Temperature Dependence of Domain Contributions as a Function of Ageing in Soft and Hard Lead Zirconate Titanate Piezoelectric Ceramics

S. Adam Qaisar, Tim P. Comyn, and Andrew J. Bell, Senior Member, IEEE

Abstract—**The stress and temperature dependence of three different PZT ceramics have been measured at 48 hours and 1 month after poling. The data were fitted to a modified Rayleigh law in which a negative quadratic stress term accounts for a saturation of the domain wall contributions at higher stress. The relative changes to the fitting parameters can be explained by the materials possessing differences in the concentration of orientable defect dipoles, but with similar distributions of relaxation time constants.**

Index Terms—**piezoelectricity**

I. INTRODUCTION

PIEZOELECTRIC materials are important contributors to electronic technology in actuator, sensor and signal processing applications. For the most widely used materials such as lead zirconate titanate ceramics, $Pb(Zr_xTi_{1-x})O_3$ or PZT, it is well established that the presence of ferroelectric domains contributes significantly to the piezoelectric effect [1–6]. Specifically, applied electric field or stress can induce local reorientation of the crystal lattice, observed as the displacement of domains walls. Non-180° domain wall motion augments the field-induced strain or stress induced charges and therefore increases the value of the most widely used measure of piezoelectric activity, the charge coefficient, d_{ij}. Piezoelectric materials are generally categorized as either "soft" or "hard". Soft materials are engineered to maximize the charge coefficient at the expense of increasing the dielectric and mechanical losses, whilst hard materials are designed to have low losses and a high electromechanical Q factor, at the expense of a reduced charge coefficient. The observed differences between hard and soft piezoelectric materials are strongly correlated with the defect chemistry of the materials which is thought to control domain wall mobility [7]. In soft, donor

doped PZT, there is evidence to suggest that up to 50% of the value of the d coefficient can be accounted for by non-180° domain wall motion.

It is also widely accepted that the observed non-linearity of the piezoelectric effect with respect to applied field and stress is principally due to the influence of domain walls [7]. However, the form of the non-linearity is dependent on a number of issues. Whilst many materials, including soft PZTs, exhibit a linear increase in the d coefficient with increasing field or stress, known as the Rayleigh law, others, notably hard materials, exhibit higher order stress/field dependence, but with significant evolution over time.

The non-linear behavior of piezoelectric materials facilitates an understanding of how the material will perform in real world scenarios where the material may be subject to a variety of static or dynamic mechanical loads and fields over time. As many applications call for wide operating temperature range, it is also important to understand how non-linear behavior is modified by temperature. Hence the work presented here investigates the non-linearity of the direct piezoelectric effect of 3 types of commercial PZT ceramics as a function of temperature and ageing.

These measurements were conducted up to a maximum of 150°C for all samples in a single experimental step, and after two different ageing periods.

II. EXPERIMENTAL

The material selection consisted of a soft (Navy Type VI - Noliac A/S, Kvistgaard, Denmark), a hard (Navy Type I - PI Ceramic GmbH, Lederhose, Germany) and an intermediate (Navy Type II - PI Ceramic GmbH, Lederhose, Germany) PZT compositions, as shown in Table I.

All materials were obtained off the shelf and cut to ensure an aspect ratio of at least 1:1 (height ≥ width) to minimize

S. Adam Qaisar is now with the National Nuclear Laboratory, Sellafield, Cumbria, CA20 1PG, UK (adam.qaisar@nnl.co.uk)

Tim P. Comyn is now with Ionix Advanced Technologies Ltd., 3M Buckley Innovation Centre, Firth St, Huddersfield, HD1 3BD, UK (tim.comyn@ionix.at).

TABLE I: MANUFACTURER MATERIAL PARAMETERS.

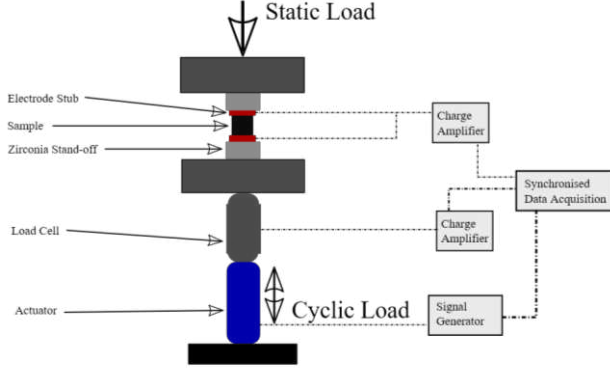| Material	Type	d_{33} / pC N^{-1}	$\varepsilon_{33}/\varepsilon_0$	s_{33} / TPa^{-1}	k_{33}	tan δ	Q_m	T_C / °C
PI PIC181	Hard	265	1200	14.2	0.66	0.003	2000	330
PI PIC255	Intermediate	400	1750	20.7	0.69	0.020	80	350
Noliac NCE55	Soft	670	5000	21.0	0.72	0.022	70	159

Fig. 1. Schematic of the test apparatus - comprising of band heater, stainless steel and zirconia stand-offs and thermal isolation.

clamping effects [1], [8]. The soft and intermediate samples took the form of a cylinder (Ø 4.5mm and Ø 4 mm respectively), with the hard PZT as a rectangular prism (2 x 2 x 4 mm). For consistency, they were thermally de-poled by progressive heating to beyond the material-specific depolarization temperature. All three were then re-poled at 2.25 kV mm^{-1} in silicone oil for 10 minutes at 70°C. All materials were left at room temperature for 48 hours before further measurements.

Direct longitudinal charge coefficient measurements were carried out as a function of stress amplitude using an in-house constructed system comprising a material test frame (3382, Instron) capable of providing a constant stress pre-load and a PZT-based actuator (P-225, Physik Instrumente UK Ltd, UK) to apply a cyclic stress at 1 Hz, measured using an in-line quartz load cell and charge amplifier (9641B and 5011B, Kistler Instruments Ltd, UK). The charge generated by the sample was measured using an identical charge amplifier connected directly to the material under test. The sample was positioned within a temperature controlled region within the test apparatus shown in Fig. 1.

To mitigate non-parallel loading of the sample surfaces, the apparatus was designed with a ±5° accommodation in the orientation of the platens contacting the sample. The experimental temperature was measured using a thermocouple, connected directly to thermal acquisition hardware. All signal generation and data acquisition was synchronous to 1 ms, with data saved in a streaming time division multiplexed format. Fig. 2 shows a typical example of raw data obtained from one complete stress cycle, with a linear regression fit to calculate d_{33}.

The direct piezoelectric coefficient of all samples was measured 48 hours after poling, from room temperature to 150°C in 25°C increments, using the apparatus described above, with a 10 MPa compressive pre-stress and an additional cyclic compressive stress, varying sinusoidally between zero and a maximum "amplitude" with a frequency of 1 Hz, as shown in Fig. 2. The measurements on each sample were conducted in one experimental run, to ensure consistency between measurements at different stresses and to minimize the influence of thermal cycling on the material behavior. The measurements were then repeated after 1 month ageing at room temperature.
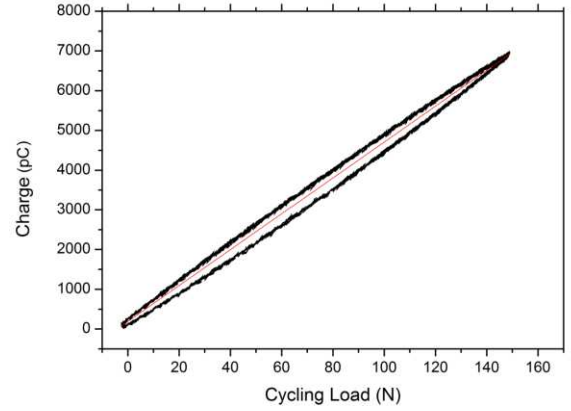
Fig. 2. Typical example of raw data collected from the experimental apparatus, showing one complete stress cycle charge response and linear regression fit (red) to calculate d_{33}.

III. RESULTS

The experimental data are presented in Fig. 3 as plots of d_{33} vs stress amplitude X_0 as a function of temperature at both 48 hours and 1 month after poling. We attribute the differences between the manufacturers' own values of d_{33} and our measured values to the probable differences in poling regimes. After the initial measurements at 48 hours, the samples were re-measured using the Berlincourt meter at room temperature and found to have no more than a 3% change in charge coefficient compared to the value before the temperature excursion.

On initial analysis, the hard composition exhibits substantially linear behavior between d_{33} and X_0, that is it conforms to the Rayleigh law:

$$d_{33} = d_i + \alpha X_0, \tag{1}$$

where d_i is the piezoelectric charge coefficient at zero stress and α is the Rayleigh coefficient. However, the intermediate
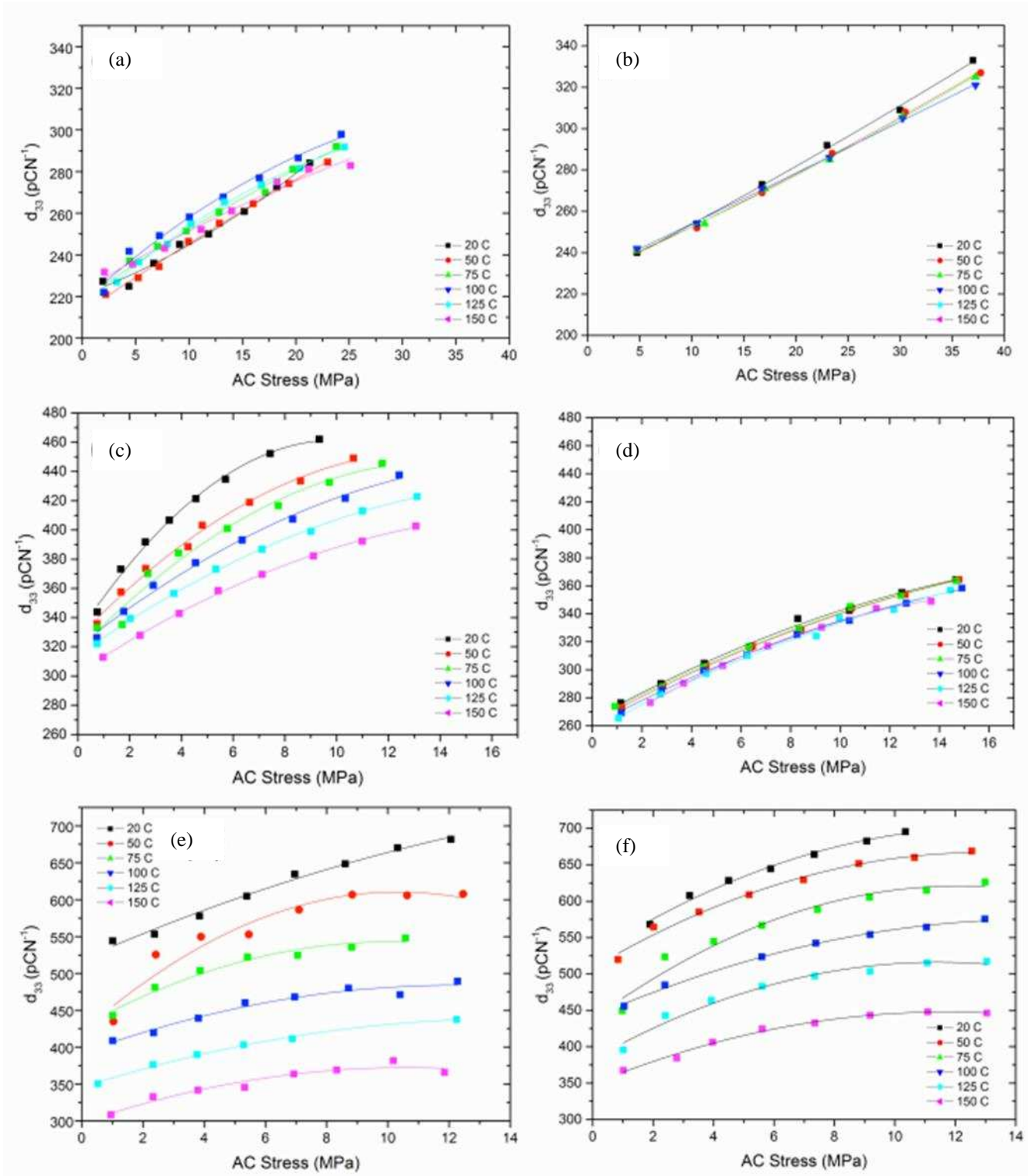
Fig. 3. d_{33} as a function of stress amplitude at 1 Hz and temperature for (a) Hard PZT at 48 hours; (b) Hard PZT at 1 month; (c) Intermediate PZT at 48 hours; (d) Intermediate PZT at 1 month; (e) Soft PZT at 48 hours; (f) Soft PZT at 1 month ageing.

and soft compounds are initially non-linear, with higher order stress dependence, hence all the data have been analyzed according to:

$$d_{33} = d_i + \alpha X_0 + \beta X_0^2. \qquad (2)$$

The coefficients d_i, α and β are compared in Fig. 4 for all three materials as a function of temperature. It can be observed that at 48 hours the hard material is substantially linear in terms of the stress dependence of the charge coefficient, hence the value of β is insignificant. There is also little temperature dependence of both d_i and the first order coefficient α. After 1

month the value of d_i has increased slightly but with somewhat less temperature dependence. If it is assumed that d_i represents the reversible contribution to piezoelectricity, whilst the value of α indicates the size of the extrinsic, or irreversible contribution, often associated with domain wall motion, then both contributions are relatively stable as a function of time and temperature.

At 48 hours the intermediate material exhibits non-linear behavior with low temperature dependence of d_i but significant temperature dependence of both α and β. The former has a positive value and decreases with increasing temperature, whilst the latter is negative and increases with increasing temperature. However, after 1 month, there is a substantial decrease in d_i and both the amplitude and temperature dependence of both α and β has decreased markedly.

The soft material exhibits the largest magnitudes and the greatest temperature dependence of all three parameters. The initial value of charge coefficient, d_i, decreases with increasing temperature, with little change between the 48 hour and 1 month values. Ageing for 1 month sees an approximate threefold reduction in the value of α and a reduction in its temperature dependence, whilst the magnitude of β decreases with increasing temperature, but is relatively unchanged during the ageing period.

IV. Discussion

The most widely employed interpretation of the difference in properties between hard and soft piezoelectric materials relies on the model of the ferroelastic domain wall motion contribution to the charge coefficient being pinned to a greater or lesser extent by defect dipoles formed between oxygen vacancies and acceptor dopants or impurities. Under this model, following poling, defect dipoles align themselves with the direction of local polarization. As the time constant for reorientation of such dipoles is usually much longer than the period of the signal used to measure the charge coefficient, the defect dipoles inhibit the domain wall motion. In hard materials, it is assumed that there is a high concentration of such dipoles, whilst soft materials have a lower defect dipole concentration. The ageing process in piezoelectric ceramics, by which the piezoelectric activity decreases as a function of time is therefore associated with the gradual alignment of defect dipoles with the local polarization.

Whilst the Rayleigh law (Eqn. (1)) is cited by a number of authors as indicative of domain wall processes, it is clear that the majority of data here do not adhere to a simple linear dependence of charge coefficient upon stress, hence a higher order term has been introduced (Eqn. (2)). This term is introduced as the simplest means of characterizing the departure from Rayleigh linearity; it is not assigned any mechanistic significance. It is assumed that d_i is a purely reversible contribution to the piezoelectric coefficient and is dominated by the lattice contributions, which, in addition to extensions of the polarization vector along the polar axis, include polarization rotation.

The coefficients α and β represent the extrinsic contributions

due to the ferroelastic domain wall motion. A positive value of α represents increasing strain contributions (i.e. greater domain wall motion) as a function of increasing stress amplitude. We interpret β, which in the current analysis is always negative, as being the extent to which this effect diminishes or saturates at
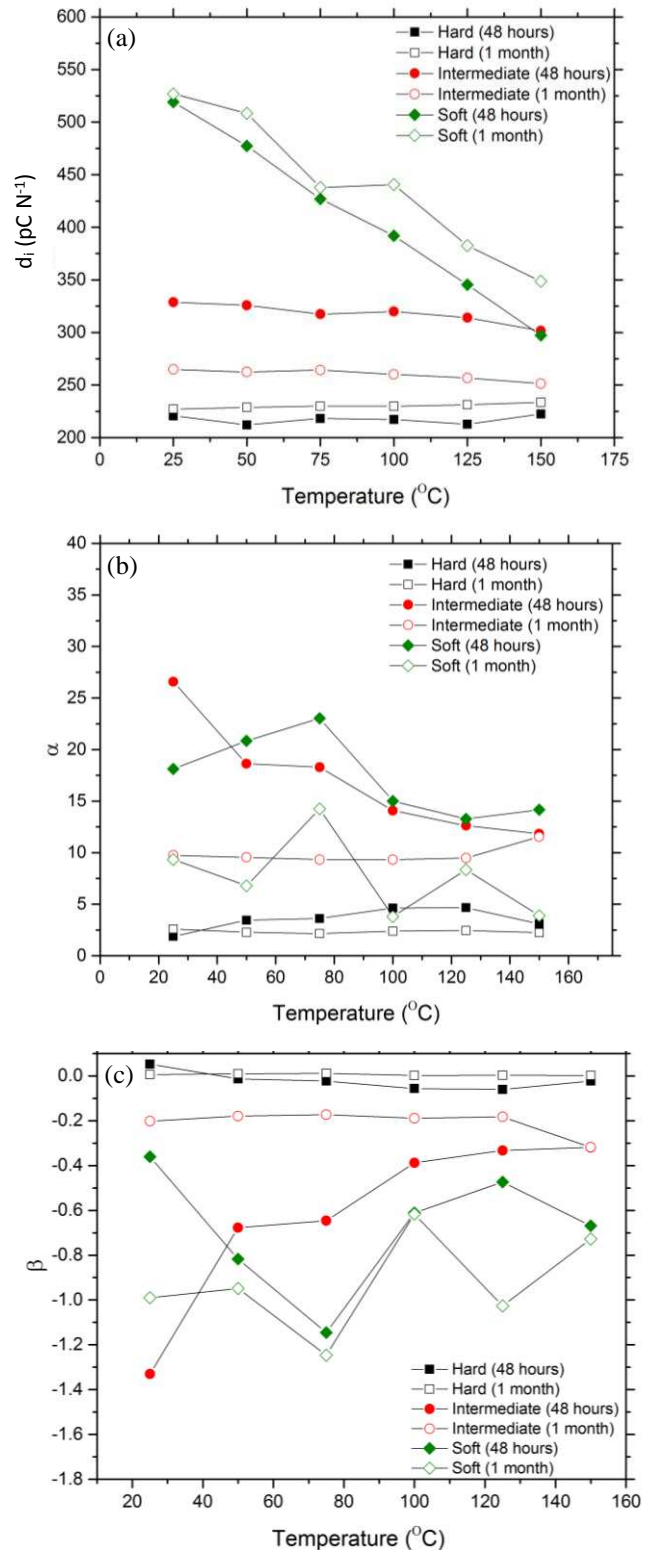

Fig. 4. Coefficients of the second order "Rayleigh fit" (a) d_i, (b) α and (c) β as a function temperature.

higher stresses. Whilst in soft materials, the low density of defect dipoles allows relative ease of domain wall translation, occasional "deep traps" can completely prevent further motion of individual walls, thereby leading to saturation at high stress. The soft and intermediate materials have significant values of β, reflecting a sparse population of defects but with sufficient deep traps to diminish the extrinsic contributions at higher field. The hard material exhibits a vanishingly small β value, characteristic of a material in which a high concentration of homogeneously distributed defects effectively inhibits domain wall motion at all stress levels; hence there is no diminution at higher stress. Furthermore, in the hard material, the value of α does not change as a function of time or temperature. This suggests that the time constant for orientation of the defect dipoles is very short compared to the timescale of these experiments ($<<$ 48 hours). Also, any extrinsic contribution that may be present is not thermally activated, as may be expected for domain wall motion. Indeed, it may be that the Rayleigh behavior exhibited in the hard material may not be domain related, but is due to intrinsic non-linearity in the elastic constants. This effect may be masked in softer materials by the domain contributions.

In the soft material, α and d_i have similar negative temperature dependence. According to simple phenomenological arguments, their values both depend upon the spontaneous polarization, P_s. As the Curie temperature of the soft materials is approximately 150°C less than the intermediate and hard samples, the decrease of P_s as a function temperature dominates their behavior more than in the higher T_C materials. The small change in d_i as a function of ageing is not regarded as significant in this case. The reduction in both the amplitude and temperature dependence of α after 1 month may indicate some stabilization of the orientation of the dipole population. However, β stays approximately constant indicating that the sparse distribution of deep traps still results in diminution of the extrinsic contribution at higher stress. As demonstrated mainly by the values of α, there appears to be a marked change in the material around 75°C. This has not been investigated further, but may be indicative of a shift in the morphotropic phase boundary as a function of temperature.

The intermediate material has many similarities to the soft at 48 hours and certainly fulfils its categorization as being intermediate to the hard and soft behaviors. However, after 1 month it is almost indistinguishable from the hard material, other than having slightly higher values of both d_i and α. This suggests that the defect dipoles take longer to orient with the local polarization than in the hard material; i.e. after 48 hours the defects are still randomly oriented and so do not act to inhibit extrinsic contributions, whereas after 1 month they are completely oriented.

Hence, we might express the differences in the three materials simply in terms of the time constant for defect dipoles to align with the local polarization (τ); the hard material has τ $<<$ 1.7 x 10^5 s, for the soft τ > 2.5 x 10^6 s and for the intermediate, 1.7 x $10^5 < \tau < 2.5$ x 10^6 s. It is widely understood that the origin of the difference between hard and soft materials
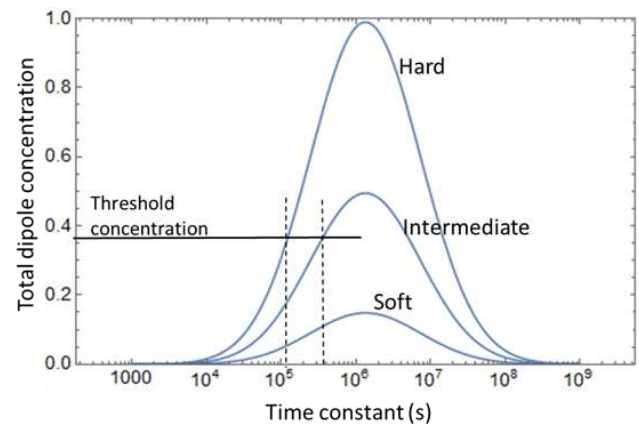

Fig. 5 Conceptual plot of distribution of dipole orientation time constants for the three materials.

is in concentration of acceptors and oxygen vacancies. So how is the behavior described here manifest itself as a difference in alignment time constants ? We can assume that each material has a different total concentration of defect dipoles, but with a similar distribution of alignment time constants and that a threshold concentration of aligned dipoles is required to completely eliminate domain wall contributions (Fig. 5). For a large total concentration of dipoles, as in the hard material, a sufficient number of dipoles have time constants below 48 hours and therefore exhibit the hard state within that period. However, in the intermediate material the threshold concentration of aligned dipoles is not achieved until some time between 48 hours and 1 month. In the soft material, the concentration is so low that the threshold is never achieved, although some hardening is observed before 1 month.

V. CONCLUSIONS

The stress and temperature dependence of three different PZT ceramics have been measured at two different post-poling intervals. The data were fitted to a modified Rayleigh law in which a negative quadratic stress term accounts for a moderation in the domain wall contributions at higher stress. The relative changes to the fitting parameters can be explained by the materials possessing differences in the concentration of orientable defect dipoles, but with similar distributions of relaxation time constants.

REFERENCES

[1] D. Damjanovic and M. Demartin, "The Rayleigh law in piezoelectric ceramics," Ferroelectrics, vol. 29, pp. 2057–2060, 1996.

[2] T. P. Comyn and A. J. Bell, "Study of intrinsic / extrinsic piezoelectric contributions in La-doped BiFeO₃- PbTiO₃ ceramics using the Rayleigh method", Proc. IEEE 16th ISAF, Nara, 2007 pp 402-403. IEEE, 2007.

[3] K. Kobayashi, K. Hatano, Y. Mizuno, and C. a. Randall, "Rayleigh Behavior in the Lead Free Piezoelectric $Li_x(Na_{0.5}K_{0.5})_{1-x}NbO_3$ Ceramic," Appl. Phys. Express, vol. 5, no. 3, p. 031501, Feb. 2012.

[4] F. Li, S. Zhang, Z. Xu, X. Wei, J. Luo, and T. R. Shrout, "Composition and phase dependence of the intrinsic and extrinsic piezoelectric activity of domain engineered $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$-$xPbTiO_3$ crystals.," J. Appl. Phys., vol. 108, no. 3, Aug. 2010.

[5] M. Davis, D. Damjanovic, and N. Setter, "Direct piezoelectric effect in relaxor-ferroelectric single crystals," J. Appl. Phys., vol. 95, no. 10, p. 5679-5684, 2004.

[6] A. Pramanick, D. Damjanovic, J. E. Daniels, J. C. Nino, and J. L. Jones, "Origins of Electro-Mechanical Coupling in Polycrystalline Ferroelectrics During Subcoercive Electrical Loading," J. Am. Ceram. Soc., vol. 94, no. 2, pp. 293–309, Feb. 2011.

[7] H. Jaffe, W. R. Cook and B. Jaffe, Piezoelectric Ceramics, Academic Press, London 1971.

[8] A. Barzegar, D. Damjanovic, and N. Setter, "The effect of boundary conditions and sample aspect ratio on apparent d_{33} piezoelectric coefficient determined by direct quasistatic method.," IEEE Trans. Ultrason. Ferroelectr. Freq. Control, vol. 51, no. 3, pp. 262–70, Mar. 2004.