Probing local and global ferroelectric phase stability and polarization switching in ordered macroporous PZT

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ABSTRACT

We describe the characterization, ferroelectric phase stability and polarization switching in strain-free assemblies of $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$ (PZT) nanostructures. The 3-dimensionally ordered macroporous structures present uniquely large areas and volumes of PZT where the microstructure is spatially modulated and the composition is homogeneous. Variable temperature powder X-ray diffraction (XRD) studies show that the global structure is crystalline and tetragonal at room temperature and undergoes a reversible tetragonal to cubic phase transition on heating/cooling. The measured phase-transition temperature is 50 – 60 °C lower than bulk PZT of the same composition. The local ferroelectric properties were assessed using piezoresponse force spectroscopy that reveal an enhanced piezoresponse from the nanostructured films and demonstrate that the switching polarization can be spatially mapped across these structures. An enhanced piezoresponse is observed in the nanostructured films which we attribute to the formation of strain free films, thus for the first time we are able to assess the effects of crystallite-size independently of internal stress. Corresponding polarization distributions have been calculated for the bulk and nanostructured materials using a direct variational method and Landau-Ginzburg-Devonshire (LGD) theory. By correlating local and global characterization techniques we have for the first time unambiguously demonstrated the formation of tetragonal *and* ferroelectric PZT in large volume nanostructured architectures. With the wide range of materials available that can be formed into such controlled architectures we conclude that this study opens a pathway for the effective studies of nanoscale ferroelectrics in uniquely large volumes.

KEYWORDS Ferroelectric Materials, Porous Materials, Polarization Switching, Structure-Property relationships

MAIN TEXT

Ferroelectric nanostructures have recently attracted attention owing to both fundamental scientific interest, as well as the possibility of well-regulated energy and information storage.^[1] The potential applications for these new materials include sensors, actuators, compact electronics, pyrosensors and thermal imaging devices.^[2-6]

Lead zirconate titanate (PZT) systems have been studied extensively because of their outstanding ferroelectric, piezoelectric and pyroelectric properties coupled with their thermal stability and relative ease of synthesis.^[4, 7-9] The continued development of PZT and other ferroelectric nanostructures requires the knowledge of both the average (global) response of the system and the local nanoscale properties. We describe the characterization, ferroelectric phase stability and polarization switching in strain-free assemblies of $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$ (PZT) macroporous structures. Our studies correlate global and local characterization revealing that in the macroporous material tetragonal *and* ferroelectric PZT is stabilized, this opens a pathway for the effective study of nanoscale ferroelectrics in large volumes.

Traditional forms of nanostructured ferroelectrics include thin films, nanowires and nanodots. For nanowires and dots the effective volume of material is extremely small, hindering in-depth quantitative studies of physical properties using macroscopic scattering and spectroscopic techniques. Furthermore, the electrical boundary conditions of low-dimensional ferroelectric materials immobilized on solid substrates

are strongly affected by the electric and elastic interaction with the substrate.^[10] At the same time, unsupported systems are difficult to study and are prone to rapid degradation through Ostwald ripening and sintering processes.

The Curie temperature (T_c) of ferroelectric materials and the stabilization of the tetragonal/ferroelectric phase is known to be highly sensitive to crystallite size, strain, composition and contamination.^[11-14] In bulk PZT systems the tetragonal phase would display ferroelectric behavior as the displacement of the central cation (Ti/Zr) results in the formation of an electric dipole. However in macroporous BaTiO_3 prepared using the same methodology described herein there has been debate over whether a tetragonal structure is stabilized as crystallite size is reduced,^[14, 15] and indeed whether tetragonality is an unambiguous indicator of ferroelectric behavior. As an example, tetragonal centrosymmetric structures can be induced by biaxial pressure in the centrosymmetric materials.^[16] Alternatively, large built-in fields can stabilize polar non-ferroelectric phases.^[17]

In this article, we report on the synthesis and characterization of macroscopic assemblies of 50-100 nm wide ferroelectric nanostructures arranged in a 3D periodic porous lattice. In these structures, the open porosity of the structure as well as the distance between the lower electrode and the upper surface allows relaxation of substrate induced strain *i.e.* clamping effects are significantly reduced. Additionally a macroscopically large volume of material can be obtained with pre-defined nanoscale architectures, *e.g.* wall thickness and pore spacing, whilst the composition remains homogeneous. The local and global ferroelectric properties are explored by combining switching spectroscopy piezoresponse force microscopy (SSPFM) and

structural analysis by variable temperature X-ray diffraction (XRD). The demonstration of switching behavior confirms that ferroelectric structures are stabilized and shows that clean surfaces have been prepared. The XRD measurements demonstrate a lowering of the T_c , induced by a reduction in crystallite size, and from these data the thermodynamic parameters of the process are derived.

Substrate supported PZT films with thicknesses 4-6 μm were prepared by a sol-gel route using colloidal crystal templating to define the structure.^[18] Briefly, the PZT precursor solution^[19] is used to impregnate an ordered self-assembled template of polystyrene (PS) spheres, with a subsequent one-step densification of the PZT and removal of the organic components. The process results in characteristic volume-spanning macroporous PZT architecture, (**Fig. 1**). Densification of the PZT precursor during crystallization results in the formation of isolated macroporous regions of typical area less than 1000 μm^2 , (Fig. 1a). Significantly the densification process occurs simultaneously with the porosity development (by degradation of the PS spheres) and so the films are able to relax to relieve any inherent growth or interface stress. Higher magnification images (Fig. 1b) show an interconnected PZT structure with hexagonal symmetry on the surface and underlying layers demonstrating the three-dimensional ordering. The walls of the macroporous PZT structures exhibit a polycrystalline rod-like morphology (Fig 1b); the crystallite sizes at room temperature are summarized in **Table 1**. The edges of the isolated regions show terraces that confirm three-dimensional ordering and porosity (Fig. 1c). The macroporous structure extends over several microns without defects (Fig. 1d). For comparison a 350 nm thick continuous film was also prepared using standard conditions.^[9] The SEM and all other subsequent characterization were carried out on the as prepared, substrate

supported, thin films without the need for substrate removal. Thus the local and long-range structure and ordering is not perturbed by the analysis.

XRD data for the porous and bulk films show a reversible tetragonal-cubic phase transition on heating/cooling (**Fig. 2a**). The tetragonality and the T_c , can be determined by plotting the temperature dependence of the c/a axis ratio on thermal cycling; the system is fully cubic when $c/a=1$. The reported T_c for PZT of this composition is around 450°C^[20], however the measured T_c of our continuous film was around 470 °C. There is no hysteresis observed in the 2θ plots on cooling back to 25°C, this has been verified by carrying out two heating-cooling cycles. In the macroporous PZT the measured T_c was some 50-60 °C lower (Fig. 2b-c). The c/a plot shows a hysteresis of around 20 °C near the T_c that widens to 40 °C during the heating-cooling cycle. It should be noted that there is no hysteresis observed after thermal cycling (Supplemental information).

The crystallite size as a function of temperature has been calculated by Rietveld refinement of the XRD data using HighScore Plus™ and a LaB₆ size standard (Fig. 2d). The data are fitted to a tetragonal model^[21], which is valid up to T_c . Fig. 2d shows a hysteresis similar to that observed in the c/a axis plots which collapses beyond the T_c . X-ray peak broadening can result from both small crystallite size and/or microstrain. The Rietveld analysis indicated that size, not strain, was the dominant effect, but the reversibility of the crystallite size is unusual. The formation of twins appears the most reasonable explanation for the reversible reduction in the coherent domain size on cooling^[22]. The small crystallite size and the associated effects of line broadening do not mask the tetragonal peak splitting.^[12] Previous reports of crystallite

size affecting T_c have been for crystallite sizes almost an order of magnitude greater than those measured in this study.^[23] The calculated lattice parameters and crystallite sizes obtained from the XRD measurements are summarized in Table 1.

TEM characterization confirms that the prepared films are polycrystalline (**Fig 3. a-c**) and the measured crystallite size, 10-20 nm, (Fig. 3b) are consistent with the values obtained from the XRD data. Electron diffraction patterns (Fig. 3c) obtained from individual grains show well defined single crystal orientation, whilst diffraction patterns from overlapping regions show a polycrystalline structure with some local texture, which is not observed by XRD. Our studies have shown a small $\text{Ti}_{0.65-0.75}$ local variation when analysed by EDX in the TEM. When the phase diagram is consulted such local variations should result in a change in T_c of only $\pm 15^\circ\text{C}$, which would not account for the large T_c reduction of (50 – 60 $^\circ\text{C}$) that we have observed.

As discussed, above the T_c of ferroelectric materials stabilization of the tetragonal/ferroelectric phase is sensitive to crystallite size, strain, composition and contamination.^[11-14] The XRD data show that the tetragonal phase has been formed in both the continuous (not shown) and nanostructured films. To unambiguously demonstrate that ferroelectric material has been prepared and to explore the spatially resolved ferroelectric response switching spectroscopy piezoresponse force microscopy (SSPFM)^[7] - a spatially resolved imaging version of PFM spectroscopy - was used. To establish the height set-point and to ensure defect free regions^[24] were analysed, the macroporous films were first imaged in contact mode (Fig. 4a-b). During PFM measurement, a small periodic bias is applied to the tip, resulting in electromechanical response of the surface detected by the scanning probe microscopy

(SPM) electronics. The extremely high vertical resolution of SPM allows displacements as small as $\sim 3\text{-}10$ pm in the 1 kHz bandwidth to be detected locally (ultimately on the length scale of the tip-surface contact radii of 5-20 nm). In piezoresponse force spectroscopy (PFS), this AC signal is superimposed on the top of the DC switching signal.

The latter induces local switching below the tip, allowing ferroelectric functionality to be probed on the nanoscale. The evolution of electromechanical response with an applied periodic DC bias (triangular wave) provides the local analogue of an electromechanical hysteresis loop.^[25] In SSPFM the hysteresis loops are acquired point-wise on a grid, providing spatially-resolved information of switching behavior.^[7] Characteristic hysteresis loops obtained over an applied voltage range of ± 30 V from the continuous and nanostructured film, over the wall, and from the pore region are compared in **Fig. 5a**. The hysteresis loop of the continuous film shows a relatively small piezoresponse, an elongated shape and a relatively small nucleation bias. This behavior is consistent with a strongly clamped film with a high density of defects or other inhomogeneities that act as nucleation centers. In contrast, the loops obtained from the macroporous PZT are almost square, indicating a well-defined nucleation bias and show a large piezoresponse. This behavior is expected for strain-free high-quality materials, and unambiguously indicates the ferroelectric nature of the structures. In comparison, data extracted from the pores show no switching/ferroelectric behavior as expected.

Here, to allow for the variation of resonance frequency between dissimilar locations, we have used the band excitation (BE) version of PFS. In BE, a range of frequencies

is excited, as opposed to a single frequency in standard SPM. Each spatial pixel in the SSPFM map corresponds to the simultaneous measurement of response as a function of frequency and DC bias (2 sweeps ± 30 V, 1 second sweep rate), the corresponding spectrograms illustrate the variation in the contact resonance frequency of the cantilever during measurement (Fig. 5b-c). The stability of the resonance frequency over the continuous film (Fig. 5b) confirms that contact is maintained as the applied voltage is altered. In contrast, the average response from the entire macroporous 2D map shows a large variation frequency indicating changes in contact during measurement (fig. 5c). Such large fluctuations (~ 20 kHz, as compared to 5 kHz peak width) could not be measured and hysteresis loops could not be obtained without the use of the band excitation technique.^[26]

The SSPFM maps of effective work of switching (WoS) are shown in Fig. 4c-d.^[7] The effective WoS contrast in the continuous film is uniform and relatively small, this indicates the uniformity of the switching behavior. The crystallite shape and some macroscopic grain boundaries can be resolved from the maps (Fig. 4c). SSPFM maps recorded from the nanostructured material show large and relatively uniform effective WoS within the walls and, as expected, no switching over the pores (Fig. 4d). These observations indicate the ferroelectric nature and uniformity of ferroelectric phase. In addition, they clearly demonstrate the absence of any surface contamination or segregation layers that would preclude PFM imaging and spectroscopy.^[27] The piezoresponse loops obtained at several positions in the continuous and macroporous films are shown in Fig. 4e-f.

The macroporous structure is modeled as an assembly of rod-like ligaments arranged to form a 3-D lattice. Using the direct variational method ^[16] and the expressions for the spontaneous strain originating from the surface tension (u_{11}) and electrostriction effects (u_{33})^[28], ($u_{11} = u_{22} = -(s_{11} + s_{12})(\mu/R) + Q_{12}P_3^2$, $u_{33} = -s_{12}(\mu/R) + Q_{11}P_3^2$), where Q_{ij} are the components of the electrostriction strain tensor, s_{ij} are the elastic compliances and μ is the surface tension coefficient. An approximation for the average spontaneous polarization ($\bar{P}_3(R)$) and the paraelectric-ferroelectric transition temperature in the nanostructures formed from rods of radius R were derived as:

$$\bar{P}(R) \approx \sqrt{\frac{2\alpha_T(T_{cr}(R) - T)}{\beta + \sqrt{\beta^2 + 4\gamma\alpha_T(T_{cr}(R) - T)}}}. \quad (\text{equation 1})$$

Where the T_c of the nanorod, is:

$$T_{cr}(R) \approx T_C - Q_{12} \frac{4\mu}{\alpha_T R} - \frac{2}{\alpha_T} \left(\frac{g}{R\lambda + 2R^2/k_{01}^2} \right). \quad (\text{equation 2})$$

The Landau-Ginzburg-Devonshire LGD free energy bulk expansion coefficient (γ) and the gradient term (g) are both positive. In the coefficient $\alpha(T) = \alpha_T(T - T_C)$, T is the absolute temperature and the Curie temperature of the bulk material is T_C . Note that for the second order phase transition the Curie temperature coincides with the critical temperature (T_{cr}) at which the transition between paraelectric and ferroelectric phases takes place. The constant k_{01} is the minimal root of Bessel function $J_0(k)$, $\lambda = g/\alpha_s$ is the so-called extrapolation length that depends on the expansion coefficient α_s in the LGD surface energy (for example see^[29]) In Eqn. (1) we took into account the possible increase of coefficient β related to any inhomogeneous internal

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¹¹ $u_{11} = u_{22} = -(s_{11} + s_{12})(\mu/R) + Q_{12}P_3^2$, $u_{33} = -s_{12}(\mu/R) + Q_{11}P_3^2$

stresses. The simple estimation for $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$ solid solution shows that the expansion coefficient (β) increases from $2.58 \times 10^7 \text{ m}^5/(\text{C}^2\text{F})$ in a strain free system^[30] to $4.69 \times 10^9 \text{ m}^5/(\text{C}^2\text{F})$ in a clamped system.

The tetragonality of the unit cell thus acquires the form:

$$\frac{c}{a} = \frac{1 + u_{33}}{1 + u_{22}} = \frac{1 - s_{12}(\mu/R) + Q_{11}\bar{P}^2}{1 - (s_{11} + s_{12})(\mu/R) + Q_{12}\bar{P}^2} \approx 1 + s_{11}\frac{\mu}{R} + (Q_{11} - Q_{12})\bar{P}^2. \quad (\text{equation 3})$$

In Fig. 2 (b-c) the comparison of eqn. (3) with experimentally obtained results for macroporous $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$ structures are shown. Bulk values of $\alpha_T = 6.01 \cdot 10^5 \text{ m}/(\text{F K})$, $\gamma = 1.41 \cdot 10^9 \text{ m}^9/(\text{C}^4\text{F})$, $Q_{11} = 0.07887 \text{ m}^4/\text{C}^2$, $Q_{12} = -0.0248 \text{ m}^4/\text{C}^2$, $s_{11} = 8 \cdot 10^{-12} \text{ m}^2/\text{N}$ were used, while β and T_{cr} were treated as fitting parameters. There is some variation in the calculated T_{cr} between structures of different pore diameter and also on heating and cooling owing to the thermal hysteresis. Extracting the parameter $\delta t = s_{11}(\mu/R) \sim (2-2.2) \times 10^{-3}$ from experimental data at high temperatures ($T > T_{cr}$) i.e. when $P_3 = 0$ allows an estimation of the surface tension coefficient as $\mu \approx 9.4 \text{ N/m}$. The value is reasonable for PZT family (see e.g. recent results on *ab initio* simulations of PbTiO_3 nanowires).^[31] These data allow us to estimate the extrapolation length $\lambda \approx 2-3 \text{ nm}$ from the difference $T_g \approx T_C - T_{cr} - 4\mu Q_{12}/(\alpha_T R)$, when $T_C = 440^\circ\text{C}$, $T_{cr} \approx 390^\circ\text{C}$ for cooling and $T_{cr} \approx 420^\circ\text{C}$ for heating are used. The calculated β values of $3.8 \times 10^8 \text{ m}^5/(\text{C}^2\text{F})$ for the 420 nm templated film and $4.0-4.2 \times 10^8 \text{ m}^5/(\text{C}^2\text{F})$ for the 500 nm templated film indicate that there is significantly less strain than in a continuous thin film, in agreement of the SSPFM studies of the loop shape. The difference between the obtained values of β and those for the mechanically free system could be related to the partial clamping imposed by either

non-ferroelectric intergranular media or constraints due to the joints between rods. The calculated values of δt (0.002206 and 0.0020) for 420 and 500 nm template diameters are consistent with this model. A summary of the calculated ferroelectric parameters is given in **table 2**.

The geometry of the structures is too complex to allow rigorous calculations of size related effects on T_{cr} . For example there may be an effect of coupling. The crystallites in the continuous film are strongly coupled compared with the macroporous films, which have small isolated domains. In addition, the continuous film is highly strained and the calculated inhomogeneous internal stresses are greater than in the nanostructured material. Our theoretical model and experimental observations lead us to conclude that the reduction in T_{cr} is due primarily to a reduction in the crystallite size. This effect is observable in these films only because the nanostructuring allows formation of effectively strain-free films.

The properties of PZT nanostructures have been probed using complementary experimental techniques that provide unique information about the global and local ferroelectric properties. Tetragonal peak splitting is observed by XRD in samples with a measured crystallite size of 27-28 nm. During preparation of the PZT sol a 10% excess of Pb is typically added^[9] to compensate for Pb loss during synthesis. If present the Pb would be found in either the surface of the films or on the B sites of the PZT lattice and would lead to a degradation of the ferroelectric properties^[32], thus we conclude that the possibility of excess Pb affecting T_c is not the origin of our observations. As the switching response across the porous films is uniform and is coupled within the rods, ferroelectric phase stabilization is confirmed and importantly this demonstrates that clean surfaces (*e.g.* Pb free) have been prepared. The films

undergo a reversible phase transition during thermal cycling and a reduction of T_{cr} is seen in the nanostructured films, which is attributed to the small crystallite size. The open porosity of the structures allows the formation of very low strain material compared to conventional thin films and so effects of substrate clamping and internal stresses are eliminated. Using a two-parametric direct variational method based on LGD theory the corresponding polarization distributions have been calculated for the bulk and nanostructured materials that correlate well with experimental results. The formation of these types of nanostructure and the characterization methods provide a convenient and reproducible method for the characterization and correlation of global and local behavior in complex ferroelectric nanostructured systems.

Experimental

PZT film preparation: Ordered arrays of polystyrene spheres (diameter 420 and 500 nm) were assembled using a controlled drying technique^[33] on planar indium tin oxide coated glass substrates (Psiotec UK Ltd). The PZT sol ($\text{Pb}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3$) was diluted by addition of 30% vol. dry methanol and mixed to ensure homogeneity. The polystyrene arrays were immersed in the solution for 2-3 seconds, removed and allowed to dry under ambient conditions.^[18] This process was repeated three times, following which the films were heated under flowing air to 510°C (1°C/minute) and held for 180 minutes.

Global Characterization: The SEM measurements were carried out on films coated with 20 nm Cr using a LEO 1525 field emission SEM at an accelerating voltage of 10kV. Variable temperature θ -2 θ XRD scans were collected over the 20-80°2 θ range under air at 20°C intervals between 30 – 470 °C on heating and cooling using a PANalytical X'Pert Pro MPD diffractometer with a Cu tube at 45 kV and 40 mA, an X'Celerator RTMS detector, and an Anton Paar XRK-900 heating stage. Topography images and switching

spectroscopy piezoresponse force microscopy (SSPFM) data sets were obtained at room temperature.

Local Ferroelectric Measurements: To obtain quantitative and high signal to noise data, we utilize the recently developed band excitation method as applied to PFM spectroscopy [26, 34]. The PFM signal is the oscillatory surface response, determined as a product of driving voltage, V_{ac} , electromechanical response, d_{eff} , and cantilever transfer function, $F(\omega)$, as $PR = V_{ac} d_{eff} F(\omega)$. The use of large excitation voltages necessarily leads to low energy resolution. At the same time, the use of resonance enhancement ($F(\omega) = 1$ for low frequencies and $F(\omega) = Q$ at the cantilever resonance, where Q is of the order of 30-100 for contact resonances) is limited by the strong position dependence of contact resonance.^[26] The use of band excitation method^[7] or dual-resonance frequency tracking^[35] allows efficient tracking of the resonance response in PFM, and hence high-fidelity cross-talk free spectroscopic measurements. The PFM and BE-SSPFM was implemented on a commercial Asylum MFP-3D system with an additional in-house electronics for BE and SSPFM measurements based on NI PXI platform (National Instruments). Pt coated tips (Olympus Electrilever AC240) were used to measure the piezoelectric response of the ferroelectric film in contact mode. A high voltage amplifier module (Asylum Research HVA220) was used to enable bias voltages greater than 10 V. A LABVIEW-MATLAB code developed in-house and synchronized with the controller through TTL channel was used for generating the probing signal and for data acquisition and analysis. The bias was applied directly through the SPM probe, with the bottom ITO electrode being grounded. The magnitude of the AC probe field was 3V at a frequency of 380 kHz and each loop was measured over a ~10 ms time period.

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Figure 1. SEM images of macroporous PZT arrays obtained after high temperature XRD and SSPFM measurements showing, a) isolated ordered macroporous regions, areas highlighted illustrate the rod-like morphology, b) hexagonal wall structure, c) the edge of a region to illustrate film thickness and reveal 3D structure, d) that the regular structure extends over several microns without defects.

Figure 2. a) XRD 2θ scans of macroporous PZT prepared from 500 nm template recorded at 25°C (tetragonal phase) and 470°C (cubic phase), selected peaks, {211} and {200}, are indexed to illustrate the phase transition. b-c) Plots of c/a ratio for macroporous PZT formed from b) 500 nm and c) 420 nm templates. The red and blue curves show the data obtained on heating and cooling, respectively. The dotted lines show the curves calculated from equation (3). The T_c of bulk $\text{Pb}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3$ is 440°. d) Plot of the crystallite size during thermal cycling for macroporous PZT from 500nm diameter template obtained by Rietveld refinement of the XRD data.

Figure 3 a) Bright-field TEM image shows rod-like hexagonal structure of the films and confirms that they are polycrystalline, b) axial dark-field image showing lattice contrast from wall region in the hexagonal array, and c) Bright field image of 3D macroporous region, inset images show electron diffraction patterns from the circled regions.

Figure 4. Topography images showing a) region of a continuous PZT film and b) an area of a macroporous PZT (the height range for each image is shown independently), the boxed areas approximately indicate the areas analysed by SSPFM. The spatially resolved SSPFM maps have been processed to show WoS over a c) 60 x 60 and d) 40 x 40 grid (the WoS values are shown independently for each image), e-f) the measured piezoresponse from the areas indicated on the maps are shown.

Figure 5. a) Typical piezoresponse hysteresis loops obtained from a continuous PZT film, the wall of macroporous PZT over a pore in the macroporous PZT. The hysteresis loop for the macroporous has been flipped to maintain orientation, as phase offset is not controlled during acquisition. The phase of the resonant response of the cantilever as a function of b) varying DC-bias applied to obtain the ferroelectric hysteresis loops obtained from c) solid region of macroporous PZT, c) average response from macroporous PZT (including pores).

Table 1. A summary of the calculated unit cell parameters for the continuous and macroporous PZT films obtained from the XRD measurements.

Sample	a [Å]	c[Å]	c/a	Crystallite size @ 25°C [nm]	Crystallite size @ 470°C [nm]
Continuous	3.9907(4)	4.1484(5)	1.039	48	59
500 nm	3.9958(7)	4.1251(9)	1.033	14	28
420 nm	3.9913(7)	4.122(1)	1.033	14	27

Table 2. Ferroelectric parameters calculated for the macroporous films on heating and cooling.

Sample	Rod radius [nm]	$\delta c/a^2$	μ [N/m]	ΔT_μ [°C] ³	T_{cr} [°C]	Tg ⁴	λ [nm] ⁵
500 nm	37.5	0.00200	9.375	41.2	420	61.2	2.8 (heating)
					390	91.2	1.9 (cooling)
420 nm	34.0	0.002206	9.375	45.5	420	65.5	2.7 (heating)
					385	100.5	1.8 (cooling)

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² at T = 440 °C, $\delta t = s_{11} \frac{\mu}{R}$

³ $\Delta T_\mu \approx -\frac{4\mu Q_{12}}{\alpha_T R}$

⁴ $T_g \approx T_C + \Delta T_\mu - T_{cr}$, for Tc = 440 °C

⁵ $\lambda = \frac{2g}{\alpha_T T_g R}$, at $\alpha_T = 6 \cdot 10^5$ m/(FK) and $g = 10^{-9}$ m³/F

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