Leakage current, ferroelectric and structural properties in Pb$_{1-x}$Ba$_x$TiO$_3$ thin films prepared by chemical route

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A R T I C L E   I N F O

Article history:
Received 19 November 2007
Received in revised form 27 June 2008
Accepted 4 July 2008

Keywords:
A. Thin films
B. Chemical synthesis
D. Electrical properties
D. Phase transition

A B S T R A C T

Single-phase perovskite structure Pb$_{1-x}$Ba$_x$TiO$_3$ thin films ($x = 0.30$, 0.50 and 0.70) were deposited on Pt/Ti/SiO$_2$/Si substrates by the spin-coating technique. The dielectric study reveals that the thin films undergo a diffuse type ferroelectric phase transition, which shows a broad peak. An increase of the diffusivity degree with the increasing Barium contents was observed, and it was associated to a grain decrease in the studied composition range. The temperature dependence of the phonon frequencies was used to characterize the phase transition temperatures. Raman modes persist above tetragonal to cubic phase transition temperature, although all optical modes should be Raman inactive. The origin of these modes was interpreted in terms of breakdown of the local cubic symmetry by chemical disorder. The absence of a well-defined transition temperature and the presence of broad bands in some interval temperature above FE–PE phase transition temperature suggested a diffuse type phase transition. This result corroborates the dielectric constant versus temperature data, which showed a broad ferroelectric phase transition in these thin films. The leakage current density of the PBT thin films was studied at different temperatures and the data follow the Schottky emission model. Through this analysis the Schottky barrier height values 0.75, 0.53 and 0.34 eV were obtained to the PBT70, PBT50 and PBT30 thin films, respectively.

1. Introduction

Lead barium titanate (PBT) thin films have attracted a lot of attention nowadays because of their good dielectric, ferroelectric and piezoelectric properties [1–6]. The role of dopants concentration, i.e., barium ions in the lead titanate (PT) has a strong influence in the dielectric, structural, microstructural properties as well as in the phase transition temperature in these ferroelectric materials [7–9]. It is also interesting to note that many ferroelectric materials exhibit relaxor behavior characteristics as a function of the dopant concentration by a maximum broad in the temperature dependence of the dielectric constant, and a strong frequency dispersion of the dielectric constant at temperatures around the phase transition temperature [10]. These materials show a relaxor-type phase transition. Lead magnesium niobate (PMN), lead zinc niobate (PZN) and their solid solutions with PT are the most widely relaxor materials studied [11–13].

Although, there have been several earlier investigations on the preparation of PBT by different techniques to obtain homogeneous ceramics, there has been very little effort to study and characterize the detailed dielectric properties in thin films. Most of the reports discuss only the synthesis and structural aspects of PBT thin films with few or no correlation with dielectric and structural properties as function of temperature [14–16]. Moreover, the knowledge phase transitions temperature in PBT thin films is considered an important key to fabricate several optical and electronic devices.

Xing et al. discussed the solid solution limit of PBT ceramics prepared by a state-solid reaction at high temperatures [15]. Fuflygin et al. [6] reported a study on electro-optic properties in Ba$_{1-x}$Pb$_x$TiO$_3$ thin films grown on R-Al$_2$O$_3$ substrates. Significant improvement of the thin films crystallinity and optical quality was observed. The thin films showed to be transparent at 350–2000 nm, indicating the possibility of its application in light controlling devices at wavelengths used in optical...
communication. Recently, Pillai et al. [17] reported a new sol–gel procedure incorporating diethanolamine as a chelating agent for the synthesis of a stable Pb0.3Ba0.7TiO3 precursor sol–gel. Highly oriented Pb0.3Ba0.7TiO3 films were obtained by a spin-coating technique on single-crystal MgO, after calcination at 600 °C.

However, to the best of our knowledge, there has been no report on the ferroelectric, structural behavior and the leakage current characteristics of PBT thin films prepared by soft chemical as a temperature function. In addition, leakage measurements are a crucial part of any electrical characterization of a ferroelectric device. A number of electric conduction mechanisms have been proposed for ferroelectric thin films, including ohmic conduction, space-charge-limited current (SCLC), Schottky emission, Poole–Frenkel emission and grain-boundary-limited conduction [18–21]. In spite of the leakage, current behavior of ferroelectric oxide thin films have been studied extensively in recent years, the transport mechanism of charge carriers is still not well understood.

It is well known that the interface barrier in a capacitor has a crucial influence on the dielectric properties including polarization, dielectric constant, dielectric loss and leakage current. Recently, Pabst et al. [22] reported results of transport on high quality, fully epitaxial BiFeO3 thin films grown via pulsed laser deposition on SrRuO3/DyScO3 (110) substrates. The authors suggest a Poole–Frenkel emission as the limiting leakage current mechanism which yields ionization energies of 0.65–0.8 eV. Calzada et al. [23] reported that leakage current mechanism of strontium bismuth tantalate (SBT) thin films on Pt/TiO2/Si(10 0) substrate are governed by a Schottky emission model, with a barrier height of 0.89 eV.

For comparison, a large number of researches have been focusing on the leakage current behavior of PZT, SBN, SBT and BST thin films [24–27]. In this paper, the temperature dependence of dielectric constant and Raman spectra in the study of phase transition of polycrystalline Pb1−xBaxTiO3 (PBT) thin films was studied. The current conduction mechanism based on the limited interface Schottky emission theory as well as the physical parameters involved were investigated.

2. Experimental procedure

The Pb0.7Ba0.3TiO3 (PBT70), Pb0.5Ba0.5TiO3 (PBT50) and Pb0.3Ba0.7TiO3 (PBT30) thin films studied in the present work were derived from a soft chemical process which details can be found in the literature [28,29]. The polymeric precursor solution was spin-coated on substrates [Pt (140 nm)/Ti (10 nm)/SiO2 (1000 nm)/Si] by a commercial spinner operating at 7000 rev/min for 30 s (spin-coater KW-4B, Chemat Technology) and 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 as following: 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 600 °C for 2 h for crystallization. The film thickness was controlled by adjusting the number of coatings meaning that the coating/drying operation was repeated until the desired thickness was obtained.

The thin films were structurally characterized by X-ray diffraction (XRD) (Cu Kα radiation) in the mode of 0–2θ scan and recorded on a Rigaku diffractometer (D/max-2400).

An atomic force microscopy—Digital Instruments Multimode Nanoscope IIIa (Santa Barbara, CA)—was used to obtain an accurate analysis of the sample surface and the evaluation of some parameters, such as roughness and mean grain size. The film thickness was measured by a thin film cross-section analysis made by SEM (Zeiss, DSM940A).

Electrical characterizations were carried out for PBT70, PBT50 and PBT30 thin films with 380, 330 and 300 nm thicknesses, respectively. The temperature dependent dielectric constant of the thin film was studied in metal–ferroelectric-metal (MFM) configuration through a Keithley 3330 (LCR) meter at a temperature range of 298–750 K. For these measurements, circular Au electrodes of approximately 4.9 × 10−2 Z m2 area were deposited, by evaporation process through a shadow mask, on the surfaces of the heat-treated films as top electrodes. The ferroelectric properties and capacitance–voltage curves were measured in a MFM configuration, using an HP4192A impedance/gain phase analyzer; hysteresis loop measurements were carried out using Radiant Technology equipment.

The Raman measurements were performed using a T-64000 Jobin–Yvon triple-monochromator coupled to a charge-coupled device (CCD) detector. An optical microscope with a 50X objective was used to focus the 514.5 nm line of Coherent Innova 90 Argon ion laser on the sample, keeping the power at 20 mW. An oven TMS 93 from Linkam Scientific Instruments LTD was used under the microscope for the measurements at the 298–748 K temperature range. A source-measuring unit (Keitlkey 237) was used to study the leakage current parameters of the thin films.

3. Results

The crystal structure of the thin films was examined by a Rigaku X-ray diffractometer with Cu Kα radiation. Fig. 1 shows that the thin film was well crystallized without any unexpected phases. By increasing the concentration of barium ions in the lattice, it can be observed a possible effect of the overlapping of the peaks (1 0 1)/(1 1 0), which has been attributed to the tetragonal transition. In addition, the AFM analysis showed a variation in the morphology of PBT70, PBT50 and PBT30 thin films as a function of the barium ions content (inset in Fig. 1) given that, with its increase, a slight reduction of the average grain size and the roughness (rms) was observed. Regarding the pinholes and microcracks, the thin films indicate a good microstructure for the different barium ions contents, which, with its increasing, makes...
this morphology smoother and denser. The average grain size and surface average roughness values are shown in Table 1.

The impact of substitution of the lead ions by barium ions on the ferroelectric properties of the Pb$_{1-x}$Ba$_x$TiO$_3$ thin films is illustrated in Fig. 2. The remanent polarization and coercive electric field decrease with increasing of the barium content. However, the thin films are assumed to be ferroelectric nature. Remanent polarization ($P_r$) and coercive field ($E_c$) values of the PBT70, PBT50 and PBT30 thin films were 13.03, 8.36, 3.68 and 58.90, 77.30, 47.74, respectively.

The dielectric constant ($\varepsilon$) was measured as a function of temperature for various compositions of the Pb$_{1-x}$Ba$_x$TiO$_3$ thin films at 10 kHz (see Fig. 3). Several interesting features are evident in the dielectric constant ($\varepsilon$) versus the temperature curves of Pb$_{1-x}$Ba$_x$TiO$_3$ thin films with different Ba$^{2+}$ concentrations. Qualitatively, disregarding the Ba$^{2+}$ concentrations, the strongly broadened dielectric peak indicates that the phase transition is of a diffuse type near the transition temperature. This is clearer in samples PBT50 and PBT30.

In addition, the order of the ferroelectric to paraelectric phase transition can be determined from the temperature dependence of the ferroelectric to paraelectric phase transition temperature, $T_0$, can be obtained directly. The fact that the Curie–Weiss temperature, $T_0$, is lower than the transition temperature, $T_C$, the first-order phase transition between the paraelectric and ferroelectric phases for the thin films is expected. Furthermore, for a diffuse transition, the following empirical modification of the Curie–Weiss Law was proposed to describe the diffuseness of the phase transition as [30]:

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_0} + (T - T_{\text{max}})^\gamma,$$

where $\gamma$ is the critical exponent, which is a measure of the degree of the diffuse transition, and $\varepsilon_0$ is a Curie–Weiss constant. For a sharp transition, $\gamma = 1$ and for a diffuse transition it lies in the range $1 < \gamma \leq 2$. The plot of $\ln(1/\varepsilon - 1/\varepsilon_0)$ versus $\ln(T - T_{\text{max}})$ at 10 kHz for different compositions is shown in Fig. 4. Linear relationships were observed. The values of $\gamma$ at 10 kHz were found to be 1.37, 1.73 and 1.82 for PBT70, PBT50 and PBT30 thin films, respectively. These data indicate that the transition is relatively diffuse, but the ferroelectric phase is not relaxor in these thin films. The observed broad curve behavior displayed by the thin film, unlike the bulk behavior, suggests that the smaller grain size of thin film relative to the bulk causes some type of strain between the grain–boundary interfaces, which is generally responsible for the observed transition. In addition, the broadened dielectric maximum for PBT50 and PBT30 thin films associated with large $\gamma$ values can be attributed mainly to the compositional fluctuation and structural disordering due to the arrangement of cations (Pb and Ba) in one or more crystallographic sites of the perovskite structure. These sites can act as additional spatial fluctuations of the Pb and Ba ions in the solid solution of PBT leading to the coexistence of nano-regions of different Curie temperatures.

In order to study the ferroelectric to paraelectric phase transition by Raman spectroscopy, Raman spectra of Pb$_{1-x}$Ba$_x$TiO$_3$ thin films were obtained at different temperatures and the results

![Fig. 2. Ferroelectric hysteresis loops of the Pb$_{1-x}$Ba$_x$TiO$_3$ thin films. The inset shows the dielectric constant-applied voltage curves.](image1)

![Fig. 3. Dielectric constant as a function of temperature at 10 kHz for Pb$_{1-x}$Ba$_x$TiO$_3$ thin films with different compositions.](image2)

![Table 1](image3)

<table>
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<th>Parameters</th>
<th>PBT70</th>
<th>PBT50</th>
<th>PBT30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average grain size (nm)</td>
<td>140</td>
<td>115</td>
<td>85</td>
</tr>
<tr>
<td>Roughness (nm)</td>
<td>17</td>
<td>13</td>
<td>6</td>
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![Table 2](image4)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>PBT70</th>
<th>PBT50</th>
<th>PBT30</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C$ (K)</td>
<td>2.38 x 10$^{-5}$</td>
<td>9.12 x 10$^{-6}$</td>
<td>2.42 x 10$^{-5}$</td>
</tr>
<tr>
<td>$T_0$ (K)</td>
<td>647</td>
<td>418</td>
<td>382</td>
</tr>
</tbody>
</table>
are showed in Fig. 5. The room temperature Raman spectra of all thin films are in agreement with the literature, showing all Raman active optical modes [31]. In the other hand, according to the selection rules, all optical modes must make Raman inactive above the transition temperature.

Increasing the temperature, the Raman modes in all thin films became broad and gradually lost intensity. However, some modes disappear completely at a certain temperature which can correspond to the ferroelectric to paraelectric phase transition one. Given that the soft mode belongs to E(1TO) symmetry, this behavior is most prominent for the lowest frequency Raman lines at 69 and 50 cm\(^{-1}\) for PBT70 and PBT50 thin films, respectively. Furthermore, it was not possible to follow the evolution of the soft mode for the PBT30 thin films, being B1+E mode used in this case. However, increasing temperatures causes frequency downshifts (E(1TO)), and finally its disappearance above the transition temperature can be clearly seen in Fig. 5. The downshifts are due to the instability of the E(1TO) mode in the paraelectric cubic phase. However, in all thin films, there is a persistence of phonon modes at temperatures above the transition temperature, which can be attributed to short-range structural disorder in the
paraelectric cubic phase. This disorder destroys the perfect cubic local symmetry and thus it allows Raman activity in the paraelectric phase, which seems to be a characteristic of the disordered paraelectric phase. In perovskite type compounds, this can be attributed to the disorder on A sites when at least two cations (Pb and Ba) with large difference in ionic radius of Ba\(^{2+}\) (0.253 nm) and Pb\(^{2+}\) (0.154 nm) occupy the same crystallographic site. Similar observation was reported by.

The phase transition temperature of Pb\(_{1-x}\)Ba\(_x\)TiO\(_3\) thin films from the characteristics changes in their Raman spectra near the phase transition by monitoring the softening of the E(1TO) modes (see Fig. 6) was also estimated. Due to the persistence of the broad bands in temperature intervals above phase transition, it is believed that the phase transition in Pb\(_{1-x}\)Ba\(_x\)TiO\(_3\) thin films is of diffuse nature and Ba concentration dependent.

This typical soft mode behavior is responsible for the ferroelectric to paraelectric phase transition. Furthermore, aiming determine the damping factor \(\gamma\) as a function of temperature, important information can be obtained by a detailed examination of the temperature dependence of the line shape of the soft mode in the light of the damped classical harmonic oscillator model. This information can be modeled according to following equation [32]:

\[
I(\omega) \propto \frac{kT \varepsilon(0)\varepsilon^2}{(\omega_{TO}^2 - \omega^2)^2 + \gamma^2 \omega^2},
\]

where \(I\) is the intensity, \(k\) is Boltzmann constant, \(T\) is the temperature, \(P_s\) is the spontaneous polarization, \(\varepsilon\) is the imaginary part of the dielectric constant and \(\gamma\) is the damping factor.

A computer fitting of Eq. (2) of the line shape was carried out and the damping factors \(\gamma\) were obtained for the soft mode E(1TO) as a function temperature, as it is displayed in Fig. 6. Concerning the damping factor, \(\gamma\), a marked increase was observed near the phase transition temperature. Such an increase of the damping was observed in a wide range of solid solution perovskite ferroelectrics for the soft mode E(1TO). A similar observation was reported by Yu et al. [33] in SrBi\(_2\)Ta\(_2\)O\(_9\) nano-particles and in PT thin films on sapphire, reported by Dobal et al. [34]. A different value to phase transition temperature was estimated from the temperature dependence of the damping factor using the damped classical oscillator model. Fu et al. [35] reported phonon mode behaviors similar to PbTiO\(_3\) thin films deposited on Pt/Si substrates where the phase transition temperature was estimated by damping factor.

The computer fitting using Eq. (2) for the obtained data, was carried out and \(\omega_{TO}^2\) could be obtained for the E(1TO) soft mode as a function temperature, as shown in Fig. 6. This typical E(1TO) soft mode behavior is responsible for the ferroelectric phase transition that could fade in the paraelectric cubic phase. However, in the case of PBT thin films, the persistence of phonon modes far beyond the transition temperature lies in a short-range structural disorder in the paraelectric cubic phase can be noticed. This disorder destroys the perfect cubic local symmetry and thus allows Raman activity in the paraelectric phase. Due to the persistence of the broad bands at temperature intervals above the phase transition, it is believed that the phase transition in PBT thin films is of diffuse nature. The significant changes of the Raman spectra and the vanishment of the E(1TO) soft mode indicated that the PBT70, PBT50 and PBT30 thin films underwent a ferroelectric-to-paraelectric phase transition at around 673, 548–573 and 498–523 K, respectively.

In addition, it is noticed that the lowest frequency peak, E(1TO) soft mode, disappears well below the Curie temperature, as obtained from the temperature and frequency dependence of the dielectric constant (see Fig. 3). This has been observed because Raman spectroscopy is highly sensitive to the local structure change and allows for the characterization of thin films with high spatial resolution, as compared to other techniques.

It is well established that no first-order Raman scattering is allowed by the symmetry for the ideal cubic paraelectric perovskite phase [36]. However, PBT thin films showed an intense Raman activity, characteristic of first-order scattering above the ferroelectric to paraelectric phase transition temperature, as evidenced by the temperature dependence of the Raman spectra (Fig. 5). Moreover, the broadbands have a tendency to hardening with increasing of temperature above the phase transition temperature. This behavior could be interpreted assuming that the wavevector selection rules break in the PBT thin films due to the disordering in lattice caused by the A-cation substitution. As a result, it induces the loss of the inversion center in the perovskite structure. This effect might produce the appearance of “forbidden” lines in a cubic paraelectric perovskite phase. Thus, a contribution to light scattering from some points in the Brillouin zone becomes possible. Consequently, the persistent weak Raman spectra that have been observed for the cubic paraelectric phase can be related to a phase transition considered as diffuse.

The conduction mechanism of the current through the ferroelectrics thin films has been often explained by the Schottky emission, space-charge-limited conduction and Poole–Frenkel
emission [20,37–40]. In Pt/PCT24/Au, Pt/SBT/Pt and Pt/PZT/Au capacitors, which have a layered perovskite type ferroelectric structure, the main conduction mechanism has been known to be Schottky emission [19,41,42]. To clarify the conduction mechanism of PBT70, PBT50 and PBT30 thin films, the Schottky emission dominantly operated in our thin films was investigated. The current–voltage characteristics were obtained at different diode temperatures for applied voltages up to 10 V and the results are plotted in Fig. 7. At higher field region, the current increased exponentially. The metal/PBT/metal structure usually constitutes a back-to-back Schottky diode. The current density in such system is given by

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

where $V$ is the applied voltage, $T$ is the temperature, $n$ is the ideality factor, $\phi_B$ is the Schottky barrier height and $A^*$ ($= 120 m/m_0$, $m_0$ is the free hole mass) is the Richardson constant.

As expected from the Schottky current emission theory, the current increases by increasing temperature as this thermally activated conduction is further enhanced by the applied field. Fig. 8 shows the relation of $\ln(I_0)$ versus $V^{1/2}$ for the high current emission measured at different temperatures. The logarithm of current ($\ln(I_0)$) was found to be linearly dependent on the square root of applied voltage in the interest region. This indicates that leakage is controlled at least by Schottky barrier limited conduction. In this sense, in Fig. 9 the $\ln(I_0/T^2)_{V=0}$ versus $1/T$ curves were plotted for the different PBT compositions (high field region). The Schottky equation provides a good fit to the data, as indicated by solid lines (Fig. 9). The barrier height and the Richardson constant $A^*$ can be calculated from the slope of the plot of $\ln(I_0/T^2)_{V=0}$ versus $1/T$. The preexponential factor of the fit is a measure of the Richardson constant, $A^*$. As shown in Fig. 9, the extracted value of $A^*$ is 0.022, 0.048 and 4.95 A/m² K² for PBT30, PBT50 and PBT70, respectively. From these curves, the barrier heights were evaluated from the slopes of the plots $\ln(I_0/T^2)_{V=0}$ versus $1/T$. In fact, the barrier height (at $V = 0$) reflects the Schottky barrier heights of 0.75, 0.53 and 0.34 eV for PBT70, PBT50, and PBT30 thin films, respectively, considering at least the thermionic emission only. Referring to this model, Pintilie et al. [20] experimentally observed in epitaxial PZT thin films the dominance of the Schottky emission at high temperatures. The authors reported value of 0.133 eV for the potential barrier at zero voltage. In the other

![Fig. 7. The characteristics of positive $I$–$V$ curves obtained at different temperatures for the Pb$_{1-x}$Ba$_x$TiO$_3$ thin films.](image-url)
hand, McCormick suggested that the leakage mechanism combined characteristics of Poole–Frenkel and Schottky emission controlled process to polycrystalline BaTiO3 thin films prepared by hydrothermal process [39] with barrier height even 0.64 eV and trap depth 0.72 eV for Schottky and Poole–Frenkel models, respectively. Wu and Shy [43] reported that the current emission of the BZT12 thin films deposited on LaNiO3 followed the relation of Schottky emission, and a Schottky barrier height of 0.73 eV was evaluated from the temperature dependence of the current emission. Kim and Kim reported the Schottky barrier height for Bi3.25La0.75Ti3O13 (BLT) thin films on Pt/Ti/SiO2/Si substrate to be approximately 1.06 eV [44]. Recently, Zubko et al. [45] have analyzed leakage current mechanism of PbZr0.4Ti0.6O3 thin films capacitors with Pt bottom and Ir/IrO2 top electrodes. The authors concluded that Poole–Frenkel emission of carriers from traps, which energy was found to be 1.0 eV, was the most likely conduction mechanism. Wu et al. [46] reported leakage current characteristics of Pt/Bi3.25La0.75Ti3O13/Pt thin films capacitors as a function of temperature. Schottky emission dominated the leakage current above the ohmic conduction regime with a barrier height of 0.84 eV.

In addition, Scott et al. reported values of the Schottky barrier (at $V = 0$) for SrBiTa2O9 (SBT), Ba$_{1-x}$Sr$_x$TiO3 (BST) and PbZr0.4Ti0.6O3 (PZT) to be about 1.6, 1.62 and 1.5 eV, respectively [47]. Moreover, Das et al. studied the leakage characteristics of SrBiTi2O6 thin films at elevated temperatures and the data were fitted by the Schottky emission model [48]. The Schottky barrier heights of the films on Pt and LaNiO3 substrates were estimated to be 1.27 and 1.12 eV, respectively.

![Figure 8](image1.png)  
Fig. 8. Variation of $\ln(I_0)$ as a function of $V^{1/2}$ for the Pb$_{1-x}$Ba$_x$TiO$_3$ thin films at different temperature.

![Figure 9](image2.png)  
Fig. 9. Plot of $\ln(I_0/T^2)$ versus $1/T$ for Pb$_{1-x}$Ba$_x$TiO$_3$ thin films in which the Schottky barrier height was estimated.
4. Conclusions

In summary, the dielectric study revealed that polycrystalline PBT70, PBT50 and PBT30 thin films grown by a soft chemical processing underwent a diffuse type of ferroelectric phase transition. A higher diffuse character was observed in the PBT50 and PBT30 compositions when compared to the PBT70. This behavior was attributed to a grain smaller size and local structural disorder effects. The Raman scattering was used to probe the phase transition. The transition temperature was estimated using the disappearance and wavenumber variation of the soft mode belonging to the tetragonal phase. The fact that Raman broad bands are seemed to persist far beyond the transition temperature in the thin film samples was also found. This was attributed to the breakdown of selection rules due to the presence of disorder in these materials can be controlled by the Ba concentration.

Acknowledgment

The authors gratefully acknowledge the financial support of the Brazilian financing agencies FAPESP/CEPID. FAPESP process no. 06/5926-4.

References