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NON-LINEAR CHARACTERISATION OF PIEZOELECTRIC CERAMICS FOR ACOUSTIC TRANSDUCERS

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Abstract

Acoustic sensors and actuators often utilize piezoelectric transducers in active methods of noise and vibration control and in other smart applications. The increasing range of these applications requires the piezoelectric materials to be used under a variety of conditions that include large applied AC fields, DC bias fields, applied stresses and a large range of frequencies and temperatures. Such conditions will result in a non-linear response in the material properties. It is therefore necessary to understand the behaviour of these materials under the afore-mentioned conditions. Both quasi-static and resonance methods have been used to characterize the response of soft and hard doped piezoelectric ceramics as a function of temperature, stress and applied fields. Significant non-linear behaviour was observed in the ceramics' material constants. Almost all the non-linear phenomena can be understood on the basis of domain dynamics in the material that lead to extrinsic effects.

INTRODUCTION

Piezoelectric materials produce a strain under the influence of an external electric field or become electrically polarised under the influence of an external stress. Piezoelectricity can be mathematically derived from a phenomenological model of thermo-dynamical potentials. The derivations are not unique and the set of equations describing the direct and converse piezoelectric effect depend on the choice of potential and the independent variables used [1], [2]. For example, one set of such linear constitutive relations will yield a 9 x 9 matrix of the material constants with subscripts 1, 2, 3 designating the orthogonal directions and 4, 5, 6 designating the shear directions. For the commonly used piezoelectric ceramics with C_{∞} symmetry, such as lead zirconate titanate or PZT, there are ten non-zero, independent matrix elements consisting of 5 independent elastic coefficients ($s^E_{11}, s^E_{12}, s^E_{13}, s^E_{33}, s^E_{55}$), 3 independent piezoelectric coefficients (d_{31}, d_{15}, d_{33}) and 2 independent dielectric constants ($\varepsilon^T_{11}, \varepsilon^T_{33}$)[3]. While the linear constitutive relations can be written in many ways, there are only 10 independent constants. The full, reduced, matrix for these materials can be found in the IEEE standard [3], which also contains the equations that allow one to convert from one set of constitutive equations/matrix to another.

Ideally, under small fields and stresses and for materials with low losses within a limited frequency range, these 10 constants contain all the information required to predict the behaviour of the material when a stress, strain or electric field is applied to it. However, the continuing increase in applications has seen the use of piezoelectric materials under a growing range of conditions. These include the application of large fields and stresses as well as a wider range of frequencies and temperatures. In practice most piezoelectric materials display dispersion and non-linearities, have measurable losses and their properties are temperature dependent. The last two decades has also seen the development of finite element packages to model piezoelectric materials, such as PZFlex [4], and some of these are sufficiently precise so as to require very accurate material constants. All of the above has pointed to the need for better characterisation of piezoelectric materials. The Laboratory for Ferroelectric Materials at the Royal Military College of Canada has a continuing programme for improving the characterisation of these materials and at ICSV-5 (1997) two invited papers reported on the work of this laboratory [5], [6]. This paper presents a summary of some of this group's work in recent years. Fuller details can be obtained from the references mentioned in this paper.

TEMPERATURE DEPENDENCE OF THE MATERIAL CONSTANTS

The most widely used technique for determining all the 10 relevant constants for piezoelectric ceramics is the resonance technique outlined in the IEEE standard on piezoelectricity [3]. Basically, a small AC electrical signal is used to excite an elastic wave in the piezoelectric material via an electromechanical coupling. A resonance condition, which occurs at a critical frequency depending on the sample dimensions, is monitored by measuring the impedance or admittance of the sample as a function of the frequency (usually the scanned frequency range is from 10 kHz to 5 MHz depending on the resonance mode). By changing the conditions at which the resonance measurement is taken, such as varying the temperature, the piezoelectric ceramic material constants are calculated and the non-linear response is studied over a wide range of possible conditions [5].

In our experiments soft (EC-65) and hard (EC-69) doped PZT samples from EDO Ceramics were pre-cut to four resonance geometries: radial mode, thickness extensional mode, length extensional mode and length thickness extensional mode and several piezoelectric (d_{33}, d_{31}), elastic (s^E_{11}, s^E_{12}, s^E_{33}, σ_E) and dielectric ($\varepsilon^T_{33}/\varepsilon_0$) constants, as well as the corresponding electromechanical coupling factors (k_{31}, k_{33}, k_p, k_t) were obtained as a function of temperature ranging from 15 °C to –165 °C, up to 195 °C and back down to 15 °C for both soft and hard PZT compositions. The temperature cycle used allowed the observation of any thermal hysteresis in the material constants, which is generally expected in ferroelectrics [7]. Sherrit et al [8] conducted studies on the effect of multiple heat cycles on some material constants for PZT samples and they found that, during the first heat cycle for a given sample, the temperature variations induce an internal stress build-up that is gradually relieved by irreversible domain wall dynamics, causing a hysteresis to appear. However, according to that same study, this hysteresis was greatly reduced in subsequent heat cycles on the same sample, since contributions of the irreversible domain wall motion became lesser in ensuing cycles.

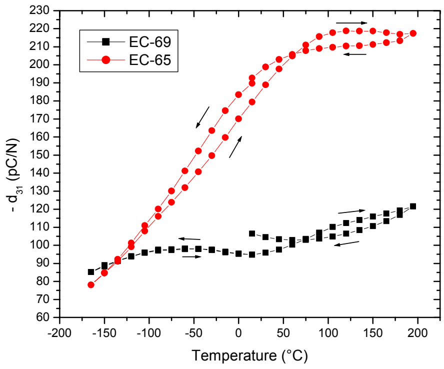

Figure 1. The temperature dependence of -d_{31} for soft (EC-65) and hard PZT (EC-69) obtained from the radial mode (f_s ~ 73 kHz; f_p ~ 83 kHz).

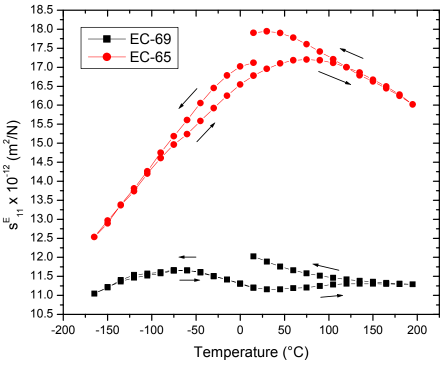

Figure 2. The temperature dependence of s^E_{11} for soft (EC-65) and hard PZT (EC-69) obtained from the radial mode (f_s ~ 73 kHz; f_p ~ 83 kHz).

Our results for a few constants are discussed in this paper and more complete results have been published elsewhere [8]. The piezoelectric constant -d_{31}, seen in figure 1, shows signs of decline with decreasing temperature that are more pronounced in soft PZT (the negative sign in - d_{31} indicates compression of the sample). Essentially, as the temperature declines, the domains become clamped and their motion is hindered. Their thermal energy decreases and a higher activation energy is required to engage changes in the domain structures, thus, reducing the extrinsic piezoelectric response, which is known to be more significant in soft rather than hard PZT [9]. For soft PZT in figure 1, as the temperature climbs back up from –165 °C, the overall domain motion is gradually restored over time as the sample heats up, until a maximum in the extrinsic response, including the irreversible domain dynamics, is reached (between 100 °C and 195 °C). On the other hand, when heating hard PZT from –165 °C, its d_{31} response seems to be more instantaneous since the cooling and heating values of d_{31}, below 15 °C, coincide almost on top of each other for identical temperatures. This is because extrinsic contributions are smaller in hard PZT. Furthermore, given that figure 1 shows the first heating cycle applied onto the samples, upon cooling from 195 °C to 75 °C, both soft and hard PZT exhibit a decrease in - d_{31} due to a reduction in the irreversible domain dynamics during this cooling process. Finally, the slight increase in - d_{31} from 75 °C to 15 °C, for both soft and hard PZT, is attributed to the de-pinning effect. Usually, during the samples' manufacturing process, some of the domains become trapped or pinned by impurities or structural defects with time [10]. When a high temperature is applied onto the samples, structural changes or redistribution of impurities occur, causing the de-pinning of certain domains that were previously restricted motion and sometimes increasing the piezoelectric, elastic and dielectric response.

In figure 2, the greater variation of s^E_{11} in soft PZT, compared to hard PZT, is due to the quicker domain wall motion attributed to the easier transfer of atoms by the Pb vacancies in soft PZT, rather than by the O vacancies in hard PZT. Basically, two broad peaks are distinguished: the first is located around –75 °C for hard PZT and the second, around 60°C for soft PZT. These peaks correspond to a tetragonal-to-rhombohedral phase change in the lattice structure. The occurrence of this phase change in soft and hard PZT at dissimilar temperature ranges is due to their doping differences. In addition, the decrease in s^E_{11}, observed for soft PZT at temperatures from 60 °C to 195 °C and for hard PZT at temperatures from –75 °C to 25 °C, is also attributed to this tetragonal-to-rhombohedral phase change. Finally, upon cooling from 195 °C to 15 °C, both samples exhibit signs of the de-pinning effect.

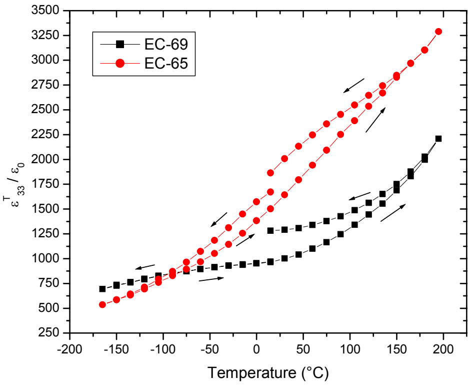

Figure 3. The temperature dependence of $\varepsilon^T_{33}/\varepsilon_0$ for soft (EC-65) and hard PZT (EC-69) obtained from the radial mode (f_s ~ 73 kHz; f_p ~ 83 kHz).

The origin of the temperature dependence of ε^T_{33} can be considered from the crystal structure point of view. Basically, as the temperature increases, the restrictions on the ionic movements are weakened, thus, raising the ionic polarisability and the dielectric constant of the tested samples [11]. This phenomenon also explains the rise in the d_{31} piezoelectric constant as the temperature increases in figure 1. However, the substantially higher increase of ε^T_{33} with temperature, seen in figure 3, compared to the other piezoelectric and elastic constants is attributed to the fact that both 180° and non-180° domain walls contribute to the dielectric properties of these ceramics, while only non-180° domain walls contribute to the piezoelectric and elastic properties. In figure 3, the relative dielectric constant of both sample compositions increases with temperature as expected. This increase is almost linear in the soft PZT curve throughout the tested temperature range. On the other hand, $\varepsilon^T_{33}/\varepsilon_0$ of hard PZT stabilizes somewhat and increases with temperature at a much smaller rate in the sub-zero range. However, upon heating from 15 °C to 195 °C, the hard PZT $\varepsilon^T_{33}/\varepsilon_0$ curve increases at an almost identical rate to the soft PZT curve. Finally, the de-pinning effect is also present for both PZT compositions upon cooling from 195 °C to 15 °C.

STRESS DEPENDENCE OF THE PIEZOELECTRIC EFFECT

It has been shown that mechanical stress can cause re-orientation of polarisation and de-poling in piezoelectric ceramics [12], [13], [14]**.** If the electric field is kept constant or is set to zero (short circuit condition), the dielectric displacement and the strain can be measured and the piezoelectric, dielectric and elastic constants can be determined as a function of stress [15]. Our measurements were carried out on soft and hard doped ceramics similar to those in the previous section. The basic experimental set-up for making these measurements has been described earlier [16]. The dynamic response to a small AC stress superimposed on a DC pre-stress was based on the method described by Audigier et al [17].

Due to space constraints, only our dynamic measurements are discussed here. Figure 4 shows the experimental variation of the piezoelectric constant d_{33}, the elastic constant s^E_{33}, the dielectric constant ε^T_{33} and the electromechanical coupling coefficient k_{33}, all as a function of the pre-stress for the hard EC-69 and the soft EC-65 PZT ceramics.

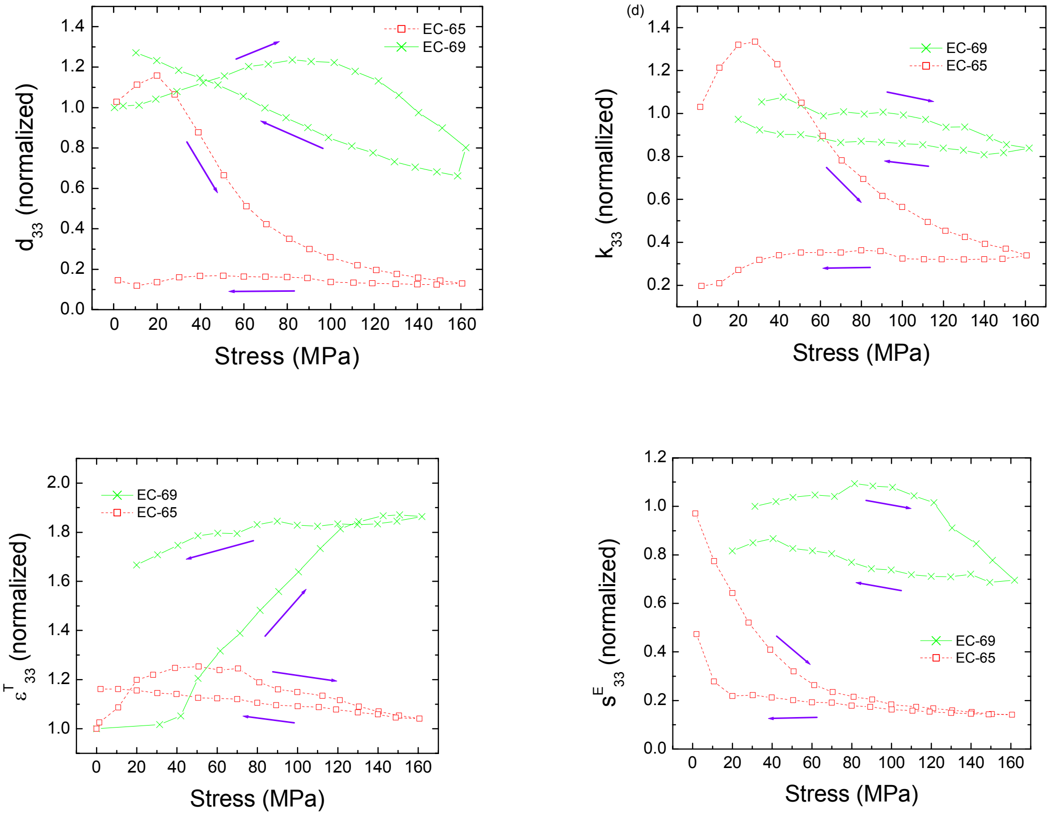

Figure 4. The stress dependence of the electromechanical properties of EC-69 and EC-65 PZT ceramics.

When a stress is applied to the hard EC-69 ceramic, domain switching can lead to the production of new non-180° domain walls [18], [19]. Also, the stress can cause de-ageing (de-pinning of domain walls) and both effects lead to an increase in d_{33} as seen in Fig. 4. This increase in the extrinsic contribution also causes the dielectric constant and the loss to increase, as observed earlier [20], [21] and shown in Fig. 4. As the stress is further increased the domain walls become progressively clamped by the stress and causes a decrease in the d_{33}. The figure also shows that when the stress is released the value of d_{33} recovers and indeed after a full stress cycle, the EC-69 ceramic shows a net increase in d_{33}. This confirms that there has been no de-poling and the decrease in d_{33} under high stress is due to stress-induced clamping of domain walls. Just like EC-69, the soft EC-65 also shows an initial increase in d_{33} as the pre-stress is increased but the d_{33} begins to decrease at a fairly low stress level and there is little recovery of the d_{33} when the stress is released. It is clear that in this case the stress has caused significant de-poling. This is the dominant effect at high stress, although a small recovery of d_{33} when the stress is being reduced suggests that some reversible stress-induced clamping of domain walls has also occurred. But it is clearly stress-induced de-poling that causes the dramatic reduction in d_{33} in EC-65 ceramic after a stress cycle. The significant drop in s^E_{33} after a full cycle is further evidence of the depoling of the specimen. On the other hand EC-69 shows little change in s^E_{33} but it shows a strong increase in its dielectric constant ε^T_{33} that is normally an indication of de-ageing in the material [21]. Our measurements of the average and differential values of d_{33} as a function of stress have been described elsewhere [16], [22].

STRAIN RESPONSE UNDER LARGE ELECTRIC FIELDS

The determination of the piezoelectric response under large applied fields requires direct measurement of the strain. In our laboratory, we have different experimental methods of measuring strains including the relatively simple optical lever [23], the differential variable reluctance transducer (DVRT) and laser Doppler interferometry. The latter is the most versatile of the direct strain measuring instruments as it allows the measurement of AC strains [24]. Our measurement system uses a Zygo ZMI 2000 heterodyne laser Doppler interferometer [25] with a resolution of 0.62 nm and it has been described elsewhere [26]. The system may be used to directly measure linear strains as well as shear strains and thus it allows us to determine all the piezoelectric d coefficients.

Figure 5 shows the variation of the average values of the d_{33}, d_{31} and d_{15} as a function of applied electric fields up to about 1 MV/m for the same type of PZT ceramics described in the previous sections: the fairly soft EC-65 and the hard EC-69 ceramics. Soft PZT is characterised by a high piezoelectric constant and mobile domain boundaries [27] so that extrinsic contributions are inherently more important and their effect is increased at higher fields [28]. The observed increase in the d coefficients in the soft PZT, EC-65, is likely due to the larger extrinsic contribution resulting from increased domain switching under the influence of large fields. The non-linearities observed are stronger than what would be predicted by the Rayleigh law as can be seen from the following polynomial fits to the curves for the EC-65 PZT:

$$d_{15} = 560 + 1170E - 205E^2 + 142E^3,$$
$$d_{33} = 455 + 529E - 153E^2 + 43E^3,$$
$$d_{31} = -192 - 312E + 126E^2 - 12E^3.$$

Although figure 5 does not show any significant non-linearity in the d coefficients of the hard EC-69 ceramic, this is only because the applied fields here were not high enough. The acceptor doped hard PZT suppresses domain wall response so that higher fields are required for the same effects to be observed.

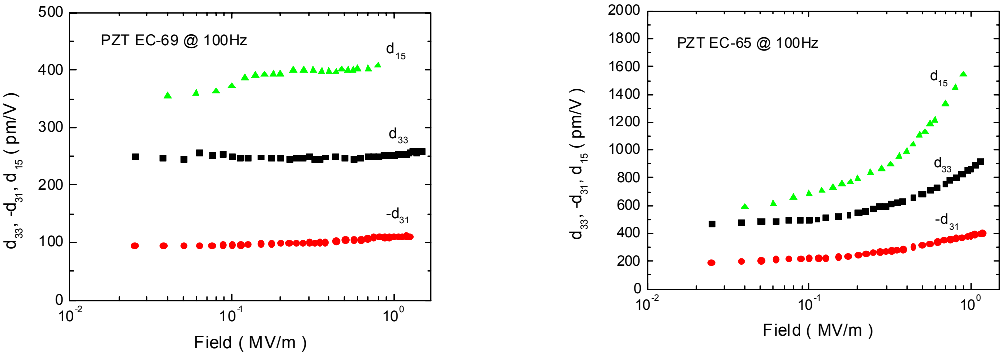

Figure 5. Piezoelectric d coefficients of hard EC-69 and soft EC-65 PZT ceramics as a function of an applied 100 Hz AC electric field.

CONCLUSION

This paper has presented experimental observations to show that, except when very small excitation signals are applied, the piezoelectric, dielectric and elastic responses of a piezoelectric ceramic are essentially non-linear. The material constants have also been shown to change as a function of temperature. It is clear that, from the point of view of an applications/design engineer, it would be appropriate to have the material characterised under the same conditions as the material would be exposed to during the application. For reasons of space, only some examples of the non-linear properties of PZT ceramics have been discussed here. Further details may be found in the references.

REFERENCES

1. A.F. Devonshire, Phil. Mag. Supp., 3, 85-130 (1952).
2. W.P. Mason, “Physical Acoustics and the Properties of Solids”, D. Van Nostrand Co. Inc. (Princeton, New Jersey) (1958).

3. IEEE Standard on Piezoelectricity (1987), ANSI/IEEE Standard 176-1987.
4. PZFlex, from Flex Support, Weidlinger Associates, Inc., 4410 El Camino Real, Suite 110, Los Altos, CA 94022, USA, see http://www.wai.com/AppliedScience/Software/Pzflex/index-pz.html.
5. B.K. Mukherjee, S. Sherrit, "Characterization of Piezoelectric and Electrostrictive Materials for Acoustic Transducers: I. Resonance Methods", *Proceedings of the Fifth International Congress on Sound and Vibration (ICSV-5),* 385-393 (1997).
6. B.K. Mukherjee, S. Sherrit, "Characterization of Piezoelectric and Electrostrictive Materials for Acoustic Transducers: II. Quasistatic Methods", *Proceedings of the Fifth International Congress on Sound and Vibration (ICSV-5)*, 395-403 (1997).
7. H.L.W. Chan, Y. Chen, C.L. Choy, "Thermal Hysteresis in the Permittivity and Polarization of PZT and PVDF Composites", IEEE Trans. On Dielectrics and Electrical Insulation, **3**, 800-805, 1996.
8. R.G. Sabat, G. Yang, W. Ren, B.K. Mukherjee, "Temperature Dependence of the Piezoelectric, Dielectric and Elastic Properties of PZT", To be published in *Smart Atructures and Materials 2006: Active Materials: Behavior and Mechanics: SPIE Proceedings Vol. 6170*, 2006. SPIE Press, Bellingham, WA., USA.
9. Q.M. Zhang, H. Wang, N. Kim, L.E. Cross, "Direct Evaluation of Domain-Wall and Intrinsic Contributions to the Dielectric and Piezoelectric Response and their Temperature Dependence on lead Zirconate Titanate Ceramics", J. Appl. Phys., **75**, 454-459, 1994.
10. B. Jaffe, W.R. Cook, H. Jaffe, "*Piezoelectric Ceramics*", Academic Press, London and New York, 1971.
11. T. Kamiya, R. Michima, T. Tsurumi, M. Daimon, T. Nishimura, "Mechanism of Temperature Dependence of Piezoelectric Properties for PZT", Jpn, J., Appl. Phys., **32**, 4223-4226, 1993.
12. A.G. Luchaninov, A.V. Shil'nikov, L.A. Shuvalov and V.A. Malyshev, Ferroelectrics, **145**, 235-239, 1993.
13. H. Cao and A. Evans, J. Amer. Cer. Soc., **76**, 890-896, 1993.
14. S.C. Hwang, C.S. Lynch and R.M. McMeeking, Acta Metall. Mater., **43**, 2073-2084, 1995.
15. D. Guyomar, D. Audigier and L. Eyraud, *Proceedings of the Eleventh Int. Symp. on the Applications of Ferroelectrics, ISAF'98*, 307-310 (1998). IEEE, Piscataway, N.J., USA.
16. G. Yang, S-F. Liu, W. Ren and B.K. Mukherjee, *Smart Structures and Materials 2000: Active Materials: Behavior and Mechanics: SPIE Proceedings Volume* **3992**, 103-113 (2000). SPIE Press, Bellingham, WA., USA.
17. D.Audigier, C. Richard, C. Descamps, M. Troccaz and L. Eyraud, Ferroelectrics, **154**, 219-224 (1994).
18. A. Schaufele and K.H. Hardtl, J. Amer. Cer. Soc., **79**, 2637-2640 (1996).
19. C.S. Lynch, Acta Mater., **44**, 4137-4148 (1996).
20. H.H.A. Krueger, J. Acoust. Soc. Am.,**42**, 636-645 (1967).
21. Q.M. Zhang and J. Zhao, IEEE Trans. on Ultrasonics, Ferroelectrics, and Frequency Control, **46**, 1518-1526 (1999).
22. G. Yang, S-F. Liu, W. Ren and B.K. Mukherjee, Ferroelectrics **262**, 1181-1186 (2001).

23. H.D. Wiederick, S. Sherrit, R.B. Stimpson and B.K. Mukherjee, Ferroelectrics, **186**, 25-31 (1996).
24. K.M. Rittenmyer and P.S. Dubbelday, J. Acoust. Soc. Am., **91**, 2254-2260 (1992).
25. Zygo Corp., Laurel Brook Rd., Middlefield, CT 06455-0448, USA.
26. A.J. Masys, W. Ren, G. Yang and B.K. Mukherjee, J. Appl. Phys., **94**, 1155-1162 (2003).
27. Q.M. Zhang, W.Y. Pan and L.E. Cross, J. Appl. Phys., **63**, 2492-2496 (1988).
28. Q.M. Zhang, H. Wang, N. Kim and L.E. Cross, J. Appl. Phys., **75**, 454-459 (1994).