This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

Bingcheng Luo $^a$, Xiaohui Wang $^a$, Enke Tian $^a$, Guowu Li $^c$, Longtu Li $^{a*}$

The electronic structure, lattice vibrations, optical, dielectric and thermodynamic properties of BaTiO$_3$/CaTiO$_3$/SrTiO$_3$ (BT/CT/ST) ferroelectric superlattices are calculated by using first-principles. The lattice parameters after relaxation are in good agreement with the experimental and other theoretical values within error of 1%. The band structure shows an indirect band gap with the value of about 2.039 eV, and a direct band gap of 2.39 eV at the $\Gamma$ point. The density of states and the electron charge density along [001] axis are calculated and show the displacement of Ti ions along the [001] axis. The strong hybridization between O 2p and Ti 3d contributes to the ferroelectricity of BT/CT/ST ferroelectric superlattices. The $\Gamma$ modes are stable, while the vibration modes at A, M, R, and X point are unstable governing the nature of phase transition. The static dielectric tensor including the ionic contribution is calculated and the permittivity parallel to the optical axis is almost eight times more than the permittivity vertical the axis, exhibiting the strong anisotropy. The thermodynamic enthalpy, free energy, entropy, and heat capacity are also investigated based on the phonon properties.

1. Introduction

Ferroelectric materials with ABO$_3$-type perovskite structure have been extensively studied for their application in sensors, actuators, FRAM memories, capacitors, and energy harvesting and storage devices$^7$. Ferroelectric superlattices have received much attention because of their dramatic distinct electric properties from the bulk materials, such as dielectric constant, polarization, Curie temperature, domain and tunability$^2$-3. Recently, much research in the ferroelectric superlattices has been focused on the several two-component superlattices, such as BaTiO$_3$/SrTiO$_3$ 2-4, KTaO$_3$/KNbO$_3$, PbTiO$_3$/PbZrO$_3$, SrTiO$_3$/NaNbO$_3$ 5, and PbTiO$_3$/SrTiO$_3$. Furthermore, few three-component ferroelectric superlattices, such as CaTiO$_3$/BaTiO$_3$/SrTiO$_3$, LaTiO$_3$/SrTiO$_3$/YTiO$_3$, have also been studied theoretically and experimentally.

BaTiO$_3$ was discovered during World War II in 1941 and 1944 in the United States, Russia, and Japan, and found ferroelectric behaviour in 1945 and 1946, and recently paid attention again for the lead-free ferroelectric material which has a successive ferroelectric transition with the temperature reducing$^{12,13}$. It has a cubic perovskite structure with no net polarization which transforms to tetragonal phase with a polarization along the [100] direction at 120$^\circ$C. Then it transforms to the orthorhombic and rhombohedral phase with the polarization along [111] and [110] direction at -5$^\circ$C and -90$^\circ$C, respectively. The polarization is mainly caused by the displacement of Ti$^{4+}$ cation from the [TiO$_6$] octahedron center to an off-center position. SrTiO$_3$ is a well-known perovskite material for the quantum paraelectricity which has a very large dielectric constant with the saturation at $\varepsilon=20000$, associated with the softening of a long-wave length transverse optic phonon mode$^{14}$. It can remains paraelectric until the temperature is below 0.3K, while the ferroelectric polarization could easily occurred with the balance of forces broken by the slight perturbation in the lattice structure, such as doping, strain and oxygen isotope substitution$^{15}$. CaTiO$_3$ is also a well-known incipient ferroelectric with a dielectric constant of $\varepsilon=180$ in bulk crystal$^{16}$, which shows no ferroelectric phase transition in spite of the intriguing dielectric constant behavior$^{17}$. Contrast to SrTiO$_3$, the paraelectric phase of CaTiO$_3$ is much more difficult to be destroyed by the slight perturbation. The difference in dielectric permittivity of CaTiO$_3$ compared to SrTiO$_3$ is caused by the tilted [TiO$_6$] octahedrons, which prevent any long-range coupling to neighbouring unit cells$^{18}$.

Ferroelectric thin films and the superlattices of these materials with other ABO$_3$-type perovskite compound have exhibited the enhancement in the dielectric, piezoelectric, and ferroelectric properties. The remanent polarization was enhanced in epitaxial asymmetric BaTiO$_3$/SrTiO$_3$ strained superlattices, which was ascribed to the increase of lattice parameter $c$ of the BaTiO$_3$ layer due to interface strain as well as the increase in the proportion of BaTiO$_3$. Neaton and Rabe used the first-principles density-functional theory within the local density approximation to study the spontaneous polarization of epitaxial BaTiO$_3$/SrTiO$_3$ superlattices as a function of composition, revealing the theoretical evidence for the enhancement in the computed superlattice polarization above that of bulk BaTiO$_3$ for superlattices with BaTiO$_3$ fraction.
larger than 40%. Epitaxial strain plays an important role in the physical properties of artificial superlattice structures. Ortega et al presented a way to control the local stress in epitaxial films by altering the lattice parameter by doping and had grown the BaTiO$_3$/Ba(Sr)TiO$_3$ ferroelectric superlattices. Meyer and Vanderbilt studied the cubic perovskite compounds with the form $\left( A_{1/3} A'_{1/3} A''_{1/3} \right) B O_3$ and $A \left( B_{1/3} B'_{1/3} B''_{1/3} \right) O_3$ using first-principles methods, and found the strong variation of the strength of the symmetry breaking with the strength of the compositional perturbation. Lee et al fabricated the three-component ferroelectric BaTiO$_3$/CaTiO$_3$/SrTiO$_3$ (BT/CT/ST) superlattices using pulsed laser deposition method, and revealed the subtle effects of a non-inversion-symmetric environment and the role of a large number of coupled heterointerfaces, and verified the theoretical predictions of strain-enhanced ferroelectric polarization of BaTiO$_3$. However, the research that focused on the three-component superlattices is quite few, especially the three-component BT/CT/ST superlattices. Shah et al studied the short-period three-component SrTiO$_3$/BaTiO$_3$/PbTiO$_3$ (ST/BT/PT) perovskite superlattice using first-principles density functional approach. Nakhmanson studied the composition-dependent structural and polar properties of epitaxial short-period BT/CT/ST superlattices grown on a SrTiO$_3$ substrate using first-principles methods. The presence of highly polar CT and BT layers induced substantial polarization and the polarization in the (ST)$_3$(JT)$_1$(BT)$_1$ superlattices started to decrease at $m$=7, indicating the strongest polarization enhancement can be tuned by the delicate balance between concentration and layer thickness. Experimentally, Liu et al also showed that the dielectric constant and dielectric loss of the BaTiO$_3$/SrTiO$_3$/MgO superlattices were highly dependent upon the stacking period numbers and layer thicknesses, and the strong interface effect were found in the heterostructures with the combination period larger than 16 or each STO layer less than 6.0 nm. Similarly, the dielectric constant, dielectric loss, and tunabilities of the Mn:BST/Mn:ZT/MgO heterostructures are highly dependent upon the sequences of Mn:BST to Mn:ZT. Obviously, Nakhmanson only focused the polarization enhancement while Gao only concentrated on the intrinsic asymmetric ferroelectricity together with the heterostructure between metal and ferroelectric superlattices. But the band structure, elastic properties, optical dielectric function, lattice vibration, and thermodynamics properties of BT/CT/ST ferroelectric superlattices are still not reported. Thus, in this work, we perform first-principles calculations to study the properties of BT/CT/ST ferroelectric superlattices. The structural, electronic, optical properties are investigated using standard density functional theory. The lattice vibrations and thermodynamics properties are analyzed with the density functional perturbation theory.

3. Results and discussion

3.1. Structural and electronic properties of BT/CT/ST ferroelectric superlattices

We first relaxed the superlattice to obtain the geometry optimized atom configuration. The calculated lattice parameter of BT/CT/ST ferroelectric superlattices are $a=b=3.88$ Å, $c=11.85$ Å and the $c/a$ ratio is 3.05, which is in great agreement with the experimental value of 3.02 and other theoretical value of 3.018. This error within of 1% confirmed the validation and reliability of our methods.

The calculated band structure of BT/CT/ST ferroelectric superlattices is shown in Fig. 1. The Fermi level is fixed to zero at the top of valence band. The maximum of valence band and minimum of conduction band are located at A point and $\Gamma$ point, respectively, which indicates the BT/CT/ST ferroelectric superlattices are an indirect band gap materials with the value of about 2.039 eV. It is also clear that the smallest direct band gap is 2.39 eV at the $\Gamma$ point. Our results are in consistency with

2. Method and computational details

The first-principle calculations were performed by employing the pseudopotential plane-wave (PP-PW) approach based on the density functional theory (DFT) framework as implemented in the Cambridge Serial Total Energy (CASTEP) code. The generalized gradient approximation (GGA) with the PBE exchange-correlation functional was used. The norm-conserving pseudopotentials adopted for the ferroelectric superlattices were constructed by the electron configurations as Ca 3s$^2$3p$^6$4s$^2$ states, Sr 4s$^2$4p$^6$5s$^2$ states, Ba 5s$^2$5p$^6$6s$^2$ states, Ti 3s$^2$3p$^3$3d$^4$4s$^2$ states, and O 2s$^2$2p$^4$ states. The structure was fully relaxed with a 6×6×1 special k-point mesh grid and 880 eV energy cutoff for the plane-wave basis, which had been carefully tested to ensure the well-converged total energy and geometrical configurations. The energy tolerance was $5\times10^{-6}$ eV/atom, the force tolerance was 0.01 eV/Å, and the stress tolerance was 0.02 GPa, and the displacement tolerance was 5×10$^{-4}$ Å. Then the band structure, density of states, electron density, and optical properties were calculated. In order to strengthen the validation of calculation, we also used VASP code to relax the structure and calculate the properties. The phonon, dielectric and thermodynamic properties were calculated by using the density functional perturbation theory (DFPT) with a linear response method implanted in CASTEP code. Fig. 1 shows the schematic crystal structure of BT/CT/ST ferroelectric superlattices. The BT/CT/ST superlattices with P4mm symmetry were constructed based on the cubic BaTiO$_3$, SrTiO$_3$, and CaTiO$_3$ crystal. The lattice constant of the superlattice is fixed to the bulk cell parameter of bulk SrTiO$_3$, to implicitly include the SrTiO$_3$ substrate.

![Schematic crystal structure of BT/CT/ST ferroelectric superlattices before (a) and after (b) relaxation. Pictures drawn with VESTA](image-url)
the band gap of 2.3 eV according to Gao et al., but they didn’t show the band structure. Considering that there is no detailed report about the experimental band gap, we compared with the gaps of BaTiO$_3$, CaTiO$_3$, and SrTiO$_3$. According to the literature, these three components are indirect band materials, indirectly revealing the rationality of present calculation of band gaps. It is well known that the band gap can be underestimated due to the choice of exchange correlation functional. The total density of states (DOS) and the partial density of states (PDOS) of BT/CT/ST ferroelectric superlattices are shown in Fig. 3 information in the energy region nearer the Fermi level. It can be seen that the valence band from -6~0eV mainly consists of O 2p states, together with small contribution from Ti 3d states. Considering that the partial density of states for the Ba, Sr, and Ca ions is lower than 0.3 electrons per cell, these contributions can be ignored. The conduction band minimum from 0~6eV is mainly originated from Ti 3d states, together with small contribution of O 2p states. The density of Ti 3d is much higher than that of O 2p, indicating that some electrons of O atom move from valence band to conduction band and hybrid with Ti 3d electrons. It can be also seen that the PDOS difference between O 2p states and Ba (also Sr, Ca) states is much larger than that between O 2p states and Ti 3d state, indicating that the Ti-O bonding is covalent and the Ba-O (also Sr-O, Ca-O) bonding is ionic. The strong hybridization between O 2p and Ti 3d contributes to the ferroelectricity of BT/CT/ST ferroelectric superlattices.

To better understand the charge distribution and the nature of the chemical bonding, the electron charge density for BT/CT/ST ferroelectric superlattices along [001] axis is calculated and the results are shown in Fig. 4. It can be seen that the charge distribution around Ti site reveals that the bonding between Ti and O is covalent, while the charge distribution around Ba site shows the ionic behavior between Ba and O. Similarly, the bonding between Ca and O and the bonding between Sr and O are also mainly ionic. Furthermore, the interatomic distance between Ti and O1 is 1.773 Å, which is much smaller than the interatomic distance of 2.765Å between Sr and O1, indicating the covalent nature of the Ti-O bonding. It can also be seen that the interatomic distance between Ti and O1 atom is much shorter than the interatomic distance between Ti and O2 atom, indicating the displacement of Ti ions along the [001] axis. This shows the evidence for the ferroelectricity of BT/CT/ST ferroelectric superlattices.
3.2. Optical properties of BT/CT/ST ferroelectric superlattices

The optical properties of BT/CT/ST ferroelectric superlattices can be calculated from the complex dielectric function

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$$  \hspace{1cm} (1)

where $\varepsilon_1$ and $\varepsilon_2$ are the real part and the imaginary part of the dielectric function, respectively. The imaginary part of dielectric function is dependent on the frequency and can be calculated by

$$\varepsilon_2(\omega) = \frac{2\pi e^2}{\Omega \varepsilon_0} \sum_{k,v} \left| \Psi_k^v \right|^2 \delta(E_k^c - E_k^v - \hbar\omega)$$ \hspace{1cm} (2)

where $\varepsilon_0$ is the vacuum dielectric constant, $\Omega$ is the volume, $v$ and $c$ represents the valence and conduction band, respectively, $\hbar\omega$ is the energy of the incident phonon, $\mathbf{u}$ is the vector defining the polarization of the incident electric field, $\mathbf{u} \cdot \mathbf{r}$ is the momentum operator, $\Psi_k^c$ and $\Psi_k^v$ are the wave function of conduction band and valence band at $k$ point, respectively. According to the imaginary part of dielectric function, all optical properties such as refractive index $n(\omega)$, extinction coefficient $k(\omega)$, absorption coefficient $\alpha(\omega)$, reflectivity $R(\omega)$, energy loss spectrum $L(\omega)$, and the optical conductivity $\sigma(\omega)$ can be given by

$$n(\omega) = \frac{1}{\sqrt{2}} \left[ (\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega))^\frac{1}{2} + \varepsilon_1(\omega) \right]^\frac{1}{2}$$ \hspace{1cm} (3)

$$k(\omega) = \frac{1}{\sqrt{2}} \left[ (\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega))^\frac{1}{2} - \varepsilon_1(\omega) \right]^\frac{1}{2}$$ \hspace{1cm} (4)

$$\alpha(\omega) = \frac{\sqrt{2}\omega}{c} \left[ (\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega))^\frac{1}{2} - \varepsilon_1(\omega) \right]$$ \hspace{1cm} (5)

$$R(\omega) = \frac{\sqrt{\varepsilon_1(\omega) + i\varepsilon_2(\omega) - 1}}{\sqrt{\varepsilon_1(\omega) + i\varepsilon_2(\omega) + 1}}$$ \hspace{1cm} (6)

$$L(\omega) = \text{Im} \left( \frac{-1}{\varepsilon(\omega)} \right) = \frac{\varepsilon_1(\omega)}{\varepsilon_1(\omega) + i\varepsilon_2(\omega)}$$ \hspace{1cm} (7)

$$\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega) = -\frac{1}{4\pi} \frac{\varepsilon_1(\omega) + i\varepsilon_2(\omega) - 1}{\varepsilon_1(\omega) + i\varepsilon_2(\omega) - 1}$$ \hspace{1cm} (8)

Fig. 5 shows the dielectric function, absorption coefficient, reflectivity, conductivity, refractive index, and electron energy-loss spectrum. From Fig. 5 (a), it can be seen that the peaks for the imaginary part dielectric function at 4.3 eV and 6.7 eV is much stronger than other peaks, which is mainly originated from the transition from O 2p valence band to Ti 3d conduction band. The peak at high energy (≈20.0 eV) arises from the transition from O 2s to the Ti 3d states, while the peak at even much higher energy around 36.9 eV should derive from the transition from the Ti 3p level to conduction band, which is consistent with the reflectivity in Fig. 5 (c). These also explains the origin of the peak structures in the refractive index and extinction coefficient spectra as shown in Fig. 5 (c). From the real part of dielectric function in Fig. 5 (a), it can be clearly seen the static dielectric constant is 4.5, which only contains the contributions of electrons. The contributions of ionic vibrations to the dielectric constant will be discussed in the following section. From the real part of the refractive index, the static refractive index is 2.1. This large refractive index in the low energy range exhibiting the high band gap, which is in good accordance with the band calculations as shown in Fig. 2.

In the range from 0 to 2.4 eV and above 11 eV the reflectivity for BT/CT/ST ferroelectric superlattices is lower than 20%, displaying that BT/CT/ST superlattices are transparent for photons at these ranges. The energy loss spectrum describes the energy lost by an electron passing from a homogeneous dielectric materials, the peaks in the energy loss spectrum locates at 10.7 eV, 20.2 eV, and 38.0 eV. The peak at 10.7 eV is high and sharp, indicating the energy loss range is narrow and it is useful for the optical storage efficiency. The main peak is defined as the bulk plasma frequency $\omega_p$, above and below
which the material exhibits dielectric \(\varepsilon_1(\omega) > 0\) and metallic \(\varepsilon_1(\omega) < 0\) behavior\(^{40}\). The sharp structure located at 10.7 eV is related with the sharp decrease in the reflectivity as shown in Fig. 5 (c). This process is associated with the electrons transition from O 2s and Ba 6s, lying below the valence band, to the empty conduction band as shown in Fig. 3.

### 3.3. Lattice vibrations and dielectric properties of BT/CT/ST ferroelectric superlattices

To better understand the lattice dynamics and dielectric properties of BT/CT/ST ferroelectric superlattice, the phonon dispersion curves and phonon density of states are calculated using density functional perturbation theory\(^{30}\). According to the literature\(^{41-44}\), the phonon properties can be obtained using a harmonic approximation by:

\[
D_{\mu\nu}(\mathbf{R} - \mathbf{R}^\prime) = \left. \frac{\partial^2 E}{\partial u_\mu(\mathbf{R}) \partial u_\nu(\mathbf{R}^\prime)} \right|_{u=0}
\]

where \(u\) refers to the displacement of a given atom and \(E\) is the total energy in the harmonic approximation. This force constants matrix can be written in reciprocal space and usually referred to as the dynamical matrix:

![Graphs showing dielectric function, absorption coefficient, reflectivity, conductivity, refractive index, and electron energy-loss spectrum of BT/CT/ST ferroelectric superlattices.](image-url)
The plane waves are employed to evaluate each atomic displacement:

\[ u(R,t) = \varepsilon e^{i(qR - \omega t)} \]

(11)

where the polarization vector of each mode, \( \varepsilon \), is an eigenvector with the dimension of 3N of the eigenvalue problem:

\[ M \omega(q)^2 \varepsilon = D(q) \varepsilon \]

(12)

The contribution to the partial density of state on atom \( i \), from each phonon band, is evaluated using:

\[ N_i(E) = \int \frac{dk}{4\pi^2} |e_i(i)|^2 \delta(E - E_n(k)) \]

(13)

where \( e_i \) is the eigenvector associated with the mode of energy \( E_n \). Considering the tetragonal primitive cell of BT/CT/ST ferroelectric superlattices contains 15 atoms, the complete phonon spectrum consists of 45 normal modes of vibration including 3 acoustical branches and 42 optical branches.

The Born effective charges control the amplitude of the long-range Coulomb interactions between nuclei and the splitting between longitudinal optic (LO) and transverse optic (TO) phonon modes. The Born effective charge tensors \( Z_{\alpha\beta} \) is defined as the partial derivative of the macroscopic polarization concerning a periodic displacement of all the periodic images of that ion at zero macroscopic electric field:

\[ Z_{\alpha\beta}^{\text{eff}}(\kappa) = \frac{\partial P_\alpha}{\partial \tau_\beta}(\kappa) \]

(15)

where \( P_\alpha \) is the total macroscopic polarization per unit cell generated in the \( \theta \) direction, \( \Omega_0 \) is the volume of the unit cell, \( \tau \) is the rigid displacement of the sublattice of \( x \)th atom along the \( \alpha \) direction. The Born effective charges are calculated through linear response method with density functional perturbation theory, and the diagonal tensors are shown in Fig. 6 along high-symmetry lines of tetragonal Brillouin zone are shown in Fig. 6, together with the phonon density of states. It is clear that no imaginary frequency is found at \( \Gamma \) point showing stable character. However, there exists imaginary frequency at A, M, R, and X point, whose phonon dispersion curves are shown below zero frequency, indicating the unstable modes. These unstable modes govern the nature of phase transition, dielectric and ferroelectric response of BT/CT/ST ferroelectric superlattices. The phonon DOS in the frequency region below 20 THz is mainly contributed by the Ti-O hybridization of [TiO_6] octahedron.
Table I, together with the nominal charges. The Born effective charges of all the atoms in ferroelectric superlattices are larger than their nominal ionic values owing to the ions displacement during phase transition, favouring the ferroelectric instability. The large values of $Z_1$ and $Z_2$ further revealing the strong hybridization between O 2p and Ti 3d states and the dynamic charge transfer along Ti-O bonds, which also explains that the Mulliken charges are lower than the Born effective charges. Combining the ionic contribution to the dielectric properties, the static dielectric tensor is calculated with two different components, $\varepsilon_{||}^0 = 25.5$ and $\varepsilon_{\perp}^0 = 203.4$. Obviously the static dielectric permittivity is larger than the optical dielectric permittivity. The static dielectric tensor parallel to the axis is electronic, while that perpendicular the optical axis is ionic. Polarization enhancement with respect to bulk tetragonal BaTiO$_3$ has been reported for two- and three-component superlattices with a BaTiO$_3$ concentration of more than 30%$^{21}$. The concentration and layer thickness of individual layer are identified as an important factor governing the polarization improvement. The polarization of the (ST)$_x$(BT)$_{1-x}$(CT)$_y$ superlattices increases with the increase of the (CT) layer thickness, while the (ST)$_z$(CT)$_y$ system is substantially more polar than (ST)$_x$(CT)$_z$, and (BT)$_z$(CT)$_y$ is more polar than (ST)$_z$(BT)$_y$. Gao et al$^{22}$ studied the intrinsic asymmetric ferroelectricity of the BT/CT/ST tricolour superlattice at the nanoscale and showed the relationship between the polarization directions and geometric stacking sequences of the superlattices. Similar polarization enhancement has been reported in (ST)$_x$(BT)$_z$(PT)$_y$ system, and the lattice distortion in superlattices can be manipulated by changing the layer thicknesses.$^{21}$

Table I The calculated Born effective charge tensors, average of their eigenvalues, nominal charges and Mulliken charges of Ba, Sr, Ca, Ti and O in BT/CT/ST ferroelectric superlattices in unit e.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>$Z$</th>
<th>$\lambda$</th>
<th>Nominal charge</th>
<th>Mulliken charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>[2.752 2.752 3.013]</td>
<td>2.839</td>
<td>+2</td>
<td>1.53</td>
</tr>
<tr>
<td>Sr</td>
<td>[2.518 2.518 3.013]</td>
<td>2.609</td>
<td>+2</td>
<td>1.34</td>
</tr>
<tr>
<td>Ca</td>
<td>[2.515 2.515 2.590]</td>
<td>2.540</td>
<td>+2</td>
<td>1.41</td>
</tr>
<tr>
<td>Ti1</td>
<td>[6.637 6.637 4.616]</td>
<td>5.963</td>
<td>+4</td>
<td>1.3</td>
</tr>
<tr>
<td>Ti2</td>
<td>[6.667 6.667 5.226 ]</td>
<td>6.187</td>
<td>+4</td>
<td>0.89</td>
</tr>
<tr>
<td>Ti3</td>
<td>[6.619 6.619 5.306]</td>
<td>6.181</td>
<td>+4</td>
<td>1.27</td>
</tr>
<tr>
<td>O1</td>
<td>[-2.038 -2.038 -4.095]</td>
<td>-2.724</td>
<td>-2</td>
<td>-1.12</td>
</tr>
<tr>
<td>O2</td>
<td>[-1.695 -1.695 -4.402]</td>
<td>-2.598</td>
<td>-2</td>
<td>-0.75</td>
</tr>
<tr>
<td>O3</td>
<td>[-1.702 -1.702 -4.741]</td>
<td>-2.715</td>
<td>-2</td>
<td>-0.74</td>
</tr>
<tr>
<td>O4</td>
<td>[-2.001 -1.768 -5.460]</td>
<td>-3.077</td>
<td>-2</td>
<td>-0.9</td>
</tr>
<tr>
<td>O5</td>
<td>[-1.963 -1.700 -5.474]</td>
<td>-3.045</td>
<td>-2</td>
<td>-0.77</td>
</tr>
<tr>
<td>O6</td>
<td>[-2.017 -1.685 -5.359]</td>
<td>-3.020</td>
<td>-2</td>
<td>-0.9</td>
</tr>
</tbody>
</table>

3.4. Thermodynamic properties of BT/CT/ST ferroelectric superlattices

With the calculation of phonon properties, the thermodynamic enthalpy $H$, free energy $F$ and entropy $S$ at finite temperature can be computed. The vibration contribution to the free energy is derived by$^{17}$

$$H(T) = E_\omega + \frac{1}{2} \int g(\omega) h_0 d\omega + \int \frac{h_0}{e^{\omega/kT} - 1} g(\omega) d\omega$$  \hspace{1cm} (16)$$

$$F(T) = E_\omega + \frac{1}{2} \int g(\omega) h_0 d\omega + k_B T \int g(\omega) \ln(1 - e^{-\hbar \omega/kT}) d\omega$$  \hspace{1cm} (17)$$

$$S(T) = k_B \left[ \int \frac{h_0}{e^{\hbar \omega/kT} - 1} g(\omega) d\omega - \int g(\omega) \ln(1 - e^{-\hbar \omega/kT}) d\omega \right]$$  \hspace{1cm} (18)$$

where $g(\omega)$ is the phonon density of states, $k_B$ is the Boltzmann constant. Fig. 7 shows the Temperature dependence of the calculated thermodynamic enthalpy, free energy, and temperature times entropy for BT/CT/ST ferroelectric superlattices. It is clear that the enthalpy and free energy increase with the temperature increase, while the entropy decreases with the temperature increase. All these three terms in Fig. 7 yields to zero when the temperature approaches zero, which is in accordance with Third law of thermodynamics. Fig. 9 shows the temperature dependence of Debye temperature and heat capacity derived from phonon model for BT/CT/ST ferroelectric superlattices. It can be seen that the heat capacity approaches Dulong–Petit classical limit at high temperature. All these thermodynamic properties can be compared with experimental results and predict the phase stability.

This journal is © The Royal Society of Chemistry 20xx J. Name., 2013, 00, 1-3 | 7
4. Conclusions

In this work, we investigated the electronic structure, lattice vibrations, optical, dielectric and thermodynamic properties of BaTiO$_3$/CaTiO$_3$/SrTiO$_3$ ferroelectric superlattices by employing the pseudopotential plane-wave approach based on the density functional theory framework. After relaxation, the lattice parameters are in good agreement with the experimental and other theoretical values within error of 1%. The band structure shows an indirect band gap with the value of about 2.039 eV between A and $\Gamma$ point, and a direct band gap of 2.39 eV at the $\Gamma$ point. The density of states shows that the Ti-O bonding is covalent and the Ba-O (also Sr-O, Ca-O) bonding is ionic. The electron charge density for BT/CT/ST ferroelectric superlattices along [001] axis is calculated and the results show the displacement of Ti ions along the [001] axis. The strong hybridization between O 2$p$ and Ti 3$d$ contributes to the ferroelectricity of BT/CT/ST ferroelectric superlattices. The dielectric function, absorption coefficient, reflectivity, conductivity, refractive index, and electron energy-loss spectrum are also calculated and discussed. The phonon dispersion curves and phonon density of states are calculated using density functional perturbation theory. No imaginary frequency is found at $\Gamma$ point showing stable character, while the imaginary frequency at A, M, R, and X point indicates unstable modes, which governs the nature of phase transition. Combing the ionic contribution to the dielectric properties, the static dielectric tensor including the ionic contribution is calculated and the permittivity parallel to the optical axis is almost eight times more than the permittivity vertical the axis, exhibiting the strong anisotropy. The thermodynamic enthalpy, free energy, entropy, and heat capacity are also investigated based on the phonon properties. Given that there are few experimental results of BT/CT/ST ferroelectric superlattices reported, especially the optical, phonon, and thermodynamic properties, we hope this predictive first-principles calculations will attract the attention and motivate the experimental investigations.

Acknowledgements

The work was supported by Ministry of Sciences and Technology of China through National Basic Research Program of China (973 Program 2015CB654604), National Natural Science Foundation of China for Creative Research Groups (Grant No.51221291), National Natural Science Foundation of China (Grant No. 51272123), the Fundamental Research Funds for the Central Universities (Grant No.2652013105), and also supported by CBMI Construction Co., Ltd.

Notes and references

43. M. Born, Dynamical theory of crystal lattices, Oxford Univ. Press, 1966.