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Application of the X-ray combined analysis to the study of lead titanate based ferroelectric thin films

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Abstract

Lead titanate based ferroelectric thin films are well known for their excellent piezo and pyroelectric properties. In order to obtain a complete characterisation of the structural, micro structural and texture parameters of these films, a recently developed combined analysis of the X-ray diffraction data is carried out. The advantages of this approach reside in the fact that we obtain simultaneously quantitative and more reliable information of these parameters than with more conventional methods. Results obtained for ferroelectric thin films are analysed and compared with those obtained with other methods of analysis. The conclusions show that the texture of the films obtained with the combined method is able to separate the contributions of close texture components, like ⟨100⟩ and ⟨001⟩, or to study components with low contribution to the texture of the film.

Keywords: Quantitative texture analysis; Combined approach; Ferroelectric materials; Thin films

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1. Introduction

Ferroelectric materials and specifically ferroelectric thin films, have attracted a great deal of attention recently due to their excellent polarisation, dielectric, piezoelectric, pyroelectric and optical properties, used in a wide range of technological applications, from ferroelectric random access memories (FeRAM) [1] to microelectromechanical systems [2]. The study of the crystallographic preferential orientation or texture plays a major role in these materials because the polar character of ferroelectrics characterised by a spontaneous electric polarisation, whose value greatly determines the performance of ferroelectrics in applications. Due to the interest of the texture analysis for the control and optimisation of ferroelectric thin film performance, a number of works using advanced X-ray diffraction analysis methods like the quantitative texture analysis (QTA) on ferroelectric thin films have been published recently [3–7]. However, the application of classical diffraction approaches to anisotropic polycrystalline samples such as the ferroelectric thin films, may be problematic. For example a usual Bragg–Brentano diffraction diagram of a strongly textured film may not reveal all possible diffraction reflections, making its structural determination impossible, which in turn prevents any quantitative analysis. This can be solved with the relatively recently developed combined approach [8], which is now proved to be a viable tool [9], and has been successfully applied to ferroelectric thin films [10]. The advantage of this method, which consists in the combination of adequate refinement procedures, resides in the simultaneous and more accurate determination of the structure and texture of the films, which allows to obtain information not attainable by other means.

In this work we have applied successfully the combined method to the analysis of X-ray diffraction data of a series of ferroelectric lead titanate based thin films to show the advantages of the method over more traditional approaches. The separation of the contributions of the associated ⟨100⟩ and ⟨001⟩ texture components, or the study of the evolution of the structural and texture parameters of the deposited films with the

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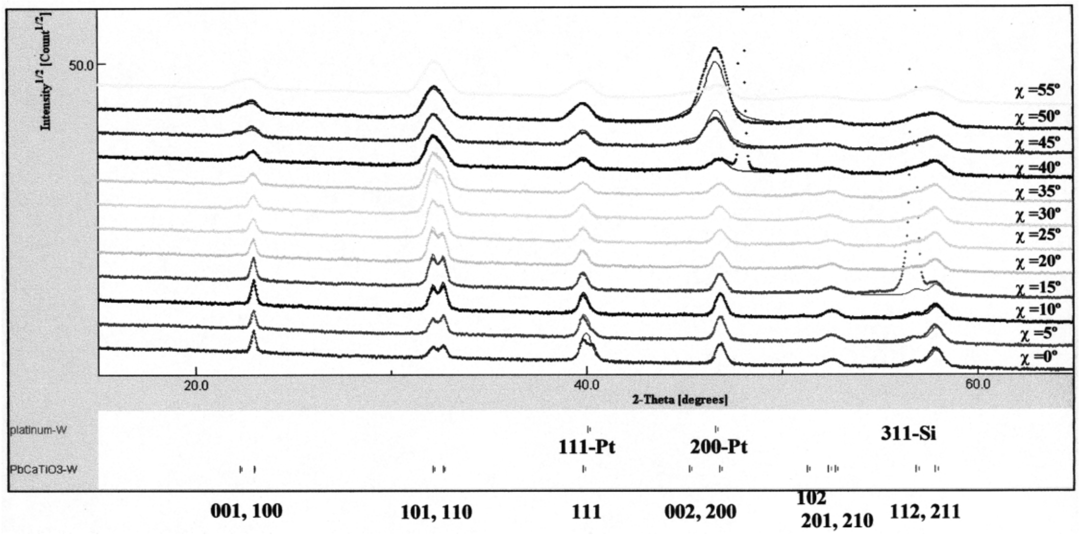

Fig. 1. Experimental (dotted line) and fitted (solid line) X-ray diffraction diagrams for $\chi = 0°$ to $\chi = 55°$ of a PCT film deposited on a platinised Si based substrate. The refinement was carried combining Rietveld and E-WIMV analysis. (Reliability factors Rietveld: $R_w = 13\%$, $R_B = 12\%$, $R_{exp} = 22\%$; E-WIMV: $R_w = 5\%$, $R_B = 6\%$).

recrystallisation process, are two clear examples shown here of the large possibilities of analysis of this method.

2. Experimental procedure

2.1. Materials

Thin films of Ca-modified lead titanate (PCT) were obtained by spin-coating deposition of sol–gel processed solutions of $Pb_{0.76}Ca_{0.24}TiO_3$ with 10% excess PbO [11] on substrates of $Pt/TiO_2/(100)Si$ (PCT-Si) and Pt/(100)MgO (PCT-Mg). Crystallisation was carried out at 700 °C for 50 s by rapid thermal processing (RTP), with a heating rate of ~30 °C/s for all films. Film PCT-A_0 was prepared on a $Pt/TiO_2/(100)Si$ substrate without any previous treatment. All the rest of the films (PCT-B) were deposited on substrates that were previously annealed at 650 °C for 30 min (heating rate = 10 °C/min). A recrystallisation process at 650 °C (heating rate = 10 °C/min) has been applied to some of these films: PCT-B_1 for 1 h; PCT-B_2 for 2 h; and PCT-B_3 for 3 h. PCT-B_0 was left without recrystallisation for comparison.

2.2. X-Ray diffraction characterisation

Experimental pole figures were obtained using a Huber four-circle goniometer mounted on an X-ray generator at a fixed incident angle of 11°. A 5×5° grid measurement was carried out to cover the whole pole figure. A position sensitive detector (INEL CPS-120), covering an angle of 120°, is used (angular resolution 0.03°). Pole figure data are normalised into distribution densities, and expressed as multiple of a random distribution (m.r.d.), which is equivalent to volume percentage per 1% area. From the experimental pole figures we obtain by the WIMV (Williams-Imhof-Matthies-Vinel) iterative method [12], or the entropy modified WIMV (E-WIMV) [13], the orientation distribution (OD) of the sample. From the OD we can determine the texture index F^2, which is an indication of the degree of orientation of the material [4,7]. In this paper we describe the application of an alternative method of analysis of the X-ray diffraction data, the so-called combined approach [8]. In the case of chemical solution deposited films it has been shown that they present fibre textures, i.e. axial symmetry [4]. This means that intensities are varying effectively only with one rotation angle, allowing us to sum all X-ray diagrams corresponding to that angle, in order to refine first background, 2θ offset and defocusing effects. In the refinement we used the nominal compositions and the starting cell parameters were derived from equivalent bulk ceramics. A first cycle was applied to all the diagrams to extract the integrated intensities using the Le Bail algorithm [14]. These intensities were used for a first OD refinement. The OD is then introduced into the cyclic Rietveld refinement. The new refined parameters are used for a new OD refinement, and so on. Calculations were carried out with the Materials Analysis Using Diffraction package (MAUD) [15], in which the layered method [16] was implemented. This allows the analysis not only of the reflections coming from the ferroelectric thin film but also from the Pt layer beneath. An example of the application of the combined method on a ferroelectric PCT film deposited on a platinised Si-based substrate can be seen in Fig. 1.

Table 1
Estimated values of the contribution of ⟨001⟩ and ⟨100⟩ texture components obtained by conventional quantitative texture analysis (QTA) and by the combined approach

Method of analysis	Film	Estimated contribution of texture components (%)	
		⟨001⟩	⟨100⟩
Conventional QTA	PCT-Si	62	38
	PCT-Mg	55	45
Combined approach	PCT-Si	7	93
	PCT-Mg	68	32

3. Results and discussion

3.1. Separation of the contributions of texture components in PCT thin films

In tetragonal lead titanate based compositions, the polar axis is along the ⟨001⟩ direction. Therefore, we ideally search for a preferential orientation along this axis perpendicular to the film surface. The problem is that, in chemical solution deposited films on substrates with un-related structures (without any obvious lattice match), orientation along this direction is always accompanied by an undesirable texture component along ⟨100⟩ [7]. This results in a high number of crystals that do not contribute to the net polarisation of the film. The distribution of crystals along these two directions, ⟨001⟩ and ⟨100⟩, seems to be directly related to the stress state present during the film processing [17]. As that stress state is mainly due to the different expansion coefficients of film and substrate, we can increase the contribution of the desired ⟨001⟩ texture component by changing from a Si-based substrate (PCT-Si), which produces a tensile stress, to a MgO-based one (PCT-MgO), whose stress state is compressive. It has been reported that the use of MgO-based substrates results in a substantial improvement of the ferroelectric behaviour of the PCT films deposited on top [18].

However, the conventional quantitative texture analysis (QTA) of the X-ray pole figures gives similar estimated contributions for both directions regardless of the substrate used (see Table 1). A study of the evolution of the diffracted intensities of 100 and 001 reflections with the χ angle concluded that these results did not reflect the real situation. The solution is the use of the combined method (Table 1), whose results are consistent with both the measured peak intensity evolution and the reported tendencies explained above.

Integration in the conventional QTA is carried out over the overlapped 001, 100 reflection, separating both contributions during the WIMV iterative process. This introduces a large ambiguity as the calculations are based on the orientation distribution coverage obtained with the measurements, which is always limited due to the influence of reflections from the substrate, blind areas, and so on. In contrast to this 'integral approach', the combined method deconvolute first the 001, 100 peaks using the Rietveld refinement, improving greatly the number of constraints in the determination of the peak intensities. Then the WIMV process that follows is a second check for the coherency between intensities, resulting in an overall better evaluation of the texture and of the contributions of these two important texture components. The same would be applicable to any texture components of directions with close reflections: the combined method is the best approach to obtain reliable results.

3.2. Effects of the processing parameters on the structure and texture of PCT thin films

In the search for methods to produce highly oriented thin films, the authors propose the annealing of the substrate previous to the film deposition. The increase of the surface roughness resulting of this process will disrupt the usual nucleation process of the deposited film on the substrate. As a result, it has been reported the inducement of preferential orientation along the ⟨111⟩ direction, not observed in the non-treated substrate [6]. In order to increase the degree of orientation, we study the effect of the recrystallisation of the film, which in the case that the texture is growth controlled (oriented grains grow at the expense of the others) will produce an increase of the texture index [6].

The conventional QTA does not allow us to obtain information on the Pt layer of the substrate. With the use of the combined method, it is possible to compare the structural and texture characteristics of Pt before and after the different annealing process to which film and substrate are subjected to in this study. And we can refine the thickness and the lattice parameter of this layer, whose values do not vary significantly with the thermal treatments (see Table 2). Regarding the texture, we obtain a clear ⟨111⟩ orientation, as the recalculated pole figures in Fig. 2 show. The annealing at 650 °C of the substrate produces a relatively important increase of the texture index, which is less affected by the recrystallisation for different times, although the highest value is achieved for the longest crystallisation time (Table 2). This may be a consequence of a preferential growth of the ⟨111⟩ oriented crystals over the other.

The comparison of the PCT structural variations shows first the importance of the surface state of the substrate on which the deposition takes place. Both a and c values decrease when the film is deposited on a rougher Pt surface (annealed substrate) (Table 3). This may be a consequence of the increase of the stress present during the film formation on the rough Pt surface. The recrystallisation of the film seems to relax

Table 2
Structural, microstructural and texture results of the Pt layer after different annealing treatments obtained by the X-ray combined analysis

Pt layer	a (Å)	Thickness (nm)	Reliability factors (Rietveld analysis) (%)	Texture index-F^2 (m.r.d.^{2})	R factors (Texture) (%)
Non-treated substrate					
Pt layer	3.9108 (1)	45.7 (3)	$R_w=13$ $R_B=12$ $R_{exp}=22$	129	$R_w=5$ $R_B=6$
Annealed substrate					
Pt layer	3.9100 (4)	46.4 (3)	$R_w=8$ $R_B=14$ $R_{exp}=21$	199	$R_w=16$ $R_B=18$
Pt (recryst. 1 h)	3.9114 (2)	47.8 (3)	$R_w=9$ $R_B=20$ $R_{exp}=21$	199	$R_w=20$ $R_B=26$
Pt (recryst. 2 h)	3.9068 (1)	46.9 (3)	$R_w=9$ $R_B=14$ $R_{exp}=22$	195	$R_w=8$ $R_B=9$
Pt (recryst. 3 h)	3.9141 (4)	47.5 (9)	$R_w=27$ $R_B=12$ $R_{exp}=21$	222	$R_w=14$ $R_B=17$

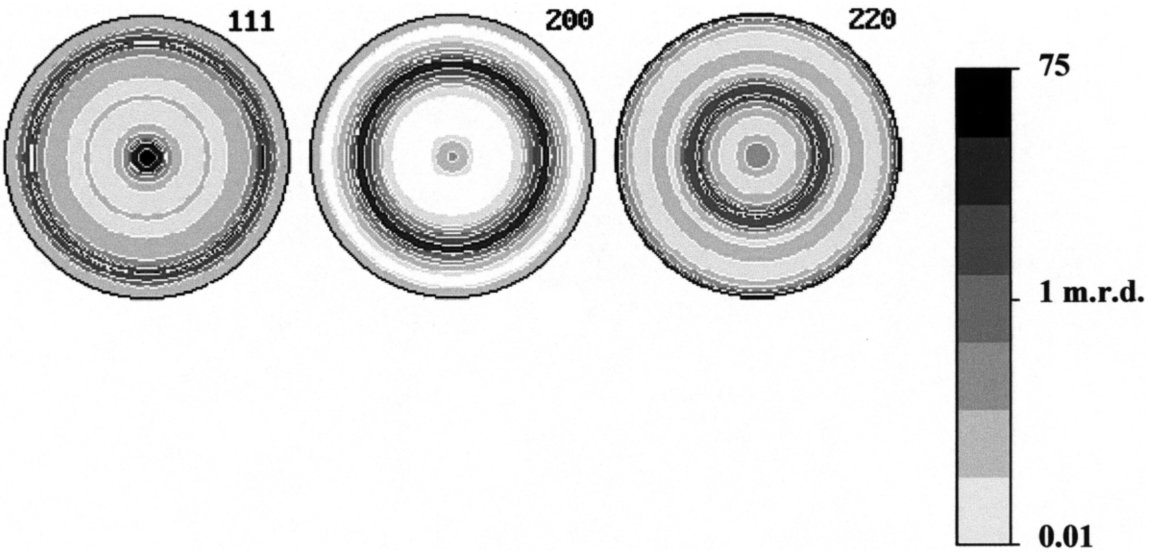

Fig. 2. Recalculated pole figures of the Pt layer from the orientation distribution (OD) obtained by the combined analysis. Equal area projection and logarithmic density scale.

Table 3
Structural, microstructural and texture data of a series of PCT films deposited obtained by the X-ray combined analysis. (For reliability factors see Table 2)

Pt layer	a (Å)	c (Å)	Thickness (nm)	Texture index-F^2 (m.r.d.^{2})	Main texture component
Non-treated substrate					
PCT-A_0	3.9156 (1)	4.0497 (6)	272.5 (13)	5.2	⟨100⟩
Annealed substrate					
PCT-B_0	3.8920 (6)	4.0187 (8)	279.0 (9)	2.1	⟨111⟩
PCT-B_1 (recryst. 1 h)	3.8929 (2)	4.0230 (4)	266.1 (11)	2.1	⟨111⟩
PCT-B_2 (recryst. 2 h)	3.8982 (2)	4.0227 (4)	258.4 (9)	2.5	⟨111⟩
PCT-B_3 (recryst. 1 h)	3.9001 (4)	4.0228 (11)	253.6 (3)	2.5	⟨111⟩

the stress present in the film, shown by a continuous increase of the lattice parameters with the annealing time, which is also reflected in a decrease of the film thickness (Table 3).

Fig. 3 shows the recalculated pole figures of two PCT films deposited on untreated and annealed substrates. While the film on the untreated substrate has a texture dominated by an orientation along ⟨100⟩, the one formed on a previously annealed substrate has a strong texture component along the ⟨111⟩ direction, accompanied by a decrease of the texture index (Table 3). This confirms previous results obtained with the conventional

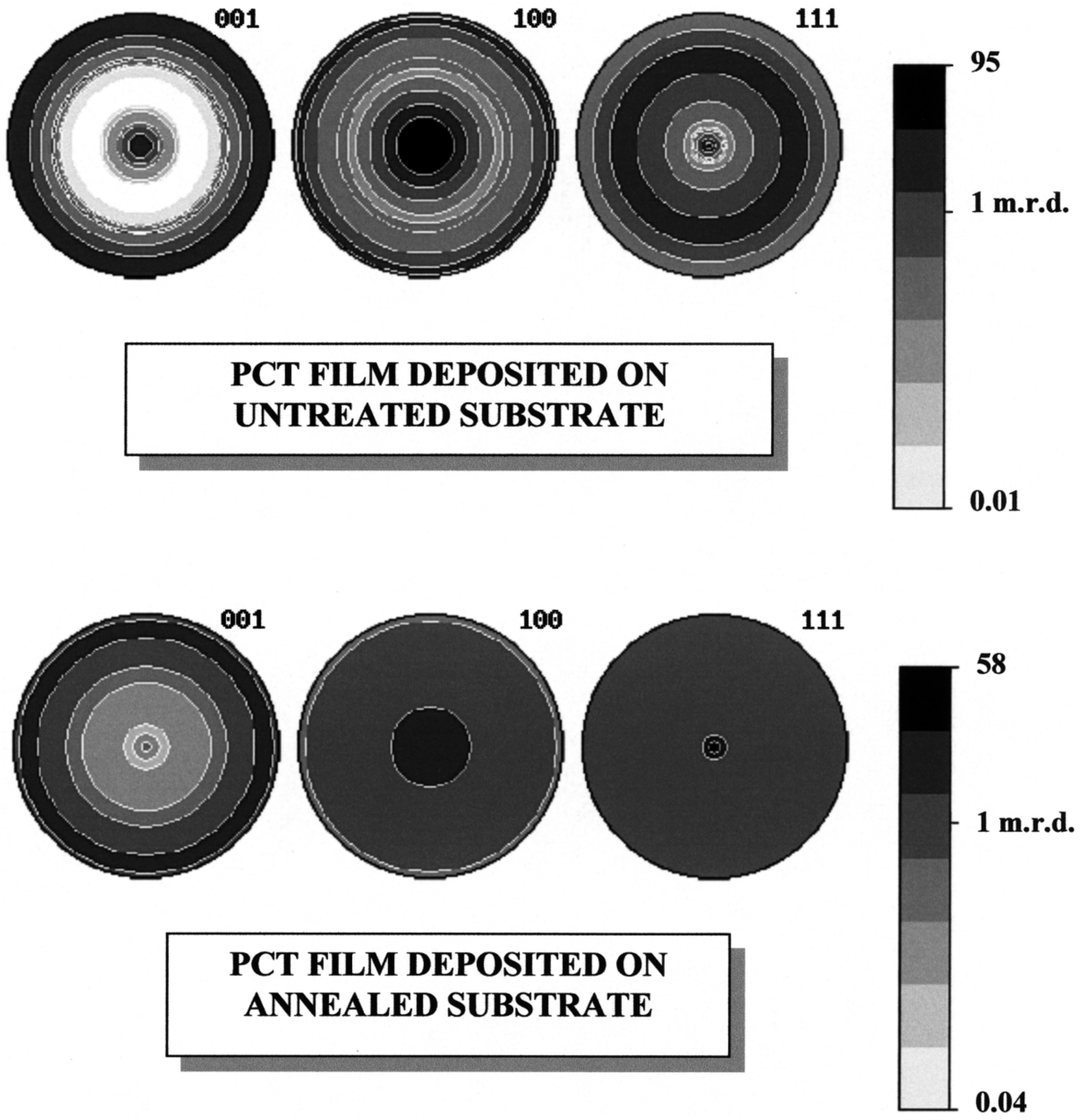

Fig. 3. Recalculated pole figures of the PCT films from the OD obtained by the combined analysis. Equal area projection and logarithmic density scale.

QTA [6]. However, while the tendencies obtained are equivalent, we can observe that, although in a very small quantity, the ⟨111⟩ texture component is already present in the PCT film deposited on an ordinary substrate. Its small contribution, together with the fact that the 111 reflection of PCT is very close to the 111 of Pt, results in an underestimation of its contribution by conventional QTA, which makes that in fact this texture component has not been observed. This new information sheds light onto the origin of the ⟨111⟩ texture component, which is therefore not induced by the rougher surface of the annealed substrate, as concluded before. Instead, it seems that ⟨111⟩ becomes the most important texture component as the main ⟨100⟩ texture component does not appear in the annealed substrate. The decrease of the ⟨100⟩ contribution to the texture results also in a decrease of the overall texture index. The reasons behind this change in the choice of texture components on the annealed substrate are not fully understood and it will be the focus of further work.

4. Conclusions

The application of the combined method to ferroelectric calcium modified lead titanate thin films has proved to produce more accurate and reliable results than more traditional X-ray diffraction analysis approaches. It also provides simultaneously information on the structure, microstructure and texture of both the deposited film and the substrate, revealing important characteristics of the Pt layer used in this study as bottom electrode.

An important aspect covered in this paper is the better resolution of the texture and, specifically of the contribution of the different texture components, obtained by the combined method. The separation of the contributions of two important texture components in the lead titanate based materials, as ⟨001⟩ (containing the polar axis) and ⟨100⟩, has only been possible by the use of this method. The same is true for any other texture components derived from directions whose reflections are close, which results in an overall better quantitative determination of the texture of the films. Texture components that can be difficult to measure due to its low contribution and/or the overlap of their corresponding reflections with other from the substrate, like ⟨111⟩ texture component of PCT, and that the conventional QTA is not able to treat, are also revealed with the combined method.

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References

[1] J.F. Scott, Ferroelectric Memories. Springer Series in Advanced Microelectronics, 3,, Springer-Verlag, 2000.
[2] D.L. Polla, L.F. Francis, MRS Bull. 21 (7) (1996) 59.
[3] D. Chateigner, H.R. Wenk, A. Patel, M. Todd, D.J. Barber, Integr. Ferroelectr. 19 (1998) 121.
[4] J. Ricote, D. Chateigner, Bol. Soc. Esp. Cerám. Vidrio. 38 (6) (1999) 587.
[5] J. Ricote, D. Chateigner, L. Pardo, M. Algueró, J. Mendiola, M.L. Calzada, Ferroelectrics 241 (2000) 167.
[6] J. Ricote, M. Morales, M.L. Calzada, Mater. Sci. Forum 408–412 (2002) 1543.
[7] J. Ricote, R. Poyato, M. Alguero, L. Pardo, M.L. Calzada, D. Chateigner, J. Am. Ceram. Soc. 86 (2003) 1571.
[8] H.R. Wenk, S. Matthies, L. Lutterotti, Mater. Sci. Forum 157–162 (1994) 473.
[9] S. Matthies, L. Lutterotti, H.R. Wenk, J. Appl. Cryst. 30 (1997) 31.
[10] L. Cont, D. Chateigner, L. Lutterotti, J. Ricote, M.L. Calzada, J. Mendiola, Ferroelectrics 267 (2002) 323.
[11] R. Sirera, M.L. Calzada, Mater. Res. Bull. 30 (1) (1995) 11.
[12] S. Matthies, G.W. Vinel, Phys. Stat. Sol. B 112 (1982) K111.
[13] L. Yansheng, W. Fu, X. Jiazheng, L. Zhide, J. Appl. Cryst. 26 (1993) 268.
[14] A. Le Bail, H. Duroy, J.L. Fourquet, Mater. Res. Bull. 23 (1998) 587.
[15] L. Lutterotti, S. Matthies, H.R. Wenk, in: J.A. Szpunar (Ed.), Textures of Materials, 2, NRC Research Press, 1999, pp. 1599–1604.
[16] A. Tizliouine, J. Bessières, J.J. Heizmann, J.F. Bobo, Mater. Sci. Forum 157 (1994) 227.
[17] C.M. Foster, Z. Li, M. Buckett, D. Miller, P.M. Baldo, L.E. Rhen, et al., J. Appl. Phys. 78 (4) (1995) 2607.
[18] R. Jiménez, M.L. Calzada, J. Mendiola in: E. Colla, D. Damjanovic, N. Setter (Eds.), Proceedings of the Eleventh IEEE International Symposium on Applications of Ferroelectrics, IEEE Catalog number 98CH36245, 1998, pp. 155–158.