

Characterisation of Screen Printable Piezoelectric Thick-Films

P.G. Dargie¹, N.R. Harris², N.M. White², J.K. Atkinson¹, R.P. Sion³

¹Department of Mechanical Engineering, University of Southampton, Highfield, Southampton SO17 1BJ, UK

²Department of Electronics and Computer Science, University of Southampton, Highfield, Southampton SO17 1BJ, UK

³Systems Engineering Faculty, Southampton Institute, East Park Terrace, Southampton, UK.

Abstract

Experimental techniques for measuring the piezoelectric coefficient d_{33} of screen printed thick-film lead zirconate titanate (PZT) pastes are described, together with a comparison of these values for different paste formulations. In particular, the effect of type and concentration of the binder has been observed. Concentrations of between 0 and 30% binder by weight have been analysed for two different binders, lead(II) oxide and lead borosilicate. The results show that sensors utilising the piezoelectric effect of PZT have a greater sensitivity if formulated with a lead(II) oxide binder.

Introduction

Thick-film technology has been used as a method of fabricating both physical and chemical sensors for several years^[1,2,3]. Many of these have been based on the piezoresistive properties of thick-film resistor pastes. Recently, thick-film materials have been developed that exploit the ferroelectric nature of PZT. There is documented evidence of the use of PZT-based thick-film sensors for accelerometers, couplers, acoustic wave devices, pressure and humidity sensors^[4-9]. A particularly novel application is its use as an actuator in a micromachined pump.^[11]

The PZT powder is typically mixed with a glassy binder and an organic vehicle to enable it to be screen printed in exactly the same manner as traditional thick-film materials. This paper presents some results from a study of the effect of both binder type and concentration on the sensitivity of PZT pastes. Throughout this paper, sensitivity is taken as being proportional to the magnitude of the d_{33} coefficient. This is fully described, along with many other parameters in the IEEE standard on piezoelectricity^[10]. The results from two different binder types are presented in this paper, lead borosilicate, which is often used as a binder in thick-film pastes, and lead(II) oxide (PbO).

Paste Preparation

A series of paste samples with varying binder concentrations was made for both binder types. In each case, the concentrations were 3%, 10%, 20% and 30% binder by weight. The dry mixture of PZT powder (Ferropem type 27, 1.75 μm mean particle size) and binder was mixed in a container prior to the addition of 5% (by weight) Electro Science Laboratories' ESL 400 vehicle. In addition to these samples a mix of 100% PZT was also used for comparison purposes. The resultant paste was then transferred onto a Pascal Engineering triple roll mill for final mixing.

Test samples comprised of a layer of PZT between two electrodes were printed onto alumina substrates as shown in figure 1.

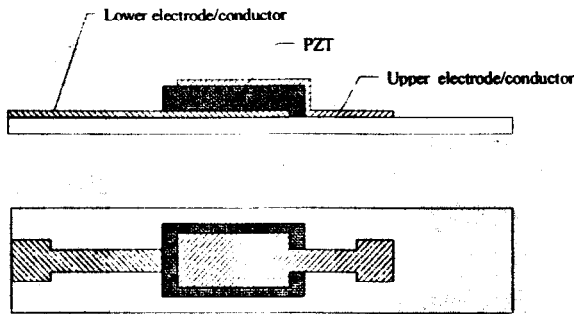


Figure 1. Sample construction

ESL 8836 gold paste, processed in accordance with the manufacturer's recommendations was used for the lower electrode. A relatively thick (100-150 μm) layer of PZT was deposited over the lower electrode area by printing and firing repeatedly at 950° C until the desired thickness was achieved. Finally, the devices were overprinted with the upper gold electrode. The nature of

ferroelectric ceramics means that after firing the samples have no remnant polarisation and it is therefore necessary to polarise the devices. Optimal conditions for polarisation are currently under investigation, but for this investigation the following procedure was standardised. The devices were placed in a box oven and allowed to become thermally stable at 150°C. An electric field of 3MV m^{-1} was then applied across the PZT in a direction perpendicular to the substrate. The samples remained in this state for 30 minutes, before being allowed to cool to ambient, at which point the electric field was removed.

The d_{33} coefficient may be defined as the ratio of either strain resulting from an applied electric field (mV^{-1}) or short circuit charge density resulting from an applied stress (CN^{-1}), in each case both terms act in the plane perpendicular to the substrate. Two techniques for measuring d_{33} were investigated. Firstly by the application of an electric field and measurement of the resultant strain and secondly by stressing a sample and measuring the resultant charge.

The first technique involved clamping the sample to a flat base, and applying an electric field. Using a high-resolution capacitive displacement probe it was possible to measure the deformation of the sample due to the applied field. Knowing the original thickness of the PZT layer it was possible to calculate the strain in the material and hence the d_{33} coefficient. A series of measurements of strain as a function of applied electric field was taken for each binder concentration of both the lead borosilicate and the lead(II) oxide samples. The displacements measured were typically 20-30 nm, agreeing with theoretical values calculated assuming a PZT thickness of 100 μm and d_{33} coefficient of 150 pC N^{-1} . Such small displacements are at the limit of resolution of the probe and particular difficulty was experienced in measuring the very small displacements occurring with higher concentrations of binder.

The second technique of stressing the sample required a means of applying a known load to the sample under test. This was accomplished using the rig shown in figure 2.

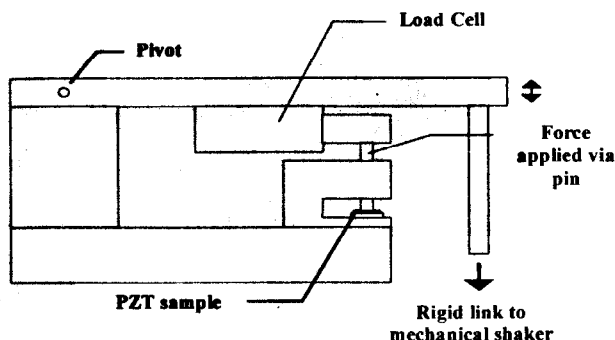


Figure 2. Charge measuring rig

measurements to be made on samples having d_{33} coefficients as low as 10 pC N^{-1} . In order to validate the measurement technique, tests have been performed on samples of commercially available bulk PZT having known characteristics. These measurements have yielded values of d_{33} within the manufacturers standard tolerance of $\pm 20\%$.

Results

Figure 3 shows strain as a function of applied electric field for a typical sample obtained using the application of an electric field.

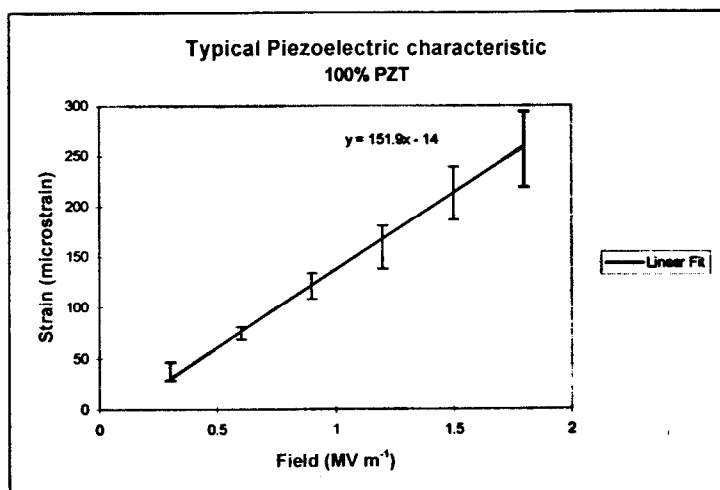


Figure 3. Typical variation of strain with field

The value of the d_{33} coefficient is given by the slope of the linear fit line and, in the case illustrated, is approximately 150 pC N^{-1} . This figure compares well with the d_{33} figure obtained using the charge measurement technique (140 pC N^{-1}). For comparison the value for commercial Morgan Matroc PZT-5A is 374 pC N^{-1} .

Figure 4 shows the variation of d_{33} as a function of binder concentration for both lead borosilicate and lead(II) oxide binders. These measurements were made using the charge measurement technique.

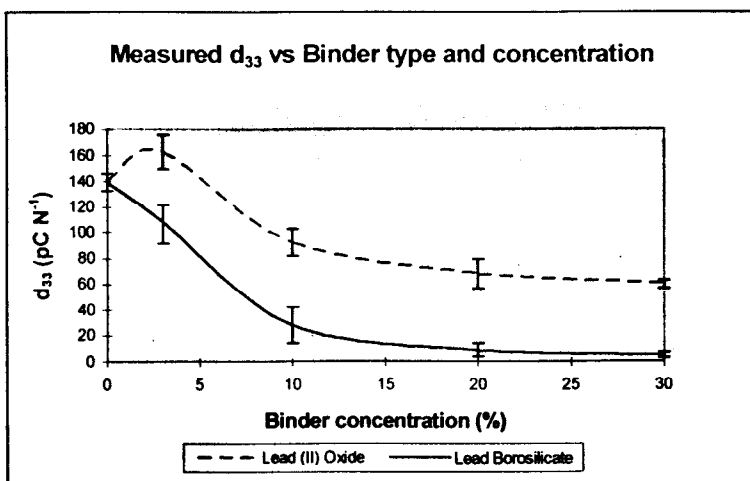


Figure 4. Effect of binder concentration

lead. It is of particular interest that a small amount of Pb(II)O enhances the sensitivity above that of 100% PZT. This is not due to the bonding effects of the binder, as it does not occur for lead borosilicate.

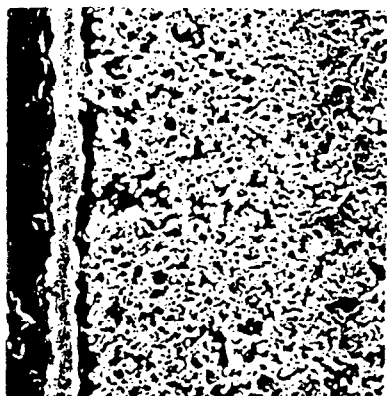
Samples of each of the various PZT/binder combinations have been observed using a scanning electron microscope (SEM), a selection of which are shown in figure 5. All the SEM micrographs shown in figure 5 are at a magnification of 500 times actual size and show cross-sections of the samples taken at approximately the same position on each sample. The alumina substrate is to the left hand side of each picture with the lower metal electrode being discernible as a light coloured vertical band situated between the substrate and the PZT layer. Figures 5(a) to 5(g) show thick-film devices whilst a section through a piece of bulk Morgan Matroc PZT 5A material has also been included at figure 5(h) for comparison.

It may be observed that an increased binder concentration leads to a denser sample, with fewer but much larger voids. This is to be expected, as the binder is able to melt at the firing temperature thus forming a denser structure. No significant structural differences are evident for different binders. The bulk PZT-5A has a denser structure than the 100% PZT thick-film sample, due to the compression techniques used in its manufacture, and this accounts for the difference in sensitivity between the thick-film samples and the bulk material.

Conclusion

Research at the University of Southampton is aimed at identifying the material properties and processing parameters required to maximise the d_{33} characteristic of screen printed thick-film piezoceramics. This paper has presented techniques for measuring this parameter. Results show that an addition of various quantities of binder change the morphology of the PZT layer, in addition to changing the sensitivity of the layer. The use of Pb(II)O however, appears to be preferable to lead borosilicate owing to a significant increase in sensitivity. A contributing factor is likely to be in the chemistry between the binder and the PZT, particularly in the area of lead loss/replacement, as lead loss is known to occur in PZT sintering. Research in this area is continuing.

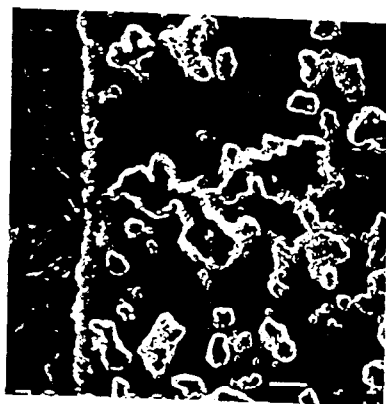
It is apparent that the use of lead (II) oxide gives a significant improvement in sensitivity over the use of lead borosilicate. Reasons for this are currently under investigation, but it is felt that the use of lead (II) oxide may reduce the effects of lead evaporation from the PZT during firing^[12], by either inhibiting lead loss, or replacing the



a) 97:3

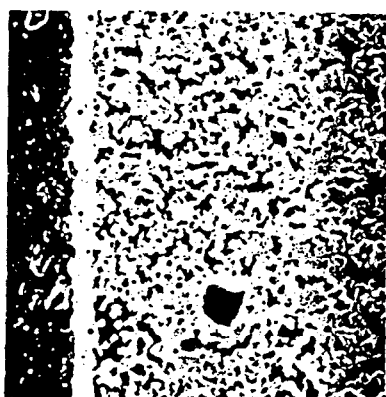


b) 90:10

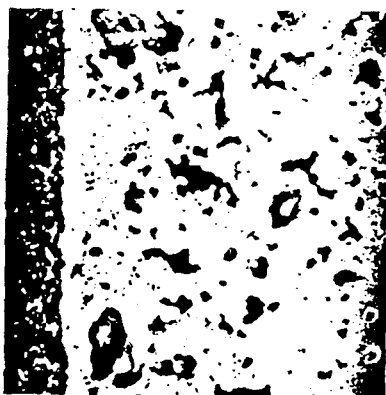


c) 70:30

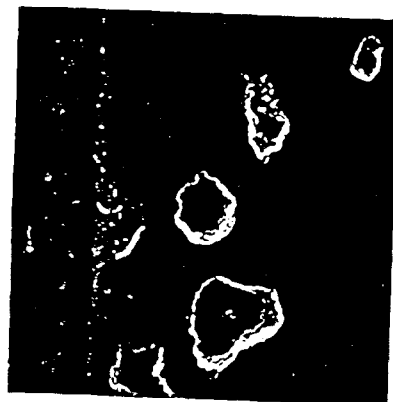
PZT:PbO %wt



d) 97:3



e) 90:10



f) 70:30

PZT:Lead Borosilicate % wt



g) 100% PZT



h) Bulk PZT 5A

Scale:

— = 10 μ m

Figure 5. SEM micrographs of cross-sections through various sample devices.

Acknowledgements

The authors wish to thank Morgan Matroc Limited and Ferroperm Limited of Denmark for providing the PZT samples used in these experiments.

References

1. *A Novel Accelerometer Using Thick-film Technology*, R.P. Sion, J.K. Atkinson, J.D. Turner, *Sensors And Actuators A*, 37-38, pp348-251, 1993.
2. *Sensor Applications Of Thick-Film Technology*, J.E. Brignell, N.M. White, A.W.J. Cranny, *IEE Proceedings, Part I*, Vol 35, No. 4, pp77-84, 1988.
3. *Hybrid Chemical and Physical Sensor Arrays*, J.K. Atkinson, *Hybrid Circuits*, No.32, pp 21-25 and 32, 1993.
4. *Resonant Pressure Sensor Based on Piezoelectric Properties of Ferroelectric Thick-films*, B. Morten, G. De-Cicco, M. Prudenziati, *Sensors and Actuators A*, 31, 1992 pp 153-158.
5. *Thick-film Acoustic Wave Sensor Structure*, N.M. White, V.T.K. Ko, *Electronics Letters*, August 1993 pp 1807-1808.
6. *Thin and Thick-film Sensors*, B. Morten, A. Alberigi Quaranta, M. Prudenziati and G. De Cicco, *Proceedings of PROMETHEUS Pro-Chip Workshop*, Stuttgart, 1991, pp 91-94.
7. *A thick-film resonant sensor for humidity measurements*, B. Morten, G. De Cicco and M. Prudenziati, *Sensors and Actuators A*, 37-38 1993 pp 337-342.
8. *Screen Printing Piezoelectric Devices*, H. Baudry, *Hybrid Circuits*, No. 14, September 1987 pp 71-74.
9. *PZT Based Thick-Films and the Development of a Piezoelectric Pressure Sensor*, B. Morten, G. De-Cicco, A. Gandolfi, C. Tonelli, *Hybrid Circuits*, No 28, 1992.
10. *IEEE Standard on Piezoelectricity*, ANSI/IEEE Std. 175-1987, Publ. The Institute of Electrical and Electronic Engineers, 1987.
11. *A Novel Micropump Design with Thick-Film Piezoelectric Actuation* M. Koch, N. Harris, R. Maas, A. G. R. Evans, N. M. White, *A Brunnschweiler Meas. Sci. Tech.* 8(1997) pp49-57
12. *Thick Film Printing of PZT onto Silicon* R. Maas, M. Koch, N. Harris, A. G. R. Evans, N. M. White *Mater. Lett.* accepted for publication