Cation ratio and ferroelectric properties of TbMnO₃ epitaxial films grown by pulsed laser deposition

K. Shimamoto,¹ M. Döbeli,² T. Lippert,^{1,3} and C. W. Schneider¹

¹Energy and Environment Research Division, Paul Scherrer Institut, CH 5232 Villigen-PSI, Switzerland

²Laboratory of Ion Beam Physics, ETH Zürich, CH 8093 Zurich, Switzerland

³Laboratory of Inorganic Chemistry, Department of Chemistry and Applied Biosciences, ETH Zürich, CH 8093 Zurich, Switzerland

(Received 17 March 2016; accepted 26 April 2016; published online 12 May 2016)

The cation ratio, crystal structure, and ferroelectric properties of TbMnO₃ films on (010) oriented YAlO₃ substrates grown by pulsed laser deposition were investigated. We found that the cation ratio is altered by the background gas pressure, and that stoichiometric films have larger critical thicknesses than Tb-rich films. The ferroelectric order was severely disturbed in Tb-rich films showing a lower transition temperature and a smaller polarization. In addition, frequency dispersion was observed in the dielectric response of relaxed stoichiometric TbMnO₃ films, which may be introduced by defects due to strain relaxation. *Published by AIP Publishing.*

[<http://dx.doi.org/10.1063/1.4948961>]

I. INTRODUCTION

The versatile electric, magnetic, and ionic properties of complex oxides provide an attractive research field, in particular, for epitaxial thin film growth and device applications. Atomic scale engineering and design of strained films^{1–3} and hetero-interfaces^{4–6} has been widely investigated in order to cultivate new functionalities. The rise of novel properties in complex oxide films and hetero-structures reminds thin film researchers about the importance of precise control of the cation ratio in addition to the compensation of potential oxygen vacancies. Since cation off-stoichiometry causes defects in a crystal, it critically modifies structural and physical properties, e.g., crystalline properties,^{7–12} conductivity,^{9,13–16} ferroelectric (FE) polarization,^{10,17} and transition temperature of an ordered phase.^{8,18} Thus, it is indispensable to control the cation ratio to obtain films with the desired functionality.

Pulsed laser deposition (PLD) is one of the most widely used techniques to grow complex oxide films. A so-called stoichiometric transfer (or congruent transfer) of the target composition to the as-grown film is often mentioned as a virtue of PLD.^{19–24} This virtue allows us to easily obtain films with multiple elements such as YBa₂Cu₃O_{7–δ}²⁵ and SrBi₂Ta₂O₉.²⁶ On the other hand, this is a misleading statement in a sense that the “stoichiometric transfer” cannot be taken for granted.^{27,28} It is recognized from the early stage of oxide film growth by PLD that the materials with light or volatile elements (Li, Na, K, Zn, Pb, Bi) require special solutions, e.g., using an off-stoichiometric target or a segmented target to compensate the loss of those elements^{20,21,29–31} and precise control of PLD parameters.^{17,32–34} Further research revealed that the window for optimum growth conditions is rather small even if the oxide does not contain the aforementioned elements. Processes which contribute to a change in the cation ratio are material ejection by a laser beam from the target, scattering by the background gas or within the plasma plume, (re)sputtering of adsorbed elements by

plasma species with high kinetic energy, and evaporation of adsorbed elements from the substrate surface.³⁵ The corresponding PLD parameters known to have an influence on cation ratios are laser fluence,^{7,9–11,15,16,33,34,36–42} background gas pressure,^{17,31–34,42–47} and substrate temperature.^{31,32,36,48,49} Since a high temperature is usually required in order to obtain films with good crystal quality, the control of the cation ratio ought to be performed by the other parameters. Here, we re-emphasize the importance of exploring growth parameters to control the cation ratio of complex oxide films by demonstrating the relationship between the film composition and structural/ferroelectric properties of TbMnO₃ films grown on (010) oriented YAlO₃ substrates.

II. EXPERIMENT

TbMnO₃ films were grown on (010) oriented YAlO₃ substrates (Crystec Co. Ltd., *Pbnm* space group) by PLD. Pulsed beams from a KrF excimer laser ($\lambda = 248$ nm) were focused onto a stoichiometric TbMnO₃ ceramic target to the size of ≈ 2 mm² ($\approx 1.2 \times 1.67$ mm) at a repetition rate of 2 Hz. The target-substrate distance was fixed at 41 mm. The substrate was mounted at the plume center and heated to 690 °C by a lamp heater (heating area: $\phi \approx 6$ cm). Laser fluence and a N₂O background gas pressure were chosen as variables. The chemical composition of films was verified by Rutherford backscattering spectrometry (RBS). The lattice parameters of each film were investigated by x-ray diffraction using a Cu K α x-ray source. In order to evaluate the in-plane electric properties, Au (56 nm)/Ti (4 nm) interdigitated electrodes were patterned on the film surface. The capacitance was measured with an AC voltage of 100 mV using an Agilent E4980A LCR meter. FE hysteresis loops were probed using a Sawyer-Tower circuit and the Positive-Up Negative-Down (double-wave) method.⁵⁰

FIG. 1. The cation ratio of TbMnO₃ films as a function of (a) laser fluence with fixed N₂O pressure (0.7 mbar) and (b) N₂O pressure with fixed laser fluence (2.05 J cm⁻²) investigated by RBS. The corresponding raw data are shown in Fig. S1.⁵¹ (c) Out-of-plane x-ray θ -2 θ diffraction pattern of 14 nm films grown at different N₂O pressures.

III. RESULTS AND DISCUSSIONS

The influence of the N₂O pressure with respect to the cation ratio of the TbMnO₃ films is investigated from 0.1 to 0.9 mbar with a fixed laser fluence of 2.05 ± 0.05 J cm⁻² (Fig. 1(a)).⁵¹ There is a boundary between 0.3 and 0.7 mbar where the cation ratio changes from Tb-rich to stoichiometric. The amount of Tb ions in the films grown at 0.3 mbar is 13% larger than the stoichiometric composition. On the other hand, the cation ratio does not significantly change in the fluence range between 1.8 and 2.5 J cm⁻² at a N₂O background of 0.7 mbar (Fig. 1(b)).⁵¹ At the investigated pressure range, the mean free path in N₂O gas is smaller than 2 mm (~ 1.5 mm for 0.1 mbar at a gas temperature of 1000 K). This means that there are a considerable number of collisions between plasma species and the N₂O molecules until the species reach the substrate. Following the Schou's review report on the transfer of materials by laser ablation,³⁵ the most-likely reason for the Mn loss at 0.3 and 0.1 mbar is preferential scattering of the lighter element, i.e., Mn, by background gas molecules while the effect of scattering is not as pronounced for the heavier element, Tb. By introducing more

FIG. 2. Reciprocal space maps of (130) and (041) reflections of 200 nm (a, b) Tb-rich and (c, d) stoichiometric TbMnO₃ films. The maps of a YAlO₃ (010) substrate for the respective reflections are shown above each map.

gas, the heavier element Tb is also scattered more so that the number of elements arriving to the substrate becomes comparable for both elements. In the following discussion, we will compare the properties of Tb-rich and stoichiometric TbMnO₃ films made with a laser fluence of ~ 2.05 J cm⁻² at the N₂O pressure of 0.3 and 0.7 mbar, respectively.

First, their crystalline properties are compared. Fig. 1(c) shows θ -2 θ x-ray scans of Tb-rich and stoichiometric 14 nm films where out-of-plane lattice parameters are larger for stoichiometric films (Tb-rich: 5.887 Å, stoichiometric: 5.94 Å). Thicker films exhibit an additional difference in their crystalline properties. Reciprocal space maps of 200 nm films are displayed in Fig. 2. Both Tb-rich and stoichiometric films exhibit diffraction from three layers as summarized in Table I, consisting of a coherently grown (Layer A), a partially relaxed (Layer B), and a fully relaxed layer (Layer C). There are two intriguing properties. First, the intensity of the coherently grown layer is stronger for the stoichiometric film, which implies that the critical thickness where a strain relaxation occurs is larger for the films with a stoichiometric composition. This is a reasonable assumption

TABLE I. Lattice parameters and unit cell volumes of 200 nm TbMnO₃ films derived from Fig. 2 in comparison to the bulk TbMnO₃.

	Tb-rich (grown at 0.3 mbar)			Stoichiometric (grown at 0.7 mbar)			Bulk ^a	YAlO ₃ ^b
	Layer A	Layer B	Layer C	Layer A	Layer B	Layer C		
<i>a</i> (Å)	5.181	5.307	5.31	5.183	5.291	5.30	5.306	5.180
<i>b</i> (Å)	5.899	5.857	5.85	5.939	5.872	5.86	5.854	5.329
<i>c</i> (Å)	7.369	7.369	7.41	7.368	7.368	7.40	7.413	7.371
volume (Å ³)	225.2	229.1	230.2	226.8	228.9	229.8	230.4	

^aReference 52.

^bReference 53.

FIG. 3. Ferroelectric hysteresis curves of 14 nm (a) Tb-rich and (b) stoichiometric TbMnO₃ films at 20 K. The effective polarization values shown were calculated as $Q/(tL)^{-1}$, where Q is the measured charge, t is the film thickness, and L is the total length of the finger pairs.^{67–69} Effective remnant polarizations along the a -axis plotted as a function of temperature for both Tb-rich and stoichiometric (c) 14 nm (d) 200 nm films. The c -axis components of the 200 nm films are shown in the inset of (d). (e) Ferroelectric hysteresis curve of the stoichiometric 200 nm film taken along the a -axis at 15 K.

considering that the cation off-stoichiometry is likely to result in defects in a crystal⁹ triggering strain relaxation. To maintain a thick coherently grown layer, films must therefore be grown with the appropriate composition. Second, the unit-cell volume of the coherently grown layer is smaller for Tb-rich films (Table I). Some perovskite films exhibit a larger unit cell volume by introducing cation off-stoichiometry.^{9,16} The expansion of the lattice can be explained by local electrostatic repulsion or the formation of additional layers.⁹ However, some other off-stoichiometric perovskites may exhibit a smaller unit cell.^{8,10,12} Thus, the influence of the cation ratio to the unit cell can be material dependent or is to be considered with the appropriate analysis of the chemical composition including the amount of oxygen, which must be carefully quantified especially when oxide substrates are used.

The electric properties also change with the cation ratio (Fig. 3). For both Tb-rich and stoichiometric 14 nm films, FE hysteresis curves were observed along the a -axis, showing a flip of the direction of polarization from along the c -axis in bulk⁵⁴ (Figs. 3(a) and 3(b), details are discussed elsewhere⁵⁵). However, there are remarkable differences in the magnitude of the polarization and the FE transition temperature (T_{FE}) for the films with different composition. The Tb-rich film has a smaller polarization by one order of magnitude and T_{FE} of the Tb-rich film is lower than that of the stoichiometric films (Figs. 3(a)–3(c)). The same difference appears for 200 nm films except for a trace of polarization appearing along the c -axis for both Tb-rich and stoichiometric films (Fig. 3(d)). These results indicate that the FE long range order of the Tb-rich films is disturbed by potential defects due to the cation off-stoichiometry.

Here, we would like to focus on the electric properties of the stoichiometric 200 nm film, which exhibits a unique behavior. It shows an additional increase in the FE polarization below ~ 23 K compared to the 14 nm film (Figs. 3(c) and 3(d)). The distinct FE feature from the relaxed layer is also observed in the FE hysteresis curve at 15 K, which exhibits a superposition of two hysteresis curves (Fig. 3(e)). Since the lattice parameter of the fully relaxed layer almost corresponds to bulk TbMnO₃ which has a c -axis polarization, we may assume that the second FE component reflects the properties of the partially relaxed layer. Capacitance measurements provide detailed information about the FE properties. Fig. 4(a) shows the capacitance measured along the a -axis plotted as a function of temperature in the frequency range of 100 Hz to 2 MHz. The figure displays the signs of two different types of FE features. One is the sharp divergent behavior at ~ 40 K which corresponds to the FE transition temperature of the coherently grown layer. The location of the peak does not depend on the measurement frequency, indicating that the transition at 40 K reflects long range order. At lower temperatures, there is a broad hump whose peak location is frequency dependent. This feature is a specific characteristic for the thick films and does not appear for coherently grown films,⁵⁵ i.e., the property is related to the relaxed layer. This glass-like response of dielectric properties can be analyzed by using the Vogel-Fulcher equation,^{56,57}

$$f(T_{\max}) = f_0 \exp [-E/k_B(T_{\max} - T_f)],$$

where $T_{\max}$ is the temperature for the maximum in the dielectric constant ($\propto$ capacitance), f_0 is the cut-off

FIG. 4. (a) Temperature dependent capacitance of the stoichiometric 200 nm TbMnO₃ film measured at various frequencies. (b) Vogel-Fulcher fit of the relaxational behavior of the capacitance.

frequency of the distribution of relaxation times, E is the energy barrier for the dipole reorientation, and T_f is the so-called static freezing temperature.⁵⁸ The measurement frequency vs. $T_{\max}$ plot and the fitting curve are shown in Fig. 4(b). Fitting the data with the Vogel-Fulcher relation gives $f_0 = (2.4 \pm 1) \times 10^{10}$ Hz, $E = 6.2 \pm 0.5$ meV, and $T_f = 9.8 \pm 0.2$ K (Fig. 4(b)). Although the fitting coefficients f_0 and E are smaller for typical relaxors,^{56,59,60} all coefficients are reasonable to assume that the glass-like response of the relaxed layer originates from nano-scaled polar-regions.^{58,61,62} This dielectric response should be correlated to the FE feature of the partially relaxed layer which started at around 23 K (Fig. 3(d)).

The origin of the relaxational behavior from the relaxed layer is an open question. The frequency dispersion converges above ~ 20 K (Fig. 4(a)), which implies that the effect does not originate from the potential charge carriers in the film. It is also supported by the frequency dependent dielectric loss (Fig. S2(a)⁵¹). The dielectric loss is 0.03 at a maximum within the measured temperature (8–50 K) and frequency (10^2 – 10^6 Hz) range. Thus, the observed frequency dispersion is not an artifact such as the Maxwell-Wagner effect.^{63,64} Typical bulk relaxors are either multi-element ferroelectrics, e.g., $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$,⁶² or doped dielectrics with a soft phonon mode, e.g., $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$.⁵⁸ In both cases, the dispersed and fluctuating distribution of mixed/doped elements generates polar nano-regions causing a relaxational behavior in their dielectric response.^{58,61} The stoichiometric 200 nm TbMnO_3 film, however, does not have such a chemical feature. Strained SrTiO_3 films are reported to show the relaxor ferroelectricity,^{65,66} in which the origin of the relaxational behavior is recently reported to be correlated to small off-stoichiometry (3%–5%) of the cation composition.¹⁸ We cannot exclude this possibility in our film due to the error bar of the RBS measurements (Fig. 1, $\pm 4\%$ – 5%) as a result of the background signal from the YAlO_3 substrate. But it seems less likely since the transition temperature at 40 K is frequency independent (Fig. 4(a)). Considering the significant mosaicity of the relaxed layer (Figs. 2(c) and 2(d)), it is likely that the relaxor behavior can be attributed to the defects in the crystal. Potential dislocations in the relaxed layer may act as barriers between polar nano-regions, disturbing the long range ordering of the polarization. Interestingly, the Tb-rich 200 nm film does not exhibit relaxational behavior in the capacitance measurements (Fig. S2(b)⁵¹), even though the film also has considerable mosaicity and cation off-stoichiometry as a source of defects. This result suggests that the large off-stoichiometry ($\sim 10\%$) disturbs the generation of polar order even on the nano-scale. These results reveal the importance of controlling the cation ratio to achieve the desired ordered state in complex oxide films since changes in composition induce different properties.

IV. CONCLUSION

We confirmed that the background gas pressure has a significant influence on the cation ratio of PLD-grown TbMnO_3 films. Crystalline properties of TbMnO_3 films

change accordingly, e.g., the coherently grown layer can be grown thicker for the stoichiometric films as compared to the Tb-rich films. The cation ratio also has an influence on the ferroelectric order in films. A higher transition temperature and a larger polarization were found in stoichiometric films. Poor cation stoichiometry thus disturbs the coherent growth, ferroelectric order, and formation of a polar state in TbMnO_3 films, demonstrating that a careful investigation of PLD parameters is indispensable to obtain the desired functionalities in complex oxide thin films.

ACKNOWLEDGMENTS

The financial support and CROSS funding to K.S. from PSI are gratefully acknowledged. We would like to thank D. Marty (PSI, Laboratory for Micro- and Nanotechnology) for the support with optical lithography and U. Greuter for the implementation of a Sawyer-Tower circuit for ferroelectric hysteresis measurements. The use of the LCR-meter belonging to the Laboratory for Scientific Developments and Novel Materials, PSI is acknowledged.

- ¹D. G. Schlom, L.-Q. Chen, C.-B. Eom, K. M. Rabe, S. K. Streiffer, and J.-M. Triscone, *Annu. Rev. Mater. Res.* **37**, 589 (2007).
- ²J. M. Rondinelli and N. A. Spaldin, *Adv. Mater.* **23**, 3363 (2011).
- ³D. G. Schlom, L.-Q. Chen, C. J. Fennie, V. Gopalan, D. A. Muller, X. Pan, R. Ramesh, and R. Uecker, *MRS Bull.* **39**, 118 (2014).
- ⁴H. Y. Hwang, Y. Iwasa, M. Kawasaki, B. Keimer, N. Nagaosa, and Y. Tokura, *Nat. Mater.* **11**, 103 (2012).
- ⁵P. Zubko, S. Gariglio, M. Gabay, P. Ghosez, and J.-M. Triscone, *Annu. Rev. Condens. Matter Phys.* **2**, 141 (2011).
- ⁶J. M. Rondinelli, S. J. May, and J. W. Freeland, *MRS Bull.* **37**, 261 (2012).
- ⁷T. Ohnishi, M. Lippmaa, T. Yamamoto, S. Meguro, and H. Koinuma, *Appl. Phys. Lett.* **87**, 241919 (2005).
- ⁸J. H. Song, T. Susaki, and H. Y. Hwang, *Adv. Mater.* **20**, 2528 (2008).
- ⁹T. Ohnishi, K. Shibuya, T. Yamamoto, and M. Lippmaa, *J. Appl. Phys.* **103**, 103703 (2008).
- ¹⁰D. Kan and Y. Shimakawa, *Appl. Phys. Lett.* **99**, 081907 (2011).
- ¹¹E. Breckenfeld, A. B. Shah, and L. W. Martin, *J. Mater. Chem. C* **1**, 8052 (2013).
- ¹²L. Qiao, K. H. L. Zhang, M. E. Bowden, T. Varga, V. Shutthanandan, R. Colby, Y. Du, B. Kabius, P. V. Sushko, M. D. Biegalski, and S. A. Chambers, *Adv. Funct. Mater.* **23**, 2953 (2013).
- ¹³W. Siemons, G. Koster, A. Vailionis, H. Yamamoto, D. H. A. Blank, and M. R. Beasley, *Phys. Rev. B* **76**, 075126 (2007).
- ¹⁴M. P. Warusawithana, C. Richter, J. A. Mundy, P. Roy, J. Ludwig, S. Paetel, T. Heeg, A. A. Pawlicki, L. F. Kourkoutis, M. Zheng, M. Lee, B. Mulcahy, W. Zander, Y. Zhu, J. Schubert, J. N. Eckstein, D. A. Muller, C. S. Hellberg, J. Mannhart, and D. G. Schlom, *Nat. Commun.* **4**, 2351 (2013).
- ¹⁵E. Breckenfeld, N. Bronn, J. Karthik, A. R. Damodaran, S. Lee, N. Mason, and L. W. Martin, *Phys. Rev. Lett.* **110**, 196804 (2013).
- ¹⁶H. K. Sato, C. Bell, Y. Hikita, and H. Y. Hwang, *Appl. Phys. Lett.* **102**, 251602 (2013).
- ¹⁷L. You, N. T. Chua, K. Yao, L. Chen, and J. Wang, *Phys. Rev. B* **80**, 024105 (2009).
- ¹⁸C.-H. Lee, V. Skoromets, M. D. Biegalski, S. Lei, R. Haismaier, M. Bernhagen, R. Uecker, X. Xi, V. Gopalan, X. Martí, S. Kamba, P. Kuzel, and D. G. Schlom, *Appl. Phys. Lett.* **102**, 082905 (2013).
- ¹⁹H.-U. Krebs, M. Weisheit, J. Faupel, E. Súske, T. Scharf, C. Fuhse, M. Störmer, K. Sturm, M. Seibt, H. Kijewski, D. Nelke, E. Panchenko, and M. Buback, *Advances in Solid State Physics* (Springer-Verlag, Berlin, Heidelberg, 2003), Vol. 43, p. 505.
- ²⁰D. P. Norton, *Mater. Sci. Eng., R* **43**, 139 (2004).
- ²¹H. M. Christen and G. Eres, *J. Phys.: Condens. Matter* **20**, 264005 (2008).
- ²²M. Opel, *J. Phys. D: Appl. Phys.* **45**, 033001 (2012).
- ²³S. Shahidi, B. Moazzenchi, and M. Ghoranneviss, *Eur. Phys. J. Appl. Phys.* **71**, 31302 (2015).

- ²⁴C. A. F. Vaz, F. J. Walker, C. H. Ahn, and S. Ismail-Beigi, *J. Phys.: Condens. Matter* **27**, 123001 (2015).
- ²⁵D. Dijkkamp, T. Venkatesan, X. D. Wu, S. A. Shaheen, N. Jisrawi, Y. H. Min-Lee, W. L. McLean, and M. Croft, *Appl. Phys. Lett.* **51**, 619 (1987).
- ²⁶S. B. Desu, D. P. Vijay, X. Zhang, and B. He, *Appl. Phys. Lett.* **69**, 1719 (1996).
- ²⁷D. G. Schlom, L.-Q. Chen, X. Pan, A. Schmehl, and M. A. Zurbuchen, *J. Am. Ceram. Soc.* **91**, 2429 (2008).
- ²⁸S. A. Chambers, *Adv. Mater.* **22**, 219 (2010).
- ²⁹S. Yilmaz, T. Venkatesan, and R. Gerhard-Multhaupt, *Appl. Phys. Lett.* **58**, 2479 (1991).
- ³⁰Y. E. Lee, D. P. Norton, and J. D. Budai, *Appl. Phys. Lett.* **74**, 3155 (1999).
- ³¹H. Beá, M. Bibes, A. Barthelémy, K. Bouzehouane, E. Jacquet, A. Khodan, J.-P. Contour, S. Fusil, F. Wyczisk, A. Forget, D. Lebeugle, D. Colson, and M. Viret, *Appl. Phys. Lett.* **87**, 072508 (2005).
- ³²J. S. Horwitz, K. S. Grabowski, D. B. Chrisey, and R. E. Leuchtner, *Appl. Phys. Lett.* **59**, 1565 (1991).
- ³³T. Ohnishi, B. T. Hang, X. Xu, M. Osada, and K. Takada, *J. Mater. Res.* **25**, 1886 (2010).
- ³⁴T. Ohnishi and K. Takada, *Appl. Phys. Express* **5**, 055502 (2012).
- ³⁵J. Schou, *Appl. Surf. Sci.* **255**, 5191 (2009).
- ³⁶T. Ohnishi and K. Takada, *Appl. Phys. Express* **4**, 025501 (2011).
- ³⁷B. Dam, J. H. Rector, J. Johansson, J. Huijbregtse, and D. G. De Groot, *J. Appl. Phys.* **83**, 3386 (1998).
- ³⁸B. Dam, J. Rector, M. F. Chang, S. Kars, D. G. de Groot, and R. Griessen, *Appl. Phys. Lett.* **65**, 1581 (1994).
- ³⁹S. Kobayashi, Y. Tokuda, T. Ohnishi, T. Mizoguchi, N. Shibata, Y. Sato, Y. Ikuhara, and T. Yamamoto, *J. Mater. Sci.* **46**, 4354 (2011).
- ⁴⁰T. Venkatesan, X. D. Wu, A. Inam, and J. B. Wachtman, *Appl. Phys. Lett.* **52**, 1193 (1988).
- ⁴¹S. Wicklein, A. Sambri, S. Amoruso, X. Wang, R. Bruzzese, A. Koehl, and R. Dittmann, *Appl. Phys. Lett.* **101**, 131601 (2012).
- ⁴²C. Xu, S. Wicklein, A. Sambri, S. Amoruso, M. Moors, and R. Dittmann, *J. Phys. D: Appl. Phys.* **47**, 034009 (2014).
- ⁴³J. Gonzalo, R. Gómez San Román, J. Perrière, C. N. Afonso, and R. Pérez Casero, *Appl. Phys. A: Mater. Sci. Process.* **66**, 487 (1998).
- ⁴⁴Z. Marton, S. S. A. Seo, T. Egami, and H. N. Lee, *J. Cryst. Growth* **312**, 2923 (2010).
- ⁴⁵D. M. Packwood, S. Shiraki, and T. Hitosugi, *Phys. Rev. Lett.* **111**, 036101 (2013).
- ⁴⁶A. P. Chen, F. Khatkhatay, W. Zhang, C. Jacob, L. Jiao, and H. Wang, *J. Appl. Phys.* **114**, 124101 (2013).
- ⁴⁷J. Chen, D. Stender, K. Conder, A. Wokaun, C. W. Schneider, and T. Lippert, *Appl. Phys. Lett.* **105**, 114104 (2014).
- ⁴⁸F. Gunkel, K. Skaja, A. Shkabko, R. Dittmann, S. Hoffmann-Eifert, and R. Waser, *Appl. Phys. Lett.* **102**, 071601 (2013).
- ⁴⁹C. N. Mihailescu, I. Pasuk, M. Straticiu, C. R. Nita, D. Pantelica, and J. Giapintzakis, *Appl. Surf. Sci.* **320**, 852 (2014).
- ⁵⁰M. Fukunaga and Y. Noda, *J. Phys. Soc. Jpn.* **77**, 064706 (2008).
- ⁵¹See supplementary material at <http://dx.doi.org/10.1063/1.4948961> for supplementary figures.
- ⁵²J. M. Chen, T. L. Chou, J. M. Lee, S. A. Chen, T. S. Chan, T. H. Chen, K. T. Lu, W. T. Chuang, H.-S. Sheu, S. W. Chen, C. M. Lin, N. Hiraoka, H. Ishii, K. D. Tsuei, and T. J. Yang, *Phys. Rev. B* **79**, 165110 (2009).
- ⁵³M. C. Morris, H. F. McMurdie, E. H. Evans, B. Paretzkin, H. S. Parker, N. P. Pyrrhos, and C. R. Hubbard, *Natural Bureau of Standards Monograph* **25**, *Standard X-ray Diffraction Powder Patterns Section 19* (U.S. Department of Commerce, 1982), p. 7.
- ⁵⁴T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, *Nature* **426**, 55 (2003).
- ⁵⁵K. Shimamoto, S. Mukherjee, N. S. Bingham, A. K. Suszka, T. Lippert, C. Niedermayer, and C. W. Schneider, *Elastic Strain Engineering at Phase Boundaries of Material Systems* (2016).
- ⁵⁶D. Viehland, S. J. Jang, L. E. Cross, and M. Wuttig, *J. Appl. Phys.* **68**, 2916 (1990).
- ⁵⁷A. K. Tagantsev, *Phys. Rev. Lett.* **72**, 1100 (1994).
- ⁵⁸G. A. Samara, *J. Phys.: Condens. Matter* **15**, R367 (2003).
- ⁵⁹K. B. Lyons, P. A. Fleury, and D. Rytz, *Phys. Rev. Lett.* **57**, 2207 (1986).
- ⁶⁰T. Maiti, R. Guo, and A. S. Bhalla, *J. Am. Ceram. Soc.* **91**, 1769 (2008).
- ⁶¹L. E. Cross, *Ferroelectrics* **151**, 305 (1994).
- ⁶²A. A. Bokov and Z.-G. Ye, *J. Mater. Sci.* **41**, 31 (2006).
- ⁶³G. Catalan, D. O'Neill, R. M. Bowman, and J. M. Gregg, *Appl. Phys. Lett.* **77**, 3078 (2000).
- ⁶⁴G. Catalan and J. F. Scott, *Nature* **448**, E4 (2007).
- ⁶⁵M. D. Biegalski, Y. Jia, D. G. Schlom, S. Trolier-McKinstry, S. K. Streiffer, V. Sherman, R. Uecker, and P. Reiche, *Appl. Phys. Lett.* **88**, 192907 (2006).
- ⁶⁶H. W. Jang, A. Kumar, S. Denev, M. D. Biegalski, P. Maksymovych, C. W. Bark, C. T. Nelson, C. M. Folkman, S. H. Baek, N. Balke, C. M. Brooks, D. A. Tenne, D. G. Schlom, L. Q. Chen, X. Q. Pan, S. V. Kalinin, V. Gopalan, and C. B. Eom, *Phys. Rev. Lett.* **104**, 197601 (2010).
- ⁶⁷B. Xu, R. G. Polcawich, S. Trolier-McKinstry, Y. Ye, L. E. Cross, J. J. Bernstein, and R. Miller, *Appl. Phys. Lett.* **75**, 4180 (1999).
- ⁶⁸Q. Q. Zhang, S. J. Gross, S. Tadigadapa, T. N. Jackson, F. T. Djuth, and S. Trolier-McKinstry, *Sens. Actuators, A* **105**, 91 (2003).
- ⁶⁹C. M. Folkman, S. H. Baek, C. T. Nelson, H. W. Jang, T. Tybell, X. Q. Pan, and C. B. Eom, *Appl. Phys. Lett.* **96**, 052903 (2010).