

Microstructure and dielectric properties of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ films grown on LaAlO_3 substrates

Y. Gim,^{a)} T. Hudson, Y. Fan, C. Kwon,^{b)} A. T. Findikoglu, B. J. Gibbons, B. H. Park, and Q. X. Jia^{c)}

Superconductivity Technology Center, Mail Stop K763, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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We report a systematic study of the microstructure and dielectric properties of barium strontium titanate, $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$, films grown by laser ablation on LaAlO_3 substrates, where $x = 0.1-0.9$ at an interval of 0.1. X-ray diffraction analysis shows that when $x < 0.4$, the longest unit-cell axis is parallel to the plane of the substrate but perpendicular as x approaches 1. Dielectric constant versus temperature measurements show that the relative dielectric constant has a maximum value and that the peak temperatures corresponding to the maximum relative dielectric constant are about 70°C higher when $x \leq 0.4$ but similar when $x > 0.4$, compared with the peak temperatures of the bulk $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$. At room temperature, the dielectric constant and tunability are relatively high when $x \leq 0.4$ but start to decrease rapidly as x increases. © 2000 American Institute of Physics. [S0003-6951(00)01534-5]

Recently, solid solutions of barium titanate and strontium titanate, $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ (BST), have been extensively studied because of their potential applications for various microelectronic devices. Aside from the composition of $x = 1$, BST is a ferroelectric material with a Curie temperature that decreases almost linearly with increasing x . BST possesses a wide range of dielectric constants varying from a few hundred to thousands depending on the Ba/Sr ratio, the grain size, and the temperature. In addition, it exhibits a large tunability of the dielectric constant upon application of a dc electric field near the Curie temperature.¹⁻⁵ These properties make BST an attractive material for storage capacitors in next-generation dynamic random access memories and also in electrically tunable microwave devices (i.e., tunable filters, phase shifters, etc.).

For electrically tunable microwave devices with a coplanar waveguide structure, BST is used as an active dielectric layer in thin-film form.¹ To achieve a high dielectric constant and a low dielectric loss tangent ($\tan \delta$), the BST film is usually grown epitaxially on single-crystal substrates such as LaAlO_3 [(LAO) $a = 0.3793$ nm, $\alpha = 1.1$ ppm/ $^\circ\text{C}$], which has a comparatively small dielectric constant (≈ 25) and a low dielectric loss (loss tangent $< 10^{-4}$), both necessary for microwave applications.^{1,4,5} The choice of the Ba/Sr ratio in the BST dielectric layer largely depends on intended operating temperature, as the maximum tunability is typically achieved near the Curie temperature (which varies with Ba/Sr ratio). As we will describe below, however, such extrapolation from bulk to thin film is not trivial because of significantly different stresses and defects which films might possess.

When an epitaxial BST film is grown on a single-crystal

LAO substrate, the lattice mismatch and the difference in the thermal expansion between the film and the substrate introduce residual stresses within the film. One effect of these stresses is to elongate and/or shorten the unit-cell dimensions of the film, compared with those of the bulk. In most epitaxial oxide thin films, such distortions usually cause changes in the electrical properties of the films (again, compared to the bulk). In light of this, a systematic study of the structural and dielectric properties of BST thin films is necessary for the development and optimization of tunable microwave devices based on BST.

Here, we report on a systematic study of the structures and dielectric properties of BST films grown on LAO, where $x = 0.1-0.9$ at an interval of 0.1. We have found that the c axis is elongated for all x values; by crystallographic convention we define the c axis as the longest unit-cell lattice axis ($c > a = b$) in the tetragonal structure. The direction of the c axis is parallel to the plane of the substrate when $x < 0.4$ but normal to the substrate plane as x approaches 1.0. From temperature-dependent relative dielectric constant (ϵ_r) measurements, we have found that the ϵ_r has a maximum and the temperature corresponding to the maximum decreases as x increases. By comparing the maximum temperatures for the films to those measured for bulk samples of the same composition, we have found that the peak temperatures for the films are about 70°C higher when $x \leq 0.4$ but similar when $x > 0.4$. At room temperature, the $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ film exhibits the highest relative dielectric constant (≈ 1100) and tunability ($\approx 37\%$) with an applied dc electric field of about 40 kV/cm.

We used pulsed-laser deposition to grow 300-nm-thick epitaxial BST films on 0.5-mm-thick LAO substrates which are commercially available from Lucent Technology. To grow films with various Ba/Sr ratios, we used a series of sintered stoichiometric ceramic targets of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$, where $x = 0.1-0.9$ at an interval of 0.1. To eliminate other deposition variables, we kept the same conditions for film

^{a)}Currently with Jet Propulsion Laboratory, Pasadena, CA 91109.

^{b)}Currently with Department of Physics and Astronomy, California State University-Long Beach, Long Beach, CA 90840.

^{c)}Author to whom correspondence should be addressed; electronic mail: qxjia@lanl.gov

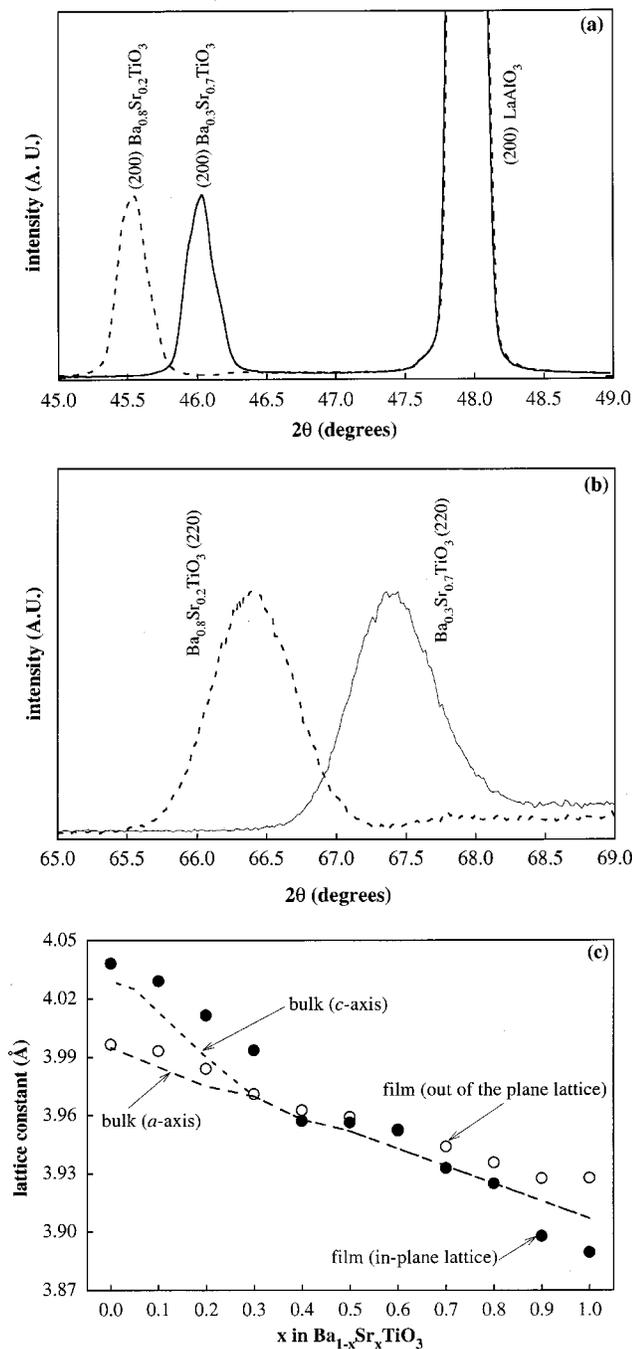


FIG. 1. (a) Normal ($\chi \approx 90^\circ$) and (b) tilted ($\chi \approx 45^\circ$) x-ray 2θ scans of the $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ (dotted line) and $\text{Ba}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ (solid line). (c) The in-plane and out-of-plane lattice constant vs x in $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ for film and bulk. Bulk data are from Ref. 6. Open circles in (c) represent the out-of-plane lattice constants of the BST films calculated based on the x-ray diffraction measurements.

growths: a deposition temperature of 800°C and an oxygen pressure of 200 mTorr. Such conditions were used for the growth of high-quality BST epitaxial films in our earlier studies.¹ Following the deposition, the films were cooled to room temperature in an oxygen pressure of 300 Torr without any further thermal treatment.

To study the dependence of the lattice constants of the BST films on x in $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$, we performed x-ray $\theta-2\theta$ scans using a SIEMENS D5000 four-circle x-ray diffractometer. Figures 1(a) and 1(b) show the typical sections of normal ($\chi \approx 90^\circ$) and tilted ($\chi \approx 45^\circ$) 2θ scans of the BST

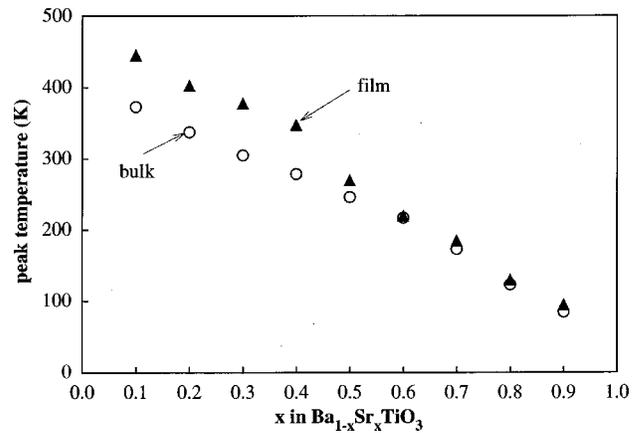


FIG. 2. Characteristic temperature vs x in $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ for film (filled triangle) and bulk (open circle). The characteristic temperatures of the bulk are from Ref. 10.

films, respectively; here, we have chosen the $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ (dotted curve) and $\text{Ba}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ (solid curve) films as examples. As a first approximation, we are able to fit each BST peak in Fig. 1(a) using a single Lorentzian curve that has three parameters: peak intensity, peak position, and peak broadening. Both BST peaks in Fig. 1(a) have a peak broadening of 0.1° and their peak positions are determined very accurately in the 2θ axis.

For the BST diffraction peaks in Fig. 1(b), unlike the diffraction peaks in Fig. 1(a), neither peak could be fitted by using a single Lorentzian curve even with a relatively large peak broadening. That is, attempts to model these peaks by optimization of the intensity and peak breadth always resulted in fits that were much too narrow compared to the experimental data below the half maximum. Instead, each diffraction peak was best fitted using two Lorentzian curves with similar peak intensities, indicating that the films have two different in-plane lattice constants. It is possible to have two different in-plane lattice constants if the c axis is in the plane; one for the c axis and the other for b axis. By taking the average of these two peak positions in the 2θ axis, we have calculated in-plane lattice constants and plotted them (represented by solid circles) in Fig. 1(c). For comparison, we also plot the a - and c -axis lattice constants of bulk BST.⁶

It is interesting to note that when $x < 0.4$, the in-plane lattice constant is larger than the out-of-plane lattice constant and changes in a similar way as do the c -axis lattice constants of bulk BST. If we define the c axis as the longest unit-cell lattice axis ($c > a = b$ for a tetragonal structure), the results suggest that when $x < 0.4$ the c axis lies in the plane of the substrate and the films are a -axis oriented. However, when $0.4 \leq x \leq 0.6$, the in-plane and out-of-plane lattice constant values are very close to each other. This implies that the crystal structures of the films are very close to cubic, as in bulk BST. Nevertheless, as x approaches 1.0, the in-plane lattice constant becomes smaller than the out-of-plane lattice constant. As a result, BST films with $x = 0.9$ and 1.0 are structurally tetragonal although their bulk counterparts are not. This is in agreement with recent work where transmission electron microscopy showed that structural distortion of SrTiO_3 film causes the out-of-plane lattice to be elongated and the in-plane lattice to shorten.⁷ The tetragonal distortion

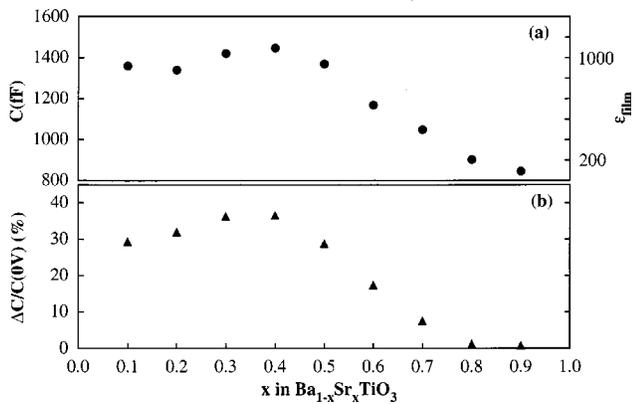


FIG. 3. (a) Capacitance and (b) tunability vs x in $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ films at room temperature.

was also observed for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ films using different oxygen pressures during deposition.⁸

To investigate the temperature-dependent dielectric properties of our BST films, we have fabricated coplanar capacitors using gold as the electrode. We first measured the capacitance and then calculated the dielectric constant using a simplified coplanar waveguide model.⁹ It was found that the dielectric constant has a maximum and that the peak temperature (T_p) corresponding to this maximum dielectric constant decreases with increasing x . The T_p of the BST films and bulk BSTs (Ref. 10) are represented by the filled triangle and open circle in Fig. 2, respectively. As shown in Fig. 2, they, however, have a similar dependence on x for $0.4 < x \leq 1$. Below 0.4, the T_p of the films is about 70 °C higher than that of the bulk. We would also like to point out that the degree of broadening of the peak in the temperature dependence of the dielectric constant decreases slightly with x . However, the broadening is not only a function of chemical composition, it is also strongly affected by the microstructural properties of the films, including the stress and grain size.

Figure 3(a) shows a plot of the room-temperature capacitance and dielectric constant versus x for $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ films measured at 1 MHz. The measured capacitance includes a substrate contribution of 750 fF. The dielectric constants of the BST films are shown on the right of Fig. 3(a). When $x \leq 0.4$, the dielectric constant is relatively high and shows a weak dependence on x . However, as x increases over 0.4, the dielectric constant shows a strong dependence on x and rapidly decreases. To test the tunability of the BST films at room temperature, we have measured the capacitance at dc bias voltages of 0 and 40 V (the maximum surface electric field is 40 kV/cm), respectively. Figure 3(b) shows the tunability, $[C(0\text{ V}) - C(40\text{ V})]/C(0\text{ V}) \times 100\%$ vs x . The tunability is around 30% when $x < 0.4$ but starts to decrease rapidly as x increases over 0.4. Among the BST films, the $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ film exhibits the highest dielectric constant (~ 1100) and tunability ($\approx 37\%$) at room temperature.

It will be interesting to study the origin of the T_p shift in the BST films. For single-crystal BaTiO_3 (BTO), the Curie temperature can be increased or decreased from the intrinsic

value (120 °C) by applying external stress. For example, when a pressure is applied in such a way that one of the BTO axes is allowed to expand (or the crystal favors tetragonality), the Curie temperature increases.^{11,12} On the other hand, when the unit-cell dimensions of the BTO are forced to shrink by applying a hydrostatic pressure, the Curie temperature decreases.¹³ For other bulk Ba/Sr composition ratios, such comprehensive data are not available. However, as a first approximation, we can expect that the dependence of the Curie temperature on the types of applied stresses should be qualitatively similar, although the amount of change in the Curie temperature may depend on the Ba/Sr ratio for the same value of an applied stress. From the previous structural analysis, we know that the c -axis lattice is elongated for all compositions and, therefore, expect that the T_p of the BST films will increase compared with those of bulk BSTs. Figure 2 does show that the T_p of the BST films is about 70 °C higher when $x \leq 0.4$. In this case, it is possible that the residual stress is larger due to the larger mismatch in lattice constant between the film and substrate. Perhaps another explanation is that the stress is likely to be relieved because of this larger mismatch. More studies are needed to resolve this issue. However, when $x > 0.4$ the T_p of the films are almost unchanged. One observation is that the response of the T_p to a structural change is not so sensitive as x increases over 0.4. For example, even though the crystal structure of the BST film of $x = 0.9$ shows a rather large deviation from the bulk's cubic structure [see Fig. 1(c)], the T_p of the film is very close to that of the bulk.

In conclusion, we have studied the microstructure and dielectric properties of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ films grown by laser ablation on LAO substrates, where $x = 0.1 - 0.9$ at an interval of 0.1. When $x \leq 0.4$, the c axis lies in the plane of the substrate. The characteristic temperature, at which the relative dielectric constant has a maximum value, is about 70 °C higher than that of bulk BST. However, for $x > 0.4$, the c axis is normal to the plane of the substrate and the characteristic temperature of the films is very close to that of bulk BST.

¹A. T. Findikoglu, Q. X. Jia, D. W. Reagor, and X. D. Wu, *Microwave Opt. Technol. Lett.* **9**, 306 (1995).

²R. A. Chakalov, Z. G. Ivanov, Yu. A. Boikov, P. Larsson, E. Carlsson, S. Gevorgian, and T. Claesson, *Physica C* **308**, 279 (1998).

³H. C. Li, W. D. Si, A. D. West, and X. X. Xi, *Appl. Phys. Lett.* **73**, 190 (1998).

⁴I. Takeuchi, H. Chang, C. Gao, P. G. Schultz, X. D. Xiang, R. P. Sharma, M. J. Downes, and T. Venkatesan, *Appl. Phys. Lett.* **73**, 894 (1998).

⁵C. L. Chen, H. H. Feng, Z. Zhang, A. Brazdeikis, Z. J. Huang, W. K. Chu, C. W. Chu, F. A. Miranda, F. W. Van Keuls, R. R. Romanofsky, and Y. Liou, *Appl. Phys. Lett.* **75**, 412 (1999).

⁶M. McQuarrie, *J. Am. Ceram. Soc.* **38**, 444 (1955).

⁷L. Ryen, E. Olsson, L. D. Madsen, X. Wang, C. N. L. Edvardsson, S. N. Jacobsen, U. Helmerson, S. Rudner, and L.-D. Wermlund, *J. Appl. Phys.* **83**, 4884 (1998).

⁸W. J. Kim, W. Chang, S. B. Qadri, J. M. Pond, S. W. Kirchoefer, D. B. Chrisey, and J. S. Horwitz, *Appl. Phys. Lett.* **76**, 1185 (2000).

⁹S. S. Gevorgian, *Electron. Lett.* **30**, 1236 (1994).

¹⁰G. A. Smolenskii and K. I. Rozgachev, *Zh. Tekh. Fiz.* **24**, 1751 (1954).

¹¹F. Jona and G. Shirane, *Ferroelectric Crystals* (Dover, New York, 1993), Chap. IV.

¹²P. W. Forsbergh, Jr., *Phys. Rev.* **93**, 686 (1954).

¹³W. J. Merz, *Phys. Rev.* **77**, 52 (1950).