

In-plane versus out-of-plane dielectric response in the thin-film relaxor $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$

K. Brinkman, A. Tagantsev,* V. Sherman, D. Su, and N. Setter

École Polytechnique Fédérale de Lausanne (EPFL), Ceramics Laboratory, CH-1015 Lausanne, Switzerland

(Received 25 March 2005; revised manuscript received 2 November 2005; published 21 June 2006)

The nature of the strongly reduced dielectric permittivity in relaxor ferroelectric thin films is addressed. This reduced response has often been attributed to passive or surface layers in series with the film capacitance. The present report presents evidence in contradiction to this scenario in relaxor thin films by comparing the properties determined in two different measurement configurations termed “out-of-plane” versus the “in-plane” dielectric response. The analysis of the dielectric properties of $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$ films processed in a similar fashion on Pt/Ir/MgO substrates measured out-of-plane, and directly on MgO substrates measured in-plane showed that a passive layer is not the predominant effect for the reduction of permittivity by an order of magnitude for thin films as compared to bulk ceramics. This conclusion is confirmed by the results of the out-of-plane dielectric response as a function of the film thickness. It is concluded that the origin of the reduced dielectric response in relaxor thin films should be sought in the structural and microstructural properties of the film itself rather than in its interfacial properties.

DOI: [10.1103/PhysRevB.73.214112](https://doi.org/10.1103/PhysRevB.73.214112)

PACS number(s): 77.80.-e, 77.55.+f, 77.84.-s, 77.90.+k

I. INTRODUCTION

The subject of relaxor ferroelectrics comprises a current challenging issue in the physics of dielectrics. With their very large dielectric permittivity, remarkable dielectric relaxation, and nonlinearity, they have long been a topic of interest from the point of view of both fundamental studies¹⁻⁷ and practical applications.⁸ Although there have been attempts to theoretically describe the macroscopic properties of relaxors in terms of collective cluster dynamics^{6,7} or by analogies with either a glassy,^{1,5} or as a nanodomain state,^{3,4} the behavior of relaxor ferroelectrics is still very much a puzzle as neither approach can describe the whole body of essential features of the relaxor behavior. An additional puzzle is encountered with relaxor materials in the thin film form, which typically exhibit dielectric permittivities reduced by an order of magnitude as compared to ceramics and single crystal specimens.^{9,10} Clarification of the origin of this phenomenon is again of importance from the fundamental and practical points of view.

Presently, the so-called passive layer scenario provides a simple explanation for this phenomenon. According to this scenario the reduced values of permittivity in ferroelectric and relaxor thin films are due to an interfacial passive layer, while the dielectric properties of the bulk of the film are assumed to be the same.¹¹⁻¹³ In fact, a report on 100–500 nm thick relaxor $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMN-PT) and $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-PbTiO}_3$ films measured in the out-of-plane configuration (in a parallel plate capacitor) by Tyunina *et al.*¹⁴ describes the passive layer as *the* principal factor, with reconstructed film values similar to those observed in ceramics and single crystals. At the present stage of investigation and potential applications of relaxor thin films, the acceptance or nonacceptance of this scenario for the interpretation of their dielectric behavior is very important for further progress in the field. For instance, thin films can be investigated under much higher electric fields than their bulk counterparts so that, if the passive layer scenario is correct, the data obtained from the films can be used for the interpretation of properties of bulk relaxors.

In this paper we report on an experimental test of the passive layer scenario for relaxor thin films of lead scandium tantalate. We have done this by the analysis of a body of experimental data obtained using two different experimental methods for dielectric permittivity determination termed the standard out-of-plane parallel plate capacitor geometry, and the in-plane measurement geometry. In the out-of-plane situation, passive layers are in series with the film capacitance thus reducing the response, while surface passive layers in the in-plane measurement geometry should not greatly affect the response of the ferroelectric capacitor.¹⁵ Therefore, the impact of any surface layers present can be tested by a comparison of both the out-of-plane and the in-plane dielectric response. It should be noted that experimentally, the measurements for the in-plane and out-of-plane geometry cannot be performed on the same sample. Specifically, the in-plane geometry requires the ferroelectric film to be deposited directly onto a low dielectric constant substrate, while the out-of-plane geometry requires the film to be deposited on a substrate with a bottom electrode. In the present study, single crystal MgO (dielectric constant ≈ 10) was used as a substrate with and without a sputtered Pt bottom electrode in order to compare the two measurement geometries. In the following, we show that the reduced dielectric permittivity in lead scandium tantalate thin films cannot be attributed to the presence of a surface passive layer, so that the nature of the reduced permittivity of relaxor thin films must originate from other effects.

II. OUT-OF-PLANE DIELECTRIC RESPONSE

The material system lead scandium tantalate (PST) is such that the dielectric response is sensitive to *B* site order as controlled by annealing conditions. It has been demonstrated in ceramics and single crystals^{16,17} that ordered PST behaves as a conventional ferroelectric, while disordered PST exhibits the relaxor ferroelectric behavior. In thin film form, relaxor behavior in PST was typically observed after low processing temperatures near 700 °C.¹⁸⁻²⁰ In order to

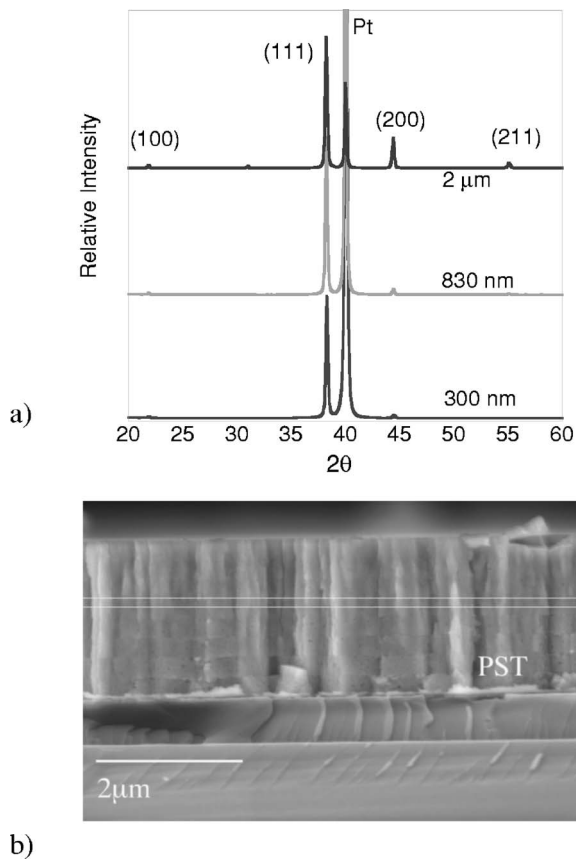


FIG. 1. PST on Pt/Si/SiO₂ substrates with thicknesses from 300 nm to 2 μm (a) x-ray diffraction spectra and (b) SEM cross section of a 2 μm thick film.

investigate the passive layer scenario for the reduction of permittivity relaxor PST films, disordered samples (characterized by the lack of superlattice reflections) were fabricated with varying the thickness from 300 nm to 2 microns on Pt/Si substrates from a mixed acetate and alkoxide sol-gel derived solution. The films were annealed at 700 °C for 1 min, and measured in the out-of-plane configuration. Top electrodes of Cr/Au were evaporated with a nominal diameter of 600 μm, and contact was made with the bottom electrode via wet etching thus defining the parallel plate capacitor geometry for measurement of the dielectric properties through the film thickness. Figure 1 displays the x-ray spectra and SEM determined microstructure of characteristic films deposited on Pt/Si substrates used in this study. No pyrochlore secondary phase was detected even after multiple annealings, and the films exhibited a global (111) orientation preference, although an increase of (100) reflections was observed with increasing film thickness. A columnar microstructure with a *thickness independent grain size* distribution of 150–300 nm was observed. Figure 2(d) displays the results of the measured thickness dependance of the out-of-plane dielectric permittivity.

The measured values of the permittivity are one order of magnitude smaller than the corresponding values for bulk ceramics¹⁶ and single crystals.¹⁷ Let us evaluate the parameters of a surface passive layer that may explain this dependence. Given the aforementioned microstructure, grain

boundary effects are negligible as they are in parallel with the measured film capacitance out-of-plane, and the effect of a surface passive layer may be then described as follows for a series connection of the film and the passive layer capacitances [see Fig. 5(a)]:

$$\frac{1}{C} = \frac{1}{C_f} + \frac{1}{C_p}, \quad (1)$$

where C is the total measured capacitance and C_f and C_p are capacitances of the film and passive layer connected in series. This leads to the following relations:

$$\frac{d}{k} = \frac{d_f}{k_f} + \frac{d_p}{k_p}, \quad (2)$$

$$\frac{1}{k} = \frac{1}{k_f} + \left(\frac{1}{k_p} - \frac{1}{k_f} \right) \frac{d_p}{d}, \quad (3)$$

where k is the measured dielectric constant, k_p and k_f are the dielectric constants of the passive layer and film, respectively, d is the total measured thickness of the film plus the surface layer, d_p and d_f are the thicknesses of the passive layer and the film, respectively. Thus, plotting $1/k$ versus $1/d$ for different values of k_f (different temperatures) one can determine $(1/k_p - 1/k_f) d_p$ and k_f . Then, by plotting the former versus $1/k_f$ one can find d_p and k_p . Such an analysis was recently performed in ferroelectric polymer films by Takahashi²¹ who found a temperature dependent passive layer. Figure 2 illustrates our implementation of this method. Figures 2(a) and 2(b) display the measured inverse dielectric constant versus the inverse of film thickness from –100 °C to 0 °C, and from 0 °C to +100 °C at 1 kHz showing a linear dependence. The following qualitative features may be observed: upon heating from –100 °C towards the phase transition²² the value of the intercept decreases, while the slope increases as a result of the increasing film permittivity. With continued heating above the phase transition, the value of the intercept increases and the slope decreases as a result of the decreasing film permittivity upon passing into the paraelectric region. A separate plot of these slopes and intercepts at different temperatures results in Fig. 2(c) which displays a linear dependence from –100 °C towards the phase transition where a strong deviation is observed. At temperatures above the phase transition this linear relationship is seen to re-emerge.

A fit of the low temperature data up to the phase transition in a linear fashion results in values of an approximately 75 nm passive layer with a dielectric constant of 636, while fitting of the data at temperatures above the phase transition results in values of 69 nm and a dielectric constant of 544. These values most likely represent the effects of a lead deficient surface layer with reduced permittivity which retains its temperature dependent dielectric response and not a true “hardening” of the polarization response at the surface.²³ Nevertheless, an examination of the ratio between the passive layer thickness and the passive layer dielectric constant reveals a value of $\sim 1 \text{ \AA}$, similar to theoretical predictions summarized in Ref. 15 from experimental data on PZT and BST thin films.

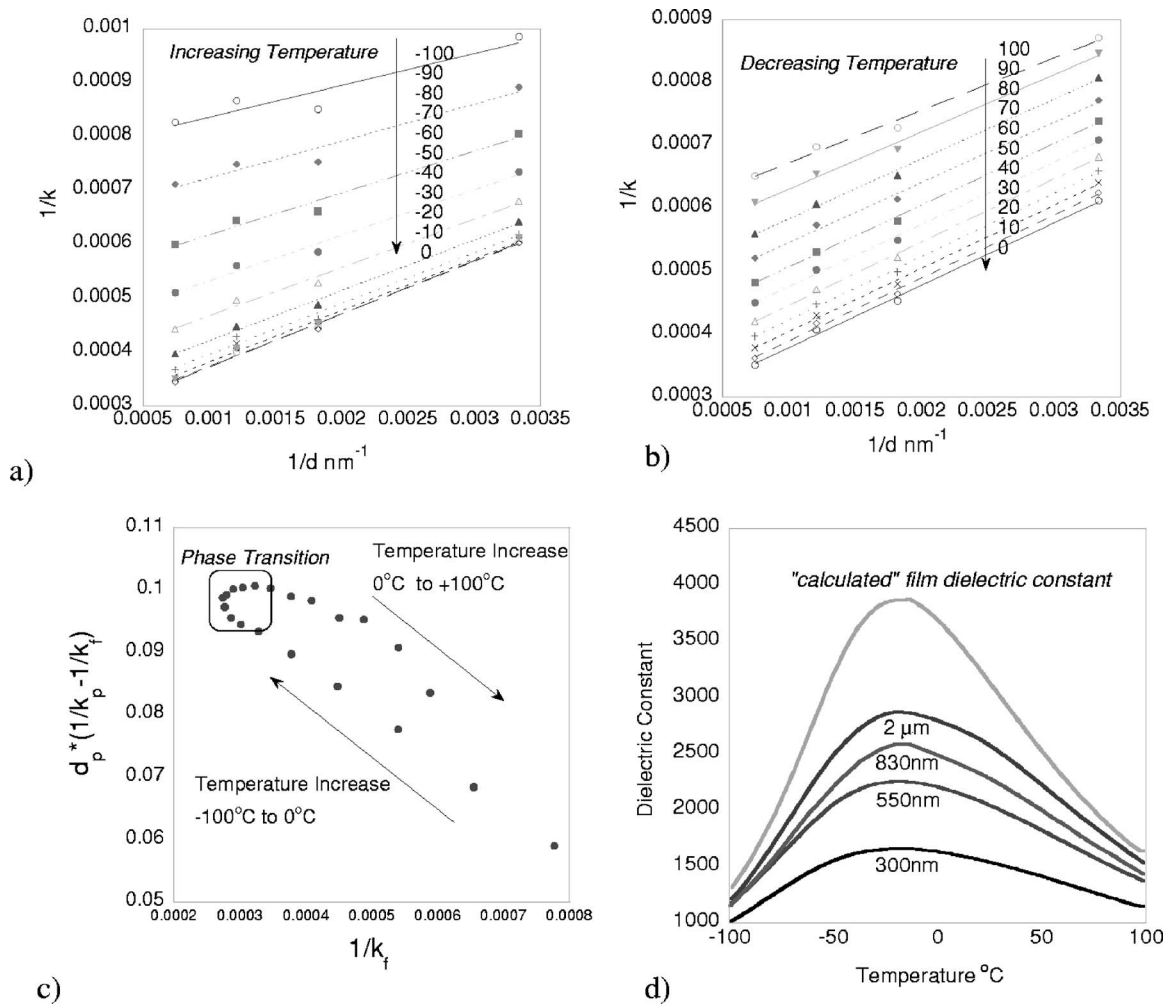


FIG. 2. Passive layer scenario: $1/k$ versus $1/d$ (a) from -100 °C to 0 °C (b) from 0 °C to 100 °C, (c) slope versus intercept of a and b at each temperature to determine parameters low temperature ($k_s=636$ and $d_s=75$ nm) and high temperature data ($k_s=544$ and $d_s=69$ nm). (d) Dielectric constant versus temperature at 1 kHz and $E_{AC}=1$ kV/cm for PST films on Pt/Si with different thicknesses as compared to the calculated dielectric constant from the passive layer model (with average values of $k_s=590$ and $d_s=72$ nm) for the 300 nm thick PST film.

Figure 2(d) displays the results of the measured thickness dependence versus the calculated film dielectric constant using averaged experimentally determined passive layer parameters (averaging slope and intercept both above and below phase transition temperature) predicting a maximum dielectric constant value of 3900 for the “bulk part” of the films. Therefore, even after taking into account experimentally determined parameters for a low dielectric constant passive layer in series with the film, the dielectric permittivity of the film is reduced by an order of magnitude as compared to the bulk material (dielectric constant in the range of 20 000). This behavior is in contrast to studies on relaxor films as reported in Ref. 14 as well as to studies on conventional ferroelectrics where Streiffer *et al.*²⁴ have reported that by taking into consideration interfacial effects in combination with the impact of strain on BST thin films, their dielectric properties are consistent with those expected in bulk ceramics.

However, it should be pointed out that the analysis in Ref. 14 was performed using measurements of films up to only

500 nm thick from which they reconstructed frequency and temperature dependencies of the film dielectric permittivity. Taking the matter one step further and (i) calculating the nominal thickness that films would need in order for passive layer effects to be negligible, and then (ii) fabricating and validating that this film thickness indeed possesses similar values as bulk ceramics, has, to the author’s knowledge, never been performed. In fact, the results in the present report show that even with films in the micron range of thickness where passive layer effects should be little, the measured dielectric permittivity is still small. A step towards such an investigation is to perform the measurements with the in-plane configuration of the electrodes.

III. IN-PLANE DIELECTRIC RESPONSE

Another test for the “passive” layer scenario of permittivity reduction is the examination of dielectric measurements performed in the in-plane geometry. The effective distance between the electrodes in this configuration is much higher

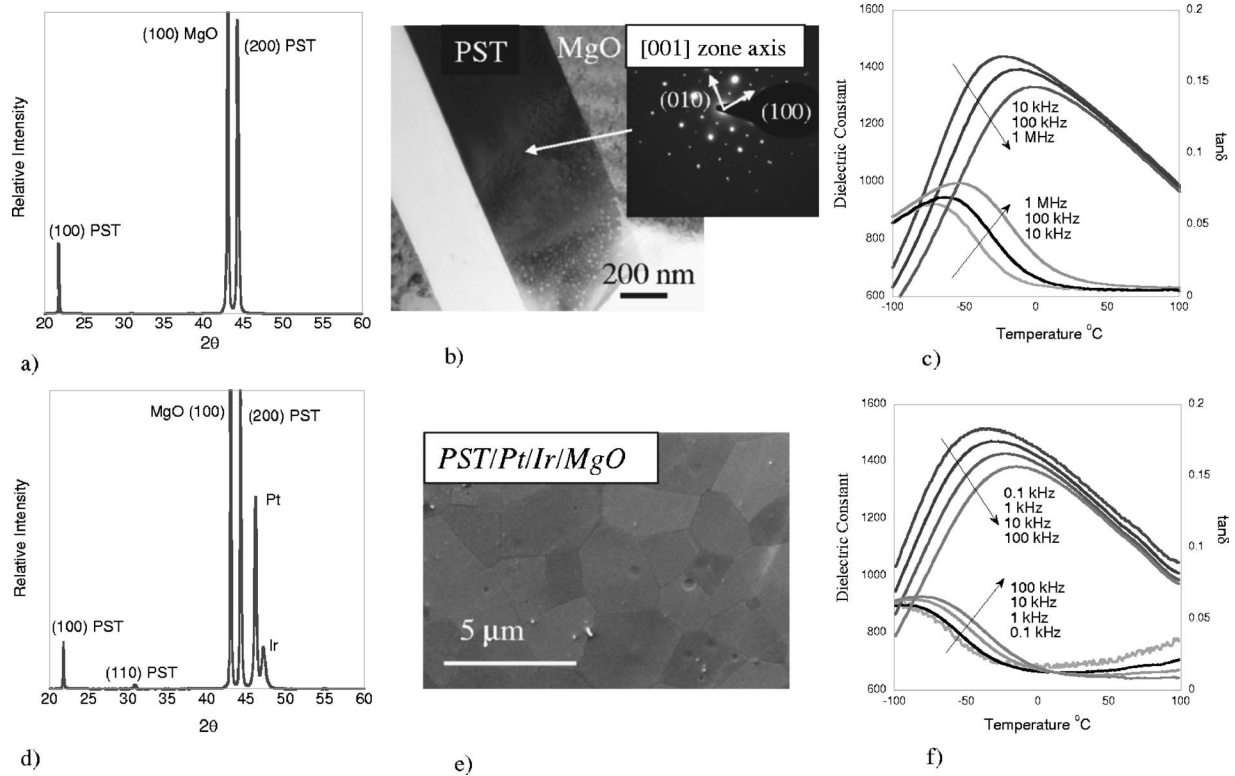


FIG. 3. Properties of 540 nm PST on the MgO single crystal substrate. (a) X-ray diffraction indicating (100) orientation, (b) bright field TEM and selected area electron diffraction images of the [001] zone axis indicating single crystal diffraction pattern, and (c) temperature dependence of film dielectric permittivity measured in-plane at $E_{AC}=1$ kV/cm. Properties of 650 nm PST film on the Pt/Ir/MgO substrate: (d) x-ray diffraction, (e) SEM determined microstructure, and (f) temperature dependence of film dielectric permittivity measured out-of-plane.

than the thickness of the film and can be easily adjusted by the photolithographic process. For these experiments we deposited sol-gel derived PST films on (100) single crystal MgO substrates annealed at 700 °C for 1 min. Two top electrodes with a length of 1500 μm and a width of 750 μm were deposited with standard photolithographic techniques used to define the gap width between the electrodes of 10, 20, and 30 μm . An important feature of this measurement configuration is that it is less sensitive to the presence of a thin electrode-adjacent passive layer as it is seen from the Appendix, where the detailed analysis of the passive layer contribution to the total capacitance of the in-plane and out-of-plane configurations is performed. From this analysis it is clear that for the parameters of our system, not taking into account the possible presence of the electrode-adjacent passive layer would cause an uncertainty in determination of k_f , whose values could lie in the range $k_{f,\text{eff}} < k_f < 2k_{f,\text{eff}}$ when k_f approaches 10 000 and in the range $k_{f,\text{eff}} < k_f < 1.3k_{f,\text{eff}}$ when $k_f=1000$. In the latter case, the error due to neglecting the passive layer would not exceed 20%–30%. Here $k_{f,\text{eff}}$ is the dielectric permittivity of the thin film calculated from the measured capacitance value using an assumption that no electrode-adjacent passive layer is presented in our in-plane measurement configuration.

Thus, the dielectric response in-plane was calculated using the partial capacitances of the thin film (C_{eff}), substrate (C_{sub}), and air (C_{air}) components [see Fig. 5(b) below] as

described by Vendik in Ref. 26. The error due to the calculations in Refs. 26 and 27 is estimated to be less than 5% in our situation, however, the actual error is increased to about 10% due to an inaccuracy in the measurements of the gap distance and its inhomogeneity. Different samples are therefore compared in order to obtain a representative value of the dielectric constant to within 10%. By this method we calculated the dielectric constant of the film using the experimental data obtained from the samples made on the same substrate but having different gap widths. No dependence of the calculated dielectric permittivity on the distance between the electrodes was found. This additionally justifies the absence, or at least negligible effect of the passive layer in our measurement configuration (see Appendix for the detailed discussion).

These measurements necessitated films of PST deposited directly onto low dielectric constant single crystal substrates [in this case (100) MgO]. The x-ray spectra of a 540 nm PST film on MgO is presented in Fig. 3(a) indicating a pure perovskite phase content with a preferred (100) orientation, matching the underlying substrate. TEM investigations are presented in Fig. 3(b) where the selected area diffraction pattern of the (001) zone axis confirms the single crystal-like nature of the film. The dielectric constant, loss tangent, and imaginary part of the loss are presented in Fig. 3(c). The dielectric maximum for this sample was near 1390 at -12 °C and 100 kHz with a room temperature loss tangent of 0.6%. The sample exhibited frequency dispersion typical for relax-

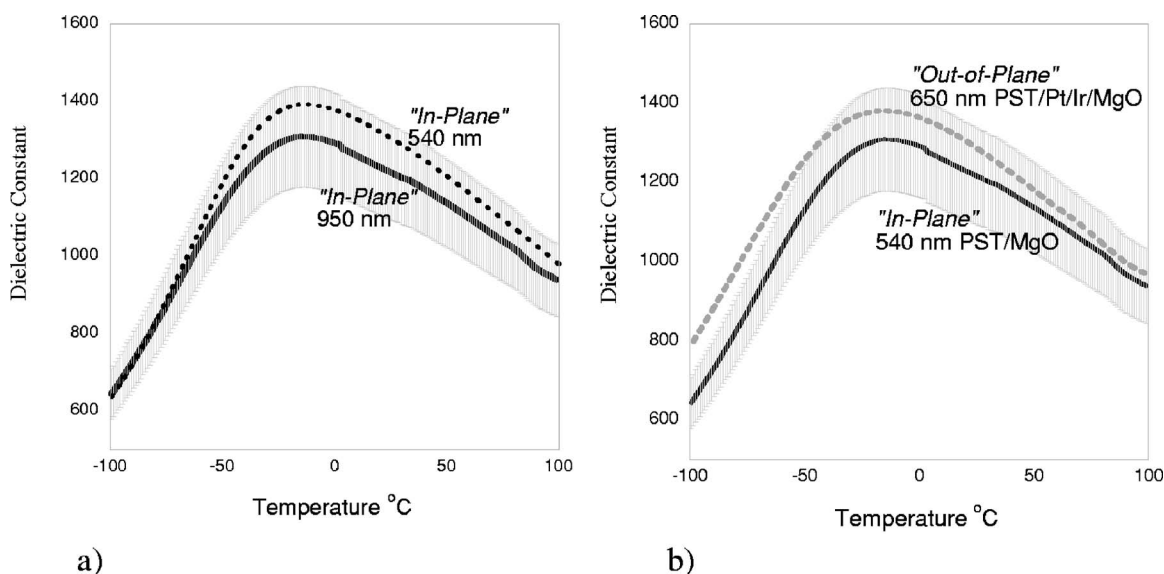


FIG. 4. (a) Thickness dependence of in-plane dielectric response, dielectric constant versus temperature at 100 kHz, and $E_{AC}=1$ kV/cm for 540 and 950 nm PST films on the single crystal MgO and (b) in-plane (950 nm PST) versus out-of-plane (650 nm PST) dielectric constant comparison at 100 kHz and $E_{AC}=1$ kV/cm; error bars indicate 10% error estimate.

ors in the dielectric constant as well as in the loss tangent.

Of particular interest is the examination of the thickness dependence of the dielectric constant as measured in-plane of the film. Figure 4(a) shows the dielectric constant versus temperature for PST films on MgO with thicknesses of 540 nm and 950 nm along with the 10% error estimate. The dielectric constant measured at the same frequency, and electric field was the *same* for both thicknesses within the range of error. This demonstrates, as is clearly expected, that there is no thickness dependence for the dielectric constant when measured in the in-plane configuration. It is of importance to notice that the value of the dielectric constant measured in this configuration is also an order of magnitude lower than that typically observed in bulk ceramics; even in a configuration where the possible presence of a passive layer would account for a maximum reduction of the measured capacitance by a factor of 2.

The final proposed test of the passive layer scenario is the examination of the question, “How does the dielectric constant measured in the in-plane and the out-of-plane configuration compare for films processed on the same substrate under similar conditions?” To examine this question, a bottom electrode of (100) platinum was deposited onto (100) MgO using an Ir adhesion layer. Figure 3(d) displays the x-ray spectra and SEM determined microstructure [Fig. 3(e)] of a 650 nm PST film deposited on Pt/Ir/MgO showing pure phase perovskite with a highly preferred (100) orientation, including the peaks of (100) MgO substrate, (100) Pt electrode, and Ir peak. The films displayed columnar grain growth, with large grains in excess of $3 \mu\text{m}$. The dielectric response of 650 nm PST is presented in Fig. 3(f) showing a maximum dielectric constant of 1470 at -28°C and 1 kHz, with a loss tangent of 1.3% in the room temperature paraelectric phase. The loss tangent increases and exhibits frequency dispersion at higher measuring temperatures, in addition to slight frequency dispersion of the dielectric con-

stant in the paraelectric region. The reduced value of the dielectric constant in this sample as compared to samples produced on Pt/Si substrates under similar conditions may be due to possible mechanical constraints or thermal induced stress.

A direct comparison of a 950 nm PST film on MgO measured in-plane and a 650 nm PST film on Pt/Ir/MgO measured out-of-plane, processed and measured under the same conditions is shown in Fig. 4(b) revealed *essentially the same values* within the range of error. This measurement provides strong evidence against the “passive” layer scenario, since a possible presence of low dielectric constant layer between film and electrode would be expected to considerably reduce the out-of-plane dielectric response, and have a much less pronounced effect on the in-plane response. Although different microstructure are seen in the two films, the very large grain size ($3 \mu\text{m}$) of the polycrystalline PST oriented in the (100) direction measured out-of-plane approximates the microstructure of (100) epitaxial PST films deposited directly on MgO substrates.

IV. DISCUSSION AND CONCLUSIONS

We have examined the reduced dielectric response in relaxor thin films in terms of the commonly cited passive layer scenario by using two methods of investigation: (1) The out-of-plane dielectric response as a function of thickness analyzed in terms of a series capacitance connection, and (2) the in-plane dielectric response as a function of thickness and distance between the electrodes. A comparison of out-of-plane versus the in-plane response of similarly processed films showed that the reduction of permittivity by an order of magnitude for relaxor thin films as compared to bulk ceramics cannot be explained by the possible presence of a passive layer.

This conclusion contradicts that by Tyunina and Levoska.¹³ Let us look closer at the argumentation presented by these authors. Essentially, their main argument in favor of the passive layer scenario is that, using the temperature dependence of the measured permittivity of the film $k(T)$, one can plot a function

$$k_{\text{mod}}(T) = \left(\frac{1}{k(T)} - \frac{\alpha}{k_m} \right)^{-1} \quad (4)$$

which reasonably imitates the temperature dependence of the permittivity of the bulk relaxor material. Here k_m is the maximum value of $k(T)$ and α , $0 < \alpha < 1$, is an adjustable parameter. It is clear that by adjusting this parameter, one can obtain any maximum value for $k_{\text{mod}}(T)$. Since the value of α cannot be determined in principle, one cannot conclude from the analysis by Tyunina and Levoska¹³ that the tremendous reduction of the permittivity in relaxor thin films is due to the passive layer effect. Thus, at present, there is no experimental data supporting the passive layer scenario in relaxor thin films; our data show that this scenario is incompatible with the behavior of PST films, the data on PMN-PT films from Ref. 13 do not contradict this scenario but do not support it either.

Another important feature of all the available data on the temperature and frequency dependencies of permittivity in relaxor thin films is that these dependencies are qualitatively similar to those for bulk materials, but with the maximum value scaled down by at least one order of magnitude. The scaling law for the whole $k(T)$ curve is similar to that of the passive layer model, Eqs. (2) and (4). Actually, this point has been used by Tyunina and Levoska¹³ as indirect evidence for the validity of the passive layer scenario. However, Eqs. (2) and (4) describe not only the case of a surface passive layer but also the case of layered composites (see, e.g., Ref. 15). In addition, a similar scaling law may also be expected in more involved composite models. In this context, a possible reason for the hardening of the dielectric response in relaxor thin films may be due to inhomogeneous transformation of material of the films into the “true relaxor” state. In other words, the crystallinity (in terms of x-ray data) and the lack of the *B*-site order may be only necessary but not sufficient condition for having full scale relaxor behavior (“true relaxor”) in a material with nominally relaxor composition. A similar situation for films of an incipient ferroelectric has been recently addressed by Ostapchuk *et al.*²⁸ who interpreted the hardening of the dielectric response in SrTiO₃ films in terms of the brick-wall composite model. We believe that the origin of the reduced dielectric response in relaxor thin films should be sought in the structural and microstructural properties of the film itself rather than in its interfacial properties.

ACKNOWLEDGMENTS

We acknowledge the Swiss National Science Foundation for funding as well as the COST 525 European Action. Pavel Mokry, currently at the Technical University of Liberec, Czech Republic is also acknowledged for helpful discussions.

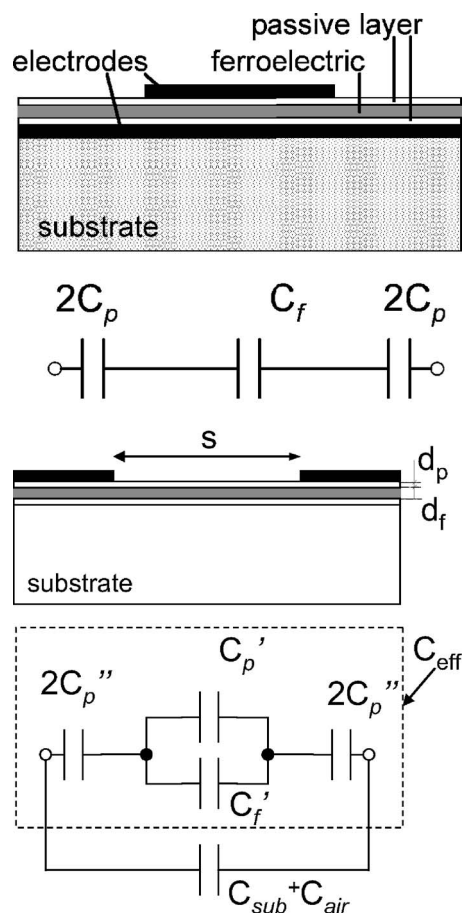


FIG. 5. The layouts and equivalent electrical circuits of the out-of-plane, (a), and in-plane, (b), test structures.

APPENDIX: MODELING THE EFFECT OF THE PASSIVE LAYER IN IN-PLANE AND OUT-OF-PLANE CONFIGURATIONS

To compare the influence of the passive layer on the total capacitance in both the in-plane and out-of-plane configurations, simple equivalent circuits presented in Fig. 5 can be used.²⁵ The out-of-plane configuration has been already addressed by Eq. (1).

In the case of the in-plane configuration [Fig. 5(b)], the part of the passive layer, which is essentially inside the gap (capacitor C_p') is connected parallel to the ferroelectric part of the film (capacitor C_f') so that its impact on the total capacitance can be neglected because the passive layer is much thinner than the ferroelectric ($d_p \ll d_f$) and it has a lower dielectric permittivity as compared to that of ferroelectric ($k_p < k_f$). Additionally, the passive layer manifests itself as a couple of capacitors $2C_p''$ connected in series with the ferroelectric capacitor C_f' . These are due to the area close to the edges of the planar electrodes where the electric field is distributed nonhomogeneously.²⁵ The capacitance C_p'' can be evaluated as $\lambda d_f w k_p / d_p$,²⁵ where w is the width of the planar capacitor and the parameter λ is a coefficient which accounts for the electric field inhomogeneity in the space near the electrode edges and is independent of w and the distance between the electrodes, s , when $d_f \ll w, s$. Thus, in both con-

figurations the contribution of the passive layer to the capacitance of the fabricated thin film capacitor can be modeled by a series connection of two capacitors (C_f , C_p or C'_f , C''_p) as in Fig. 5,

$$C^{\text{out-of-plane}} = \frac{C_f}{1 + \frac{k_f d_p}{k_p d_f}}, \quad (\text{A1})$$

$$C_{\text{eff}}^{\text{in-plane}} = \frac{C'_f}{1 + \frac{k_f d_p}{k_p s \lambda}}, \quad (\text{A2})$$

where k_f , k_p are the dielectric permittivities of the ferroelectric and the passive layer respectively, d_f , d_p are the thicknesses of the ferroelectric and passive layer, respectively, s is the distance between the electrodes in the in-plane configuration. Judging from these two equations we conclude that, in the in-plane geometry, the impact of electrode-adjacent passive layer (via C''_p) on the total capacitance is equivalent to that of the same layer in the parallel plate capacitor with the effective thickness of the ferroelectric layer $s\lambda$. In Ref. 25, Vendik has estimated the parameter λ for a series of examples which could be of practical interest. In this work, we examined the effect of a nonhomogeneous distribution of the electric field in the area close to the edges of the planar electrodes (the effect which the parameter λ accounts for) by means of finite element analysis performed using ANSYS® software.

The 2D model of the in-plane capacitor has been introduced as shown in Fig. 5(b). Using this basis, a value of zero potential has been applied to one electrode and $U=10$ V to the second electrode. The distributions of the electric field and electric displacement inside different layers of the capacitor were analyzed and the charge per unit length accumulated at one of two electrodes was calculated as

$$Q = \int_l D_n dl, \quad (\text{A3})$$

where l is a length of the electrode and D_n is a normal component of the electrical displacement. The capacitance of the in-plane capacitor then has been calculated as

$$C^{\text{in-plane}} = \frac{Q}{U} w, \quad (\text{A4})$$

where $U=10$ V and w is the width of the electrode. In order to minimize the calculation time, the meshing area was reduced by using a total capacitor length of $1000 \mu\text{m}$, width of $500 \mu\text{m}$ and a substrate thickness of $100 \mu\text{m}$ as compared to a capacitor length of $1500 \mu\text{m}$, width of $750 \mu\text{m}$, and substrate thickness of $500 \mu\text{m}$ used in the experimental section of this work. The width affects the total charge accumulated and has no impact on the conclusions of this simulation, while several independent simulations showed that the change in total capacitance of the structure was negligible after varying the substrate thickness from 500 to $100 \mu\text{m}$. The thickness of the passive layer d_p was fixed at 50 nm in

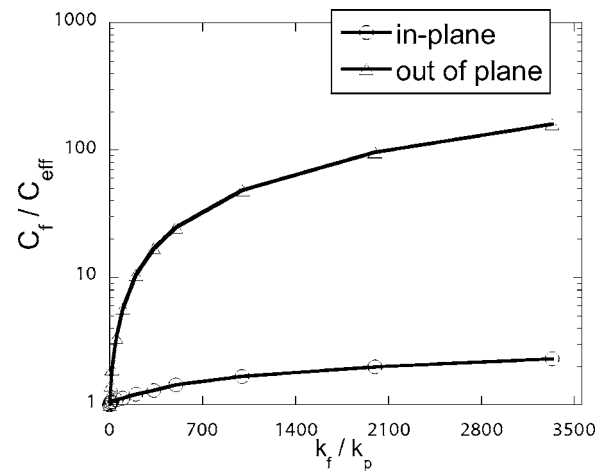


FIG. 6. The simulated reciprocal function of the calculated total capacitance of the in-plane and out-of-plane measurement structures (see Fig. 5) normalized by the capacitances calculated when $k_p=k_f$ are plotted versus the ratio k_f/k_p . The following parameters of the simulated structures were used: thickness of the ferroelectric layer $d_f=1000$ nm, thickness of the passive layer $d_p=50$ nm, distance between the electrodes in the in-plane configuration $s=20 \mu\text{m}$, permittivity of the substrate $k_{\text{sub}}=10$, thickness of the substrate $d_{\text{sub}}=100 \mu\text{m}$, length and width of one of the top electrodes $l=w=500 \mu\text{m}$.

the present situation as the use of smaller thicknesses was limited by the finite element software.

We have performed the simulation of the total capacitance of the in-plane and out-of-plane capacitors for permittivity values of the ferroelectric $k_f=1000$ and $k_f=10000$, and k_p values being in the range of $k_p=3$ to $k_p=k_f$. The reciprocal calculated total capacitance of these two configurations normalized by the capacitances calculated when $k_p=k_f$ are plotted versus the ratio k_f/k_p in Fig. 6. One can see that C_f/C for the out-of-plane configuration is a much faster increasing function of k_f/k_p as compared to that calculated for the in-plane configuration.

From Fig. 6 it is clearly seen that the total capacitance of the in-plane capacitor is reduced by a maximum factor of 2.3 when the ratio k_f/k_p approaches 3000 (value corresponding to the worst case scenario of $k_f=10000$ and $k_p=3$), whereas the out-of-plane capacitor is reduced by a factor of 100. This analysis has allowed us to make the conclusion that for known thickness of the ferroelectric film (being in the range from 500 nm to 1000 nm) and dielectric permittivities in the expected range of hundreds to tens of thousands (bulk ceramics value), the contribution of the passive layer (whose thickness and dielectric permittivity could vary from 1 nm to 10 nm and from 3 to 100 , respectively) can be neglected in the case of the in-plane configuration, when rough estimates of the value of the dielectric permittivity of the ferroelectric are needed. Furthermore, from Eq. (A2) it is seen that the effect of the possible presence of a passive layer can be easily sorted out by making a series of measurements on various in-plane capacitors having different distance between the electrodes (s). A calculated permittivity of the ferroelectric layer which is not dependent on s is evidence of the absence (or negligible effect) of the passive layer in the investigated in-plane capacitor.

*Electronic address: Alexander.Tagantsev@epfl.ch

- ¹E. Cross, *Ferroelectrics* **76**, 241 (1987).
- ²D. Viehland, S. J. Jang, L. E. Cross, and M. Wuttig, *J. Appl. Phys.* **68**, 2916 (1990).
- ³A. E. Glazounov, A. K. Tagantsev, and A. J. Bell, *Phys. Rev. B* **53**, 11281 (1996); A. Glazounov and A. Tagantsev, *Ferroelectrics* **221**, 57 (1999).
- ⁴V. Westphal, W. Kleemann, and M. D. Glinchuk, *Phys. Rev. Lett.* **68**, 847 (1992).
- ⁵R. Pirc, R. Blinc, *Phys. Rev. B* **60**, 13470 (1999).
- ⁶J. Toulouse, B. E. Vugmeister, and R. Pattnaik, *Phys. Rev. Lett.* **73**, 3467 (1994).
- ⁷B. E. Vugmeister and H. Rabitz, *Phys. Rev. B* **57**, 7581 (1998).
- ⁸S.-E. Park and T. S. Shrout, *J. Appl. Phys.* **82**, 1804 (1997).
- ⁹G. Catalan, M. Corbett, R. Bowman, and J. Gregg, *J. Appl. Phys.* **91**, 2295 (2002).
- ¹⁰V. Nagarajan, S. Alpay, C. Ganpule, B. Nagaraj, S. Aggarwal, E. Williams, A. Roytburd, and R. Ramesh, *Appl. Phys. Lett.* **77**, 438 (2000).
- ¹¹L. Francis, Y. Oh, and D. Payne, *J. Mater. Sci.* **25**, 5007 (1990).
- ¹²J. Park and S. Trolier-McKinstry, *J. Mater. Res.* **16**, 268 (2001).
- ¹³M. Tyunina and J. Levoska, *Phys. Rev. B* **63**, 224102 (2001).
- ¹⁴M. Tyunina, J. Levoska, and S. Leppavuori, *J. Mater. Sci.: Mater. Electron.* **14**, 369 (2003).
- ¹⁵A. Tagantsev, V. Sherman, K. Astafiev, J. Venkatesh, and N. Setter, *J. Electroceram.* **11**, 5 (2003).
- ¹⁶C. Stenger and A. Burggraaf, *Phys. Status Solidi A* **61**, 275 (1980).
- ¹⁷N. Setter and E. Cross, *J. Appl. Phys.* **51**, 4356 (1980).
- ¹⁸D. Liu and D. Payne, *J. Appl. Phys.* **77**, 3361 (1995).
- ¹⁹Z. Huang, P. Donohue, Q. Zhang, D. Williams, C. Anthony, M. Todd, and R. Whatmore, *Integr. Ferroelectr.* **45**, 79 (2002).
- ²⁰K. Brinkman, M. Cantoni, A. Tagantsev, P. Muralt, and N. Setter, *J. Electroceram.* **13**, 105 (2004).
- ²¹Y. Takahashi, A. Kitahama, and T. Furukawa, *IEEE Trans. Dielectr. Electr. Insul.* **11**, 227 (2004).
- ²²We use the term “phase transition” as a short hand for the temperature, at which permittivity passes through the maximum.
- ²³R. Kretschmer and K. Binder, *Phys. Rev. B* **20**, 1065 (1979).
- ²⁴S. Streiffer, C. Basceri, C. Parker, S. Lash, and A. Kingon, *J. Appl. Phys.* **86**, 4565 (1999).
- ²⁵O. G. Vendik and M. A. Nikol'skii, *Tech. Phys.* **46**, 112 (2001).
- ²⁶O. Vendik, S. Zubko, and M. Nikolski, *Tech. Phys.* **44**, 349 (1999).
- ²⁷A. Deleniv, *Tech. Phys.* **44**, 356 (1999).
- ²⁸T. Ostapchuk, J. Petzelt, V. Zelezny, A. Pashkin, J. Pokorny, I. Drbohlav, R. Kuzel, D. Rafaja, B. P. Gorshunov, M. Dressel, C. Ohly, S. Hoffmann-Eifert, and R. Waser, *Phys. Rev. B* **66**, 235406 (2002).