Coexistence of ferroelectricity and antiferroelectricity in epitaxial $PbZrO_3$ films with different orientations

Lucian Pintilie[a)]
Max Planck Institute of Microstructure Physics, Weinberg 2, D-06120 Halle (Saale), Germany, and NIMP, P. O. Box MG-7, 077125 Bucharest-Magurele, Romania

Ksenia Boldyreva, Marin Alexe, and Dietrich Hesse
Max Planck Institute of Microstructure Physics, Weinberg 2, D-06120 Halle (Saale), Germany

(Received 28 August 2007; accepted 10 November 2007; published online 16 January 2008)

The temperature dependence of the ferroelectric hysteresis and capacitance in $PbZrO_3$ epitaxial films with $(120)_O$ and $(001)_O$ orientations was investigated in the 4.2–400 K temperature range. It was found that the films with $(120)_O$ orientation show a mixture of ferroelectric and antiferroelectric phases on the entire temperature range up to room temperature, with the ferroelectric phase more stable at low temperatures. Above room temperature the $(120)_O$ oriented films seem to behave only as an antiferroelectric material. By contrast, films with $(001)_O$ orientation show only ferroelectric behavior up to a temperature of about 60 K when the single hysteresis loop splits into a double loop characteristic for antiferroelectrics. Above this temperature the $(001)_O$ oriented films show only antiferroelectric behavior up to 400 K. The temperature dependence of capacitance and loss tangent clearly shows a maximum at around 16 K in the case of the $(001)_O$ oriented film. This might be associated with a low temperature ferroelectric-antiferroelectric phase transition. However, this transition is not visible in the $(120)_O$ oriented films. © *2008 American Institute of Physics*.
[DOI: 10.1063/1.2831023]

I. INTRODUCTION

Lead zirconate ($PbZrO_3$) (PZO) is the prototype of antiferroelectric (AFE) materials, with a transition temperature to the paraelectric (PE) state of about 230 °C.[1–3] By contrast to ferroelectric (FE) materials, antiferroelectric PZO possesses a zero remnant polarization as the elementary dipoles form two polarization sublattices of the same magnitude but oriented in opposite directions.[4,5] The antiferroelectric axis lies in the *ab*-plane, being perpendicular to the *c*-direction. Typical for antiferroelectric PZO is the double hysteresis loop which occurs when the amplitude of the applied external field is larger than the critical field E_c for which the structure changes from AFE orthorhombic (AFE_O) to FE rhombohedral (FE_R).[6] This electric field-induced phase transition is possible due to the small difference between the free energies of the AFE_O and FE_R phases.[7] Also, a temperature-driven AFE-FE phase transition was observed in defect-containing PZO samples, just prior to the transition to the paraelectric state.[8–11] It was suggested that structural defects such as oxygen vacancies or impurity atoms stabilize the FE phase in a narrow temperature range before the transition to the PE phase. Therefore, the transition would not purely be AFE-PE but rather AFE-FE-PE. The width of the temperature domain in which the FE phase is stable depends on the amount of defects in the PZO sample.[12,13] It was also reported that a FE hysteresis loop can be obtained in the case of PZO films deposited on single-crystal Si substrates when the thickness of the film decreases below a critical value of about 500 nm.[14] It was suggested that in this case the FE phase is stabilized by the electric field arising at the PZO-Si interface due to interface charges. Therefore, in this case the change from double loop characteristic for AFE to single loop characteristic for FE phase seems to be related to an extrinsic effect.

However, it was suggested from the beginning that the AFE phase is not the only one present in PZO. The existence of a FE phase along the *c*-axis, viz., $[001]_O$-direction was also predicted. An estimate made by Jona *et al.* suggests a ferroelectric polarization as high as 25 $\mu C/cm^2$.[15] However, there is only one experimental report measuring a ferroelectric hysteresis loop with a saturation polarization of only 0.1 $\mu C/cm^2$, which is far below the previously mentioned estimate.[16] Therefore the question remains if there is a FE phase coexisting with the AFE one in pure PZO crystals. In recent years most of the studies on ferroelectric and antiferroelectric materials from the lead zirconate titanate (PZT) family were performed on thin films, as there is a growing interest in integrating these materials into standard semiconductor technology. The rapid advance of deposition techniques, especially pulsed laser deposition (PLD), have allowed the growth of epitaxial PZT films with crystalline quality equivalent to single crystals.[17] The careful manipulation of the substrate parameters and growth conditions allows also the deposition of PZT films with different orientations. The same is valid for PZO.[18–22] Recently the growth of high-quality PZO films with $(120)_O$ and $(001)_O$ orientations was reported.[23] This is an important achievement which made it possible to compare the properties of PZO films with the AFE axis completely in the substrate plane and with the presumed FE axis parallel to *c*-direction completely perpendicular to this plane [the case of $(001)_O$ oriented film] with

a)Electronic mails: pintilie@mpi-halle.mpg.de and pintilie@infim.ro.

 © 2008 American Institute of Physics

Downloaded 17 Jan 2008 to 85.232.23.177. Redistribution subject to AIP license or copyright; see http://jap.aip.org/jap/copyright.jsp

the properties of PZO films having the AFE axis out of the substrate plane [the case of $(120)_O$ oriented films]. Such a comparison may shed some light on the possible coexistence of AFE and FE phases in PZO.

Here we present the results of temperature-dependent electric measurements performed on $(120)_O$- and $(001)_O$-oriented epitaxial PZO films.

II. EXPERIMENTAL METHODS AND RESULTS

All samples were grown by pulsed laser deposition using a LambdaPhysik KrF laser with a wavelength of 248 nm. The $(120)_O$-oriented PZO films were grown on a (100)-oriented epitaxial $SrRuO_3$ (SRO) layer previously deposited by PLD on a $(001)_O$-oriented $SrTiO_3$ single-crystal (STO) substrate. The SRO layer plays the role of the bottom contact for the PZO capacitor. The $(001)_O$-oriented PZO films were grown on a $BaPbO_3$(BPO)/$BaZrO_3$ buffer stack previously deposited by PLD on STO substrates. The different buffer layers were used to obtain different orientations of the PZO films. The BPO layer also plays the role of a bottom electrode for the electric measurements performed on PZO. Details regarding the deposition parameters and in-depth structural investigations of the $(120)_O$- and $(001)_O$-orientated PZO films grown on the two types of buffer layers can be found in a recently published paper.[23] The $(120)_O$ sample is 120 nm thick, and the $(001)_O$ one is 200 nm thick.

Top Pt contacts were deposited onto the PZO layers by radio-frequency (rf) sputtering through a shadow mask, in this way defining the capacitors for the electric measurements. Polarization-voltage (*P*-*V*) and switching current-voltage (*I*-*V*) hysteresis loops were recorded by an AixAcct Thin Film Analyzer 2000. The capacitance was measured using a HP4194A impedance-gain analyzer. The temperature-dependent measurements were performed by placing the sample inside a Lake Shore cryogenic probe station, with open liquid He circulation, operating in the temperature range from 4.2 to 475 K. However, the temperature measurements were performed only in the temperature range between 4.2 and 400 K as above 400 K the top Pt contacts start to become damaged by the BeCu tips used for electrically contacting them in the cryogenic probe station. In the case of the *P*-*V* and *I*-*V* measurements, first the temperature was stabilized at the desired value within ±0.05 K, then the electrical measurements were performed. First measurement was performed at 4.2 K, second at 10 K, and then the measurements were performed in temperature steps of 10 K up to 400 K. In the case of capacitance-temperature measurements, the temperature was continuously varied with a heating rate of 1 K/min.

Figure 1 shows the recorded hysteresis loops at 4.2 K for the PZO films with different crystalline orientations. Surprisingly, the film with $(001)_O$ orientation shows only ferroelectric behavior, while the film with $(120)_O$ orientation shows a mixed antiferroelectric-ferroelectric behavior as suggested by the triple hysteresis loop and the six current peaks observed in Fig. 1. As the temperature was increased, significant changes were observed only in the case of the film with $(001)_O$ orientation, meaning that the hysteresis loop splits into two loops and four current peaks occur in the switching current-voltage characteristic. This fact suggests that the film with $(001)_O$ orientation undergoes a phase transition from a ferroelectric state at temperatures below about 60 K to a dominant antiferroelectric state above 60 K. The FE state might be also present above 60 K, but its presence is masked by the dominant current peaks associated with the AFE hysteresis. The films with $(120)_O$ orientation do not suffer major changes as the temperature is increased. The loops recorded for both orientations at 100 K are given as an example in Fig. 2. As can be seen the film with $(120)_O$ orientation still shows a triple hysteresis loop with six peaks in the current,

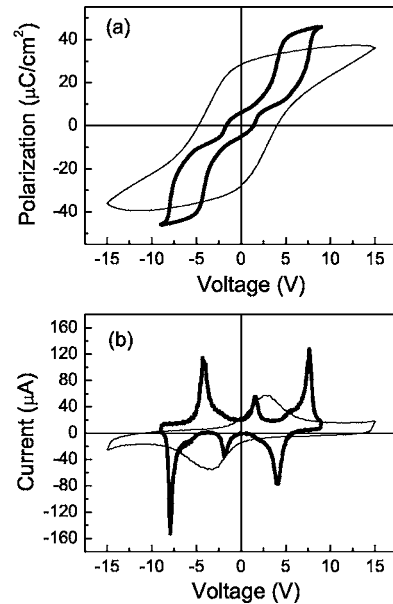

FIG. 1. The dynamic hysteresis loops at 1000 Hz (a) and the corresponding switching current-voltage characteristics (b) recorded at 4.2 K for PZO films with $(001)_O$ orientation (thin line) and $(120)_O$ orientation (thick line).

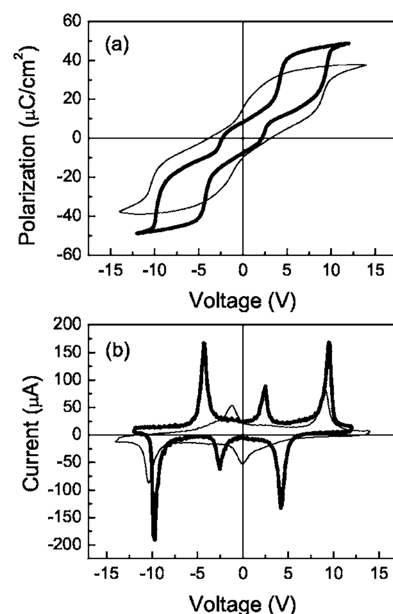

FIG. 2. The dynamic hysteresis loops at 1000 Hz (a) and the corresponding switching current-voltage characteristics (b) recorded at 100 K for PZO films with $(001)_O$ orientation (thin line) and $(120)_O$ orientation (thick line).

Downloaded 17 Jan 2008 to 85.232.23.177. Redistribution subject to AIP license or copyright; see http://jap.aip.org/jap/copyright.jsp

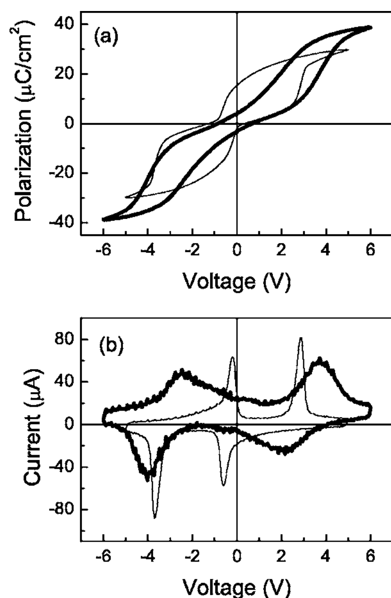

FIG. 3. The dynamic hysteresis loops at 1000 Hz (a) and the corresponding switching current-voltage characteristics (b) recorded at 400 K for PZO films with $(001)_O$ orientation (thin line) and $(120)_O$ orientation (thick line).

while the film with $(001)_O$ orientation shows a double hysteresis loop and four peaks in the switching current. With further increasing the temperature the FE behavior is more and more suppressed in the case of the PZO layer with $(120)_O$ orientation. The FE behavior is still present at room temperature, although very much reduced compared with low temperatures. At 400 K the PZO films with both orientations seem to behave only as antiferroelectrics, as shown in Fig. 3. As can be seen, a double hysteresis loop is obtained in both cases, although the polarization at zero voltage is not zero as it should be in the case of an ideal antiferroelectric. This might be due to the nonzero leakage current at small voltages, which adds a parasitic contribution to the integrated charge during the polarization switching. The switching current shows four peaks [see Fig. 3(b)] for both orientations, as it should be if only an AFE behavior is present in the PZO films.

As mentioned above the leakage current may generate some problems in the case of hysteresis measurement performed in the dynamic mode, which is based on a continuous integration of the current flowing through the ferroelectric capacitor. This can affect the polarization value and distort the hysteresis loop. One way to minimize the leakage contribution is to perform hysteresis measurements in the static mode, which is based on the integration of a current pulse generated when the polarization state changes from the one corresponding to the current applied voltage to the positive saturation state. An example of hysteresis loops measured in the static mode is shown in Fig. 4. The measurements were performed at 250 K, and show that the leakage contribution is negligible as long as the shape of the loops is very similar to those recorded in the dynamic mode. Some differences may occur in the values of remnant polarization, and coercive voltage as in the static mode the recorded polarization is the relaxed polarization after a relaxation time of 0.1 s. In any case, the sample with $(001)_O$ orientation shows only a

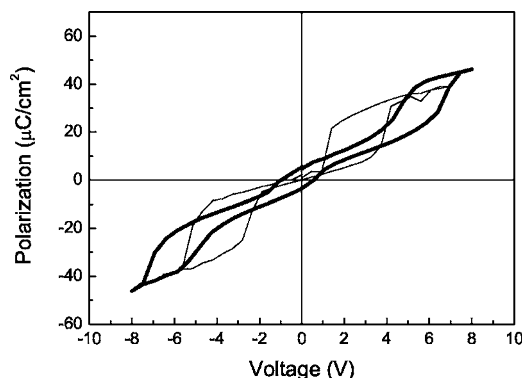

FIG. 4. The static hysteresis loops recorded with a relaxation time of 0.1 s for the PZO films with $(001)_O$ orientation (thin line) and $(120)_O$ orientation (thick line).

double loop, while the sample with $(120)_O$ orientation shows a triple loop. The results are consistent with those observed in the measurements performed in the dynamic mode.

Positive-up negative-down measurements were also tested with the Thin Film 2000 analyzer, but the results were similar to those presented in Figs. 1–3.

III. DISCUSSIONS

The results presented for the $(001)_O$ oriented film clearly show that the PZO is ferroelectric along the *c*-axis, with a remnant polarization of about 27 $\mu C/cm^2$ at 4.2 K. This value is in remarkable agreement with the estimate of 25 $\mu C/cm^2$ made by Jona *et al.* about 50 years ago.[15] However, they were very skeptical regarding the presence of ferroelectricity along the $[001]_O$ direction because of the lack of experimental results supporting this fact.

The problem is why the presence of ferroelectricity along the $[001]_O$ direction is observable only at low temperatures, especially in the case of $(001)_O$-oriented films. To better understand the possible coexistence of ferroelectricity and antiferroelectricity in PZO some schematics were drawn for the two orientations. These are shown in Figs. 5(a) and 5(b). The notation in Fig. 5 correspond to the following: AFE_O is the antiferroelectric axis in the orthorhombic phase; FE_R is the ferroelectric axis in the rhombohedral phase; FE_T is a tetragonal-like ferroelectric axis. The switching between AFE_O and FE_R is induced by the applied electric field and is responsible for the normal double loop observed in the case of antiferroelectric PZO. The switching along the FE_T axis, which is parallel to the *c* direction, is giving a single hysteresis loop. The combination of double loop with single loop leads to the triple loop observed experimentally. In the case of the $(001)_O$ oriented sample the AFE_O axis is in the substrate plane as it is shown in Fig. 5(a), while the FE_T axis is perpendicular to the substrate. It might be that the coercive field for FE_T switching is much smaller than the critical electric field necessary to induce the AFE_O-FE_R phase transition and to produce the double hysteresis loop characteristic for antiferroelectrics. If both AFE_O-FE_R and FE_T switching would take place, then a triple loop should be obtain as in the case of $(120)_O$ orientation, when the AFE_O is out of the substrate plane and the FE_T axis is in plane [see Fig. 5(b)].

Downloaded 17 Jan 2008 to 85.232.23.177. Redistribution subject to AIP license or copyright; see http://jap.aip.org/jap/copyright.jsp

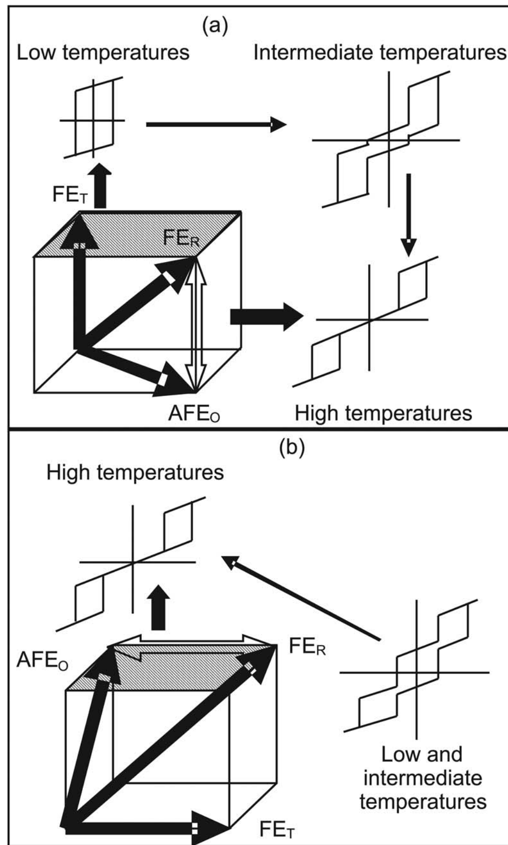

FIG. 5. Schematics of the antiferroelectric and ferroelectric axes with the resulting hysteresis loops on various temperatures domains. (a) is for the sample with $(001)_O$ orientation and (b) is for the sample with $(120)_O$ orientation. The hatched plane in (a) is $(002)_O=(001)_{pc}$ (pc-pseudocubic perovskite unit cell), and in (b) it is $(120)_O=(100)_{pc}$. These are the planes parallel to the substrate surface. For the relation between orthorhombic and pseudocubic lattices, see Refs. 3 and 4 as well as Ref. 23. AFE$_O$ is the antiferroelectric axis in the antiferroelectric orthorhombic phase; FE$_R$ is the ferroelectric axis in the field-induced rhombohedral phase; FE$_T$ is a ferroelectric tetragonal-like axis along the *c*-direction.

The presence of a triple loop at low temperatures was predicted by Fesenko, but he predicts that the field necessary to produce the triple loop should be about 750 kV/cm at −200 °C (73 K).[24] At 4.2 K the field necessary to induce the AFE$_O$-FE$_R$ transition and to produce the double loop would be around 1 MV/cm, which is higher than the observed breakdown field at this temperature [approximately 800 kV/cm for the $(001)_O$ oriented film]. We may presume that the experimentally applied field is not high enough to induce the AFE$_O$-FE$_R$ transition and to produce the triple hysteresis loop in the case of $(001)_O$ oriented sample. Therefore only the FE$_T$ switching along the $(001)_O$ axis is observed, leading to a single loop at very low temperatures. The coercive field for the FE$_T$ switching, as resulting from Fig. 1, is about 220 kV/cm at 4.2 K. This value is much smaller than the critical electric field necessary to induce the AFE$_O$-FE$_R$ transition. In other words, the applied field is too small to move the AFE$_O$ axis from the substrate plane and to change the structure from orthorhombic to rhombohedral but is high enough to switch the ferroelectric polarization perpendicular to the substrate.

It might be that increasing the temperature, the thermal energy helps in reducing the critical field for the AFE$_O$-FE$_R$ transition. At some temperature the value of the critical field may drop below the breakdown field, leading to the occurrence of the double loop characteristic for antiferroelectric materials and masking the FE$_T$ switching along the *c* axis in the case of $(001)_O$-oriented PZO films. In the case of $(120)_O$-oriented films the AFE$_O$ axis is out of the substrate plane [see Fig. 5(b)]. Probably in this case the AFE$_O$-FE$_R$ transition can be induced at lower values of the applied field. For example, the maximum field applied at 4.2 K is 750 kV/cm, while the critical field for the onset of the double loop is about 300 kV/cm. The last one is lower than the critical field predicted by Fesenko. We may conclude that the field-induced AFE$_O$-FE$_R$ transition is favored when the AFE$_O$ axis is out of the substrate plane. Regarding the coercive voltage for the ferroelectric switching along the FE$_T$ axis, we observe that this is about 160 kV/cm in the case of the $(120)_O$ sample. This value is not so different compared to the $(001)_O$ sample. We may conclude that the switching along the FE$_T$ axis is not so strongly dependent on the PZO orientation as it is the field-induced AFE$_O$-FE$_R$ transition.

It is interesting to note that at the highest tested temperature, 400 K, the saturation of the double loop for the $(001)_O$-oriented films takes place at a lower amplitude of the applied voltage than in the case of the $(120)_O$-oriented films although the $(001)_O$ films are thicker (~200 nm) than the $(120)_O$ ones (~120 nm).

It can be concluded that a saturated triple loop is clearly obtained in the $(120)_O$ films at low temperatures; with increasing temperature the ferroelectric behavior along the *c*-axis disappears faster in the $(001)_O$ films; at high temperatures the double loop is saturated at lower fields in the $(001)_O$-oriented films compared to the $(120)_O$-oriented ones.

The above discussion is mostly speculative and considers only the temperature changes of the critical field inducing the AFE$_O$-FE$_R$ transition, as well as the different orientations of the AFE$_O$ and FE$_R$/FE$_T$ axes in the two samples with different crystalline orientations. From the hysteresis measurements it is not very clear whether the $(001)_O$-oriented PZO films undergo a FE-AFE phase transition or not. Therefore we have performed some capacitance-temperature measurements at zero bias after prepoling the films in the same direction at low temperature (4.2 K). The measurements were performed at a frequency of 1 kHz with an amplitude of 50 mV for the ac probing signal. The obtained results are presented in Fig. 6. Without detailing too much the results, it can be seen that a clear peak occurs in the temperature dependence of the loss tangent of the $(001)_O$-oriented films at a temperature of about 16 K. The peak is less clear in the temperature dependence of the dielectric constant; however, a sharp drop can be observed at temperatures above 16 K. This behavior resembles very well a phase transition from a FE phase below 16 K to an AFE phase above 16 K. However, the FE phase does not totally disappear above 16 K. The two phases coexist up to about 60 K, with the AFE phase becoming stronger and stronger as the temperature increases. It seems that above 60 K only the AFE phase is present as suggested by the four peaks present in the switching current (cf. Fig. 2).

Downloaded 17 Jan 2008 to 85.232.23.177. Redistribution subject to AIP license or copyright; see http://jap.aip.org/jap/copyright.jsp

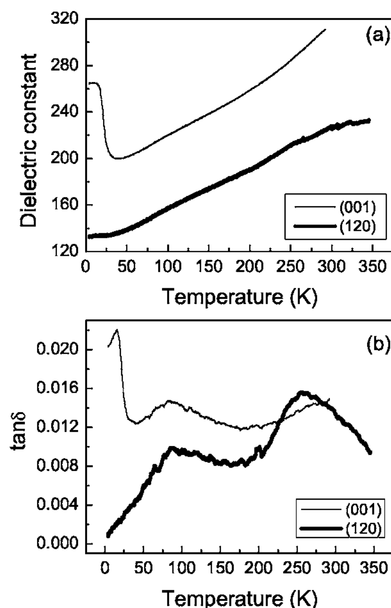

FIG. 6. The temperature dependence of the dielectric constant (a) and loss tangent (b) for PZO films with different orientations.

All the presented experimental results suggest that a structural change occurs at very low temperatures, around 16 K, accompanied by a peak in the dielectric constant and loss tangent. The shape of the hysteresis loop also changes from a simple loop characteristic for a FE phase to a double loop characteristic for an AFE phase. This apparent phase transition seems to be present in the $(001)_O$-oriented films but is not visible in the films with $(120)_O$ orientation. For the latter, there is no peak in the loss tangent around 16 K, nor a sharp drop in the dielectric constant. It appears that the low temperature FE-AFE phase transition, if present, is strongly anisotropic. This would be very unusual for a ferroelectric. It is more likely that the possible structural modifications of the PZO films induced by the changes in the strain/stress conditions at the substrate interface during the temperature scan produce significant changes in the values of the critical field and in the dielectric response. It might be that the FE and AFE phases coexist in the entire temperature range, but their "visibility" depends on the relative orientation of the two axes with respect to the direction of the applied electric field. It appears also that the FE phase along the *c* axis is more "visible" at low temperatures, while the AFE phase is more visible at high temperatures (cf. Figs. 1 and 3).

In conclusion, it was clearly shown that both ferroelectricity and antiferroelectricity coexist in epitaxial PZO films with high crystalline quality. Triple hysteresis loops were obtained at low temperatures for the films with $(120)_O$ orientation. The temperature behavior of the $(001)_O$-oriented films suggests a low temperature FE-AFE phase transition with a Curie temperature of about 16 K. However, this transition is not visible in the case of $(120)_O$-oriented PZO. In-depth structural investigations at low temperature are necessary in order to clarify this controversy.

ACKNOWLEDGMENTS

Work supported by Volkswagen Stiftung under Contract No. I/77738 and German Science Foundation (DFG) via FOR 404. L.P. acknowledges the collaboration with the DINAFER-2-CEEX-06-11-44 project funded by the Romanian Ministry of Education and Research.

[1]M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials*, (Clarendon, Oxford, 1977).
[2]E. Sawaguchi, Ferroelectrics **266**, 341 (2002).
[3]E. Sawaguchi, G. Shirane, and Y. Takagi, J. Phys. Soc. Jpn. **6**, 333 (1951).
[4]G. Shirane, E. Sawaguchi, and Y. Takagi, Phys. Rev. **84**, 476 (1951).
[5]E. Sawaguchi, H. Maniwa, and S. Hoshino, Phys. Rev. **83**, 1078 (1951).
[6]A. P. deBretteville, Jr., Phys. Rev. **94**, 1125 (1954).
[7]E. Sawaguchi, J. Phys. Soc. Jpn. **81**, 615 (1953).
[8]G. Shirane and S. Hoshino, Acta Crystallogr. **7**, 203 (1954).
[9]L. Benguigui, J. Solid State Chem. **3**, 381 (1971).
[10]G. Teisseron and A. Baudry, Phys. Rev. B **11**, 4518 (1975).
[11]K. Roledere and J. Dec, J. Phys.: Condens. Matter **1**, 1503 (1989).
[12]Z. Ujma, Phase Transitions **4**, 169 (1984).
[13]Q. Tan, Z. Xu, and D. Viehland, J. Mater. Res. **14**, 4251 (1999).
[14]P. Ayyub, S. Chattopadhyay, R. Pinto, and M. S. Multani, Phys. Rev. B **57**, R5559 (1998).
[15]F. Jona, G. Shirane, F. Mazzi, and R. Pepinsky, Phys. Rev. **105**, 849 (1957).
[16]X. Dai, J.-F. Li, and D. Viehland, Phys. Rev. B **51**, 2651 (1995).
[17]I. Vrejoiu, G. Le Rhun, L. Pintilie, D. Hesse, M. Alexe, and U. Gösele, Adv. Mater. (Weinheim, Ger.) **18**, 1657 (2006).
[18]S. S. N. Bharadwaja and S. B. Krupanidhi, J. Appl. Phys. **88**, 2072 (2000).
[19]K. Yamakawa, K. Wa Gachigi, S. Trolier–Mckinstry, and J. P. Dougherty, J. Mater. Sci. **32**, 5169 (1997).
[20]J. Zhai and H. Chen, Appl. Phys. Lett. **82**, 2673 (2003).
[21]I. Kanno, S. Hayashi, M. Kitagawa, R. Takayama, and T. Hirao, Appl. Phys. Lett. **66**, 145 (1995).
[22]E. M. Alkoy, S. Alkow, and T. Shiosaki, Jpn. J. Appl. Phys., Part 1 **44**, 8606 (2005).
[23]K. Boldyreva, D. Bao, G. Le Rhun, L. Pintilie, M. Alexe, and D. Hesse, J. Appl. Phys. **102**, 044111 (2007).
[24]O. E. Fesenko, R. V. Kolesova, and Yu. G. Sindeyev, Ferroelectrics **20**, 177 (1978).

Downloaded 17 Jan 2008 to 85.232.23.177. Redistribution subject to AIP license or copyright; see http://jap.aip.org/jap/copyright.jsp