PHYSICAL REVIEW B **69**, 214106 (2004)

Grain-size-induced relaxor properties in nanocrystalline perovskite films

C. Ziebert,[1,*] H. Schmitt,[2] J. K. Krüger,[2] A. Sternberg,[3] and K.-H. Ehses[2]
[1]*Abteilung Stoffverbunde und Dünnschichten, Institut für Materialforschung I, Forschungszentrum Karlsruhe GmbH,*
P.O. Box 3640, 76021 Karlsruhe, Germany
[2]*Fachbereich Physik, Universität des Saarlandes, 66123 Saarbrücken, Germany*
[3]*Institute of Solid State Physics, University of Latvia, LV-1063 Riga, Latvia*
(Received 14 May 2003; revised manuscript received 5 April 2004; published 18 June 2004)

Thin films of $Pb_{0.76}Ca_{0.24}TiO_3$ (PTC), which is a classical ferroelectric as a bulk material and of the relaxor material $Pb(Sc_{0.5}Nb_{0.5})O_3$, have been produced to find out whether nanocrystalline ferroelectric films show a grain-size-induced relaxor behavior. Amorphous films were deposited onto a Ti/Pt coated silicon (100) wafer by reactive rf sputtering. Different grain sizes were prepared by a controlled annealing process and they were determined by profile analysis of x-ray diffraction spectra. Temperature dependent Raman spectroscopy was used to look for phase transitions, symmetries, and stresses. Temperature and frequency dependent dielectric measurements as well as hysteresis loops show strong evidence for relaxor properties in the nanocrystalline PTC films. The different results confirmed the grain-size-induced relaxor behavior in nanocrystalline ferroelectric films.

DOI: 10.1103/PhysRevB.69.214106 PACS number(s): 64.70.Nd, 61.72.Mm, 77.55.+f, 77.22.Ch

I. INTRODUCTION

If the dimensions of a solid bulk material consisting of closed-packed crystallites are reduced to the nanometer range (10^{-9} m), both the volume fraction of the disordered interfaces between them (grain boundaries) become comparable with the volume fraction of the crystallites (interface effect) and the small size of the crystallites themselves influences the physical properties (size effect). The largest influence should be expected in such material properties which are mainly governed by long-range order interactions like, e.g., ferroelectric or ferromagnetic properties. Our goal was to investigate how the properties of ferroelectric thin films change when the crystallite size is scaled down to the nanometer range. Because the translational symmetry is a necessary condition for the development of the ferroelectric long-range order, a nanocrystalline ferroelectric film should reflect changes in its properties due to the large volume fraction of the grain boundaries disturbing the translational symmetry. There exists a class of materials closely related to the ferroelectric materials called relaxors,[1] which possess a similar intrinsically disturbed translational symmetry on the nanometer scale because of their special stoichiometry. Thus they are ideal candidates to be compared with nanocrystalline ferroelectrics. Their special properties like the diffuse phase transition and the large frequency dependence of the maximum dielectric constant are ascribed to polar regions on the nanometer scale. So we believe that it is possible to change the properties of ferroelectric films into relaxor or similar properties by reducing their grain size to the nanometer scale.

In calcium-modified lead titanate $Pb_xCa_{1-x}TiO_3$ (PTC), the large tetragonality of $c/a=1.065$ and high transition temperature of 763 K of pure lead titanate can be reduced by isovalent substitution of up to 40% of the Pb^{2+} ions by Ca^{2+} ions at the A-site of the perovskite structure ABO_3 without qualitatively changing the ferroelectric properties.[2] However, for $x>0.42$ neutron scattering[3] detected an orthorhombic distortion and relaxor behavior at $x\approx 0.5$. Therefore we have chosen the composition $Pb_{0.76}Ca_{0.24}TiO_3$ for our ferroelectric films with a moderate bulk transition temperature of 544 K. To confirm the ferroelectric poperties Fig. 1 shows the frequency dependent temperature curve of the dielectric constant of a PTC ceramic of the same composition (PTCC). There is no frequency dependent shift in the temperature T_M of the maximum dielectric constant, which gives evidence that $Pb_{0.76}Ca_{0.24}TiO_3$ is a classical ferroelectric as a bulk material. Ferroelectric or relaxor films already show differences in their dielectric properties in comparison to the bulk materials, thus it is better to compare the nanocrystalline ferroelectric PTC films with nanocrystalline relaxor films. Because of its similar perovskitic structure we used lead scandium niobate $Pb(Sc_{0.5}Nb_{0.5})O_3$ (PSN) to prepare nanocrystalline relaxor films. While PTC is formed by the partial isovalent substitution of Pb^{2+} by Ca^{2+} on the A-site of the perovskite structure, in the relaxor PSN the Ti^{4+} on the B-site is statistically completely substituted by Sc^{3+} and Nb^{5+} in the relation 1:1.

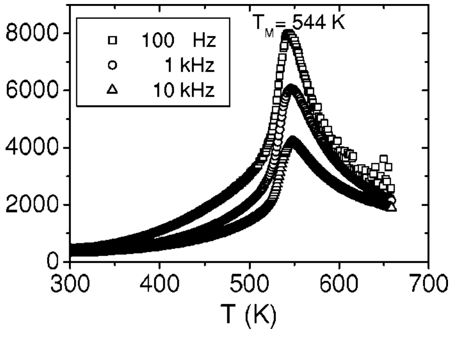

FIG. 1. Frequency dependence of the temperature curves of the real part of the dielectric constant ε' of a $Pb_{0.76}Ca_{0.24}TiO_3$ ceramic (PTCC).

0163-1829/2004/69(21)/214106(10)/$22.50

II. EXPERIMENT

rf sputtering at room temperature with argon and oxygen as a reactive component has been used to deposit the materials onto the substrate (Si/Ti/Pt) in the form of amorphous thin films.[4] Different grain sizes have been prepared by a controlled annealing process between 773 and 1023 K. After annealing circular gold top electrodes of 0.5 mm diameter have been evaporated. The film characterization included thickness measurements by spectral reflectometry, composition control by energy dispersive analysis by x-ray (EDAX), studies of the surface topography by scanning electron microscopy (SEM), and the crystallographic characterization (phase purity, crystal structure, grain size) by *x*-ray powder diffraction (XRD) in connection with a Rietveld simulation.[5] EDAX and SEM proved that the PTC films were stoichiometric with a smooth surface. The XRD revealed that the PTC films consisted of pure perovskite phase whereas the PSN films always retain some pyrochlore content. The hypothesis of grain-size-induced relaxor behavior was checked by different measurement methods. We used Raman spectroscopy to investigate symmetries and stresses in the films and to study the size and interface effects on the dielectric properties we performed frequency and temperature dependent impedance and hysteresis measurements.

III. BULK PROPERTIES OF FERROELECTRICS AND RELAXOR FERROELECTRICS

It is well-known that ferroelectric bulk materials with the perovskite structure like, e.g., lead titanate show a sharp phase transition at the Curie temperature T_C and almost no frequency dependence of the temperature curve of the dielectric constant up to the GHz region. Above T_C the temperature dependence of the dielectric constant follows the Curie-Weiss law [Eq. (1) with $p=1$]:

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_{\max}} = \frac{1}{K}(T - T_C)^p. \tag{1}$$

As has been mentioned in the Introduction the relaxors which are closely related to ferroelectrics show a different behavior because of their intrinsically disturbed translational symmetry. They are characterized by a diffuse phase transition and a large frequency dependence of the much broader temperature curve of the dielectric constant. The broad temperature dependence of the dielectric constant of the relaxors leads to a modified Curie-Weiss law[6] [Eq. (1) with $p\approx 2$ and $T_C = T_M$]. The temperature T_M is no longer a phase transition temperature but marks the temperature of the maximum dielectric constant. It has to be kept in mind that this modified Curie-Weiss law includes frequency dependence in ε and also in T_M contrary to the classical Curie-Weiss law of ferroelectrics. So there exists such a Curie-Weiss law for each fixed frequency. The temperature T_M is moving to higher values with increasing measurement frequency and the maximum value is being reduced. This pronounced frequency dependence is produced by a broad relaxation time spectrum. The diffuse phase transition of the relaxors is characterized by the fact that the macroscopic crystal symmetry (e.g., observed by XRD) does not change above and below T_M in contrast to ferroelectrics. This means that there does not exist a true phase transition and there also does not develop a spontaneous polarization below T_M nor macroscopic ferroelectric domains. However, there exist polar regions or nanodomains in a paraelectric matrix even far above T_M as has been found experimentally in the temperature dependence of the thermal expansion and the refractive index by Burns and Dacol.[7] According to Qian and Bursill[8] random field mechanisms, produced by local charge imbalance, could be the origin of the polar regions. Their polarization direction is statistically fluctuating because the energy barrier between different directions can be jumped by thermal movement.[1] When the temperature is decreased, the interaction between the polar regions is increasing and little quasi-ferroelectric domains start to develop which are still fluctuating. Without an external field the relaxor material remains macroscopically nonpolar. The fluctuations are freezing at low temperatures leading to an orientational glasslike behavior, which manifests, e.g., in a plateau in the heat conductivity at temperatures of a few Kelvin.[9] However, below a certain temperature $T_t < T_M$ by applying an electric field which is strong enough, the relaxor system can be poled, which means that it is irreversibly switched into a new phase by a field-induced phase transition. The polar regions are growing up to a macroscopic scale and the induced polarization can be switched similar to a ferroelectric. Thus this new phase does not basically differ from a classical ferroelectric phase. When recording a hysteresis loop and looking at the temperature dependence of the induced polarization of a poled relaxor it does not disappear at T_M but it slowly decays with increasing temperature above T_M. The reason for this behavior is that, even if the average value of the local polarization is zero, the average of its quadratic value $\langle P_{lok}^2 \rangle$ is different from zero.[10] Contrarily to the critical fluctuations of ferroelectrics which only occur in the vicinity of the phase transition temperature T_C, in relaxors it is possible to find fluctuations of the polar regions or their local polarization some hundred degrees above T_M. This leads to the modification of the Curie-Weiss law and the slow decay of the induced polarization. Now it is interesting to examine how the properties of ferroelectrics will change when their translational symmetry is disturbed comparable to relaxors by a large amount of grain boundaries as it is typical for nanocrystalline ferroelectric films.

IV. GRAIN-SIZE-INDUCED RELAXOR BEHAVIOR

A. Grain-size determination by XRD

At first the grain size had to be determined to relate it to the results of Raman spectroscopy and dielectric measurements. Many authors use the Warren-Averbach method[11] for this purpose. In our case this was not possible because the thin films only showed a few reflexes. In addition some of them were hidden behind substrate reflexes (Si, Pt). Therefore we determined the grain size from the full width at half

TABLE I. Annealing temperature, grain size, and thickness of the samples used in this study.

Sample	Annealing temperature T_a(K)	Grain size t (nm)	Thickness d (μm)
PTCC	1323	$\sim$1000	5000
PTC0	773	amorphous	0.97
PTC1	823	$\sim$35	1.02
PTC2	873	$\sim$46	0.79
PTC3	923	$\sim$86	0.73
PTC4	973	$\sim$111	0.77
PTC5	1023	$\sim$138	0.68
PSN1	923	$\sim$72	0.75

maximum (FWHM) by a Williamson-Hall plot.[4,12] A background polynomial was subtracted and then the complete diffraction pattern was simultaneously fitted by pseudo-Voigt profiles. In our studies as-sputtered amorphous PTC films have been annealed at different temperatures from 773 to 1023 K for a fixed time of 30 min.[13] With this procedure grain sizes between 35 ± 4 nm (PTC1) and 138 ± 10 nm (PTC5) could be prepared as summarized in Table I together with thickness data of all samples used in this study. Grain sizes in the lower nanometer range (<70 nm) showed pronounced influences on the elastic properties, which Krüger *et al.*[14] and Holtwick *et al.*[15] have studied by high resolution Brillouin spectroscopy. Figure 2 shows the evolution of the x-ray diffraction spectra of PTC films with increasing annealing temperature from 773 to 923 K. At 823 K the PTC exhibits for the first time three crystalline reflexes of the perovskite structure at $2\theta=23°$(100), 32° (110), and 57° (211), whose intensities increase with increasing annealing temperature.

Thin nanocrystalline PSN relaxor films have been prepared to compare their properties with those of thin nanocrystalline PTC ferroelectric films. It was found that an annealing time of 300 min at 923 K in lead containing atmosphere is necessary to produce the perovskite phase. In contrast to PTC where no pyrochlore phase was found the annealed PSN films always retained some percent of pyrochlore phase. The maximum amount of perovskite phase reached 70%. The XRD spectrum of such a PSN film with relaxor properties is shown in Fig. 3 (upper curve) together with simulations of the PSN perovskite phase (middle curve) and the PSN pyrochlore phase (lower curve) by a Rietveld method. The perovskite grain size is determined to 72 nm and the pyrochlore grain size to 24 nm. The following dielectric measurements have been performed on these nanocrystalline PSN films of good quality. The dielectric properties should not be largely affected by the remaining pyrochlore phase because even at contents of 90% pyrochlore the PSN films show similar properties. Of course it would have been desirable to further increase the perovskite fraction, but neither a higher annealing temperature nor a longer annealing time gave any improvements.[16]

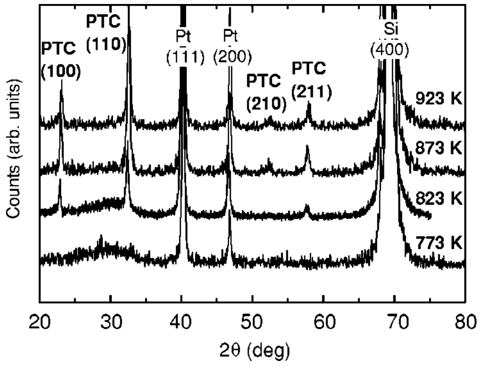

FIG. 2. Evolution of the XRD spectra of PTC films annealed for 30 min with increasing annealing temperature from 773 to 923 K (PTC0–PTC3).

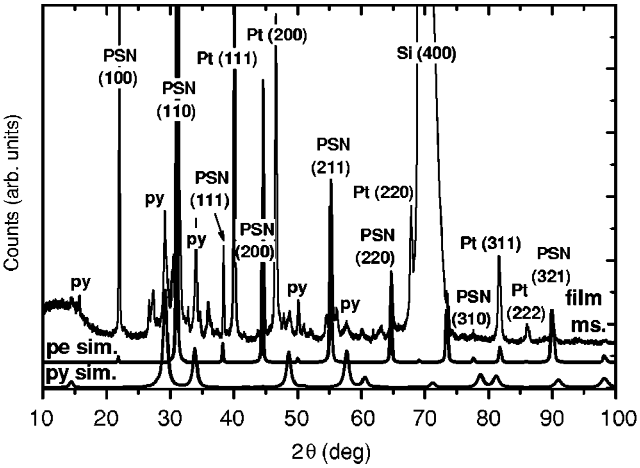

FIG. 3. XRD spectrum of a PSN film (PSN1). Upper curve: measured film spectrum (film ms.), middle curve: simulation of the PSN perovskite phase by a Rietveld method (pe sim.), and lower curve: simulation of the PSN pyrochlore phase by a Rietveld method (py sim.).

B. Frequency and temperature dependent dielectric measurements

Frequency and temperature dependent dielectric measurements and hysteresis measurements were performed to find evidence for grain-size-induced relaxor behavior in the nanocrystalline PTC films. Figure 4 compares the temperature dependence of the real part of the dielectric constant ε' of (a) a PSN relaxor film (grain size 72 nm, PSN1); (b) a nanocrystalline PTC film (grain size 35 nm, PTC1); and (c) a coarse-grained PTC film (grain size 138 nm, PTC5) measured at frequencies of 100 Hz, 1 kHz, and 10 kHz. All three curves of the nanocrystalline PTC film (b) are largely broadened, indicating a diffuse phase transition. In addition they show a strong frequency dependence of T_M from 513 K at 100 Hz to 650 K at 10 kHz. This proves that T_M shifts to higher temperatures with increasing measurement frequency.[3] Both properties are typical for bulk relaxor materials as explained in Sec. III and as it is shown as well by the nanocrystalline

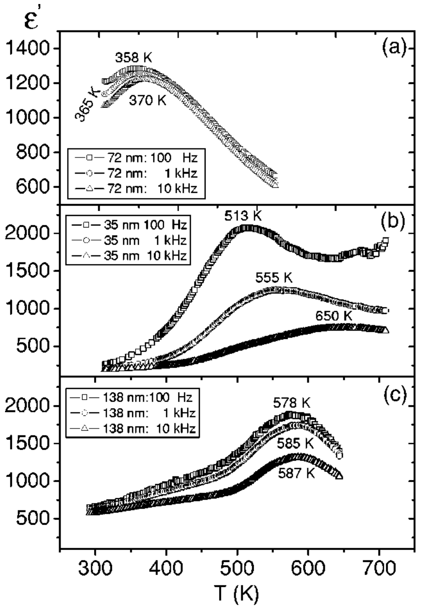

FIG. 4. Frequency dependence of the temperature curves of the real part of the dielectric constant ε' of (a) a PSN film with a grain size of the perovskite phase of 72 nm (PSN1); (b) a PTC film with a grain size of 35 nm (PTC1); and (c) a PTC film with a grain size of 138 nm (PTC5).

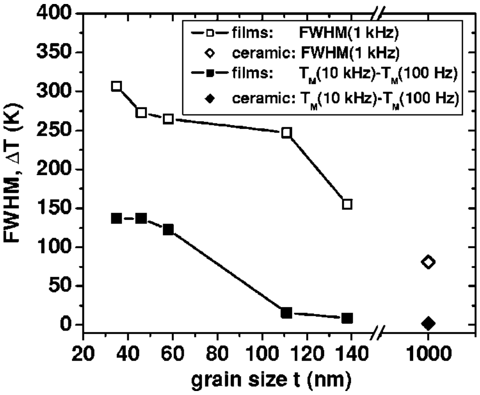

FIG. 5. Evolution of the degree of diffuseness (FWHM at 1 kHz) and the relaxor degree (difference of the temperatures of the maximal dielectric constants at 10 kHz and 100 Hz) with increasing grain size for PTC films (PTC1–PTC5) and of PTC ceramic (PTCC) as a reference.

PSN relaxor film (a). However it should be mentioned that at higher frequencies T_M shifted to lower temperature with increasing frequency in all PTC samples with annealing temperatures above 923 K and a very large increase of the loss tangent has been observed. A similar phenomenon was found by Tyunina *et al.* in films of the relaxor $Pb_{1-x}La_x(Zr_{0.65}Ti_{0.35})O_3$ (PLZT) with $x=4.5$ and 9.75.[17] They ascribed it to the rather high magnitude of increase of the loss tangent at higher frequencies due to possible changes in the Pt-film interfaces at high annealing temperatures. Therefore the frequencies above 10 kHz will be disregarded in the following. Apparently the nanocrystalline PTC film and the PSN film qualitatively show a similar dielectric behavior, however, the frequency shift is less pronounced in the case of PSN. If the driving force for the observed relaxor behavior is really the small grain size of nanocrystalline PTC films then one should expect an upper grain-size limit, where the relaxor properties disappear. It was attempted to approach this limit by increasing the annealing temperature up to 1023 K. The resulting temperature curve of the dielectric constant for such a PTC film with a grain size of 138 nm (PTC5) in Fig. 4(c) shows that the frequency dependence of T_M is largely reduced with T_M varying from 545 K at 100 Hz to 554 K at 10 kHz and that the curve shape is much smaller than the broad curves of the nanocrystalline PTC film (b). If one defines the relaxor degree of the phase transition as the difference of the temperatures of the maximal dielectric constants at 10 kHz and at 100 Hz and the FWHM of the temperature curve as the degree of diffuseness, it can be seen in Fig. 5 that both degrees decrease drastically with increasing grain size from 35 to 138 nm which indicates the increasing loss of relaxor properties. Because the PTC ceramic (PTCC) with a grain size of more than 1 μm shows ferroelectric properties, the upper grain-size limit must be somewhere in between. To get a better estimation for this limit the modified Curie-Weiss law has been investigated as another important criterion for relaxor behavior. It can be seen from the temperature dependences of the real part of the dielectric constant of the nanocrystalline PSN [Fig. 4(a)] and the nanocrystalline PTC film [Fig. 4(b)] that both do not follow the classical Curie-Weiss law. Therefore Fig. 6(a) shows a comparison of modified Curie-Weiss law exponents p [cf. Eq. (1)] of a PTC film with a grain size of 35 nm (PTC1) and a PTC film with a grain size of 138 nm (PTC5) using double logarithmic plots for $T > T_M$. Whereas $p=2$ as typical for relaxors is determined for a grain size of 35 nm, $p=1.3$ as found for a grain size of 138 nm is already close to the ferroelectric value $p=1$. In Fig. 6(b) the grain size dependence of p of the PTC films together with a fourth order polynomial fit is shown. From this data an upper grain size limit of about 150 nm can be estimated at which the relaxor properties should disappear again completely.

C. Raman spectroscopy

In addition to the dielectric measurements Raman spectroscopy was performed to study grain-size-induced relaxor properties.[18] To evaluate the Raman spectra, a background polynomial was subtracted and the Raman lines were fitted by Lorentzian profiles. This procedure allows determining frequencies, intensities, and FWHMs. Figure 7 shows Raman spectra (Stokes lines) of an amorphous PTC film (PTC0), PTC films with grain sizes of 35 nm (PTC1), 46 nm (PTC2), and 86 nm (PTC3), and of a coarse-grained PTC ceramic as a reference (PTCC), which were taken at room temperature. The amorphous sample only exhibits a broad hump between 400 and 700 cm^{-1}. Together with the initial growth of crystallites at 823 K four characteristic Raman lines appear in the Raman spectrum of the PTC film with a grain size of 35 nm. They can be related to the corresponding lines of the tetragonal ceramic in spite of a large broadening and a small shift. The intensity of these lines grows more and more with

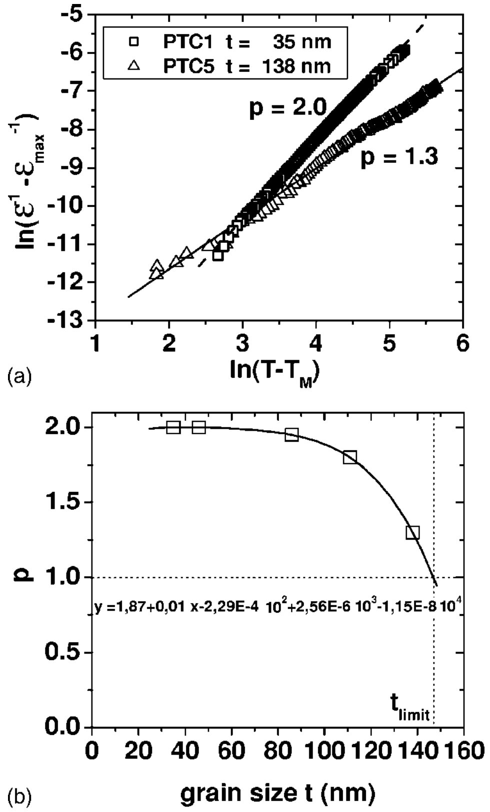

FIG. 6. (a) Comparison of modified Curie-Weiss law exponents p of a PTC film with a grain size of 35 nm (PTC1) and a PTC film with a grain size of 138 nm (PTC5) using double logarithmic plots for $T > T_M$ (b) Grain-size dependence of modified Curie-Weiss law exponents p of PTC films together with a fourth order polynomial fit.

increasing grain size. In the PTC film with a grain size of 86 nm the four lines are found at the following wave numbers: E(2TO) at 203 cm^{-1}, B_1+E at 284 cm^{-1}, A_1(3TO) at 576 cm^{-1} and E(3LO) at 741 cm^{-1}. In addition the fitting procedure revealed the following lines: E(1TO) and A_1(1TO) at 67 and 105 cm^{-1}, E(1LO) at 140 cm^{-1}, A_1(2TO) at 322 cm^{-1}, E(2LO)+A_1(2TO) at 450 cm^{-1}, E(3TO) at 514 cm^{-1}, and A_1(3LO) at 876 cm^{-1}.

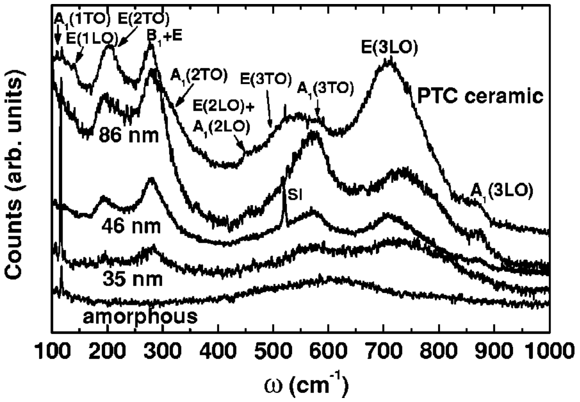

FIG. 7. Raman spectra of an amorphous PTC film (PTC0), of PTC films with grain sizes of 35 nm (PTC1), 46 nm (PTC2), and 86 nm (PTC3) and of a coarse-grained PTC ceramic as a reference (PTCC).

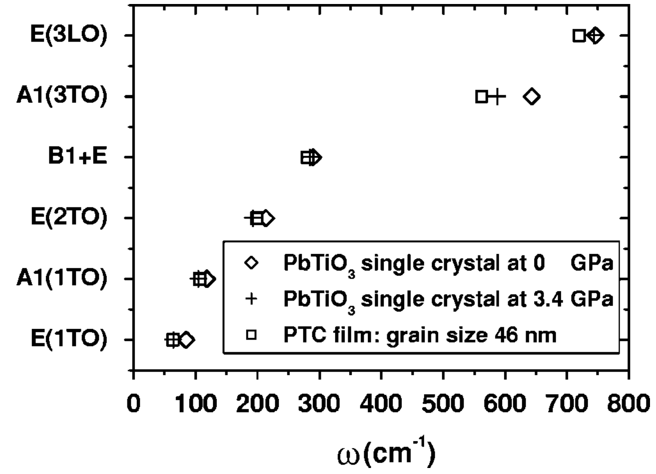

FIG. 8. Comparison of the Raman frequencies of a PTC film with a grain size of 46 nm (PTC2) with those of a $PbTiO_3$ single crystal under a hydrostatic pressure of 3.4 GPa.

Possible reasons for the large broadening of the Raman lines could be lifetime broadening and the averaging over a multitude of nanocrystallites, each of them having different internal stresses and hence Raman line shifts. In a nanocrystalline film an optical phonon cannot only decay into two acoustical phonons with opposite wave vectors of equal magnitude alone but can also decay at grain boundaries and defect sites, which reduces the lifetime and leads to peak broadening.[19]

Because it has not been possible to produce large PTC single crystals, there are no results about their Raman spectra in the literature. Thus we have taken $PbTiO_3$ single crystal Raman spectra for comparison, which should not differ too much from PTC spectra if the Ca fraction is moderate. In comparison to the Raman lines of $PbTiO_3$ single crystals under hydrostatic pressure those of the PTC films are shifted to lower wave numbers indicating tensile stress in the films.[20] Of course two different effects play a role in the observed Raman line shift which have to be separated from each other: the line shift by the Ca substitution and the one induced by stress. The smaller radius of the Ca^{2+} ions of 0.099 nm versus 0.121 nm of the Pb^{2+} ions and the higher electronegativity of the Ca–O bond of 2.5 versus 1.7 of the Pb–O bond leads to an increased binding force and consequently to a shift of the wave numbers to smaller values when substituting Pb by Ca as explained by Qin *et al.*[21] The smaller mass of the Ca ions by a factor of 5 in comparison to the Pb ions shifts the Raman lines in the same direction. The comparison of the Raman spectra of a PTC ceramic[22] and a $PbTiO_3$ ceramic[23] shows that there is a negative shift of the lines of 12% produced by the substitution of Pb by Ca, which has to be subtracted from the measured line shift of the PTC films. Figure 8 shows a comparison of the Raman frequencies of a PTC film with a grain size of 46 nm (PTC2) and those of a $PbTiO_3$ single crystal under hydrostatic pressure.[24,25] The frequencies of the PTC film showed the best agreement with the frequencies of the $PbTiO_3$ single crystal under a hydrostatic pressure of 3.4 GPa. Under consideration of the 12% contribution of the Ca substitution this gives a tensile stress of 2.5 GPa in the PTC film.

According to Ma *et al.*[26] the quasi-hydrostatic stress in thin films is similar to the internal pressure of a small particle with diameter d, produced by its surface tension γ:

$$p = \frac{2\gamma}{d}. \tag{2}$$

With a value for γ of 50 N/m taken from Uchino *et al.*,[27] this gives a pressure value of 2.2 GPa for a grain size of $d = 46$ nm. This value is close to 2.5 GPa as calculated from the Raman spectra. The PTC film with the lowest grain size of 35 nm exhibited the highest pressure values of 3.5 GPa (Raman) or 2.8 GPa (surface tension) and the film with a grain size of 86 nm the lowest of 2.1 GPa (Raman) and 1.6 GPa (surface tension). The reason for these high pressure values cannot simply be the different thermal expansion coefficients of the Si substrate and the PTC film. Another reason could be a clamping at the grain boundaries during the cooling-down after the annealing process. The PTC films annealed at temperatures higher than 723 K consist of nanocrystallites in the cubic paraelectric state because the annealing temperature is much higher than the bulk Curie temperature of 544 K. When they are quenched to room temperature, the cubic to tetragonal transformation should take place. Because the crystallites are too small to split into macroscopic ferroelectric domains, this transformation cannot happen at all or is at least hindered by the crystallites in the neighborhood which have different crystallographic orientations. This leads to a clamping at the grain boundaries and to large stresses.[28] These induced stresses at the grain boundaries produce a mainly hydrostatic pressure onto the crystallites, which could be the reason for the observed frequency shift of the Raman lines.[29] The fact that the stresses are reduced with the increase of the grain size gives evidence for this explanation, because the splitting into ferroelectric domains should then become easier which would reduce the stresses. Especially for nanocrystalline materials the phonon confinement could be another reason for the Raman line shift.[30] However, when considering the phonon dispersion curves for $PbTiO_3$ calculated by Freire and Katiyar,[31] which should not be much different from those of PTC, the shift by the Phonon confinement should appear in the opposite direction.

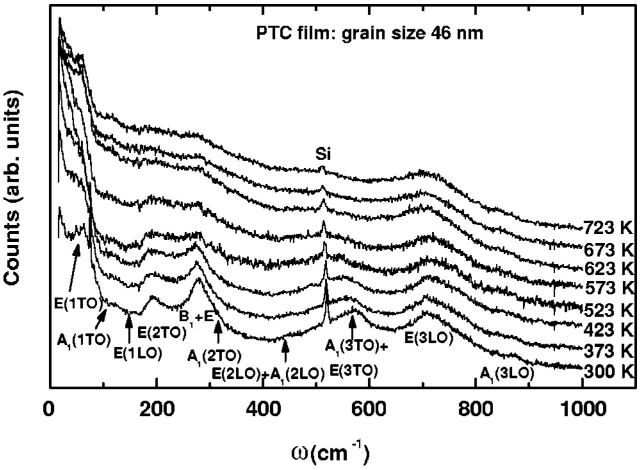

FIG. 9. Temperature evolution (from room temperature to 723 K) of the Raman spectra of a PTC film with a grain size of 46 nm (PTC2).

If the mode with the lowest energy E(1TO) is a soft mode, which is characteristic for ferroelectric materials, it should be highly sensitive to changes in pressure or temperature. The pressure dependent measurements of Sanjurjo *et al.*[22] gave a downward Raman lineshift of 6 cm^{-1} at a hydrostatic pressure of 1 GPa:

$$p = \frac{\omega_0 - \omega_p}{6}, \tag{3}$$

where ω_0 is the frequency at 0 GPa and ω_p is the frequency at a certain pressure p (in GPa). By combining the surface tension [Eq. (2)] and the pressure dependent Raman line shift [Eq. (3)] and using a value of 77 cm^{-1} for the bulk frequency, as measured by Mendiola *et al.*[25] for a PTC bulk ceramic, an empiric formula describing the frequency shift of the E(1TO) mode of PTC films with different grain sizes can be found:[27]

$$\omega_p = \omega_d = 77 - \frac{600}{d}. \tag{4}$$

For $d = 46$ nm this equation gives exactly the measured value of 64 cm^{-1}. With $d = 86$ nm the calculated value of 70 cm^{-1} coincides as well with the measured frequency. This can be interpreted as a first evidence for a soft mode behavior of the E(1TO) mode. Such a soft mode behavior should show even more significantly in temperature dependent Raman spectroscopy. In addition the diffuse phase transition found in the dielectric measurements before should have consequences for the Raman spectra as well. Figure 9 shows the evolution of the Raman spectra of the PTC film with a grain size of 46 nm from room temperature to 723 K by steps of 50 K. At room temperature the spectrum exhibits the same Raman lines as shown in Fig. 7, which are characteristic for the tetragonal phase. The amplitude of all lines is decreasing more and more with increasing temperature going hand in hand with a broadening and a shifting. Nevertheless, in contrast to a single crystal they can still be identified even at 723 K, which is 200 K above $T_M = 523$ K. Because the Raman spectra are connected to the low-frequency dielectric properties by the Lyddane-Sachs-Teller relation,[32] the T_M value of the lowest available frequency in the dielectric measurements, which was 100 Hz, was taken for evaluating the temperature dependencies of the Raman spectra. Figure 10 shows the comparison of the intensities of a $PbTiO_3$ single crystal,[33] a $PbTiO_3$ film,[33] and the PTC film in the vicinity of T_C or T_M, respectively. Contrary to the single crystal the intensity of both films does not disappear abruptly above T_M, but it is decreasing more slowly and still clearly visible even 200 K above T_M in the PTC film. A similar behavior was found by Tavares *et al.*[34] in their studies of the dependence of Raman spectra of $La_xPb_{1-x}TiO_3$(PLT) films as a function

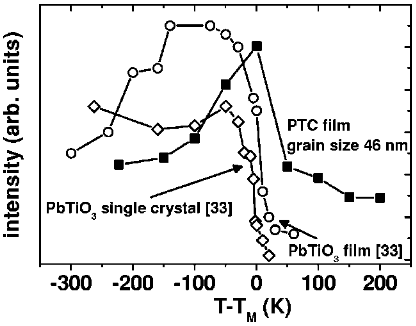

FIG. 10. Comparison of the intensities of the soft mode E(1TO) in the vicinity of T_C of a $PbTiO_3$ single crystal, a $PbTiO_3$ film, and a PTC film with a grain size of 46 nm (PTC2).

of the lanthanum concentration. They called this observation as well a diffuse phase transition and ascribed it to a disorder activated Raman effect due to the vacancies produced by the substitution of heterovalent La^{3+} ions on the sites of Ti^{4+} and Pb^{2+}. In the case of nanocrystalline PTC films the large amount of grain boundaries and the highly disturbed translational symmetry leads to a similar disorder. So these results give another evidence for the diffuse transition in nanocrystalline PTC films. The frequency and the FWHM of the E(1TO) mode shown in Fig. 11(a) versus T-T_M reveal a softening of the frequency and an increase of the FWHM when approaching T_M from below, which underlines that E(1TO) is a soft mode. The comparison of Figs. 11(b) and 11(c) shows that the temperature dependence of the squared frequency of E(1TO) can be better fitted by a modified Curie-Weiss law similar to Eq. (1), which is typical for relaxors,[35,36] than with the classical Curie-Weiss law. This gives further evidence for the grain-size-induced relaxor properties of nanocrystalline PTC films. Supposing a correlation of the soft mode intensity and the scattering volume we can conclude from Fig. 10 that a considerable amount of about 30% of the film volume remains polar above T_M. A possible origin of these polar regions, which play an essential role in the theoretical explanation of the diffuse phase transition and the relaxor behavior in general as shown above, could be the microstrain which indicates the local variation of the unit cell tetragonality.

D. Hysteresis loops

Because the temperature dependence of the induced polarization is another typical relaxor property, temperature dependent hysteresis measurements have been performed at PTC and PSN films with a Sawyer-Tower circuit.[37] At higher temperatures the increasing conductivity has to be compensated with a suited resistance connected parallel to the serial capacitor of the Sawyer-Tower circuit. Figure 12(a) shows hysteresis loops of a PSN film with a grain size of 72 nm (PSN1), recorded at different temperatures and 2 kHz. Figures 12(b) and 12(c) show the same for PTC films with grain sizes of 46 nm (PTC2) and 138 nm (PTC5) for comparison. Whereas in the case of the PSN and the nanocrystalline PTC film the hysteresis loops are still clearly visible at temperatures above their T_M values of 363 and 543 K, respectively, the hysteresis loop shows no remanent polarization above T_M=586 K in the PTC film with larger grains. This can be seen even better in the temperature dependencies of the remanent polarization P_r, which are shown for the PSN film in Fig. 13(a) and in Fig. 13(b) for the two PTC films with different grain sizes. When interpreting the P_r curve according to the Landau-Ginzburg-Devonshire (LGD)[38,39] theory, a square root law follows, which is valid only for the lower temperature range in the case of the relaxors (small grained PTC and PSN). A linear fit of P_r^2 versus T gives a value for the depolarization temperature T_0 of 371 K for the PSN film, which is just above T_M=363 K for 2 kHz. Figure 13(a) shows that starting at 358 K the measured remanent polarization, or more correctly the induced polarization, disagrees more and more with the theoretical curve (dotted line) and that P_r does still exist above T_0 and decays slowly. So as expected in PSN films both the shape of the hysteresis loop and the temperature dependence show the typical bulk relaxor behavior. Now it is tested whether the nanocrystalline PTC films behave similarly. In Fig. 13(b) the temperature dependencies of the remanent polarization of the PTC films with two different grain sizes are plotted. For a grain size of 46 nm (upper curve) the LGD theory gives a depolarization temperature T_0 of 473 K (indicated by the dotted line) which is clearly below T_M=543 K for 2 kHz.

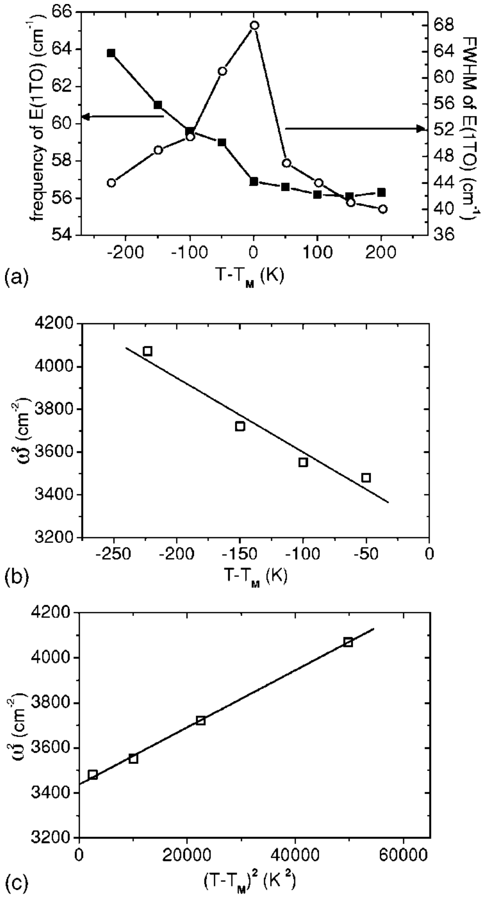

FIG. 11. (a) Dependence of the frequency and the FWHM of the soft mode E(1TO) from $T-T_M$ for a PTC film with a grain size of 46 nm (PTC2); (b) Squared frequency versus $(T-T_M)$; and (c) Squared frequency versus $(T-T_M)^2$ together with linear fits.

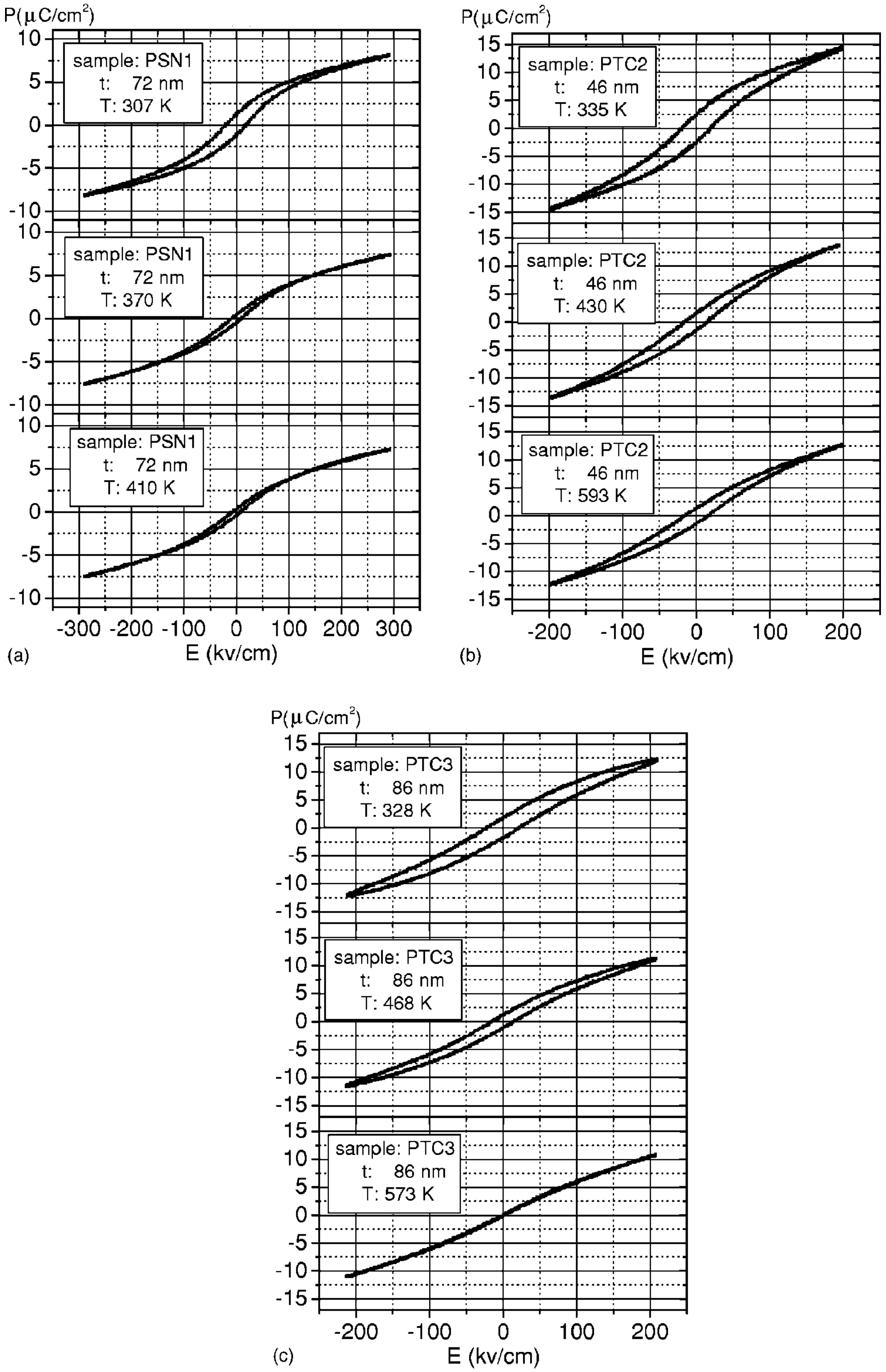

FIG. 12. Hysteresis loops recorded at 2 kHz at different temperatures of (a) a PSN film with a grain size of the perovskite phase of 72 nm and $T_M = 363$ K (PSN1); (b) a PTC film with a grain size of 46 nm (PTC2) and $T_M = 543$ K; and (c) a PTC film with a grain size of 138 nm (PTC5) and $T_M = 553$ K.

However, even 50 K above T_M there still remain considerable values of P_r, which is the same behavior as found in the relaxor PSN film. Whereas at a grain size of 138 nm (lower curve), T_0 and T_M coincide at 553 K and above T_M the remanent polarization is zero, which is typical for a ferroelectric material. This proves that the relaxor behavior of the nanocrystalline PTC films changes back to ferroelectric behavior at larger grain sizes, which has been concluded before from the temperature dependence of the dielectric constant for the same PTC film.

V. CONCLUSIONS

Our goal was to investigate how the properties of ferroelectric thin films change when downscaling the crystallite size is scaled down to the nanometer range. The starting point was the hypothesis, that when the grain size is reduced and the translational symmetry is disturbed by a large volume fraction of grain boundaries, a classical bulk ferroelectric material will show similar properties as found in relaxor materials, whose special properties are ascribed to the

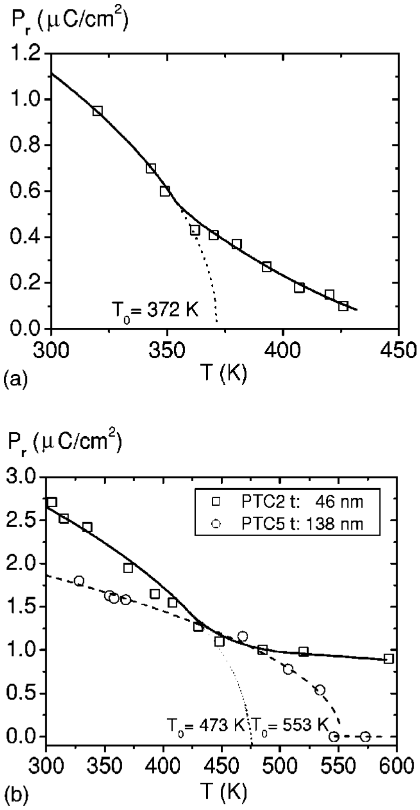

FIG. 13. (a) Temperature dependence of the remanent polarization P_r of a PSN film with a grain size of 73 nm. (b) Comparison of the temperature dependences of the remanent polarization P_r of PTC films with grain sizes of 46 nm (upper curve) and 138 nm (lower curve). The dotted line indicates the determination of T_0 when the LGD theory is applied.

existence of polar regions in the nanometer range due to an intrinsic disturbance of its translational symmetry. We prepared nanocrystalline ferroelectric PTC films and nanocrystalline relaxor PSN films for comparison. We were able to confirm the hypothesis with Raman spectroscopy and measurements of the temperature as well as the frequency dependence of the dielectric constant with different ways.

At first both the Raman spectra and the temperature dependence of the dielectric constant of nanocrystalline PTC films exhibit a diffuse phase transition.

Second the temperature curve of the dielectric constant shows a strong frequency dependence of the temperature T_M of the maximum, which is typical for relaxor materials. In addition this temperature curve follows the relaxor-typical modified Curie-Weiss law for a fixed low frequency.

Third it has been possible by increasing the grain size to more than 100 nm that the relaxor properties found before in nanocrystalline PTC films show the tendency to disappear and become similar to the ferroelectric properties of a ceramic sample.

Fourth the hysteresis loops recorded on PTC films with a small grain size show the same properties as those of the PSN films. The remanent polarization, or more correctly the induced polarization, does not disappear at T_0 but slowly decays above T_M. For larger grain size T_0 and T_M coincide and the polarization disappears at T_M.

It can be concluded that no results have been found with the experimental methods chosen that contradict the thesis of grain-size-induced relaxor behavior, i.e., that the disturbance of the translational symmetry induced by the small grain size and the large fraction of grain boundaries in nanocrystalline ferroelectric films (in our case PTC) leads to a qualitative change from ferroelectric to relaxor behavior. On the contrary it was possible to find evidences for this thesis with different experimental methods. The demonstrated grain-size-tuneable relaxor properties of nanocrystalline ferroelectric films are interesting for applications in the field on which the classical relaxor materials are already established, like, e.g., infrared detectors or electrostrictive actors, because there might be advantages compared to the classical relaxors, because it could be easier to control the grain size instead of the composition of sputtered thin films to tune their properties.

ACKNOWLEDGMENTS

We thank C. Bruch, T. Britz, H. Thedens, M. Marx, M. Kundzins, K. Kundzins, V. Zauls, and L. Shebanovs for their measurements and fruitful discussions. This work was kindly supported by the DFG in the Sonderforschungsbereich 277.

---

*Corresponding author. FAX: +49-7247-4567; Email address: carlos.ziebert@imf.fzk.de

[1] L. E. Cross, Ferroelectrics **76**, 241 (1987).
[2] E. Sawaguchi and M. L. Charters, J. Am. Chem. Soc. **42**, 157 (1959).
[3] R. Ranjan, N. Singh, D. Pandey, V. Siruguri, P. S. R. Krishna, S. K. Paranjpe, and A. Banerjee, Appl. Phys. Lett. **70**, 3221 (1997).
[4] C. Ziebert, J. K. Krüger, R. Birringer, H. Schmitt, and B. Jiménez, J. Phys. IV **8**, Pr-9-105 (1998).
[5] H. M. Rietveld, Acta Crystallogr. **22**, 151 (1967).
[6] B. Kirsch, H. Schmitt, and H. Müser, Ferroelectrics **68**, 275 (1986).
[7] G. Burns and F. H. Dacol, Solid State Commun. **48**, 853 (1983).
[8] H. Qian and L. A. Bursill, Int. J. Mod. Phys. B **10**, 2007 (1996).
[9] E. Fischer, W. Hässler, E. Hegenbarth, and V. I. Fritsberg, Phys. Status Solidi A **66**, K169 (1981).
[10] G. Burns and B. A. Scott, Solid State Commun. **13**, 423 (1973).
[11] B. E. Warren and B. Chalmers, in *Progress in Metal Physics*, edited by R. King (Pergamon, New York, 1959), p. 147.
[12] G. K. Williamson and W. H. Williamson, Acta Metall. **1**, 22 (1953).
[13] C. Ziebert, H. Schmitt, R. Birringer, J. K. Krüger, and J. Mendiola, Ferroelectrics **223**, 227 (1999).
[14] J. K. Krüger, C. Ziebert, H. Schmitt, B. Jiménez, and C. Bruch, Phys. Rev. Lett. **78**, 2240 (1997).

[15] R. Holtwick, C. Ziebert, M. Marx, H. Schmitt, J. K. Krüger, R. Birringer, and B. Jiménez, Ber. Bunsenges. Phys. Chem. **101**, 1757 (1997).
[16] C. Ziebert, A. Sternberg, H. Schmitt, K.-H. Ehses, and J. K. Krüger, Integr. Ferroelectr. **31**, 183 (2000).
[17] M. Tyunina, J. Levoska, A. Sternberg, and S. Leppävuori, J. Appl. Phys. **84**, 6800 (1998).
[18] C. Ziebert, H. Schmitt, J. K. Krüger, T. Britz, and C. Bruch, Ferroelectrics **240**, 371 (2000).
[19] E. Ching-Prado, A. Reynés-Figueroa, R. S. Katiyar, S. B. Majumder, and D. C. Agrawal, J. Appl. Phys. **78**, 1920 (1995).
[20] W. Zhu, Z. Q. Liu, W. Lu, M. S. Tse, H. S. Tan, and X. Yao, J. Appl. Phys. **79**, 4283 (1996).
[21] Z. Qin, G. A. Qiang, and M. Zhong-Yan, Acta Phys. Sin. (Overseas Ed.) **6**, 302 (1997).
[22] J. Mendiola, M. L. Calzada, P. Ramos, M. J. Martin, and F. Agulló-Rueda, Thin Solid Films **315**, 195 (1998).
[23] J. Frantti and V. Lantto, Phys. Rev. B **54**, 12 139 (1996).
[24] J. A. Sanjurjo, E. López-Cruz, and G. Burns, Phys. Rev. B **28**, 7260 (1983).
[25] J. A. Sanjurjo, E. López-Cruz, and G. Burns, Solid State Commun. **48**, 221 (1983).
[26] W. Ma, M. Zhang, and Z. Lu, Phys. Status Solidi A **166**, 811 (1998).
[27] K. Uchino, E. Sadanaga, and T. Hirose, J. Am. Chem. Soc. **72**, 1555 (1989).
[28] I. Taguchi, A. Pignolet, L. Wang, M. Proctor, P. Lévy, and P. E. Schmidt, J. Appl. Phys. **73**, 394 (1993).
[29] D. Bersani, P. P. Lottici, A. Montenero, S. Pigoni, and G. Gnappi, J. Mater. Sci. **31**, 3153 (1996).
[30] H. Richter, Z. P. Wang, and L. Ley, Solid State Commun. **39**, 625 (1981).
[31] J. D. Freire and R. S. Katiyar, Phys. Rev. B **37**, 2074 (1988).
[32] R. H. Lyddane, R. G. Sachs, and E. Teller, Phys. Rev. **59**, 673 (1941).
[33] Yu I. Yuzyuk, R. Farhi, V. L. Lorman, L. M. Rabkin, L. A. Sapozhnikov, E. V. Sviridov, and I. N. Zakharchenko, J. Appl. Phys. **84**, 452 (1998).
[34] E. C. S. Tavares, P. S. Pizani, and J. A. Eiras, Appl. Phys. Lett. **72**, 807 (1998).
[35] H. Schmitt and A. Dörr, Ferroelectrics **93**, 309 (1989).
[36] P. Pitzius, H. Schmitt, and A. Dörr, Ferroelectrics **106**, 155 (1990).
[37] C. B. Sawyer and C. H. Tower, Phys. Rev. **35**, 269 (1930).
[38] L. D. Landau, Phys. Z. Sowjetunion **11**, 26 (1937).
[39] A. F. Devonshire, Philos. Mag. **740**, 1040 (1949); **742**, 1065 (1951).