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CPM8.1 Task 6:
Evaluation of New Functional Materials

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ABSTRACT

A PMN-PT relaxor electrostrictive and a single crystal PZN-4.5%PT have been evaluated using a range of high and low field piezoelectric characterisation techniques. The performance of electrostrictives under high AC fields gives similar output to a soft PZT. The single crystal exhibited piezoelectric activity 2-3 times that of a soft PZT composition, and the maximum achievable strain was almost an order of magnitude greater. A 95/5 PZT material exhibited a field induced phase transition from antiferroelectric to ferroelectric at around 3.5kV/mm and is associated with a strain of around 0.16%. The fields needed to achieve this strain are close to the breakdown strength of the material of around 8kV/mm.

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1 INTRODUCTION

The current interest in functional materials has led to renewed interest in some previously established materials and also to the discovery and production of newer materials with improved functionality. The previous DTI sponsored functional materials work at NPL has up to now concentrated on commercially available lead zirconate titanate (PZT) compositions, and the purpose of this task is to evaluate some of these newer materials using the expertise and test methods developed in this and earlier programs.

The initial phase of this task was to carry out a survey of potential new materials[1], and this highlighted several classes of materials that have potentially been overlooked or not recognized by UK industry. One of the problems for this task was that because many of these materials are not in commercial production they have been difficult to source. The materials examined in this study were an electrostrictive composition, an AFE-FE phase change material, and a single crystal sample.

2 RESULTS AND DISCUSSION

ELECTROSTRICTIVE MATERIAL

An electrostrictive relaxor composition was obtained from Morgan Electroceramic, a lead magnesium niobate with 10% lead titanate, (PMN-PT). The samples were rectangular rods 20mm long with fired silver electrodes on the 2mm square ends. The samples were light green in colour, very different to the tan or grey colour of most PZT formulations, most probably due to the niobium. The sample density was around 7600 kg/m^3, and the microstructure of the material is shown in figure 1. The material is electrostrictive but not piezoelectric, so as expected there was no measurable d_{33} coefficient using a Berlincourt type meter.

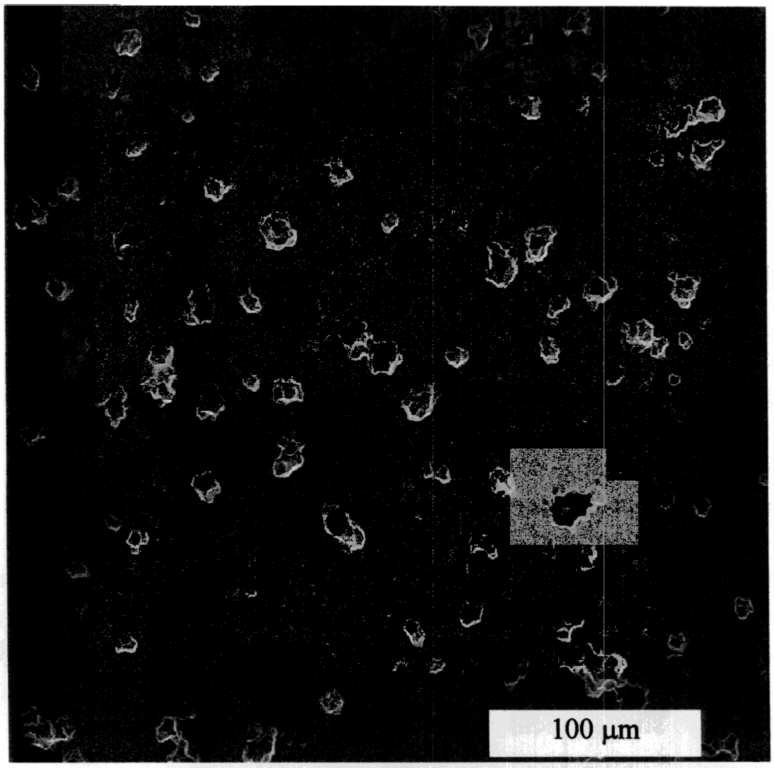

Figure Microstructure of electrostrictive PMN-PT material

The relaxor materials have very high relative permittivity, the room temperature relative permittivity at 1 kHz was around 17,000. A characteristic of relaxor behaviour is the temperature and frequency dependence of the permittivity. Figure 2 shows the dielectric behaviour of the material from –5 to +90°C. The permittivity shows a broad peak around 40°C, which is frequency dependent, going to lower temperatures with decreasing frequency, and the dielectric loss shows a step change going from high loss at low temperature to low loss at higher temperatures. This transition temperature is called T_m, the temperature of maximum permittivity, and is equivalent to the Curie temperature T_c in a piezoelectric material. The measurements were obtained with a Solartron 1260 Gain Phase Analyser with a 1296 dielectric interface, and the temperature maintained in an Environmental chamber. The dielectric measurements were integrated for a fixed time, rather than number of cycles, so the loss data for the low frequency measurements is therefore much noisier, but the trend can be seen.

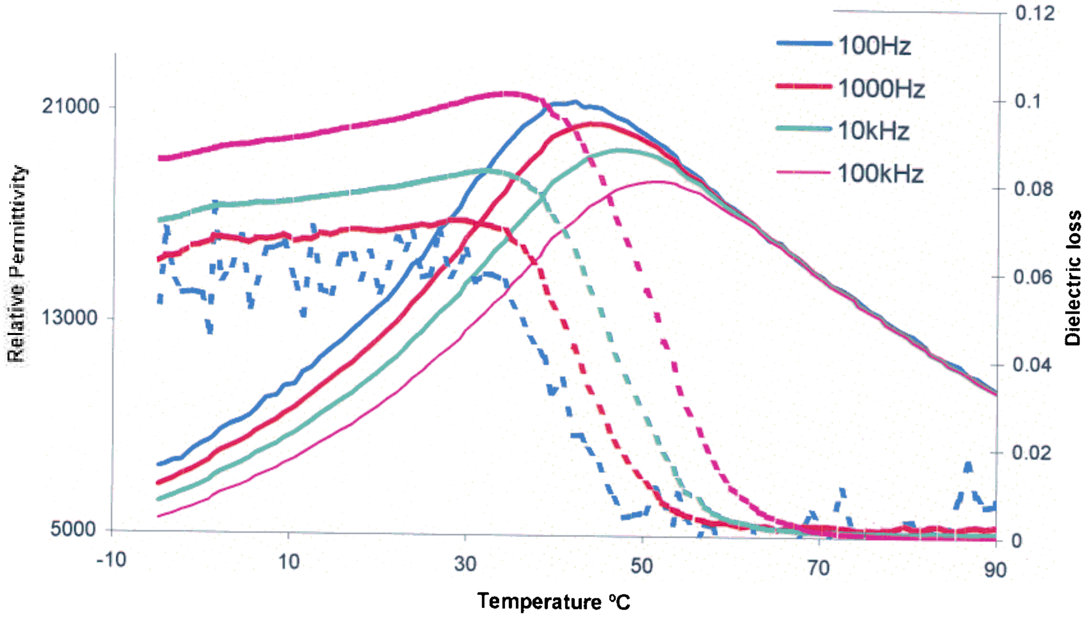

Figure 2 Dielectric behaviour of PMN-PT electrostricitive material as a function of temperature (full line relative permittivity, dashed line - dielectric loss).

It is normal practice with piezoelectric samples to perform an impedance sweep, and from the resonant behaviour of a well-defined sample shape, determine various electromechanical parameters. A low field impedance sweep using the gain phase analyser showed purely capacitative behaviour, without sample dependent resonant peaks. If electrostrictive materials are electrically biased they will exhibit piezoelectric like behaviour, so an impedance sweep was performed using a bias of 750V. Unfortunately, because of the long aspect ratio of the sample shape, this still only represents a DC bias of 37.5V/mm, and as will be seen later this is not sufficient to induce significant piezoelectric behaviour, therefore no resonant behaviour was seen in the impedance sweep. The high bias measurement set-up on the Solartron system was configured as suggested in the equipment user manual^2 with a large capacitor to block the high DC bias from the sensitive measuring electronics of the 1296. The efficacy of the system was tested on a soft PZT sample, thickness 1mm, where the application of the 750V bias was found to show a measurable change in the impedance sweep.

In order to investigate the high field behaviour of the material a polarization-strain-field measurement system, PeHys[3] developed under DTI program CAM7, was used. This set of software routines was designed to apply a high voltage to piezoelectric samples and measure the current and strain thus obtained, and based on these measurements determine several dielectric and piezoelectric constants. Figure 3 shows a set of polarization field loops taken at 10Hz using a bipolar drive of fields up to 0.35kV/mm, and shows the material behaves like a lossy capacitor. From this, the software can determine the permittivity based on the slope of the PE loop, and the loss based on the area of the loop, figure 4. The values for the high field permittivity and loss are broadly consistent with the low field measurements using the gain phase analyser. However it can be seen that the permittivity is highly dependent on the AC field, and the loss seems to decrease with increasing AC field.

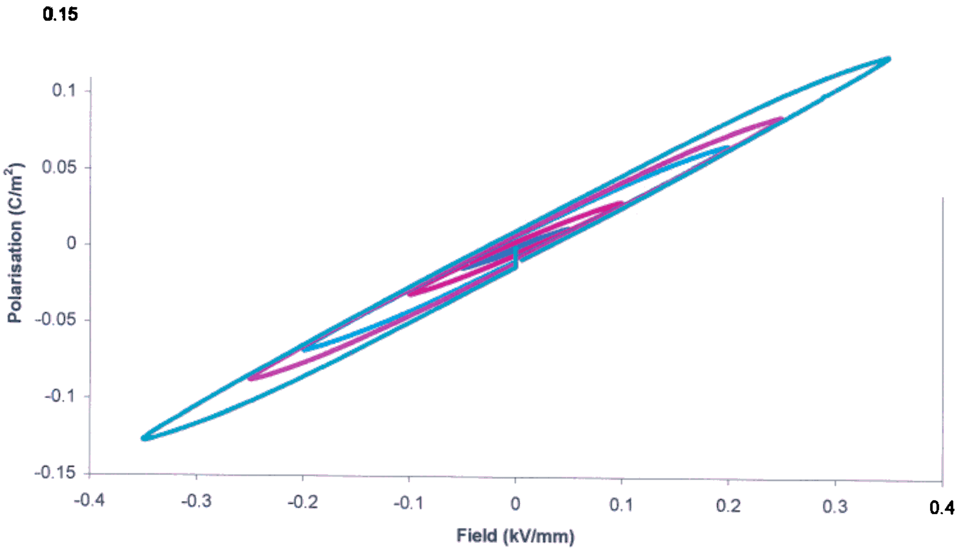

Figure 3 Polarisation Field loops for electrostrictive material at 1Hz.

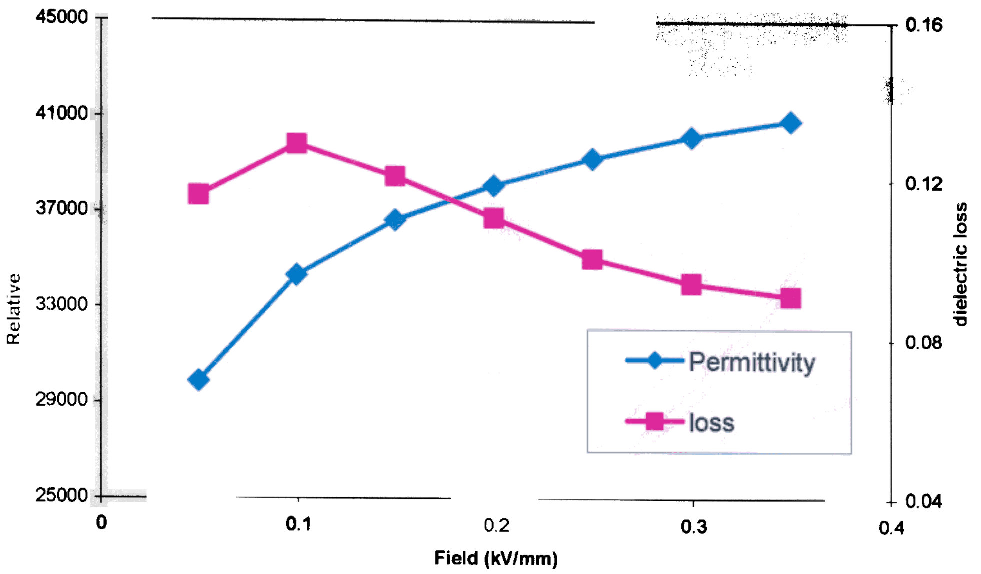

Figure 4 Relative permittivity and loss values calculated by PeHys software using PE loops from figure 3.

The PeHys can also simultaneously accept data from a strain measurement system; in this case a capacitance gauge based system with a range of 100 micrometres and an analogue output of 10μm/V. The results, figure 5, show the electrostrictive nature of the material, the behaviour is symmetrical about zero applied field, and the quadratic nature means there is very little output at low fields. The PeHys software could not be used to determine effective piezoelectric constants because the method of determination is based on the gradient of the line between maximum and minimum applied field. The software could potentially be

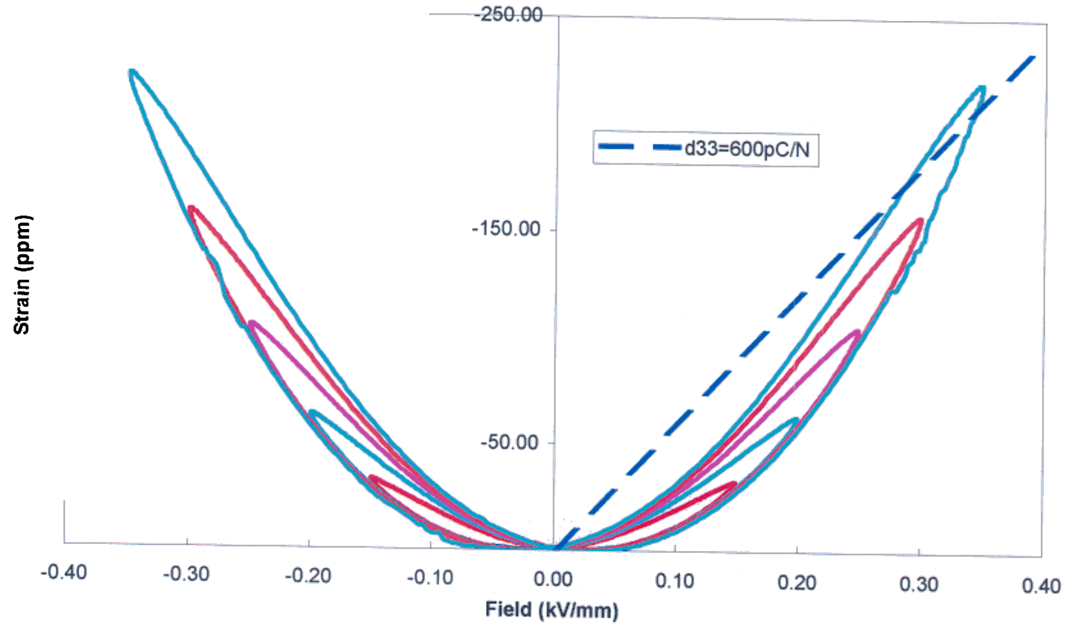

Figure 5 Strain-Field data for electrostrictive material at 1Hz. Dashed line represents a d_{33} of 600pC/N.

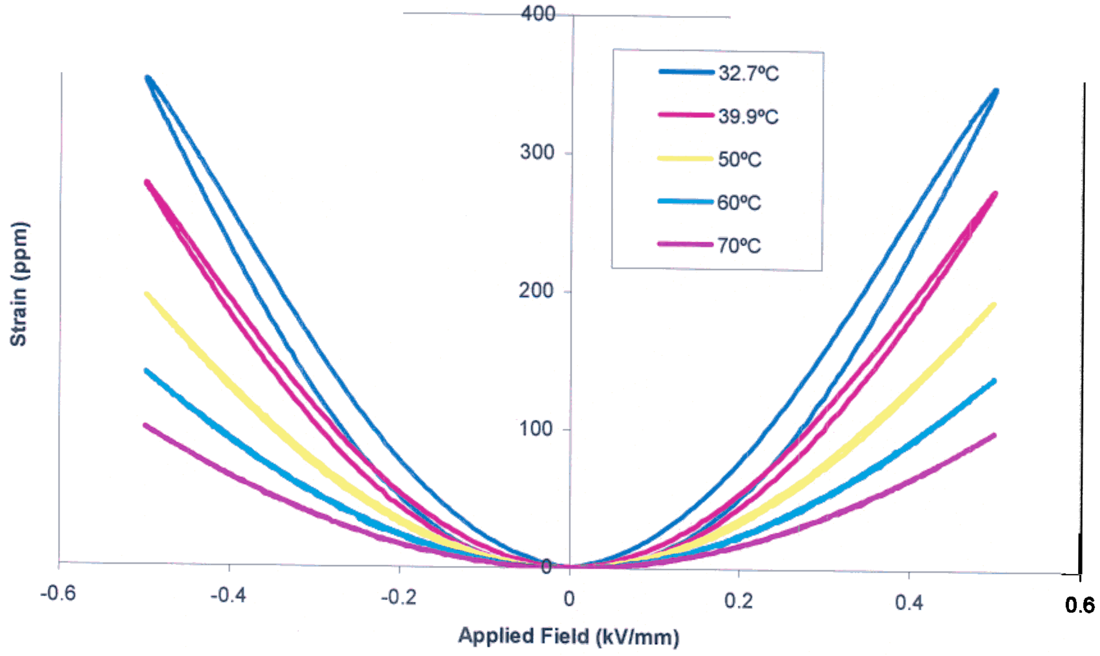

Figure 6 High field Strain Field for electrostrictive material as a function of temperature.

modified to determine the instantaneous gradient over the entire loop. Figure 5 also shows a straight line, representing the strain output of a piezoelectric material with a d_{33} of 600pC/N. As can be seen this would give a broadly comparative output over the range. However because of the quadratic field dependence of the electrostrictive materials, driving around a minor loop at a bias of around 0.35kV/mm would give a much increased d_{33} value. The material also shows a considerable piezoelectric loss when operated over this major loop, however it may be that a minor loop at a 0.35kV bias reduces this.

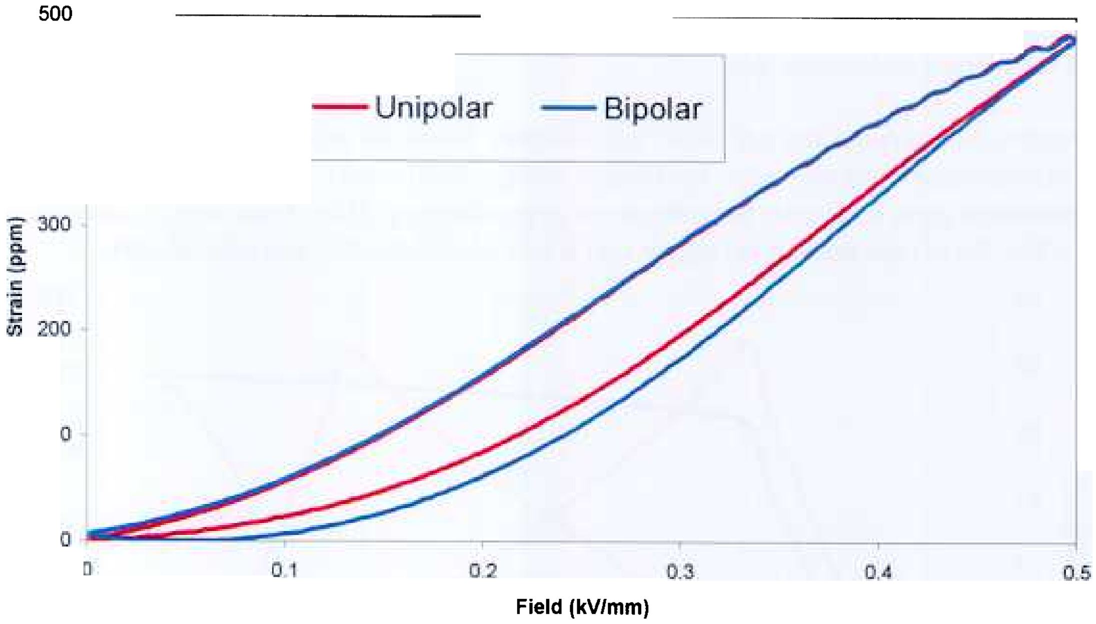

Figure 7 Comparison of unipolar and bipolar drive fields on electrostrictive material at 1Hz.

As was seen from the dielectric measurements at temperature, the relaxor material is highly temperature dependent. The high field strain measurements can also be carried out as a function of temperature, figure 6. This shows similar behaviour to the dielectric measurements, with the loss decreasing with increasing temperature, but unfortunately so does the strain output.

Most of the measurements were carried out using bipolar drive, but some measurements used unipolar drive, and a comparison of the strain output is shown in figure 7. There is a slight difference between the two, but because of the electrostrictive nature of the material this should not be the case. It may be that there is a slight phase lag associated with the reversal of the electric field. There is also a repeatable ripple at high fields in both the unipolar and bipolar drives. This is not aliasing or digitisation errors, but may be a ringing from when the sample has to change strain direction.

SINGLE CRYSTAL MATERIAL

A lead zinc niobate - lead titanate single crystal PZN-4.5%PT was obtained from TRS Ceramics. Although PZT single crystals cannot be grown, recent advances in the growth of relaxor compositions have yielded single crystals of considerable size[4,5,6]. Most of the crystal growth work has concentrated on the PZN-PT system, as it is easier to grow uniform crystals because of the low PT content. The rectangular crystal was 2.77mm thick, with gold coated electrodes on 5mm square faces. The crystal was translucent, with a density of 8260kg/m^3. The 4.5%PT composition is in the rhombohedral region on the PZN-PT phase diagram, with the morphotropic phase boundary (MPB) being about 9.5% PT at room temperature. Above this the tetragonal phase is more stable. The MPB in this system is much more temperature dependent than in the piezoelectric PZT system, and from the work of Shrout[6] it does not appear necessary to use compositions near the MPB to obtain maximum activity. The crystal orientation was <100>, and this is reported to give the highest activity, even though the <111> direction is the polar axis.

As received the crystal did not show any resonant peaks on an impedance sweep, and there was no measurable piezoelectric coefficient using a Berlincourt meter. The 1kHz capacitance measurement gave a relative permittivity of approximately 2200. From this it was concluded that either the crystal needed poling, or that it was electrostrictive not piezoelectric.

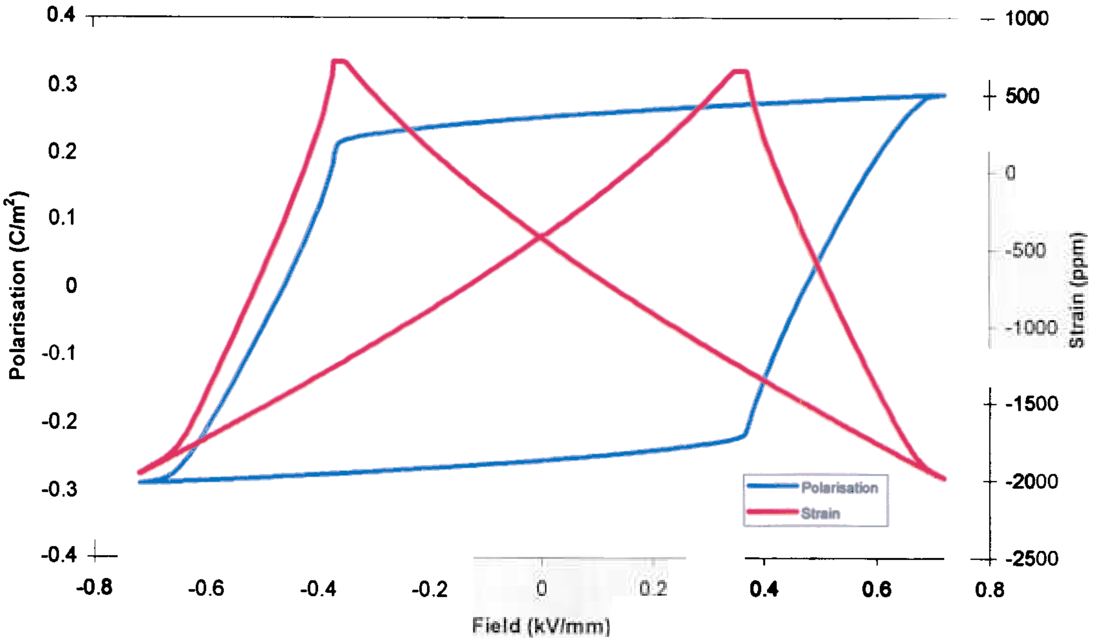

Figure 8 Polarisation and Strain field data for PZN-4.5%PT single crystal at 1Hz

High field experiments using the PeHys system confirmed the piezoelectric nature of the material, figure 8, showing a butterfly loop, and a square polarization loop. The as received crystal was unpoled, and the application of a high field has poled the crystal, even if the bipolar field has alternately poled and depoled the crystal. On a second application of a bipolar field, lower than the final poling field in the first experiment, the crystal shows increased strain output, and is reasonably linear, figure 9. As the field increases the crystal depoles and is once again poled and repoled by the bipolar field, giving a butterfly loop again. After these initial experiments the sample was removed and examined using low field measurements. The Berlincourt meter now gave a d_{33} of around 1400pC/N, however this is less than the claimed values of around 2000pC/N. This may because the material is sensitive to the static preloads necessary for the Berlincourt measurement. A low field impedance sweep using a HP4292A impedance analyser now gave several resonant peaks, although because of the aspect ratio of the sample it was not possible to determine piezoelectric coefficients from this.

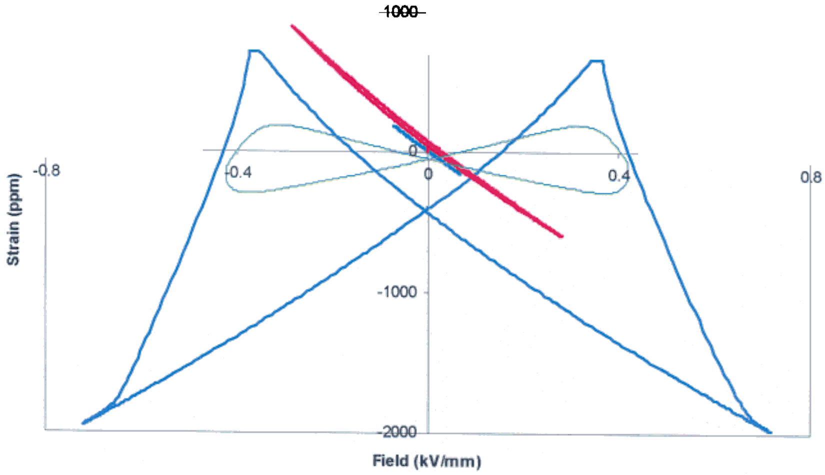

Figure 9 Strain field data for PZN-4.5%PT single crystal at 1Hz.

The previous high field experiments were carried out in air, thus limiting the maximum applied field to around 1kV/mm. This gave a strain output of approximately 2500ppm, but in order to achieve the claimed strain levels of 1%, higher fields are needed which necessitate performing the measurements in insulating oil. The capacitance measurement set up was such that the gauge was remote from the sample, contacted by a set of leaf springs. This meant it was possible to cover the sample with oil yet still maintain the capacitance gauge air gap. Figure 10 shows the strain output for voltages up to 10kV applied across the sample thickness. The strain output is significantly increased to almost 1%, but there is also increased non linear behaviour. The opening up of the loops is probably associated with the change to tetragonal phase. If the temperature is increased to 90°C, figure 11, this phase change occurs more readily and the loop opens out at much lower fields, as the increase in temperature pushes the material closer to the MPB.

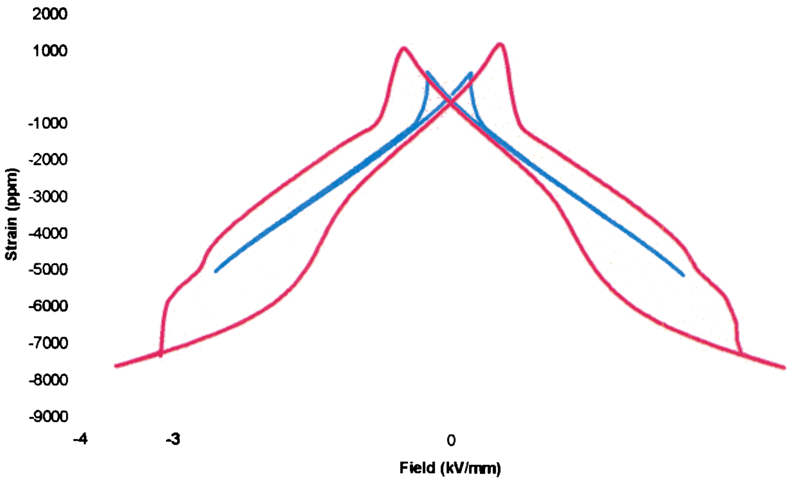

Figure 10 Strain field data for PZN-4.5%PT single crystal at 1Hz at increased fields in oil bath. Room Temperature

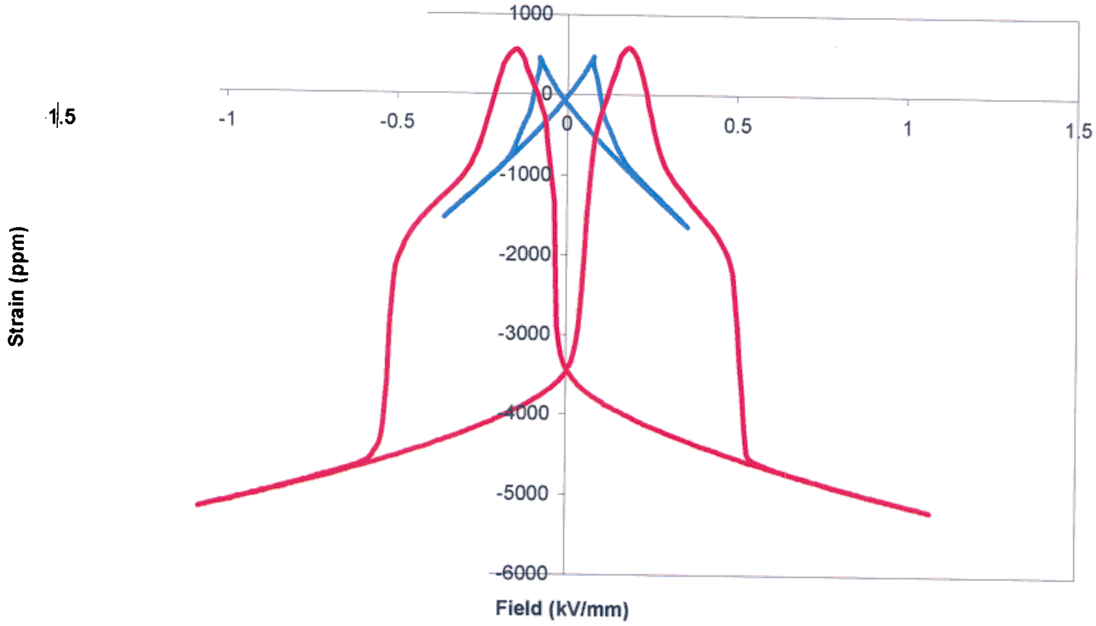

Figure 11 Strain field data for PZN-4.5%PT single crystal at 1Hz at increased fields in oil bath. Temperature = 90°C

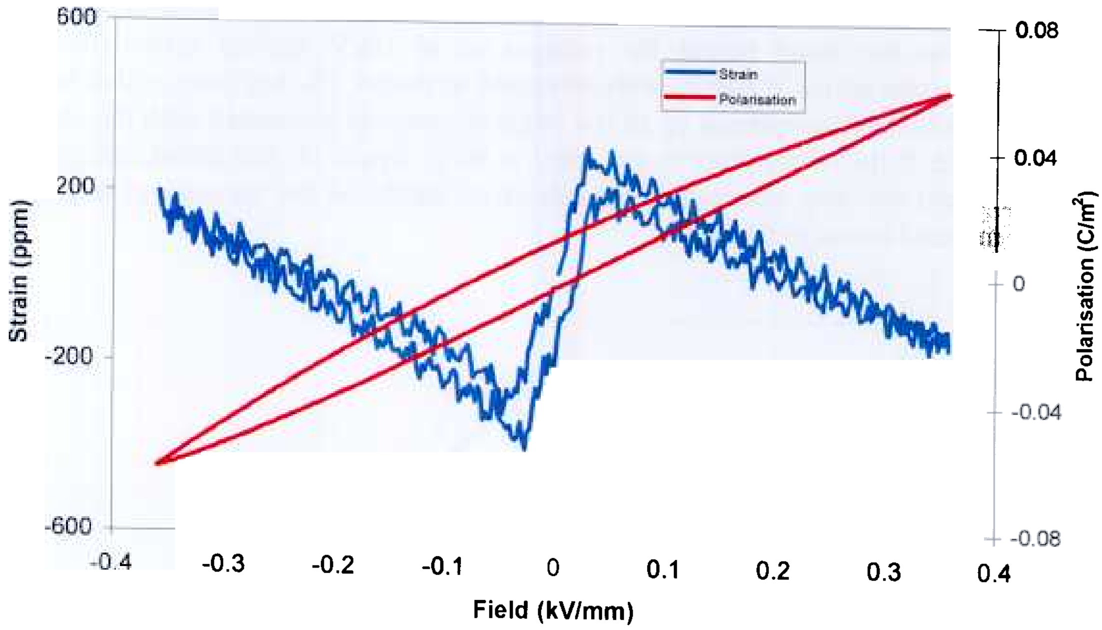

Figure 12 Strain field data for PZN-4.5%PT single crystal at 1Hz after high voltage bipolar cycling

After cooling the sample back to room temperature the crystal no longer gave a high strain output and the strain was very disjointed, figure 12. The Berlincourt value had been reduced to 1250pC/N and the resonance behaviour had been changed, figure 13. On inspection of the crystal it was seen to have extensive cracking, figure 14, although the sample was still in one piece. It appears that due to the high strains, and particularly the bipolar operation has caused mechanical failure of the crystal, and although the individual parts of the crystal are still poled, leading to a high Berlincourt d_{33}, the resonance and strain output are damped by the cracks. This behaviour in high field bipolar drive has been seen by Wan[7].

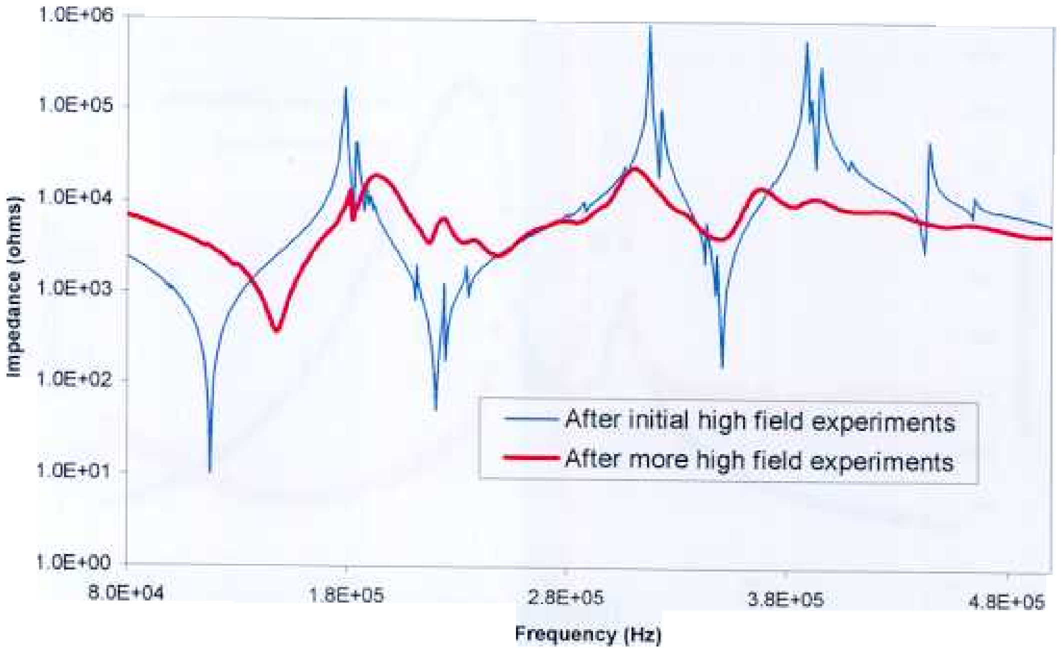

Figure 13 Impedance frequency sweep of PZN-4.5%PT single crystal, before and after high field experiments.

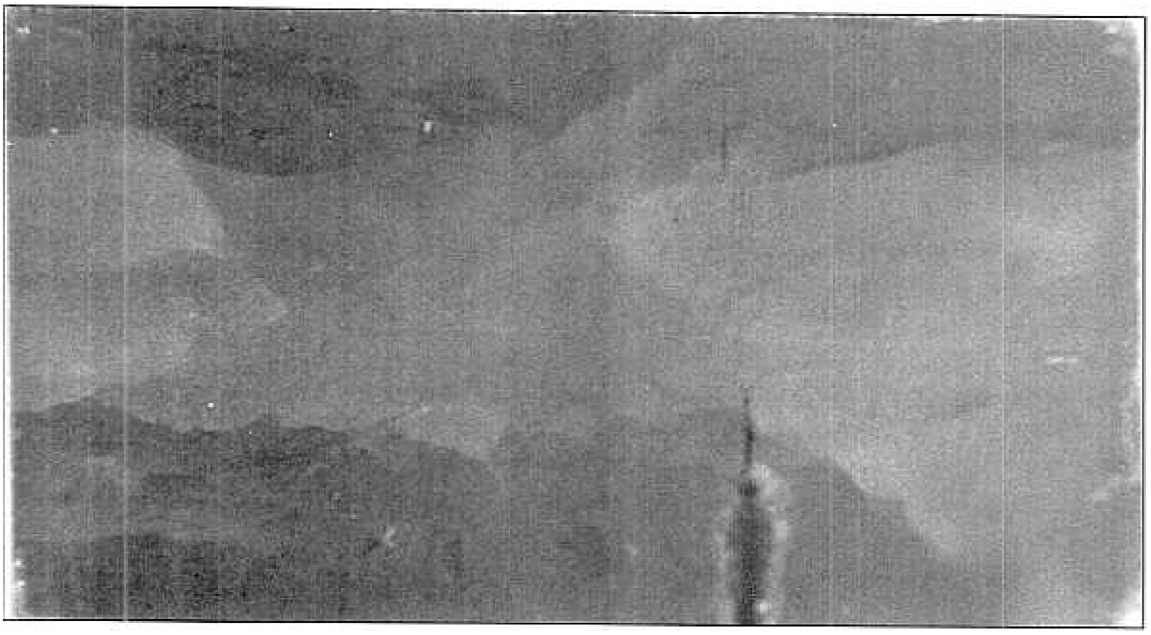

Figure 14 Cracks in PZN-4.5%PT single crystal after high voltage bipolar cycling. Full image width =5mm

Although the crystal was extensively damaged it could still be used for a low field dielectric study. Figure 15 shows the relative permittivity and loss as a function of temperature from 30 to 250°C. This shows two peaks, one at around 120°C associated with the rhombohedral to tetragonal phase transition, and the second at around 160°C is the Curie temperature T_c. As a consequence of this experiment the sample was depoled and no longer gave a reading on the Berlincourt meter.

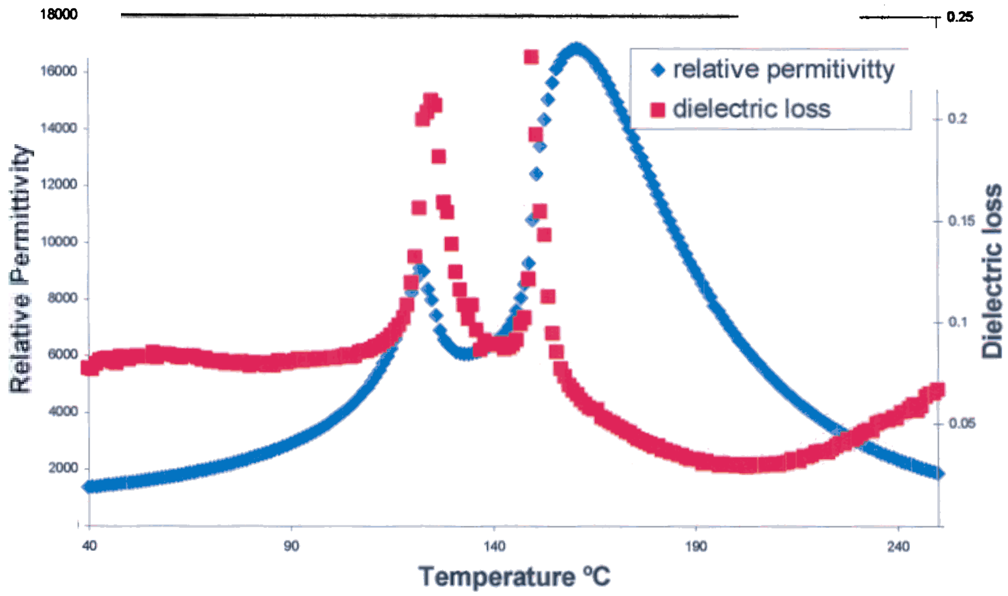

Figure 15 Low field Permittivity and loss as a function of temperature for PZN-4.5%PT single crystal.

PHASE CHANGE MATERIAL

A 95/5 PZT antiferroelectric to ferroelectric (AFE-FE) sample was obtained through AWE Aldermaston. The AFE-FE phase change materials can be used as either an actuator if it is field induced[8,9], or as a power source if it is stress induced[10]. The disk shaped sample 7mm diameter, 1mm thick, had a density of around 8200kg/m^3, and was electroded with graphite from a pencil. In its antiferroelectric state the sample has no overall polarisation and so does not give a reading on the Berlincourt meter or resonate if driven electrically.

When the sample is driven at modest field levels the sample behaves like a lossy capacitor, with elliptical P-E loops, figure 16. The permittivity is around 1500 with a loss of approximately 0.1, which is field independent for these field levels, i.e. the PE loops have the same gradient. Compare this with the electrostrictive material, figure 4, where the loops rotate anticlockwise with increasing fields. At levels below 1kV/mm there is no measurable displacement, using the present displacement measurement set-up.

At higher fields the phase change starts to occur, and this is evidenced by the appearance of a double PE loop, figure 17. At a field of around 3kV/mm the AFE-FE phase change occurs, leading to a large jump in the polarisation, and it is not until the voltage is taken back down to less than 2kV/mm does the material switch back to its antiferroelectric state. This behaviour is mirrored when the field direction is reversed. The phase change is associated with a volume change, figure 18 shows the longitudinal strain produced as result, which is of the order 1200ppm. As the field increases above this, the strain is still increasing, however at a much reduced rate. This is now probably associated with piezoelectric behaviour in the ferroelectric phase, rather than the AFE-FE phase change. The maximum strain for this sample was around 0.16% for an applied field of 6kV/mm, which is much less than the strains of almost 0.8% achieved in some AFE-FE compositions. However this strain was achieved at fields of over 20kV/mm, and is thought to be associated with a second field induced phase transformation. The material in this study was taken to higher fields but was limited to 8kV/mm by the breakdown of the sample, with no evidence of any further phase transformations.

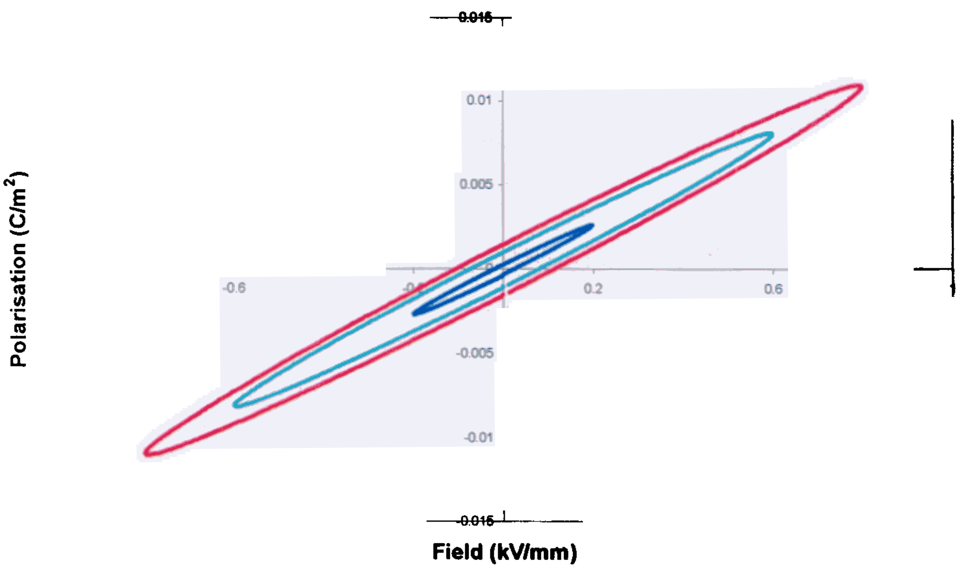

Figure 16 PE loops for phase change material for modest field levels at 1Hz

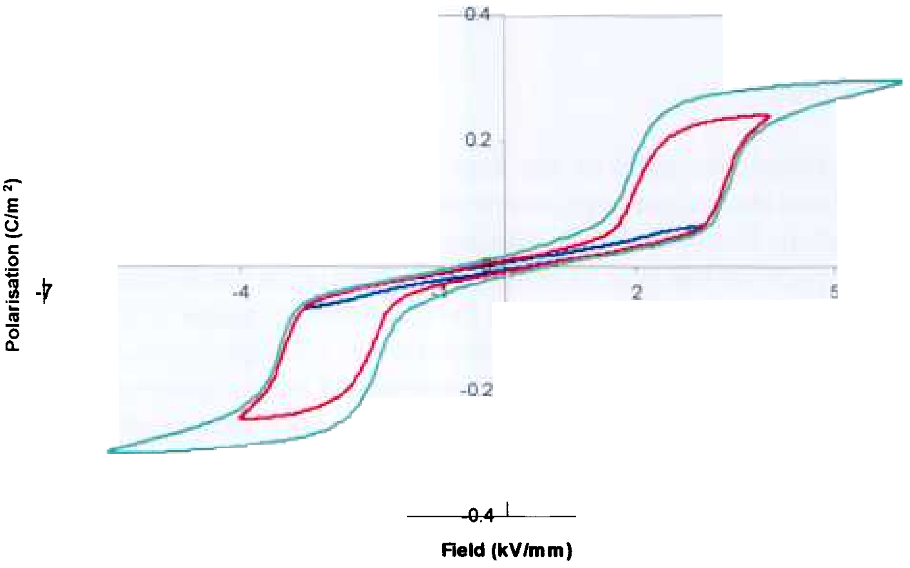

Figure 17 Polarisation field loops of phase change material at 1Hz performed in oil at room temperature.

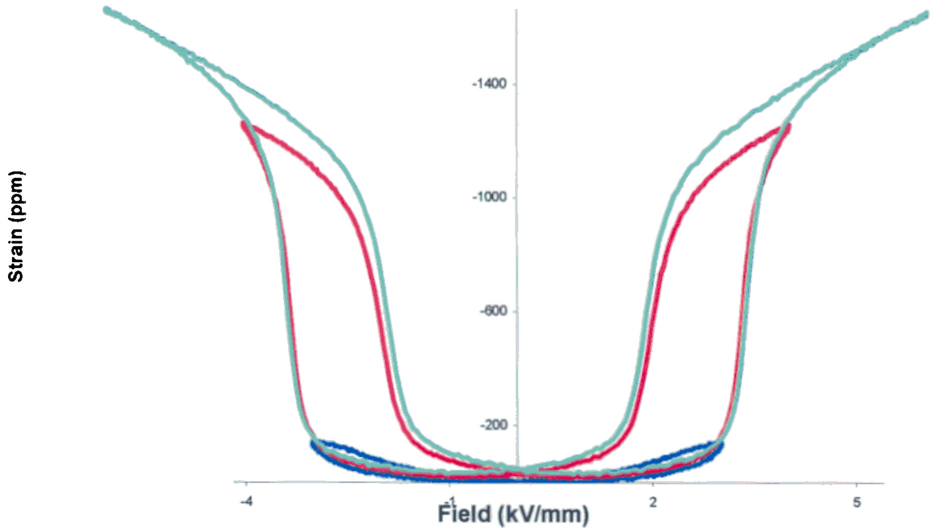

Figure 18 Strain field behaviour of phase change material at 1Hz in oil bath at room temperature.

As a potential actuator material this is slightly disappointing, in that the overall strain-field behaviour corresponds to a d33 of approximately 270pC/N. Of course as in the case of the electrostrictive it is not necessary to drive the material from zero to the switching field, but there is still a hysteresis of around 1.5kV/mm between switching on and off. Another disadvantage of this type of actuator material is that there is virtually no control over intermediate strain states, which is one of the features of using a piezoelectric actuation. The application would have to be such that the actuation is digital.

3 CONCLUSION

ELECTROSTRICTIVE

The PMN-PT electrostrictive material has been examined using a variety of measurement techniques. It has been shown that large strains are possible under a high field, equivalent to a soft PZT composition, however this is associated with a considerable hysteresis. A more suitable operating mode for this type of material would be under small signal drive, but under a high DC bias to get the material operating in the piezoelectric regime. The large temperature dependence of the material could also be a disadvantage, although the lower loss means that self heating is not such a problem. The high permittivity of relaxor materials can also present a problem to the drive electronics for these types of actuators because of the larger current requirements.

From the perspective of the measurement techniques most of the methods have proven useful in examining this class of material. It is clear that the models used in the PeHys software to derive the various coefficients must be modified to accommodate the quadratic nature of electrostrictive behaviour. The impedance analysis system was modified to operate under high DC bias, however shorter samples, giving higher fields, are needed for it to function on the electrostrictive material.

SINGLE CRYSTAL

A PZN-4.5%PT single crystal has been evaluated using a variety of high and low field techniques. The piezoelectric output of the crystal is two or three times the output of the most active PZT material, and because of the higher breakdown strength, the achievable strains are almost an order of magnitude greater. However from these experiments it is evident that these large strains are deleterious to the material, and therefore bipolar operation should be avoided. The main problem with these materials at present is the difficulty of obtaining them, and their expense. No doubt as production increases availability will increase and cost decrease, however it is still likely they will be used in small high added value devices, such as medical transducers.

AFE-FE PHASE CHANGE

The 95/5 PZT material exhibits a field induced phase transition from antiferroelectric to ferroelectric at around 3.5kV/mm and is associated with a strain of around 0.16%. The fields needed to achieve this strain are close to the breakdown strength of the material, so significant improvements in the ceramic defect microstructure are needed to improve the performance. In addition this mode of actuation does not give the close control of strain associated with piezoelectrics, but is an on-off operation.

ACKNOWLEDGEMENTS

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