

**FIFTH INTERNATIONAL CONGRESS ON SOUND AND VIBRATION**

DECEMBER 15-18, 1997  
ADELAIDE, SOUTH AUSTRALIA

*Invited Paper*

**CHARACTERISATION OF PIEZOELECTRIC AND  
ELECTROSTRICTIVE MATERIALS FOR ACOUSTIC  
TRANSDUCERS: II. QUASISTATIC METHODS**

*B.K. MUKHERJEE AND S. SHERRIT*

Department of Physics, Royal Military College of Canada,  
Kingston, Ontario, Canada K7K 7B4.

**ABSTRACT**

Piezoelectric transducers are frequently used as acoustic sensors and projectors as well as in active methods of vibration control. Their proper utilisation requires a good understanding of the non-linear properties of the material. Quasistatic experiments have been developed to determine the dependence of the more important material constants on the temperature and on the levels of voltage and stress applied singly or simultaneously to the material. The response time of the piezoelectric effect has been studied and it has been found that the observations can be understood by assuming that the domain wall movements in the material are governed by a distribution of activation energies. More recently, high strain electrostrictive materials have been developed and these are inherently non-linear. Many of the above experiments can be used to characterise these materials as well.

**INTRODUCTION**

Piezoelectric and electrostrictive materials are frequently used as the active material in acoustic transducers, which are used as sensors, actuators or as part of smart structures. Piezoelectric materials produce a strain  $S$ , under the influence of an external electric field,  $E$ , or become electrically polarised under the influence of an external stress,  $T$ . The direct and converse piezoelectric effects are often described by a set of linear constitutive relations<sup>1</sup>; one example of such a set couples the electromechanical behaviour to the stress-strain and the displacement-field relationships:

$$S_p = s_{pq}^E T_q + d_{pm} E_m \quad \text{and} \quad D_m = \epsilon_{mn}^T E_n + d_{pm} T_p, \quad (1)$$

where  $D$  is the electric displacement,  $s$  is the elastic compliance,  $d$  is a piezoelectric constant and  $\epsilon$  is the dielectric permittivity. The superscripts of the constants designate the independent variable that is held constant when defining the material coefficient and the subscripts define tensor directions that take into account the anisotropic nature of the material. The elements of the tensor form a  $9 \times 9$  matrix with 1,2,3 designating the orthonormal directions (3 is the poling direction) and 4,5,6 designating the shear directions. For the commonly used polycrystalline piezoelectric ceramic materials with  $C_\infty$  symmetry, such as lead zirconate titanate or PZT, there are ten non-zero, independent matrix elements consisting of 5 independent elastic constants, 3 independent piezoelectric constants and 2 independent dielectric constants. In an accompanying paper<sup>2</sup> we have discussed the importance of expressing the material constants as complex coefficients so as to account for all the losses in the material and we have described the experimental methods to find these constants by using resonance techniques. Piezoelectric materials generally exhibit varying degrees of non-linearity and electrostrictive materials are essentially non-linear. If the above linear equations are used to define the material constants of piezoelectric materials, then the material constants themselves are a function of applied fields and stresses as well as of the temperature of the material. Also, the piezoelectric response is not instantaneous and the response time can be important in some applications. This paper describes a number of experiments that have been used to study these effects.

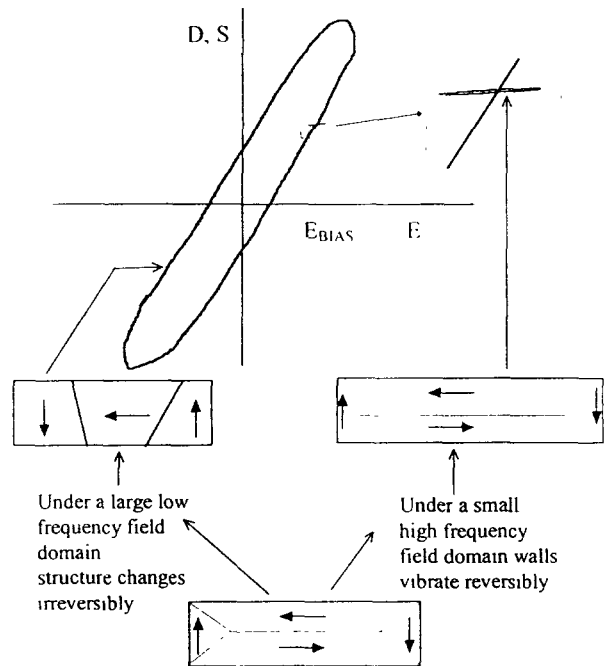
The set of equations (1) is used to interpret most quasistatic measurements. Two experimental conditions may be used to simplify the measurement. If the stress is set to zero (i.e. the sample is free to expand unhindered), the equations are no longer coupled and the strain and the electric displacement can be measured as a function of the electric field. Similarly, if the electric field is zero (the short circuit condition), the strain and the dielectric displacement can be measured as a function of the stress. These uncoupled relationships are shown in Table 1.

Table 1. The quasistatic measurements that can be made in the 33 direction (along the poling axis) on a piezoelectric material with one of the independent variables set to zero.

Boundary Condition	Simultaneous Equations	
$T = 0$ (unclamped) Apply $E$ - measure $S$ and $D$	$S = dE$	$D = \epsilon^T E$
$E = 0$ (short circuit) Apply $T$ - measure $S$ and $D$	$S = s^E T$	$D = dT$

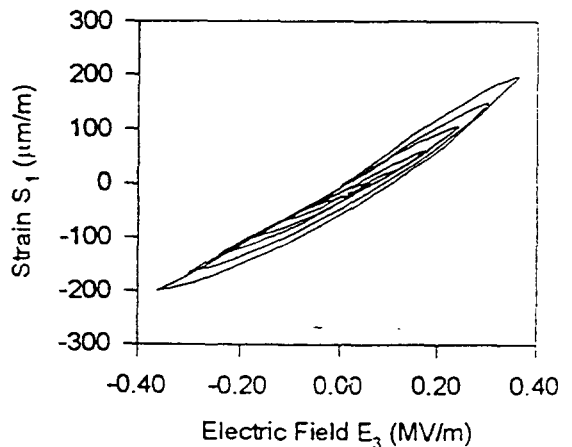
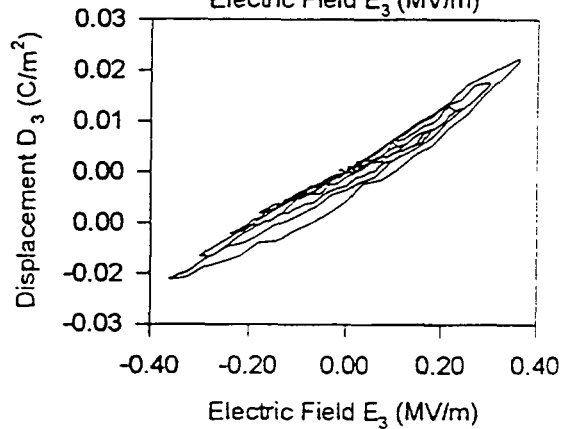
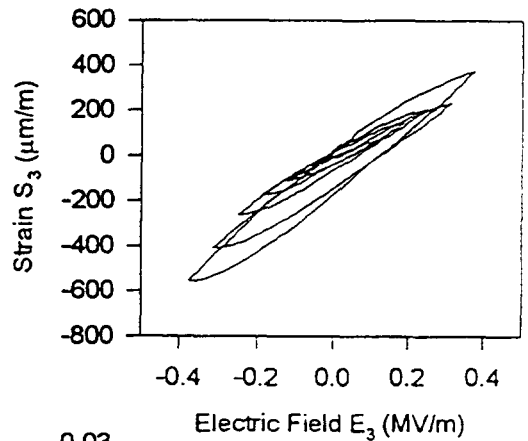
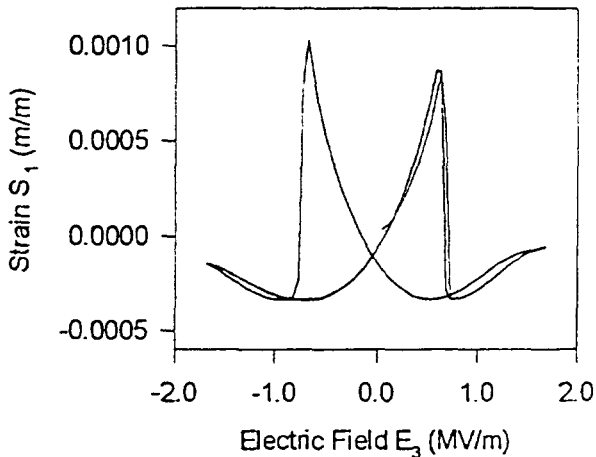
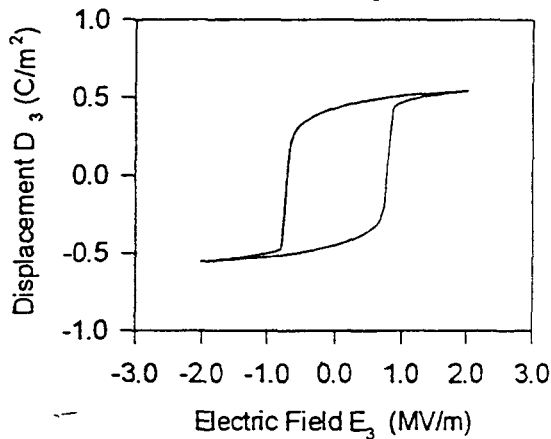
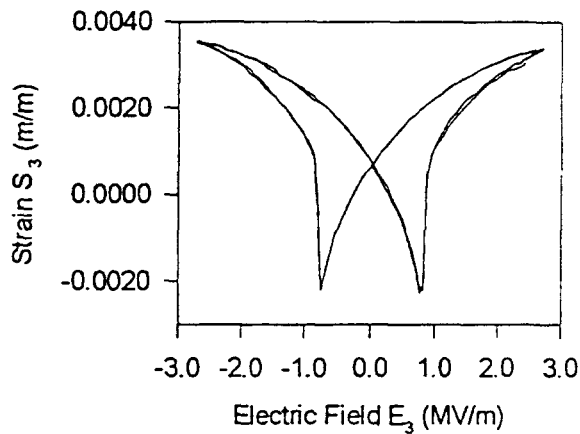
# MEASUREMENT OF THE PIEZOELECTRIC CONSTANT AND THE PERMITTIVITY AS A FUNCTION OF THE APPLIED ELECTRIC FIELD

The variation of the piezoelectric constant  $d$  and the permittivity  $\epsilon$  as a function of the applied electric field can be carried out under two different experimental situations: (a) quasistatic experiments, which gives the value of the constants under near DC conditions, and (b) resonance experiments, which yield the material constants at the appropriate resonance frequency. The difference in the significance of these two types of measurement can be understood with reference to Figure 1. The main curve in the figure shows a typical curve that is obtained when a varying electric field, below the coercive field, is applied to a piezoelectric material and the resultant strain is measured. A measurable hysteresis is found and this is due to the reversible and irreversible domain wall motions that are characteristic of ferroelectric materials. Under a large electric field the domain walls move to maintain a minimum in the domain energy and some of the domains engulf other domains or change shape irreversibly, which contributes to the net strain and polarisation. The onset of irreversibility in such materials has been studied by Zhang et al<sup>3</sup> who found that each material has a plateau region where the permittivity and the piezoelectric constant were independent of field and they attributed this field independence to reversible domain motion. In the case of resonance measurements, the AC measurement signal is small, well below the plateau region found by Zhang et al, and so the measurements correspond to reversible domain motions. Such AC resonance measurements have been carried out with an applied DC bias field to determine the variation of the material constants as a function of the DC field. The illustrative diagram in Figure 1 shows clearly that the slopes of the two types of measurement are different and therefore the material constants found from the two types of measurements cannot be the same. This discussion underlines the importance of determining the material constants under conditions appropriate for any particular application.



**Figure 1.** The relationship between the reversible and irreversible domain motion and the resultant strain or electric displacement as a function of the electric field.

The quasistatic measurements were carried out with an optical lever experiment<sup>4</sup> that allows the strains in the 1 or 3 directions to be determined directly as a function of an applied dc field in the 3 direction whose maximum value exceeds the reversibility limit. The dielectric displacement was measured at the same time. Results<sup>5</sup> for the case of Motorola PZT 3203 HD ceramic are shown in Figure 2 and they exhibit the typical hysteresis



**Figure 2.** The quasistatic field dependence of the strain  $S_3$ , the dielectric displacement  $D_3$  and the strain  $S_1$  as a function of electric field to field levels above the coercive field.

**Figure 3.** The quasistatic field dependence of the strain  $S_3$ , the electric displacement  $D_3$  and the strain  $S_1$  as a function of field to field levels below the coercive field. In each case six loops with different maximum fields are shown.

behaviour of ferroelectric materials. The shapes of the curves depend on the size and the change in the electric field.

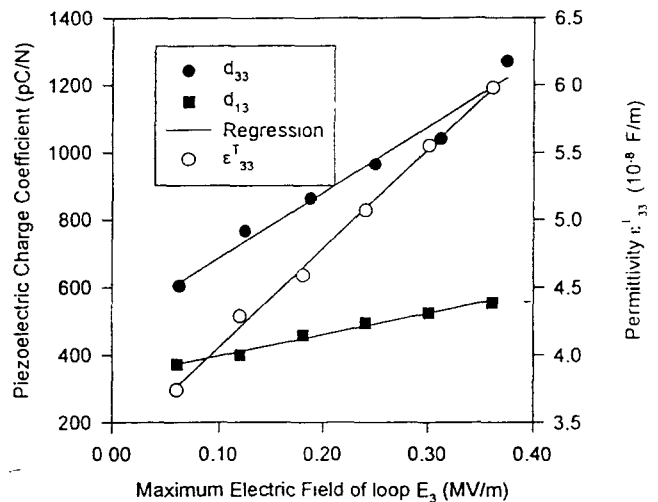
If the maximum applied field is kept below the coercive field (0.5 to 1.0 MV/m for the Motorola ceramic), the non-linearities and the hysteresis are much less significant as can be seen in the curves in Figure 3. The figures show curves (loops) for six different maximum applied fields in each case and it can be seen that the slope and the hysteresis increase as the maximum field of the loop is increased. Since the hysteresis is now less significant, an average slope can be used to determine the material constants. The piezoelectric constants and the permittivity are plotted as a function of the maximum applied field in Figure 4. Although these constants represent average values, they would be useful, for example, to an actuator designer who is mainly interested in the strain level as a function of the applied field. The piezoelectric charge coefficients and the permittivity are found to vary linearly as a function of the applied electric field. These variations can be expressed as follows:

$$S = d_{33}E + q_{33}E^2 \quad \text{and} \quad D = \epsilon_{33}E + (\kappa_{33}/2)E^2, \quad (2)$$

where  $q_{33}$  is the electrostrictive coefficient and  $\kappa_{33}$  is the second order dielectric constant which we call the electrodielectric constant. It should be noted that  $\kappa_{33}$  represents the contribution which is caused by the coupling of the polarisation to the electric field.

The non-linear properties of the piezoelectric materials have also been studied by carrying out AC resonance measurements under DC bias<sup>5</sup> but, as explained above, the material constants obtained by these measurements correspond to reversible domain motions and are different from those obtained from the quasistatic measurements. The difference is illustrated in Table 2 which gives the values of the electrostrictive and electrodielectric coefficients obtained from the two types of measurements.

As pointed out above, the non-linearities are much less significant if the applied fields are below the coercive field so that a greater range of linear behaviour can be found with materials with high coercive fields. For example, the piezoelectric copolymer PVDF-TrFE has properties<sup>6</sup> that are relatively independent of the applied electric field for fields up to  $\pm 0.4$  MV/m; however this copolymer exhibits a much greater dispersion than does the ceramic PZT. This shows that the device designer needs to choose his material carefully depending on the performance requirements of the device.



**Figure 4.** The quasistatic field dependence of the effective piezoelectric constant and permittivity as a function of the field up to field levels below the coercive field. The slopes give the higher order material coefficients.

**Table 2:** The electrostriction and electrodielectric constants determined from the quasi-static and DC biased resonance spectra.

Non linear Coefficient Real Part	Quasi-static Maximum $E_{DC}=0.39\text{MV/m}$ $f < \text{mHz}$	Length thickness Resonator $E_{DC}=0.39\text{MV/m}$ $f=72 \text{ kHz}$	Length Resonator $E_{DC}=0.016\text{MV/m}$ $f=572 \text{ kHz}$
$K_{33}(\text{Fm/V})$	$7.3 \times 10^{-14}$	$1.8 \times 10^{-14}$	$1.4 \times 10^{-14}$
$q_{33} (\text{m}^2/\text{V}^2)$	$9.5 \times 10^{-16}$	N/A	$1.4 \times 10^{-16}$
$q_{13} (\text{m}^2/\text{V}^2)$	$3.1 \times 10^{-16}$	$5.0 \times 10^{-17}$	N/A

## STRESS AND TEMPERATURE DEPENDENCE OF THE DIRECT PIEZOELECTRIC CHARGE COEFFICIENT

The relationship between the dielectric displacement  $D$  and the stress  $T$  has also been studied<sup>7</sup>; this corresponds to the second experimental condition shown in Table 1 and the results show how the piezoelectric  $d$  constant varies as a function of the applied stress and the temperature of the specimen. The experimental arrangement has been described earlier<sup>7,8</sup>; the sample is compressed by a stress  $T$  and the resulting piezoelectric current is measured by a low input impedance electrometer operating in the current mode. The sample temperature can be set by a heat lamp and it can be measured by means of a thermocouple.

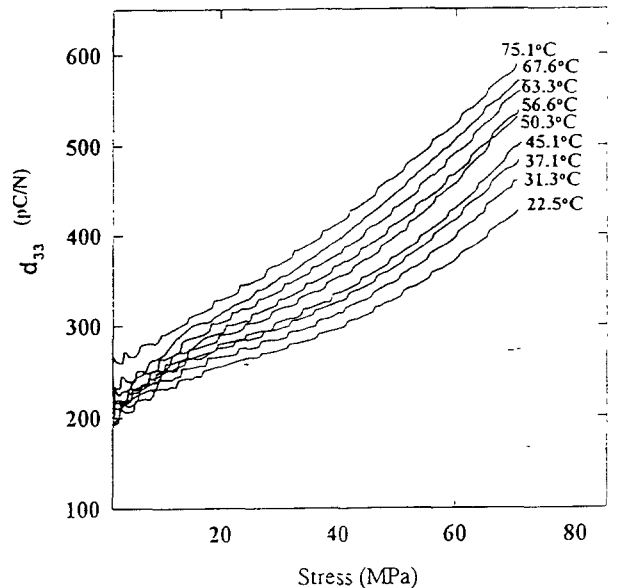
The application of a steadily increasing stress generates a polarisation that produces a current,  $I$ , through the electrometer. If the stress is increased as a function of time,  $t$ , the current produced is directly proportional to the piezoelectric charge coefficient and the relationship is given by

$$D_3 = \frac{1}{A} \int I \partial t = d_{33} T_3 \quad (3)$$

where  $A$  is the electroded area of the sample. The technique can determine an integrated average value of the charge coefficient up to the stress level  $T_3$ , as defined by

$$d_{33}(T_3) = \frac{\int I \partial t}{AT_3} \quad (4)$$

Sherrit et al<sup>7</sup> have used this technique to measure the charge coefficient,  $d_{33}$ , for a Channel 5804 PZT ceramic as a function of the applied stress and the temperature and their results are shown in Figure 5. At room temperature, the application of a stress of around 70 MPa increases the value of  $d_{33}$  by a factor of about two, once again emphasising the importance of the



**Figure 5** The value of  $d_{33}$  as a function of stress and temperature for a Channel 5804 PZT ceramic.

non-linear effects. The shape of the  $d_{33}$  curves as a function of stress appears to flatten and become more linear as the temperature is increased.

## THE PIEZOELECTRIC RESPONSE TIME

The curves shown in Figure 5 were measured under increasing stress and hysteresis was observed when the stress was ramped down. This suggested that the results would depend on the ramp rate of the stress and that time dependent effects were involved. In order to study the response time, Sherrit et al<sup>7,8</sup> applied a step stress with a rise time of less than 10 seconds and measured the current as a function of time elapsed after the application of the stress. The step stress resulted in a step increase in the current and, most interestingly, the current then decayed over a period of time, almost exactly following the inverse relationship  $I = k/t$ . Any mechanical relaxation in the experimental system or any relaxation in the elastic constant would only have resulted in a negative current. Sherrit et al were therefore able to attribute the continued current to the continued generation of charges in the specimen which is likely to result from slow changes to the domain structure in the specimen, particularly the  $90^\circ$  reorientation of domains, which require atomic motion and are therefore expected to be slower than the  $180^\circ$  reorientation of domains that require only a shift in the charge centre of the domain. When a step stress is applied, there is a near instantaneous generation of charge due to  $180^\circ$  domain changes and some  $90^\circ$  domain changes and this is followed by the slow switching of other  $90^\circ$  domains that gives rise to the observed continued generation of charge and slow decay in the current. Both the fast and the slow domain changes contribute to the piezoelectric charge coefficient and, using equation (4), this can now be expressed as

$$d_{33} = d_{33}^0 + d_{33}^t \ln(t) = d_{33}^0 + \frac{\int \frac{k}{t} \partial t}{AT_3}, \quad (5)$$

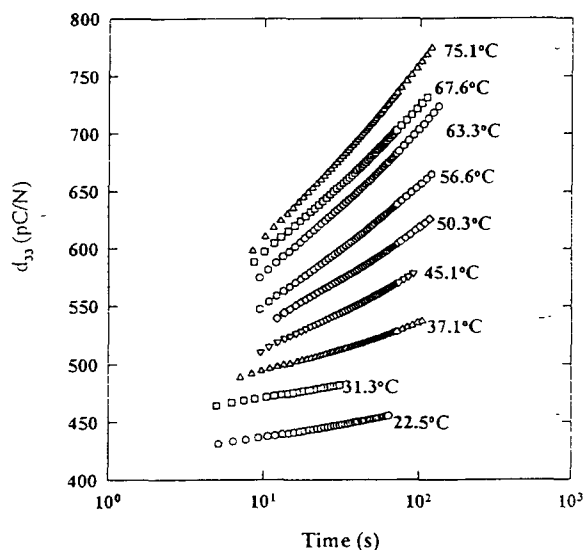
where  $d_{33}^t = k/AT_3$  is a constant that describes the time dependence of the current as well as that of  $d_{33}$ .

From the point of view of applications, it is important to note that the observed time dependence results in a frequency dependence for the piezoelectric charge coefficient. A high frequency signal will produce a charge that, to a first order, is proportional to  $d_{33}^0$ , while a low frequency will produce a charge that has contributions from both  $d_{33}^0$  and  $d_{33}^t$ .

Figure 6 shows the variation of the charge coefficient,  $d_{33}$ , for the Channel PZT 5804 PZT ceramic as a function of the temperature and the time after the imposition of the stress signal. The slope of the curves, which determines  $d_{33}^t$ , is seen to increase with increasing temperature and Sherrit et al<sup>7,8</sup> were able to obtain a roughly linear Arrhenius plot of  $\ln(d_{33}^t T)$  as a function of inverse temperature,  $1/T$ , corresponding to the expression

$$d_{33}^t = \frac{d_{33}^{t0}}{T} \exp\left(\frac{-E_a}{KT}\right), \quad (6)$$

where  $E_a$  is an average activation energy for domain motion,  $d_{33}^{10}$  is a pre-exponential factor and  $K$  is Boltzmann's constant. They found an average activation energy of 0.39 eV for the Channel 5804 PZT and their measurements on a variety of PZT types yielded activation energies in the range from about 0.2 eV to 0.7 eV. The time dependence coefficient  $d_{33}^t$  was found to be independent of the stress level while the coefficient  $k$ , which describes the time dependence of the current due to the generation of charge, was found to be linearly dependent on the stress  $T_3$  up to 60 MPa.



**Figure 6.** The value of  $d_{33}$  as a function of the time after the application of a stress step.

## CONCLUSIONS

The experimental results reviewed in this paper clearly show that piezoelectric materials have significant non-linear effects. It follows that the material constants measured under the application of small signals, which are the parameters usually provided by the manufacturers, are not sufficient to predict the behaviour of the materials when large signals are applied, as, for example, in actuators and acoustic projectors. The device designer requires material constants that are measured under the conditions which prevail during the operation of the device, and this paper has reviewed some of the experiments that are available to make such measurements.

## ACKNOWLEDGEMENT

We gratefully acknowledge funding support from the Defence Research Establishment Atlantic and the Academic Research Programme of the Department of National Defence, Canada as well as support from the Office of Naval Research, USA given through the Naval Undersea Warfare Centre, Newport, RI, USA.

## REFERENCES

<sup>1</sup> IEEE Standard on Piezoelectricity (1987): [ANSI/IEEE Standard 176-1987].

<sup>2</sup> B.K. Mukherjee and S. Sherrit, the previous paper in this volume.

<sup>3</sup> Q.M. Zhang, W.Y. Pan, S.J. Jang and L.E. Cross, *J. Appl. Phys.*, **64**, pp.6445-6451 (1988).



---

<sup>4</sup> H.D. Wiederick, S. Sherrit, R.B. Stimpson and B.K. Mukherjee, *Ferroelectrics*, **186**, pp.25-31 (1996).

<sup>5</sup> S. Sherrit, H.D. Wiederick, B.K. Mukherjee and M. Sayer, Smart Structures and Materials 1997: Smart Materials Technologies (SPIE Proceedings Volume 3040), pp.99-109 (1997), SPIE, Bellingham, Washington, USA.

<sup>6</sup> S. Sherrit, J.E. Haysom, H.D. Wiederick, B.K. Mukherjee and M. Sayer, Proc. Of the 10th Int. Symp.on Applications of Ferroelectrics: ISAF '96, pp.959-962, IEEE, Piscataway, NJ, USA (1996).

<sup>7</sup> S. Sherrit, R.B. Stimpson, H.D. Wiederick and B.K. Mukherjee, Presented at the SPIE Far East and Pacific Rim Symposium on Smart Materials, Structures and MEMS held in Bangalore, India in December 1996 and to be published in the proceedings.

<sup>8</sup> S. Sherrit, D.B. Van Nice, J.T. Graham, B.K. Mukherjee and H.D. Wiederick, Proc. of the 8th Int. Symp. on Applications of Ferroelectrics: ISAF '92: pp. 167-170, IEEE, Piscataway, NJ, USA (1992).