Evidence for the monoclinic–tetragonal phase coexistence in $Pb(Zr_{0.53}Ti_{0.47})O_3$ thin films

2008 J. Phys.: Condens. Matter 20 415203

(http://iopscience.iop.org/0953-8984/20/41/415203)

IOP Publishing
Journal of Physics: Condensed Matter
J. Phys.: Condens. Matter **20** (2008) 415203 (5pp)
doi:10.1088/0953-8984/20/41/415203

Evidence for the monoclinic–tetragonal phase coexistence in $Pb(Zr_{0.53}Ti_{0.47})O_3$ thin films

E B Araújo[1,3], E C Lima[1], J D S Guerra[1], A O dos Santos[2], L P Cardoso[2] and M U Kleinke[2]

[1] Departamento de Física e Química, Universidade Estadual Paulista (UNESP), 15385-000 Ilha Solteira, SP, Brazil
[2] Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas (UNICAMP), 13083-970 Campinas, SP, Brazil

E-mail: eudes@dfq.feis.unesp.br (E B Araújo)

Received 17 June 2008, in final form 23 August 2008
Published 12 September 2008
Online at stacks.iop.org/JPhysCM/20/415203

Abstract

The structure and ferroelectric properties of $PbZr_{0.53}Ti_{0.47}O_3$ thin films were investigated in detail by using the x-ray diffraction technique. The surface morphology of the film was studied by using the atomic force microscopy technique, showing a film with a dense morphology and a smooth surface. Based on recent results reported by Pandey *et al* (2008 *Acta Crystallogr.* A **64** 192), Rietveld refinements of the structure were conducted considering different models proposed in the literature. Results suggested the monoclinic and tetragonal (M + T) phase coexistence, with $P4mm$ and Cm space groups, respectively. The monoclinic phase (68 mol%) is dominant over the tetragonal phase (32 mol%) for this PZT film composition.

---

1. Introduction

The temperature–composition phase diagram for PZT was obtained first by Jaffe *et al* [1] in 1971. This phase diagram is characterized by a variety of different structural phases and mainly by the existence of a morphotropic phase boundary (MPB), characterized initially as a region where both tetragonal (F_T) and rhombohedral (F_R) ferroelectric phases of PZT coexist. The MPB occurs at $x \approx 0.48$, where PZT of this composition exhibits superior ferroelectric and piezoelectric properties. The recent discover of a stable ferroelectric monoclinic (F_M) phase in the PZT system close to the MPB [2–4] provides a new perspective to explain some results attributed before to the coexistence of tetragonal and rhombohedral phases, for example, the high piezoelectric response of PZT ceramics [5–7].

After the initial discovery of a monoclinic phase with space group Cm in the PZT system [2], other new monoclinic phases with Pm and Cc space groups were also discovered [8–10]. In addition, phenomenological and Raman scattering studies were also performed on different PZT compositions around the MPB to confirm the presence of the monoclinic Cm and Cc phases [11, 12]. Consequently, a new temperature–composition phase diagram for PZT was proposed [13] and more recently [14, 15] a revised phase diagram was proposed including a region of monoclinic phases with Cm and Cc symmetries at compositions corresponding to the MPB, as shown in figure 1. In addition to this, very recent studies [16] suggest the presence of a monoclinic phase with a Cm space group instead of a rhombohedral phase with a $R3m$ space group for Zr-rich compositions ($0.40 \leqslant x \leqslant 0.475$). Thus, the limits for the existence of the monoclinic phase in the temperature–composition phase diagram of the PZT are still open for discussion.

The physical and structural properties for PZT bulk ceramics were investigated experimentally and theoretically in many papers in recent years. However, there are no available reports on the structure of PZT thin films with $x = 0.47$ mol% Ti, considering the new monoclinic phase. Although the monoclinic ferroelectric phase was predicted in MPB compositions of epitaxial PZT films [17], a monoclinic phase in PZT thin films has never been effectively observed. In recent work, Yan *et al* [18] suggested that the enhanced ferroelectric properties of epitaxial $Pb(Zr_{0.52}Ti_{0.48})O_3$ thin films are related to a low symmetry monoclinic phase. In

---

[3] Author to whom any correspondence should be addressed.

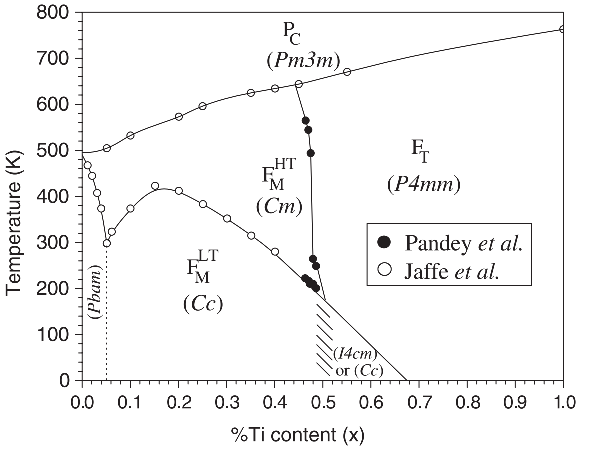

Figure 1. New phase diagram of PZT (adapted from [13] and [15]), including data from Jaffe *et al* [1] and Pandey *et al* [13, 15]. The obtained result in the present work was also added to the phase diagram (up triangle).

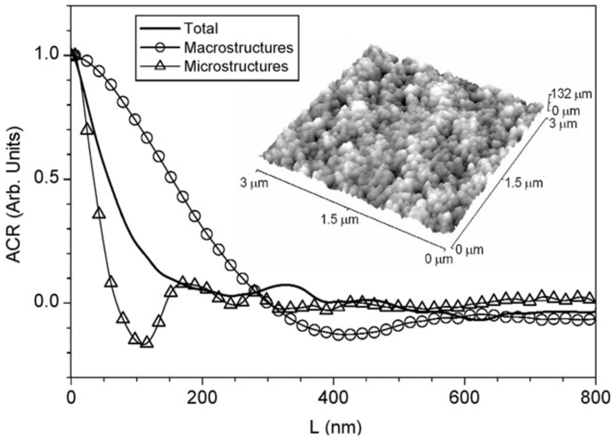

Figure 2. Auto-correlation function against length for PZT thin film. Inset shows AFM image for the same PZT film.

the spirit of this new interpretation, the present work report studies on the structural and microstructural properties of $Pb(Zr_{0.53}Ti_{0.47})O_3$ thin films prepared by a chemical method. These properties were investigated in terms of x-ray diffraction (XRD), Rietveld refinements and atomic force microscopy.

A PZT thin film was prepared with nominal composition $Pb(Zr_{0.53}Ti_{0.47})O_3$ ($Zr/Ti = 53/47$) by using a chemical polymeric method described elsewhere [19]. The film was deposited on a $Pt/Ti/SiO_2/Si$ substrate by spin-coating at 4000 rpm for 40 s and crystallized in an electric furnace at 700 °C for 1 h to obtain a film with ~400 nm thickness. The chemical method used to prepare the studied PZT film in the present work provides excellent control of the stoichiometry. For this reason, in our discussions compositional fluctuations are not considered.

2. Experimental details

The structure of the films was investigated at room temperature by using the x-ray diffraction (XRD) technique with an X'Pert PRO MRD Philips diffractometer, radiation Cu Kα (1.5405 Å), under grazing incidence geometry and a pyrolytic graphite monochromator for a diffracted beam. No preferential orientations were observed for the PZT thin films studied in the present work. For Rietveld [20] analysis, XRD data were input into the GSAS [21] structure refinement code under the EXPGUI [22] interface. Peak profiles were fitted using the Thompson–Cox–Hastings [23] pseudo-Voigt function while a sixth-order polynomial was used to fit the background. Atomic force microscopy (AFM) images were acquired using an AutoProbe CP Research SPM (from Thermo-Microscopes) operating in contact mode, with 2 line s^{-1} frequency and tips of high aspect ratio. All images (512×512 pixels) were achieved with scan lengths varying from 5.0 to 0.5 μm. All results obtained in the present work were recorded at room temperature (~300 K).

3. Results and discussions

The surface morphology of the PZT film was studied by using the AFM technique. Typical grain size length can be estimated by auto-correlation length (λ_{ACR}) which is the first zero of the auto-correlation function $ACR = \langle h(r')h(r-r')\rangle_{r'}$, where $h(r')$ is the surface height at r', $h(r-r')$ is the surface height in a circle centered at r' with radius r and $\langle\cdots\rangle_{r'}$ means averaging over r'. Figure 2 shows the auto-correlation function as a function of length for PZT thin films studied in the present work. In this figure is shown the microstructures, macrostructures and the sum of both. The inset in figure 2 shows the AFM image for the same PZT film. This AFM image presents hillocks (macrostructures) formed by small structures like grains (microstructures), with a roughness saturation value equal to 16.0 ± 0.5 nm. The total ACR presents a composition of macro-and microstructures, without a clear correlation length. The original image was smoothed to estimate the macrostructure's correlation length, and this correlation length suggests a hillock's mean diameter close to 400 nm. Microstructure correlation length was measured in the image resulting from the subtraction from the original image of the smoothed hillock image. This new image reveals the microstructure of grains and we can estimate the diameter of microstructures as 82 ± 10 nm. These results are in agreement with those reported for PZT thin films with the same composition and prepared by the sol–gel process [24].

Figure 3 depicts the selected (110), (111) and (200) profiles of PZT thin films for three possible models proposed in the literature: pure tetragonal phase (T) with $P4mm$ space group, pure monoclinic phase (M) with Cm space group and the coexistence of monoclinic and tetragonal phases (M + T) [4, 15]. In this figure is also presented the (111) and (200) reflections associated with the Pt substrate at around $2\theta = 39.7°$ and $46.2°$, respectively. Thus, the influence of the platinum substrate, $Fm\bar{3}m$ space group, was also included in all Rietveld refinements. Figure 3 also shows the observed and the calculated profiles as well as the difference between then. For the Rietveld refinements, we adopt the same convention as that used by Noheda *et al* [3]. In the tetragonal phase,

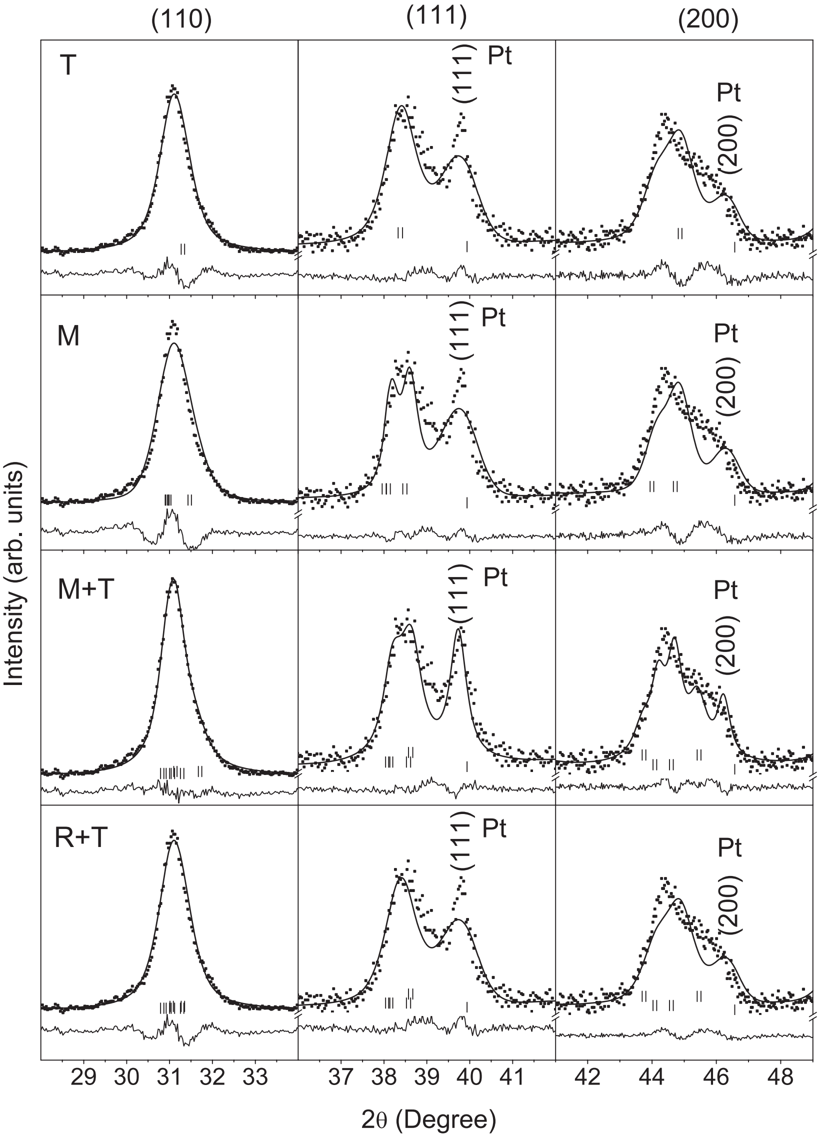

Figure 3. The observed (dots), calculated (lines) and difference (bottom lines) profiles of (110), (111) and (200) pseudo-cubic reflections for $Pb(Zr_{0.53}Ti_{0.47})O_3$ thin film using different structural models. Bars represent peak positions.

the Pb^{2+} ion occupies sites at (0, 0, 0), Ti^{4+}/Zr^{4+} and O_I^{2-} occupy sites $(1/2, 1/2, z)$ and O_{II}^{2-} occupy sites at $(1/2, 0, z)$. In the monoclinic phase, there are four ions in the asymmetric unit with Pb^{2+}, Ti^{4+}/Zr^{4+} and O_I^{2-} ions occupying sites at $(x, 0, z)$ and O_{II}^{2-} in sites at (x, y, z). Considering a Rietveld refinement, the main criteria for judging the quality of the fitting is the final fit of the calculated pattern compared to the observed data. However, the R-factor weighted profile wR_p, the statistically expected R_{exp} and the goodness-of-fit indices $\chi^2 = wR_p/R_{exp}$ are usually used to attest the quality of a fit [25]. As observed in figure 3, the refinement using a pure tetragonal phase or pure monoclinic phase leads to a poor fit, with χ^2 values relatively high, 5.12 and 6.15, respectively. On the other hand, consideration of coexisting tetragonal and monoclinic phases leads to a fit that is more reasonable (χ^2 around 4.98). The obtained wR_p and R_{exp} values were, respectively, 15.71% and 6.94% for refinement using a pure tetragonal phase, 19.75% and 7.96% for a pure monoclinic phase and 15.83% and 7.09% for refinement using the model for the coexistence of monoclinic and tetragonal phases. Finally, although the existence of the rhombohedral phase in the new PZT phase diagram shown in figure 1 is not assumed, the coexistence of both tetragonal and rhombohedral phases (R + T) was also considered. For this model, the obtained wR_p, R_{exp} and χ^2 values were 16%, 6.93% and 5.33, respectively. The selected profiles for R + T refinements were also added in figure 3. As observed, these values are slightly higher than those observed for bulk ceramics [26]. The main reasons for these differences can be associated with larger linewidth and the effects of substrates in thin films, if compared with bulk ceramics or single crystals.

Based only on profiles shown in figure 3, it is very difficult to conclude about the precise structure of the studied film. Thus, the results obtained in the present work must be discussed considering: (i) Rietveld analysis, (ii) the fact that the first-order *monoclinic* → *tetragonal* phase transition for $PbZr_{0.53}Ti_{0.47}O_3$ occurs below room temperature [4], (iii) that

Table 1. Refined structural parameters of Pb$(Zr_{0.53}Ti_{0.47})O_3$ thin film for the tetragonal and monoclinic (M + T) phase coexistence model.

	Tetragonal phase (space group $P4mm$) $a = b = 3.9915(1)$ Å, $c = 4.140(4)$ Å				Monoclinic phase (space group Cm) $a = 5.719(4)$ Å, $b = 5.7785(3)$ Å, $c = 4.1098(1)$ Å and $\beta = 90.64(5)°$			
	x_T	y_T	z_T	U (Å^2)	x_M	y_M	z_M	U (Å^2)
Pb^{2+}	0.000	0.000	0.000	$U_{11} = 0.028(8)$ $U_{22} = 0.028(8)$ $U_{33} = 0.034(0)$	0.000	0.000	0.000	$U_{11} = 0.098(4)$ $U_{22} = 0.063(9)$ $U_{33} = 0.012(8)$
Ti^{4+}/Zr^{4+}	0.500	0.500	0.457(6)	$U_{iso} = 0.050(5)$	0.578(3)	0.000	0.473(3)	$U_{iso} = 0.014(7)$
O_I^{2-}	0.500	0.500	−0.009(6)	$U_{iso} = 0.029(0)$	0.596(3)	0.000	−0.108(6)	$U_{iso} = 0.055(5)$
O_{II}^{2-}	0.500	0.000	0.452(8)	$U_{iso} = 0.029(0)$	0.280(8)	0.262(8)	0.369(8)	$U_{iso} = 0.008(7)$
Ratio	32 mol% (tetragonal)				68 mol% (monoclinic)			

the boundary [12] between the Zr-rich compositions and MPB region appears as a quasivertical line between $0.46 < x < 0.47$ and (iv) the absence of the rhombohedral phase [16] for $0.40 \leqslant x \leqslant 0.475$. Considering PZT compositions close to the MPB, the expected structures of the (111) and (200) reflections are singlet and doublet, respectively, for the tetragonal phase. On the other hand, the expected structures for these reflections are doublet and singlet, respectively, for the rhombohedral phase [15]. Considering the recent proposed possibility of monoclinic phase for PZT Zr-rich compositions [16], a similar structure is expected for reflections in figure 3 such as those observed for the rhombohedral phase.

The monoclinic and tetragonal phase (M + T) coexistence model adopted in the present work was assumed considering the possibilities investigated in the recent literature for PZT compositions at around the MPB for thin films [18] and bulk [15] ceramics. At room temperature, in detailed studies reported by earlier workers it had been assumed the M + T phase coexistence for $PbZr_{0.52}Ti_{0.48}O_3$ and $PbZr_{0.525}Ti_{0.475}O_3$ bulk compositions [15]. However, up to this moment this phase coexistence was not observed for $PbZr_{0.53}Ti_{0.47}O_3$ thin film. The obtained result in the present work for the M + T phase coexistence was also added to the PZT phase diagram in figure 1. In the past nine years, several modifications were proposed to the PZT phase diagram to include the new monoclinic phase and better define the phase coexistence regions. As a result, important works were published on this subject. The PZT phase diagram shown in figure 1, proposed by Pandey *et al* [15], summarizes several previous important studies. Within these studies, Woodward *et al* [14] revised the PZT phase diagram (see figure 8 in [14]) including a monoclinic phase with Cc symmetry, at low temperature, as a subgroup of both rhombohedral ($R3c$) and monoclinic (Cm) structures. However, the precise phase boundaries of the PZT in the vicinity and across the MPB are not trivial to solve, especially the phase coexistence phenomena. Additional problems appear when thin films are investigated, since the stress induced by different substrates affect differently the structures of PZT thin films. So, there are a limited number of studies on phase transitions at the PMB for PZT thin films [27], if compared with PZT ceramics studies. Within these studies, an experimental PZT phase diagram was also proposed around the MPB (see figure 4 in [27]), based on dielectric measurements performed on thin films.

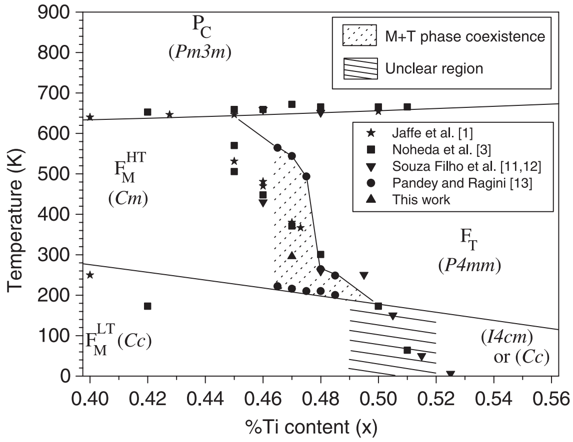

Figure 4. PZT phase diagram around MPB, including the result obtained in the present work and results from Jaffe *et al* [1], Noheda *et al* [3], Souza Filho *et al* [11, 12] and Pandey and Ragini [13]. The dotted area denotes the region where M + T phases coexist. The area below 200 K and $0.49 < x < 0.52$ remains unclear.

The refined structural parameters for the M + T phase coexistence model shows that the tetragonal unit cell has $a = 3.991$ Å and $c = 4.140$ Å, and the monoclinic phase has $a = 5.719$ Å, $b = 5.778$ Å, $c = 4.110$ Å and $\beta = 90.64°$. In addition, the calculated ratio monoclinic/tetragonal phase percentage amounts were M/T = 68/32 for the PZT studied film. This result reveals that the monoclinic phase, with Cm space group, is the dominant phase in the composition of $PbZr_{0.53}Ti_{0.47}O_3$ film (68 mol% of monoclinic phase). The refined structural parameters for the M + T phase coexistence model are given in table 1. The result obtained in the present work was summarized in the PZT phase diagram around MPB shown in figure 4, which also includes results from different authors. The dotted area in figure 4 denotes the region where M + T phases possibly coexist. Experimental studies for low temperature are necessary to define the boundaries at $0.49 < x < 0.52$ and for this reason the dashed area in figure 4 remains unclear.

At this moment it is important to discuss the possible effects of homogeneity and compositional fluctuations on phase transitions for PZT compositions near or across the MPB. Composition inhomogeneity of PZT powders, as well as their size and morphology, was found to depend strongly on the synthesis conditions. For PZT thin film synthesis these parameters are critical due to difficulties concerning stoichiometry control, substrate and other technical details intrinsic for each preparation method. The PZT composition studied in the present work is very close to the phase boundary between monoclinic and tetragonal phases. Consequently, due to a quasivertical line nature for PZT around $x = 0.47$, a small deviation to Zr-rich or Ti-rich composition can lead to different results and interpretations. While a Zr-rich composition leads to a monoclinic phase, a Ti-rich composition around $x = 0.47$ leads to an M + T phase coexistence.

4. Conclusions

In summary, results suggested the monoclinic and tetragonal phase coexistence in $PbZr_{0.53}Ti_{0.47}O_3$ thin film, with $P4mm$ and Cm space groups, respectively, with the monoclinic phase dominant over the tetragonal phase for this PZT film composition. Different to that observed for PZT ceramics, which shows an abrupt separation between the monoclinic phase and the MPB, at around $x = 0.47$, results obtained in the present work suggested the monoclinic and tetragonal (M + T) phase coexistence, where the monoclinic phase (Cm space group) is dominant over the tetragonal phase ($P4mm$ space group) for this PZT film composition. Studies are in progress to better understand the nature of the monoclinic phase in PZT thin films.

Acknowledgments

We would like to express our gratitude to Brazilian agencies FAPESP (contract nos. 2007/00183-7 and 2007/08534-3), CNPq (research grant 301382/2006-9) and CAPES for financial support.

References

[1] Jaffe B, Cook W R and Jaffe H 1971 *Piezoelectric Ceramics* (London: Academic)
[2] Noheda B, Cox D E, Shirane G, Gonzalo J A, Cross L E and Park S-E 1999 *Appl. Phys. Lett.* **74** 2059
[3] Noheda B, Gonzalo J A, Cross L E, Guo R, Park S-E, Cox D E and Shirane G 2000 *Phys. Rev.* B **61** 8687
[4] Noheda B, Cox D E, Shirane G, Guo R, Jones B and Cross L E 2001 *Phys. Rev.* B **63** 014103
[5] Guo R, Cross L E, Park S-E, Noheda B, Cox D E and Shirane G 2000 *Phys. Rev. Lett.* **84** 5423
[6] Singh A K, Mishra S K, Ragini, Pandey D, Yoon S, Baik S and Shin N 2008 *Appl. Phys. Lett.* **92** 022910
[7] Bellaiche L, Garcia A and Vanderbilt D 2000 *Phys. Rev. Lett.* **84** 5427
[8] Singh A K and Pandey D 2001 *J. Phys.: Condens. Matter* **13** L931
[9] Hatch D M, Stokes H T, Ranjan R, Ragini, Mishra S K, Pandey D and Kennedy B J 2002 *Phys. Rev.* B **65** 212101
[10] Ranjan R, Singh A K, Ragini and Pandey D 2005 *Phys. Rev.* B **71** 092101
[11] Souza Filho A G, Lima K C V, Ayala A P, Guedes I, Freire P T C, Mendes Filho J, Araújo E B and Eiras J A 2000 *Phys. Rev.* B **61** 14283
[12] Souza Filho A G, Lima K C V, Ayala A P, Guedes I, Freire P T C, Melo F E A, Mendes Filho J, Araújo E B and Eiras J A 2002 *Phys. Rev.* B **66** 132107
[13] Pandey D and Ragini 2003 *Z. Kristallogr.* **218** 1
[14] Woodward D I, Knudsen J and Reaney I M 2005 *Phys. Rev.* B **72** 104110
[15] Pandey D, Singh A K and Baik S 2008 *Acta Crystallogr.* A **64** 192
[16] Singh A K, Pandey D, Yoon S, Baik S and Shin N 2007 *Appl. Phys. Lett.* **91** 192904
[17] Pertsev N A, Kukhar V G, Kohlstedt H and Waser R 2003 *Phys. Rev.* B **67** 054107
[18] Yan L, Li J, Cao H and Viehland D 2006 *Appl. Phys. Lett.* **89** 262905
[19] Araújo E B and Eiras J A 1998 *J. Mater. Sci. Lett.* **17** 833
[20] Rietveld H M 1967 *Acta Crystallogr.* **22** 151
[21] Larson A C and Von Dreele R B 1994 *Los Alamos National Laboratory Report* LAUR 86
[22] Toby B H 2001 *J. Appl. Crystallogr.* **34** 210
[23] Thompson P, Cox D E and Hastings J B 1987 *J. Appl. Crystallogr.* **20** 79
[24] Cho C R 1999 *Mater. Sci. Eng.* B **64** 113
[25] McCusker L B, Von Dreele R B, Cox D E, Louër D and Scardi P 1999 *J. Appl. Crystallogr.* **32** 36
[26] Ragini, Ranjan R, Mishra S K and Pandey D 2002 *J. Appl. Phys.* **92** 3266
[27] Sheen D and Kim J J 2003 *Phys. Rev.* B **67** 144102