

The Variability of Piezoelectric Measurements: Material and Measurement Method Contributions

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SUMMARY

The variability of piezoelectric materials measurements has been investigated in order to separate the contributions from intrinsic instrumental variability, and the contributions from the variability in materials. The work has pinpointed several areas where weaknesses in the measurement methods result in high variability, and also show that good correlation between piezoelectric parameters allow simpler measurement methods to be used.

The Berlincourt method has been shown to be unreliable when testing thin discs, however when testing thicker samples there is a good correlation between this and other methods. The high field permittivity and low field permittivity correlate well, so tolerances on low field measurements would predict high field performance.

In trying to identify microstructural origins of samples that behave differently to others within a batch, no direct evidence was found to suggest that outliers originate from either differences in microstructure or crystallography. Some of the samples chosen as maximum outliers showed pin-holes, probably from electrical breakdown during poling, even though these defects would ordinarily be detrimental to piezoelectric output.

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INTRODUCTION

For almost all manufacturing processes it is important to have a consistent supply of raw materials/ components. For piezoelectric ceramics this will usually be achieved by specifying some sort of minimum or maximum tolerances on various parameters, depending on the intended use of the ceramic. For a DC actuator it might be a minimum d_{33} value, which defines the minimum that the actuator will move, or for a welding transducer it may be a maximum dielectric loss, to prevent the sample overheating. From a practical perspective it is simpler to specify tolerances on the most important parameter, as experience tells the designer that the other parameters are less important in his application. For example, by controlling tolerance on the piezoelectric coefficient of a material used in a medical transducer, it will achieve the desired output, and ordinarily the capacitance of the device is within the operating range of the amplifier. However a change of variability in the capacitance, whilst still maintaining the tolerance on the piezoelectric coefficient, may affect the ability of the power supply to drive the transducer. The obvious answer would be to specify tolerances on all the parameters, however because of the complexity of piezoelectric behaviour this is not always practical, and so the designer makes some judgements, based on past experience, as to how the material will vary. This work aims to look at some of the issues surrounding these assumptions, and how the measured variability may arise.

In metrology the term repeatability is the intrinsic instrument variability – a measure of the agreement between repeated measurements of the same quantity under unchanged conditions of measurement. However it is sometimes difficult with the complexity of piezoelectric measurements to separate the contributions from the intrinsic measurement variability to the intrinsic variability in the material. Often it comes down to the definition of ‘unchanged conditions of measurement’ and it may be difficult to separate, i.e. when reinserting a sample in a Berlincourt tester, is a different sample area being tested, or are the measurement conditions changed subtly?

The variability of any given property depends on the measurement, and the resolution of that measurement method, for example measuring the density of a material with an insufficiently precise balance might give the same results for a batch of material, yet is still good enough to distinguish different materials. Therefore the variability of a set of results reflects not only the real variability of a material, but also the errors associated with the measurement technique

In the following experiments selected batches of similar materials are examined to determine whether the variability seen in certain piezoelectric measurements is due to material or experimental variability.

RELATIONSHIP BETWEEN DIELECTRIC AND PIEZOELECTRIC VARIABILITY

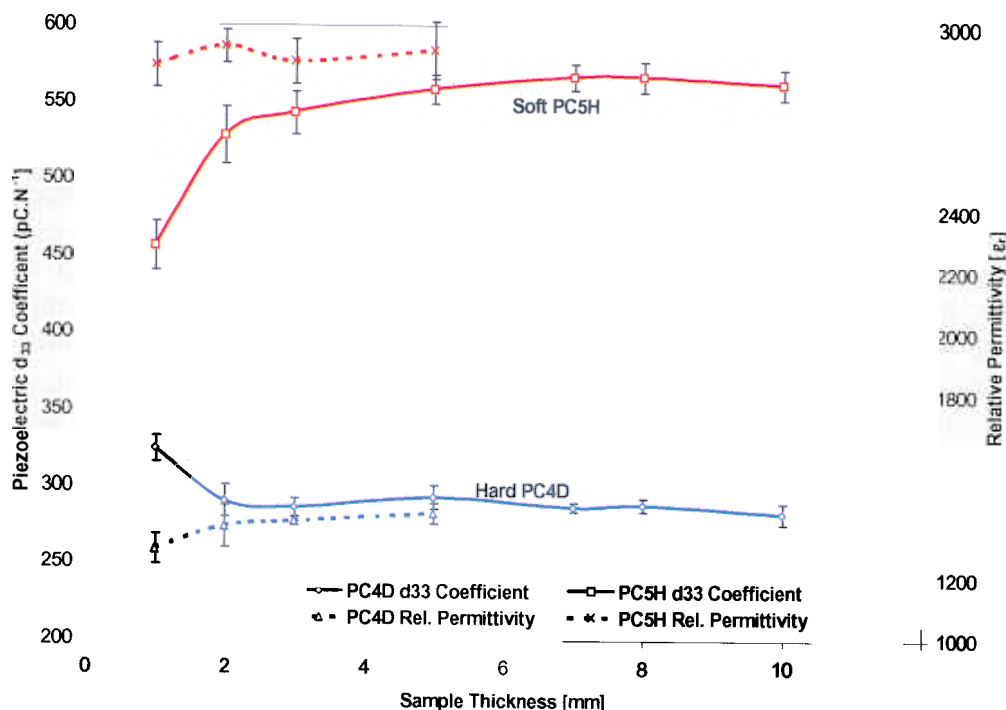


Figure 1 Comparison of relative permittivity with piezoelectric coefficient d_{33} for different thickness samples

Two batches of material (one hard and one soft) were cut to various thicknesses, electroded and poled in the conventional manner. Relative permittivity was measured at 1kHz, using an HP 4292A impedance analyser and d_{33} was measured using the Berlincourt method (outlined in GPG No.44¹).

Relative permittivity, or dielectric constant, is expected to be constant with sample thickness since the parameter is a property of the material. The piezoelectric coefficient is also expected to vary in a similar manner to the permittivity since both are intrinsically related to the materials polarisation. However, the variation in d_{33} using the Berlincourt method, exhibits departures from linearity at low values of sample thickness (< 2 mm), Figure 1. The measured d_{33} decreases with decreasing sample thickness for the soft material whilst the opposite is true for the hard material. This has been observed before and may be explained by the non-linear behaviour of d_{33} with mechanical stress, which becomes significant when the sample thickness is reduced. For thinner samples there are regions of material that are more highly stressed than the average stress state within a thicker sample. This is an attribute of the static pre load configuration of the Berlincourt test method. These observations suggest:

- The measurement of permittivity appears to be a material dependent property (measured using an impedance analyser) whilst
- The measurement of the piezoelectric coefficient d_{33} by the Berlincourt measurement method is complicated by the sample geometry effect.

This assumes that the different thickness samples are all the same, i.e. they are not different due to different poling conditions, and the variability here is due to measurement variability.

A materials permittivity and piezoelectric coefficient – for any given chemical composition – is dependent on its microstructural and chemical homogeneity, grain size, porosity, poling history (domain configuration) etc. If we assume that within a batch of similar material that the composition is constant, then the microstructural features that lead to larger permittivity values would also lead to larger piezoelectric parameters. However it is sometimes difficult to distinguish this because of the variability in the results, either from the material or the measurement technique.

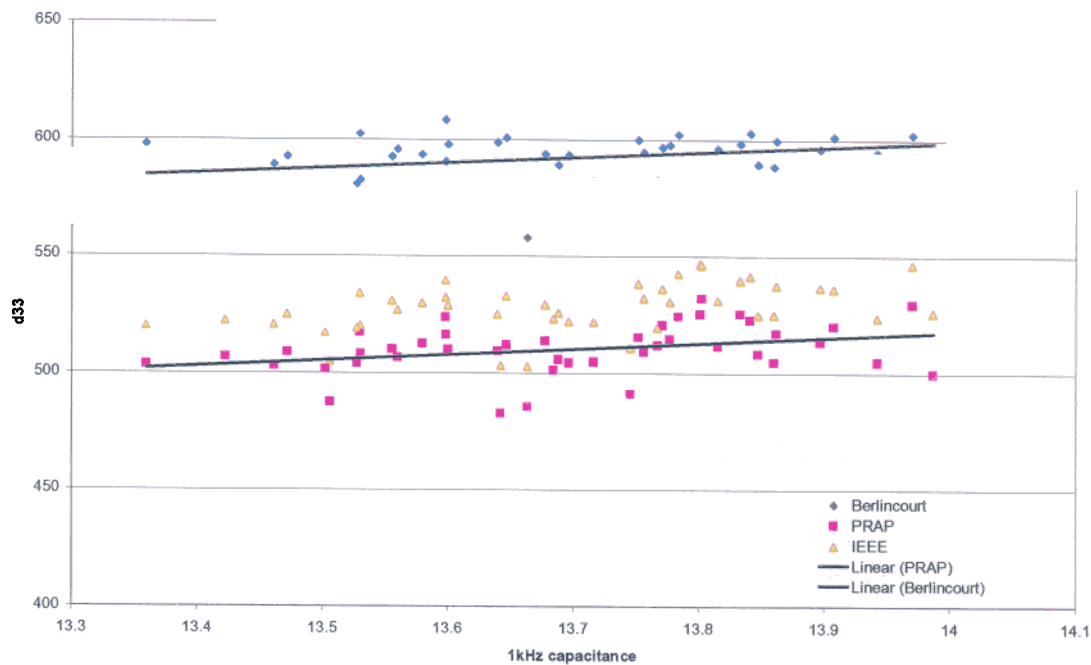


Figure 2 Comparison of Berlincourt d_{33} against low field capacitance measurements for a soft PC 5H material

The data in Figure 2 tells us that a slight linear dependence exists between d_{33} and capacitance (as expected from the relationship of polarisation with permittivity and d_{33} and the relationship $k_{33}^2 = d_{33}^2 / (\epsilon - S)$, with k_{33}^2 = coupling coefficient, ϵ = permittivity, and S = compliance).

The data in Figure 3, shows the variability in materials property measured using three different techniques. The first two methods utilise resonance data analysed in different ways, the third method uses the Berlincourt method. Ideally there should be a one to one correspondence between the methods, and the slope of the line is close to 1, although they both have non zero crossovers. This is probably due to the different conditions under which the measurements are made, the Berlincourt is at low frequency, and there is the additional pre load.

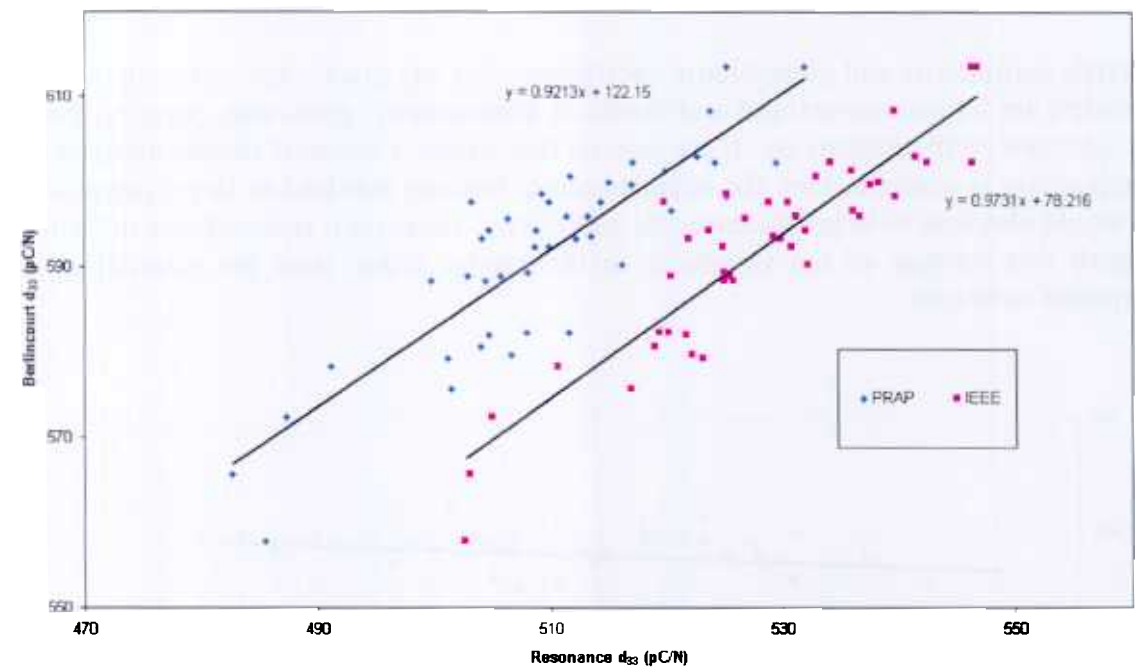


Figure 3 Variation of d_{33} measured by three different methods on a batch of PC5H material

EFFECT OF SAMPLE DENSITY

The piezoelectric coefficient is expected to vary with volume of active material in any given sample, with the implication that porosity will reduce the overall value of d_{33} .

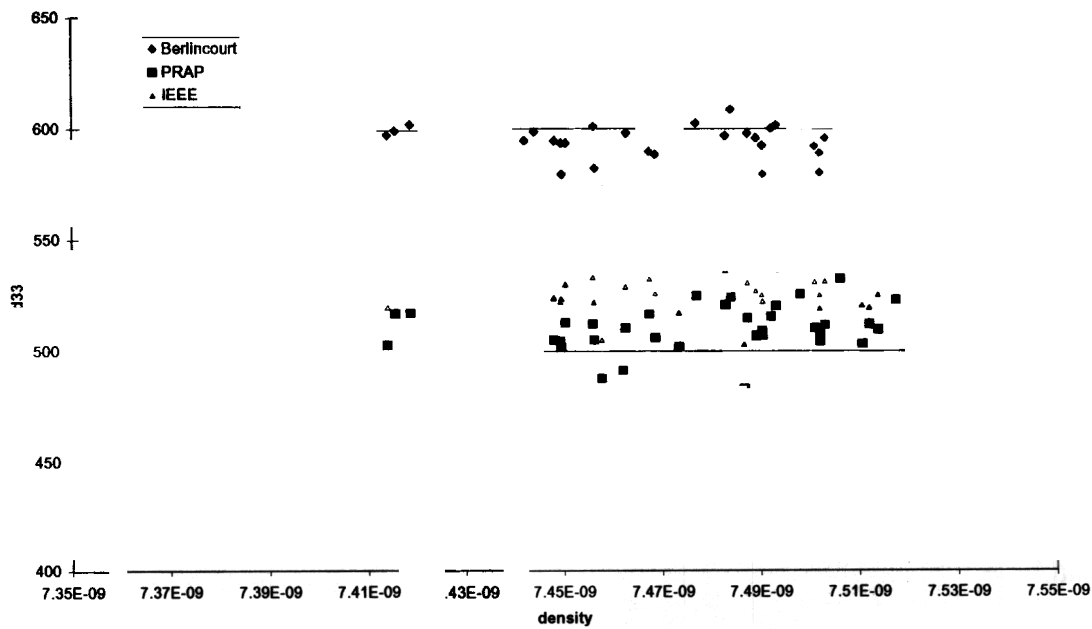


Figure 4 Variation of d_{33} with density for PC5H

The data in Figure 4, shows the d_{33} (via three techniques) verses density for the batch of material. The variation in density of this batch is only $\sim 3\%$ between min to max measured values, which is probably the order of the measurement error. The decrease in d_{33} , expected from the simple linear relationship $d_{33} \propto \text{volume fraction porosity}$, would thus be of order 3% , which is not apparent in the statistical spread of data from all the samples in the batch measured. In summary, the measurement of density is not sensitive enough to detect differences within the batch, and the d_{33} appears to be dominated by factors other than the materials bulk density.

SAMPLE GEOMETRY EFFECTS

Thickness mode resonators 3mm diameter with different sample thickness were measured using simple LCR type capacitance measurements, resonance sweeps and Berlincourt d_{33} measurements. The samples were all prepared from the same batch, so as long as the raw material is homogenous, and the poling conditions are the same, then all three sample geometries should have the same materials parameters. In practice the material has a degree of variability, and poling conditions for the different lengths may vary.

If two different methods are used to measure a materials parameter and the results agree, then is it probably safe to assume that the materials are homogeneously the same. If the results disagree then, either the materials are different, which could be detected by some microstructural/microchemical measurement, or the two measurement methods are not measuring the same parameter.

The dielectric loss of the samples can be determined in two ways, firstly by a simple LCR measurement, and secondly by the fitting of a complex quantity to the resonance curve using PRAP². The results for the three different thickness samples are shown in figure 5.

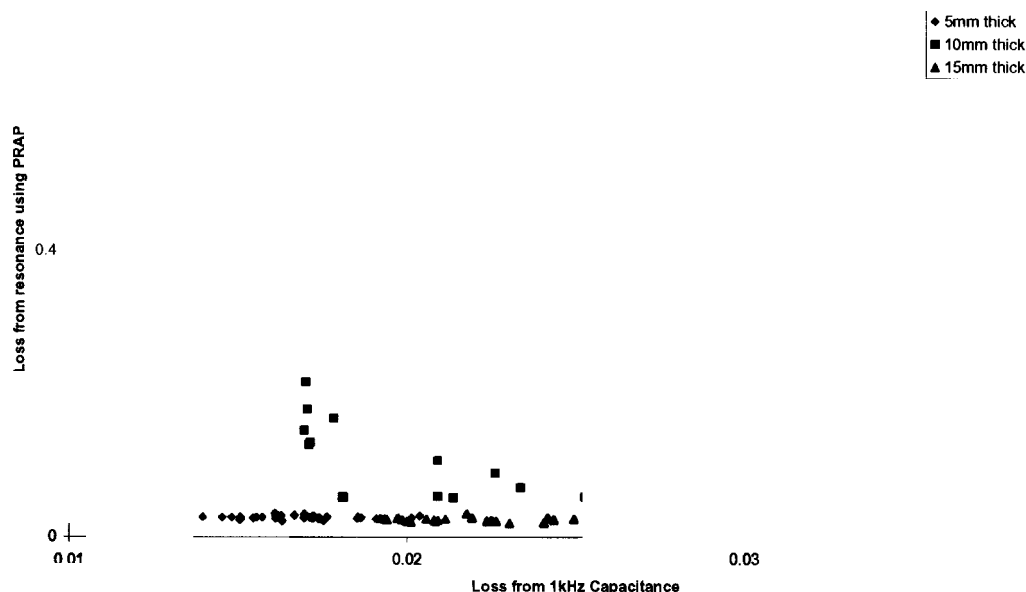


Figure 5 Dielectric loss determined by PRAP with 1kHz measurement for PC4D

At first this indicates there is a very poor agreement between the two sets of results, particularly for the 10 mm samples. On closer investigation this is due to the interference of the various resonance modes in the 10mm sample leading to a poor fit, and thus inaccurate loss predictions. In fact, of the three sample geometries only the 15 mm sample approaches the ideal shape to enable a pure resonance mode, however the 5 mm sample still gives reasonable results as can be seen in Figure 6.

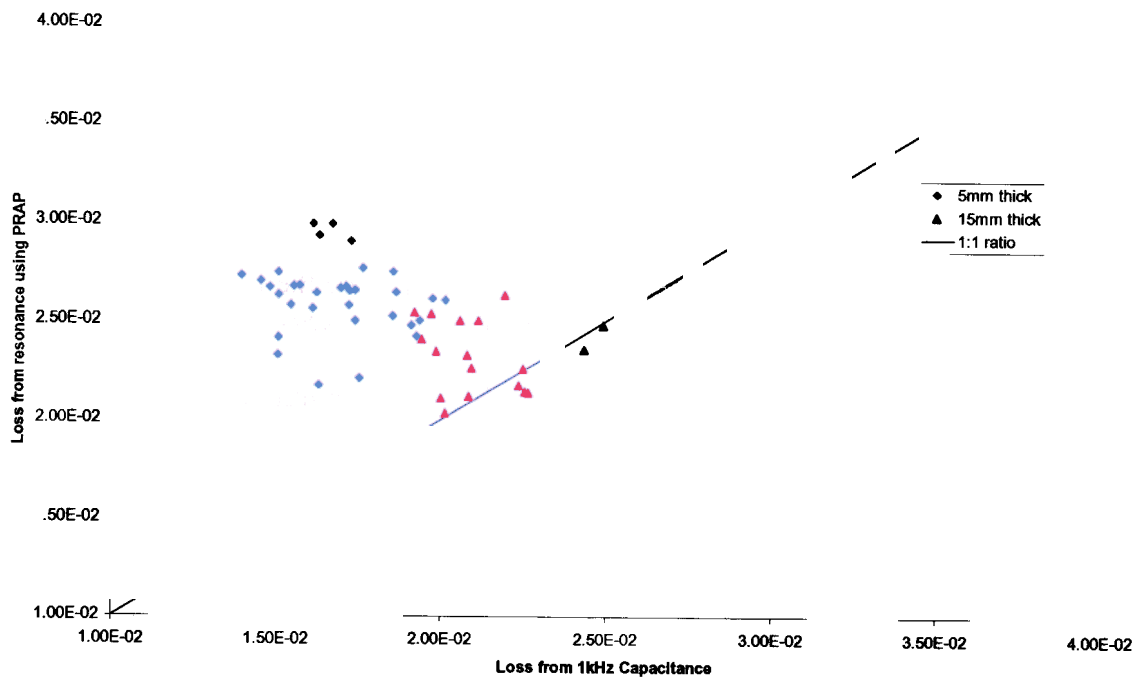


Figure 6 Comparison of loss measured by PRAP with 1kHz low field measurement for PC4D

The expanded region shows that the loss measured by resonance is reasonably consistent for the 5 and 15 mm samples whereas the LCR measurements suggest that the longer samples have a larger loss. Loss is a material parameter and so should not depend on the sample length which leads to various possibilities:-

- The loss is greater in the longer samples (due to different poling conditions?)
 - The LCR measurement of loss is inaccurate (dependent on the sample capacitance?)
- The resonance measurement of loss is inaccurate.

The measurements for the 15 mm samples lie symmetrically about the 1:1 line suggesting that these are accurate, and implies one of several conclusions

- Both measurements are inaccurate for the 5 mm samples
- Both sample sets are the same and the LCR measurement is inaccurate for 5 mm
- Both sample sets are different and the PRAP measurement is inaccurate for 5 mm.

At present the second conclusion would seem the most likely, and further tests might confirm this.

EFFECTS OF SAMPLE POROSITY

The Berlincourt test method is prone to variability in results, due to a number of reasons mostly associated with the pre load applied to perform the test. The pre load is usually applied by turning a screw clamp a number of turns, which then holds the sample in place against a spring. The variability in any set of tests can be reduced if the screw clamp is kept in position, and the samples are forced in against the spring manually. The test takes a few seconds to stabilise a reading, and after this successive readings are within 1 or 2%. However if the sample is removed and immediately replaced variations of up to 30% or more can often be seen, dependent on the sample. An explanation for this effect is that in each test the sample is placed in a slightly different position, and therefore testing a different volume of the sample. The Berlincourt test only stresses a small area of the sample underneath the loading probes, which for a 1mm thick sample equates to around 2mm³ sample volume. In order to give rise to large variations in measured d_{33} the fluctuations in microstructure would need to be of the order of the sample volume. The only features in the microstructure which approach this size are pores which can sometimes approach 0.1mm³. If porosity was responsible for the differences in behaviour then samples with different porosity levels should show different variability.

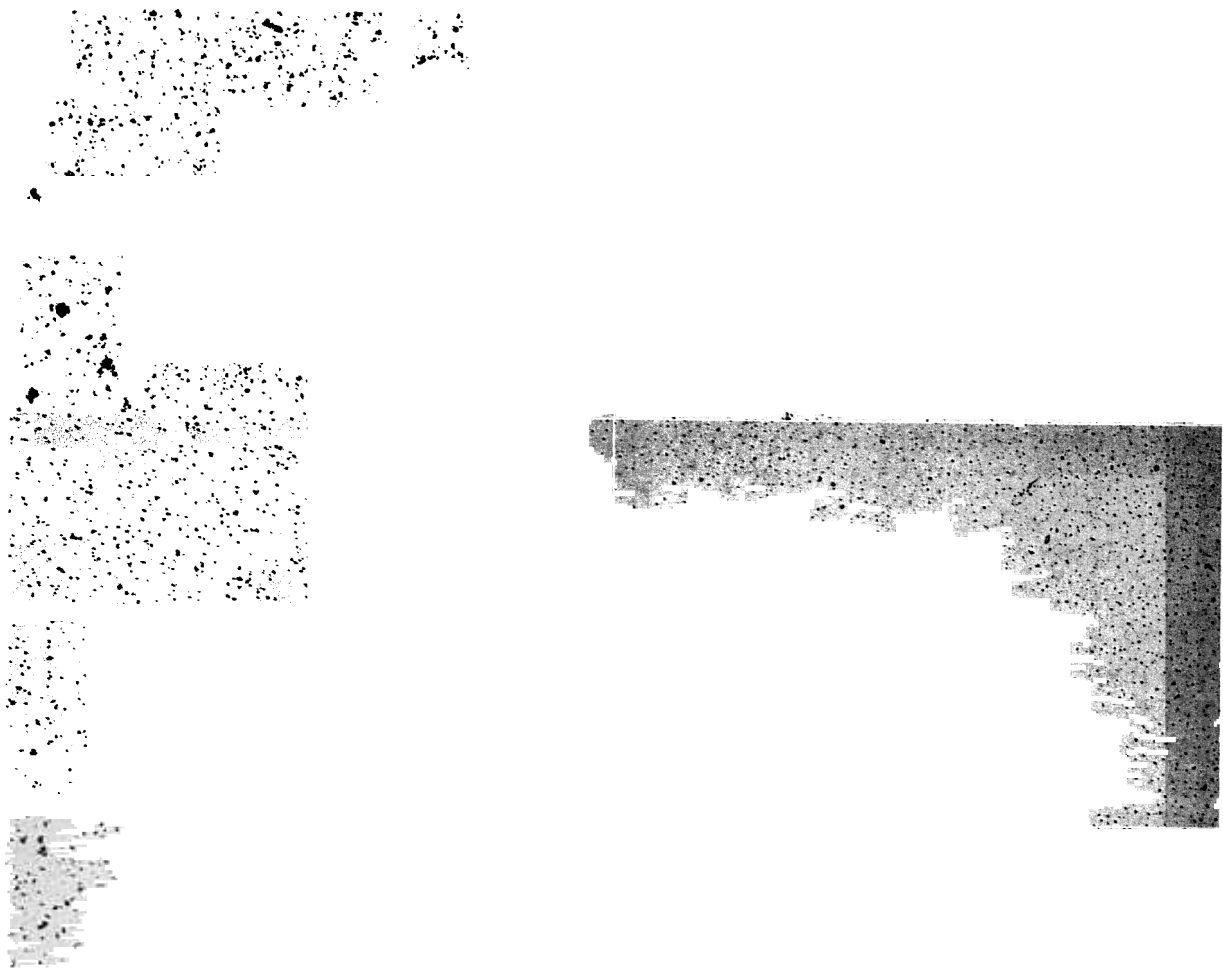
Six samples of different porosity levels were examined for the variability of results from the Berlincourt test. This included a hard and a soft composition, produced by three different manufacturers with slightly different manufacturing routes, including one hot pressed set.

	Soft			Hard		
Manufacturer	A	B (hot pressed)	C	A	B (hot pressed)	C
Average	378.0	304.4	364.2	286.3	267.8	312.5
Standard deviation	7.81	4.31	7.57	1.64	2.25	2.85

Table 1 Variation in measured d_{33} for samples with different porosity levels

As can be seen from the micrographs, Figure 7, the hot pressed samples have fewer and smaller pores, whilst the other conventionally sintered samples have similar porosity levels. The materials are not necessarily the same compositionally, but the hard is a Navy type I, whilst the soft is a Navy type II, so variability could come from different composition, rather than purely porosity.

The Berlincourt results for the soft materials have a larger standard deviation than the hard materials, and the soft hot pressed sample has a smaller standard deviation than the conventionally sintered counterparts. For the hard samples the standard deviation is similar for all the samples.



Soft

Hard

Figure 7 Micrographs of the materials one soft and one hard composition from three different manufacturers, from top to bottom A, B, C.

It is difficult to conclude that the differing porosity levels in these samples has an effect on the variability of the measured d_{33} . The soft material shows a larger variability, but this maybe because the soft materials are much more sensitive to the effects of small variations in pre load. If porosity does not play a part in the Berlincourt measurement variability, then it maybe that the measured volume is much smaller than previously estimated. The loading contact area is of the order of millimetres resulting in a large variation of stress throughout the sample. Since the method measures the charge generated throughout the sample, (d_{33} is the ratio of charge generated to applied force), then the majority of the total charge could originate from a very small proportion of the stressed volume.

EFFECTS OF SAMPLE TEXTURE

Within a batch of samples, all made using nominally the same manufacturing method there is a spread of results, with the outliers differing by as much as 20%. If the reason for this large spread can be identified and rectified, then either the spread about the mean can be reduced, or the mean of the samples could be raised.

From the previous argument we have discounted the possibility that changes in the measured porosity level (of the magnitude encountered in nominally dense samples), has an effect on the piezoelectric activity of the sample. Another cause for changes in piezoelectric activity might be the sample texture. Initially, after sample firing, the texture is random and only after poling does the texture develop that gives rise to the large piezoelectric effect. If there is some variability in the poling process from sample to sample, this could lead to differences in activity. Although low field measurements might be an indicator of the thoroughness of poling, the high field P-E loop behaviour should show both the current polarisation state and the poling capability of the sample through the polarisation saturation.

Out of a large batch of soft PC5H samples 1mm thick, several samples were selected as being either average samples, or maximum or minimum outliers based on Berlincourt measurements, and these were further investigated.

Nine samples were re measured using the Berlincourt method and the results are shown in table 2.

Sample ID	20b	23b	27b	32b	35b	47b	46b	41a	35a
Original ID	average	average	max	max	min	min	average	average	max
Mean	429	449	443	456	418	394	423	415	460
Standard Deviation	20.38	19.17	17.14	17.69	17.94	15.48	17.69	17.04	20.42

Table 2 Nine selected samples from a batch of PC5H discs

The original identification, average, maximum or minimum is also listed, and it appears that the pre selection was not sufficiently rigorous to identify outliers unequivocally, however some of the samples can be distinguished because of their different d_{33} . The low field capacitance and loss of the samples was also measured at this stage to check that PE loop measurements did not unduly change the samples.

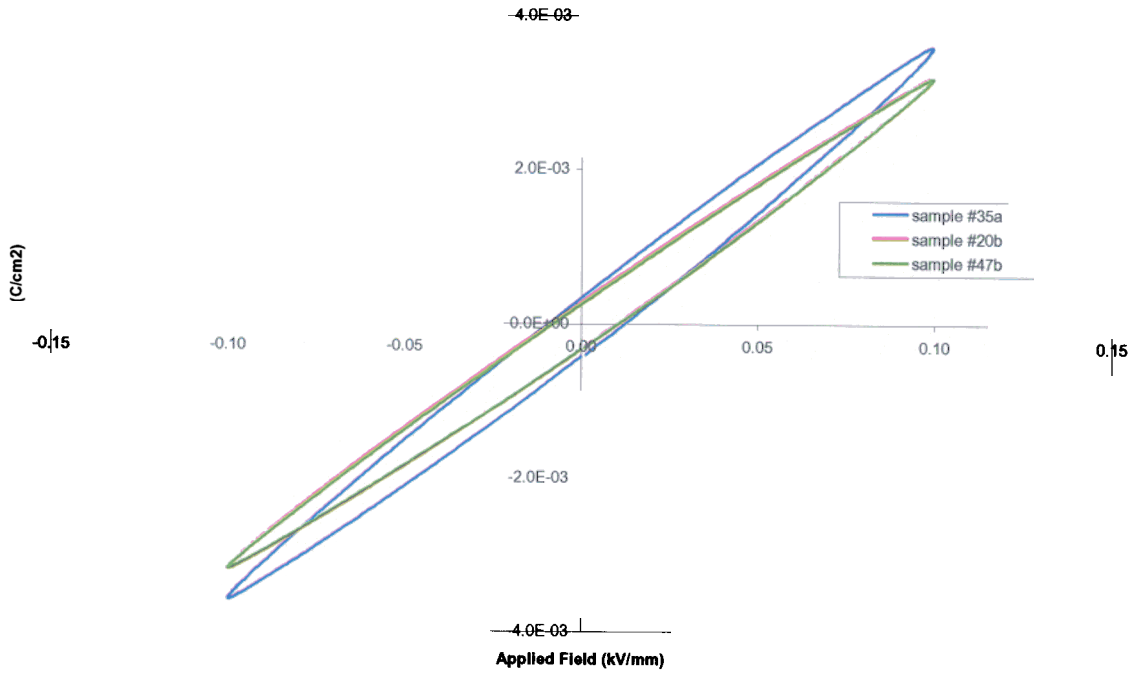


Figure 8 PE loops at 0.1kV/mm

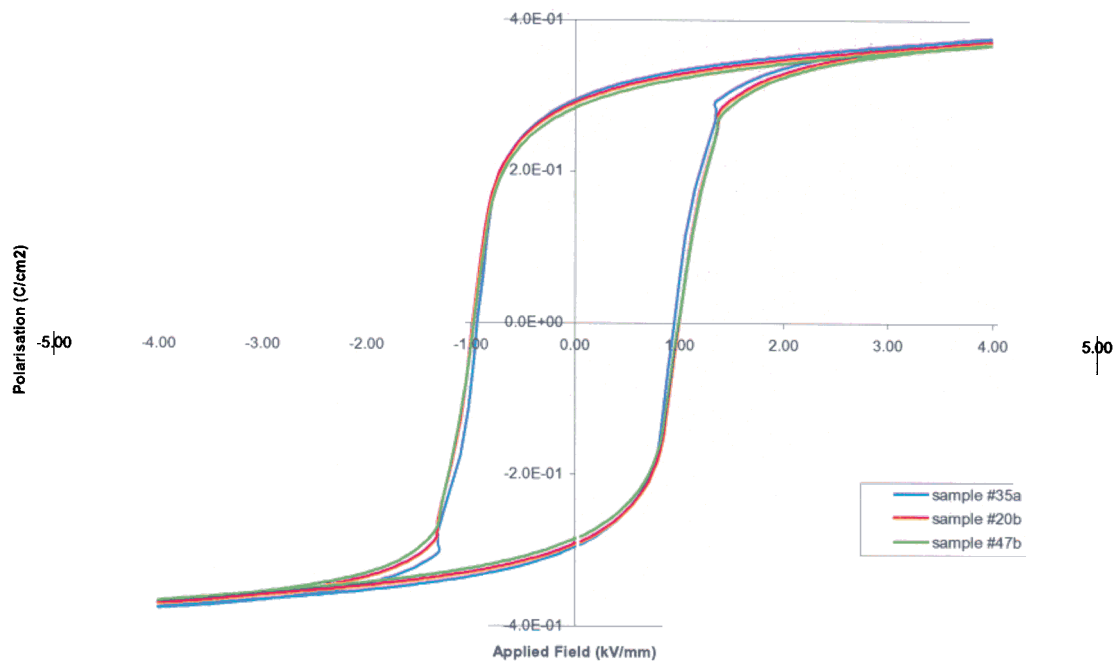


Figure 9 PE loops at 4kV/mm

PE loop measurements were carried out at 1Hz, from 0.1kV/mm to 4kV/mm, using the NPL PeHyst measurement system, which can then extract the relevant parameters from the PE

loops. Figure 8 and Figure 9 show the PE loops for the maximum and minimum field levels applied for three of the samples. At 0.1kV/mm the material is behaving as a lossy capacitor, the slope of the PE loop at any point is the permittivity of the sample, and the dielectric loss can be determined from the area within the loop. Figure 10 shows the permittivity determined by PeHyst and it is clear from this that sample 35a is different, exhibiting a higher permittivity at the lower field levels, and only when the polarisation saturates at around 1.5kV does the permittivity level approach that of the other samples. There is a strong correlation between the low field permittivity at measured at 1V/mm using an impedance analyser and the high field permittivity as determined by PeHyst, even though the behaviour at the high field level is non linear, Figure 11.

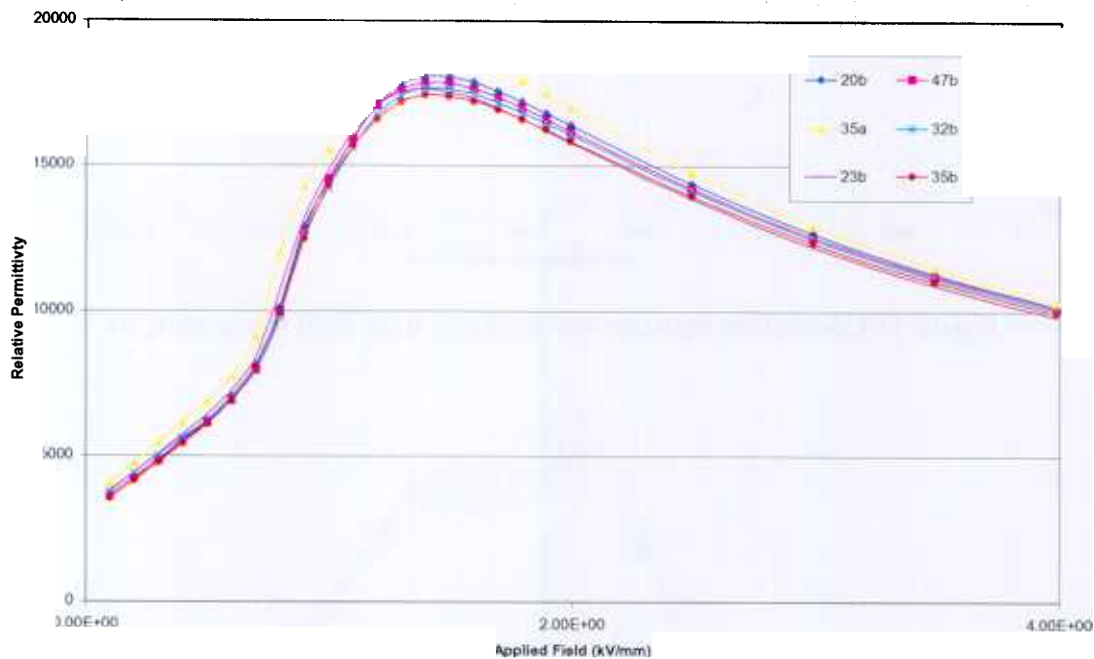


Figure 10 Relative permittivity as a function of applied field as determined by PeHyst

At 4kV/mm however all the samples show similar saturation polarisation, which suggests one of two things

- The samples are identical but one has been poled differently, suggesting that improving the poling process could improve the properties of the others.
- The saturation polarisation is the same for all samples but one sample has a different texture enabling it to maintain the remnant polarisation state

The crystallographic texture of the samples was investigated using x-ray diffraction, simply by dissolving off the silver electrodes using nitric acid, and performing an analysis of the exposed surface of the disc. The resultant scans, Figure 12, show little difference between the various samples, i.e. the poled texture of the samples is similar. Of course the x-ray diffraction only gives information from the surface of the disc, whereas the electrical measurements depend on the bulk properties.

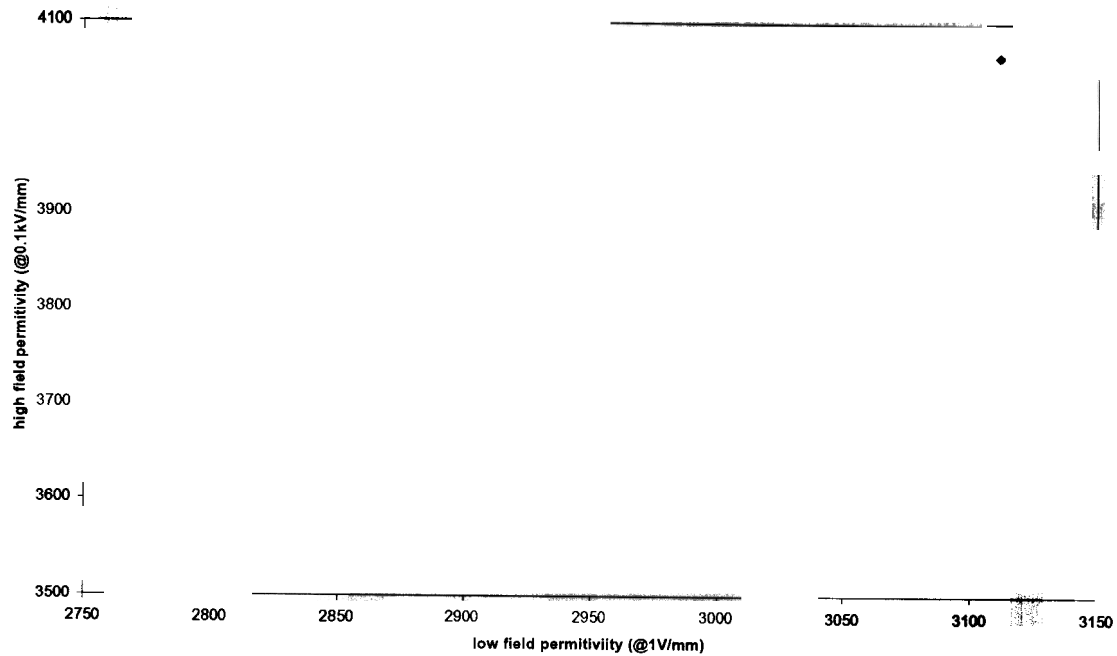


Figure 1 Correlation between low field and high field measurements

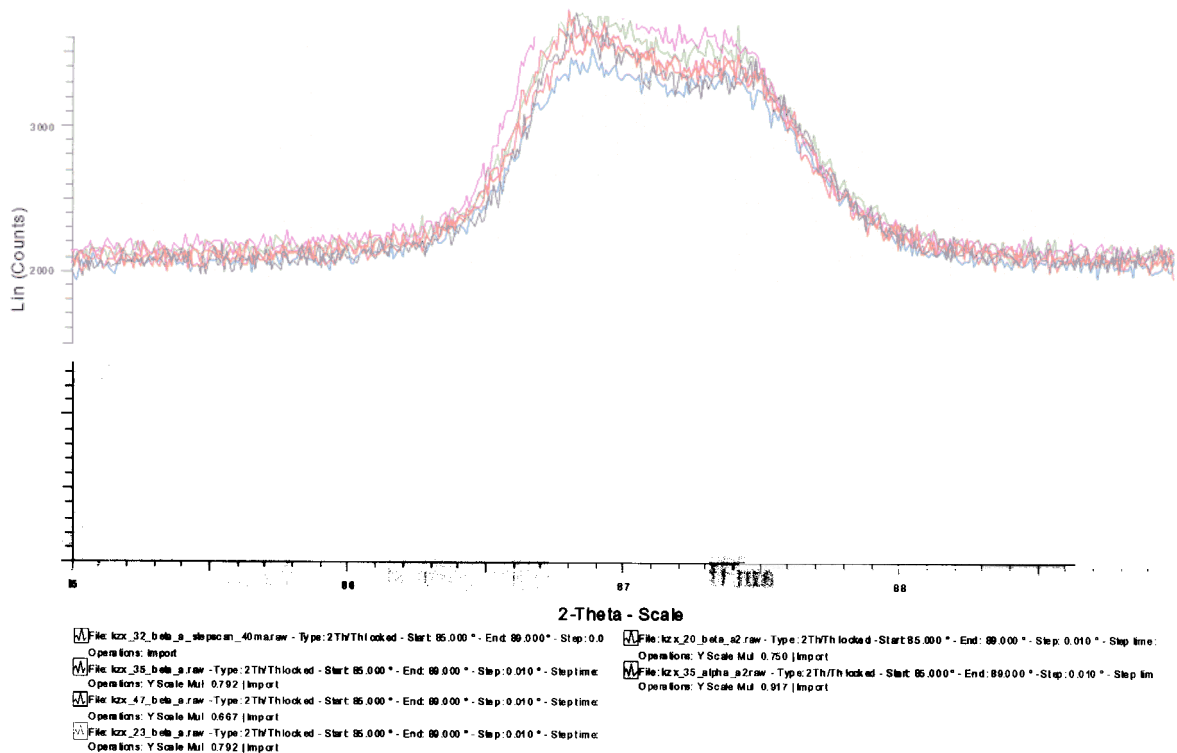


Figure 12 X-ray diffraction patterns from samples after PE loop measurements

When the electrodes were removed from the samples, some of the samples showed surface marks, that on closer inspection were holes through the thickness of the discs. At first they were thought to be due to electrical breakdown of the samples during the PE measurements, but there was no evidence of breakdown during the PE measurements, and low field measurements showed little change after the PE measurements. This means the 'breakdown'

damage was introduced in manufacture, during poling. Investigation of the other samples showed these marks without PE loop measurements, in as received samples. Normally this kind of breakdown results in a short circuit, however the samples appear to behave as those without the marks. The two samples from the nine selected that exhibited these breakdown pin holes were 35a, the sample with the highest permittivity and high Berlincourt, and sample 32b, which also had a high Berlincourt d_{33} . If these pinholes occurred during the poling process it is possible that they could have led to a different poling field, leading to the increased activity. Of the 98 samples in this batch, only one other sample showed pinholes that could be seen on the electroded sample.



Figure 13 Pinhole in sample #35a probably caused by breakdown during poling

CONCLUSION

Investigations into the variability of piezoelectric materials measurements have highlighted several areas where weaknesses in the measurement methods result in high variability, and also show that good correlation between piezoelectric parameters allow simpler measurement methods to be used.

The Berlincourt method has been shown to be unreliable when testing thin discs, however when testing thicker samples there is a good correlation between this and other methods. Use of resonance to determine materials parameters can be extended outside the 'ideal' geometries, provided that other resonance modes do not grossly interfere with the dominant

resonance peak.

The high field permittivity and low field permittivity correlate well, so tolerances on low field measurements would predict high field performance. However the piezoelectric activity measured by the Berlincourt method, and high field permittivity do not follow the same trend, although they should both be dependant on the same microscopic mechanisms.

In trying to identify microstructural origins of samples that behave differently to others within a batch, no direct evidence was found to suggest that outliers originate from either porosity or crystallography. PE loop measurements were used as a method of detecting differences in the poled state of samples, however the saturation polarisation was similar for most of the samples. Interestingly some of the samples chosen as maximum outliers showed pin-holes, probably from electrical breakdown during poling, where these defects would ordinarily be detrimental to piezoelectric output.

Most of the microstructural measurement techniques used in this work were localised, such as microscopy and X-ray diffraction, and so it is difficult to detect differences over the whole sample, whereas most of the electrical measurements are an average of the whole sample. In future, bulk methods such as neutrons or X-ray synchrotron could be used to measure the bulk crystallography, and texture.

REFERENCES

- 1 NPL Good Practice Guide No 44, Measuring Piezoelectric d_{33} coefficients using the Direct Method
2. PRAP, Piezoelectric Resonance Analysis Program, software from TASI, <http://www.tasitechnical.com>

ACKNOWLEDGEMENTS

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