Electrical conduction mechanism and phase transition studies using dielectric properties and Raman spectroscopy in ferroelectric Pb 0.76 Ca 0.24 TiO 3 thin films

F. M. Pontes, D. S. L. Pontes, E. R. Leite, E. Longo, A. J. Chiquito, P. S. Pizani, and J. A. Varela

Electrical conduction mechanism and phase transition studies using dielectric properties and Raman spectroscopy in ferroelectric Pb$_{0.76}$Ca$_{0.24}$TiO$_3$ thin films

F. M. Pontes, D. S. L. Pontes, E. R. Leite,[a)] and E. Longo
Department of Chemistry, LIEC–CMDMC, Universidade Federal de São Carlos Via Washington Luiz, km 235, CP-676, CEP-13565-905, São Carlos, S. P., Brazil

A. J. Chiquito and P. S. Pizani
Department of Physics, Universidade Federal de São Carlos Via Washington Luiz, km 235, CEP-13565-905, São Carlos, S. P., Brazil

J. A. Varela
Institute of Chemistry, UNESP, Araraquara, S. P., Brazil

We have studied the phase transition behavior of Pb$_{0.76}$Ca$_{0.24}$TiO$_3$ thin films using Raman scattering and dielectric measurement techniques. We also have studied the leakage current conduction mechanism as a function of temperature for these thin films on platinized silicon substrates. A Pb$_{0.76}$Ca$_{0.24}$TiO$_3$ thin film was prepared using a soft chemical process, called the polymeric precursor method. The results showed that the dependence of the dielectric constant upon the frequency does not reveal any relaxor behavior. However, a diffuse character-type phase transition was observed upon transformation from a cubic paraelectric phase to a tetragonal ferroelectric phase. The temperature dependency of Raman scattering spectra was investigated through the ferroelectric phase transition. The soft mode showed a marked dependence on temperature and its disappearance at about 598 K. On the other hand, Raman modes persist above the tetragonal to cubic phase transition temperature, although all optical modes should be Raman inactive above the phase transition temperature. The origin of these modes must be interpreted in terms of a local breakdown of cubic symmetry by some kind of disorder. The lack of a well-defined transition temperature suggested a diffuse-type phase transition. This result corroborate the dielectric constant versus temperature data, which showed a broad ferroelectric phase transition in the thin film. The leakage current density of the PCT24 thin film was studied at elevated temperatures, and the data were well fitted by the Schottky emission model. The Schottky barrier height of the PCT24 thin film was estimated to be 1.49 eV. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1611269]

I. INTRODUCTION

Recently, many ferroelectric thin films such as Pb(Zr,Ti)O$_3$, PbTiO$_3$, and Pb(Ca,Ti)O$_3$ have been actively investigated for application in memory integrated circuits.[1–3] Lead titanate (PbTiO$_3$) based materials are used in a broad range of electronic devices, e.g., transducers, infrared detectors, pulse generating devices, ferroelectric memories, etc.[4,5] PbTiO$_3$ has a low dielectric constant, high spontaneous polarization, and high pyroelectric coefficient. In addition, solid solutions of PbTiO$_3$ thin films with other perovskite compounds enhance various interesting properties and device feasibilities. PbTiO$_3$ shows a first-order phase transition temperature at about 763 K.[6] With the addition of SrTiO$_3$ or CaTiO$_3$ to PbTiO$_3$, the phase transition temperature decreases with increasing Ca or Sr concentration, and the ferroelectric phase transition in Pb$_{0.5}$Ca$_{0.5}$TiO$_3$ and Pb$_{0.3}$Sr$_{0.7}$TiO$_3$ systems occurs near room temperature.[7,8] It is also interesting to note that many ferroelectric materials exhibit relaxor behavior characteristics as a function of the dopant concentration by a broad maximum in the temperature dependence

of the dielectric constant, and a strong frequency dispersion of the dielectric constant at temperatures around the phase transition temperature.[9] Lead magnesium niobate (PMN), lead zinc niobate (PZN), and their solid solutions with lead titanate (PT) are the most widely studied relaxor materials.[10–12] In addition, the relaxor characteristics of PT with higher La concentration are reported in the literature.[13–15] Among the doped PbTiO$_3$ systems, Pb$_{1-x}$Ca$_x$TiO$_3$ (PCT) systems have recently received renewed attention due to the high-piezoelectric effect and excellent dielectric properties.[16–18] In addition, unlike bulk materials, thin films of PbTiO$_3$ and Pb$_{1-x}$Ca$_x$TiO$_3$ show submicron size grains resulting in a lower value of the dielectric constant. These films do not show any anomaly in the curves of the dielectric constant as a function of temperature, but they present a monotonic decrease in the dielectric constant. These observations suggest that the phase transition temperature in PbTiO$_3$ and Pb$_{1-x}$Ca$_x$TiO$_3$ thin films may not be as sharply defined as in bulk single crystals, and bulk ceramics.[7] Naik *et al.*[19] reported a study on Pb$_{0.4}$Sr$_{0.6}$TiO$_3$ thin films where the dielectric permittivity versus temperature data showed a broad peak at room temperature indicating a rather diffuse phase transition. On the other hand,

a)Electronic mail: derl@power.usfcar.br

Tenne *et al.*[20] studied vibrational properties of $Ba_{0.5}Sr_{0.5}TiO_3$ thin films prepared by pulsed laser deposition and they observed that the temperature dependence of the Raman spectra indicates a broad ferroelectric phase transition in the thin films. Dobal *et al.*[21] studied, by Raman scattering and dielectric constant as a function of the temperature, the antiferroelectric phase transition in $PbZrO_3$ thin films. These $PbZrO_3$ thin films exhibited a clear temperature-dependent phase transition from the antiferroelectric to paraelectric state, through a ferroelectric phase. Gakh *et al.*[22] reported the phase transition of $Pb_{1-x}Ca_xTiO_3$ thin films. The $x=0.15$ thin film was found to undergo a tetragonal-to-cubic phase transition at about 370 °C.

Although many authors have investigated PCT thin films and ceramic solid solutions, no systematic study of the temperature dependence of the PCT conduction current behavior was discussed in the literature. Once PCT has the highest potential for application in dynamic random access memories, because of its high dielectric constant, low leakage current, and high breakdown field, the conduction current mechanism should be studied. For comparison, a large number of research has focused on the leakage current behavior of $PbZr_{0.4}Ti_{0.6}O_3$ (PZT), (SBN), $SrBiTa_2O_9$ (SBT), and $Ba_{1-x}Sr_xTiO_3$ (BST) thin films.[23–26]

In this article, we have studied the temperature dependence of the dielectric constant and Raman spectra in the study of the phase transition of polycrystalline $Pb_{1-x}Ca_xTiO_3$ thin films. No study of the temperature dependence of the leakage current was reported on $Pb_{1-x}Ca_xTiO_3$ thin films. We have also investigated the current conduction mechanism based on the interface limited Schottky emission theory and estimated the possible physical parameters involved.

II. EXPERIMENT

The $Pb_{0.76}Ca_{0.24}TiO_3$ (PCT24) thin film studied in the present work was derived from a soft chemical processing. Details of the preparation method can be found in the literature.[18] The polymeric precursor solution was spin coated on substrates [Pt (140 nm)/Ti (10 nm)/SiO$_2$ (1000 nm)/Si] by a commercial spinner operating at 6000 rev/min for 20 s (spin-coater KW-4B, Chemat Technology), via a syringe filter to avoid particulate contamination. After spinning, the films were kept in ambient air at 150 °C on a hot plate for 20 min to remove residual solvents. A two-stage heat treatment was carried out: initial heating at 400 °C for 4 h at a heating rate of 5 °C/min to pyrolyze the organic materials, and finally, followed by heating at 700 °C for 2 h for crystallization. The film thickness was controlled by adjusting the number of coatings, and the coating/drying operation was repeated until the desired thickness was achieved.

The dielectric constant of the thin film was measured using a Keithley 3330 (LCR) meter in the temperature range of 298–653 K. The capacitance–voltage ($C-V$) curves were measured using an HP4194A impedance/gain phase analyzer at the temperature range of 298–573 K. The leakage current at various temperatures was measured using the computer Keitlhey 237 unit.
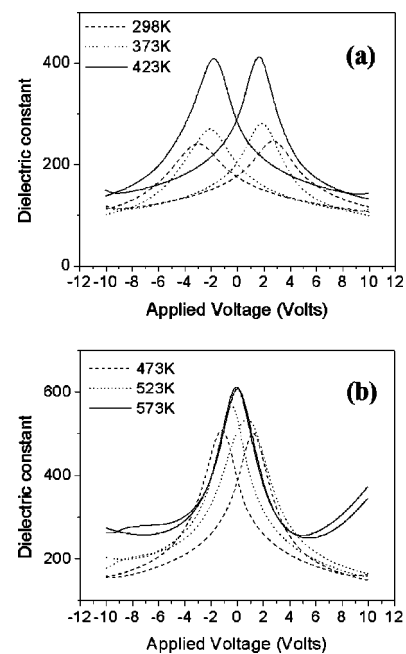

FIG. 1. Dielectric constant-voltage characteristics of the $Pb_{0.76}Ca_{0.24}TiO_3$ thin film at different temperatures at 100 kHz.

The Raman measurements were performed using a T-6400 Jobin–Yvon triple-monochromator coupled to a charge-coupled-device detector. An optical microscope with a 50× objective was used to focus the 514.5 nm line of a Coherent Innova 90 argon laser into the sample. An oven TMS 93 from Linkam Scientific Instruments, Ltd., was used under the microscope for measurements at the 298–873 K temperature range.

III. RESULTS

Figure 1 shows the capacitance–voltage ($C-V$) curves of the PCT24 thin film deposited on a Pt/Ti/SiO$_2$/Si substrate. $C-V$ curves were obtained at different temperatures at a frequency of 100 kHz with an oscillation amplitude of 50 mV. The capacitance of the film showed a strong dependence on the applied voltage. At 298 K, the $C-V$ curve showed two broad peaks, the curve was symmetric about the zero-bias axis, and hysteresis behavior was observed. Increasing the temperature, the butterfly-type shape of the curves decreased: the separation between the $C-V$ curves of the positive and negative biases decreased, and at about 573 K, the $C-V$ curves showed absence of splitting (butterfly type) for decreasing and increasing voltages for both polarities. This fact indicates that the 573 K temperature corresponds to the ferroelectric–paraelectric transition phase. Venkateswarlu *et al.*[27] observed a similar behavior for lead lanthanum titanate thin films prepared by the laser ablation technique.

The temperature and frequency variations of the dielectric constant for the PCT24 thin film are shown in Fig. 2. We may note that the peak of the dielectric constant versus temperature is broader than that corresponding peak of compositions close to PCT24 in the bulk form. However, measurements at different frequencies do not show any peak shift. Such behavior indicates that the transition is relatively dif-
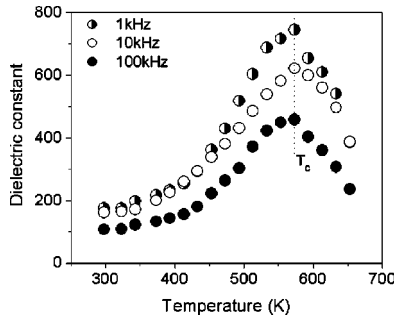
FIG. 2. Temperature dependence of the dielectric constant for the $Pb_{0.76}Ca_{0.24}TiO_3$ thin film as a function of the frequency.

FIG. 4. Characteristic positive $I-V$ curves obtained at different temperatures for the Au/PCT24/Pt thin films studied in this work.

fuse, but that the ferroelectric phase is not a relaxor in the PCT24 thin film prepared by the polymeric precursor method.

For a normal ferroelectric, in the vicinity of the transition temperature, the dielectric stiffness, $(1/\epsilon)$, follows the well-known Curie–Weiss law:[28]

$$1/\epsilon = (T - T_0)/C, \qquad (1)$$

where C is the Curie–Weiss constant and T_0 is the Curie–Weiss temperature.

In addition, the order of the ferroelectric to paraelectric phase transition can be determined from the temperature dependence of the dielectric constant inverse $(1/\epsilon)$. When T_0 is smaller than T_C we observe a first-order transition; on the other hand, when $T_0 = T_C$, a second-order transition is observed.[29]

Figure 3 shows the temperature behavior of the inverse of the dielectric constant at 10 kHz for the PCT24 thin film. The dielectric stiffness in the paraelectric phase follows the Curie–Weiss behavior. The parameters C and T_0 were fitted at a narrow temperature range near T_C. From these data, the ferroelectric to paraelectric phase transition temperature, T_C, and the Curie–Weiss temperature, T_0, can be obtained directly. The fitting parameters are $C = 1.98 \times 10^5$ K and $T_0 = 530$ K. The fact that the Curie–Weiss temperature ($T_0 = 530$ K) is lower than the transition temperature ($T_C = 573$ K) is expected from the first-order phase transition between the paraelectric and ferroelectric phases. Moreover, the value of the Curie–Weiss constant (C) for a regular ferroelectric-like barium titanate and lead titanate undergoing
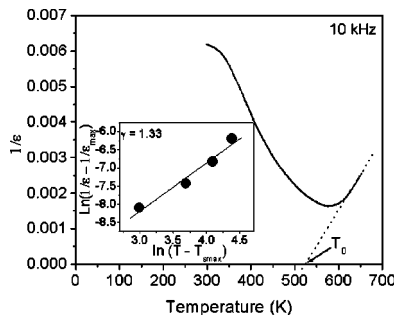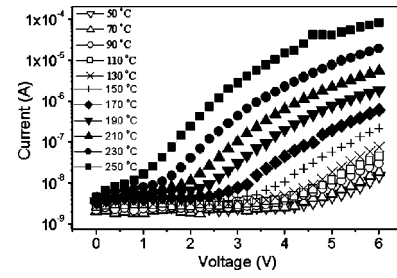
a sharp transition is usually $\leqslant 2 \times 10^5$ K, whereas for a relaxor ferroelectric like lead magnesium niobate undergoing a diffuse transition, this value is $> 4 \times 10^5$ K.[30] In our case, we obtained the parameter $C = 1.98 \times 10^5$ K.

In the literature for a diffuse transition, the following empirical relationship for the Curie–Weiss law was proposed to describe the diffuseness of the phase transition as[31]

$$1/\epsilon - 1/\epsilon_m = (T - T_{\epsilon \max})^\gamma / C^*, \qquad (2)$$

where γ is the critical exponent, which is a measure of the degree of diffuseness of the transition, and C^* is a Curie–Weiss-like constant. For a sharp transition, $\gamma = 1$ and for a diffuse transition it lies in the range $1 < \gamma \leqslant 2$.[32] We obtained the parameter $\gamma = 1.33$ by fitting the experimental data (the fitting curve is shown in the inset of Fig. 3). From these data, we may note that there is some diffuse character; but measurements at different frequencies showed that the peak temperature is not seriously affected by the change in frequency. Similar behavior was observed by Subrahmanyam and Goo for the $(Pb_xSr_{1-x})TiO_3$ system.[8] Pokharel and Pandey reported values of γ in the range of 1.25–1.50 for the diffuse behavior of the $(Pb_{1-x}Ba_x)ZrO_3$ system.[32] In addition, Ganesh and Goo reported values of γ in the range of 1.20–1.34 for the diffuse behavior of the paraelectric–ferroelectric transition region for the $(Pb_{1-x}Ca_x)TiO_3$ system.[7]

In order to study the current transport mechanism in our system, the current–voltage characteristics were obtained at different diode temperatures and the results are plotted in Fig. 4. The metal/PCT24/metal system usually constitutes a back-to-back Schottky diode. The current density in such a system is given by

$$J = \left[A^* T^2 \exp\left(\frac{-q(\phi_B - \Delta\phi_B)}{kT} \right) \right] \left[\exp\left(\frac{qV}{nkT} \right) - 1 \right], \quad (3)$$

where V is the applied voltage, T is the temperature, n is the ideality factor, ϕ_B is the Schottky barrier height, and A^* ($= 120m/m_0$, m_0 is the free-hole mass) is the Richardson constant. The term in the first bracket in Eq. (3) is usually referred to as the saturation current or J_0. When using only the thermionic emission theory to account for the electron transport over the barrier, the lowering term ($\Delta\phi_B$) in Eq. (3) should be neglected.[33] The barrier lowering due to the applied voltage V depends on the depletion region width d and on the relative dielectric constant ϵ_r as given below:

FIG. 3. Inverse of the dielectric constant, $(1/\epsilon)$, as a function of temperature for the $Pb_{0.76}Ca_{0.24}TiO_3$ thin film. Inset shows $\ln(1/\epsilon - 1/\epsilon_{\max})$ as a function of $\ln(T - T_{\epsilon,\max})$.
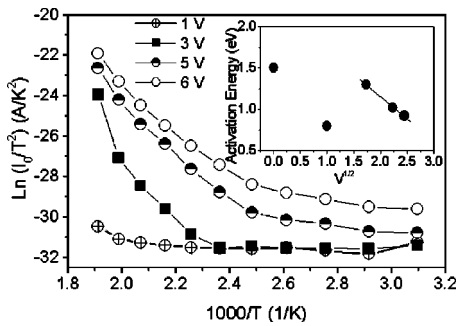
FIG. 5. Variation of $\ln(J_0/T^2)$ as a function of $1000/T$ for the Au/PCT24/Pt thin film at different voltages. These curves were used to determine the activation energies of the current transport and the obtained values are plotted in the inset.

FIG. 6. Raman spectra of the $Pb_{0.76}Ca_{0.24}TiO_3$ thin film above and below the transition temperature.

$$\Delta\phi_B = \sqrt{\frac{qV}{4\pi\epsilon\epsilon_r d}}. \tag{4}$$

According to Eq. (3), it seems clear that both temperature and voltage dependencies of J should be experimentally explored in order to explain the current mechanisms in our samples.

As expected from the Schottky current emission theory, the current increases for increasing temperatures because this thermally activated conduction is enhanced by the applied field. However, in the low voltage and low temperature ranges, the observed current cannot be explained using the Schottky mechanism. This suggests that a different conduction mechanism should be considered in that range. We have investigated the use of the Poole–Frenkel and space-charge-limited current models, but the fit of the experimental curves using these models was quite unreasonable. A similar behavior was found in Ref. 34 indicating that a more comprehensive treatment is needed. This will be the object of future work.

In Fig. 5 we plot the $\ln(J_0/T^2)$ vs $1000/T$ curves at different voltages (high field) at the temperature range from 110 to 250 °C. From these curves we can determine the activation energy for the emission of carriers over the Au/PCT24 barrier. The obtained values are plotted in the inset in Fig. 5 as a function of the square root of the applied voltages and they reveal a decreasing behavior as the voltage increases. This is expected from the Schottky theory and it is caused by the lowering of the field induced barrier ($\Delta\phi_B$). In fact, the activation energy at $V=0$ V reflects the Schottky barrier height of 1.49 eV at the Au/PCT24 interface, considering the thermionic emission only. In addition, Scott et al.[35] reported values of the Schottky barrier at $V=0$ V for SBT, BST, and PZT to be about 1.6, 1.62, and 1.5 eV, respectively. Das et al.[23] studied the leakage characteristics of $SrBi_2Ta_2O_6$ thin films at elevated temperatures and the data were fitted by the Schottky emission model. The Schottky barrier heights of the films on Pt and $LaNiO_3$ substrates were estimated to be 1.27 and 1.12 eV, respectively. Other authors have reported the Schottky barrier height of $SrBi_2Nb_2O_9$ and $(Ba,Sr)TiO_3$ thin films in the range of 1.37–1.5 eV.[24,36]

The fitting of the activation energy versus voltage curves provides an estimate of the $\epsilon_r d$ product present in Eq. (4). Our estimated value is $\epsilon_r d = 6$ nm, in agreement with previ-
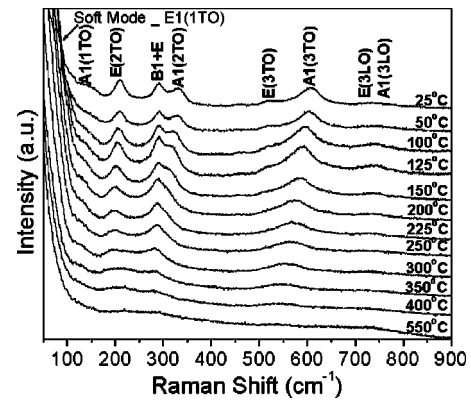
ous reported values.[34] In Ref. 34, this small value has explained in terms of a very thin interfacial layer, as proposed by Mott in 1938.[37] Our results confirm that Mott's model is also valid for the metal/PCT24/metal system.

In order to study the phase transition by Raman spectroscopy for PCT24 thin films, the evolution of Raman spectra were obtained at different temperatures and the results are showed in Fig. 6. The room temperature Raman spectrum is in agreement with the literature, showing all Raman active optic modes.[38] According to the selection rules, all optic modes become Raman inactive above the transition temperature.

As the temperature is increased, the Raman modes become broad and gradually lose intensity (see Fig. 6). However, some modes disappear completely at a certain temperature, which corresponds to the ferroelectric to paraelectric phase transition temperature. The lowest-frequency Raman line, located at 83 cm^{-1}, is the soft mode belonging to $E(1TO)$ symmetry. We can see clearly in Fig. 7 that increasing temperatures cause frequency downshifts, and finally, their disappearance at about 325 °C. We attribute these downshifts and the lack of $E(1TO)$ mode in PCT24 thin films to the ferroelectric–paraelectric phase transition temperature. The temperature dependence of the square of the soft mode frequency is shown in Fig. 8. Concerning the $E(1TO)$ mode, it can be noted that its frequency decreases rapidly up to the transition temperature. Dobal et al.[39,40] observed similar behavior for $PbTiO_3$ and $(Pb,La)TiO_3$ thin films prepared by the sol–gel method. In addition, the ex-
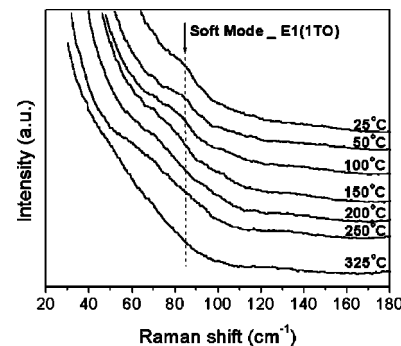

FIG. 7. Expanded view of the Raman spectra of Fig. 6 for the soft mode peak.
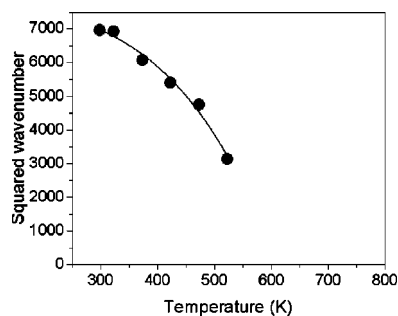
FIG. 8. Temperature variation of the squared wave number of the soft $E(1TO)$ mode in the $Pb_{0.76}Ca_{0.24}TiO_3$ thin film.

trapolation of the curve in Fig. 8 to the zero-squared wave number yields the phase transition temperature as about 598 K. However, we can see that in the case of PCT24 thin films, the persistence of phonon modes well beyond the transition temperature is owed to a short-range structural disorder in the paraelectric cubic phase. This disorder destroys the perfect cubic symmetry and thus allows Raman activity in the paraelectric phase (see Fig. 6). A similar observation was reported in thin films by Naik *et al.*[41] for $(Pb,Sr)TiO_3$ and in bulk $(Pb,La)TiO_3$.[42]

The disappearance of the 83 cm^{-1} soft modes at about 598 K indicates the transformation from the ferroelectric to the paraelectric phase at this temperature, which is consistent with the Curie temperature determined by the electrical characterization.

IV. CONCLUSION

In conclusion, a PCT24 thin film grown by soft chemical processing exhibits a diffuse type of phase transition. However, the dielectric constant values as a function of temperature and frequency revealed that the ferroelectric phase is not a relaxor, once the transition temperature was independent of the frequency (classical ferroelectric). We also have used Raman scattering to probe the phase transition. The transition temperature was estimated using the disappearance and wave-number variation of the soft mode belonging to the tetragonal phase. We also found that broad Raman bands are seen to persist well beyond the transition temperature in our thin film. This is attributed to the breakdown of selection rules due the presence of disorder in the paraelectric phase. Both dielectric and Raman studies showed a diffuse type of phase transition. Also, the temperature dependence of the $I-V$ curves of the PCT24 thin film was studied. The leakage current data are in agreement with the Schottky emission model and the Schottky barrier height was estimated to be 1.49 eV at the Au/PCT24 interface.

[1] I. Boerasu, L. Pintilie, M. Pereira, M. I. Vasilevskiy, and M. J. M. Gomes, J. Appl. Phys. **93**, 4776 (2003).
[2] R. Poyato, M. L. Calzada, and L. Pardo, J. Appl. Phys. **93**, 4081 (2003).
[3] X. Chen, W. Zhu, O. K. Tan, and X. Yao, Mater. Chem. Phys. **75**, 90 (2002).
[4] D. Fu, T. Ogawa, H. Suzuki, and K. Ishikawa, Appl. Phys. Lett. **77**, 1532 (2000).
[5] V. R. Palkar, S. C. Purandare, P. Ayyub, and R. Pinto, J. Appl. Phys. **87**, 462 (2000).
[6] Y. Kuroiwa, S. Aoyagi, A. Sawada, J. Harada, E. Nishibori, M. Takata, and M. Sakata, Phys. Rev. Lett. **87**, 217601-1 (2001).
[7] R. Ganesh and E. Goo, J. Am. Ceram. Soc. **89**, 653 (1997).
[8] S. Subrahmanyam and E. Goo, Acta Mater. **46**, 817 (1998).
[9] I. W. Chen, J. Phys. Chem. Solids **61**, 197 (2000).
[10] E. Ching-Prado, J. Cordero, R. S. Katiyar, and A. S. Bhalla, J. Vac. Sci. Technol. A **14**, 762 (1996).
[11] D.-S. Paik, S.-E. Park, S. Wada, S.-F. Liu, and T. R. Shrout, J. Appl. Phys. **85**, 1080 (1999).
[12] A. L. Kholkin, E. K. Akdogan, A. Safari, P.-F. Chauvy, and N. Setter, J. Appl. Phys. **89**, 8066 (2001).
[13] T.-Y. Kim, H. M. Jang, and S. M. Cho, Solid State Commun. **119**, 527 (2001).
[14] S. Bhaskar, S. B. Majumder, and R. S. Katiyar, Appl. Phys. Lett. **80**, 3997 (2002).
[15] P. S. Dobal, R. R. Das, B. Roy, R. S. Katiyar, S. Jain, and D. C. Agrawal, J. Raman Spectrosc. **31**, 965 (2000).
[16] H. Y. Guo, J. B. Xu, Z. Xie, E. Z. Zuo, I. H. Wilson, and W. L. Zhong, Solid State Commun. **121**, 603 (2002).
[17] H. Y. Guo, J. B. Xu, I. H. Wilson, Z. Xie, and E. Z. Luo, Phys. Lett. A **294**, 217 (2002).
[18] F. M. Pontes, D. S. L. Pontes, E. R. Leite, E. Longo, E. M. S. Santos, S. Mergulhão, A. Chiquito, P. S. Pizani, F. Lanciotti, Jr., T. M. Boschi, and J. A. Varela, J. Appl. Phys. **91**, 6650 (2002).
[19] V. M. Naik, D. Haddad, R. Naik, J. Mantese, N. W. Schubring, A. L. Micheli, and G. W. Auner, J. Appl. Phys. **93**, 1731 (2003).
[20] D. A. Tenne, A. M. Clark, A. R. James, K. Chen, and X. X. Xi, Appl. Phys. Lett. **79**, 3836 (2001).
[21] P. S. Dobal, R. S. Katiyar, S. S. N. Bharadwaja, and S. B. Krupanidhi, Appl. Phys. Lett. **78**, 1730 (2001).
[22] S. G. Gakh, T. P. Myasnikova, O. A. Bunina, T. A. Yusman, and I. A. Cherepkova, Inorg. Mater. (Transl. of Neorg. Mater.) **33**, 416 (1997).
[23] R. R. Das, P. Bhattacharya, R. S. Katiyar, and A. S. Bhalla, J. Appl. Phys. **92**, 6160 (2002).
[24] R. R. Das, P. Bhattacharya, W. Perez, R. S. Katiyar, and A. S. Bhalla, Appl. Phys. Lett. **81**, 880 (2002).
[25] K. H. Ahn, S. S. Kim, and S. Baik, J. Appl. Phys. **93**, 1725 (2003).
[26] Y. S. Yang, S. J. Lee, S. Yi, B. G. Chae, S. H. Lee, H. J. Joo, and M. S. Jang, Appl. Phys. Lett. **76**, 774 (2000).
[27] P. Venkateswarlu, S. S. N. Bharadwaja, and S. B. Krupanidhi, Thin Solid Films **389**, 84 (2001).
[28] M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (1977).
[29] J. Ravez, C. Brouster, and A. Simon, J. Mater. Chem. **9**, 1609 (1999).
[30] K. Uchino, L. E. Cross, R. E. Newnham, and S. Namura, J. Appl. Phys. **52**, 1455 (1981).
[31] K. Uchini and S. Namura, Ferroelectr. Lett. Sect. **34**, 2551 (1982).
[32] B. P. Pokharel and D. Pandey, J. Appl. Phys. **88**, 5364 (2000).
[33] S. M. Sze, *Physics of Semiconductors Devices* (Wiley, New York, 1981).
[34] C. S. Hwang, B. T. Lee, C. S. Chang, K. H. Lee, H.-J. Cho, H. Hideki, W. D. Kim, S. I. Lee, and M. Y. Lee, J. Appl. Phys. **85**, 287 (1999).
[35] J. F. Scott, K. Watanabe, A. J. Hartmann, and R. N. Lamb, Ferroelectrics **225**, 83 (1999).
[36] J. F. Scott, Jpn. J. Appl. Phys., Part 1 **38**, 2277 (1999).
[37] N. F. Mott, Proc. Cambridge Philos. Soc. **34**, 568 (1938).
[38] L.-S. Qiang, D.-Y. Tang, X. He, and H. H. Fu, Spectrosc. Lett. **34**, 159 (2001).
[39] P. S. Dobal, S. Bhaskar, S. B. Majumder, and R. S. Katiyar, J. Appl. Phys. **86**, 828 (1999).
[40] P. S. Dobal, R. R. Das, B. Roy, R. S. Katiyar, S. Jain, and D. C. Agrawal, J. Raman Spectrosc. **31**, 965 (2000).
[41] R. Naik, J. J. Nazarko, C. S. Flattery, U. D. Venkateswaran, V. M. Naik, M. S. Mohammed, G. W. Auner, J. V. Mantese, N. W. Schubring, A. L. Micheli, and A. B. Catalan, Phys. Rev. B **61**, 11367 (2000).
[42] E. C. S. Tavares, P. S. Pizani, and J. A. Eiras, Appl. Phys. Lett. **72**, 897 (1998).