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# Technological Challenges of Making PZT Based Piezoelectric Wafers

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## ABSTRACT

In recent future, piezoelectric wafers are going to play a pivotal role in nondestructive evaluation (NDE) of structures in defence, aerospace and industrial sectors. Structural health monitoring (SHM) or integrated vehicle health monitoring (IVHM) requires small, light-weight, minimally invasive sensors which can be embedded in or mounted on the surface of the structure. Especially, for the NDE of thin-wall structure, piezoelectric wafers look very promising for Lamb wave excitation and sensing. Incidentally, piezoelectric wafers are normally required in large numbers for NDE of structures and hence, a proven and cost-effective technology of making such wafers is the need of the hour. Though the standard tape casting (doctor-blade) technique is expected to serve the purpose, some typical problems, which crop up during fabrication of PZT based wafers, need to be sorted out to make high performance wafers. Just by following the standard process of fabrication of alumina/zirconia substrates, one does not get quality products in the present case owing to volatilization of lead from PZT at the sintering temperature, warpage and adhesion of the wafers with the setter plate. Such problems are quite alarming in the present case as the effective exposed surface of a single-layer wafer is much higher compared to that of a bulk or stacked multilayered structure. In the present work, important processing parameters to make good quality PZT wafers have been discussed. The dielectric and piezoelectric properties of the wafers have been studied and compared with those of bulk PZT ceramics.

**Keywords:** PZT, wafer, tape-casting

## 1. INTRODUCTION

Piezoelectric materials are currently used in a variety of applications as sensors and actuators and they play a pivotal role in the arena of smart materials and structures. Generally, multilayered structure[1] (alternate layers of piezoelectric wafers and electrodes) is preferred in most of the actuator applications so that excitation can be done at a low voltage. Though wafers or substrates of alumina are common items in electronic industry[2-3], piezoelectric wafers are seldom used in real-life applications. However, recently, PZT based piezoelectric wafers have opened new opportunities for ultrasonic testing of structures. Piezoelectric wafer active sensors (PWAS) can act as both sensors and actuators. Several investigators[4-6] have explored the generation of Lamb waves with PWAS. Piezoelectric wafers are non-intrusive, nominally invasive and non-resonant wide band devices with surface pinching in-plain strain and can be surface-mounted on existing structures or inserted between the layers of the lap joints or inside composite materials. PWAS can act as both the generator and detector of Lamb wave. Incidentally, guided waves (like Lamb waves in thin plates) have certain advantages for NDE of structures, e.g., they travel long distances and follow the contour of the structure in which they are propagating and these modes allow inspection in regions that are inaccessible, such as buried structures.

Tape casting or doctor-blade process is generally employed to produce thin flat ceramic sheets (substrates/wafers). Tape-casting is advantageous for preparing relatively large-area uniform thin sheets with high density[2]. Tape casting[2-7], basically, consists of preparing a suspension of a ceramic powder in a solvent with addition of dispersants,

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binders and plasticizers. The suspension is cast onto a stationary or moving surface. After the evaporation of the solvent, the dried green tape is stripped from the surface followed by cutting to the appropriate shape. The green tapes are sintered after removal of organic components at a low temperature. Apparently, this simple process of making substrates/wafers turns out to be not so-simple when one tries to prepare dense flat PZT wafers. Keeping in mind the requirements of indigenous source of low-cost PZT wafers for NDE of thin wall structures like aircraft shells, pressure vessels, industrial tubes, pipes etc, we highlight in the present article the technological challenges of making thin, dense PZT wafers in a cost-effective way.

## 2. EXPERIMENTAL

PZT powder of composition $Pb(Zr_{0.52}Ti_{0.48})O_3$, which is close to morphotropic phase boundary and hence having optimum piezoelectric coefficients, was prepared by a mixed route comprising citrate-nitrate gel method followed by solid state mixing and calcination. The details of the processing steps have been given elsewhere[8].The synthesized powder was characterized by an XRD (Philips) and the powder morphology was analyzed in a SEM (Leo 430i).

Suspensions of PZT were prepared using reagent grade solvent consisting of an azeotropic mixture of methyl ethyl ketone (MEK) and ethanol (66:34 by volume). PZT and the solvent in the weight ratio of 1:15 along with 1-3 wt% phosphate ester (Emphos PS21-A, Witco Chemicals, USA) were ball milled for 20 h using zirconia balls to get the desired suspension. Electrophoretic mobility of the particles in the above suspensions was studied using a microelectrophoresis apparatus (Zetameter 3.0+, Zetameter Inc., USA). A typical PZT tape casting slurry was made as per the composition given in Table 1. An excess PbO was used as a sintering aid [9-10] in the batch composition. To prepare the tape casting slurry, PZT powder along with the excess PbO and dispersant was ball-milled in the solvent for 20 h using zirconia balls. The binder, plasticizer and homogenizer were then added to the slurry followed by further milling for 2 h. The viscosity of the slurry was measured by using a concentric cylinder rotational viscometer (VT 500 Haake, Germany) at a shear rate 40.34 $s^{-1}$. The slurry was tape-cast using a moving doctor-blade at a speed in the range of 20-25 mm/sec. The dried tapes were cut into square shapes (10-15 mm square) and fired in air at a slow heating rate (5$^o$C/h) from room temperature to 600$^o$C so as to remove the organics. The fired tapes were then sintered at a temperature in the range of 1150$^o$C-1200$^o$C with heating rates between 150-400$^o$C/h under controlled atmosphere (created by using a mixture of lead zirconate and lead oxide powders inside a closed crucible).

**Table 1**: Composition of PZT tape casting slurry

| Ingredients | Function | Wt% |
|---|---|---|
| PZT [$Pb(Zr_{0.52}Ti_{0.48})O_3$] | Ceramic | 75.00 |
| PbO | Sintering additive | 2.25 |
| Phosphate Ester | Dispersant | 1.93 (Equivalent to 2.5 wt% of PZT) |
| Methyl Ethyl Ketone (E. Merck India Ltd) + Ethanol (Bengal Chemicals & Pharmaceuticals Ltd) | Solvent | 14.56 |
| Polyvinyl Butyral (Hipol B-30, Hindustan Inks and Resins Ltd. Gujarat, India) | Binder | 2.47 |
| Polyethylene Glycol ( S. D. Fine-Chem Pvt. Ltd). | Plasticizer | 2.66 |
| Butyl Benzyl Phthalate (Merck-Schuchardt) | Plasticizer | 0.74 |
| Cyclohexanone (S. D. Fine-Chem Pvt. Ltd.) | Homogenizer/ Skin inhibitant | 0.39 |

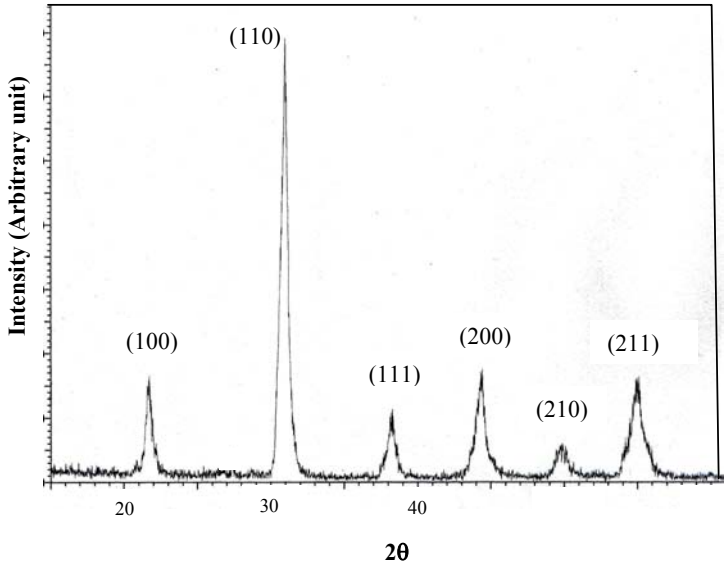
The bulk density of the fired wafers was calculated geometrically and the microstructures were viewed in the SEM. The dielectric studies of the fired wafers were made using a Hioki 3532-50 LCR Hitester in the frequency range of 100-1MHz after electroding with gold paste. The piezoelectric strain constant ($d_{33}$) was measured by a $d_{33}$ meter (Pennbeker 8000 $d_{33}$ tester) after poling the samples in silicone oil at a temperature of 120$^o$C at 3kV/mm field for 30 min. The planer electrochemical coupling coefficient ($k_p$) was determined from the resonance ($f_r$) and antiresonance ($f_a$) frequencies using the formula

$$K_p = \sqrt{2.51\frac{\Delta f}{f_r}} \qquad (1)$$

where $\Delta f$ is equal to $(f_a - f_r)$. Ferroelectric hysteresis studies of the wafers were carried out in a loop tracer (Precision LC, Radiant Technologies Inc.)

## 3. RESULTS & DISCUSSION

The synthesized PZT powder was phase pure as observed from the X-ray diffractorgram (Fig.1). The average particle size of synthesized PZT powder was around 200 nm (Fig.2). The electrophoretic mobility (Fig.3) and the viscosity of the slurry (Fig.3) justify the amount of dispersant added in order to get proper dispersion of the slurry. Apparently, making satisfactory tapes by controlling the slurry rheology[12] does not ensure good quality final products. Some of the problems unique to fabrication of dense, flat PZT wafers are given below.

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First, the loss of PbO due to volatilization at high temperatures can alter[13] the stoichiometry and degrade the piezoelectric and dielectric properties. Incidentally, lead volatilization problem is critical in case of thin wafers due to more exposed surface. Second, thin tapes easily curl and warp due to differential shrinkage [14] during sintering. Third, tapes often stick to the setter plates and may crack or break during removal.

The standard method of tackling lead volatilization is to sinter the material in a closed crucible surrounded with lead containing atmosphere powder[15]. Other efforts have focused on decreasing sintering temperature by adding different liquid-phase-sintering aids among which PbO plays an important role [16]. Because of low thickness (0.3 mm) and high exposed surface (10 mm x 10 mm) of PZT tapes, it needs utmost control of the parameters like heating schedule, composition and the amount of surrounding atmosphere powder and the amount of excess lead oxide in the batch composition so that dense and flat PZT wafers with unaltered composition and above all, which do not stick to the setter plates, can be obtained. Table 2 gives a glimpse of the characteristics of sintered wafers under varying processing parameters. It is evident from table 2 that a fine tuning of processing parameters is required to get high performance PZT wafers. Fig 4 depicts the polarization-electric field hysteresis of PZT wafers confirming their ferroelectric nature in the thick film form. Table 3 shows the comparison of the dielectric and piezoelectric properties of PZT wafers with bulk samples. Fig 5 depicts the dielectric properties of the wafers at different frequencies. From table 3 it is evident that the dielectric constant of the wafer is comparable (especially samples a & b) with that of the bulk samples. However, the dissipation factor (DF) of the wafers is higher than that of bulk samples. The high DF of the wafers 'a', 'b'and 'c' may arise from lead deficiency in the sample leading to p-type conduction[18] in PZT. The higher DF of lead excess sample'd' dissipation factor (DF) of the wafers is higher than that of bulk samples. Incidentally, the planar coupling coefficient ($k_p$) of the wafers is inferior to that of bulk samples. It is well-known [19] that with the decrease in grain size, $k_p$ decreases. However, from the SEM micrographs (Figs 6&7) of wafers and bulk samples, no spectacular difference in grain size was observed. The low $k_p$ value of the wafers probably arises from low domain wall mobility[19] due to domain wall stabilization by defect dipoles[15], the latter being present in more numbers in wafers as evident from the higher DF of wafers.

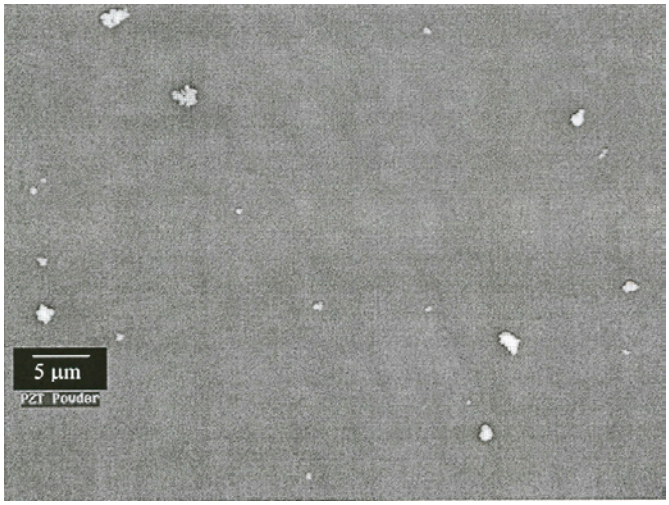


**Figure 2**: SEM photograph of synthesized powder.

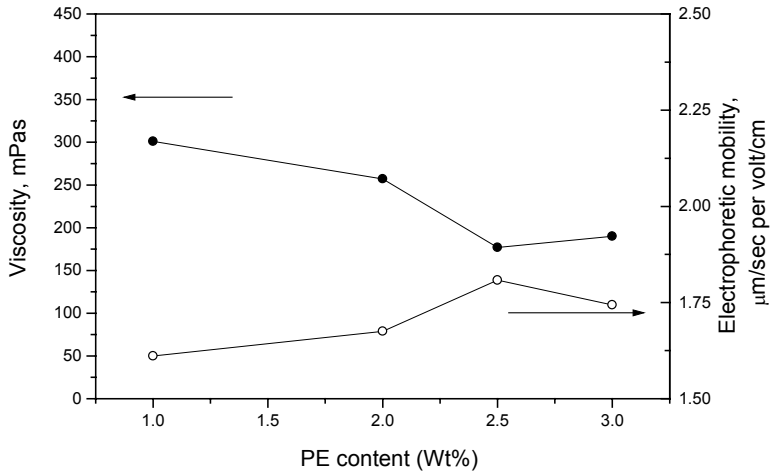


**Figure 3**: Electrophoretic mobility and viscosity of the slurry with varying amounts of phosphate ester.

**Table 2**: Characteristics of Sintered Wafers Under Varying Processing Parameters

| **Sorrounding Powder, [Batch wt / Powder wt]** | **Firing Schedule** | **PbO (wt%) excess or deficient (with respect to PZT) after firing** | **Remarks** |
|---|---|---|---|
| *PZ:PbO (1:1) , [0.064] | Heated @ 150° C/h to 1200° C (3h soaking) and cooled @ 150° C/h | - 6.7 to -7.4 | High PbO loss |
| PZ:PbO (1:1) , [0.0213] | Heated @ 150° C/h to 1200° C (3h soaking) and cooled @ 150° C/h | - | Tapes stick to the setter Plate# |
| PZ:PbO (1:1) , [0.0213] | Heated @ 150° C/h to 1200° C (3h soaking) and cooled @ 150° C/h | - | Tapes stick to the setter plate |
| PZ:PbO (1:1) , [0.064] | Heated @ 300° C/h to 1200° C (4min soaking) and cooled @ 300° C/h | | Tapes stick to the setter plate |
| PZT:PbO (1:1) , [0.064] | Heated @ 300° C/h to 950° C (1 h) then heated @ 300° C/h to 1200° C (10 min) and cooled @ 300° C/h | -2.38 to -2.5 | Could not be removed from the setter plate |
| PZT:PbO (1:1) , [0.08] | Heated @ 300° C/h to 950° C (1 h) then heated @ 300° C/h to 1200° C (10 min) and cooled @ 300° C/h | - 1.8 to -2.0 | Some regions of the tapes stuck to the setter plate while others could be easily removed. |
| PZT:PbO (1:1) , [0.213] | Heated @ 300° C/h to 950° C (1 h) then heated @ 300° C/h to 1175° C (10 min) and cooled @ 300° C/h | - 1.4 to -1.6 | Tapes could be removed easily from the setter plate. |
| PZT:PbO (1:1) , [0.213] | Heated @ 400° C/h to 950° C (1 h) then heated @ 400° C/h to 1175° C (10 min) and cooled @ 400° C/h | + 0.37 to -0.47 | Tapes could be removed easily from the setter plate. |
| PZT:PbO (1:1) , [0.085] | Heated @ 400° C/h to 950° C (1 h) then heated @ 400° C/h to 1175° C (10 min) and cooled @ 400° C/h | + 1.08 to +1.51 | Still some tapes got stuck to the substrate while others could be easily removed. |

(*PZ = $PbZrO_3$) (#dense zirconia)

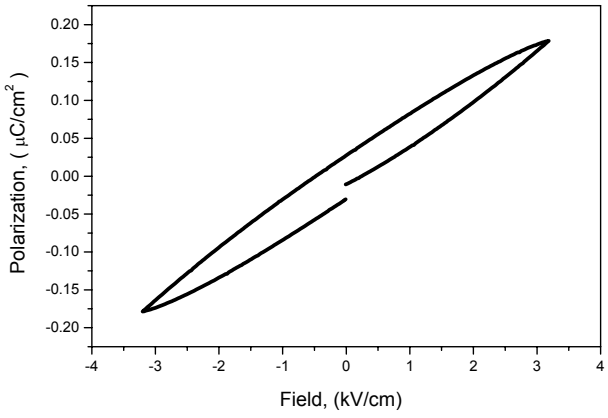


**Figure 4**: Polarization – electric field hysteresis of PZT wafers.

**Table 3**: Dielectric and piezoelectric properties of PZT wafers and bulk samples

| Sample Code | Excess / deficient PbO content* (wt %) | Density (% of $\rho_{th}$) | Dielectric Constant (K) ( at 1 kHz) | Dissipation Factor (D) ( at 1 kHz) | $d_{33}$ (pC/N) | Coupling Coefficient ($k_p$) |
|---|---|---|---|---|---|---|
| a (wafer) | -1.523 | 97.03% | 668.41 | 0.031 | 220-230 | 0.35 |
| b (wafer) | -1.405 | 96.39% | 613.00 | 0.029 | 201-208 | 0.35 |
| c (wafer) | -0.50 | 96.19% | 570.98 | 0.037 | 200-205 | 0.35 |
| d (wafer) | +1.26 | 95.35% | 479.83 | 0.073 | 142-146 | 0.31 |
| Bulk[#] | Near morphotropic | - | 612.00 | 0.004 | 223 | 0.52 |

([#] as per ref 17)
(* with respect to morphotropic PZT)

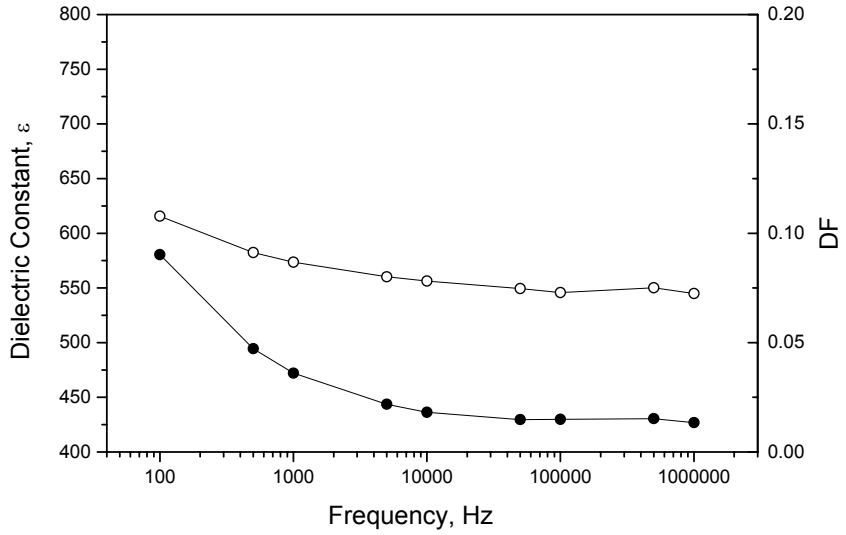


**Figure 5**: Variation of dielectric constant and dissipation factor of the wafers with frequency.

## 4. CONCLUSION

For NDE of thin wall structures in aerospace, industrial and civil sectors, PZT based piezoelectric wafers are going to play a key role as sensors and actuators. As the wafers are required in large numbers for surface mounting and embedding inside the structures, it is essential to develop a technology of making dense PZT wafers in a cost-effective way. In the present work, it has been shown that standard tape casting followed by sintering may not produce dense, flat high performance PZT wafers. It needs fine tuning of the processing parameters like sintering schedule, composition and the amount of surrounding atmosphere powder and the amount of excess PbO in the batch composition to get PZT wafers of acceptable properties.

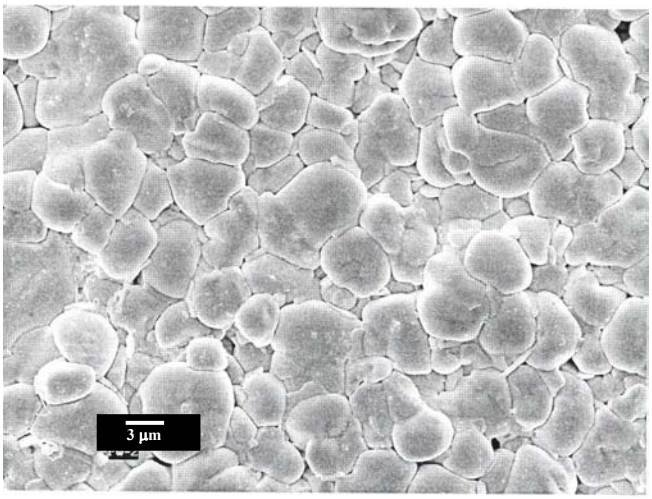


**Figure 6**: SEM micrograph of PZT wafer.

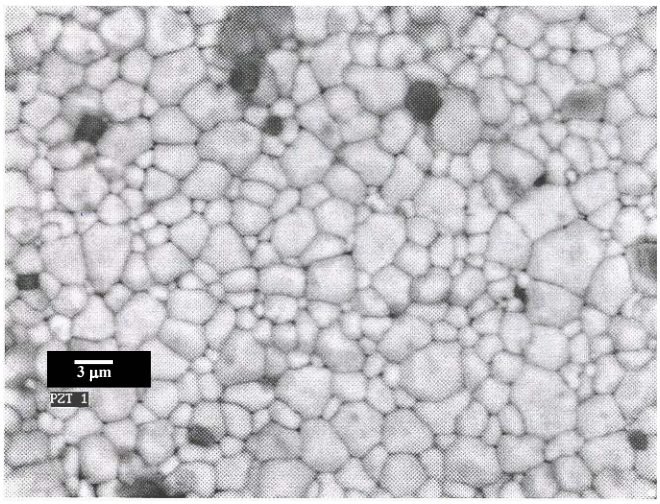


**Figure 7**: SEM micrograph of bulk PZT.

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