

Folded acoustic phonons and soft mode dynamics in BaTiO₃/SrTiO₃ superlattices

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A series of BaTiO₃/SrTiO₃ superlattices with stacking periodicity of 6–10 unit cells were fabricated on (001)MgO substrates using pulsed-laser-deposition technique. Polarized Raman spectra revealed BaTiO₃-like optical vibrations and confirmed tetragonal symmetry of the superlattices with the *c* axis being normal to the layers. Due to in-plane compressive stresses generated by the lattice mismatch of the constituting layers, the *E*(1TO) soft mode was underdamped and markedly shifted to higher frequencies with respect to its analogs in the bulk. The existence of perfect superlattice structure was evident from the observation of the folded acoustic phonons in Raman spectra. The frequencies of the folded phonons matched well with the calculated transverse-acoustic branches of the constituent materials. No phase transitions were revealed in the superlattices below room temperature, while phase transition to the paraelectric state is shifted up to 650–700 K and it is diffused.

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Artificial superlattices (SL's) of ferroelectric perovskites have attracted great attention due to their superior structural and electrical properties^{1,2} of interest for a variety of thin-film device applications. The multilayered heterostructures of epitaxial BaTiO₃ (BT) and SrTiO₃ (ST) have shown an elevated dielectric constant with low tangential loss and high remanent polarization that cannot be achieved in conventional single-layer ferroelectric thin films.^{2–6} Perovskites are known to be very sensitive to even small structural distortion and their properties can be modified by mechanical constraints within SL. The observed enhancement of dielectric properties of BT/ST SL's in comparison to conventional single-layer BT thin films was attributed to the nature of strain within the constituting layers.² The remarkably enhanced remanent polarization was observed in epitaxial “asymmetric” BT/ST SL's with the variation of thickness ratio of BT and ST layers.⁴ The first-principles calculations⁷ predicted the tetragonal and polar character of ST layers within BT/ST SL's. However, by varying the deposition parameters and the substrate (or substrate orientation) one can obtain a wide variation of the lattice distortions within the heterostructures. Both BT and ST layers can be tetragonal and ferroelectric with polar axis normal to the layers^{2,5} or, alternatively, ST layers can be orthorhombic with polar axis parallel to [110] and [1 $\bar{1}$ 0] pseudocubic directions.^{8,9} Nakagawara *et al.*¹⁰ have observed a relatively high dielectric constant and low remanent polarization of epitaxial (111) oriented BT/ST multilayers on Nb-doped ST(111) substrates. The various bulk properties of BT and ST have been extensively studied for last 50 years; therefore, in addition to practical interest, BT/ST SL's are very attractive as model systems for investigations of unusual and sometimes surprising properties of multilayered ferroelectrics.

In the paraelectric cubic phase bulk ST and BT have a similar crystal structure but exhibit quite different phase-transition sequences on cooling. Lattice-dynamical properties, in particular, soft-mode behavior in bulk BT and ST, are well understood. Infrared, Raman, and hyper-Raman spectra of bulk BT and ST are well documented (see Ref. 11 and references therein). An important difference is that some vibrational modes in BT (including the soft mode in the cubic

and tetragonal phases) are heavily damped due to disorder of Ti ions, while all peaks in ST are very sharp. Far-infrared and Raman investigations of BT and ST thin films revealed remarkable deviation of the soft-mode behavior with respect to the bulk compounds.^{12–14} The ferroelectric soft mode is usually very sensitive to the strain field in thin films,¹⁵ and, therefore, information concerning the soft-mode behavior in ferroelectric multilayered heterostructures is very useful for better understanding of their physical properties. Although Raman spectroscopy has been successfully applied for the investigations of semiconductor multilayered heterostructures,¹⁶ surprisingly little attention has been paid so far to perovskite SL's. To the best of our knowledge, only a few papers concerning Raman-scattering characterization of PbTiO₃/BaTiO₃ (Ref. 17) and (La,Sr)MnO₃/SrTiO₃ (Ref. 18) multilayers have been published up to date. In this paper we report a polarized Raman study of BT/ST SL's grown on MgO substrates. We have observed significant hardening of the *E*(1TO) soft mode due to the strain between constituting layers. The folded acoustic phonons were observed in the Raman spectra of several SL's with different stacking periodicity.

Epitaxial BT/ST SL's were grown on cubic MgO(001) substrates using a pulsed-laser-deposition technique. The stacking periodicity *d* was precisely maintained by controlling the number of laser shots and laser energy density after appropriate calibration. In this study we have designed several SL's in which each layer has a similar periodicity ($d_1 = na_1$, $d_2 = na_2$, where *n* represents number of unit cells, a_1 and a_2 represent unit-cell parameters of constituting materials) varied from $n = 6$ to $n = 10$ unit cells. Irrespective of the stacking geometry, the total thickness of each film was ~600 nm. The orientation and phase purity of the films was confirmed by x-ray diffraction (XRD) using a Siemens D5000 diffractometer. XRD patterns of SL's showed diffraction peaks accompanied by the satellite peaks, which is a characteristic of SL structure. The in-plane epitaxial relation between the SL and the substrate were confirmed by four-circle pole figure measurements. Both BT and ST layers are found to be tetragonal with the *c* axis normal to the layers, in agreement with XRD data of Kim *et al.*^{5,6} on similar films grown on MgO.

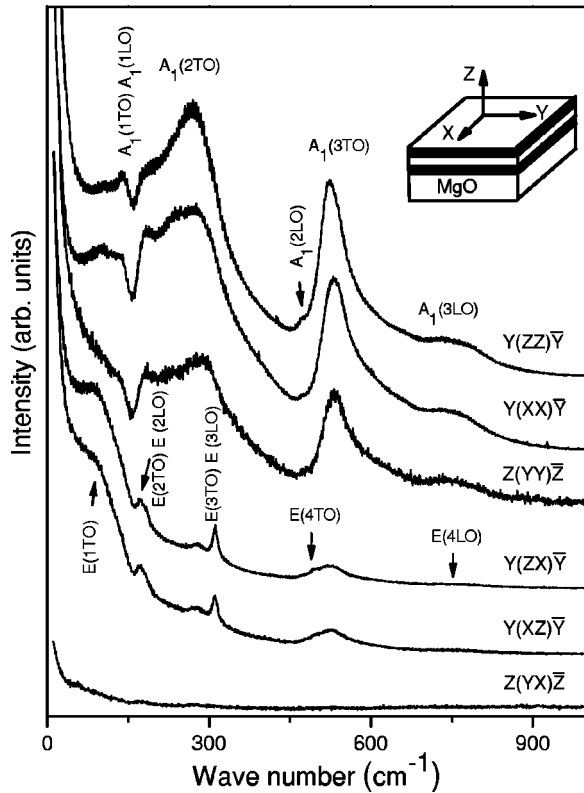


FIG. 1. Polarized Raman spectra of BT/ST ($n=10$) SL for six scattering geometries at room temperature.

Raman spectra were excited using the polarized light of a Coherent INNOVA 99 Ar⁺ laser ($\lambda=514.5$ nm) and analyzed using a Jobin Yvon T64000 spectrometer equipped with a charge coupled device. Polarized Raman spectra have been measured on samples carefully oriented according to the crystallographic axes of c -domain films ($X\parallel[100]$, $Y\parallel[010]$, and $Z\parallel[001]$). An optical microscope with a $80\times$ objective was used to focus the incident light as a spot of about $2\ \mu\text{m}$ in diameter on the sample. Polarized Raman spectra were obtained in normal and side-view backscattering geometries (for details see Ref. 15). For temperature-dependent micro-Raman measurements we used Linkam FDCS 196 cryostat and TS 1500 hot stage.

Since the Raman selection rules are strictly associated with the orientation of the polar axis, the presence of only one kind of domain with the polarization normal to the substrate (c domains) or parallel to the substrate (a domains) can be easily determined from the polarized Raman studies.^{11,14,15} In the tetragonal ferroelectric BT, one can expect $3A_1(xx,yy,zz) + B_1(xx,yy) + 4E(xz,yz)$ Raman-active optical phonons. Due to the presence of an electric field the polar A_1 and E modes split into transverse optical (TO) and longitudinal optical (LO) components. As one can see in Fig. 1, the polarized Raman spectra of BT/ST ($n=10$) SL at room temperature are very close to those of bulk BT crystals¹⁹ and proved tetragonal symmetry of the SL with the c axis being normal to the substrate. In the xx spectrum we have observed $A_1(3LO)$ peak at $730\ \text{cm}^{-1}$, $A_1(3TO)$ at $525\ \text{cm}^{-1}$, very weak $A_1(3LO)$ peak at $473\ \text{cm}^{-1}$, and

$A_1(2TO)$ band centered at $270\ \text{cm}^{-1}$. The latter peak exhibits much stronger coupling with the lowest lying $A_1(1TO)$ mode, and the interference dip at $160\ \text{cm}^{-1}$ is much more pronounced in xx and zz spectra of SL with respect to similar interference dip at $\sim 180\ \text{cm}^{-1}$ in a single-crystalline BT. In agreement with the selection rules, no Raman peak was found in the xy geometry. Both xz and zx spectra contain E symmetry modes and leaked $A_1(2TO)$ and $A_1(3TO)$ bands from diagonal geometries. Very weak $E(4TO)$ and $E(4LO)$ peaks were observed at 495 and $740\ \text{cm}^{-1}$, respectively. The sharp $E(3TO)=E(3LO)$ peak has practically the same frequency ($309\ \text{cm}^{-1}$) as in BT, while the $E(2TO)=E(2LO)$ peak at $173\ \text{cm}^{-1}$ is slightly downshifted. The most significant difference with respect to BT crystal appeared at lower frequencies where the $E(1TO)$ soft mode was observed as an underdamped peak with the frequency being $115\ \text{cm}^{-1}$ and the half-width of $70\ \text{cm}^{-1}$. It is worth noting that in ST the lowest-lying F_{1u} soft mode is an underdamped peak at $88\ \text{cm}^{-1}$ at room temperature,²⁰ in contrast, in bulk BT crystals¹⁹ this mode is overdamped with the damped harmonic-oscillator fitted frequency being $35\pm 5\ \text{cm}^{-1}$ and the half-width larger than $100\ \text{cm}^{-1}$.

Apparently, BT layers are compressed in plane parallel to the substrate and showed enhanced tetragonal distortion with out-of-plane parameter larger than in bulk BT. Being polarized by BT layers, ST layers exhibit tetragonal distortion and all triply degenerated modes of cubic ST are split into Raman-active A_1 and E components. As a result, both layers exhibit BT-like optical vibrations. Most vibrational modes in BT/ST SL have intermediate frequencies between corresponding BT and ST values, while the low-frequency $E(1TO)$ soft mode is markedly altered with respect to its analogs in bulk BT and ST. The $E(1TO)$ soft mode corresponds to Ti displacement with respect to oxygens in the xy plane,²¹ the plane being parallel to the substrate. In the c -domain films, the $E(1TO)$ soft mode can exhibit upward shift due to significant two-dimensional (2D) clamping caused by the mismatch between the thermal-expansion coefficients of the film and MgO substrate.¹⁵ In the case of BT/ST SL, the upward shift of the soft mode in BT layers is believed to be larger due to in-plane compressive stress generated by the lattice mismatch with ST layers.

The most relevant result is the activation of folded acoustic phonons in the Raman spectra of SL's, as illustrated in Fig. 2. The bulk dispersion transverse-acoustic (TA) branches of BT and ST are similar, and the resulting SL acoustic phonons are propagating modes with a sound velocity that is approximately the weighted average of the constituents. Due to the new periodicity, the bulk Brillouin zone is folded into a new SL Brillouin zone, with the zone edge at $k_z=\pi/d$, where $d=d_1+d_2$ is the superlattice period. As a result, a number of opticlike phonon branches can be measured by means of Raman scattering near the zone center. The TA phonon-dispersion curve is approximately linear below $k=0.1(2\pi/a)$ in both BT and ST crystals,²²⁻²⁴ and the slope of the TA branch is determined by the corresponding sound velocity. Figure 3 shows the plot of the TA branches for BT and ST calculated using available sound velocities

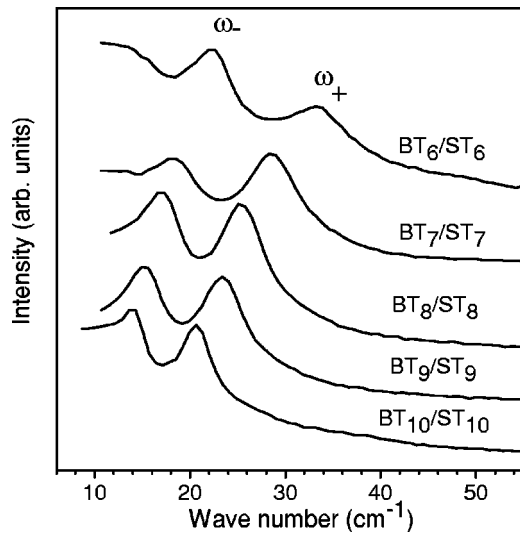


FIG. 2. Folded acoustic phonons in Raman spectra of SL's with different stacking periodicity.

[$v_t = 4.8 \times 10^{-3} \text{ ms}^{-1}$ for ST (Ref. 25), $v_t = 3.1 \times 10^{-3} \text{ ms}^{-1}$ for BT along the [001] direction²⁶]. Due to the normally small acoustic mismatch at the interfaces, a small band gap appears at the zone center and edge. Therefore, doublets can be observed in the parallel-polarized spectra with the frequencies determined by $\omega_{\pm} = v_{\pm} (2\pi m/d)$, where v_+ and v_- are the transverse sound velocities of bulk ST and BT, respectively. Only first-order doublets are usually observed ($m=1$) because the intensity of the high-order folded modes is very low. The observed frequencies match well with the calculated TA branches as shown in Fig. 3. Therefore, the observed frequencies of the folded acoustic phonons provide precise determination of the SL's periodicity. Also, the observation of the folded acoustic phonons is an evidence of high-quality SL structure with sharp boundaries and no interdiffusion at the interfaces.

In the high-frequency region of optical phonons, one can

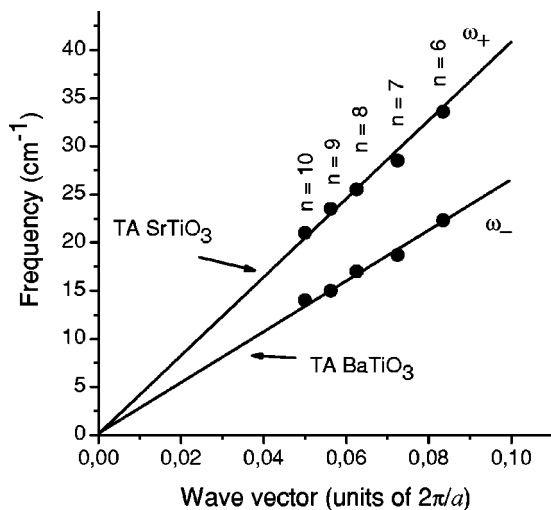


FIG. 3. The folded-acoustic-phonon frequencies (full circles) and calculated dispersion TA branches for bulk BT and ST (solid lines).

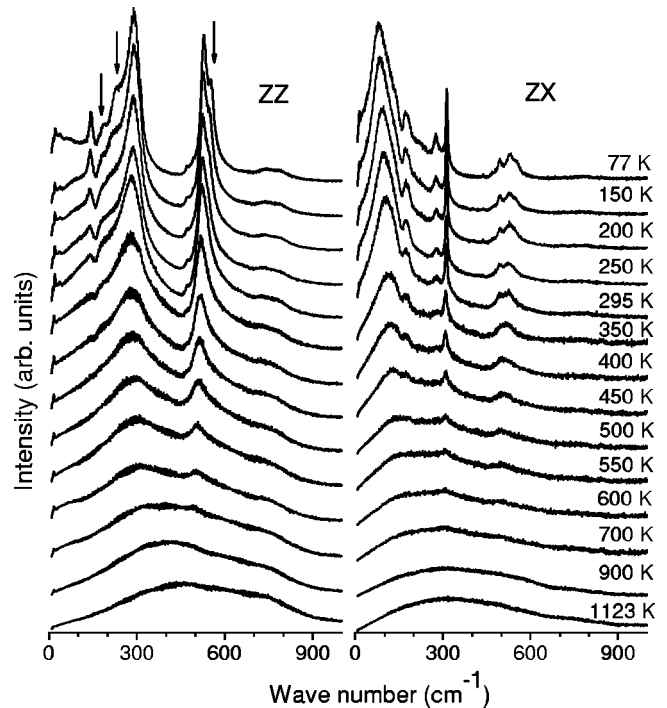


FIG. 4. Polarized Raman spectra of BT/ST ($n=10$) SL at selected temperatures. Arrows indicate new peaks detected at low temperatures.

expect activation of confined modes in the Raman spectra if no overlap of the phonon-dispersion curves of the constituent compounds occurred. Due to intrinsic disorder as well as Brillouin-zone folding most of the peaks are essentially broad at room temperature and no mode splitting was revealed. However, on cooling below 200 K, additional peaks start to appear at the low-frequency side of the $A_1(2\text{TO})$ band and on the high-frequency side of the $A_1(3\text{TO})$ peak. At 77 K all peaks are narrower and additional peaks (186, 233, and 551 cm^{-1}) are better resolved, as shown in Fig. 4. Apparently, these additional peaks are confined modes related to individual layers within the SL. Unfortunately, lack of dispersion curves for optical phonons in bulk BT prevents any detailed assignment.

As can be seen in Fig. 4, Raman spectra are polarized in the whole temperature interval studied (77–1123 K). In contrast to bulk BT and ST, Raman spectra of SL revealed a gradual temperature dependence. The folded acoustic modes are temperature independent in the whole temperature range studied. Below room temperature, we found no evidence of any structural transformation in SL down to 77 K. The $E(1\text{TO})$ showed a slight downshift, while all other peak frequencies were practically temperature independent. Apparently, ST layers prevent tilts of polar axis in BT layers, and no transformation to the low-symmetry orthorhombic or rhombohedral phases occurs. In turn, BT layers stabilize the neighboring ST layers and prevent structural phase transition associated with the tilting of octahedra in ST layers. At elevated temperatures, the $E(1\text{TO})$ component of the soft mode in the SL shows a hardening from 106 cm^{-1} at room temperature up to $\sim 140 \text{ cm}^{-1}$ at 600 K. All other peaks

showed no remarkable frequency variation. The intensity of all polar modes steadily decreases on heating. All polar modes gradually disappear in the temperature interval 650–700 K, implying that stability of the ferroelectric state in SL is markedly higher than in the bulk BT ($T_c = 395$ K). It should be emphasized that the upward shift of T_c in true epitaxial thin films is expected because of 2D clamping imposed by the substrate.²⁷ In case of BT/ST SL's the upward shift of T_c seems to be more significant due to the interlayer strain. Above 700 K, we observed very broad bands (disorder-activated background), usually observed in bulk BT due to intrinsic disorder of Ti ions, in agreement with the eight-site model.²⁸

In summary, the polarized Raman spectra of BT/ST SL's are very similar to those observed in BT single-domain crystals and confirmed tetragonal symmetry of the SL with the c

axis being normal to the layers. All peaks have intermediate frequencies between the corresponding BT and ST values, while the low-frequency $E(1TO)$ soft mode is markedly altered with respect to its analogs in bulk BT and ST due to in-plane compressive stress generated by the lattice mismatch of the constituting layers. The presence of the folded acoustic phonons in the Raman spectra confirmed the perfect periodicity within the SL's. The observed frequencies match well with the calculated TA branches. On cooling down to 77 K, no phase transition was revealed in BT/ST($n=10$) SL, while the phase transition to the paraelectric state is diffused and shifted up to 650–700 K.

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