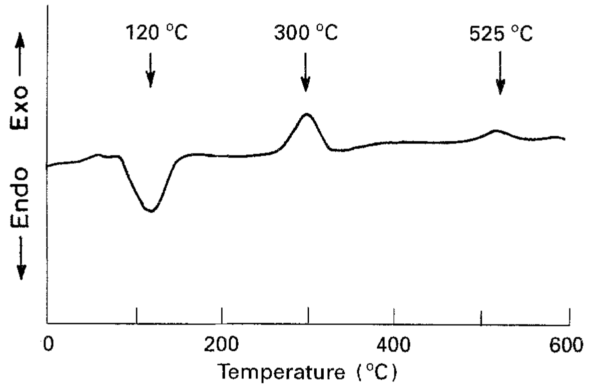

*Figure 3* DTA plot of coated powders (US-1) prepared at pH 10.5.

### 3.2.2. Density and microstructure

The densities of the samples made from washed powder were higher (7.75–7.84 g cm$^{-3}$) as compared to those made from unwashed powders (7.5–7.68 g cm$^{-3}$).

Fig. 5a and b show the fractured surfaces of the sintered PZT samples prepared at pH 3 and pH 7, respectively. At pH 7, the microstructure is highly dense and the internal porosity is almost absent. The grain size, as measured by the line intercept method, varied from 1.0–3.0 µm. But at pH 3, voids are observed in the microstructure and the size of the grains is about 3 µm.

### 3.2.3. Phases present in the sintered samples

The sintered samples (from powder US-2) were monophasic tetragonal at $x = 0.525$. Both tetragonal and rhombohedral phases coexist for $x$ between 0.535 and 0.545 (Fig. 6). The morphotropic phase boundary in these samples, therefore, extends at least between $x = 0.535$ and 0.545.

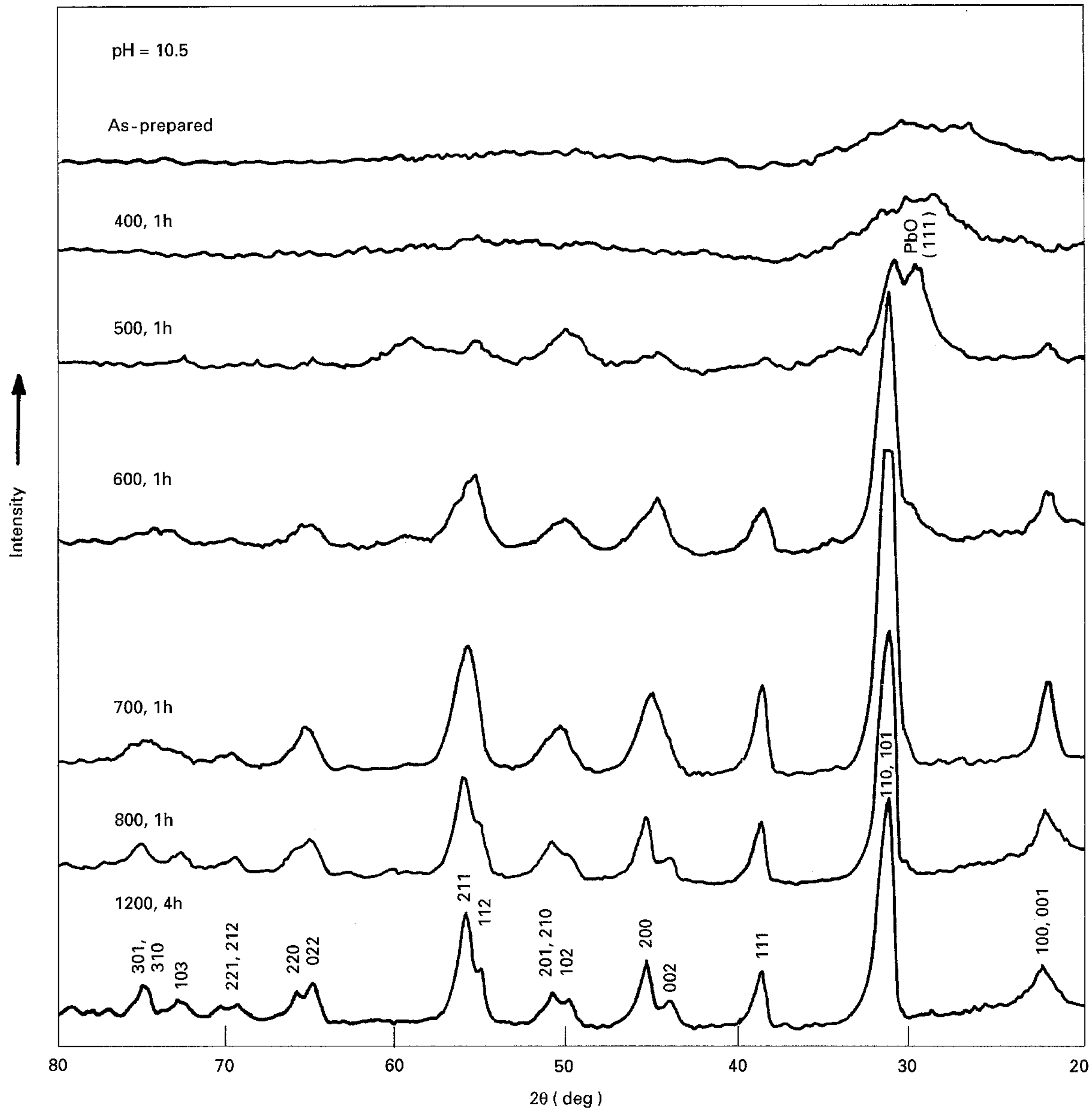

*Figure 4* X-ray diffractograms of coated powders (US-1) after heating to different temperatures ($x = 0.535$, pH = 10.5).

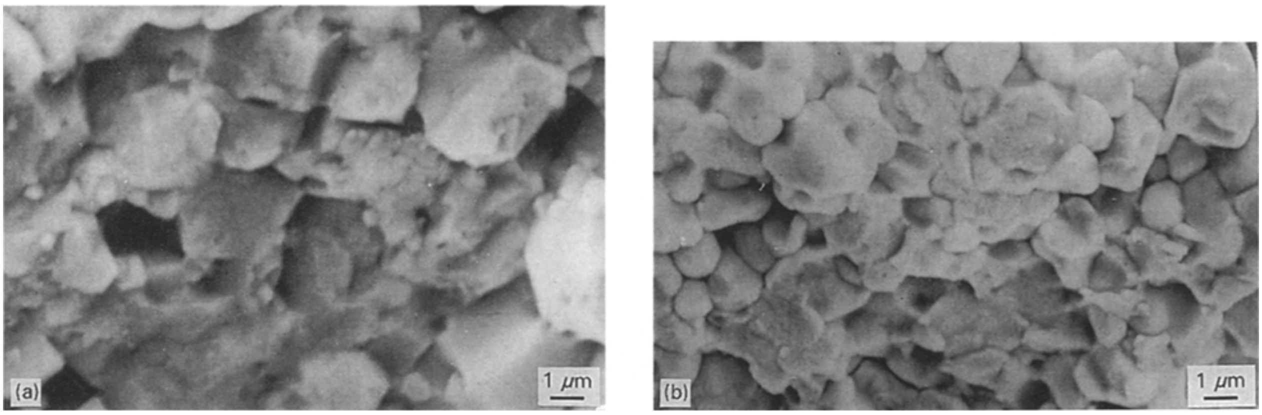

*Figure 5* Fracture surfaces of sintered samples made from powders (US-1, $x = 0.535$) prepared at pH (a) 3 and (b) 7.

### 3.3. Response to poling

The most significant difference in the sintered samples prepared from different powders was found to be in their response to poling and in their piezoelectric and dielectric properties.

Thus, when an attempt was made to pole the sintered pellets prepared from stabilized sols (powder S) calcined with or without pelletizing, it was found that these samples conducted an appreciable amount of current which increased during poling to levels such

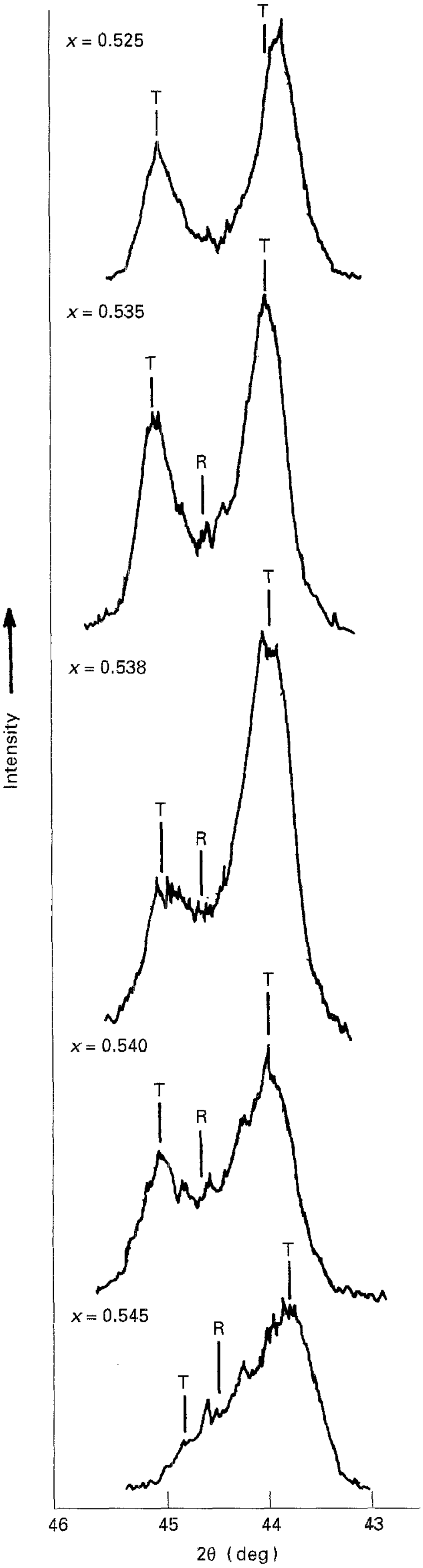

*Figure 6* X-ray scans between $2\theta = 43°$ and $46°$ showing the coexistence of tetragonal and rhombohedral phases as $x$ is increased from 0.535 to 0.545 (US-2 powders).

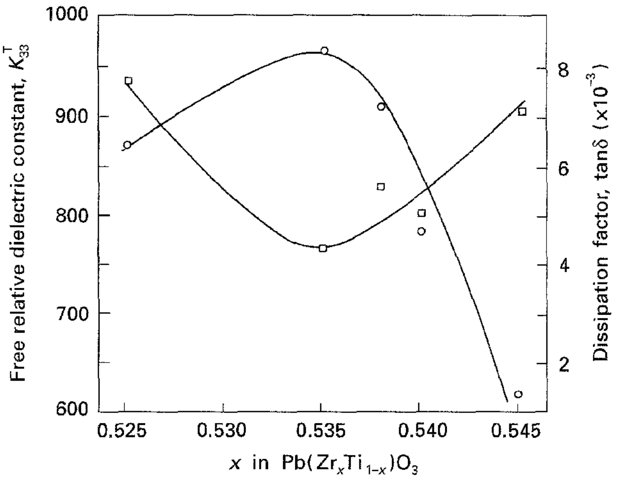

*Figure 7* (○) Free relative dielectric constant, $K^T_{33}$, and (□) tan δ for samples of different compositions (US-2 powders).

that the poling had to be discontinued after a few minutes. The relatively high conductivity of the samples was due to the presence of metallic lead particles which were produced by the reduction of lead oxide by residual carbon from the incompletely hydrolysed alkoxides, as discussed later. Various calcination and sintering schedules were attempted to remove the residual carbon. However, these were not very successful.

Similarly, in the samples made from powder US-1, calcined in the pellet form, while applying the high d.c. voltage, the current was found to increase as before, to unacceptable levels and the poling could not be carried on. This indicates that in the pellet form, the removal of the organics is difficult during calcination.

The above problem of high conductivity during poling was not encountered in the samples prepared from the unstabilized sol powders (US-1 and US-2) calcined loose (without pelletizing).

## 3.4. Dielectric and piezoelectric properties

The properties of samples prepared from unwashed powders (US-2) are reported here in detail. Those from the washed powder samples (US-1) were found to be very poor and are also indicated. As mentioned above, the samples from the stabilized sols could not be poled and so no measurements were done on them.

### *3.4.1. Dielectric constant and dissipation factor*

The free relative dielectric constant, $K^T_{33}$, along with the dissipation factor, tan δ, was measured at 100 kHz. A maximum value of 965 for $K^T_{33}$ was obtained for $x = 0.535$ which also had minimum tan δ ($4.30 \times 10^{-3}$). Fig. 7 shows the results. In contrast, the dielectric constant for washed powder samples ranged from 382 (pH 3) to 616 (pH 10.5).

### *3.4.2. Piezoelectric coefficients*

The longitudinal strain coefficient $d_{33}$, the lateral strain coefficient $d_{31}$, the longitudinal electromechanical coupling factor, $k_{33}$, the radial electromechanical

TABLE I Strain and coupling coefficients (US-2 powders)

| $x$ in $Pb(Zr_xTi_{1-x})O_3$ | Strain coefficients | | Coupling coefficients | | |
|---|---|---|---|---|---|
| | $d_{33}$ ($pC N^{-1}$) | $d_{31}$ ($pC N^{-1}$) | $k_{33}$ | $k_{31}$ | $k_p$ |
| 0.525 | 121 | 48 | 0.26 | 0.16 | 0.27 |
| 0.535 | 166 | 59 | 0.31 | 0.19 | 0.32 |
| 0.538 | 190 | 77 | 0.33 | 0.20 | 0.33 |
| 0.540 | 182 | 62 | 0.35 | 0.21 | 0.36 |
| 0.545 | 152 | 43 | 0.27 | 0.17 | 0.28 |

TABLE II MPB in different methods

| Method of preparation | Range of $x$ for MPB | Reference |
|---|---|---|
| PbO + spray pyrolysed product | 0.52–0.55 | [4] |
| PbO + coprecipitated product | 0.53–0.54 | [2] |
| Spray drying | 0.51–0.52 | [5] |
| Mixed oxide | 0.47–0.58 | [2] |
| Present work | 0.535–0.545 | – |

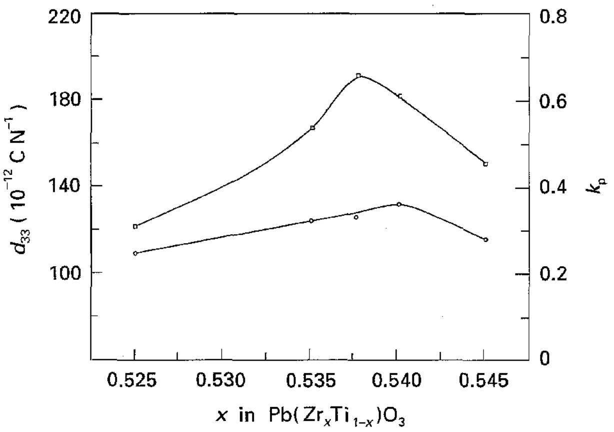

*Figure 8* (□) Longitudinal strain coefficient, $d_{33}$ and (○) planar coupling coefficient $k_p$, for samples of different compositions (US-2 powders).

coupling factor, $k_{31}$ and the planar electromechanical coupling factor, $k_p$, were calculated for all compositions and are given in Table 1. Plots of $d_{33}$ and $k_p$ are shown in Fig. 8. $d_{33}$ and $d_{31}$ attain a maximum of 190 and 77 $pC N^{-1}$, respectively, for the composition $x = 0.538$. Samples of composition $x = 0.54$ show maximum $k_{33}$, $k_{33}$ and $k_p$ (the maximum values obtained from the washed powders were much lower at $d_{33} = 40$ $pC N^{-1}$ and $k_p = 0.32$).

## 4. Discussion

The absence of PbO peaks in the as-coated powder and its total change of colour to white from yellow of the PbO powder indicates that a strongly adherent coating is forming on the PbO particles. The coating is amorphous, as shown by X-ray diffraction, and comprises of fine particles which are agglomerated, as seen in scanning electron micrographs. The size of the particles in the coating increases from 10 nm to about 100 nm as the pH is increased from 3 to 10.5. In the alkoxide sol–gel process, the high pH increases the rate of condensation and favours the formation of compact particles [12]. The coating is quite adherent and is not much affected by repeated washing. However, piezoelectric properties achieved from sintered samples made from washed powders are quite low as it is suspected that the washing may cause loss of some material leading to uncertain stoichiometry.

DTA and XRD of these coated powders suggest that the coating consists of particles in which titanium and zirconium are mixed at an atomic level, as no intermediate products such as $TiO_2$, $ZrTiO_4$, $PbTiO_3$ or $PbZrO_3$ are formed on heating. PZT forms directly upon heating to about 520 °C, the reaction being nearly complete by 600 °C. Higher calcination temperatures cause growth of crystallites producing sharper X-ray peaks.

Some free PbO peaks also appear at $\simeq$ 500 °C and persist up to 800 °C (Fig. 4). This most probably happens because of the exposure of the PbO surface at locations where the coating is thin. The coating diffuses away or into PbO and exposes the free PbO which persists until the reaction is complete at $\simeq$600 °C.

While the width of the MPB in the samples prepared by the mixed oxide route can be quite large ($x = 0.47$–$0.58$, [2]) it is much narrower in powders prepared by other methods as shown in Table II. The region of MPB observed in our samples agrees well with the results for powders made by methods other than the mixed oxide route [2, 4, 5].

The compositional homogeneity and the low calcination temperatures as observed here are distinct advantages of the powders prepared from the alkoxide precursors. However, the hydrolysis of the alkoxides during the powder preparation is usually not complete. The trapped organic groups are difficult to remove during the subsequent calcination and sintering steps. This leads to problems, such as low density and, in the case of PZT, reduction of an easily reducible ion such as $Pb^{2+}$ to metallic state. Thus the presence of pores in the samples from powders prepared at pH 3 indicates that the amount of residual organics is higher in this case than in the powders prepared at pH 7 or 10. At low pH, the hydrolysis and condensation reactions occur preferentially at the ends of the chains leaving unhydrated alkoxy groups in the middle [12]. This leads to large amounts of residual organics in the powders prepared at low pH.

A more positive indication of the residual organics in the present experiments is the flow of large currents through the samples during poling. This happens because of the presence of metallic lead formed due to the reduction of PbO by carbon from the organics. In the extreme cases, globules of metallic lead were found to form on the surface of the calcined pellets. The increase in current during poling indicates that paths of lower resistance form, due to the field-induced migration of metallic lead.

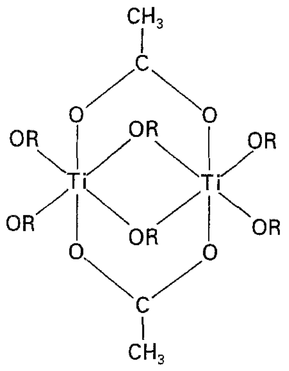

*Figure 9* Structure of chelated titanium *iso* propoxide [12].

High poling currents were observed for all samples calcined after pelletizing. Calcination without pelletizing removed this problem for the powders US-1 and US-2 but not for powder "S", from the sols using chelating agents such as acetic acid or DEA.

The role of stabilizers such as acetic acid and acetylacetone (AcAc) has been studied for the case of titanium *iso* propoxide, Ti(OPr$^i$). The acetic acid combines with Ti(OPr$^i$) monomer to give a structure (Fig. 9) in which the acetate ion acts as a bidendate (bifunctional) ligand, bridging two titaniums and terminal as well as bridging OPr$^i$ ligands are present. This alters the condensation pathway and promotes the formation of linear polymers suitable for fibre drawing but also leads to larger amounts of residual organics in the product.

Similarly when AcAc is used as a stabilizer, it is found that with Ti(OPr$^i$), singly chelated and dichelated precursors are formed. Addition of water causes (OPr$^i$) ligands to be preferentially hydrolysed, whereas not all (AcAc) ligands bonded to titanium are hydrolysed even if excess water is used. This again leads to large amounts of residual organics.

The above results show that the powders prepared from the alkoxide precursors should be calcined without pelletizing; furthermore, use of chelating agents such as acetic acid, while helpful in allowing the processing to be carried out in an open atmosphere makes the removal of organics difficult and is to be avoided.

The sintered samples in the present experiments show negligible lead loss and can be sintered without the use of atmosphere powders. The grain size is much smaller (1–3 μm) as compared to that obtained from the MO route (5–10 μm) which is useful for many applications. The piezoelectric and dielectric properties are comparable to that obtained from the MO route samples despite their low grain size.

## 5. Conclusion

The hybrid sol–gel route using powder of PbO and alkoxides of titanium and zirconium yields powders which on calcination at low temperatures form phases of lead zirconate titanate directly without the formation of any intermediate phases. The powders have good compositional homogeneity as reflected by a small width of the MPB. However, care has to be taken to ensure complete removal of residual organics to avoid problems such as low sintered density and reduction of PbO, which makes it difficult to pole the samples. Use of chelating agents (DEA, acetic acid) exacerbates this problem. The problem can be overcome by eliminating the chelating agents from the process and calcining the powders without pelletizing. Washing of powders is not necessary and, in fact, leads to degraded properties, most probably due to change in composition by loss of some coating during washing. The piezoelectric and dielectric properties are comparable to those obtained by the mixed oxide route with the added advantage of negligible lead loss during sintering and low grain size, which are crucial for many applications. It should be possible to introduce various dopants easily by use of suitable salts or oxides. The advantages, such as easy one-step processing requiring no grinding or mixing of solids, no necessity of washing of powders, low calcination temperature, high homogeneity, low grain size, low lead loss and the possibility of easy incorporation of dopants, make the powders prepared by the hybrid sol–gel route potentially attractive for many applications.

## Acknowledgement

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