Local hardening of Raman phonons in $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ thin films deposited by r.f. sputtering

O Zelaya-Angel$^{1,3}$, M Melendez-Lira$^1$, J Reséndiz-Muñoz$^2$, J I. Fernández-Muñoz$^{3,6}$ and F Caballero-Briones$^4$

$^1$ CINVESTAV Departamento de Física, Av. IPN 2508, Zacatenco, Z.P. 07000, Ciudad de México, México
$^2$ Ingeniería-Química, COARA—Universidad Autónoma de San Luis Potosí, Matehuala, San Luis Potosí, México
$^3$ Instituto Politécnico Nacional, GESMAT, CICATA-IPN Legaria, Av. Calzada Legaria No. 694, Colonia Irrigación, Z.P. 11500, Ciudad de México, México
$^4$ Instituto Politécnico Nacional, GESMAT, CICATA-IPN Altamira, Km14.5 Carretera Tampico-Puerto, Z.P. 89600 Altamira Tamaulipas, México
$^5$ Facultad de Ingeniería, Universidad Autónoma de Querétaro, Centro Universitario, Z.P. 76010, Santiago de Querétaro, Qro. México
$^6$ Author to whom any correspondence should be addressed.

E-mail: fcaballero@ipn.mx and jlfernandez@ipn.mx

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Abstract

Thin films of nanometric order of a solid solution of barium-strontium titanate $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (BSTO), in the entire $0 \leq x \leq 1$ range, were deposited at 495 °C on quartz by RF reactive co-sputtering. The composition was controlled through the RF power ($P$) applied to the targets. X ray diffractograms (XRD) reveal that all the samples show the cubic perovskite crystalline structure. The percentage of elements ($x$) in the films were evaluated by using of electron dispersion spectroscopy, also through the change of the (110) lattice interplanar spacing determination of BSTO by means of XRD patterns. Experimental data points of concentration of Ba ($x$) and Sr ($1-x$) as a function of $P$ describe a symmetric sigmoidal curve. The average crystal size for the whole composition is around 20 nm as estimated from XRD data. Raman measurements in the 100–900 cm$^{-1}$ range show that optic phonons experience local hardening in the $x$ interval 0.6–0.8. Around this region of $x$ it is, in general, expected in BSTO a crystalline cubic-tetragonal phase transition when is prepared at low substrates temperatures. Distortion of the unit cell is observed in that interval, which probably originates the local hardening of phonons.

1. Introduction

The design of desired material properties such as band gap, hardness, melting point, etc can be carried out by means of alloying, which is a process amply and always used word wide, for the search of advanced materials. The variety of applications of perovskite oxides is broad, which includes solar cells, photocatalysis, optoelectronic devices, resistive memories, sensors, etc [1–3]. Even though the physical properties of $\text{BaTiO}_3$ (BTO), $\text{SrTiO}_3$ (STO) and their solid solutions $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (BSTO) have been widely studied, the researching on these oxides is still far from exhausted. Recently, the perspective of being applied in the search of new high critical temperature superconductors [4], and in colossal permittivity materials [5], has promoted an increase in the interest on these oxides. Nowadays, the study of perovskite oxides alloys has a regained importance due to the possibility to obtain a better performance of devices using materials with optimal properties. The similar structure of BTO and STO has motivated the research to produce the alloy $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ to improve the control of properties such as ferroelectricity and band gap [6, 7]. Greater flexibility in the control of BSTO properties is obtained through the deposit as thin films because films can induce stress or nanostructure formation [8]. The possibility to control ferroelectric properties directly through the composition of the BSTO alloy makes the production and characterization of this material very interesting [7]. BSTO films has been produced by sol-gel, RF sputtering, laser ablation, MBE, among others, growth methods [9–11]. The sputtering technique has been
employed for the thin films preparation for more than a century [12], and in the BSTO layers deposition is even a useful process with excellent results [13, 14].

In this work the Raman phonons characterization of BSTO thin films, in the entire $0 \leq x \leq 1$ range, deposited by reactive RF co-sputtering, is reported. The final composition of the films was controlled by the power applied to the BTO and STO targets. The successful production of the BSTO solid solution is confirmed by the shift of diffraction peaks on the 2θ axis. Experimental data on the Ba and Sr content in the films versus the applied RF power describe a sigmoidal function, and the Vegard’s law is employed to determine the content of the components. Raman spectroscopy allowed for the frequency versus the x content measurements, for various Raman optical modes in the wavenumbers 200–900 cm$^{-1}$ interval. The data obtained reveal a relative maximum of Raman shift versus x in the 0.6 ≤ x ≤ 0.8 interval, for the different modes studied. This maximum has been associated to distortion of the lattice into that interval.

2. Experimental details

BSTO films were deposited on 1.5 × 2.5 cm$^2$ quartz substrates by means of RF reactive co-sputtering employing a cylindrical stainless-steel chamber with diameter and height of 36 cm and 24 cm, respectively. Substrates were supported on a circular stainless-steel substrate holder (radius of 8 cm) rotating at 100 rpm and located at 8 cm from the two sputtering guns. An off-axis configuration was employed with a 3 cm separation between the sputtering gun axis. The chamber was evacuated to a pressure better than 1.2 × 10$^{-3}$ Pa, afterwards a flushing was applied using 3.9 Pa of argon for 10 min. The reactive working atmosphere was a mixture of Ar/O$_2$ with a ratio Ar/O$_2$ = 9 at a pressure of 3.9 Pa. Both, argon and oxygen gases were ultra-high purity grade. The source materials were 2” targets of 99.95% BTO and 99.9% STO (SCI Engineered Materials, Inc.). Prior to the films deposition targets were subjected to 15 min of a pre-sputtering process. 100% STO films (x = 0) were obtained applying 120 W to the STO target and no power to the BTO target. 100% BTO films (x = 1) were obtained using the inverse procedure. Values in the 0 ≤ x ≤ 1 interval for the BSTO films were obtained by changing the power applied to each target in 15 W steps in a complementary way, keeping always the total power applied to both targets at 120 W. The films were deposited employing a substrate temperature of 495 °C. The thickness of the films was measured using a Dektak3ST profilometer from Veeco Instruments. Chemical composition was analyzed with a scanning electron microscope (SEM) Jeol JSM-5300 equipped with a Kevex energy dispersive spectrometer (EDS) model Delta 1, calibrated by using semiconductor standards. An electron energy of 15 keV, enough to excite the Lo-X-ray emission of the elements of interest, to probe just the films was employed. The thickness of the samples, normalized to one min of growth, was obtained by processing the transmission spectra (not showed here) employing the program SCOUT. The X-ray diffractograms were obtained by a Phillips X’Pert diffractometer using the CuKα = 1.54060 Å wavelength. In order to calculate the particle size, the full width at half maximum (FWHM) of the (110) X-ray diffraction peak for each composition was obtained by a deconvolution procedure employing Gaussian profiles. The center of the peak was also obtained by means of this process. The particle size was obtained by using the Scherrer’s formula: $d = 0.9 \lambda / (b \cos \theta)$; where $\lambda$ is the wavelength of the X-ray radiation, b is the FWHM of the peak, and $\theta$ the Bragg’s angle. Room temperature Raman spectroscopy was carried out in a Horiba Jobin Yvon LabRAM micro-Raman system equipped with a He–Ne laser emitting at 632.8 nm and a He–Cd laser at 442 nm. For data analysis and the Origin 8 software was utilized.

3. Results and discussion

From STO to BTO, the thickness ($\tau$) of the samples varied from 180 to 530 nm, the variation of thickness is due to the plasma erosions more rapid BTO target than that of STO under the same conditions [15]. In figure 1, the XRD patterns for the whole set of BSTO samples deposited are displayed. All the films show the cubic structure of perovskite. In the right inset, the shift of the position of the peak as the composition of Ba$_x$Sr$_{1-x}$TiO$_3$ films changes from $x = 0$ (STO) to $x = 1$ (BTO) is observed, with no appreciable increase in the FWHM. The aforementioned characteristics of the XRD patterns indicate that the gradual incorporation of Ba in the STO lattice, and vice versa, preserves the perovskite structure without promoting structural disorder, which in turn assures an effective substitutional incorporation. As XRD is volume sensitive, it is plausible to assume that the films are mainly formed by the BSTO alloy as there is no evidence of the superposition of BTO or STO diffractograms on those of the BSTO alloy. The inset (a) of figure 1 shows the behavior of the XRD peak associated to the (200) plane along with all the composition values, that is, from BTO to STO ($\Delta \theta$) ≅ 44.5° to 46.5°) [16]. The inset (a) does not show the (002) XRD peak at lower 2θ values, next to the (200) one for all the x values, which indicates that the films are constituted only by the cubic phase [17, 18]. The inset (b) shows two small peaks, pointed out with asterisks, sited in the 55 ≤ 2θ ≤ 75° interval, which were discarded as coming
from other BSTO phases, these signals more probable are impurities that were originated by carbon-based oxides from the chamber ambient \cite{19, 20}.

The inset of figure 2 shows a linear connection between the (110) interplanar distances of BTO and STO (green line), considering that the lattice parameter of the BSTO alloy satisfies the Vegard’s law \cite{21, 22}. In the same inset, the values of the RF power applied to the BTO target as a function of the (110) interplanar spacing, calculated from XRD data, are shown (left scale). This arrangement is employed to obtain the values of the

Figure 1. X-ray diffractograms displayed in the $2\theta < 2\theta < 90$ range of all the BSTO samples studied. The inset (a) shows a detail, obtained from all spectra, in the 44–47 degrees interval. The inset (b) shows also an XRD detail in the $2\theta$ range 55–75 degrees.

Figure 2. Experimental $x$ and $1-x$ values measured by using the Vegard’s law (red open circles) and the interplanar spacings of the (110) plane, and by EDS technique (blue squares). The green triangles represent the same values fitted by a growth model. The inset shows the interpolation method used to determine the $x$ values.
composition \((x)\) by interpolation through the Vegard’s law linear relation. These \(x\) values, together with those provided by the EDS measurements are plotted as a function of the power applied to the BTO target \((P_{-BTO})\) in figure 2. Triangles are data fitted with a sputtering growth model used to explain the origin of the sigmoid form of the line-shape of \(x\) versus \(P_{-BTO}\) function \([15]\). The \(x\) and \(1-x\) as a function of the r.f. power data can be coupled to the Boltzmann equation, which allows for simpler analysis \([23]\).

The Raman spectra of the set of samples studied, excited by using the 632.8 nm line of a He-Ne laser, in the 100–900 cm\(^{-1}\) interval, are shown in figure 3. The penetration of the red light is, generally, greater than that of more energetic wavelengths, so that the information provided is more likely to be originated from all the volume of the film. The inset (a) illustrates the change of position of the mode at about 490 cm\(^{-1}\) for the different values of \(x\). The inset (b) exhibits the deconvolution process, in the 400–500 cm\(^{-1}\) region as an example, for a representative sample used for a better determination of the position of modes.

![Figure 3. Raman spectra obtained using a red laser (632.8 nm line) as an excitation source, for all the samples studied. The inset (a) illustrates the change of position of the mode at about 490 cm\(^{-1}\) for the different values of \(x\). The inset (b) exhibits the deconvolution method, in the 400–500 cm\(^{-1}\) region as an example, for a representative sample used for a better determination of the position of modes.](image)

In most cases, the line-shape of the frequency of vibrational modes as a function of \(x\) in cubic \(\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3\) solid solutions for STO to BTO decreases monotonically \([24]\), in the case of figures 4(a) and (b), a protuberance is observed in the 0.6–0.8 region of \(x\). In BSTO solid solution, this region is characterized by strong distortions, since there it occurs the cubic to the tetragonal phase transition of thin films grown or/and annealed at lower temperatures \([25, 26]\). In the present case, the transition stays as a tendency. This region has the property that high permittivity values can be reached \([27]\). The Raman spectra of all the samples excited with the blue line at 442 nm of a He-Cd laser are shown in figure 5(a). By comparison with the spectra of figure 3(a) an evident difference can be observed mainly at lower frequencies. This fact can occur when the samples absorb more photons, coming from the blue laser, by localized states placed in a wider energy interval, than those by localized ones placed in a narrower interval, from photons emitted by the red laser (photons from both red and blue beams have energy lower energy than the bandgap of all the BSTO films). Then, the electronic transition of blue-excited electrons across the forbidden energy band originates a major number of phonons than when red-light is used. Which, in turn, can excite other modes that are not excited by the red-
beam [18, 24, 28]. Figure 5(b) displays in an enlarged size the 450–550 cm\(^{-1}\) interval of the spectra of figure 5(a), the band outlined at around 500 cm\(^{-1}\) corresponds to the A1(\(\text{TO}_3\)) + E(\(\text{TO}\)) modes [29].

To have a better definition of the center of the Raman modes of figure 5 the deconvolution was carried by means of the fitting using eleven Lorentzians, as depicted in figure 6(a) for a representative sample. In figure 6(b) the position of the band-centers versus the power, for all the samples, is plotted for the better defined and fitted modes. A similar tendency to that followed in figure 4 by the frequency against the power is described in this case. This result supports the hardening of the Raman vibrational modes in the vicinity of \(x = 0.7\), observed formerly.

The (110), (111) and (200) interplanar spacings (IS) against \(P\)-BTO are displayed in the inset (A) of figure 7, which shows a sigmoid path as expected. The inset (B) exhibits the IS versus \(x\) plot, where right lines are observed
as confirmation that Vegard’s law is valid for other crystalline planes. Figure 7 illustrates the cubic unit cell volume (UCV), calculated using the cubic lattice parameter calculated from the average of the three IS data, as a function of P-BTO. A linear tendency is clearly shown. Nevertheless, the inset (C) exhibits the derivative of UCV with respect to x (left vertical axis), where an inverse sigmoid is evidenced. \( \frac{d(UCV)}{dx} \) reveals the negative and positive deviations from the expected derivative \( (5.4 \times 10^{-3} \text{ nm}) \) followed by the UCV if the Vegard’s law had been exactly satisfied along with all the 0 \( \leq x \leq 1 \) range, and represented here by the green dashed line. The hardness of BSTO for the pseudocubic perovskite phase, data from Jian et al [30] is also included in this inset (right vertical axis). The positive and negative deviations of \( \frac{d(UCV)}{dx} \) from the green line can be interpreted as tensile and compressive stress of the lattice, respectively, which could be produced by the tendency of the cubic crystalline phase of BSTO to transform to the tetragonal phase, whose developing did not progress into the films, except as very small crystals. Stress in the BSTO films are in general introduced by temperature deposition [31] and by the x values. The RF sputtering power significantly influences the x and \( 1-x \) distribution along with all the 0.0–1.0 interval of x, as shown in figure 2 and in its inset, also in figure 7 Ba and Sr do not have symmetric concentrations within this interval. Above (below), the green line the UCV has a larger (lower) value than expected. At \( x = 0.75 \) the hardness has the minimum value, followed by a rapid increment when x moves to 1.0, i.e., after an increase of the UCV follows a rapid contraction, which, probably, could be the cause of the local
hardening of the vibrational modes in the region 0.6–0.8 of x. As aforementioned, these distortions are caused by stress provoked by the attempt of lattice to change the phase in that interval [32].

The inset (a) of figure 8 shows the absorbance spectra of four BSTO samples plus the glass substrate. The average absorbance looks to be larger in the high energy region than in the lower energies; specifically, absorbance in the closeness of 2.81 eV (442 nm from-blue-laser) is larger than in the closeness of 1.96 eV (632.8 nm from-red-laser). This result can explain, in some way, the difference between spectra shown in figure 3 with those of figure 5. The \((\alpha h\nu)^2\) versus \(h\nu\) data is displayed in figure 8, for all the x values, Tauc’s method, employed to calculate the direct bandgap energy \(E_g\) of BSTO. Here, \(\alpha\) is the optical absorption coefficient and \(h\nu\) the photon energy. The \(E_g\) values versus x are depicted in the inset (b). The curve \(E_g\) versus x shows an inverse sigmoid aspect. Unfortunately, there is very little information on bandgap types and values in the ferroelectric BSTO, probably because the \(E_g\) in BSTO is very sensitive to the conditions of preparation [33, 34]. BSTO possesses non-linear and electrooptical characteristics because of the interaction between spontaneous polarization and the polarized induced by the electromagnetic field of light [35]. Direct and direct band gaps in the entire 0 \(\leq x \leq 1\) interval are characterized, like Raman modes, by a monotonic variation [36, 37]. In the case of this work, the inverse sigmoid curve observed for \(E_g\) versus x is similar to the \(d(UCV)/dx\) one. Therefore, it could be concluded that the \(E_g\) in the solid solution studied here, is sensitively modulated by the stress present in the samples. The general importance of this property lies in tuning the bandgap in this type of oxides, where alloying plays a fundamental role in generating stress by means of the formation of the different phase in a sample. Alloying is, until a certain point, a quite accessible process because of the well-known variety of growth and post-growth techniques to prepare, for many purposes, materials in micro-or-nanostructured films, crystals, powders, glasses, etc.

4. Conclusions

Thin films of a solid solution of BSTO crystallized in the perovskite cubic phase was successfully deposited on quartz, on all the 0 \(\leq x \leq 1\) range, by the RF sputtering growth technique. A substrate temperature of 495 °C was used for the growth of all samples. Diffractograms reveal the cubic phase of the perovskite of the Ba\(_{1-x}\)Sr\(_{x}\)TiO\(_3\) solid solution. Two series of Raman spectroscopy measurements, using a red laser (632.8 nm line) in the first series, and the 442 nm line of a He-Cd laser in the second one, allowed to achieve the vibrational spectra in the 200–900 cm\(^{-1}\) interval of all the samples studied. The positions of modes, fitted by means of Lorentzian curves for a better position determination, show a local enhancement of frequencies around the 0.6 \(\leq x \leq 0.8\) interval. This localized increase of the vibrational modes has been found to be originated by tensile-compressive stress variation in the lattice due to the attempt of a lattice change of phase within that
interval. The direct optical bandgap as a function of x exhibits an inverse sigmoid line-shape similar to that of \(d(U_{\text{UCV}})/dx\) versus x, which suggests that the bandgap of BSTO is strongly modulated by lattice distortions promoted by the stress, which in turn was provoked by the crystalline phases mixing.

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**ORCID iDs**

J L Fernández-Muñoz @ https://orcid.org/0000-0002-2039-3222

F Caballero-Briones @ https://orcid.org/0000-0003-4340-1050

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