Chapter 4

HR-EELS Investigation of BaTiO$_3$/SrTiO$_3$ Multilayers

The dielectric properties of BaTiO$_3$ thin films and multilayers are different from bulk materials because of nanoscale dimensions, interfaces, and stress-strain conditions. In this study, BaTiO$_3$/SrTiO$_3$ multilayers deposited on SrTiO$_3$ substrates by pulsed laser deposition have been investigated by high energy resolution electron energy-loss spectroscopy. The fine structures in the spectra are discussed in terms of crystal-field splitting and misfit strain. The near-edge structure of the oxygen K edge in BaTiO$_3$ thin layers and in bulk BaTiO$_3$ are simulated by Ab-Initio self-consistent full multiple-scattering calculations.

4.1 Introduction

Ferroelectric thin films are used for the development of next generation microwave controllers, frequency-agile filters, voltage-controlled oscillators, tunable microwave filters, non-volatile random access memories, etc. [69]. The dielectric permittivity can be controlled by applying a sufficiently high electric field. This field can be easily achieved in thin film structures using low control voltages below 50 V, which is necessary for high-density integrated electric devices. Recent investigations have been focused on barium strontium titanate (Ba,Sr)TiO$_3$ (BST) because of its high permittivity and specific capacitance. One of the most promising applications of BST is the use for very-high-density dynamic random-access memories [70]. High integration requires very small sizes of the electric devices, but the dielectric properties of many existing materials are different at nanoscale dimensions.

In order to grow high quality thin films on a certain substrate, many new techniques have been developed. Among them, pulsed laser deposition (PLD) is widely and successfully used. High-quality ceramic thin films can be obtained by PLD with carefully optimized oxygen pressure, substrate temperature, laser spot size, as well as other parameters like pulse repetition rate.

BaTiO$_3$/SrTiO$_3$ (BTO/STO) multilayers are promising in view of unique properties different from thin films and from bulk materials [71]. The dielectric properties of BTO/STO multilayers are predominated by the crystallization of the BTO layers and the interfaces between the BTO and STO layers. In this study, fine structures of the titanium L$_{23}$ edges and the oxygen K edge are investigated by EELS/STEM in multilayers consisting of BTO/STO layers deposited on SrTiO$_3$ (001) substrates by PLD.
4.2 Experiment

Two series of multilayer films were deposited on SrTiO\(_3\) (001) substrates in the sequences STO (50 nm)/BTO (10 nm) and STO (100 nm)/BTO (10 nm) by PLD, respectively, as shown in Fig. 4.1(a) and Fig. 4.1(b). Details of the growth and the TEM (transmission electron microscopy) preparation of the specimens studied in this work were similar to those described in Ref. [1]. For optimizing the probe size with a sufficient beam current, a 50 \(\mu\text{m}\) objective aperture is used to restrict the convergence semiangle (\(\sim 14\) mrad). The details of the general experimental conditions of acquiring EEL spectra can be found in Chapter 3.

4.3 Results and Discussion

The cross-sectional TEM dark-field and STEM bright-field images of the multilayers are shown in Fig. 4.1(a) and (b), respectively. Fig. 4.1(c) gives the selected area diffraction pattern (SAD) taken from the region including both substrate and BaTiO\(_3\) layer with the incident electron beam parallel to the [010] direction. The orientation relationship between BTO layers and the STO substrate can be obtained from the diffraction pattern: (001)

![Fig. 4.1](image-url)
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BTO || (001) STO, and [100] BTO || [100] STO. The [400] and [004] reflections (magnified in the insets) from BaTiO$_3$ and SrTiO$_3$ are well separated. The sharp reflections confirm that the BaTiO$_3$ layer is a high-quality single crystal layer. Because the lattice parameter ($a=3.905$ Å, Ref. [72]) of the SrTiO$_3$ substrate is stable and known very well, the reflections from SrTiO$_3$ can be used as a standard ruler to determine the lattice parameters of the BaTiO$_3$ layer without calibration of the camera length. The calculated lattice parameters of BaTiO$_3$ layers are summarized in Table 4.1. The lattice parameter $a$ is close to that of a 12 nm thick BaTiO$_3$ single layer deposited on a SrTiO$_3$ substrate reported by Yoneda [71]. But the lattice parameter $c$ in Ref. [71] might be overestimated since the volume of the unit cell should be a little smaller than that of bulk BaTiO$_3$ due to the presence of misfit strain (note that the lattice parameter $a$ of the STO substrate is 2.3% smaller than that of bulk BTO). From Table 4.1, one can see that the lattice parameter is shortened in the growth plane and elongated along the growth direction ($c$ axis) by the strain at the interfaces. In comparison with the BaTiO$_3$ thin film, the smaller lattice parameter in the growth plane indicates that the misfit strain is stronger in the BaTiO$_3$ layer than in the thin film due to the deposited SrTiO$_3$ film.

Table 4.1: Lattice parameters ($a$, $b$ and $c$) of a 10 nm thick BaTiO$_3$ layer. For comparison, the data of a 12 nm thick BaTiO$_3$ thin film [71] and bulk BaTiO$_3$ (Ref. [73]) are given. $V$ is the volume of the unit cell.

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<tr>
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<th>BTO layer (10 nm)</th>
<th>BTO film (12 nm)</th>
<th>Bulk BTO</th>
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<tr>
<td>$c$ (Å)</td>
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<td>4.038</td>
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<tr>
<td>$V^{1/3}$ (Å)</td>
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<td>4.008</td>
</tr>
<tr>
<td>$c/a$</td>
<td>1.032</td>
<td>1.053</td>
<td>1.011</td>
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4.3.1 Ti L$_{23}$ Edges

The ferroelectric properties of BaTiO$_3$ layers are related to the distortion of oxygen octahedra [74]. Although the lattice parameters can be obtained from the SAD pattern, the atomic positions within the unit cell cannot be extracted in a similar way. The ligand-field multiplet model has been successfully applied to identify the symmetry of oxygen octahedra in transition metal compounds [51]. It is derived that multiplet effects dominate the profile of the Ti L$_{23}$ near-edge structure in titanate perovskites. The density of unoccupied states of the Ti atoms are sensitive to short-range coordination. The four well split peaks in the Ti L$_{23}$ edges are attributed to excitations of $2P_{3/2}$ and $2P_{1/2}$ subshells to unoccupied $t_{2g}$ and $e_g$ states [75]. Peak positions, FWHM, asymmetry of the peak shape, satellite structures, and branch ratios [76] contain information about the atomic arrangement. As well known, bulk BaTiO$_3$ is found in a cubic perovskite phase above the Curie point ($T_c=120^\circ$C) and in a tetragonal phase at room temperature (cf. Fig. 4.2). The Ti atom lies in the center of the regular octahedron of oxygen atoms in the cubic perovskite structure, while the octahedron of oxygen atoms is distorted along the $c$ axis in the tetragonal perovskite structure.

30 spectra were acquired along the direction indicated by the white arrow in Fig. 4.1(d). The acquisition time per spectrum was set to 10 s. A small spatial drift of the specimen due to the local charging effect has been corrected by the help of the raster image (inset in Fig. 4.1d). The BaTiO$_3$ layer of definite thickness can be used as a ruler mark. Thus, the position of the acquired spectrum can be corrected assuming a continuous drift of the specimen along the line scan direction. The average scanning step corrected by this method
Fig. 4.2: (a) Cubic perovskite structure of bulk BaTiO$_3$ above the Curie point 120°C. The crystal data take from Ref. [77]. (b) Tetragonal perovskite structure of bulk BaTiO$_3$ at room temperature. The crystal data take from Ref. [73]. The labeled lattice parameters and Ti-O bond lengths are given in units of Å.

amounts to about 1 nm, which is close to the estimated probe size. In order to correct the intrinsic energy drift of the electron beam, the zero-loss peak was monitored at the position marked in Fig. 4.1(d). However, this method can only limit the energy drift below ±0.3 eV because of the slight asymmetry of the zero-loss peak. Therefore, all EEL spectra contained in the raster image were normalized and energetically aligned to the $t_{2g}$ peak in the L$_3$ edge, which was fitted by a Lorentzian function. By this method, changes in the crystal-field splitting smaller than 0.1 eV could be identified unambiguously.

For quantitative analysis, the Ti L$_{23}$ edges are separated into four peaks by multi-peak

Fig. 4.3: Crystal-field splitting in the L$_3$ and L$_2$ edges across the BaTiO$_3$ layer. The vertical dotted lines indicate the interfaces positions. Additionally, the measured values for bulk BaTiO$_3$ are given as open and solid triangles.
Lorentzian fitting. Other fitting models, such as δ functions [75], could also be used. The coefficient of determination ($R^2$) of the Lorentzian fitting is better than 0.99 in this work, which means that the Lorentzian function is a reasonable model for the separation of Ti L$_{23}$ peaks. For bulk BaTiO$_3$ (see Fig. 4.3), the crystal-field splitting of the Ti L$_{23}$ edges amounts to only about 2.15 eV. Therefore, a high energy resolution is necessary to detect variations in the crystal-field splitting. The variation in the crystal-field splitting across the BaTiO$_3$ layer is shown in Fig. 4.3, where the abscissa gives the relative distance from the center of the BaTiO$_3$ layer. Note that the crystal-field splitting of the L$_3$ edge is obtained more accurately than that of the L$_2$ edge due to sharper peaks, more accurate pre-edge background fitting, and negligible plural scattering artifacts. The crystal-field splitting of the Ti L$_2$ edge is slightly larger (by $\sim$0.12 eV) than that of the Ti L$_3$ edge in all layers. According to the results of crystal-field multiplet calculations of the Ti L$_{23}$ edges for octahedral coordination of Ti with oxygen atoms [78], this small discrepancy is due to the different effect of the crystal field on the L$_3$ and L$_2$ edges. In Fig. 4.3, one can see that the slope of the lower interface is different from that of the upper interface. This slope is related to the relaxation of misfit strain at the BaTiO$_3$/SrTiO$_3$. The length of the relaxation is about 6 nm, which is in agreement with the TEM results of Visinoiu et al. [1]. Additionally, the crystal-field splitting of the BaTiO$_3$ layer is a little larger with respect to that of bulk BaTiO$_3$. This difference can be interpreted by the misfit strain, which compresses the octahedra to reduce the Ti-O bond length. As known, the shorter Ti-O bond length leads to the stronger crystal field, which finally results in the larger crystal-field splitting.

Fig. 4.4 shows the L$_{23}$ edges of Ti$^{4+}$ in differently distorted octahedral coordinations. The octahedra share two edges with other octahedra in rutile, three edges in brookite, and four edges in anatase. They share six corners in the perovskite structure. The crystal

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**Fig. 4.4:** (a) Experimental spectra of bulk BTO and STO compared to TiO$_2$ anatase, brookite, and rutile. The splitting of the $e_g$ peak in the L$_3$ edge is indicated by vertical dotted lines. Satellite structures appear above the white lines. (b) Comparison of the fine structure of the titanium L$_{23}$ edges measured in STO, BTO, and at the BTO/STO interface.
structures of rutile, brookite, and anatase are sketched in Fig. 4.5. In the distorted cubic crystal field, the second main peak ($e_g$ in the $L_3$ edge) is split into two peaks. Using atomic multiplet theory including the crystal field, de Groot calculated the Ti$^{4+} L_{23}$ edge in $O_h$ and $D_{4h}$ symmetries, respectively [51]. No such splitting was found in $O_h$ symmetry. The reproduced splitting of the $L_3 e_g$ peak in $D_{4h}$ symmetry was in good agreement with the experimental spectra of rutile TiO$_2$, even though the octahedron in rutile is actually of $D_{2h}$ symmetry. Therefore, this splitting is believed to be related to the distortion of the octahedral coordinations. With respect to molecular orbitals, the low-energy orbitals point to the ligands with the longer bond length, while the high-energy orbitals point to the ligands with the shorter bond length. In bulk BTO, the octahedron is in a $D_4$ symmetry, which can be regarded as a distortion of the $D_{4h}$ symmetry. But a splitting has never been observed in the Ti $L_3 e_g$ edge, neither in the experimental spectra of BTO layers nor in spectra of bulk BTO. This unidentified splitting in BTO might be due to the following reasons: (1) The splitting in perovskite titanate ceramics is too small to be separated in the spectrometer, or core-hole lifetime broadening and instrumental broadening smear out the small splitting. (2) The effect of crystal-field splitting in the edge-sharing structures is stronger than that in the corner-sharing structures. The low-energy peak relates to the shared edges, while the high-energy $e_g$ peak relates to the ligand atoms. The relative intensity of the low-energy peak increases with the number of shared edges from rutile to anatase. Due to these reasons, the splitting of the $e_g$ peak in other similar perovskite titanate ceramics, such as PbTiO$_3$ or ZrTiO$_3$, may be also difficult to be observed. Fig. 4.4(b) shows the spectra taken at the BTO/STO interface and in the 10 nm thick BaTiO$_3$ layer. Spectra taken from SrTiO$_3$ (substrate) and bulk BaTiO$_3$ are also given for comparison. All of the spectra are also aligned to the first peak. The centers of the peaks are indicated by vertical dotted lines. There is no discriminable difference between the spectra from the BTO layer and bulk BTO. The spectrum at the interface can be regarded as the superposition of BTO layer and STO substrate spectra. Special fitting techniques, such as the multiple linear least-squares
(MLLS) fitting, may be appropriate for this case [79].

The Ti $L_{23}$ edges can be reproduced by the Ab-Initio full multiple-scattering commercial code Feff8.20 (Ref. [80]). In SrTiO$_3$, there are two satellite peaks above the Ti $L_{23}$ edges with an energy separation of about 5.5 eV, which corresponds to the energy separation of the $L_{23}$ edges. The Ti $L_{23}$ edges were calculated shell by shell using the FMS method. The definition of the shell model is schematically illustrated in Fig. 4.6. The first shell contains six nearest-neighbor oxygen atoms with a distance of 1.952 Å to the central Ti atom. The second shell consists of eight Sr atoms with a distance of 3.382 Å. The third shell contains six Ti atoms with a distance of 3.905 Å. The result of calculations up to the sixth shell is shown in Fig. 4.7(a). The satellite structures can be well reproduced when the third shell (labeled 21 atoms) was considered in the cluster. In the simulation, the satellites of $L_{23}$ edges were calculated, then weighted by a branching intensity ratio ($I_{L_3}/I_{L_2}$) of 0.8 (Ref. [81]) and then summed up. The result is in a good agreement with the experimental spectrum without any manual energy shift (cf. Fig. 4.7b). With regard of multiple-scattering, the satellites originate from backscattering at neighbor atoms; and the charge transfer process dominates the satellite structures. The satellites are shifted to lower energies by about 1.5 eV in BaTiO$_3$ with respect to bulk SrTiO$_3$ (cf. Fig. 4.4b). This means that the longer inter-atomic distance leads to a smaller charge transfer. The energy shift of the satellite peaks is more significant than that of the white-line peaks. In the near edge onset region (0-10 eV above the Fermi energy), the four main peaks can also be reproduced (not shown in the left part of the spectra in Fig. 4.7), but the relative intensity of the peaks is not in agreement with the experimental spectrum due to the neglect of multiplet effects (i.e., intra-atomic interactions redistribute the intensities of the peaks) which are more important than the charge transfer process for 3$d$ transition metal atoms [54]. In other words, the excited electrons with a low kinetic energy are easily localized in unoccupied 3$d$ states above the Fermi level. For the simulation of the $L_{23}$ edges of transition-metal atoms, the agreement with experiment can be improved not only for the main peaks but also for the satellites by the charge-transfer and multiplet (CT-M) model [82] or multichannel multiple-scattering theory [83].

![Fig. 4.6: Atomic coordinations up to three-shell around the Ti site in the FMS calculations of SrTiO$_3$.](image)
Fig. 4.7: (a) Satellite structures of the Ti L\textsubscript{2}\textsubscript{3} edge of SrTiO\textsubscript{3} calculated in the shell-by-shell model of the FMS method. The spectra are labeled by the total number of the atoms in the clusters. The number of atoms in the new shell with respect to the previous cluster is indicated in parenthesis. (b) The experimental satellite structures of the Ti L\textsubscript{23} spectrum compared with the FMS calculations of SrTiO\textsubscript{3}.

4.3.2 O K Edge

The fine structure of the O K edge was acquired with an energy dispersion of 0.2 eV/channel. The acquisition time per spectrum was set to 10 s for sufficient intensity. The fine structures of the O K edge are compared in Fig. 4.8(a). The spectra are aligned with respect to peak A1. The peaks A1 and A2 are related to the 3d orbitals of the Ti atoms. The separation between A1 and A2 amounts to about 2.4 eV, what reasonably coincides with the crystal-field splitting in the Ti L\textsubscript{23} edges. The identical separation is one of the evidences of the hybridization of the oxygen 2p orbitals with the Ti 3d orbitals. This interpretation corresponds to the explanation of de Groot in terms of ligand-field splitting [84].

In order to identify the origin of the features B1, B2, C1 and C2, the O K edge of bulk BaTiO\textsubscript{3} was simulated by FMS calculations shell by shell using the parameters given in Table 4.1. Overlapped self-consistent muffin-tin potentials were used to reduce the effects of potential discontinuities at the muffin-tins. As shown in Fig. 4.8(b), there are two unequal positions for oxygen atoms in the tetragonal perovskite structure, labeled O1 and O2. One O1 and two O2 oxygen atoms are included in one unit cell. The spectra from the two unequal oxygen atoms were calculated, respectively. Then the spectra were multiplied by the corresponding number of atoms in the unit cell and summed up. The results of the calculation of BaTiO\textsubscript{3} layers and bulk BaTiO\textsubscript{3}, including 107 atoms in the individual cluster, are in a good agreement with the main features of the experimental spectra, as shown in Fig. 4.8(b).
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Fig. 4.8: (a) Comparison of the fine structure of the oxygen K edge. The reference spectra measured in bulk BTO and STO were averaged from 5 spectra taken from different positions. (b) Experimental and simulated oxygen K edges of bulk BaTiO$_3$ and BaTiO$_3$ thin film. The lattice parameters for simulations are given in Table 4.1.

The difference in the spectra calculated for a BTO layer and bulk BTO is very small, which agrees with the experimental results. This means that the strain-induced distortion of the BTO structure is not the main reason for the difference in the dielectric properties of a BTO layer and bulk BTO. Interface effects have to be taken into account. The details of the FMS calculations will be discussed in Section 4.4. The origins of peaks A1-C3 are discussed in the following. Peak A1 is related to the hybridization of the O 2$p$ and Ti 3$d$ orbitals. Peak A2 is also related to the hybridization, but its intensity is very low, which is consistent with the experimental spectrum. Peaks B1, B2 and B3 originate from the backscattering of the electron wave at the nearest Ba shell. The peak C1 arises from the backscattering at the nearest oxygen shell. The experimental energy splitting between C1 and C2 amount to about 3.8 eV. However, this splitting cannot be well reproduced in the FMS simulations. This disagreement might be caused by the fact that the polarization potential along the c axis is neglected in the FMS calculations of BaTiO$_3$. The polarization potential is generated by the displacement of Ti atoms in the octahedra along the same direction, which breaks the symmetry of the nearest oxygen atoms around the excited oxygen atom [85]. Peak C3 is mainly related to scattering at the third oxygen shell. In multiple-scattering calculations, the fine structure in the spectra predominantly arises from strong backscattering at neighbor oxygen atoms. Contributions from distant cations are usually small.
4.3.3 [Ti]/[O] Ratio

The [Ti]/[O] element ratio was calculated by a standard procedure which was implemented in the DigitalMicrograph software packages. In this procedure the total counts of the core edge signals of two elements are integrated in an energy window (\( \sim 50\, \text{eV} \)) above the threshold energy, which are assumed to be \( I_a \) and \( I_b \). The corresponding cross sections, \( \sigma_a \) and \( \sigma_b \), are calculated by a Hartree-Slater model. Then, the element ratio is given by \( \frac{I_a \sigma_b}{I_b \sigma_a} \). The details of the calculations can be found in Ref. [64]. A 10 eV energy window in the pre-edge was used to fit the background for both core-loss edges. The integrated intensities of the Ti L\(_{23}\) edges and the O K edge were calculated up to 45 eV and 60 eV above the corresponding threshold energies, respectively. Fig. 4.9 shows the element ratios across the BaTiO\(_3\) layer. A slight slope caused by the nonuniform thickness has been corrected by subtracting a fitted line. A significant increase (around 6\%) of the [Ti]/[O] ratio is found reproducible at several different positions at the upper interface of the BaTiO\(_3\) layer, while no detectable increase is found at the lower interface. The increased [Ti]/[O] ratio implies that oxygen vacancies are aggregated at the upper interface. Similar results have been reported for grain boundaries [20, 86] and dislocation cores [23]. The [Ti]/[O] element ratio in the region far from the interface fluctuates in the range of 0.33\( \pm \)0.03, which is mainly caused by the removal of the background.

Since the surface of the STO substrate was prepared to terminate at the TiO\(_2\) plane [1],

Fig. 4.9: [Ti]/[O] ratio across the BaTiO\(_3\) layer. The vertical dotted lines indicate the upper and lower interfaces. The abscissa denotes the relative distance from middle of the BTO layer.
the molecules were deposited at the beginning of the growth process on the STO surface in the stacking sequence BaO–TiO$_2$–BaO–TiO$_2$ . . . due to energetic reasons. In the first few layers (< 5 nm), the misfit strain from the interface makes the energetic preference strong, which causes that this region is free of defects. When the BTO layer becomes thicker, the misfit strain is relaxed. However, the misfit-strain-induced polarization along the growth direction retains in the whole BTO layer. In perovskite oxides, oxygen vacancies can order at the grain boundaries [87]. Oxygen vacancy ordering mechanism may occur in the BaTiO$_3$ thin layer under the influence of misfit strain because the stacking sequence is not rigorous [88]. This may be one of the possible explanations for the formation of space charge layers [71] at the rough upper interface of BaTiO$_3$ layers [1]. The presence of a space charge at the upper interface dominates the difference of dielectric properties between multilayers and bulk BaTiO$_3$.

4.4 Explanation of Fine Structures of the O K Edge

In the previous section, FMS calculations have been performed to interpret the fine structures of the oxygen K edge in BaTiO$_3$. However, the accuracy of the FMS calculations is not very high. Therefore, some details of the fine structures have been smeared out, especially for the peaks C1-C3 in BaTiO$_3$. More accurate theoretical calculations are needed to explain the splitting feature. In this section, the combination of FMS and band-structure methods will be used to interpret the features of the oxygen K edge in BaTiO$_3$. As a starting point, the calculations are performed for SrTiO$_3$ firstly, and then extended to BaTiO$_3$.

4.4.1 Bulk SrTiO$_3$

For the oxygen K edge, only $1s \rightarrow 2p$ transition is allowed according to the dipole selection rule. Multielectron effects, transition matrix elements and the core-hole potential have a negligible influence on the fine structures of the oxygen K edge [55]. Therefore, the partial density of states can be reasonably compared with the experimental oxygen K edge directly.

In this work, a widely used FLAPW code, Wien2K, is used to do the work due to its high accuracy on electronic structure calculations. As a starting point, the oxygen pDOS of SrTiO$_3$ is firstly calculated, because SrTiO$_3$ has a perfect perovskite structure. BaTiO$_3$ has a similar perovskite structure except a small distortion along the Z-axis (cf. Fig. 4.2(b)). The unit cell parameters of SrTiO$_3$ are taken from Ref. [72] and listed in Table 4.2 including the muffin-tin radius of each different atom used in the present calculations. The atomic structure of unit cell is schematically shown in Fig. 4.10. The three oxygen sites have the equivalent coordinations. Indeed, for reducing the computing afford in the actual calculation, the (1/2,0,1/2) and (0,1/2,1/2) oxygen sites have been rotated onto (1/2,1/2,0) by a so-called “local rotation matrix”. The (1/2,0,1/2) site changes to (1/2,1/2,0) by a 90° rotation about Y axis, and the (0,1/2,1/2) site by a 90° rotation about X axis. The muffin-tin radii for Sr, Ti and O are listed in Table 4.2 in units of the Bohr radius. The self-consistent calculation is performed by using a 10×10×10 k-point
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sampling in the irreducible Brillouin zone (IBZ). The present calculation with 1000 k-points is close to the calculation with a 20×20×20 k-point sampling in the literature [89].

Table 4.2: Unit cell parameters of bulk SrTiO3 with a perovskite structure (Space Group Pm3m), taken from Ref. [72]. The lattice parameter is a=3.905 Å. The muffin-tin radii $R_{MT}$ used in the FLAPW calculations are given for all different atoms in units of the Bohr radius.

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<tr>
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<th>x</th>
<th>y</th>
<th>z</th>
<th>$R_{MT}$</th>
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</tr>
<tr>
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The oxygen pDOS at (1/2,1/2,0) site compared with the ELNES of the oxygen K edge is shown in Fig. 4.11. Note that the same Cartesian coordinate is used for the orientation-projected DOS as that of the unit cell. The orientation-decomposed components are also shown in this figure. The same series of labels as in Fig. 4.8 are adopted for the features in the spectrum. One can see that the peaks A1-A2, B1-B3, and C1-C3 are well reproduced in the calculated oxygen pDOS. The spectra have been aligned to the position of the first peak. The present calculation by FLAPW method are well consistent with the results of Ref. [55] by localized spherical wave (LSW) method. The oxygen pDOS has been broadened by 0.1 eV FWHM with a Gaussian distribution. Herein, a smaller broadening is used in order to show the details of the structures. The calculated band gap in this work is about 2.0 eV which is reasonable in comparison with the experimental value of 3.2 eV. The underestimation of the band gap is a well-known feature of LDA method due to the inadequacy to describe the electron excitation directly by the ground state density of states with an one-electron approximation [41].

The orientation-decomposed pDOS provides the possibility of analyzing the origin of the individual feature in the spectrum. The oxygen pDOS can be decomposed into three components along X, Y and Z axes. The label “PZ” means the projection of the pDOS on Z-axis. The label “PX+PY” indicates the PX or PY projection of the pDOS. The features in the oxygen pDOS are related to the Sr-O, Ti-O and O-O interactions. Thus, the site-projected DOS of SrTiO3 are drawn in Fig. 4.12 in order to analysis the relationships. The total DOS of the Sr and Ti sites are decomposed into the corresponding partial DOS, and the $d$DOS of Sr and Ti are additionally decomposed into D-eg and D-t2g components. The orientation-decomposed pDOS of oxygen at (1/2,1/2,0) is drawn again for completeness.

In Fig. 4.11, peak A1 at 3.8 eV is almost entirely from the PX+PY component. At the same time, this peak relates to the D-t2g component in the Ti dDOS (cf. Fig. 4.12b). That means that peak A1 originates from the $pd$ hybridization between titanium and oxygen with a $\pi$-bonding character. Similarly, peak A2 is only found in the PZ component and relates to the $e_g$ component in the Ti dDOS. Therefore, peak A2 arises from the Ti-O $pd$ hybridization with a $\sigma$-bonding character. The $e_g$ component of the Ti dDOS is spread out from 4.0 to 9.0 eV, which can be seen in Fig. 4.12(b). The double peaks at 5.2 and 6.8 eV can also be found in the PZ component of the oxygen pDOS. In the calculated Ti dDOS, the intensity of peak $e_g$ is much weaker than that of peak $t_{2g}$, which is not correct in comparison with the ELNES of the Ti L23 edges in bulk SrTiO3 in Fig. 4.4(a). This disagreement is caused by the neglect of multiplet effects (or the interactions between core-hole and the crystal-field) for the titanium cations in the ground state calculations. Multiplet effects predominate the Ti L23 white lines. However, there is no significant multiplet effects on the oxygen K edge. The intensity of peak A2 is much weaker than that of peak A1, which is consistent with the relative intensity of peak $e_g$ and $t_{2g}$ in the Ti dDOS. This result is in agreement with the
Fig. 4.11: Ground state oxygen p-projected density of states compared with the ELNES of the oxygen K edge for SrTiO$_3$. The oxygen pDOS is decomposed into three components along X,Y,Z-axis.

Now, let’s look at the peak B1 in Fig. 4.11. Firstly, peak B1 is spread out in the range of 5.0-8.5 eV. It is overlapped with the peak A2. Peak B1 arises from both PZ and PX+PY components of oxygen pDOS. The PX+PY contribution is related to the Sr D-eg component, which can be seen from Fig. 4.12(a) and (c). The peak at about 8.0 eV in the PX+PY component can also be found in the Sr D-eg component at the same energy position. The B1 contribution from the PZ component of oxygen pDOS is mainly related to the Sr D-t2g component. Similar to the Ti-O bonding, the interactions between oxygen PZ and Sr D-t2g projected orbits have a $\pi$-bonding character, as well as the interactions between oxygen PX+PY and Sr D-eg orbits have a $\sigma$-bonding character. In the oxygen pDOS, peak B2 is almost entirely related to the PX+PY component. Mainly the Sr dDOS and partially the Ti D-t2g component contribute to this peak. Peak B3 is entirely from Sr DOS, which can be seen from Fig. 4.12(d). According to the decomposed Sr DOS in 4.12(a), peak B3 is contributed from Sr sDOS (s-character density of states) and dDOS components. Thus, peak B3 in oxygen pDOS has s and d characters indeed, which is forbidden by the dipole-transition rule. This is the reason why peak B3 almost disappears in the experimental spectrum. In comparison with the ELNES in Fig. 4.11, peak B1 is shifted to a lower energy by about 1.0 eV as well as 1.5 eV for peak B2. This difference is caused by the neglect of the core-hole effect in the DOS calculations. The core-hole potential trends to hamper the electron transition from a core level to the unoccupied density of states. That causes a little higher energy loss in the EELS experiments.

Peak C2 and C3 can not be well separated in SrTiO$_3$ due to intrinsic and instrumental broadenings. It might be difficult to assign the peaks in the range of 12-25 eV to C1, C2 and C3. Fortunately, a clear assignment can be given in the calculations for BaTiO$_3$, which will be discussed later. Due to similar atomic structures of BaTiO$_3$ and SrTiO$_3$, the assignment...
for peaks C1–C3 can be given as labeled in Fig. 4.11. Peak C1 is located at about 16.7 eV which is very close to the experimental value of 16.3 eV. Peak C2 is located about 21 eV in the calculated pDOS. This peak is overlapped by the peak C3 at about 22.5 eV. The energy separation between C1 and C2 amounts to about 4.3 eV. Due to the larger broadening at higher energies, the separation between C2 and C3 is completely smeared out in the electron energy-loss spectrum. Peak C1 comes partly from PX+PY and PZ components, while peak C2 is mainly related to the PX+PY component with a small contribution from the PZ component. According to the partial DOS of Sr and Ti atoms, peak C1 might be related to Sr pDOS, Sr D-t2g, Ti sDOS and Ti D-t2g components, while peak C2 is related to Sr dDOS, Ti pDOS, and Ti dDOS components according to the identical peak positions. Peak C3 is spread out in the range from 22 to 27 eV. The peak position is at about 22.5 eV in comparison with the experimental value of 23.5 eV. The explanation of the energy shift of 1.0 eV is the same as those of peaks B1 and B2 mentioned above in terms of core-hole effect. Peak C3 is entirely from the PX+PY component, which may be also related to Sr dDOS, Ti pDOS, and Ti D-t2g components. Even though peaks C1-C3 have been interpreted by Sr-O and Ti-O interactions, the relative intensities of peaks C1-C3 are not correct if the interpretation is only given by the Sr-O and Ti-O interactions. The fine structures above 12 eV should be dominated by O-O interactions.

The discussion above shows a reasonable way to interpret the fine structures by cation-anion interactions. But oxygen-oxygen interactions cannot be directly incorporated. O-O interactions are usually important in oxide compounds. They dominate the fine structures in the high-energy region in the electron energy-loss spectrum. It is not surprising because the repulsion between the ejected electron and the negatively charged oxygen neighbors has
the trend to increase the energy loss of the oxygen K edge. In fact, the fine structures of the oxygen K edge should be interpreted by the combination of Ti-O, Sr-O and O-O interactions. As known, the multiple-scattering method can get an excellent consistency with the experiments in the extended energy-loss fine structure (EXELFS) region. The combination of multiplet-scattering and band-structure methods should give a better understanding of the features in the oxygen ELNES spectrum.

The FMS method has the ability to consider the backscattering of the individual shell. The present FMS calculations take into account six shells around the oxygen site. The shell structure is shown in Fig. 4.13. The first shell only includes two titanium atoms along the Z-axis with the distance of 1.592 Å to the excited oxygen atom. The second shell (the 1st oxygen shell) includes eight nearest-neighbor oxygen atoms with a distance of 2.761 Å. The eight oxygen atoms occupy the eight corners of a rhombohedron with the lateral lengths of 2.761 Å in the X- and Y-axis and 3.905 Å in the Z-axis. The third one contains four strontium atoms lying in the XY plane. The distance to the central atom amounts to 2.761 Å. The fourth shell (the 2nd oxygen shell) contains six oxygen atoms in octahedral symmetry around the central atom. The shell-distance is 3.905 Å. The fifth shell is comprised of eight titanium atoms, which occupy the eight corners of a rhombohedron with the lateral lengths of 3.905 Å in the Z-axis and 5.523 Å in the X- and Y-axis. The distance to the central atom of this shell is 4.366 Å. The last shell has a distance of 4.783 Å to the central atom. Sixteen oxygen atoms are included in this shell and occupying the sixteen corners of a decahedron.

In the FMS calculations, the scattering potential is self-consistently calculated in a cluster with a radius of 5.0 Å, which contains 53 atoms. The FMS calculations of the oxygen K edge in SrTiO₃ following this shell model are shown in Fig. 4.14. The labels for the individual spectrum at the right side indicate the total number of atoms in the FMS cluster. When the six shells with 45 atoms are included in the cluster, all major peaks are reproduced in comparison with the 165-atom cluster. In the FMS calculations, the core-hole effect is taken into account. Peaks A1 and A2 can be reproduced in the 3-atom cluster. Peak A1 is sharp, but peak A2 spreads over a wide range of 535-540 eV. When the eight nearest-neighbor
oxygen atoms are appended, peak C1 is well reproduced. As the four nearest-neighbor barium atoms are considered, Peaks B1, B2 and B3 are reproduced, but peaks B1 and B2 are strongly overlapped the broadened peak A2. The second nearest-neighbor oxygen shell has a small contribution between peaks C1 and C3. This contribution is assigned to the peak C2, which is strongly overlapped the peak C3 according to the calculated oxygen pDOS in Fig. 4.11. The second nearest-neighbor titanium atoms have a very small influence on the fine structures above 12 eV. This is caused by their small scattering cross sections for the electron wave. Peak C3 is mainly related to the third nearest-neighbor oxygen shell, which can be seen from the 45-atom spectrum.

In conclusion, peaks A1-A2 are dominated by Ti-O bonding, peaks B1-B3 by Sr-O bonding. Peaks C1 is mainly related to the nearest-neighbor oxygen shell, as well as peaks C2 and C3 are mainly related to the second and the third nearest-neighbor oxygen shells, respectively. Although peaks C1-C3 have identical peak positions to the corresponding peaks in Sr DOS and Ti DOS, the amplitudes are mainly dominated by the surrounding oxygen atoms. Herein, the term of a “shell field” is introduced, which represents the local field of the corresponding shell felt by the excited electron from the core level. This definition is similar to the conventional definition of “ligand field” or “crystal field”. For a neighbor cation shell, the shell field has a trend to facilitate the electron excitation due to the attraction on the ejected electron. That makes the corresponding excitation slightly easier. Vice versa, the neighbor anion shell has a trend to hamper the corresponding excitation by repulsion, which makes the corresponding excitation energy slightly higher. For the Ti$^{4+}$ shell, its shell field is slightly stronger than that of the Sr$^{2+}$ shell. Therefore, the Ti-related features are located in the lower-energy region and the Sr-related features in the higher-energy region. Due to the repulsion of the negatively charged oxygen shell on the ejected electron, the O-O interaction related features C1-C3 present in the higher-energy region of the spectrum. The

**Fig. 4.14**: FMS calculations of the oxygen K edge for SrTiO$_3$ in shell-by-shell model.
CHAPTER 4. HR-EELS INVESTIGATION OF BATIO$_3$/SRTIO$_3$ MULTILAYERS

energetic sequence of peaks C1-C3 may be explained by the electron hopping mechanism. The ejected electron can be more easily transferred to the nearest-neighbor oxygen atoms than the other oxygen atoms. From the point of view of the multiple-scattering, higher energy of the photoelectron wave is needed to reach higher oxygen shells.

4.4.2 Bulk BaTiO$_3$

The interpretation of the fine structures of the oxygen K edge in BaTiO$_3$ is similar to that of SrTiO$_3$ due to the similar atomic structure. Firstly, the unit cell parameters of bulk BaTiO$_3$, which are listed in Table 4.3, are taken from Ref. [73]. The atomic structure of the unit cell can be seen in Fig. 4.2(b). There are two inequivalent oxygen positions in the unit cell, which are labeled O1 and O2, respectively. O1 takes the position (1/2,1/2,-0.024) and O2 takes the positions (0,1/2,0.48) and (1/2,0,0.48). The atomic coordinations of O1 and O2 sites are schematically shown in Fig. 4.15. The major difference between the local environments of the O1 and O2 sites is the rotation of the nearest-neighbor oxygen atoms which surround the O1 site in a tetrahedral symmetry and the O2 site in a distorted tetrahedral symmetry.

In the DOS calculations, the muffin-tin radii of Ba, Ti and O are set to 2.4, 1.9 and 1.6 in units of the Bohr radius, respectively. A $10 \times 10 \times 9$ k-point sampling is used in the irreducible Brillouin zone. The total of 900 k-points are sufficient in the present calculations by comparing with the results of the 8000 k-points calculations in the literature [89]. The site-projected DOS are shown in Fig. 4.16. The O1 pDOS is decomposed into PZ and PX+PY components. For the O1 site, the PX and PY components are equal, and they are represented by the PX+PY component together.

As known, the electron beam is converged on the specimen in the STEM image mode. The EELS/STEM spectrum in the image mode is angularly averaged because the convergent beam eliminates the coherence of the electrons [64]. Therefore, the total oxygen DOS should be compared with the experimental spectrum. The comparison between oxygen pDOS and the measured ELNES of the oxygen K edge is shown in Fig. 4.17. The total oxygen pDOS is given by the summation of O1 and O2 pDOS weighted with the corresponding multiplicity of equivalent positions. The interpretation of the fine structures in oxygen pDOS is similar to that of SrTiO$_3$. Peaks A1 and A2 are related to the hybridization of the titanium 3d orbitals and the oxygen 2p orbitals. The intensities of peaks A1 and A2 are slightly smaller than those of SrTiO$_3$ due to the larger bond length which reduces the Ti-O hybridization. The weak peak A2 is smeared out by the overlapping peak B1. Peaks B1 and B2 are dominated by the Ba-O bonding interactions. The calculated splitting of the peaks B1 and B2 in BaTiO$_3$ is about 2.0 eV compared to the splitting of about 1.0 eV in SrTiO$_3$. Due to the stronger broadening of the peak B1 in BaTiO$_3$, this splitting is not discriminable in the ELNES spectrum, in contrast to the well separated peaks B1 and B2 in SrTiO$_3$. In comparison

<table>
<thead>
<tr>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$R_{MT}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>0.0</td>
<td>0.0</td>
<td>2.4</td>
</tr>
<tr>
<td>Ti</td>
<td>0.5</td>
<td>0.5</td>
<td>0.515</td>
</tr>
<tr>
<td>O1</td>
<td>0.5</td>
<td>0.5</td>
<td>-0.024</td>
</tr>
<tr>
<td>O2</td>
<td>0.5</td>
<td>0.0</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Table 4.3: Unit cell parameters of bulk BaTiO$_3$ with a space group P4mm, taken from Ref. [73]. The lattice parameters are $a=3.994$ Å, $b=4.038$ Å. The muffin-tin radii $R_{MT}$ used in the DOS calculations are given for all different atoms in units of the Bohr radius.
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Fig. 4.15: (a) Atomic coordination of O1 site. (b) Atomic coordination of O2 site. The lateral lengths of the oxygen hexahedron are scaled in units of Å.

Fig. 4.16: Ground state site-projected density of states of bulk BaTiO$_3$. The pDOSs of the O1 and O2 sites at (1/2,0,0.48) are decomposed into PX, PY and PZ components. The O2 site at (0,1/2,0.48) is equivalent to the O2 site at (1/2,0,0.48) except a 90° rotation about the Z-axis.
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Fig. 4.17: Ground state oxygen $p$-projected density of states of the bulk BaTiO$_3$ in comparison with the ELNES of the oxygen K edge.

with SrTiO$_3$, the intensity of the peak B2 is a little stronger in BaTiO$_3$. This result is well consistent with the experimental finding. The small energy shift of the peaks B1 and B2 is caused by the core-hole effect. Peak B3 is mainly related to the $f$ DOS ($f$-character density of states) of Ba atoms, which can be seen in Fig. 4.16(a). Since the $1s \rightarrow 4f$ transition is forbidden by the dipole selection rule, peak B3 is not present in the experimental spectrum. The interesting features in the oxygen K edge are peaks C1 and C2. The 3.8 eV-splitting of C1 and C2 is well reproduced. In comparison with the ELNES spectrum, the calculated peaks C1 and C2 are shifted to higher energy by about 2.5 eV, and the intensity of peak C2 is underestimated. The underestimated intensity of the peak C2 might be caused by the neglect of the dipole transition matrix. When the dipole selection rule is applied, the relative intensities of peaks C1 and C2 should have a better consistency with the experiment.

The oxygen $p$-projected density of states in bulk (P4mm), Pm3m and layer BaTiO$_3$ have been compared in this thesis. The lattice parameter ($a=4.009$ Å) of the Pm3m BaTiO$_3$ was determined by taking the same unit cell volume as bulk BaTiO$_3$. The lattice parameters of the layer BaTiO$_3$ have been determined by the selected-area diffraction pattern (cf. Table 4.1). The atomic positions in the unit cell of the layer BaTiO$_3$ have been assumed to be same as those of bulk BaTiO$_3$. The comparison is given in Fig. 4.18. One can see that the three spectra are very close except a small energy shift in the high-energy region. In comparison with bulk and the Pm3m BaTiO$_3$, the oxygen $p$ DOS of the layer BaTiO$_3$ is slightly shifted to higher energy by about 0.2 eV. This shift is caused by the misfit strain which compresses the lattice in the XY plane. However, this slight shift is difficult to recognize in the ELNES spectra due to the spectral broadening at the high-energy tail of the core-loss edge.

The relationship between the peaks C1-C3 and the surrounding oxygen shells can be determined following the similar procedures like for SrTiO$_3$. FMS calculations in the shell-by-shell model have been done for O1 and O2 sites, respectively. The calculations have been performed from 3 up to 49 atoms. The 49-atom cluster is divided into six shells. The
Fig. 4.18: Comparison of oxygen $p$DOSs in bulk (P4mm), Pm$\bar{3}$m and layer BaTiO$_3$. The spectra have been normalized by the intensity of peak A1.

definition of each shell is similar to that in Fig. 4.13, except the different distance to the central atom and a slight distortion of the symmetry. The details are listed in Table 4.4. The results of the FMS calculations are given in Fig. 4.19. The FMS calculation in a 169-atom cluster is given for comparison. Similar to SrTiO$_3$, peak C1 can be assigned to the nearest-neighbor oxygen shell, peak C2 is assigned to the second nearest-neighbor oxygen shell and peak C3 is assigned to the third nearest-neighbor oxygen shell. The main difference between the fine structures of the O1 and O2 K edges is that the intensity of the peak A1 of the O1 K edge is higher than that of the O2 edge. This is caused by the shorter Ti-O1 bond length which enhances the $pd$ hybridization.

Table 4.4: The definition of each shell surrounding O1 and O2 sites. The distance is given in units of Å.

<table>
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<tr>
<th>Shell</th>
<th>O1 Distance</th>
<th>O2 Distance</th>
</tr>
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<tbody>
<tr>
<td>1$^{st}$</td>
<td>2 Ti 1.86-2.18</td>
<td>2 Ti 2.00</td>
</tr>
<tr>
<td>2$^{nd}$</td>
<td>4 Ba 2.83</td>
<td>4 Ba 2.78-2.90</td>
</tr>
<tr>
<td>3$^{rd}$</td>
<td>8 O2 2.83-2.85</td>
<td>4 O1 + 4 O2 2.82-2.85</td>
</tr>
<tr>
<td>4$^{th}$</td>
<td>6 O1 4.00-4.04</td>
<td>6 O2 4.00-4.04</td>
</tr>
<tr>
<td>5$^{th}$</td>
<td>8 Ti + 4 Ba 4.40-4.85</td>
<td>8 Ti + 4 Ba 4.40-4.87</td>
</tr>
<tr>
<td>6$^{th}$</td>
<td>16 O2 4.89-4.91</td>
<td>8 O1 + 8 O2 4.89-4.93</td>
</tr>
</tbody>
</table>
4.5 Summary

High-energy resolution electron energy-loss spectroscopy has been applied to investigate BaTiO$_3$/SrTiO$_3$ multilayers. The near-edge fine structures are discussed based on experimental results and Ab-Initio full multiple-scattering and band-structure calculations. It reveals that the crystal-field splitting can be used to characterize the misfit strain in BaTiO$_3$ layers. The crystal-field splitting of the BaTiO$_3$ thin layer is a little larger than that of bulk BaTiO$_3$ due to the present of the misfit strain. This result is confirmed by the lattice parameters of the BaTiO$_3$ thin layer determined by the selected-area diffraction. This finding proves that the crystal structure of the BaTiO$_3$ layer is compressed in the growth plane by the misfit strain.

From the increased [Ti]/[O] ratio obtained, oxygen vacancies are found to preferably aggregate at the rougher upper interface of BaTiO$_3$ layers. Oxygen vacancy ordering occurs in the BaTiO$_3$ thin layer under the influence of the misfit strain. Near the lower interface, the BaTiO$_3$ layer is revealed to be defect free due to the presence of the misfit strain. It is concluded that the difference of dielectric properties between multilayers and bulk BaTiO$_3$ is dominated by the aggregation of oxygen vacancies (related to a space charges region) at the rough upper interface.

The near-edge fine structures of the multilayers are discussed based on experimental results and theoretical calculations. According to the full multiple-scattering and band-structure calculations, the fine structures of the oxygen K edge above 12 eV and the satellite structures of the Ti L$_{23}$ edges in SrTiO$_3$ and BaTiO$_3$ are partly related to Ti-O and Sr-O or Ba-O interactions and mainly reflecting oxygen-oxygen interactions. The results give a better
understanding of the origin of the fine structures. The theoretically derived results are fairly well consistent with the experimental findings. For the oxygen K edge, the band-structure method has a better accuracy in the energy range of 0-12 eV above the Fermi level while the full multiplet-scattering method is suitable to analyze the oxygen-oxygen interactions in the higher energy range. In the different compounds with a perovskite structure, the fine structures of the oxygen K edge are very similar. The relationship between spectral features of the oxygen K edge and the coordination around the oxygen site is summarized in Table 4.5.

Table 4.5: The relationship between the fine structures of the oxygen K edge and the surrounding coordination around the oxygen site in perovskite oxides MTiO$_3$. M indicates the metal element such as Ba, Sr, Pb, Zr, etc.

<table>
<thead>
<tr>
<th>Peak</th>
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<tbody>
<tr>
<td>A1,A2</td>
<td>The nearest Ti atoms</td>
</tr>
<tr>
<td>B1,B2 and B3</td>
<td>The nearest M atoms</td>
</tr>
<tr>
<td>C1</td>
<td>The 1$^{st}$ O shell</td>
</tr>
<tr>
<td>C2</td>
<td>The 2$^{nd}$ O shell</td>
</tr>
<tr>
<td>C3</td>
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