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Self Polarization in $Pb(Sc_{1/2}Ta_{1/2})O_3$ Relaxor Thin Films: Impact on the Dielectric and Piezoelectric Response

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The phenomenon of "self-polarization" was studied in chemical solution derived $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST) thin films on Pt/Si substrates. PST films exhibited field induced pyroelectric coefficients of $300\,\mu C/(m^2\,K)$, with a detectivity figure of merit $F_d = 1.5 \times 10^{-5}\,Pa^{-1/2}$ at 100 kV/cm bias fields. The piezoelectric coefficient d_{33} was found to saturate at a value of 60 pm/V at 100 kV/cm applied field and the electrostriction coefficient Q_{33} was found to be $\sim 0.025\,m^4/C^2$. The presence of self polarization was confirmed by piezoelectric and pyroelectric activity under zero applied bias fields, resulting in a pyroelectric coefficient of $50\,\mu C/(m^2\,K)$, or an equivalent internal field of ~25 kV/cm. The impact of this internal bias field on the dielectric constant at temperatures near the dielectric maximum corresponds to a ~10% reduction in the dielectric constant. It is concluded that the "self-polarization" observed in relaxor PST films cannot be the origin of the order of magnitude reduction in the dielectric constant of thin films as compared to ceramics. [DOI: 10.1143/JJAP.45.7288]

KEYWORDS: PST thin films, relaxor ferroelectric, pyroelectricity, self-polarization, electrostriction

1. Introduction

Relaxor materials are candidates for thin film actuator applications due to their predicted non-hysteretic and high field induced strain values.[1] However, their use in this capacity is limited by the observed low dielectric constant and field induced piezoelectric and electrostrictive coefficients as compared to bulk and single crystal specimens.[2–8] The presence of self polarization first observed in relaxor $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) has been proposed as a possible contribution to the experimentally observed differences between thin film and bulk relaxor properties.[2] The purpose of this report is to confirm and investigate the nature of self polarization in chemical solution derived $PbSc_{1/2}Ta_{1/2}O_3$ (PST) relaxor thin films and quantify its impact on film properties.

PST has a cubic perovskite structure and has been shown to display either a sharp paraelectric to ferroelectric transition, or a diffuse relaxor transition depending on the degree of ordering.[9,10] This ordering of Sc and Ta cations along the (111) direction occurs at intermediate temperatures (~900 °C) and long annealing durations resulting in the doubling of the unit cell and the appearance of superlattice peaks apparent in X-ray diffraction (XRD) and transmission electron microscope (TEM) studies. This ordering phenomenon is to be avoided in applications desiring high strain/low hysteresis actuators which require disordered PST exhibiting relaxor behavior.

PST thin films have been prepared from a variety of methods including chemical solution deposition,[7,8,11] chemical vapor deposition (CVD)[11] sputtering,[12] and pulsed laser deposition (PLD).[13] Relaxor behavior was typically observed at processing temperatures near ~700 °C as slightly higher temperatures (~900 °C) led to ordering, and extreme higher annealing conditions paralleling those in the processing of disordered PST ceramics (1500 °C) are not possible due to both the damage to the film and underlying substrate/electrode layers.

Relaxor's possesses a centrosymmetric material symmetry so that in absence of a DC bias field, no pyroelectric or piezoelectric effects should be observed. Kighelman first observed piezoelectric active relaxor PMN thin films and attributed this effect to existing polar regions in the film which were partially oriented by a processing induced charge gradient, so called "Self Polarization".[2] Recent studies at the nano-scale using piezoresponse force microscope revealed the absence of a surface piezo response in epitaxial PMN films suggesting the importance of the film/substrate interface.[14]

Self polarization in conventional ferroelectrics has been reported by many authors with a variety of mechanisms being proposed including different work functions of film and bottom electrode,[15] and sputter deposition induced defects of the top electrode.[16] In addition, recent theoretical work concerning thin films of conventional ferroelectrics reveal that the surface state of thin films is itself a defect resulting in an electric field, with variations of scalar quantities such as concentration gradients (lead loss typical in lead based perovskites) increasing the level of internal field.[17] This type of analysis has been recently extended to relaxor thin films where it was found that misfit strain between the film and substrate due to the lattice constant mismatch and thermal expansion mismatch between the film and substrate lead to the appearance of a build in internal field.[18]

It is clear that whether the origins reside in processing induced defects, or mismatch strain due to the thin films state; the "real" state of as deposited relaxor thin films from a variety of deposition methods consists of a film with a built in internal field or self polarization. From both a practical as well as a fundamental viewpoint it is of importance to experimentally evaluate the level of self polarization in relaxor thin films and to examine what impact this has on other film properties. This manuscript uses pyroelectric studies to examine self polarization in chemical solution derived PST thin films on Pt/Si substrates and quantifies its impact on the dielectric and piezoelectric properties.

2. Experimental Procedure

PST relaxor thin films were fabricated by a chemical

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solution deposition method using scandium acetate hydrate, tantalum ethoxide, and lead acetate hydrate precursors in 2-methoxyethanol solvent. Solutions made with 30% excess lead were spun onto Pt/Si substrates and rapid thermal annealed (RTA) annealed to 700 °C in oxygen for 1 min as described in ref. 8. Au top electrodes were sputter deposited at room temperature and post-annealed at 350 °C for 5 min.

Pyroelectric measurements were performed under a DC bias in a dynamic mode to avoid thermally stimulated conduction. The temperature of the sample was cycled at 10 mHz in the form of a triangular signal with an amplitude of 1 °C by using a Peltier element. The pyroelectric coefficient was calculated from the induced pyroelectric current and actual measured temperature rate from eq. (1)

$$p = \frac{i}{A\dfrac{dT}{dt}} \tag{1}$$

where i is the induced pyroelectric current (A), A is the sample area (m^2), and dT/dt is the rate of temperature change (°C/s). Dielectric measurements were performed as a function of temperature at 1 kHz an AC field of 1 kV/cm with various DC fields. The dielectric contribution to the pyroelectric coefficient was calculated from the temperature dependence of the dielectric constant under DC bias fields, eq. (2).[8]

$$p = \varepsilon_0 \int_0^E \left(\frac{dk}{dT}\right)_E dE \tag{2}$$

where p is the pyroelectric coefficient C/(m^2 K), T is the temperature, ε_0 is the permittivity of free space 8.85×10^{-12} F/m, k is the dielectric constant, and E is the electric field bias V/m. The detectivity figure of merit FD was calculated by eq. (3)

$$F_\mathrm{d} = \frac{p}{c(k\varepsilon_0 \tan\delta)^{1/2}} \tag{3}$$

where c is the volume specific heat $\sim 2.5 \times 10^6$ J/(m^3 K) and $\tan\delta$ is the dielectric loss tangent.

Dielectric measurements were made through the film thickness using an impedance analyzer (HP 4284A precision LCR meter) connected to a temperature chamber (Delta 9023) with controlled cooling rates of 2°/min from 100 to −100 °C. The dielectric constant was measured under DC bias upon cooling through the phase transition. The effect of the applied DC field on the dielectric constant was characterized by difference between the dielectric constant with and without DC bias normalized by dielectric constant at zero bias; described as eq. (4)

$$\frac{\Delta k}{k_0} = \frac{k_\mathrm{DC} - k_0}{k_0} \tag{4}$$

where Δk is the difference between the bias and unbiased dielectric constant, k_DC is the dielectric constant under bias field, and k_0 is the zero bias field dielectric constant.

The converse piezoelectric coefficient d_{33} (electric field induced) was measured using a double beam laser interferometer and polarization curves were measured using a standard Saywer tower circuit. The electrostrictive coeffient Q_{33} (m^4/C^2), was calculated via the piezoelectric and polarization data using eq. (5)

$$d_{33} = 2Q_{33}k\varepsilon_0 P \tag{5}$$

where d is the piezoelectric coefficient m/V, and P is the polarization C/m^2.

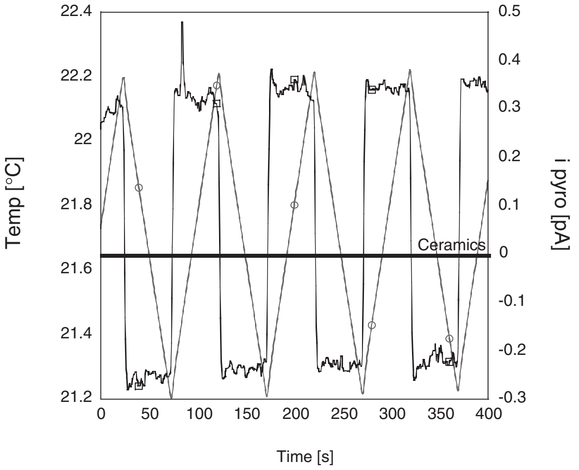


Fig. 1. Pyroelectric current (pA) for a 500 nm PST film on Pt/Si substrate, and PST bulk ceramic at room temperature and zero bias field with 1 °C oscillating temperature at a 10 mHz frequency.

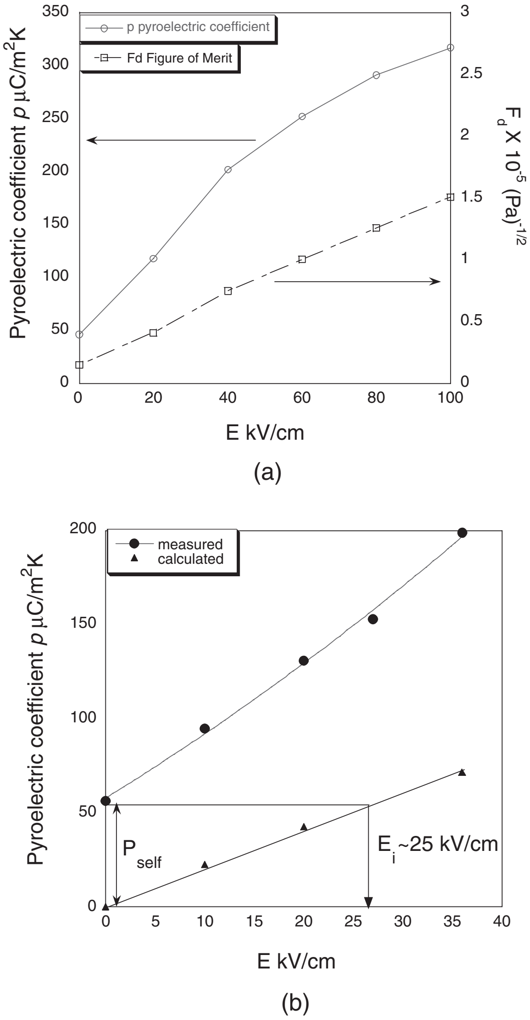
3. Results

3.1 Pyroelectric measurements

Figure 1 displays the pyroelectric measurement results for a 500 nm PST/Pt/Si thin film and a ceramic at zero bias field, with the temperature oscillating 1 °C at approximately 22 °C. The ceramic displays zero pyroelectric current as expected for a cubic material above the phase transition, while the thin film sample displays a current signal corresponding to a pyroelectric coefficient of 50 μC/(m^2 K). This unexpected pyroelectric signal appearing with zero applied field is prohibited in a centrosymmetric material; its presence reflects an inherent polarization present in the film termed "self polarization".

Figure 2(a) shows the pyroelectric coefficient and figure of merit for PST thin film on Pt/Si substrate as a function of applied DC field. The field induced pyroelectric coefficient of 300 μC/(m^2 K) at 100 kV/cm and $F_\mathrm{d} = 1.5 \times 10^{-5}$ Pa$^{-1/2}$ are comparable to sol–gel, CVD and sputtered PST film data in the literature.[11] The maximum figure of merit shown $F_\mathrm{d} = 1.5 \times 10^{-5}$ Pa$^{-1/2}$ at 100 kV/cm is greater than that previously reported for sol–gel PST on Pt/Si in the bolometer mode, greater than that for PbTiO$_3$ in the ferroelectric phase, and comparable with PZT pyroelectric sensors in the ferroelectric phase.[19] This enhanced figure of merit in our samples as compared to previous studies in the literature is due to low loss tangent values of ~0.8% at room temperature, 100 Hz and 1 kV/cm AC probing field.

The dielectric contribution to the pyroelectric coefficient was calculated using eq. (2) and is presented in Fig. 2(b) revealing a discrepancy between the measured and theoretical pyroelectric coefficient as a function of applied field. At low bias field near 10 kV/cm, the measured pyroelectric coefficient is approximately equal to the self polarization contribution plus the dielectric contribution, whereas above 10 kV/cm the measured response reflects an additional contribution believed to be the result of the reorientation of



(a)

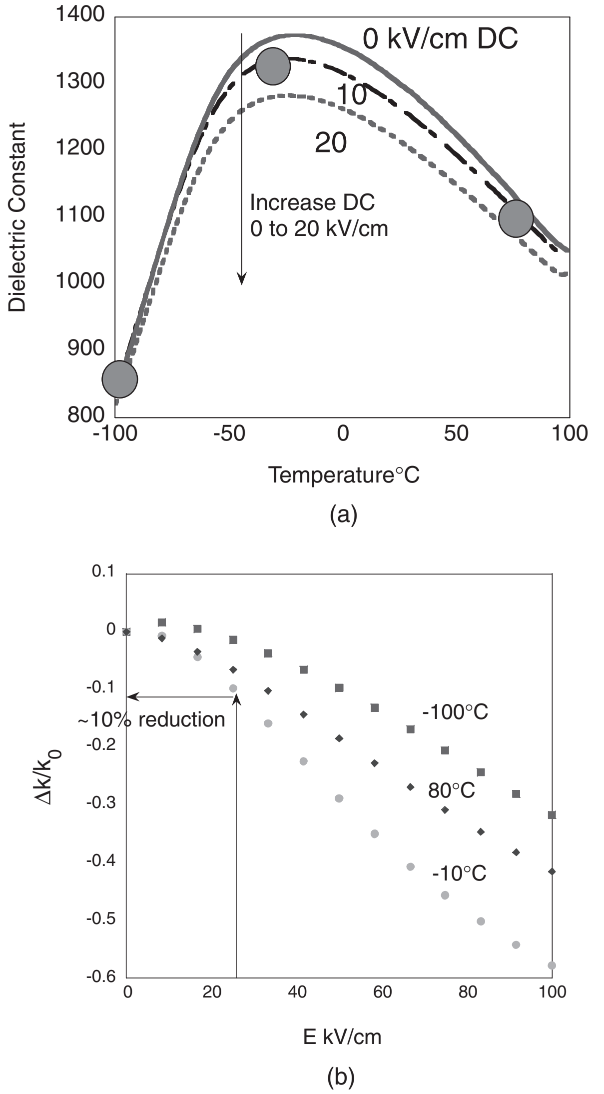
(b)

Fig. 2. (a) Pyroelectric coefficient p μC/(m² K) [eq. (1)], and figure of merit F_d [eq. (3)], for 500 nm PST thin film on Pt/Si substrate as a function of applied DC bias at 22 °C and (b) measured p versus theoretical p calculated from dielectric data [eq. (2)] as in ref. 8.

polar regions under applied bias as discussed in ref. 8. Using the calculated dielectric contribution to the pyroelectric coefficient presented in Fig. 2(b) we can estimate that an electric field of ~25 kV/cm (termed E_i, internal bias field) would be necessary to induce a pyroelectric coefficient of magnitude 50 μC/(m² K). This field level is similar to theoretical estimates,[17] and experimental data[16] in conventional ferroelectrics; and agrees well with the voltage offset seen in capacitance versus applied voltage (*C–V*) measurements in PST relaxor thin films.[20]

3.2 *DC bias permittivity*

With this information and the field dependence of the dielectric constant we can estimate the impact of self polarization on the dielectric properties of our thin films. Figure 3(a) shows the temperature dependence of the dielectric constant at DC fields of 0, 10, and 20 kV/cm. Figure 3(b) shows the quantitative reduction of the dielectric constant $\Delta k/k_0$ from eq. (4) versus applied bias at different temperature regions for PST thin films. It is seen that the maximum impact of the internal field is felt at temperatures near the phase transition; however this amounts to a relatively small 10% reduction in the dielectric constant.



(a)

(b)

Fig. 3. (a) Dielectric constant versus temperature at 1 kHz, $E_{AC} = 1$ kV/cm at 0, 10, and 20 kV/cm applied DC bias, and (b) impact of DC bias on the dielectric constant; $\Delta k_{DC}/k_{\text{low-field}}$ [eq. (4)] versus applied DC bias in the paraelectric region (80 °C), phase transition region (−10 °C) and low temperature relaxor region (−100 °C).

3.3 *Piezoelectricity and electrostriction*

The converse piezoelectric effect is presented in Fig. 4(a). It is seen that the curve is offset along the positive *d* axis, or that is displays a piezoelectric response in the absence of an applied field due again to the self-polarization/or internal bias previously discussed. The curve saturates near 100 kV/cm to a value of 60 pm/V, comparable to previous reports in the PSN (58 pm/V at 100 kV/cm) neighbor system,[5] and slightly less than those reported in PMN (90 pm/V at 40 kV/cm).[2] The hysteretic response is indicative of polar region switching at temperatures above the dielectric maximum, seen in large field PE measurements, and the measured versus dielectric contribution to the dielectric response.[8,20]

Electrostrictive coefficients may be extracted from the data using eq. (5). Thus a plot of d/k versus field induced polarization should result in a linear relation with the slope equal to $2Q_{33}$. Figure 5 shows the results of this analysis for a 550 nm PST/Pt/Si film with the calculated electrostrictive coefficient $Q_{33} = 0.025\,\text{m}^4/\text{C}^2$. This is slightly higher than

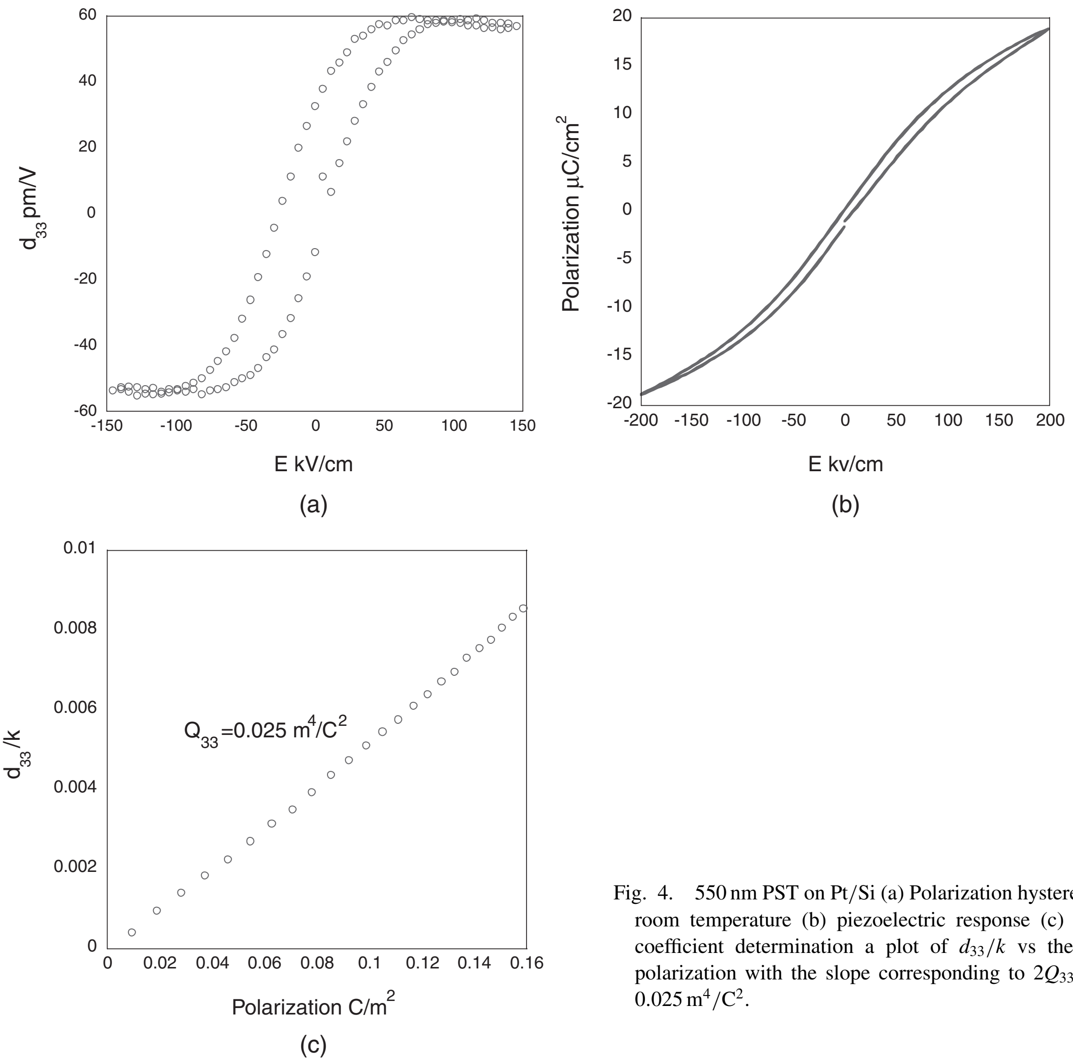


Fig. 4. 550 nm PST on Pt/Si (a) Polarization hysteresis response at room temperature (b) piezoelectric response (c) electrostrictive coefficient determination a plot of d_{33}/k vs the field induced polarization with the slope corresponding to $2Q_{33}$ [eq. (5)] $Q = 0.025\,\mathrm{m^4/C^2}$.

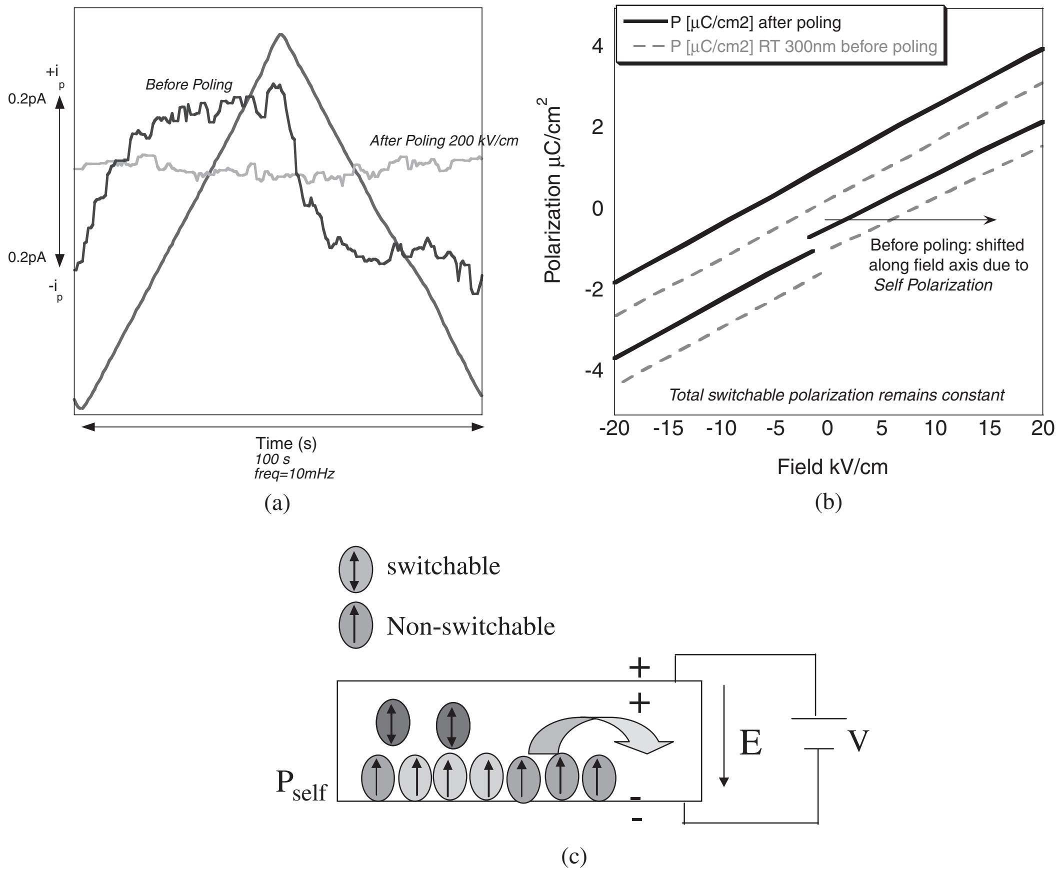
the reported values for PMN thin film ($Q_{33} = 0.0118\,\mathrm{m^4/C^2}$) and single crystal ($Q_{33} = 0.00115\,\mathrm{m^4/C^2}$),[2)] and well within the range of reported values for PMN–PT thin film, single crystals and ceramics from (0.01–$0.09\,\mathrm{m^4/C^2}$).[22)] Table I shows the piezoelectric and electrostrictive coefficients determined from PST in this report as compared to literature values for other relaxor thin films.

The reported value for Q_{33} in PST thin films, which is similar to related perovskite relaxor compounds such as PMN and PMN–PT lends credence to the claim that the reduced strain response in thin films is ultimately linked to the reduced permittivity. It is seen by the relation $M = k^2Q$ that while Q in thin films and single crystal/bulk are of the same order of magnitude, M is significantly different due to differences in the dielectric constant. These differences contribute to the induced strain variation from 0.3% in thin films to over 1.4% in single crystals.

The similarity in Q_{33} between thin film and bulk relaxors has been reported by other authors,[2,22)] however it was thought that the relaxor film's inability to strain under driving fields which had an adverse effect on the permittivity. We would like to emphasize that the permittivity and strain response of thin film relaxors in the high field region is not very well understood and small data sets exist. In contrast, the small signal permittivity of relaxors and thin films has been extensively studied consistently showing thin films with drastically reduced permittivity as compared to ceramics and single crystals.[2–8)] This consensus, performed with small signal AC field in the absence of DC field induced strain indicate that it is the film permittivity itself which is really small; and points to the role of the reduced permittivity in thin films as the origin of reduced strain response. The impact of self polarization determined from this report is to reduce the dielectric constant maximum by approximately 10%, thus similarly affecting the electrostrictive strain response. It is concluded that the presence of self polarization in relaxor thin films cannot be responsible for the differences between the strain response in ceramics and thin films.

4. Discussion

Is this "self-polarization" seen in a number of relaxor and ferroelectric thin films systems a fixed or switchable layer, and how can we see these changes? The sign, or phase of the pyroelectric coefficient is determined by the direction of the current, and thus the polarization direction in the film (top down, or bottom up). This provides an easy way to monitor the switching of the polarization. Attempts were made to pole the film in direction opposite to the polarization direction at various field levels up to 400 kV/cm at 100 °C for 10 min and monitor the subsequent pyroelectric response of the self polarization, results are presented in Fig. 5(a).



(a) (b)

(c)

Fig. 5. 300 nm PST on Pt/Si substrate (a) zero applied bias pyroelectric response 1) before and 2) after poling at 200 kV/cm and 100 °C for 10 min (b) polarization measurements before poling show loop shifted along the positive field axis, after poling procedure a re-centering of the loop occurs (c) schematic of poling process depicting both switchable and non-switchable layers of self-polarization.

Table I. Thin film piezoelectric and electrostrictive coefficients.

Material	d_{33} (pm/V) (Field kV/cm)	Q (m^4/C^2)	Reference
PST	*60 (100)*	*0.025*	*This work*
PST	13–15 (100)		11, 21
PSN	58 (100)		5
PMN	90 (40)	0.0118	2, 22

The results showed a coercive field like behavior for the reduction of the pyroelectric signal, with no reduction seen at field levels below 200 kV/cm. At this field or higher there was a reduction of the pyroelectric current from 0.2 to ~0 pA, but not a phase change. The results of this experiment suggest that there is indeed a fixed layer of polarization which cannot be switched, and the subsequent reduction to zero under poling conditions is due to a switchable layer thus compensating the contribution of the fixed layer. This result is also represented in polarization loop measurements in Fig. 5(b) where before poling the loop is shifted along field axis due to self polarization, and after poling it is re-centered. The total switchable polarization remains constant, with only a change in the initial state of polarization. Similar phenomena was observed by Abe[23)] in epitaxial sputter deposited $BaTiO_3$ thin films, and was attributed to the relaxation of the lattice misfit strain in the heteroepitaxial thin film.

5. Conclusions

The presence of a fixed layer of polarization, or an equivalent internal bias field was observed in sol–gel derived PST thin film by pyroelectric measurements and piezoelectric activity under zero applied field. Estimates of the equivalent internal field resulting in the self polarization signal from pyroelectric and dielectric data revealed a bias field of ~25 kV/cm, in good agreement with theoretical calculations. However, dielectric measurements under DC bias conditions showed that this field level results in only a ~10% reduction in the dielectric constant at temperatures near the dielectric maximum. Therefore in the case of chemical solution derived PST thin films in this study, although self-polarization clearly has a demonstrated impact on pyroelectric, piezoelectric and dielectric properties; it cannot be responsible for the differences between the strain response and drastically reduced permittivity of thin films as compared to bulk relaxors.

Acknowledgements

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