

## Phase transitions and domain evolution in (Pb, La)(Zr, Sn, Ti)O<sub>3</sub> single crystal

Yuanyuan Li, Qiang Li, Qingfeng Yan, Yiling Zhang, Xiaoqing Xi et al.

Citation: *Appl. Phys. Lett.* **101**, 132904 (2012); doi: 10.1063/1.4755759

View online: <http://dx.doi.org/10.1063/1.4755759>

View Table of Contents: <http://apl.aip.org/resource/1/APPLAB/v101/i13>

Published by the [American Institute of Physics](http://www.aip.org).

---

### Related Articles

Manganese induced modifications in yttria stabilized zirconia

*Appl. Phys. Lett.* **101**, 131606 (2012)

Fabrication and photoluminescence of SiC quantum dots stemming from 3C, 6H, and 4H polytypes of bulk SiC

*Appl. Phys. Lett.* **101**, 131906 (2012)

Phase transition of FePt/Ag nanocomposite thin films: Kinetics, activation volume, and atomic processes

*J. Appl. Phys.* **112**, 063907 (2012)

Effect of A-site La and Ba doping on threshold field and characteristic temperatures of PbSc<sub>0.5</sub>Ta<sub>0.5</sub>O<sub>3</sub> relaxor studied by acoustic emission

*J. Appl. Phys.* **112**, 064107 (2012)

Mn doping-induced structural and magnetic transformations in the antiferroelectric phase of the Bi<sub>1-x</sub>NdxFeO<sub>3</sub> perovskites

*J. Appl. Phys.* **112**, 064105 (2012)

---

### Additional information on *Appl. Phys. Lett.*

Journal Homepage: <http://apl.aip.org/>

Journal Information: [http://apl.aip.org/about/about\\_the\\_journal](http://apl.aip.org/about/about_the_journal)

Top downloads: [http://apl.aip.org/features/most\\_downloaded](http://apl.aip.org/features/most_downloaded)

Information for Authors: <http://apl.aip.org/authors>

## ADVERTISEMENT



**Goodfellow**  
metals • ceramics • polymers • composites  
70,000 products  
450 different materials  
**small quantities fast**

[www.goodfellowusa.com](http://www.goodfellowusa.com)

## Phase transitions and domain evolution in (Pb, La)(Zr, Sn, Ti)O<sub>3</sub> single crystal

Yuanyuan Li,<sup>1</sup> Qiang Li,<sup>1,a)</sup> Qingfeng Yan,<sup>1</sup> Yiling Zhang,<sup>2</sup> Xiaoqing Xi,<sup>2</sup> Xiangcheng Chu,<sup>2</sup> and Wenwu Cao<sup>3</sup>

<sup>1</sup>Department of Chemistry, Tsinghua University, Beijing 100084, China

<sup>2</sup>State Key Laboratory of New Ceramics and Fine Processing, Tsinghua University, Beijing 100084, China

<sup>3</sup>Condensed Matter Science and Technology Institute, Harbin Institute of Technology, Harbin, Heilongjiang 150080, China and Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania 16802, USA

(Received 9 July 2012; accepted 11 September 2012; published online 27 September 2012)

Antiferroelectric (Pb, La)(Zr, Sn, Ti)O<sub>3</sub> (PLZST) single crystal has been grown and characterized. From dielectric measurements, x-ray diffraction analysis, and *in situ* observation of domain structures, we found two first-order phase transitions during heating from room temperature to 250 °C: orthorhombic (O) → rhombohedral (R) → cubic. Coexistence of O and R phases, with the R phase region strongly restricted inside the O phase matrix, has been observed within a broad temperature range above 123 °C. In addition, much denser domain walls appeared in the PLZST crystal when the O-R transition takes place. © 2012 American Institute of Physics.

[<http://dx.doi.org/10.1063/1.4755759>]

Antiferroelectric (Pb,La)(Zr,Sn,Ti)O<sub>3</sub> (PLZST) has gained a lot of attention recently because of its large field induced longitudinal strain (up to 0.9%) and short response time (1-2 μs).<sup>1</sup> Usually, these promising properties occur when the phase transition between antiferroelectric (AFE) and ferroelectric (FE) phases takes place.<sup>2,3</sup> This transition can be driven by temperature, electric field, or mechanical stress.<sup>4-6</sup>

Up to now, all previous investigations on PLZST have focused on polycrystalline materials, including ceramics<sup>7,8</sup> and thin films.<sup>9,10</sup> Their applications are limited by the crystallographic isotropy. It has been demonstrated that single crystals with specific crystallographic orientations could have much superior properties than its polycrystalline counterparts, for example, the [001]-oriented relaxor based ferroelectric Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-PbTiO<sub>3</sub> (PMN-PT) and Pb(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-PbTiO<sub>3</sub> (PZN-PT) single crystals have giant piezoelectric properties.<sup>11,12</sup> This intrigued us to grow PLZST single crystals. Recently, we have grown PLZST single crystals with the size of 2.0 × 2.0 × 1.5 mm<sup>3</sup>.<sup>13</sup> Some basic properties have been characterized.<sup>14,15</sup>

In the past few years, there is an increasing interest on domain structures in PZN-PT,<sup>16,17</sup> PMN-PT,<sup>18-21</sup> and BaTiO<sub>3</sub><sup>22</sup> single crystals, because its dielectric, piezoelectric, and many other functional properties are closely related to domain structures. Domain observation has been used as a visual method to characterize the temperature or electric field induced phase transitions.<sup>23-27</sup>

Up to date, the domain structures and phase transition behaviors of antiferroelectric PLZST crystals have not been reported. Investigation on these two aspects is of great importance for the understanding of the origin of those excellent properties found in PLZST. In this work, we performed dielectric measurements and high-temperature x-ray diffraction (XRD) analysis to study the phase transition behaviors

of PLZST crystals. Moreover, temperature-dependent domain structures of PLZST single crystal were observed *in situ* with the help of a polarized light microscope (PLM). Domain evolution clearly revealed the phase transition sequence in PLZST single crystal on heating.

PLZST single crystals with the nominal composition of Pb<sub>0.97</sub>La<sub>0.02</sub>(Zr<sub>0.66</sub>Ti<sub>0.07</sub>Sn<sub>0.27</sub>)O<sub>3</sub> were grown by flux method using PbO-PbF<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> as the flux. The experimental setup is similar to the one described in Ref. 14. The obtained crystals were polished along the (001) plane into thin plates with a thickness of 0.1 mm. Careful investigations of domain structures were carried out using a polarized light microscope (Jiangnan, XJZ-6) equipped with a hot stage (Linkam, THMS600). Angles of the crossed polarizer/analyzer (P/A) pair measured in this work were referred to pseudo-cubic [100] direction, which can be determined along the crystal edges on the habitual faces. X-ray diffraction analysis was performed on crashed PLZST crystal powders, using a PANalytical X'Pert PRO diffractometer equipped with a doomed hot-stage. The wavelength of the incident radiation was Cu K<sub>α</sub> = 0.154 nm. Dielectric properties were measured using a LCR meter (Agilent, HP4294) on Ag-electroded specimen.

Fig. 1 shows the temperature-dependent dielectric properties and there are two anomalies in the measured temperature range. The higher temperature anomaly around 185 °C corresponds to the Curie temperature (*T<sub>c</sub>*), where the amplitude of the dielectric constant decreases with frequency but the transition temperature remains the same. Paraelectric cubic (C) phase appears above *T<sub>c</sub>*. The lower temperature anomaly (as highlighted in the circle) occurs in the temperature range of 116–123 °C, which indicates that another phase transition took place. The variation of reciprocal of ε<sub>r</sub> during heating and cooling at 100 kHz is shown in the inset of Fig. 1. Two thermal hysteresis loops were observed near 123 °C (115 °C) and 185 °C (180 °C) upon heating (cooling), with the former to be more evident. The thermal hysteresis indicates that the two phase transitions are of first-order.

<sup>a)</sup> Author to whom correspondence should be addressed. Electronic mail: qiangli@mails.tsinghua.edu.cn. Tel.: +86-10-62797871. Fax: +86-10-62771149.

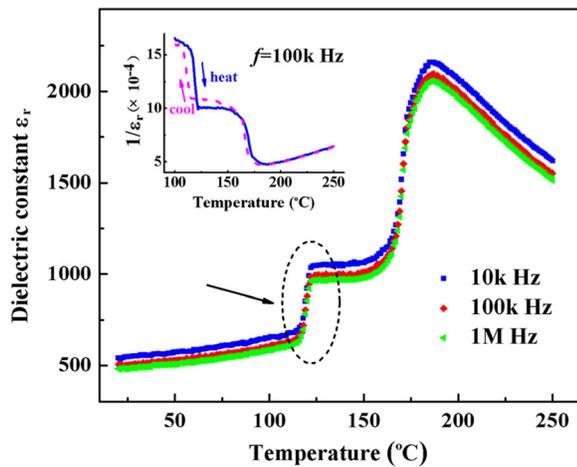


FIG. 1. Temperature-dependent dielectric properties. The reciprocal of  $\epsilon_r$  during heating and cooling is shown in the inset.

High-temperature XRD was performed at a series of temperatures to clarify the phase transition behaviors observed around the two dielectric anomalies. The results are shown in Fig. 2, where the major peaks are indexed based on the cubic perovskite structure. The pattern at room temperature shows an orthorhombic (O) symmetry, as found in many  $\text{PbZrO}_3$ -based compounds.<sup>28,29</sup> This is different from the previous reported tetragonal (T) phase, which may be attributed to the complex growth conditions and the easy deviation of  $\text{Ti}^{4+}$  content during crystal growth.<sup>30</sup> A certain amount of weak peaks in the x-ray patterns, which are regarded as superlattice diffractions when using the cubic indexing and marked by stars, can differentiate the O phase from the T one.<sup>31</sup> The intensity of superlattice diffractions decreased gradually with increasing temperature, which can be easily seen from the enlarged profiles around the (110) diffraction in Fig. 2(b). At 130°C, above the lower transition temperature observed in the dielectric measurement, the major peaks can be indexed with a rhombohedral (R) symmetry. However, close examination revealed the residual presence of trace amount of O phase, as can be seen from the remaining weak superlattice diffractions in Fig. 2(b). Fig. 2(c) shows the (200) diffraction at around  $2\theta = 44^\circ$ , where the two dotted lines separately indicate the splitting of the (200) diffraction. As the temperature increases, the left splitting peak does not show obvious change but the right peak shifts slowly to the left. The junction of these two peaks, as marked by arrows, is rising slowly before the O-R phase transition takes place. It shows that the lattices are undergoing a slow distortion from O to R structure, which results in the generation of R-phase nuclei in the O matrix. The amount of R phase increases sharply above the O-R transition temperature, as evidenced by the abrupt rising junction of the splitting peaks at 130°C. Upon further heating, however, typical single peak of R structure was not observed. This clearly indicates that some O phase regions still remain and coexist with the R phase in a wide temperature range even above 123°C. When the temperature is higher than 160°C, the R phase becomes dominant, at which nearly single peak appears. The paraelectric C phase should appear above  $T_c$ , as the XRD pattern obtained at 200°C was

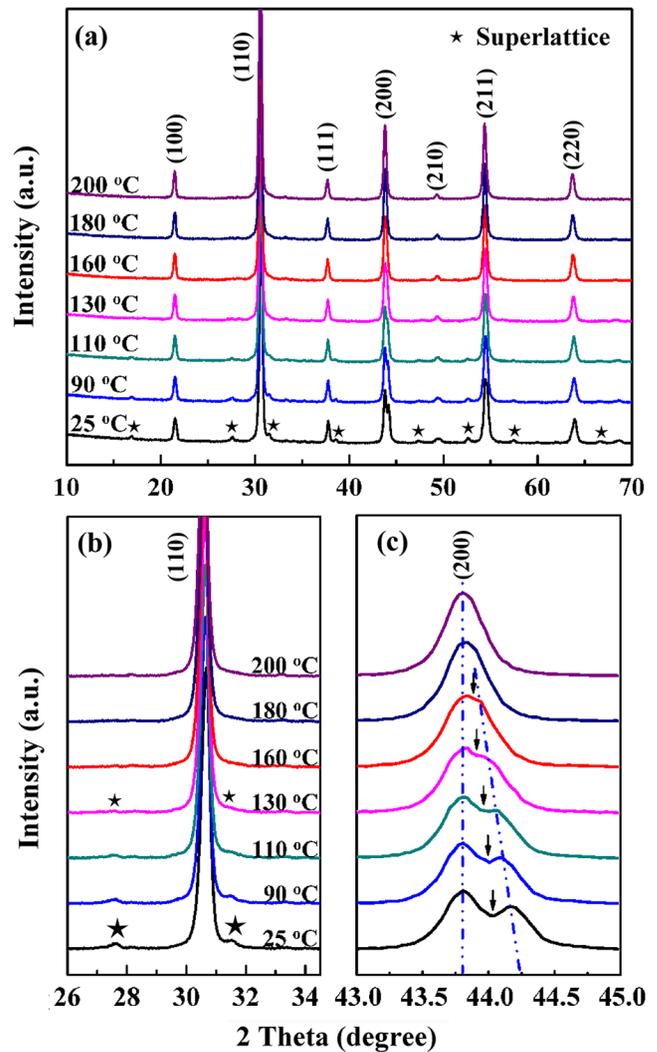


FIG. 2. (a) X-ray diffraction patterns at a series of temperatures, the stars mark the superlattice diffraction peaks. (b) The enlarged profiles around the (110) diffraction. (c) The enlarged profiles around the (200) diffraction. The two dot lines separately indicate the (200) splitting peaks and the arrows highlight the obvious changes in the junction of these two peaks.

indexed with a C symmetry, which is in accordance with the dielectric measurement results in Fig. 1.

Temperature-dependent domain structures, which were observed *in situ* along pseudo-cubic [001] direction of PLZST crystal, are shown in Fig. 3. The photo of crystal in the inset of Fig. 3(a) shows the polished crystal used for the domain observation. As had been seen in the antiferroelectric orthorhombic ( $A_O$ )  $\text{PbZrO}_3$  crystals, the [100] walls belong to  $90^\circ$ -type domains while [110] walls are of  $60^\circ$ -type.<sup>32</sup> Thus, the strip-like domain walls along [110] at room temperature are regarded as  $60^\circ$  domain walls, with the domain width of 10-40  $\mu\text{m}$ . Typical extinction for the  $60^\circ$  orthorhombic domains was observed at P/A:  $0^\circ$ , which can be seen from the insets of Figs. 3(a) and 3(b). As the temperature increases, the domain size, shape, and domain wall position are somewhat unchanged below 123°C. A gradual variation of optical interference colors was observed at P/A:  $45^\circ$ , which may be caused by the appearance of R-phase nuclei, as observed in the XRD analysis, as well as the possible generation of R-phase micro-domains. Upon further heating, remarkable transformation of domain structures takes place at

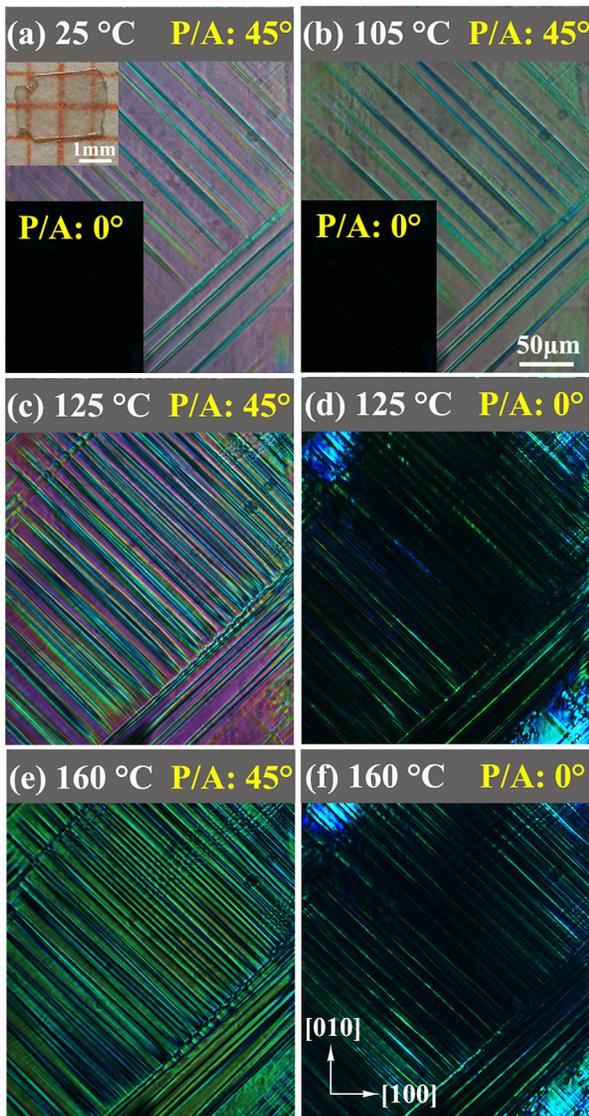


FIG. 3. Temperature-dependent domain structures at P/A: 0° and 45° at different temperatures of 25 °C, 105 °C, 125 °C, and 160 °C upon heating. The photo of crystal in the inset of (a) shows the polished crystal used for domain observation.

about 124 °C. More domain walls are clearly seen and narrow domains with different interference colors are intertwined with each other, as shown in Fig. 3(c). However, the crystal is not totally in the R phase because extinction at P/A: 45° for the R phase did not occur and only a fraction of R domains are embedded in the O matrix, as can be seen in Fig. 3(d) when P/A = 0°. The interference colors of the domains vary continuously with the increasing temperature, but still no total P/A: 45° extinction (Fig. 3(e)). Besides, the bright regions for the R phase at P/A: 0° are still inconspicuous in Fig. 3(f). In other words, the O phase persists after the O-R phase transition. These findings clearly demonstrated that the R phase regions are strongly restricted by the O-phase matrix and could not organize further into large-domain platelets or bands. This result is consistent with the high-temperature XRD measurements discussed above. On further heating, the domain matrix becomes darker and darker under cross polarizer at P/A: 45°, suggesting an increase of the amount of R phase. A total optical extinction

spread over the crystal above 185 °C when the PLZST crystal transformed to the C phase.

We can see that more domain walls are generated at the O-R phase transition. Domain formation follows the basic principle of total energy minimization, i.e., the periodicity of domains is correlated with the minimization of total energy ( $E_{\text{Tot}}$ ) in the crystal.<sup>33</sup> The total energy may be written as follows:

$$E_{\text{Tot}} = E_V + E_W, \quad (1)$$

where  $E_V$  mainly represents elastic energy in the antiferroelectric crystal and  $E_W$  means domain wall energy. The variation of total energy with the number of domain walls ( $n$ ) is schematically illustrated in Fig. 4. It can be seen that  $E_V$  monotonically decreases with the increase of domains while the domain wall energy  $E_W$  is proportional to the number of domain walls:  $E_W = nA\gamma$  (where  $A$  is the area of the wall and  $\gamma$  is the domain wall energy per unit area, namely, wall energy density). The dash lines in Fig. 4 correspond to a situation with lower wall energy density. It is known that without domains, the transformation strain will create large elastic energy. On the other hand, domain walls have positive energy. So increase of the number of domain walls will increase  $E_W$ . The balance of the two determines the domain size or domain wall numbers and results in total energy minimization. As proposed by Cao *et al.*,<sup>34</sup> the energy density of the walls decreases with temperature and the structure with a symmetry much closer to the high symmetric cubic should exhibit lower wall energy density. This can be applied to the PLZST crystal as the high temperature rhombohedral structure has a higher symmetry than orthorhombic and is usually regarded as a pseudo-cubic structure. Therefore, above the O-R phase transition temperature, the R phase has lower wall energy density and corresponds to more domain walls in the crystal to achieve the minimization of total energy, as can be seen in line  $E'_W$  and line  $E'_{\text{Tot}}$  in Fig. 4. It was observed that the formation of R phase is strongly restricted by the O phase matrix, which produces phase mixture. The O-R mixed domain structure with much more number of domain

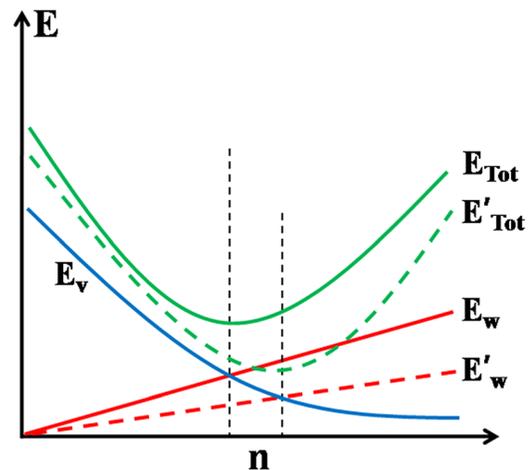


FIG. 4. The total energy ( $E_{\text{Tot}}$ ) as a function of the number of domain walls ( $n$ ).  $E_V$  mainly represents the elastic energy and  $E_W$  represents the domain wall energy.

walls in the PLZST crystal is a particular self-adjusting case of energy minimization.

In summary, the dielectric measurements, high-temperature XRD analysis, together with the *in situ* observation of domain structures clearly indicated that the PLZST crystal experienced phase transitions in the sequence of O  $\rightarrow$  R  $\rightarrow$  C upon heating. The coexistence of O and R phases with much more number of domain walls was observed in the crystal within a broad temperature range above 123 °C. The R phase was strongly restricted by the O phase matrix and could not organize into large domains immediately above the O-R phase transition temperature.

This work was supported by the National Natural Science Foundation of China under Grant Nos. 50272030, 50572048, 50972071, and 51172118 and also financially supported by the State Key Laboratory of New Ceramics and Fine Processing, Tsinghua University.

- <sup>1</sup>W. Y. Pan, C. Q. Dam, Q. M. Zhang, and L. E. Cross, *J. Appl. Phys.* **66**, 6014 (1989).
- <sup>2</sup>T. Q. Yang and X. Yao, *Ferroelectrics* **381**, 105 (2009).
- <sup>3</sup>H. L. Zhang, X. F. Chen, F. Cao, G. S. Wang, X. L. Dong, Z. Y. Hu, and T. Du, *J. Am. Ceram. Soc.* **93**, 4015 (2010).
- <sup>4</sup>C. T. Blue, J. C. Hicks, S. E. Park, S. Yoshikawa, and L. E. Cross, *Appl. Phys. Lett.* **68**, 2942 (1996).
- <sup>5</sup>W.-H. Chan, Z. K. Xu, J. W. Zhai, and H. Chen, *Appl. Phys. Lett.* **87**, 192904 (2005).
- <sup>6</sup>Z. K. Xu, J. W. Zhai, W.-H. Chan, and H. Chen, *Appl. Phys. Lett.* **88**, 132908 (2006).
- <sup>7</sup>L. H. Xue, Q. Li, Y. L. Zhang, R. Liu, and X. H. Zhen, *J. Eur. Ceram. Soc.* **26**, 323 (2006).
- <sup>8</sup>H. L. Zhang, X. F. Chen, F. Cao, G. S. Wang, X. L. Dong, Y. Gu, and Y. S. Liu, *Appl. Phys. Lett.* **94**, 252902 (2009).
- <sup>9</sup>X. H. Hao, J. W. Zhai, F. Shang, J. Zhou, and S. L. An, *J. Appl. Phys.* **107**, 116101 (2010).
- <sup>10</sup>M. S. Mirshekarloo, K. Yao, and T. Sritharan, *Appl. Phys. Lett.* **97**, 142902 (2010).
- <sup>11</sup>S.-E. Park and T. R. Shrout, *J. Appl. Phys.* **82**, 1804 (1997).
- <sup>12</sup>D. Zhou, J. Chen, L. H. Luo, X. Y. Zhao, and H. S. Luo, *Appl. Phys. Lett.* **93**, 073502 (2008).
- <sup>13</sup>L. H. Xue, Q. Li, Y. L. Zhang, X. H. Zhen, R. Liu, and L. Wang, *J. Cryst. Growth* **283**, 378 (2005).
- <sup>14</sup>L. Wang, Q. Li, and Y. L. Zhang, *Cryst. Res. Technol.* **43**, 1011 (2008).
- <sup>15</sup>Y. Y. Li, L. Qiang, L. Wang, Z. Yang, and X. C. Chu, *J. Cryst. Growth* **318**, 860 (2011).
- <sup>16</sup>Y. Xiang, R. Zhang, and W. W. Cao, *Appl. Phys. Lett.* **96**, 092902 (2010).
- <sup>17</sup>J. H. Yin and W. W. Cao, *J. Appl. Phys.* **87**, 7438 (2000).
- <sup>18</sup>S. J. Zhang, G. Liu, W. H. Jiang, J. Luo, W. W. Cao, and T. R. Shrout, *J. Appl. Phys.* **110**, 064108 (2011).
- <sup>19</sup>D. B. Lin, H. J. Lee, S. J. Zhang, F. Li, Z. R. Li, Z. Xu, and T. R. Shrout, *Scr. Mater.* **64**, 1149 (2011).
- <sup>20</sup>F. Li, S. J. Zhang, Z. Xu, X. Y. Wei, J. Luo, and T. R. Shrout, *J. Appl. Phys.* **108**, 034106 (2010).
- <sup>21</sup>J. P. Han and W. W. Cao, *Appl. Phys. Lett.* **83**, 2040 (2003).
- <sup>22</sup>B. J. Rodriguez, L. M. Eng, and A. Gruverman, *Appl. Phys. Lett.* **97**, 042902 (2010).
- <sup>23</sup>C. S. Tu, F. T. Wang, C. M. Hung, R. R. Chien, and H. Luo, *J. Appl. Phys.* **100**, 104104 (2006).
- <sup>24</sup>J. J. Yao, L. Yan, W. W. Ge, L. Luo, J. F. Li, D. Viehland, Q. H. Zhang, and H. S. Luo, *Phys. Rev. B* **83**, 054107 (2011).
- <sup>25</sup>J. J. Yao, W. W. Ge, L. Luo, J. F. Li, D. Viehland, and H. S. Luo, *Appl. Phys. Lett.* **96**, 222905 (2010).
- <sup>26</sup>C. S. Tu, C. M. Hsieh, R. R. Chien, V. H. Schmidt, F. T. Wang, and W. S. Chang, *J. Appl. Phys.* **103**, 074117 (2008).
- <sup>27</sup>R. R. Chien, V. H. Schmidt, L. W. Hung, and C.-S. Tu, *J. Appl. Phys.* **97**, 114112 (2005).
- <sup>28</sup>U. Sukkha, R. Muangthua, S. Niemcharoen, B. Boonchom, and N. Vittayakorn, *J. Am. Ceram. Soc.* **94**, 3397 (2011).
- <sup>29</sup>W. Qu, X. Tan, N. Vittayakorn, S. Wirunchit, and M. F. Besser, *J. Appl. Phys.* **105**, 014106 (2009).
- <sup>30</sup>L. Wang, Ph.D. dissertation (Tsinghua University, Beijing, 2009).
- <sup>31</sup>E. Breval, C. Wang, J. P. Dougherty, and K. W. Gachigi, *J. Am. Ceram. Soc.* **88**, 437 (2005).
- <sup>32</sup>M. Tanaka, R. Saito, and K. Tsuzuki, *Jpn. J. Appl. Phys.* **21**, 291 (1982).
- <sup>33</sup>G. Arlt, *J. Mater. Sci.* **25**, 2655 (1990).
- <sup>34</sup>W. W. Cao and G. R. Barsch, *Phys. Rev. B* **41**, 4334 (1990).