

**Electromechanical properties of calcium bismuth titanate films: A potential candidate for lead-free thin-film piezoelectrics**

A. Z. Simões, M. A. Ramírez, A. Ries, J. A. Varela, E. Longo, and R. Ramesh

Citation: [Applied Physics Letters](#) **88**, 072916 (2006); doi: 10.1063/1.2172071

View online: <http://dx.doi.org/10.1063/1.2172071>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/88/7?ver=pdfcov>

Published by the [AIP Publishing](#)

---



## Re-register for Table of Content Alerts

Create a profile.



Sign up today!



## Electromechanical properties of calcium bismuth titanate films: A potential candidate for lead-free thin-film piezoelectrics

A. Z. Simões,<sup>a)</sup> M. A. Ramírez, A. Ries, J. A. Varela, and E. Longo  
 Departamento de Química, Universidade Estadual Paulista, UNESP, P. O. Box 355, 14801-970,  
 Araraquara, SP, Brazil

R. Ramesh  
 Department of Materials Science and Engineering and Department of Physics, University of California,  
 Berkeley, California 94720

(Received 13 September 2005; accepted 11 January 2006; published online 17 February 2006)

CaBi<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> (CBTi144) thin films were evaluated for use as lead-free thin-film piezoelectrics in microelectromechanical systems. The films were grown by the polymeric precursor method on (100) Pt/Ti/SiO<sub>2</sub>/Si substrates. The *a/b*-axis orientation of the ferroelectric film is considered to be associated with the preferred orientation of the Pt bottom electrode. The *P<sub>r</sub>* and *E<sub>c</sub>* were 14 μC/cm<sup>2</sup> and 64 kV/cm, respectively, for a maximum applied field of 400 kV/cm. The domain structure was investigated by piezoresponse force microscopy. The film has a piezoelectric coefficient, *d*<sub>33</sub>, equal to 60 pm/V and a current density of 0.7 mA/cm<sup>2</sup>. © 2006 American Institute of Physics. [DOI: 10.1063/1.2172071]

Recently, more and more efforts are being made to develop nontoxic lead-free piezoelectric materials. Bismuth-layered ferroelectrics are considered to be candidate materials.<sup>1</sup> CaBi<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> (CBTi144) is a member of the Aurivillius family, (Bi<sub>2</sub>O<sub>2</sub>)<sup>2+</sup>(A<sub>*n*-1</sub>B<sub>*n*</sub>O<sub>3*n*+1</sub>)<sup>2-</sup>, in which A represents mono-, di-, tri-valent ions and B represents tetra-, penta- or hexa-valent ions. The *n* value is the number of stacking oxygen octahedrons along the *c* axis in one crystal unit cell, and is equal to 4. For practical applications, a large piezoelectric coefficient is desired.<sup>2,3</sup> CBTi144 is characterized by its high Curie point of about 790 °C and is therefore expected to be useful for special applications at relatively high temperatures.<sup>4</sup> Compounds in this family have anisotropic ferroelectricity, which is strongly associated with the crystal structure, especially the compounds with *n* equal to an even number which have no polarization along the *c* axis because there is a mirror plane perpendicular to the axis.<sup>5</sup> The polarization of the compounds is along the *a* axis. Therefore, thin films with *a*-axis orientation are preferred for use in many kind of devices, such as ferroelectric random access memories, piezoelectric microactuators, and resonators.

Among various methods such as metalorganic chemical vapor deposition, pulsed laser deposition and sol gel, the polymeric precursor method has advantages such as the possibility of working in aqueous solutions with high stoichiometry control. Moreover, it is a low-temperature process and a cost-effective method due to inexpensive precursors and equipments.<sup>6</sup>

In the present work, we describe the fabrication and characterization of polar-axis-oriented CBTi144 films without any nucleation layer by the polymeric precursor method. Calcium citrate (Synth), titanium isopropoxide (Hulls AG) and bismuth nitrate (Aldrich) were used as raw materials. The precursor solutions of calcium, bismuth and titanium were prepared by adding the raw materials to a mixture of

ethylene glycol and concentrate aqueous citric acid under heating and stirring. The molar ratio of metal: citric acid: ethylene glycol was 1:4:16. The viscosity of the resulting solution was adjusted to 20 cP by controlling the water content using a Brookfield viscosimeter. The CBTi144 thin films were spin coated on Pt/Ti/SiO<sub>2</sub>/Si substrates by a commercial spinner operating at 5000 rpm for 30 s (spin coater KW-4B, Chemat Technology). The thin films were annealed at 700 °C for 2 h in a conventional furnace. Through this process, we have obtained thickness values of about 310 nm for CBTi144, reached by repeating the spin-coating and heat treatment cycles. Phase analysis was performed at room temperature by x-ray diffraction (XRD) in Bragg-Brentano geometry (Rigaku 2000) at CuK<sub>α</sub> radiation. Furthermore, topography and thickness were examined using atomic force microscopy (AFM) (Digital Instruments, Nanoscope IV) and scanning electron microscopy (Topcom SM-300), respectively. The top Pt electrodes were prepared by photolithography with 8\*10<sup>-4</sup> mm<sup>2</sup> dot area. The AFM module is also capable of providing piezoresponse force microscopy (PFM) characterization of polarized region ferroelectric films. When an external ac voltage is applied across a ferroelectric film through the tip, the region under the tip will vibrate with the applied voltage due to the converse piezoelectric effect, Δ*Z*(*t*) = ±*d*<sub>33</sub>*V* sin(*ωt*), where Δ*Z* is the longitudinal displacement, *d*<sub>33</sub> the piezoelectric coefficient and *V* amplitude of the ac voltage, respectively. This small displacement can be detected by AFM with a standard lock-in technique. A silicon cantilever with a tip radius less than 40 nm, a force constant of 0.15 N/m, and a resonance frequency around 12 kHz, was coated with Ti and Pt for electrical conductivity. A function generator (Hewlett-Packard, model 33120A) produced an ac field of 1.5 V to induce the converse piezoelectric response and also served as the reference signal for the lock-in amplifier. We selected a dc field of 12 V to ensure a high fraction of local domain switching.<sup>7</sup> Such a poling process should improve the piezoelectric properties. To reduce the interference of surface roughness, an ac field with a frequency far from the resonant frequency of the cantilever was selected

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: alezipo@yahoo.com

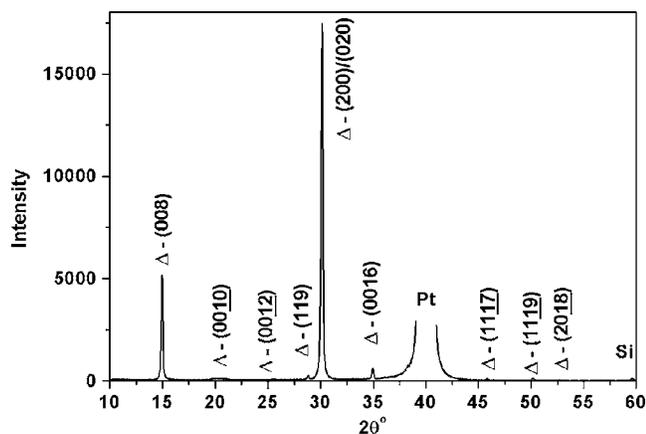


FIG. 1. X-ray diffraction for CBTi144 thin film.

for domain visualization. Artifacts could be obtained by the clamping effect due to the substrate, which leads to the significant decrease in the effective longitudinal piezoelectric coefficient. Also if the force constant of the cantilever is too low, for some instants an air gap between the tip and the sample may arise that lowers the actual voltage drop in the sample. The ferroelectric properties of the capacitors were examined by a Radiant Technology Tester RT6000 A in a virtual ground mode.

Figure 1 shows the XRD pattern of a CBTi144 thin film annealed at 700 °C for 2 h. CBTi144 films on the platinum coated silicon substrates showed a high intensity of the (200)/(020) diffraction line compared to the other lines, although the (200) and (020) diffraction lines could not be distinguished from each other. The characteristic orientation is considered to be due to good matching of atomic arrangements in CBTi144 (100)/(010) and underlying Pt planes. The characteristic peak for platinum coated silicon (100) substrates was observed in the range of  $38^\circ < 2\theta < 41^\circ$  and no preferred orientation of CBTi144 films was noticed. Since the lattice constants of (a) [or (b)] and (c) of the CBTi144 film is close to 0.5417 and 4.086 nm, the lattice mismatches between the ferroelectric phase and Pt lattice were given as remarkably small as 1.1% and 4.9%, respectively. The characteristic (100)/(010) orientation of the CBTi144 film is based on the good lattice matching of CBTi144 (001) with Pt (100) planes. Ferroelectricity of the calcium bismuth titanate thin films was observed with remanent polarization equal to  $14 \mu\text{C}/\text{cm}^2$  and coercive field equal to  $64 \text{ kV}/\text{cm}$  (Fig. 2).

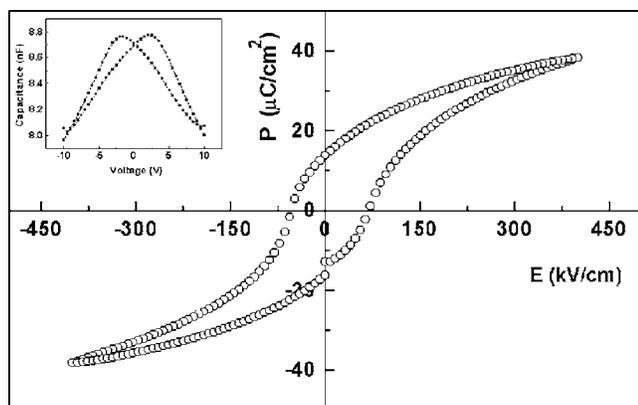


FIG. 2. P-E hysteresis loop for CBTi144 thin film. Inset shows the corresponding C-V curve.

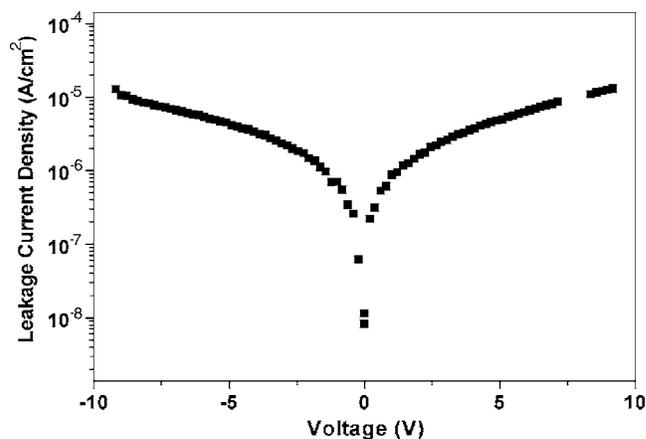


FIG. 3. Leakage current density as a function of applied voltage for CBTi144 thin film.

Almost absent is the imprint effect which causes a significant shift along the electric field axis towards the positive side. This indicates that our films present only a very small concentration of space charges at the electrode-film interface. The  $P_r$  and  $E_c$  values were improved compared with the values obtained for CBTi144 thin films with random orientation.<sup>8</sup> The higher  $P_r$  value suggests that the (100) orientation is preferred rather than the (010) orientation with respect to the present CBTi144 film. However, our  $P_r$  values are much lower than those found by Kato *et al.*<sup>2,3</sup> ( $25 \mu\text{C}/\text{cm}^2$ ). This can be explained with the lower grain size of 100 nm of our films. Kato *et al.* prepared their films by sol-gel method and reported grain sizes of 200 nm. The inset of Fig. 2 illustrates the C-V curve for CBTi144 films obtained at 100 kHz and dc sweep voltage from +10 to -10 V. The capacitance dependence on the voltage is strongly nonlinear, confirming the ferroelectric properties of the film resulting from the domain switching. The C-V curve also indicates the symmetry in the maximum capacitance values that can be observed in the vicinity of the spontaneous polarization switching. This confirms that the films contain few movable ions or charge accumulation at the film-electrode interface. A typical leakage current characteristic for a ferroelectric thin film is given in Fig. 3. Here, the measured logarithmic current density ( $\log J$ ) versus the voltage (V) is shown. It can be seen that there are two clearly different regions. The current density increases linearly with the external electric field in the region of low electric field strengths, suggesting an ohmic conduction. This ohmic behavior occurs in insulating films as long as the films are quasi neutral, that means, as long as the bulk generated current in the film exceeds the current due to injected free carriers from the electrode. This current would be due to the hopping conduction mechanism in a low electric field, because thermal excitation of trapped electrons from one trap site to another dominate the transport in the films. At higher field strengths the current density increases exponentially, which implies that at least one part of the conductivity results from Schottky or Poole-Frenkel emission mechanisms. The leakage current density at 1.0 V is equal to  $10^{-7} \text{ A}/\text{cm}^2$ . The low current density is caused by a low defect concentration, particularly by a small derivation from ideal oxygen stoichiometry due to the oriented growth in the  $a/b$ -axis direction. Figure 4 shows the out-of-plane [inset (a)] and in-plane [inset (b)] piezoresponse images of the as-grown films

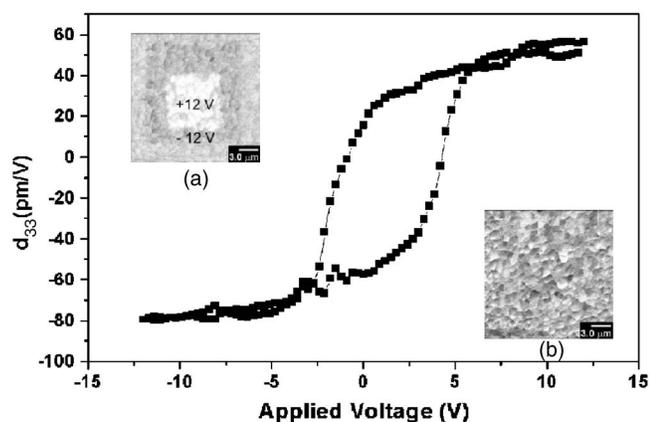


FIG. 4. Piezoresponse loop of CBTi144 thin film. Inset shows the out-of-plane (a) and in-plane (b) PFM images.

after applying a bias of  $-12$  V, on an area of  $2$  mm  $\times$   $2$  mm, and then an opposite bias of  $+12$  V in the central  $1$  mm  $\times$   $1$  mm area. To obtain the domain images of the CBTi144 films, a high voltage in order to exceed the coercive field was applied during scanning. The contrast in these images is associated with the direction of the polarization.<sup>7</sup> The white regions in the out-of-plane PFM images correspond to domains with the polarization vector oriented toward the bottom electrode hereafter referred to as down polarization [Fig. 4, inset (a)] while the dark regions correspond to domains oriented upward referred to as up polarization.

The  $d_{33}(V)$  hysteresis loop is also given in Fig. 4. The maximum  $d_{33}$  value,  $\approx 65$  pm/V, approaches the reported value for a CBTi144 single crystal.<sup>9</sup> The enhancement of polarization could be caused by the  $a/b$ -axis orientation of the ferroelectric films due to the preferred orientation of the Pt substrates. As can be seen, the hysteresis loop shows an offset in the vertical direction which can be caused by non-switchable domains pinned near the electrode-film interface.<sup>10</sup> A vertical shift in the  $d_{33}$  hysteresis loop can also be associated with different materials of the bottom electrode and the PFM tip. However, in our measurements, both materials were the same. The presented values reported for our

CBTi144 films suggest that this material can be considered as a viable alternative for lead-free piezo-ferroelectric devices. In comparison with other lead-free ferroelectrics,  $65$  pm/V is higher than the  $d_{33}$  value of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> films<sup>11</sup> ( $17$  pm/V) and Nd-doped Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub><sup>11</sup> ( $38$  pm/V). On the other hand, this value is much lower than that obtained for sol-gel-derived films deposited onto Pt foil which present an extremely high piezoelectric coefficient of  $d_{33}$ , equal to  $180$  pm/V.<sup>12</sup>

In conclusion, polar-axis-oriented CBTi144 films were fabricated on Pt substrate using a polymeric precursor method. The  $700$  °C annealed CBTi144 thin films showed polar-orientation and exhibited P-E hysteresis loops. The  $a/b$ -axis orientation of the ferroelectric films is considered to associate with the preferred orientation of the Pt substrate. The films showed improved ferro- and piezoelectric properties. The  $P_r$ ,  $E_c$ , and  $d_{33}$  values were enhanced compared to those of the CBTi144 thin film with random orientation. The polar-axis-oriented CBTi144 films would open possibilities for devices as Pb-free piezoelectric materials.

The authors gratefully acknowledge the financial support of the Brazilian agencies FAPESP, CNPq and CAPES.

- <sup>1</sup>K. Kato, K. Suzuki, D. Fu, K. Nishizawa, and T. Miki, Appl. Phys. Lett. **81**, 3227 (2002).
- <sup>2</sup>K. Kato, D. Fu, K. Suzuki, K. Tanaka, K. Nishizawa, and T. Miki, Appl. Phys. Lett. **84**, 3771 (2004).
- <sup>3</sup>K. Kato, K. Tanaka, K. Suzuki, T. Kimura, K. Nishizawa, and T. Miki, Appl. Phys. Lett. **86**, 112901 (2005).
- <sup>4</sup>L. Korzanova, Ferroelectrics **134**, 175 (1992).
- <sup>5</sup>W. Xu, W. I. Lee, T. Ko, and J. K. Lee, Appl. Phys. Lett. **82**, 3496 (2003).
- <sup>6</sup>A. Z. Simoes, A. Ries, F. M. Filho, J. A. Varela, and E. Longo, Appl. Phys. Lett. **85**, 5962 (2004).
- <sup>7</sup>A. Gruverman, O. Auciello, and H. Tokumoto, Annu. Rev. Mater. Sci. **28**, 101 (1998).
- <sup>8</sup>K. Kato, K. Suzuki, K. Nishizawa, and T. Miki, Appl. Phys. Lett. **78**, 1119 (2001).
- <sup>9</sup>D. Fu, K. Suzuki, and K. Kato, Jpn. J. Appl. Phys., Part 1 **42**, 5994 (2003).
- <sup>10</sup>A. L. Kholkin, E. L. Colla, A. K. Tagantsev, D. V. Taylor, and N. Setter, Appl. Phys. Lett. **96**, 2577 (1996).
- <sup>11</sup>H. Maiwa, N. Iizawa, D. Togawa, T. Hoyashi, W. Sakamoto, M. Yamada, and S. Hirano, Appl. Phys. Lett. **82**, 1760 (2003).
- <sup>12</sup>D. Fu, K. Suzuki, and K. Kato, Jpn. J. Appl. Phys., Part 1 **43**, 3519 (2004).