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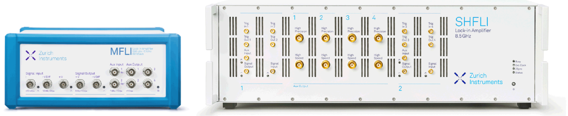

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The Impact of chemical ordering on the dielectric properties of lead scandium tantalate $Pb(Sc_{1/2}Ta_{1/2})O_3$ thin films

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The impact of chemical ordering on the dielectric properties of the thin film relaxor $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST) was investigated. It was found that the dielectric permittivity increased with increased *B* site order, directly opposite the behavior observed in ceramics. Highly ordered PST thin films on sapphire substrates were found to behave as conventional ferroelectrics with dielectric permittivities near 7000 and well developed polarization hysteresis loops below the phase transition temperature. In contrast, disordered thin films were found to exhibit relaxor behavior with the thin film permittivity reduced by an order of magnitude as compared to ceramic specimens. The direct experimental evidence of highly ordered films and ceramics possessing similar properties under similar processing conditions points to intrinsic differences in the thin film relaxor state as compared to the ceramic relaxor state. It is proposed that the low processing temperatures employed in thin film fabrication do not provide sufficient energy to achieve the same state of "disorder" which is found in ceramic specimens sintered at high temperatures. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2770834]

I. INTRODUCTION

Relaxor ferroelectrics are a special case of ferroelectric materials which are presently understood to be a composite structure consisting of polar nanoregions (PNRs) embedded in a nonpolar matrix.[1–3] The dynamics of these PNRs which give rise to large dielectric permittivity and dielectric relaxation have long been a subject of interest for both fundamental studies as well as practical applications such as high strain actuators.[4] The fabrication of these materials in the thin film form poses a problem as virtually all published reports reveal a drastic reduction in the permittivity of thin film relaxor materials. Presently, a debate exists as to whether the degradation of properties in the thin film form is due to extrinsic effects, or is a result of an intrinsic difference in the thin film and ceramic relaxor state.

Although the dielectric constant in thin films relaxors is reduced by an order of magnitude as compared to ceramics,[5–9] direct comparisons between thin films and bulk materials are complicated because the origin and dynamics of polar regions in relaxors, which give rise to their large dielectric response, are still the subject of controversy.[3,10–12] At a fundamental level, recent evidence of PNR formation at temperatures above the dielectric maximum was recently observed in lead scandium tantalate[13] (PST) and lead magnesium niobate[14] (PMN) thin film relaxors, indicating that qualitatively, the thin film and bulk relaxor states are similar.

If the intrinsic response is similar, it is logical to look for outside influences which may be responsible for the thin film permittivity reduction. These effects are referred to as "extrinsic" effects in this study, and have been the focus of current research on thin film relaxors. However, an examination of common extrinsic effects such as interfacial capacitance layers,[8,15] substrate induced strain,[6,16,17] and grain size effects have not yet yielded a convincing explanation for the low permittivity in thin film relaxors.

For instance, an examination of the most commonly used scenario for explaining the reduced thin film properties revealed that an interfacial passive layer is not the predominant effect in PST thin film permittivity reduction.[8] This confirms the work performed by Saad *et al.*[18] on free standing, single crystal barium titanate with film thickness less than 100 nm. The free standing thin film was prepared from focused ion beam sectioning of thin layers from the parent single crystal. The dielectric measurements of the film and crystal were identical, ruling out interfacial capacitance arguments in this conventional ferroelectric system. This reinforces theoretical formulations on the impact of strain on the nature of the phase transition characteristics for conventional ferroelectrics.[19] Although the impact of strain in relaxor ferroelectric thin films is far from being understood, experimental data available on a number of relaxor material systems including PMN (Ref. 6) and PST (Ref. 16) indicate that while the temperature of the dielectric maximum (analogous to the phase transition in conventional ferroelectrics) is shifted down to lower temperatures under compressive or tensile strain, the value of the dielectric maximum is hardly affected.

Therefore, in order to give on insight into the phenomena of low permittivity in relaxor thin films, we have performed the comparison of *relaxor* (disordered) thin films to *ferroelectric* (ordered) thin films using the phenomenon of *B* site chemical ordering in PST thin films. Using these results we further comment on the nature of the thin film relaxor state and the differences between bulk and thin film relaxors.

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The PST material system has been used as a "tool" in this study because by tailoring the arrangement of B site species Sc and Ta, we can produce thin films that behave as either a conventional ferroelectric [ordered PST (PST-O)] or a relaxor ferroelectric [disordered PST (PST-D)]. This phenomenon of ordered ferroelectric PST was initially demonstrated by Stenger and Burggraaf[20] and Setter and Cross[21] in ceramics and single crystals. Ordering was initially observed during slow cooling from sintering temperatures, in contrast to completely disordered samples prepared by fast cooling rates often referred to as quenching. Further experiments revealed that one could produce an ordered state by postannealing disordered samples at an intermediate temperature near 1000 °C for extended periods. Accompanying the increased periodicity were an upward shift of the dielectric maximum to higher temperatures and a reduced value of the maximum permittivity. Further work on the ordering phenomenon showed that defects such as lead vacancies could impede the relaxor to ferroelectric transition.[22] Ordering of the B site has also been observed in PST thin films.[23] However, the application oriented work in the field of pyroelectric detectors operated in the bolometer mode[24] produced little dielectric data that are available for the comparison of thin film behavior with ceramics.

In this paper, the chemical ordering of thin films performed at temperatures near those used to order bulk ceramic samples in a PbO rich atmosphere resulted in thin films with similar dielectric properties to their ceramic counterparts. Disordered films processed at 700 °C (temperatures over 800 °C below the sintering temperature of ceramics, 1500 °C) showed relaxor behavior, however, their permittivity maximum was shifted down by an order of magnitude. An examination of the available data in the PST material system points to intrinsic differences in the state of disorder found in thin films and bulk ceramic forms of the material. Specifically, it is proposed that the low processing temperatures employed in thin film fabrication do not provide a sufficient driving force to achieve the same state of "disorder" which is found in ceramic specimens. The thin film disordered state may be characterized by point defects of oxygen and lead vacancies which stabilize larger stoichiometric fluctuations of B site species than is expected when the disorder is entropy driven as in ceramic specimens. The origin of these stoichiometric deviations in chemical solution derived thin films may be a result of both the solution inhomogeneity and the amorphous to pervoskite transformation which passes through a Ta-rich intermediate phase. Once these defects are formed during film crystallization they may be locked into place; the low temperatures employed do not allow for sufficient energy to reach equilibrium.

II. EXPERIMENT

The PST films were prepared using a modified alkoxide solution precursor method, details are available in Refs. 16, 23, and 25. Films were deposited on Pt/Si, MgO (100), sapphire (0001) and strontium titanate (STO) (111) substrates by spin coating at 3000 rpm for 40 s followed by pyrolysis at 400 °C for 1 min between layers. After four subsequent spin-coated layers the films were heated in a rapid thermal annealing furnace (with a ramp rate of 1 min) to temperatures between 700 and 850 °C for durations from 1 to 20 min. In studies where temperatures exceeded 850 °C for durations longer than 20 min, films were first rapid thermal annealed to crystallinity at 700 °C for 1 min before being further heat treated in a box furnace. The samples were placed in a double shelled sealed ceramic container with a pellet of $PbO/PbZrO_3$ between the first and second ceramic covers providing a control of the processing atmosphere in the system, while eliminating PbO deposits on the film surface. Thin (2 nm) TiO_2 seed layers were sputter deposited on sapphire substrates to aid with perovskite phase formation.[26] The small amount of TiO_2 was absorbed into the PST crystal lattice during film annealing and did not lead to a low dielectric constant layer at the film/substrate interface.

The degree of order was determined using the integrated area of the superlattice peak compared to a reference peak in the material (usually the adjacent 100 peak in bulk specimens). In textured thin films, the degree of orientation is best seen in films which have at least some degree of (111) reflections. In this case, there is a convenient basis to compare the intensity of the superlattice peak to the principal (111) reference peak which removes any effect due to preferential orientation. The order degree in this case is described by the S parameter,

$$S^2 = \frac{I_{(1/2,1/2,1/2)}/I_{(111)}(\text{observed})}{I_{(1/2,1/2,1/2)}/I_{(111)}(\text{calculated, } S=1)}, \qquad (1)$$

where $S=1$ for complete order, $S=0$ for a completely disordered material, and I is the integrated intensity area of the relevant diffraction peak.

The microstructure and crystallinity of the films were characterized by x-ray diffraction (XRD; Siemens Cu $K\alpha$, 40 kV, 30 mA), scanning electron microscopy (SEM; Philips XL30), and transmission electron microscopy (TEM; Philips CM300).

Dielectric properties were measured in the *out-of-plane* parallel plate capacitor configuration in samples with bottom electrodes of Pt deposited on Si, as well as 0.5 at. %Nb doped STO substrates. The dielectric response *in plane* was calculated using the partial capacitance of the film, substrate, and air components, as described by Vendik *et al.* in Ref. 27 for PST films deposited on single crystal MgO, and sapphire substrates by depositing two top electrodes of length 1500 μm and width 750 μm using standard photolithographic techniques to define the gap width between the electrodes. The in-plane polarization has been calculated on the basis of the measured charge using methods in Ref. 27.

III. STRUCTURE

In general, it was observed that an increase in the annealing temperature, even for short durations, increased the amount of B site order in films. A thermal treatment at 1000 °C is typically carried out in order to obtain the ordered structure in bulk ceramics. In this work, evidence of ordering was already observed in thin films processed at 800 °C. An example of the structural evolution that occurs

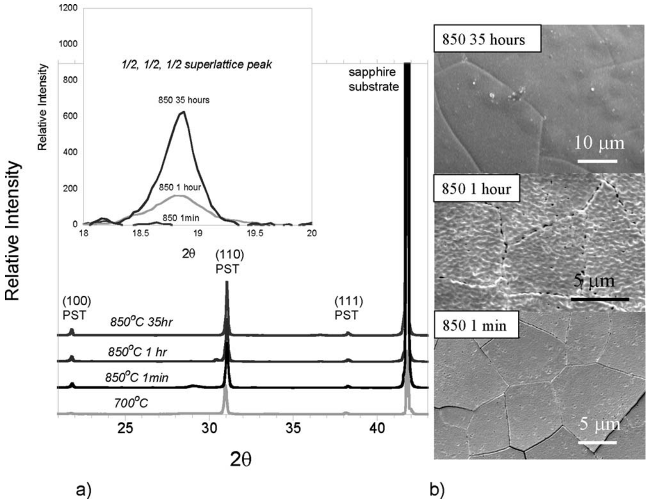

FIG. 1. PST on sapphire substrates (a): X ray of films annealed at 700 and 850 °C for 1 min ($S=0$), 850 °C for 1 h ($S=0.55$), and 850 °C for 35 h ($S=0.78$); (b) SEM determined microstructure films annealed at 850 °C for 1 min, and 1 and 35 h.

upon increased annealing temperature and ordering is presented for PST films on sapphire substrates in Fig. 1. Samples annealed for 1 h displayed an order parameter $S=0.55$, increasing to $S=0.91$ after 35 h. The 5 μm grain size was maintained after annealing durations of up to 1 h, accompanied by a homogenization of the surface and grain boundary structure which is highly evident after 35 h of annealing. TEM dark field investigations shown in Fig. 2 allow us to directly see the degree of ordering as a volume percentage in a single grain and the size distribution of ordered regions. As seen in Fig. 2(a) the x-ray estimated order degree of roughly 50% is visually represented, with roughly half of the space being occupied by ordered regions.

The ordering of PST thin films was observed on a number of substrate systems. In the Pt/Si, system ordering was observed starting at temperatures as low as 750 °C with an ordering degree of $S=0.19$, increasing to a ordered degree of $S=0.22$ at 800 °C for 20 min. Higher temperatures led to the degradation of the film/electrode interface and were not possible with the Pt/Si substrate system. To achieve higher levels of ordering, it was necessary to use single crystal substrates without bottom electrodes. By annealing for long durations in a PbO saturated atmosphere, ordering degrees up to $S=0.91$ at temperature of 850 °C for 35 h were achieved for PST films on sapphire substrates. Order degrees greater than $S=0.6$ for PST on MgO substrates after 24 h of annealing were also observed. The details of the dielectric measurements and comparison of the long range ordered state in thin film and bulk as compared with the disordered state will be presented in the following section.

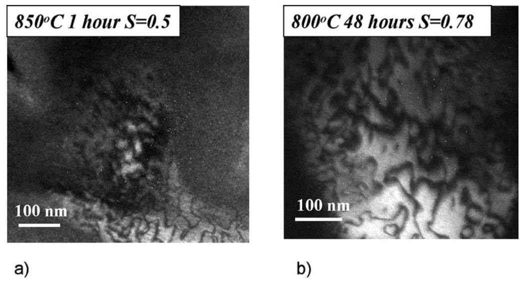

FIG. 2. TEM dark field images (1/2,1/2,1/2) of PST on sapphire substrates: (a) films annealed at 850 °C for 1 h ($S=0.5$) and (b) 800 °C for 48 h ($S=0.78$). The diffracted beam from the superlattice was used to image the ordered regions (ordered=white and disordered=black).

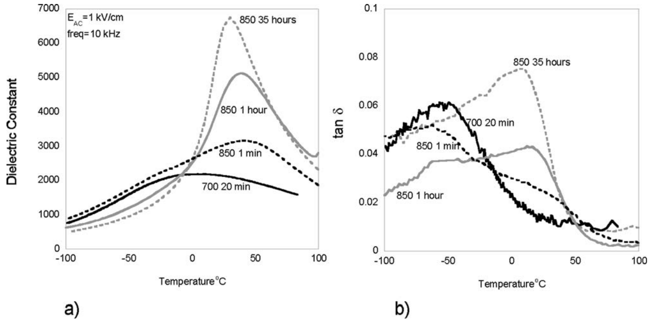

FIG. 3. 650 nm PST on sapphire substrates annealed at 700 °C for 20 min ($S=0$) and 850 °C for 1 min ($S=0$), 1 h ($S=0.55$), and 35 h ($S=0.91$): (a) dielectric constant and (b) loss tangent at measurement frequency 10 kHz and $E_{AC}=1$ kV/cm.

IV. DIELECTRIC

The dielectric properties of PST thin films were greatly affected by the degree of chemical order. Figure 3 displays the dielectric constant and loss tangent for PST films on sapphire substrates discussed in the previous section with varying degrees of B site order measured at 10 kHz and 1 kV/cm measuring field. The main feature seen was an increase in the value of the dielectric maximum with an increase in the degree of B site order. The dielectric constant increases from 2210 for the disordered ($S=0$) sample annealed at 700 °C to 6750 for the highly ordered ($S=0.91$) sample annealed in PbO saturated atmosphere at 850 °C for 35 h. The temperature at which the dielectric constant maximum occurs increased with increasing annealing temperature from 700 to 850 °C. However, as the annealing time was increased at a constant temperature of 850 °C and the order parameter was increased from $S=0$ to $S=0.91$, the temperature of the dielectric maximum decreased slightly.

Another important point concerning Fig. 3 is that although the films, processed at 700 and 850 °C for 1 min, are disordered according to the absence of x-ray superlattice reflections, they have a significant difference in the dielectric response. A close examination of the dielectric constant and loss tangent reveals a "composite" -type behavior showing phase transition characteristics of both ordered and disordered samples. In the sample annealed at 850 °C, the dielectric constant reaches a maximum near 30 °C as in highly ordered samples, however, its subsequent drop below the dielectric constant maximum is more gradual. The loss tangent also shows an increase near 30 °C, but only decreases near −50 °C coinciding with the decrease in the loss tangent of the disordered film annealed at 700 °C. This sample seems to feel the presence of disordered and ordered regions at the same time; even though the ordered regions are undetectable by x-ray and TEM investigations. Similar behavior has been

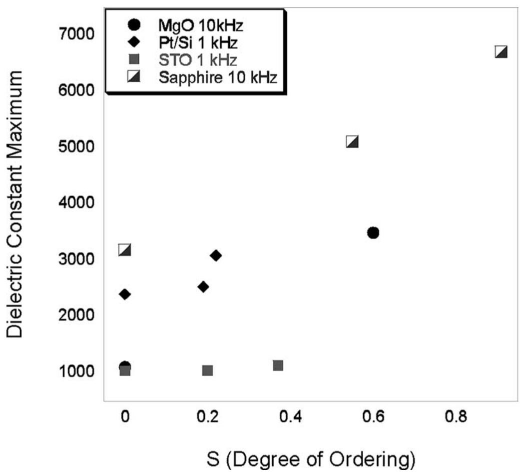

FIG. 4. Dielectric constant maximum vs degree of *B* site ordering for films deposited on (111) Pt/Si (500 nm thick PST), (0001) sapphire (650 nm PST), (111) STO (600 nm PST), and (100) MgO (550 nm PST) substrates.

recently observed in BST thin films and was also explained by the coexistence of ferroelectric and relaxor states.[28]

One can pose the question as to whether the shift in the temperature in Fig. 3 of the dielectric maximum is due to *B* site ordering or to changes in microstructure and homogeneity? The shift in the dielectric maximum in thin film relaxors is a dynamic phenomena and thus easily influenced by processing conditions inducing defects. Therefore, films annealed at different temperatures, or fabricated with different amounts of excess lead, may exhibit differences in the value and temperature of the dielectric maximum. In addition, stress or strain effects have been shown to play a role.[6,7] In the present case, films identically processed from 30% excess lead solutions on Pt/Si substrates with only the annealing temperature altered resulted in an increase in grain size. From studies of similarly processed films using different seed layers on Pt/Si substrates,[16] an increase in grain size from 140 to 325 nm resulted in no significant change in the value or position of the dielectric maximum. As in bulk materials,[22] the presence of defects such as lead vacancies in the system, as well as stress/strain in the film, tends to shift *down* the temperatures of the dielectric maximum, while increasing *B* site order shifts the temperature *up*. One can therefore conclude that the shift of the dielectric maximum to higher temperatures is due to *B* site ordering.

In addition, this general trend of an increase in the dielectric constant with increase in *B* site order was confirmed for PST films on a number of substrate systems including Pt/Si, MgO, sapphire, and STO, and is presented in Fig. 4. It is clear that as the order degree increases with increased annealing time, the dielectric properties of ordered thin films approach the dielectric properties of ordered bulk ceramics. The values of the dielectric constant for most of the disordered ($S=0$) PST films agree with numerous published reports to vary between 1000 and 5000.[23,24] The relatively low values of the dielectric constant for PST on STO substrates may be due to the built-in field resulting from the metal/ferroelectric/*n*-doped semiconductor structure. Estimates for the reduction of dielectric response due to the built-in field may be from 10% to 20%.[29,30] A reduction of this magnitude may contribute to the unusually low values of dielectric response in this work. In addition, thermal induced modification of the Nb doped substrates may produce an additional interfacial capacitance effect which cannot be ruled out.[16]

In order to distinguish between the effect of ordering and microstructure on the magnitude of the dielectric constant, let us review the evidence for films processed on (i) Pt/Si substrates and measured in the out-of-plane configuration, (ii) in-plane measurement of polycrystalline PST on sapphire, and (iii) in-plane measurement of epitaxial PST films.

(i) Increasing the annealing temperature from 700 to 800 °C for short times resulted in an increased order parameter from $S=0$ to $S=0.2$ and a microstructural change of an increased grain size from 300 to 500 nm with no appearance or evidence of surface cracks. From previous studies using TiO_2 and $PbTiO_3$ seed layers to change the grain size at constant annealing temperature, this change in grain size did not impact the measured permittivity.[16,29]

(ii) Polycrystalline PST on sapphire substrates presented in Fig. 3, annealed at low temperature (disordered 700 °C), exhibited cracks on the surface and a low value of dielectric constant. However, the dielectric constant of these films is similar to that of samples measured out of plane with dense 300 nm grain microstructures without the presence of surface cracks.

(iii) Epitaxial samples provide the best evidence since there is no change of grain size or observable microstructure with increased annealing temperatures. As seen in Fig. 4, PST on STO and MgO substrates show an increased value of permittivity with increased values of the order parameter *S*, with no observable microstructural changes other than ordering observed.

An additional clue to this discussion is provided by the sample PST on sapphire annealed at 850 °C for 1 min as seen in Fig. 3, which is disordered according to x-ray diffraction studies, but which shows traits of both ordered and disordered dielectric behaviors. In this case, the microstructure is approximately the same after being annealed at 700 and 850 °C for 1 min, however, with the onset of ordering there appears a new peak at higher temperature with a higher value of dielectric constant. After an examination of the data it is concluded that both the shift in temperature of transition and the increased magnitude of the dielectric constant is due to the onset of chemical ordering in the samples.

V. POLARIZATION

Polarization measurements below the temperature of the dielectric maximum may confirm the development of a long range ferroelectric state in highly ordered thin films. The polarization measurements in-plane of the film are shown for the disordered sample annealed at 700 °C [Fig. 5(a)], and for the highly ordered specimen ($S=0.91$) [Fig. 5(b)]. The disordered sample [Fig. 5(a)] showed a linear-type polarization response at +100 °C (paraelectric) and −100 °C with no evidence of hysteresis. The highly ordered sample [Fig. 5(b)] displayed a linearlike hysteresis in the high temperature paraelectric phase (50 °C), and a slim loop hysteresis near the temperature of dielectric maximum of 30 °C. However,

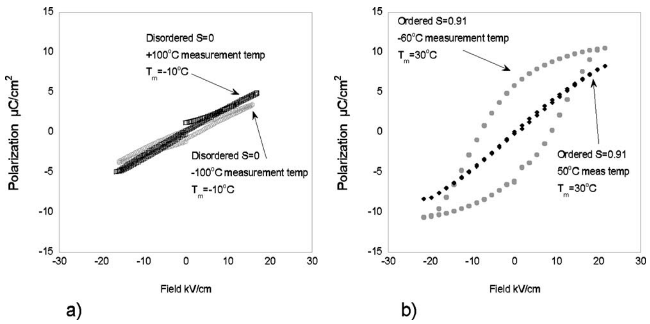

FIG. 5. Polarization vs electric field for 650 nm PST on sapphire substrates; (a) annealed at 700 °C ($S=0$ and $T_m=-10$ °C) and measured at +100 and −100 °C; (b) annealed at 850 °C for 35 h ($S=0.91$ and $T_m=30$ °C) measured at 50 and −60 °C.

in the low temperature region near −60 °C, the ordered sample displayed a remanent polarization $P_r=1$ μC/cm^2 and a well developed hysteresis loop with $P_r=5.8$ μC/cm^2. These measurements confirm that highly ordered films behave as conventional ferroelectrics.

VI. DISCUSSION

It has been shown that ordered PST films behave as conventional ferroelectrics and have dielectric properties similar to bulk ceramic specimens. What has consistently puzzled researchers in the field is why disordered PST films obtained at typical thin film deposition temperatures of 600–700 °C exhibit relaxor behavior with much lower values of permittivity as compared to their disordered bulk counterparts which are processed at high temperatures near 1500 °C. Recent work has shown that a passive layer in series with the film cannot account for such a large difference between the thin film and bulk,[8] and an examination of thermal induced stresses due to thermal expansion mismatch between the film and substrate indicated that stress is not the predominant factor in thin film permittivity reduction.[16] The work presented in the present paper, comparing ordered and disordered PST thin films, suggests that there may be intrinsic differences in the thin film and ceramic state of disorder leading to relaxor behavior.

We believe that these differences are due to the low temperature processing of thin films, which leads to an incomplete ordering due to a diffusion limitation. This incomplete ordering is not equal to the disorder driven by entropy at high temperatures where diffusion is not a limiting factor. The low temperature disorder includes vacancies and concentration variations in Ta and Sc on a length scale that is longer than two lattice constants, thus departing considerably from true atomic level disorder found in disordered bulk ceramics annealed near 1500 °C.

Thin films are subject to a postanneal at low temperatures as compared to ceramic sintering temperatures (i.e., 600–700 °C instead of 1200 °C and more) and exhibit inhomogeneities of mainly three origins. The first origin is linked to sol-gel processing and solution chemistry. In the sol-gel process, the as prepared solution may contain clusters of one precursor species, as shown for the Pb(Zr,Ti)O$_3$ system.[31] A second origin can be attributed to a concentration dependent free energy of formation of a solid solution system.[32] The third case is of primary importance for PST. The perovskite phase formation is preceded by the nucleation of other phases. In the ideal picture of postanneal techniques, an amorphous phase is transformed directly to the desired final phase, however, this is rarely the case. The transition from the amorphous phase to the perovskite phase often passes through a transient phase of a fluorite and/or defective pyrochlore phase.[33,34] We think that these phases, preceding the formation of the final perovskite phase, are the origin of inhomogeneities in PST.

Most likely, a fluorite phase M$_n$O$_{2n-x}$ with complete disorder on the metal site (mixture of Pb, Ta, and Sc in our case) is initially formed, adapting with oxygen vacancies in order to compensate charge. In lead compounds, the ambiguity of the lead valence varying between +2 (above 470 °C) and +4 (below about 300 °C) (Ref. 35) may even increase the tendency to form a fluorite phase, given that this phase is stoichiometric for Pb^{4+}. In the pyrochlore phase the metal ions are at least partially ordered, differentiating between a *B* site in the center of corner-shared oxygen octahedra and tetrahedrons of A sites containing an oxygen ion in the center. The six-fold coordination of the *B* ion is analogous with that seen in the perovskite phase.

Experiments have shown that the Pb–Ta–O system exhibits a defective pyrochlore phase Pb$_{1.3-1.5}$Ta$_2$O$_{6.3-6.5}$ (Ref. 36) (defective in O and Pb) and or pyrochlore related phases of Pb$_{22}$Ta$_{18}$O$_{67}$ and Pb$_{14}$Ta$_{10}$O$_{39}$.[37] However, no Pb–Sc–O compound is known according to the JCPDS database and the current literature. The dominant *B*-site species in the pyrochlore phase is thus the Ta. Therefore, even excluding the polymerization of Ta clusters in the solution, thermodynamic reasons lead to Ta-rich clusters when Pb–Ta pyrochlores are formed. The Ta centered oxygen octahedra may then act as a template for the final perovskite phase.

Such a scenario was indeed seen in a detailed compositional analysis by Huang *et al.* with sputtered PST thin films, in which a Ta-rich and Pb deficient grain boundary regions were consistently observed.[38] In a further study concerned with the postannealing of sputtered PST, Huang *et al.* examined the phase transition kinetics of PST which rapidly converts to pyrochlore (Ta-rich regions) upon annealing, followed by the desired perovskite phase.[39] This investigation indeed confirms that the preceding pyrochlores are Ta rich, and that the Sc-rich regions are composed of essentially scandium oxide and lead oxide.

Figure 6 attempts to visually represent this situation in terms of the Gibbs free energy ΔG. As reference value ($\Delta G=0$) we consider a homogeneous mixture of the pure oxides. The figure includes a baseline for the completely mixed compounds (Pb–Ta–Sc–O) including PbO. All experimental evidence indicates that on the scandate side ΔG is positive, thus no Pb–Sc–O compound exists, and that instead a phase mixture is installed, as identified in Ref. 39 as Sc$_6$TaO$_{11.5}$+PbO. The lead containing transient compound exists on the Ta-rich side only and was identified in Ref. 39 as Pb$_2$Ta$_{1.5}$Sc$_{0.5}$O$_7$. It is clear that the formation of the perovskite phase must start from a mixture of phases, which is inhomogeneous on the scale of a few nanometers to a few

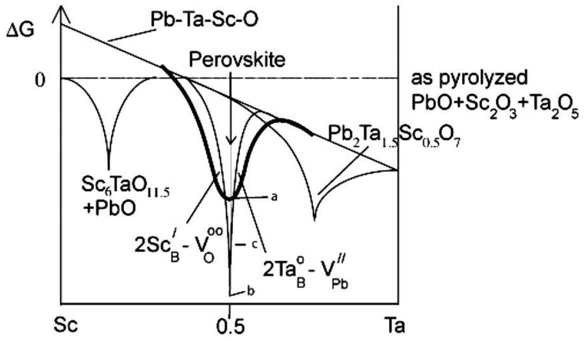

FIG. 6. Schematic drawing of the free energy (ΔG) density of crystal phase formation (change in free energy from amorphous to crystalline material) as a function of the B-site atomic ratio in the ideal case (no vacancies, thin line) as compared to the case with vacancy inclusions (bold line). Point(a) corresponds to the disordered state with vacancy inclusions (thin film disordered relaxor processed near 700 °C), (b) corresponds to the lowest free energy state ordered, and (c) corresponds to the high temperature disordered state due to entropy maximization (bulk relaxor disorder).

tens of nanometers (see TEM of Ref. 39). Figure 7 graphically depicts the changes in free energy as a function of temperature. The highest free energy state corresponds to point (a), the low temperature disorder found in thin films with point defects stabilizing large Sc and Ta stoichiometric deviations. Point (b) corresponds to the ordered state obtained by cation ordering in a lead rich environment, and point (c) corresponds to the high temperature disorder state found in ceramic relaxors.

The inhomogeneity of the starting flourite/pyrocholore and final perovskite phases has an additional impact on the formation of defects in the material. In contrast to B-site ions of the lead zirconic titanate (PZT) system, Ta and Sc have different charges, and therefore no long range variations in B-site occupancy are possible without charge compensation. In the ideal case, Ta-enriched regions must be compensated by Sc-enriched regions. This is, however, not the only possibility to compensate charges. Ta enrichment may also be compensated by lead vacancies (e.g., with four cells: $Pb_3V_{Pb''}Ta_4O_{12}$) and Sc enrichment by oxygen vacancies (e.g., with four cells: $Pb_4Sc_4O_{11}V_O$). Formally one PbO molecule is missing per eight perovskite unit cells in this example with 12.5% lead vacancies. PbO loss to the gas phase is especially enhanced by the presence of pure PbO phases in the scandium rich regions. Given that the charge compensation among the B-site ions works as expected in the boundary regions between clusters, the deficiency is expected to be limited to a few percent only, a concentration that hardly can be detected. This scenario is graphically depicted point (a) in Fig. 6, where the bold line of the PST minimum reflects the broadening of composition at lower temperature, at which vacancies are expected to compensate charges. The minimum is also more shallow because the required PbO is missing in order to reach the perfect stoichiometric structure.

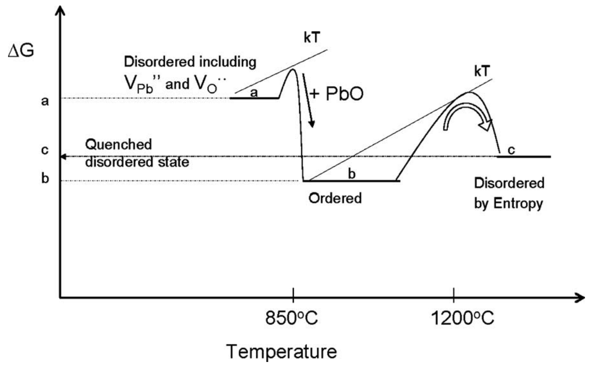

FIG. 7. Schematic drawing of the free energy (ΔG) density as a function of temperature with points (a), (b), and (c), labeled corresponding to that described in Fig. 6.

Pb vacancy diffusion is possible above 800 °C, therefore the only possibility for the improvement of film stoichiometry is through anneals in a PbO saturated atmosphere above this temperature to compensate Pb–O vacancies. Through this procedure, the ordered structure of PST can be obtained as described in this paper. This is graphically depicted in Fig. 6, where as the temperature increases above 800 °C in a PbO saturated atmosphere, lead vacancies are removed, and B site cation mobility is sufficient to order the B-site occupancy (state b in Figs. 6 and 7). Further heating from this point to temperatures near 1500 °C induces a dynamical disordered B-site occupancy through the effect of entropy maximization. In order to lock into this dynamical disordered cation arrangements, samples are quenched from high temperature so that they do not order and reoccupy the lowest corresponding free energy state, but form the disordered state (c) representing the true relaxor state.

From the above analysis and an examination of Figs. 6 and 7, comparing the free energy states as a function of composition and temperature, we can identify three important states: points (a), (b), and (c), corresponding to the low temperature thin film disorder, ordered state (same in thin films and bulk), and quenched ceramic high temperature disordered state, respectively.

According to above scenario, the low temperature disordered phase of thin films is thus characterized by clustering of Ta and Sc cations on a length scale that is larger than in the quenched high temperature disordered state. In addition, defects are present, which may pin local ferroelectric ordering. Both phenomena together can explain the occurrence of pyroelectricity above the relaxor phase transition in previously poled films.[30] The breathing or dynamics of polar nanoregions, believed to be the origin of the large dielectric constant in relaxors, is also hindered by vacancies. Additional differences between the thin films and bulk relaxor state may be seen with reference to the impact of defects: the lack of a field induced phase transition in thin films even at field levels ten times greater than those used in bulk ceramics, and peculiar contribution of polar regions at low temperatures in thin film relaxor PST.[41] These results point to a defect mediated mechanism, which inhibit both the field induced coalescence of polar nanoregions to a long range polar state as well as inhibiting the normal “freezing” process between polar nanoregions at low temperatures.

In thin films, the true relaxor phase consisting of dynamically active polar nanoregions may be therefore quantitatively reduced to the small areas between the nonstoichiometric regions. This quantitative reduction in true relaxor regions may explain why thin film relaxors show similar features of relaxor behavior, such as dielectric dispersion associated with the formation of polar regions at temperatures above the dielectric, but with this the maximum is suppressed by an order of magnitude as compared to ceramic relaxors.

VII. CONCLUSIONS

An increase in permittivity with increasing *B* site order was observed in thin film PST. Highly ordered samples ($S = 0.91$) on sapphire substrates behaved as conventional ferroelectrics with dielectric constants near 7000 with well developed polarization hysteresis below the dielectric maximum. In contrast, disordered thin films were found to behave as relaxor ferroelectrics, with their dielectric maximum shifted down by an order of magnitude as compared to ceramics. Processing induced difference in the state of “disorder” of thin film and ceramic forms of the material is proposed to be responsible for this phenomenon. Specifically, the thin film relaxor state may be characterized by inhomogeneities Sc and Ta species due to low temperature processing which necessitate charge compensating defects in the material. The impact of these defects and the quantitative reduction of the area of true relaxor regions may be responsible for the observation of low permittivity thin film relaxors which possess similar qualitative features to ceramic relaxor behavior.

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