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Improving the piezoelectric properties of thick-film PZT: the influence of paste composition, powder milling process and electrode material

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Abstract

This paper details improvements of the d_{33} coefficient for thick-film Lead–Zirconate–Titanate (PZT) layers. In particular, the effect that the powder milling process has on particle size, shape and distribution has been investigated. Ball milled, jet milled and attritor milled powders were obtained from Morgan Electro-Ceramics Ltd. These powders were mixed with various ratios of lead borosilicate glass in the range of 5–20% by weight and an appropriate quantity of Electro-Science Laboratories (ESL) 400 solvent to formulate a screen printable thixotropic paste. The use of a polymer top electrode to reduce the number of firing cycles the PZT layer is subjected to was also investigated. The results show that the highest values of d_{33} were obtained from the ball milled powder with 10% glass content, but the most consistent results were obtained from the attritor milled samples. The samples printed with a polymer top electrode have shown an average increase of around 15% in the value of d_{33}.

Keywords: Piezoelectric; Thick-film; d_{33}; Milling

1. Introduction

Bulk piezoceramic sensors are presently used in many existing applications [1] but future devices are constrained by the existing geometries available with traditional fabrication techniques [2]. Screen printable thick-film lead–zirconate–titanate (PZT) layers provide a cost-effective, simple and flexible method for many sensor and actuator applications [3–5]. Studies have shown [6] however, that the type 5H powder thick-film samples possess lower d_{33} coefficients (10–250pC/N) than their bulk (593pC/N) counterparts, due to differences in processing and composition. It is, however, notoriously difficult to obtain accurate and repeatable measurements with thick-film devices due to the influence of the substrate and clamping effects on the piezoelectric film. These factors, if not considered, can have an exaggerating effect on the resulting measurements.

This paper describes research at the University of Southampton on improving the characteristics of the thick-film devices by optimising the powder milling process and the preparation of the PZT pastes prior to screen-printing. It also looks at the effect of poling conditions on the piezoelectric properties of the film and the influence of electrode material and firing temperature. The aim of the investigation is to improve both the level of piezoelectric activity and the consistency and repeatability of the films.

2. Processes

2.1. Powder milling

PZT 5H powders of the same $PbZr_xTi_{1-x}O_3$ composition (where x is propriety of Morgan Electro-Ceramics Ltd.) were prepared by ball milling, jet milling, and attritor milling processes [7]. The ball milling process involves the PZT materials being mixed in a slurry and tumbled or shaken with a suitable milling media such as sand, steel, zirconia or alumina in a horizontally rotating mill. Ball milling results

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in smooth particles due to the nature of the process. The smoothness of the particles is controlled by the type of liquid suspension selected and the speed at which the process runs. Jet milling is a more abrasive process that includes the powder particles being suspended in a high-pressure jet of air; the particles are either directed at a target or collide and wear against themselves. The mill is constructed in such a way that when the particles have been sufficiently reduced in size they will drop out of the mill. This process produces fine particles, exhibiting uneven edges in comparison to the ball milled powder. Attritor milling is a similar process to ball milling but instead of the mill itself rotating it has a vertical shaft that rotates inside. It is used to reduce the existing powder particles into a more uniform size distribution, but will also reduce the size of the particles. It is standard practice to feed the resultant milled powder back into the mill to achieve a tighter distribution. This investigation has evaluated powders that have been attritor milled once and three times. These are subsequently denoted as attritor1 and attritor3 respectively.

2.2. Powder sizes

The four types of 5H powder, ball, jet, attritor1 and attritor3 particle distributions are shown in Fig. 1. They have an average particle size of 2, 4.3, 1.2 and 1 μm, respectively. Fig. 1 indicates the reduction effects on the particle size and distribution with each pass through the attritor mill.

A Ferro 7575 lead borosilicate glass, having an average particle size of 10.2 μm, was added to the piezoelectric powder. The glass acts as a binding matrix in the thick-film process, which melts and then binds the PZT particles together upon cooling. If the glass content is too low, the film will be poorly sintered and the mechanical quality of the film will be weak. However, the higher the percentage weight of glass the less active material in the film and the lower the resulting piezoelectric properties.

2.3. Paste composition

The powders were prepared for printing by mixing each milled powder type with 5, 10, 15 and 20% by weight of glass. This percentage range of glass was chosen to study the effect that the glass level had on the porosity of the film and the subsequent piezoelectric properties.

It is necessary to mix the powders with a standard thick-film vehicle (ESL 400) thereby forming a thixotropic paste. The viscosity of this will vary at different stages during the printing process, enabling it to pass through the screen during the print step and retaining the printed geometry during the drying phase. Between 5 and 8 ml of solvent was used for each batch to create a screen printable paste.

The pastes were mixed using a triple roll mill, which disperses the powders evenly throughout the paste. This is an important factor in obtaining a consistent quality screen-printed film since it evenly distributes the glass amongst the PZT and results in a smooth paste that is compatible with the printing process.

3. Printing and firing

The PZT pastes were printed on a 96% alumina substrate using a standard thick-film process with a DEK 1200 printer. The devices were printed in the form of a capacitor structure, with ESL 9633B, low migration silver/palladium bottom and top electrode fired with the same profile as the PZT layer. For

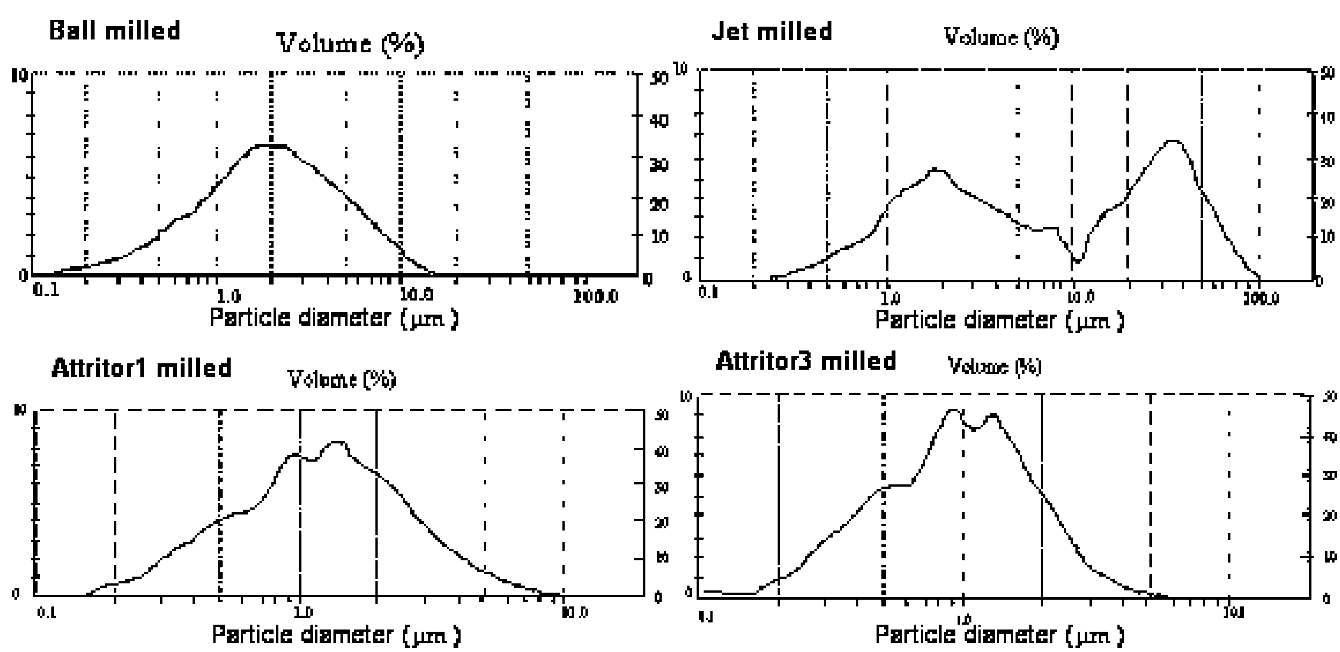

Fig. 1. Particle size distributions for ball, jet, attritor1 and attritor3 milled powders, respectively.

Table 1
Furnace firing profiles for Dupont 60 and 750PK

Stage	Temperature (°C)	
	Dupont 60	750PK
1	350	330
2	600	550
3	885	750
4	883	750
5	890	550
6	870	350

an industrial system, gold would be used for the electrodes, as it possesses improved long-term stability, although this is not a cost-effective approach for small-scale research work.

Two PZT layers were printed and dried in a DEK 1209 IR drier at 140 °C and subsequently fired on a belt furnace with a furnace profile (denoted as 'Dupont 60' henceforth) shown in Table 1. Each furnace stage is 5 min 40 s long. Care was taken to ensure that each batch underwent the same firing process to reduce any inconsistencies that may have influenced the level of sintering obtained such as drying time and time between drying and firing.

An additional sample set was fired using a reduced temperature profile denoted 750PK, shown in Table 1, to investigate the effect of reducing the lead loss typically observed in thick-film devices fired in an air atmosphere. As part of this experiment the top electrode layer was printed using ESL 1110-S silver polymer which was dried using the IR drier at 135 °C for 10 min followed by curing at 200 °C for 1 h. This process allowed the PZT layer to be subjected to only a single firing cycle and therefore reduce the lead loss whilst maintaining the high firing temperature to maintain a good level of sintering. The use of a silver polymer top electrode minimises the effect of silver migration associated with high temperature cermet silver/palladium electrodes.

Each paste batch was printed on two substrates, as shown in Fig. 2, so that a range of samples would be obtained and the repeatability of the pastes could be assessed.

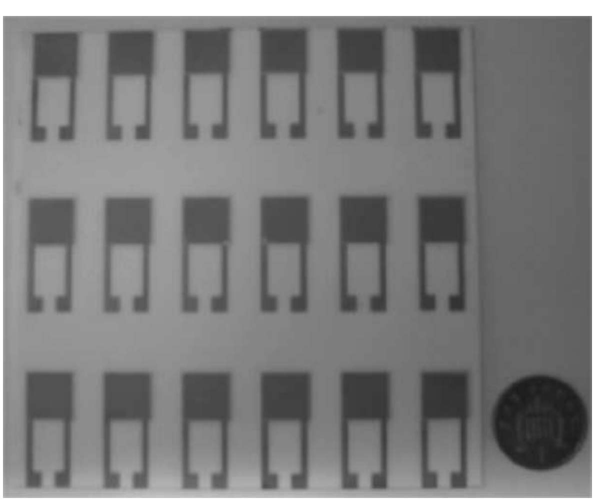

Fig. 2. Layout of the printed layers on the substrate.

Work by Tanaka et al. [8] has shown that drying the PZT layer in a vacuum can improve the density of the film and therefore improve the piezoelectric properties. A batch of ball milled pastes was printed and then dried in a vacuum chamber with 2×10^{-4} mbar of pressure at 190 °C for 10 min. This experiment was undertaken to determine if the porosity of the thick-films could be reduced as a result of imposing a vacuum during the drying stage. These samples were then fired with a Dupont 60 furnace profile as described previously. Top electrodes were, however, not printed on these samples as they were used for observing the changes in the density of the PZT layer.

This entire process took place within the Southampton University Microelectronics Centre class 1000 clean room to further reduce any inconsistencies from possible sources of contamination in the pastes. Samples from each batch were viewed in a scanning electron microscope (SEM).

4. Poling

Each sample was poled at 150 °C with field strength of $4\,\mathrm{MV\,m^{-1}}$ for 30 min and then allowed to cool to room temperature with a continuously applied electric field, this gives a balanced poling process to enable observations of any changes in piezoelectric properties independent of poling levels [6].

The d_{33} values were measured using a Take Control PM35 piezometer [9]. The piezometer is designed for bulk devices but gives consistent results for thick-film devices to enable a comparison between samples. Previous methods for d_{33} measurement [10] have proven to be less suitable given the high number of samples measured and therefore the piezometer is ideal. The limitations in this method of measurement result from the substrate clamping effects, which reduce the effective d_{33} coefficient thereby reducing the effective d_{33} [11].

The standard poling parameters used with the thick-film samples are different to those used in the Morgan Electro-Ceramics Ltd. factory poling process for bulk 5H samples. This proprietary process uses a lower temperature and applied electric field strength for a shorter period of time than our process. It was important to observe the effects on the thick-film samples with these factory conditions so a number of samples were poled under these conditions. The process is conducted using a Techne oil bath that allows higher poling fields than those used in air due to the increase in breakdown voltage.

5. Experimental results

5.1. Milling type and glass percentage

The average measured d_{33} values for each milling process and percentage weight of glass in the film were obtained

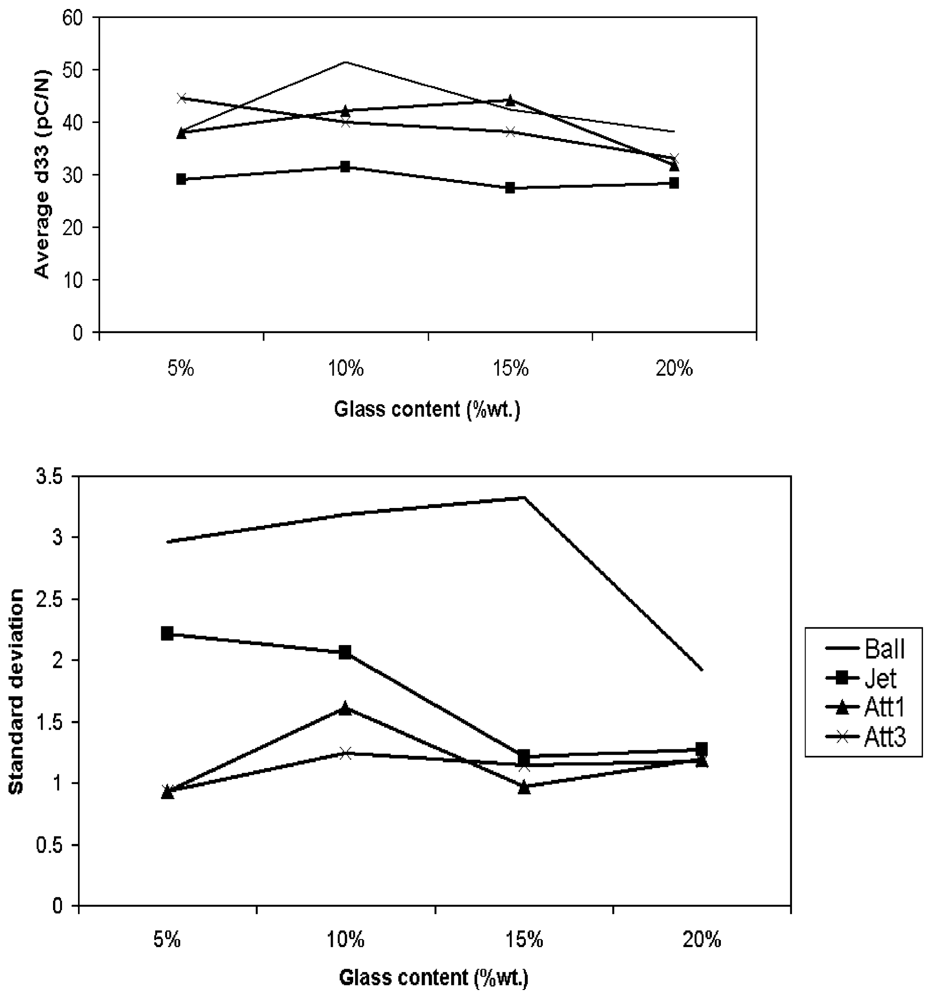

Fig. 3. Average d_{33} and standard deviation of d_{33} for different milling processes and glass percentages.

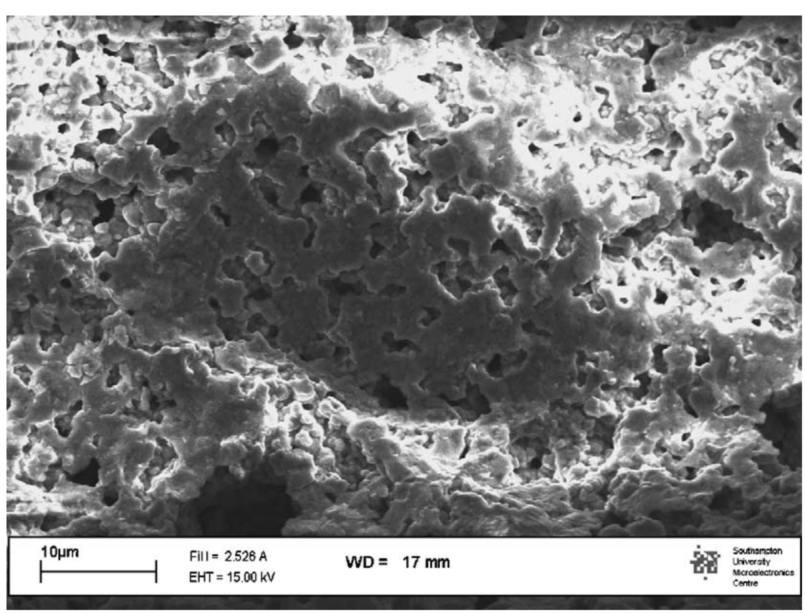

Fig. 4. Ten percent ball cross sectional PZT layer.

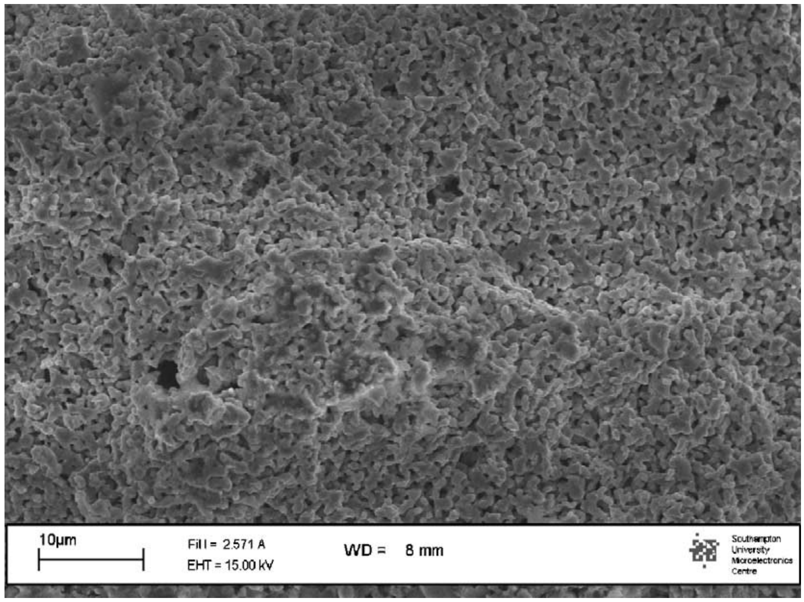

Fig. 5. Five percent attritor3 cross sectional PZT layer.

from a minimum of 20 samples. The consistency of the measured results from each process was observed with the standard deviation of the results obtained. Fig. 3 indicates the milling type and glass combination that produced the highest and most consistent results.

The highest d_{33} values were obtained from the 10% ball milled samples but the most consistent results were obtained from the attritor3 samples. Figs. 4 and 5 show the SEM micrographs of a 10% ball and 5% attritor3 sample respectively. These are both cross-sectional views of the PZT layer at the same magnification, indicating the size and quality of the films.

Fig. 4 shows that the ball milled film is well bonded but shows an increased porosity compared to an equivalent bulk device and this is a contributing factor to the reduced piezoelectric properties.

Fig. 5 indicates that the attritor milled films have good mechanical density, but the sintering is relatively poor due to the lower temperatures used (in comparison to the bulk process) and the size of the glass particles available, 10.2 μm, which is not ideally compatible with the PZT powder size. This glass frit is not required in the bulk process because the firing temperatures are high enough to produce sintering between the PZT particles resulting in greater density and therefore improved mechanical and piezoelectric properties.

The glass content has a significant effect on the different powders with the exception of jet milled PZT which displays relatively consistent d_{33} values for each glass percentage. As the amount of glass increases, the binding matrix between the PZT particles should strengthen but the adverse effect of too much glass is that the overall piezoelectric content of the film is reduced and thus the d_{33}. The ball milled powders have shown that an optimum of 10% provides enough glass to form a satisfactory bond but that 15 and 20% begin to reduce the overall piezoelectric properties. This effect is increased with the smaller attritor particles because the distance between the PZT particles is greater with increasing glass content. This causes a reduction in the net piezoelectric effect of the film by reducing the amount of transferred mechanical force into the particles for the direct effect and reducing the net deformation of the film for the indirect effect.

5.2. Drying in a vacuum

The samples dried under vacuum conditions were compared from the same substrate that were dried under normal conditions and then both halves of the substrate were fired with the Dupont 60 process. Once fired, the samples were analysed using the SEM and these micrographs are shown in Figs. 6 and 7.

There appears to be no significant increase in the density of the film from this simple experiment. The use of more sophisticated techniques, such as hot isostatic pressing, may yet yield more encouraging results.

5.3. Low-temperature firing and polymer electrodes

Following the results of Section 5.1, two substrates of 10% ball pastes were printed and fired as previously described with polymer top electrodes. One substrate was fired using the 750PK furnace profile.

Table 2 shows the average d_{33} values for each sample. The results show that the lower temperature profile has reduced the piezoelectric properties of the PZT layer but the polymer electrode has increased the d_{33} values for those fired using the Dupont 60 profile.

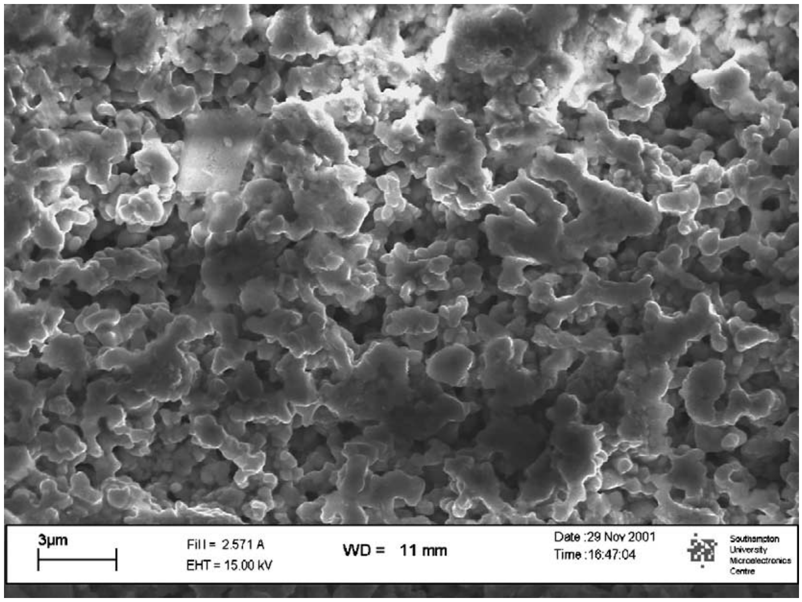

Fig. 6. PZT layer of thick-film dried in IR drier.

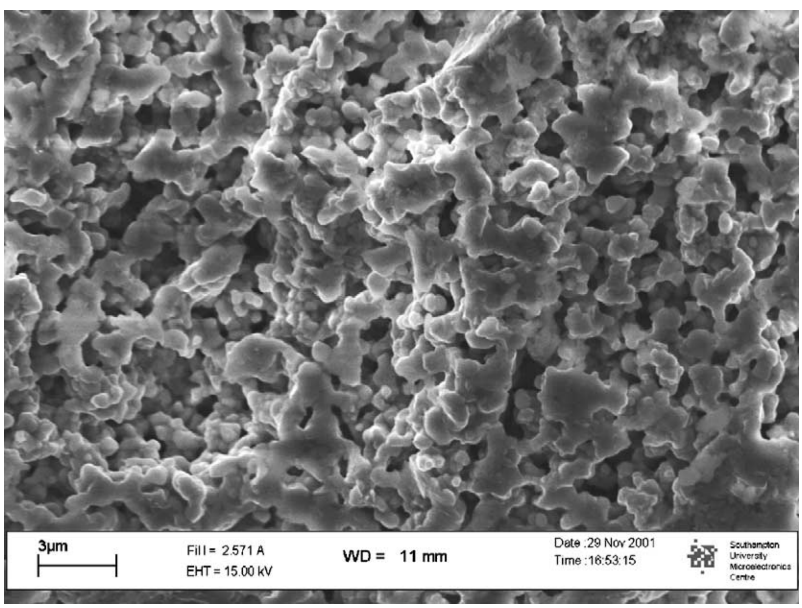

Fig. 7. PZT layer of thick-film dried under vacuum conditions.

5.4. Factory poling conditions

A set of samples were poled in a Techne oil bath using Morgan Electro-Ceramics Ltd. factory poling conditions for bulk 5H samples. This process was conducted with the maximum field that could be applied before breakdown occurred, $30\,\mathrm{MV\,m^{-1}}$, in comparison to the standard field of $4\,\mathrm{MV\,m^{-1}}$ used in air.

The resulting d_{33} values, shown in Table 3, are lower than that obtained with existing poling parameters.

Table 2
Average d_{33} results for polymer electrode and lower firing temperature samples

Sample	Firing profile	Thickness (µm)	Poling field (MV/m)	Average d_{33} (pC/N)
1	750PK	45	4	33
2	750PK	45	4	33.4
3	Dupont 60	50	4	64.2
4	Dupont 60	51	4	62
5	Dupont 60	50	4	69.2

Table 3
Comparison of d_{33} values for different poling processes

Sample	Average d_{33} (pC/N) (standard poling process)	Average d_{33} (pC/N) (Morgan Electro-Ceramics poling process)
1	49.4	31.2
2	55.6	30.8
3	55.2	31
4	45.6	29.4

6. Conclusions

Ball milled powder with 10% glass content produces the highest d_{33} coefficient with an average measured value of 52pC/N. Fig. 3 shows that the influence of the glass content on the d_{33} coefficient is different for each powder type. The ball milling process produces a larger particle size distribution compared with the attritor milling process. The increased percentage of large particles results in improved d_{33} values as the net effect of each piezoelectric response is increased. However, this results in a wider deviation in the value of d_{33} as Fig. 3 indicates. The jet milling process produces more porous and less uniform films, hence lower levels of piezoelectric activity.

Experiments with a polymer top electrode to reduce lead loss and silver migration have given positive results. Increases of 15–20% in d_{33} values have been observed with an average measured value of 65pC/N. This is thought to arise as a direct result of the improved stability of PZT stoichiometry to the reduced number of firing cycles.

The poling of the thick-film devices under bulk conditions resulted in lower piezoelectric properties. This is thought to be due to the reduction in the length of time the samples are poled for and the manner in which the samples are removed from the poling bath. This tends to reduce the overall effect the poling has in creating a significant piezoelectric effect. Use of our process parameters and factory voltages may yield an increase in piezoelectric levels.

Further work will investigate the effects of the substrate clamping on the reduction in d_{33} compared to the 5H bulk samples, and also the effects of combining different particle size powders and glass together in an attempt to produce less porous films and therefore improve the mechanical and piezoelectric properties.

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Biographies

R.N. Torah obtained the degree of BEng (Hons) in Electronic Engineering in 1999 and an MSc in Instrumentation and Transducers in 2000 at the University of Southampton. Russel is currently researching for a PhD on the optimisation of piezoelectric properties in thick-film PZT ceramics within the Electronic Systems Design Group at the University of Southampton.

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N.M. White is Professor of Intelligent Sensor Systems within the Department of Electronics and Computer Science at the University of Southampton and also Director of the Institute of Transducer Technology. He was awarded a PhD in 1988 for a thesis on the application of thick-film piezoresistors for load cells. Professor White was appointed as Lecturer in 1990, Senior Lecturer in 1999, Reader in 2000 and currently holds a Personal Chair. He has published extensively in the area of thick-film sensors and intelligent instrumentation and is author or co-author of over one hundred scientific publications. He is a Fellow of the Institute of Physics, a Chartered Engineer and a Senior Member of the IEEE and has served of several committees in various professional bodies.