



Synchrotron radiation topography study of temperature-induced phase transformation in unpoled $0.92\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.08\text{PbTiO}_3$ crystals

Jingzhong Xiao^{a,c,d,*}, Xinyi Zhang^a, Peiping Zhu^b, Wanxia Huang^b, Qingxi Yuan^b

^a Synchrotron Radiation Research Center, National Key Laboratory of Surface Physics, Department of Physics, Fudan University, Shanghai 200433, China

^b Beijing Synchrotron Radiation Laboratory, Institute of High Energy, Chinese Academy of Sciences, Beijing 100039, China

^c National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210008, China

^d International Centre for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, China

ARTICLE INFO

Article history:

Received 13 August 2007

Received in revised form

26 June 2008

Accepted 29 July 2008 by E.L. Ivchenko

Available online 3 August 2008

PACS:

77.80.Bh

61.72.Ff

77.80.Dj

Keywords:

A. Ferroelectrics

D. Phase transition

E. Synchrotron radiation

ABSTRACT

Through real time synchrotron radiation topography observation, dynamical behavior of ferroelectric domains as a function of temperature in unpoled $0.92\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.08\text{PbTiO}_3$ (PZN-8% PT) crystals is investigated. A sequence of temperature-induced monoclinic phase transformations is observed, and verified by combining this method with temperature-dependence Raman scattering, capacitance measurement, and X-ray diffraction. This phase evolution picture seems remarkably unique as the monoclinic phase is able to coexist with the cubic phase well above T_C .

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

Recently, relaxor ferroelectrics such as $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-\text{PbTiO}_3$ (PZN-PT) and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-\text{PbTiO}_3$ (PMN-PT) crystals, have been considered as a new generation of piezoelectric materials, due to their extremely excellent piezo-ferroelectric and electrostriction properties superior to those of the traditional PZT ceramics [1–4]. The maximum piezoelectric properties lie in the rhombohedral side of the morphotropic phase boundary (MPBs), which separates the rhombohedral and tetragonal regions in the phase diagram. The nature of the ultra-high properties in these systems, however, is still recognized as an important and unsolved problem. Very recently, some theoretical and experimental breakthroughs promoted a better understanding of this issue. H. Fu and R. Cohen applied a first principles method to calculate the most favorable polarization rotation path in BaTiO_3 [5], and they proposed an assumption that the large piezoelectric response in

relaxor ferroelectric crystals could be driven by polarization rotation induced by an electric field. It was also indicated that the high-piezoelectricity can be ascribed to the existence of low symmetry phases between rhombohedral and tetragonal phases near MPBs [6]. The novel low symmetry structures (monoclinic or orthorhombic phases) were proved by some high-resolution synchrotron X-ray diffraction experiments and neutron diffraction experiments [4,7–9]. Although it was noted that the statements with respect to the existence of monoclinic phases are not consistent among different reported works [10], these novel findings have, apparently, awakened a new wave of interest in exploring the origin and structural nature of the high piezoelectric response in materials.

It is well known that low symmetry phases near MPB can be easily driven not only by appropriate electric fields, but also by other variables such as temperature and composition [7,11–14]. B. Noheda's group and other research institutes had employed X-ray diffraction techniques to study intermediate phases in $(1-x)\text{PZN}-x\text{PT}$. For instance, R. Bertram et al. reported that below $x = 0.06$, PZN-PT had only rhombohedral structure; while above $x = 0.11$, they had tetragonal structure; the monoclinic Pm phase was formed during the rhombohedral-to-tetragonal phase transition as x changing between 0.07 and 0.11 [10]. For the phase

* Corresponding author at: Synchrotron Radiation Research Center, National Key Laboratory of Surface Physics, Department of Physics, Fudan University, Shanghai 200433, China. Tel.: +86 21 65643521; fax: +86 21 65643522.

E-mail addresses: xiaojz66@hotmail.com, jzxiao@fudan.edu.cn (J. Xiao), xy-zhang@fudan.edu.cn (X. Zhang).

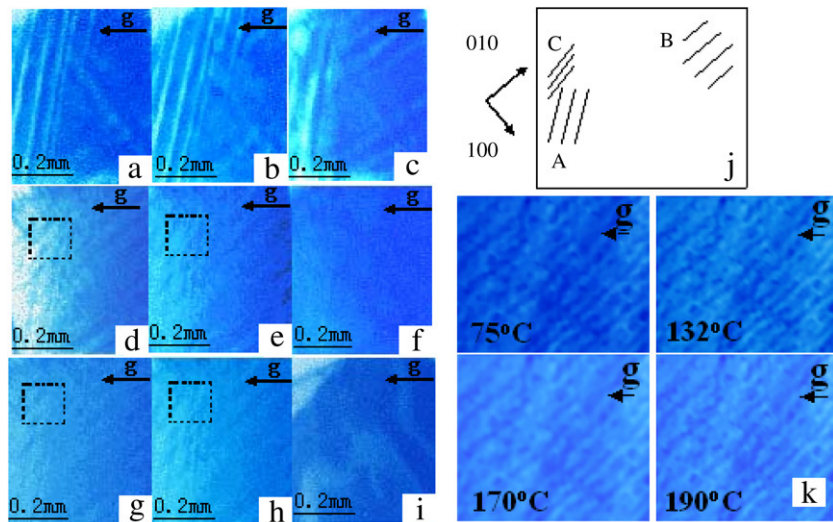


Fig. 1. (Colour on the web only) Images of the in situ synchrotron radiation topography in PZN–8% PT crystals, the x-rays incident direction to the crystal is [001], the diffraction vector is $\mathbf{g} = (1\bar{1}\bar{2})$: (a) room temperature (20 °C); (b) heating to 75 °C; (c) heating to 131 °C; (d) heating to 132 °C; (e) heating to 190 °C; (f) heating to 262 °C; (g) cooling to 190 °C; (h) cooling to 75 °C; (i) cooling to room temperature; (j) Schematic picture for presenting the ferroelectric domain configurations in the topography images of PZN–8% PT crystals; (k) enlarged images of C domain walls from 75 °C to 190 °C.

evolution as a function of temperature in 0.92PZN–0.08PT (PZN–8% PT) crystal, B. Noheda et al. described that the T_c of this system is 170 °C. Between 110 and 160 °C, there is a tetragonal phase, but between 30 and 110 °C, there occurs a possible transition to monoclinic symmetry at about 90 °C [14].

As well as the X-ray diffraction method, however, observing ferroelectric domains is also an effective approach for discovering symmetry [15]. Actually, the existence of a monoclinic phase in relaxor systems, can be directly indicated by observing domain configurations under various conditions [16–18]. The aim of this present work is to investigate temperature-dependence phase evolution in unpoled PZN–8% PT crystals, by employing a real time white-beam synchrotron X-ray radiation topography method (WBSRT) [19–21]. By combining this technique with other complementary structural experiments, a novel picture of low symmetry phase transformation and phase coexistence is suggested.

2. Experimental procedure

PZN–8% PT single crystals used in this experiment were grown by the PbO flux method [22]. A plate perpendicular to [001] axis is cut and well polished to approximately 200 μm in thickness. Real time observation is performed at the topography station at the 4W1A beam line of Beijing Synchrotron Radiation Laboratory (BSRL). The storage ring is 2.2 GeV with beam current varied from 50 mA to 90 mA. A cylindrical furnace with coiled heating elements arranged axially around the sample space is used for in situ topography investigation [23]. After carefully mounted the samples on the hot-stage, we heat them at a slow rate of 0.5 °C/min, observe and record the dynamic topography images by photo films. Through the topography images obtained by this method, we can clearly observe the ferroelectric domain configurations and their evolution as a function of temperature in PZN–8% PT crystals. In addition, other temperature-dependent experiments such as Raman scattering, capacitance measurement, and conventional X-ray diffraction are performed.

3. Results and discussion

Fig. 1 shows a series of synchrotron radiation topography images with $(1\bar{1}\bar{2})$ reflection of the (001) crystal plate taken at

different temperatures. From Fig. 1(a) to (i), we find that the domain structures are very complex. They can be categorized into three kinds of domains and addressed as A, B, and C, as shown in Fig. 1(j).

The A domain walls, which are at approximately 45° to the [100] axis, can be obviously observed at room temperature. These domain walls are considered to be the 71° (or 109°) ones in rhombohedral PZN–PT crystals, and can be clearly observed before heating the sample to 132 °C. With increasing temperature from 75 °C to 131 °C, as shown in Fig. 1(b)–(c), the B domain laminates become progressively obvious and coexist with the A domains. On the other hand, these domain laminates are along the [010] axis, which can be classified into 90° tetragonal domain walls. At the point of 131 °C, the tetragonal domains become most clear. With heating the sample to above 132 °C, as shown in Fig. 1(d), we find that the rhombohedral 71° (or 109°) domain walls (A laminates) become vague, and the image background becomes brighter than before. However, the tetragonal domain walls are still clear. This phenomenon shows that the phase transition from rhombohedral to tetragonal phase (R–T transition) starts at 75 °C, and the tetragonal domains grow gradually.

Most particularly, a set of unique domain walls (C domain walls) appear at this temperature, which is quite different from the A and B domains. This kind of domain walls is shown in Fig. 1(k), through the enlarged images taken from 75 °C to 190 °C. As the figures show, the C domain laminates deviate from the $\langle 010 \rangle$ direction at 15°–20°. According to the knowledge of domains orientation in crystals with different symmetry and X-ray diffraction extinction relations, these laminates can be considered to be neither rhombohedral nor tetragonal domain structures, but a new monoclinic phase domain structure [17,18]. The extinction condition for a domain wall is $\Delta\mathbf{p} \cdot \mathbf{g} = 0$, where \mathbf{g} is the reciprocal vector of the diffracting plane, $\Delta\mathbf{p} = \mathbf{p}_1 - \mathbf{p}_2$ is the difference of the polarization vectors across the domain wall [24].

With further heating of the system to about 132 °C, we find this domain structure is very stable and coexists with B tetragonal domains. Upon further heating to above T_c (~ 170 °C), the monoclinic C domain structure also remains. This case shows that a monoclinic phase not only appears in the process of ferroelectric–ferroelectric phase transformation, but also coexists with the cubic phase well above T_c . With the temperature elevating to about 262 °C, we find nearly all the ferroelectric domains disappear, as shown in Fig. 1(f).

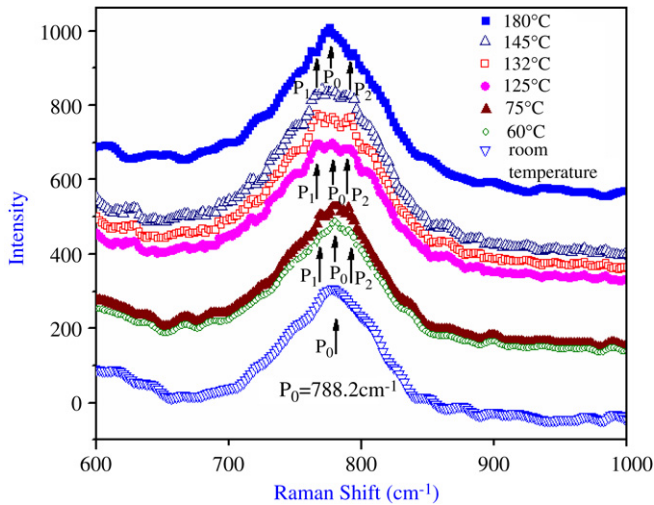


Fig. 2. (Colour on the web only) Raman spectrum of PZN-8% PT crystals obtained at different temperatures.

Whilst cooling the sample from 262 °C to 75 °C, the monoclinic domains (*C* laminates), as well as the tetragonal domains (*B* laminates), are found to reappear, whereas the rhombohedral domains (*A* laminates) cannot be recovered by cooling to room temperature. During the crystal growth, a rapid cooling process was employed for quick crystallization and to avoid the generation of a pyrochlore phase, which results in a strain field in the crystal [22]. The rhombohedral *A* domains are expected to be induced by this kind of strain field and preserved at room temperature. Thus *A* domains do not reappear after the crystals are re-cooled from 260 °C to room temperature with a slow cooling rate, since this cooling process possibly releases the crystal strain field. However, the monoclinic phase was not generated by the strain field induced during the crystal growth, since the particular *C* domains as well as *B* domains can be recovered at 75 °C by slow cooling.

In order to provide other evidence that indicates a monoclinic phase is induced by varying temperature, a Raman scattering experiment is performed. Fig. 2 shows the Raman spectra under various temperatures of the PZN-0.08PT crystal. One dominant Raman feature is the band at approximately 788.2 cm⁻¹ (as peak *P*₀ shows), which is assigned to the Nb-O-Zn stretching mode [25]. This band shows a strong temperature dependence, split into three peaks (*P*₁, *P*₂, and *P*₀) at 75 °C, 132 °C and about 180 °C, which indicates the splitting issue of the band at these temperatures is more complex than that at room temperature, and further demonstrates that the crystal structure seems to undergo a transition to a low symmetry phase.

Fig. 3 shows the capacitance–temperature curve (*C*–*T* curve) at 100 kHz. Since the capacitance is directly proportion to the dielectric constant, the curve implies the evolution of the dielectric constant with respect to temperature. One small capacity peak appears with the temperature elevating to 75 °C and about 132 °C, as shown in the figure. This capacitance anomaly shows a phase transformation at these two temperatures. We also find there appears a maximum Capacity peak near 170 °C, which clarifies the *T*_c is about 170 °C. Initially, we consider the *T*_c is about 260 °C according to that observed by the topography experiments.

In order to further determine the evolution of the crystal structure, we perform an in situ powder X-ray diffraction experiment on PZN-8% PT under different temperatures. Fig. 4 (a–d) shows the X-ray diffraction curves near the (100) peak position. At room temperature (20 °C), the strong (100) peak indicates the rhombohedral phase is dominant, with a cell of *a*_r = 4.0556 Å and *α* = 89.90°. Although at the low-angle side of the

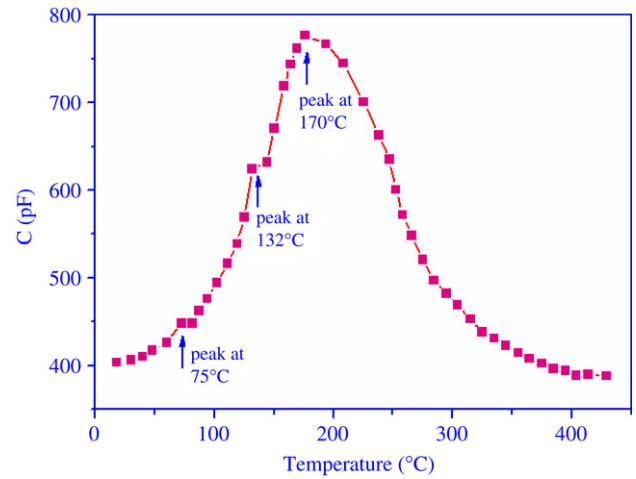


Fig. 3. (Colour on the web only) The capacitance–temperature curve (*C*–*T* curve) of PZN-0.08PT crystal at 100 kHz.

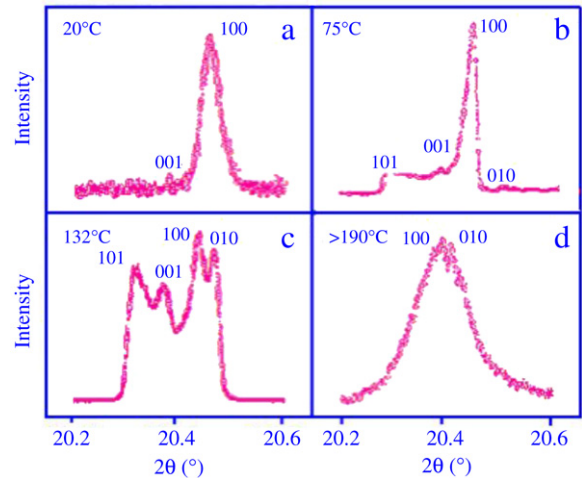


Fig. 4. (Colour on the web only) X-ray diffraction curve of (100) PZN-0.08PT crystal under different temperature.

(100) peak, one small (001) peak exists, which can be considered as a tetragonal one, as a cell with *a*_t = 4.043 Å and *c*_t = 4.068 Å. At 75 °C, one peak lying on the left side of the (001) and (100) peaks occurs. According to the angle position, it can be assigned to another tetragonal (101) peak. But at this temperature, the (100) peak is still very strong and sharp. This implies that the tetragonal phase co-exists with the rhombohedral phase at room temperature, and the portion of the tetragonal phase begins to increase and also co-exists with the rhombohedral phase from 75 °C to 131 °C.

Furthermore, on the right of the (100) peak, another peak also appears and becomes relatively strong with the temperature reaching to about 132 °C, this can be indexed to be the (010) peak. These profiles are characterized by an (00*h*) peak on the low-angle side of an (*h*00) peak, as well as an (0*h*0) peak on the high-angle side of an (*h*00) peak, which is suggestive of the existence of an orthorhombic phase with parameters of *a*_o, *b*_o, and *c*_o [13]. But this issue can also be described as a monoclinic structure. So we prefer to conclude that a monoclinic phase will co-exist with a tetragonal phase from 132 °C, since the tetragonal (101) peak does not disappear and also becomes very strong. From the splitting and angle shift of the pseudo-cubic reflections, a primitive monoclinic cell (*Pm*) with *a*_m = *c*_m = 4.058 Å, *b*_m = 4.039 Å, *β* = 90.20°, co-existing by a tetragonal cell with *a*_t = 4.045, *c*_t = 4.071 can be deduced. Upon heating the sample to a temperature

above T_c (190 °C), the (100) becomes broader and the (001) and (101) peaks seem to vanish. But prominently, the monoclinic (010) peak does not disappear, as shown in Fig. 4(d). So it seems that the monoclinic phase co-exists with the cubic phase at above T_c . In fact, this monoclinic (010) peak exists when the temperature increases to 75 °C and it is very weak, which reveals that the R–T transitions occur through the meta-stable monoclinic phase. We also conclude that the monoclinic phase found in the unpoled PZN–8% PT samples is M_C type. Previously, such a type of monoclinic phase (Pm) of poled PZN–8% PT has been reported [4], where the polarization rotates in a monoclinic plane. This is not the same type of monoclinic phase (M_A) as found in the PZT system, which has Cm symmetry [9,26,27].

Therefore, these experimental results obtained from in situ domain observations, Raman scattering, capacity characterization, and X-ray diffraction, provide a unique picture of a temperature-dependent phase transition sequence: Below 75 °C, it seems that the rhombohedral phase is dominant, with a small fraction of tetragonal phase. Between 75 and 131 °C, the rhombohedral phase will be gradually transformed into a tetragonal one via a monoclinic phase as the temperature increases. Up to 132 °C, the monoclinic phase will co-exist with the tetragonal phase. Most interestingly, when over-heating the sample to above the temperature of tetragonal–cubic phase transition ($T_c = 170$ °C), the monoclinic phase does not disappear but co-exists with the cubic phase.

According to the traditional phase diagram reported by Kuwata et al. [2], only the Rhombohedral–Tetragonal (R–T) and Tetragonal–Cubic (T–C) phase transitions will occur with heating the PZN–PT samples. For 0.92PZN–0.08PT crystal, B. Noheda et al. recently reported that between 30 and 110 °C, there occurs a possible transition from rhombohedral to monoclinic symmetry at about 90 °C. With heating the sample to temperatures above the T_c point (~ 170 °C), only the cubic phase appears and the monoclinic phase will disappear [14]. Thus, in comparison, an apparent discrepancy exists between the previous and the present work, which shows that the monoclinic phase not only co-exists with the rhombohedral and tetragonal phases, but also co-exists with the cubic phase during the ferroelectric–paraelectric phase transition, or at a temperature well-above T_c .

A simple analysis, from the point view of structural symmetry, indicates the possibility of the appearance of a monoclinic phase at high temperature ($>T_c$). It is well known that, at room temperature, the rhombohedral $R3m$ phase coexists with that of the tetragonal $P4mm$ as $x = 0.08$ in $(1 - x)$ PZN- x PT system [10]. However, the coexistence of R and T phases can also be interpreted in terms of a monoclinic phase, as B. Noheda et al. reported elsewhere [4,13]. It is also reported that the direct transition between the rhombohedral phase ($R3m$) and tetragonal one ($P4mm$) cannot occur, because there is no subgroup relation between the two crystallographic point groups ($4mm$ and $3m$) [10]. Thus the R–T phase transition has to pass via intermediate subgroups subordinated to point groups $3m$ and $4mm$. Since the monoclinic phase (m) is a subgroup of $3m$ and $4mm$, therefore, R–T phase transition can occur through a monoclinic (m) served as a bridge of $3m$ and $4mm$. On the other hand, the monoclinic phase (m) also becomes a subgroup of the tetragonal $4mm$ and cubic $m3m$. Thus the monoclinic phase will appear during the R–T and T–C phase transitions, and will possibly appear at temperatures above the T_c point.

The concept of polar nano-regions (PNRs) is anticipated to play an important role in explaining the reason why the monoclinic phase co-exists with the cubic phase. The PNRs are due to

chemical and/or structural disorder in relaxors, and appear during the temperature duration between T_c and the Burns temperature T_d , which is a few hundred degrees above T_c . Furthermore, in relaxor ferroelectrics, these order–disorder regions may lead to the occurrence of the phase transitions from the ferroelectric structure (tetragonal) to paraelectric structure (cubic) in a wide temperature range between T_c and T_d . Thus as a bridge between the tetragonal structure and cubic structure, the monoclinic phase has the possibility of coexisting with the cubic phase at well above T_c .

4. Conclusion

Through in situ synchrotron radiation topography under various temperatures, the complex configuration and dynamic evolution of ferroelectric domains in PZN–8% PT crystals are obtained. Combining this technique with Raman scattering, capacitance measurement, and XRD experiment, a unique picture of temperature-dependence phase transition sequence in PZN–0.08PT crystals is revealed. Most significantly, that monoclinic phase appearing below and above T_c , has revealed an interesting case that is worthy of further investigation. It is expected that the present results will encourage more research interest in exploring the origin of the ultra-high piezoelectric and electrostriction properties in relaxor ferroelectrics and other advanced materials.

Acknowledgments

The support of this work by the National Natural Science Foundation of China (No. 10401004) and China Postdoctoral Science Foundation (No. 20040350122) is grateful acknowledged.

References

- [1] S.-E. Park, T.R. Shrout, J. Appl. Phys. 82 (1997) 1804.
- [2] J. Kuwata, K. Uchino, S. Nomura, Jpn. J. Appl. Phys. 21 (1982) 1298.
- [3] R.F. Service, Science 275 (1997) 1878.
- [4] D.-E. Cox, B. Noheda, G. Shirane, Y. Uesu, K. Fujishiro, Y. Yamada, Appl. Phys. Lett. 79 (2001) 400.
- [5] H.F., R.E. Cohen, Nature 403 (2000) 201.
- [6] M.K. Durbin, J.C. Hicks, S.-E. Park, T.R. Shrout, J. Appl. Phys. 85 (2000) 8159.
- [7] B. Noheda, D.E. Cox, G. Shirane, S.-E. Park, L.-E. Cross, Z. Zhong, Phys. Rev. Lett. 86 (2001) 3891.
- [8] Y. Lu, D. Jing, Z. Cheng, Q. Zhang, H. Luo, Z. Yin, D. Viehland, Appl. Phys. Lett. 78 (2001) 3109.
- [9] Z.-G. Ye, B. Noheda, M. Dong, D.-E. Cox, G. Sjrane, Phys. Rev. B. 64 (2001) 184114.
- [10] R. Bertram, G. Reck, R. Uecker, J. Cryst. Grow. 253 (2003) 212.
- [11] A. Renault, et al., J. Appl. Phys. 97 (2005) 044105.
- [12] C.S. Ganpule, et al., Phys. Rev. B 65 (2001) 014101.
- [13] B. Noheda, et al., Proceedings of the IMF-10, Madrid, 2001, p. 11.
- [14] D. La-Orauttapong, et al., Phys. Rev. B 65 (2002) 144101.
- [15] C. Medrano, et al., Phys. Rev. B 59 (1999) 1185.
- [16] K. Fujishiro, R. Vlokh, Y. Uesu, Y. Yamada, J. Kiat, B. Dkhil, Y. Yamashita, Jpn. J. Appl. Phys. 37 (1998) 5246.
- [17] J. Yin, W. Cao, J. Appl. Phys. 87 (2000) 7438.
- [18] G. Xu, H. Luo, H. Xu, Z. Yin, Phys. Rev. B 64 (2001) 020102.
- [19] D. Bowen, S. Stock, S. Davis, E. Pantos, H. Birbaum, H. Chen, Nature 309 (1984) 336.
- [20] M. Sutton, S. Mochire, T. Greytak, S. Nagier, L. Berman, G. Held, G. Stephenson, Nature 352 (1991) 608.
- [21] Z. Hu, S. Jiang, P. Huang, X. Huang, D. Feng, J. Wang, L. Li, Appl. Phys. Lett. 64 (1994) 55.
- [22] J. Xiao, et al., J. Phys: Condens. Matter. 13 (2001) 11567.
- [23] J. Xiao, et al., Phys. Lett. A 300 (2002) 456.
- [24] J. Zhao, et al., Appl. Phys. Lett. 59 (1991) 1952.
- [25] A. Lebon, et al., J. Appl. Phys. 89 (2001) 3947.
- [26] B. Noheda, D.E. Cox, G. Shirane, J.A. Gonzalo, L.E. Cross, S.-E. Park, Appl. Phys. Lett. 74 (1999) 2059.
- [27] B. Noheda, J.A. Gonzalo, L.E. Cross, R. Guo, S.-E. Park, D.E. Cox, G. Shirane, Phys. Rev. B 61 (2000) 8687.