Investigating Surface Properties and Lithium Diffusion in Brookite-TiO₂Corinne Arrouvel^{*,a,b} and Stephen Charles Parker^a^aDepartment of Chemistry, University of Bath, BA2 7AY Bath, UK^bDepartamento de Física, Química e Matemática, Centro de Ciências e Tecnologias para a Sustentabilidade, Universidade Federal de São Carlos, Campus Sorocaba, 18052-780 Sorocaba-SP, Brazil

Surfaces properties of TiO₂ in the brookite phase and the lithium diffusion are studied using density functional theory (DFT) and interatomic potential simulations. Simulations predict that the brookite surfaces have a higher intrinsic Lewis acidity compared to the other polymorphs due to the presence of four coordinated Ti atoms on the surface in contrast to the most stable surfaces of anatase and rutile which have five coordinated Ti surface atoms. The surface reactivity of the brookite is then expected to be higher for catalysis. The (210) surface is the most stable calculated surface and some experimental morphologies have been revisited. Regarding Li intercalation, the migration occurs along the c-direction and open channel surfaces are desired, therefore particles exposing the (001) surface. Those differences on chemical/physical properties highlight the importance to control the nanoparticle shapes for a given application.

Keywords: density functional theory, interatomic potentials, surface properties, morphologies, lithium battery

Introduction

The anatase and rutile phases have been widely studied¹ because they are often used in photocatalysis,² as a catalyst support,³ in dye-sensitized solar cell⁴ and for medical application (the photocatalyst can be seen as the bactericidal,⁵ the oxide surface of Ti is used for biocompatibility).⁶ There are fewer experimental studies on brookite despite its potential for use in photocatalysis,⁷⁻⁹ catalysis,^{10,11} for photovoltaic applications¹²⁻¹⁴ and lithium rechargeable batteries.^{15,16} Brookite is a metastable phase of stoichiometric TiO₂ and is less common than the other phases, anatase and rutile. Experimental studies have derived the thermodynamic properties from 298 K¹⁷ to high temperatures.¹⁸ They confirm that rutile is the most stable phase followed by brookite and then by anatase.

Although studies have succeeded in synthesizing brookite, most of them also obtain the other phases, anatase and rutile. Furthermore, as the occurrence of the exposed surfaces is highly dependent on the synthesis conditions under which brookite is prepared (e.g., hydrothermal or hydrolysis), it is difficult to assess the relative stabilities of the different surfaces from experiment. This is further

exemplified by very different morphologies that have been observed such as tablet/sheet,¹⁹⁻²¹ stick,^{9,22} pseudo-cubic²³ and spherical.⁸ Some authors^{19,20,24} have been able to identify the exposed surfaces using TEM (transmission electron microscopy) and XRD (X-ray diffraction). Moret *et al.*²⁵ have used X-ray methods and found that the dominant surfaces are (210), (111), (211) and (102). In contrast, Kominami *et al.*²⁴ have identified the (121) surface along with the (120) or (111) surface. Shibata *et al.*²⁰ have analysed brookite with a plate-like habit in which the major surface was (010). Finally, Pottier *et al.*¹⁹ have obtained nanocrystals of brookite dominated by a basal face, supposed to be an unusual (301) facets with only two exposed surfaces surrounded by four (111) surfaces.

To better link the structures of brookite surfaces with their stabilities and reactivities, we aim to generate reliable models to express the shape of the particles regarding the experimentally observed surfaces. We combine DFT (density functional theory) and force field methods. The diffusion path of lithium in brookite using DFT methods is compared to the results by Arrouvel *et al.*¹⁵ using force field methods. We focus with DFT on the (210), (100) and (010) surfaces but also on the (301) and (111) surfaces that have been identified by Pottier *et al.*¹⁹ A comparison of brookite with previous simulations on TiO₂ polymorphs²⁶⁻⁴⁰ is also

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addressed to enable us to infer the potential of brookite for catalysis and energy materials.

Methodology

DFT calculations

Total energy calculations are performed within the density functional theory (DFT) implemented in the Vienna *ab initio* simulation package (VASP).⁴¹⁻⁴³ Different functionals have been tested: the generalized gradient approximation (GGA) of Perdew and Wang (PW91),⁴⁴ the revised Perdew-Burke-Ernzerhof functional (RPBE)⁴⁵ and local density approximation (LDA).⁴⁶ PW91 is the most accurate on the bulk study (see Results section) and is mainly used for this study. Another approach is to use DFT+U⁴⁷ which combines the GGA functional with U, the site Coulomb parameter, for the electronic correlation for d orbitals. U is a value adjusted by hand to reproduce some experimental properties. The influence of the U value on some properties is tested. To solve the Kohn-Sham equations, VASP performs an iterative diagonalization of the Kohn-Sham Hamiltonian via unconstrained band-by-band minimization of the norm of the residual vector to each eigenstate and via optimized charge density mixing routines. The convergence criterion for the electronic self-consistent cycle is fixed at 0.1 meV *per* cell. The eigenstates of the electron wave functions are expanded on a plane-waves basis set using pseudopotentials to describe the electron-ion interactions within the projector augmented waves (PAW) approach.⁴⁸ For total energy calculations with PW91, we use a cutoff energy of 312.5 eV. The optimization of the atomic geometry at 0 K is performed by determining the exact Hellman-Feynman forces acting on the ions for each optimization step and by using a conjugate gradient algorithm. A full relaxation of all atomic positions in the cell is performed until the geometric convergence criterion on the energy (1 meV *per* cell) is reached. A convergence on the k-point meshes using Monkhorst-Pack scheme⁴⁹ is also ensured on bulk structural optimization and it is even overvalued for the band gap calculations (see the values in the Results section).

ZPE contributions

The zero point energy (ZPE) contribution is calculated using the well-known lattice dynamics approach of Born and Huang,⁵⁰ where the vibrational frequencies are calculated by diagonalizing the dynamic matrix at different points in k-space and then integrated over k-space to yield the energy contribution. The problem is that

the direct calculation of the vibrational frequencies as a function of k-space is CPU (central processing unit) time consuming when using *ab initio* approaches. However, model potentials⁵¹ can achieve virtually the same level reliability, certainly when integrated over k-space, and have the advantage of being very quick and efficient. We used PARAPOCS program,^{52,53} which was developed to perform free energy minimization of solids using numerical derivatives, as a consequence gives the vibrational frequencies and the different components of the free energy suitably evaluated over the whole Brillouin zone. This code has also been previously used in conjunction with DFT calculations modelling two low index surfaces of ZnO.⁵⁴

Interatomic potential methods

The simulations are upon a Born model of solid where ions interact via long-range electrostatic forces and short range-forces including both the repulsions and the van der Waals attractions between neighboring electron charge clouds.⁵⁰ We have used interatomic potentials derived by Matsui and Akoagi⁵⁵ which were successfully used to model the surfaces of rutile⁵¹ and adapted to model the rutile-water interface.⁵⁶ Those potentials have been described by Oliver *et al.*⁵¹ and our atomistic simulations have been undertaken with the same code, METADISE (minimum energy techniques applied to dislocation, interface, and surface energies).⁵⁷

The potentials follow the relation:

$$V_{r_{ij}} = \sum \frac{q_i q_j}{r_{ij}} + A_{ij} \exp(-r_{ij} / \rho_{ij}) - \frac{C_{ij}}{r_{ij}^6} \quad (1)$$

with q_i , q_j the charges of each ion, r_{ij} the separation of the ion centers, and A, ρ , C the ion-ion parameters in the Buckingham relation. And they are given in Table 1.

Those potentials do not have a shell model and their validity for brookite-TiO₂ has been compared to DFT on surface energy calculations.

Table 1. Interatomic potentials for TiO₂

	$q / e $	A / eV	$\rho / \text{\AA}$	$C / (\text{eV \AA}^6)$
Ti	+2.196	31120.2	0.154	5.25
O	-1.098	11782.76	0.234	30.22
Ti-O		16957.53	0.194	12.59

q: ion charge; A, ρ , C: Buckingham parameters.

Surface energy calculations

The surface energy in vacuum, Γ_{hkl}^0 , for a given crystal orientation (hkl), is given as follows:

$$\Gamma_{hkl}^0 = \frac{G_{hkl} - NG_{bulk}}{2A_{hkl}} \quad (2)$$

G_{hkl} is the Gibbs free energy of the (hkl) surface and the G_{bulk} is the Gibbs free energy of the bulk normalized to the number N of atoms used in the supercell. A_{hkl} is the surface area. We note that a slab of the supercell contains two (hkl) surfaces.

The calculations are performed at 0 K and neglect the zero point energy which is valuable considering that the ZPE difference between the surface and the bulk is negligible. Finally, the slab energies assume constant surface area. Therefore, we can write: $G = E$, with E the energy of the bulk or the slab. The equation 2 becomes:

$$\Gamma_{hkl}^0 = \frac{E_{hkl} - NE_{bulk}}{2A_{hkl}} \quad (3)$$

From the k-point grid optimization of the bulk energies (in Table 2) we can evaluate the k-point grid necessary for the calculations of each surface. To avoid the interaction between slabs along the z axis, we make a vacuum gap higher than 26 Å for each surface and ensure that the slabs have mirror symmetry (vacuum and slab sizes are summarized in Table 3). In each simulation, all of the atoms are allowed to relax. Another point to take into account is the eventual oscillation of the surface energy with the parity of the number of layers. When a surface has an oscillating surface energy, the minimum is observed for even numbers of layers and a maximum for odd numbers of layers, whatever functional or pseudopotential is chosen (for example on the (110) surface of rutile,^{31,34,37,39} (110) and (100) surfaces of anatase).⁵⁸ In order to ensure that we had a reliable value of surface energy, we chose a relatively high and even number of layers in the case of the brookite and rutile phases, as the case of the anatase phase having been carefully detailed in a previous study.²⁶ The (101) and (001) surfaces of anatase do not oscillate and from a previous study²⁶ the required slab depth is known to have a reliable value for the surface energy. The details for each calculated surface are given in the following Results section. The value of the surface energy may vary with both slab thickness and with different functionals. However, the variation of energy is the same so it is important to keep the methodology consistent when comparing different surfaces. For that consistency, we choose the method from Arrouvel *et al.*²⁶

Gibbs-Curie-Wulff construction

The Gibbs-Curie-Wulff law⁵⁹ provides an approach determining the equilibrium morphology of an ideal crystal

according to the following relationship,

$$\frac{\Gamma_{hkl}}{d_{hkl}} = \alpha \quad (4)$$

where Γ_{hkl} is the surface energy for the (hkl) orientation, d_{hkl} is for the normal distance from the surface to the center of mass of the solid, and α is a constant independent from h, k, l .

The METADISE⁵⁷ code allows us to express the equilibrium shape of the oxide using the surface energies from DFT and atomistic calculations and indeed to compare it with predictions using simplified pair potentials. Previous theoretical studies^{58,60} have shown that the shape at the thermodynamic equilibrium depends strongly on the working conditions. However, the first step is to consider the material under vacuum.

Results

TiO₂ bulk

The crystal structure of brookite is orthorhombic ($a = 9.184$ Å, $b = 5.447$ Å, $c = 5.145$ Å).⁶¹ Before constructing the surfaces of brookite, it is necessary to optimize the bulk cell from X-ray data⁶² using the simulation approach described above. A comparison with the bulk crystal structure of anatase^{63,64} and rutile⁶⁵ obtained from X-ray data are summarized in Table 2. From the convergence criteria on bulk calculations, the convergence on ionic forces is ca. 1 meV Å⁻¹.

The rutile phase is the densest of the three phases with the highest symmetry. The bulk cell (Figure 1) contains 2 TiO₂ units and there are two different Ti–O distances (calculated Ti–O distances with GGA/PW91 functional and PAW pseudopotentials are: 1.961 and 1.997 Å). The anatase phase has also two different Ti–O distances (calculated Ti–O: 1.946 and 2.005 Å). The brookite phase has 6 different Ti–O lengths, calculated distances between 1.873 and 2.081 Å (1.873, 1.925, 1.944, 2.000, 2.025 and 2.081 Å).

From the calculated total energy E_T , the relative stability of each phase can be deduced and compared with the experimental enthalpy differences. Effectively, the calculated total energy corresponds to the internal energy and can be simply linked to the enthalpy by neglecting the effect of temperature and zero point energy (ZPE). The experiment for the enthalpy data is given at ambient temperature and the extrapolation at 0 K does not reverse the order of stability between anatase and rutile. The calorimetric work has also shown that the standard entropy of the different phases are similar and hence entropic

Table 2. Calculated structural and energetic characteristics of TiO₂ polymorphs

	Brookite	Anatase	Rutile
Space group	Pbca (61)	I 4 ₁ /amd (141)	P4 ₂ /mmn (136)
Crystal system	orthorhombic	tetragonal	tetragonal
<i>a</i> , <i>b</i> / Å	9.241, 5.489	3.801	4.637
<i>c</i> / Å	5.182	9.697	2.971
Internal coordinate <i>u</i>	–	0.207	0.305
Cell volume / Å ³	263.13	140.10	63.86
Number of TiO ₂ units	8	4	2
<i>E_T</i> / (eV per cell)	–215.25	–107.78	–53.72
<i>E_T</i> / (kJ mol ^{–1} per TiO ₂)	–2596.05	–2599.79	–2591.59
Band gap <i>E_g</i> / eV	2.32 (3.78) ^a	2.22 (3.59) ^a	1.91 (3.24) ^a
k-point meshes up to	8 × 8 × 8	8 × 8 × 8	14 × 14 × 14
<i>E_T</i> (RPBE/PAW) / (kJ mol ^{–1} per TiO ₂)	–2383.42	–2390.17	–2377.39
<i>E_T</i> (DFT+U ^b) / (kJ mol ^{–1} per TiO ₂)	–2032.34	–2032.22	–2039.21
ZPE / (kJ mol ^{–1} per TiO ₂)	24.75	24.50	24.94

^aFrom Beltrán *et al.*,⁶⁶ B3LYP/6-31G; ^bU = 9.0 eV, J = 0.3 eV fitted on rutile; *E_T*: total energy; RPBE: revised Perdew-Burke-Ernzerhof; PAW: projector augmented waves; DFT: density functional theory; ZPE: zero point of charge; B3LYP: Becke 3 Lee-Yang-Parr.

Figure 1. Structure of the calculated bulk of (a) rutile; (b) anatase; (c) brookite. Light balls: Ti atoms; dark balls: O atoms (same colors for all figures).

differences will not affect the order of stability (values are available for rutile and anatase).^{17,67}

The calculations show that anatase is more stable than rutile by 8 kJ mol^{–1} (ΔE_T per TiO₂ unit) and less surprising is more stable than brookite by 3 kJ mol^{–1}. We found that the ZPE, calculated empirically with PARAPOCS,^{52,53} does not affect the order of stability. We have also tested the RPBE (revised Perdew-Burke-Ernzerhof) functional with a PAW pseudopotential and a cutoff of 353.6 eV; and still found that the anatase phase was the most stable one at 0 K. In addition, the cell parameters are less well represented compared to PW91. Using DFT+U⁴⁷ we found, in agreement with Vu *et al.*,⁶⁸ that the rutile phase becomes the most stable phase with the increase of the U value. However, the choice of the Coulomb site U and the

exchange site J on Ti is somewhat empirical. We chose to fit to the band gap of rutile phase at 3.0 eV using the values of U = 9 eV and J = 0.3 eV, but the fitted values give less reliable band gaps for the other phases, the anatase at 3.4 eV and the brookite 3.3 eV, i.e., the band gap of anatase is overestimated. A high value of U (U = 10 eV) has been reported with LDA by Person and Ferreira da Silva⁶⁹ in order to reproduce the band gap of rutile. From our results, U is not reliable enough to compare different polymorphs. Tables S2 and S3 in Supplementary Information (SI) section resume the calculated values of band gaps and cell volumes regarding different U values.

There are some theoretical studies on the bulk electronic properties but few reproduce the experimental band gap due to the choice of the functional. The LDA functional

underestimates the band gap (anatase: 2.0 eV;^{70,71} rutile 1.5-2.0 eV),^{71,72} and Hartree-Fock calculations overestimate it (anatase: 10 eV).⁷³ The result with a hybrid method B3LYP (Becke 3 Lee-Yang-Parr, functional combining three thermodynamic experimental parameters)⁷⁴ shows a better agreement (anatase: 3.7 eV).²⁷ The calculation close to experimental value is the one using LMTO (linear muffin-tin orbital) method on rutile (3.06 eV)⁷⁵ but complementary results are not available for anatase and brookite.

There are many experimental references in the literature to the band gap of bulk rutile, 3.0 eV² and anatase, 3.2 eV.⁷⁶ From our DFT calculations with GGA/PW91 functional, the band gap is also underestimated. The relative order is however consistent with experimental data. The band gap of anatase is 0.3 eV higher than the rutile. There is no experimental data on large crystals of brookite due to the lack of experimental pure specimens and that most experimental syntheses generate nanoparticles. Indeed, some studies of the band gap on nanoparticles of brookite by Koelsch *et al.*¹³ give 3.4 or 3.26 eV,²⁰ which is still in agreement with the calculated relative order. Koelsch *et al.*⁷⁷ showed also that the band gap varies with the nanoparticle size. The authors do not know if the band gap variation is due to the direct or indirect transition. The direct transition increases when the size decreases. For the indirect transition, the variation is less pronounced but the tendency is similar on anatase and brookite, and more variable on rutile. Other authors report for nanoparticles of brookite band gap at 3.11 eV,⁷⁸ 3.13 eV.²² The study from Koelsch *et al.*⁷⁷ has suggested that the morphology plays a key role on the electronic properties and then, it becomes important to compare the different surfaces of each phase. Furthermore, as we want to explore whether brookite is more reactive and hence potentially a technologically more important material, we needed the simulations to

be consistent with previous studies.²⁶ As the GGA/PW91 functional has been shown to be able to describe the surface structures and their reactivity we report the surface energies with this functional and PAW pseudopotentials. Some tests have been undertaken with DFT+U and the surface energy varies with the U value but the structure of the surface remains the same (not shown in the present paper).

Li diffusion in brookite-TiO₂

From a previous study,¹⁵ we have identified the lithium pathway using force field. The lithium is diffusing along the c direction and two channels are interconnected. The optimized path is reproduced with 15 positions following the c direction in one of the channels and the connection between two channels, see Figure 2. For each calculation, the spin-polarization is considered, all ionic positions are relaxed and only the z coordinated is keeping fixed for Li to be able to evaluate the path and energies along the c direction. Some key Li positions have been fully relaxed in order to reach the fully relaxed stable intercalated lithium. We report an activation energy of 0.73 eV, slightly lower than the activation energy obtained with force field ($E_{ac} = 1.07$ eV).¹⁵ This difference is consistent with calculated activation energy barriers on TiO₂-B, comparing the same methods (DFT and force field).^{15,79} The most stable site at the center the unit cell relaxed at fractional coordinates 0.59 0.62 0.55 (see Figure 2b). This result agrees with the previous study from Arrouvel *et al.*,¹⁵ this site having been identified as the C site, with the Wyckoff notation 8c. The center of the unit cell is in fact a barrier between two c-channels, agreeing with force field methods, site M, Wyckoff notation 4b. The 6 oxygen atoms in the first coordination sphere are at distances 1.83, 1.86, 2.01, 2.03, 2.16 and 2.66 Å. We note that there are four equivalent positions. Another stable position is found at

Figure 2. (a) 15 Li positions along a channel, where Li was allowed to relax in the *x-y* plane but fixed in *z*, to illustrate the nonlinear diffusion. (b) Most stable position. Li in purple, O in red, Ti in grey.

$z = 0.4$ in fractional coordinates. The lithium is surrounded by 6 oxygen ions in a distorted environment, 3 pairs of distances 1.8, 2.1 and 2.4 Å. The barrier is at $z = 0.2$ in fractional coordinates (the second barrier in the same channel being at $z = 0.7$).

The DFT results are in excellent agreement with force field methods for geometrical properties. No magnetic moment is observed in the stable sites. During the diffusion, the total magnetic moment of the unit cell can reach $0.26 \mu_B$ in some positions close to the stable sites.

Brookite-TiO₂ surfaces

We will characterize the main surfaces which have been observed experimentally on particles from different methods. There is special interest in (301) and (111) surfaces because the synthesis of the brookite at low pH (pH = 1) from TiCl₄ induces the formation of well-defined nanoparticles exhibiting mainly those surfaces with the (301) identified as the basal face^{19,77} by TEM. However, other studies from Ohno *et al.*²³ and Lin *et al.*²¹ also demonstrate morphologies exposing the (210) surfaces. Resultantly, we describe other important surfaces, such as (210), (100) and (010) surfaces of brookite (Table 3). Brookite has the least symmetrical crystal structure than anatase and rutile, therefore more atoms are required in the simulation cells (higher number of layers and higher surface area) in order to have a good description of the surfaces. All the surfaces relax considerably, which means that a larger number of layers is required. Only the most stable terminations are presented. In those slabs, we can see that

the surface energies before the ionic relaxation are twice the surface energies after relaxation. The convergence on ionic forces is ca. 10 meV on each atom for the surfaces.

We denote the acid Lewis sites by Ti_V the five coordinated Ti atoms and by Ti_{IV} the four coordinated Ti atoms. The basic sites generated are bridging oxygen μ_2O .

(301) surface

Modelling the (301) surface has been our first focus because it is the dominant surface of nanoparticles synthesized using TiCl₄ as discussed above. This surface has a large energy Γ_{301}^0 (after relaxation: 1.03 J m^{-2}) in comparison to surfaces with lower Miller indices (Figure 3 and Table 3). Before relaxation, the surface energy is 2.28 J m^{-2} and has the six different Ti–O distances seen in the bulk (1.873, 1.925, 1.944, 2.000, 2.025 and 2.081 Å). Upon relaxation, all the surface bond distances shorten, up to 0.3 Å. For example, a Ti_{IV}–O bond has an initial long distance of 2.081 Å and becomes the shortest distance of the surface at 1.771 Å. We note that these longest Ti–O distances are reduced to the greatest extent. The surface Ti–Ti distances also become significantly shorter (around 0.2 Å). The environment of the 2/3 of the Ti_{IV} atoms is similar to the Ti_{IV} on the (110) surface of anatase. As the (110) surface of anatase is highly reactive with adsorbed molecules (such as H₂O and H₂S),^{26,60} we would expect the brookite surface to behave similarly. The dissociative chemisorption of one isolated H₂O molecule leads to Ti_V– μ_1OH and μ_2O –H, with an adsorption energy of -1.37 eV .²⁶ This face of brookite is less symmetric than the (110) surface of anatase because of the presence of various

Table 3. Calculated characteristics of various brookite surfaces

(hkl) surfaces	(301)	(111)	(210)	(100)	(010)
Atom number	96	96	96	72	72
k-point meshes	$1 \times 3 \times 1$	$2 \times 2 \times 1$	$4 \times 3 \times 1$	$6 \times 6 \times 1$	$6 \times 6 \times 1$
Surface area / Å ²	99.26	75.33	74.35	28.47	47.92
Slab thickness / Å	8	9	13	27	16
Vacuum thickness / Å	32	26	32	33	44
Γ_{hkl}^0 / (J m ⁻²)	2.28	1.74	1.58	2.13	1.58
Γ_{hkl}^0 / (J m ⁻²)	1.03	0.78	0.71	0.95 (1.27) ^b	0.83 (0.97) ^b
μ_2O / (μmol m ⁻²)	13.38	11.02	8.93	11.68	13.87
Ti _{IV}	5.02	2.20	0	0	6.94
Ti _V	3.35	6.61	8.93	11.68	0
Number of broken Ti–O bonds	26.8	22.0	17.9	23.4	27.7
k-point meshes	$10 \times 20 \times 1$	$16 \times 20 \times 1$	$20 \times 16 \times 1$	$20 \times 20 \times 1$	$16 \times 10 \times 1$
E_g / eV	2.27	2.51	2.47	2.33 (3.69) ^b	2.74 (4.63) ^b

^aBefore relaxation; ^bfrom Beltrán *et al.*,⁶⁶ B3LYP/6-31G, with E_g bulk = 3.78 eV; Γ_{hkl}^0 : surface energy under vacuum; B3LYP: Becke 3 Lee-Yang-Parr; E_g : band gap.

Figure 3. (a) Side view; (b) top view of the (301) surface of brookite.*Similarity of Ti_{IV} with those on the (110) surface of anatase.

Ti_{IV} and Ti_V sites. In our surface unit cell (surface area of $99.26 \text{ \AA}^2$), the four Ti_{IV} atoms and the two Ti_V atoms are non-equivalent (Figure 3) whereas on the (110) surface of anatase, all the Ti_{IV} are equivalent.

We denote the number of broken Ti–O bonds which corresponds in fact to double the number of μ_2O , being at $26.8 \text{ } \mu\text{mol m}^{-2}$. Effectively, Hu *et al.*⁸⁰ have shown on the various clays that the point zero of charge (PZC, also assimilated in that case to the isoelectric point) is linked to the number of broken bonds. Considering this hypothesis, we should be able to predict a relative order of the acidity of each surface.

(111) surface

The (111) surface of brookite has been characterized by different authors.^{19,24,25} The slab unit cell is monoclinic ($\alpha = \beta = 90^\circ$, $\gamma = 70.38^\circ$) and is more stable than the (301) surface (0.78 J m^{-2}). The number of broken bonds is similar to the (301) surface, at $22.0 \text{ } \mu\text{mol m}^{-2}$. The surface has also different sites (Figure 4). In each surface unit cell, there are four surface Ti sites, one Ti_{IV} and three different Ti_V .

The presence of Ti_{IV} indicates that this surface should also be reactive to small molecules. Effectively, a Ti_{IV} should be able to adsorb two basic groups (such as OH or SH groups) to complete its bulk coordination of 6. Those sites are clearly more acidic than Ti_V sites and as with the (110) surface of anatase, H_2O or H_2S molecules will dissociate on Ti_{IV} sites.⁶⁰ Before relaxation, the surface energy is 1.74 J m^{-2} . This surface shows the six different Ti–O distances found in the bulk. The relaxation results in most of the distances being shortened by $0.1 \text{ \AA}$, except for the two longest distances on the Ti_V which become even longer. The distances corresponding to the $2.081 \text{ \AA}$ bond lengths stretch to $2.211 \text{ \AA}$. Thus the Ti_V atoms relax so that they are more similar to Ti_{IV} which will increase the Lewis site quality.

(210) surface

The (210) surface has also been characterized using electron diffraction.²⁰ The surface is the most stable surface ($\Gamma_{210}^0 = 0.71 \text{ J m}^{-2}$, in agreement with other theoretical work),^{40,81,82} and has four Ti_V sites in one unit

Figure 4. (a) Side view and (b) top view of the (111) surface of brookite.

area ($8.93 \mu\text{mol m}^{-2}$) which seems similar (Figure 5). In fact, there are two different $\mu_2\text{O}$ sites and two Ti_V on the surface. One $\mu_2\text{O}$ site has two Ti–O distances: 1.927 and 2.081 Å before relaxation that become 1.833 and 1.865 Å after relaxation. The two Ti–O distances on the second $\mu_2\text{O}$ site are initially 2.000 and 2.025 Å and relax to 1.847 and 1.829 Å. As the Ti–O distances are similar we expect the Ti_V to exhibit the same reactivity. The number of broken bonds is the smallest, at $17.9 \mu\text{mol m}^{-2}$.

(100) surface

The (100) surface is terminated by Ti_V and $\mu_2\text{O}$ at a high density ($11.68 \mu\text{mol m}^{-2}$, Table 3) and is scarcely observed.⁸³ The number of broken bonds is then at $23.4 \mu\text{mol m}^{-2}$.

The surface is more stable (at 0.95 J m^{-2}) than the (310) and (111) surfaces and it is isostructural with the (112) surface of anatase. Figure 6 shows that each octahedral unit in anatase is aligned in the same direction whereas in brookite, the orientation of the octahedra changes every two layers. The Ti–Ti and Ti–O distances are regularly spaced. The Ti–Ti distance is 3.095 Å before relaxation and shortens to 2.800 Å after relaxation. All the Ti_V atoms are identical. The $\mu_2\text{O}$ are also similar with initial Ti–O distances of 1.927 and 2.081 Å which become, respectively, 1.799 and 1.884 Å after relaxation.

The (112) surface of anatase is also rarely seen.^{84,85} Gao and Elder⁸⁵ observed the {112} face on anatase (and {103} face) synthesized at high pH. Furthermore, because the structure of the (100) surface of brookite is epitaxially matched to the (112) surface of anatase, it is not surprising that brookite has been observed at the surface of anatase.^{83,86} If those surfaces are exposed, they should exhibit the same properties, but, as yet, there is no experimental data to confirm this fact.

(010) surface

The (010) surface (see Figure 7) has been detected by

Shibata *et al.*²⁰ as the dominant surface in their sample. This surface is energetically the most stable (0.83 J m^{-2}). This surface gets the highest number of broken bonds ($27.7 \mu\text{mol m}^{-2}$). The acid sites are the Ti_IV atoms with a high density ($6.94 \mu\text{mol m}^{-2}$). That explains why the brookite from their study²⁰ is predominant and very hydrophilic especially when it has been stored under high vacuum or been exposed to UV light radiation. These conditions clean the surface of adsorbed molecules and the Lewis sites are free to accept water molecules. The Ti–O distances are 2.025 and 1.927 Å before relaxation and shorten at 1.829 and 1.858 Å after relaxation.

This surface has also been calculated by other authors.^{66,87} They also found that the (010) surface has a lower surface energy than (100) surface.

Gibbs-Curie-Wulff morphologies

Figure 8 shows the predicted morphology of brookite under vacuum using the five surfaces described above. It is similar to a bipyramid with a hexagonal base. The {100} and {010} surfaces should exhibit two faces, the {210} and the {301} both express four faces and the {111} eight faces. From the calculation, only four surfaces appear. The (100) surface is not appearing, which is not surprising because it is not observed on the pure brookite sample. The main exposed surfaces are the (111) and the (210) (Figure 8). Those surfaces have been often observed.^{19,20,24,25} The (010) is also present to a small extent, 5%. This surface has been strongly stabilized during the synthesis by Shibata *et al.*²⁰ as a flat particle exposing the (010) surface with the (210) surface at the side. The (301) surface appears with a small surface area (1%).

Atomistic calculations using Matsui potentials give the almost same trend on the surface energy. We are able to simulate a higher number of surfaces (21 surfaces have been calculated, see Figure S1 in SI section). The surface

Figure 5. (a) Side view and (b) top view of the (210) surface of brookite.

energies are in the range of 1.61 J m^{-2} ((210) surface) and 2.51 J m^{-2} ((112) surface). Other surfaces appear in the morphology (see Figure 8b). The lowest surface energies

are as follows: $(210) < (110) = (101) < (001) < (212) < (211) < (201)$. Apart from the (210) surface, the surface energies are very close in energy. The dominant surface is

Figure 6. Side views and top views of (a) (100) surface of brookite; (b) (112) surface of anatase.

Figure 7. (010) surface of brookite. (a) Side view along x; (b) side view along z; (c) top view.

Figure 8. Morphology under vacuum of (a) the 5 calculated surfaces with DFT (b) the 21 surfaces calculated with force field.

still the (210) surface at 29.2% of the surface area followed by the (110) surface at 14.2%. Twelve other surfaces are present for less than 10% such as the (101) and (212) surfaces, others can be even negligible such as the (100) and (011) surfaces being at less than 1%.

From Pottier *et al.*¹⁹ study, the authors attribute the (301) surface as the basal from TEM analysis and the four sides surfaces belonging to (111) family. From our calculations, these surfaces are not the most stable ones. In addition, to obtain the tablet obtained experimentally, only two faces of (301) orientation should appear instead of four facets. To reproduce this morphology, the (301) surface needs to be strongly stabilized (i.e., the surface energy becoming the lowest). To obtain the same morphology as in the experiment (Figure 9), we have fixed a surface energy ratio (111)/(301) at 1.5. We note also that the edges are perpendicular to the basal surfaces, which correspond to the $\{1\bar{1}1\}$, $\{\bar{1}11\}$ and $\{11\bar{1}\}$, $\{\bar{1}\bar{1}1\}$ planes perpendicular to the $\{301\}$ and $\{\bar{3}1\bar{1}\}$. However, another possibility more likely to explain the tablet shape is to consider that the basal plane is the (001) surface and the side surfaces are the (210) facets. A morphology with an angle of 80 degrees between the side facets and perpendicular to the basal plane has been observed by Ohno *et al.*²³ in some particles. This angle correspond the intersection of two (210) planes, measured at 80.6 degrees from our DFT calculations. The morphology obtained by Pottier *et al.*¹⁹ is then revisited in Figure 9.

Surface electronic calculations of rutile, anatase and brookite phases

Electronic calculations require a high number of k-point meshes to converge the band gap to within 0.03 eV. Our study on the bulk of TiO₂ shows that it is important to keep the same methodology to compare the different phases and surfaces. We have reported in Table 3 the five surfaces of brookite. In addition, tests on the influence of the slab thickness on the band gap show that it modifies by 0.1 eV

Figure 9. Morphology of the lozenge tablet reproducing the brookite-TiO₂ from TiCl₄ and HCl^{19,77} with a revision of the surface indexation.

(the difference observed between the slab of (110) surface of rutile at 6 and 8 layers). It has been not possible to compare band gap of similar slab thickness due to steric effect and to reduce the (100) surface to 10 Å will not be appropriate (the slab is not thick enough and the surface energy is not converged).

The test on the rutile (110) agrees with previous experimental and theoretical studies^{1,37,88} where the band gap of the (110) surface is similar to the bulk values. We found, for the slab with 6 layers of TiO₂, a band gap at 2.06 eV (with k-point meshes at $(15 \times 10 \times 1)$) and at 1.97 eV for the 8 layers model which converges to the bulk value at 1.91 eV. Another study using hybrid DFT methods with a slab with 5 layers has reported that the gap is slightly smaller than the bulk by 0.2 eV.⁸⁹ The difference might come from the functional used or might be due to the odd number of layers. But by increasing the number of layers to 9, the band gap converges to the bulk value.

For the anatase phase, the band gaps of the (101) surface and the (001) surface are very different. The band gap, E_g , on the (101) surface is higher than the bulk by 0.26 eV ($E_g = 2.48$ eV) whereas the (001) surface is more conductive, being lower by 0.69 eV ($E_g = 1.53$ eV).

The values for each surface of brookite phase are reported in Table 3. Only the (301) surface has a band gap slightly lower than the bulk value by 0.05 eV ($E_g = 2.27$ eV). However, the (100) surface has a band gap close to the bulk, at 2.33 eV, which is similar to the relative order found by Beltrán *et al.*⁶⁶ The order for E_g in Table 3 is given as follows: (301) < bulk ca. (100) < (210) < (111) < (010).

In fact, if we consider slabs with similar thickness, the order changes mainly with an increase of the (100) value when its thickness decreases. The E_g for (100) surface at 10.3 Å and (010) at 10.2 Å become, respectively, 2.79 and 2.89 eV. The order for similar slab thickness is: (301) < bulk < (210) < (111) < (100) < (010).

Discussion

Rutile is the densest phase of the three considered. $\Delta_f H^\circ$ values¹⁷ indicate that rutile is more stable at 298 K by 2 kJ mol⁻¹ than brookite and by 5 kJ mol⁻¹ than anatase. Brookite should therefore be more stable than anatase. $\Delta_f S^\circ$ values are similar for rutile and anatase (ca. 50 J mol⁻¹ K⁻¹)^{17,67} which will not influence the stability order (no value is available for brookite). In contrast with experimental measurements, we find from calculations and in agreement with various theoretical studies,^{29,73,90} that the anatase phase is more stable than the rutile by 8 kJ mol⁻¹ and the brookite phase more stable by 4 kJ mol⁻¹. The difference is small and the functionals (GGA PW91 and RPBE) may be at the origin from this discrepancy. The work by Muscat *et al.*⁹⁰ also shows that the choice of the basis set can influence the order, with a good basis set the anatase is still the most stable phase. Fahmi *et al.*⁷³ also found some differences when using HF, the anatase, being more stable, becomes less stable when the parameters are calculated with correlation density functional. The introduction of the ZPE correction does not change the stability order but emphasizes that we should be careful when comparing the energetics of different bulk polymorphs with DFT. However, we find that fitting the band gap on rutile at 3.0 eV with DFT+U, the rutile is the most stable phase but the corrections by U and J need to be the same to provide a meaningful comparison between the different phases. The band gap of anatase deviates from the experimental value when U and J are fitted to the rutile phase band gap. This is not surprising because the Ti environment is different for each phase. Titanium atoms are in an octahedral environment with a D_{4h} symmetry in rutile, but C_{2v} in anatase and C_1 in brookite. This implies that U should be different because the d orbitals interact differently. However, to our knowledge, there are no calculated values on U and J for Ti⁴⁺ in TiO₂. In reproducing the experimental

band gap, some authors have found that U = 7.0 eV for Ti⁴⁺ in SrTiO₃.⁹¹ Other authors report U values but for cases in which Ti has been reduced (by oxygen vacancies^{92,93} with GGA/LDA $U_{\text{eff}} = (U - J) \geq 4.2$ eV or with dopants⁹⁴ with LDA $U_{\text{eff}} = 5.6$ eV). It is clear that the use of DFT+U is empirical, but the development of a non-empirical method for assigning the parameter would be useful for taking this forward. In addition, experiments with low temperature calorimetry of the titania phases would be also be valuable for comparison purposes.

In our calculations, the temperature is not taken into account, which can introduce more differences. The calculated structures with GGA/PW91 functional are in agreement with experiments and with previous theoretical work by Beltrán *et al.*⁶⁶ (using B3LYP functional), by Gong and Selloni⁸⁷ (using PWSCF functional) by Zhu *et al.*⁹⁵ (using GW methods) and by Mohamad *et al.*⁹⁶ (using Perdew-Burke-Ernzerhof (PBE) method). GGA functionals are known to systematically underestimate the band gap. However, the relative order of the calculated band gaps is also consistent with experiments. We must be cautious about over interpreting this result as it has been shown, for example, that the optical band gap is dependent on particle size and hence the bulk crystal value can differ (anatase: 3.2 eV,⁷⁶ 3.34 eV).¹³ That has led us to the determination of the band gap of surfaces in order to better understand some trends.

The Ti–O bulk distances will play a key role in determining the energetic cost of forming surfaces. Generally, it is energetically more favorable to cut the longest distance, which is given by the surface energy Γ_{hkl}^0 before the ionic relaxation. The (001) surface is the most stable of anatase before relaxation²⁶ and the (210) surface is the most stable in the case brookite. The relaxation can change the stability order. The relaxation depends on the surface symmetry and the type of Lewis sites. For example, the (001) surface of anatase is flat and has equivalent surface Ti_v atoms and equivalent surface $\mu_2\text{O}$ atoms. The surfaces with low coordination of Ti species (i.e., Ti_{lv}) have the higher surface energies. For example, the (301) and (111) surfaces of brookite, having Ti_{lv} sites, are less stable than the (210) surface having only Ti_v surface sites.

The surface energies and the coordination of the surface species are therefore linked to their stability and reactivity; less stable is the surface, more reactive it is expected. The comparative adsorption energies of water and formic acid on (101) surface of anatase and (210) surface of brookite confirms this trend.⁹⁷ With the surface (210) of brookite being more reactive, it is expected to be a better catalyst compared to an anatase phase exposing (101) surfaces. A similar fact is observed by Lin *et al.*,²¹ nanosheets of

brookite exposing {210}, {101} and {201} facets are more efficient catalyst than Degussa P25 TiO₂.

The bulk of the brookite phase has six different distances between 1.873 and 2.081 Å. The variation of the surface Ti–O distances can be used in the interpretation of EXAFS spectra. The main difference between the (301) and (111) surfaces is that the mean Ti–O distances is shorter on the (301) surface and some bonds stretch (ca. 0.1 Å) on the (111) surface which means that the Ti_v is predicted to become more acidic. There are also more Ti_{iv} ions on the (301) surface and therefore a higher intrinsic acidity. The brookite offers a wide variety of Ti and O geometries that will result in the different reactivity of each species (more or less acidic and more or less accessible).

As noted above, one visual way of comparing the relative stability of surfaces is to combine the Gibbs–Curie–Wulff law with the calculated surface energies and cell parameters to give the equilibrium morphology of the crystal. In natural samples of rutile, the (110) surfaces are predominant while the common form of anatase is a bipyramid with a squared base. To our knowledge, the brookite phase does not have a typical form but some particles seem to have a large proportion of the (010) surface.^{98,99} Ziolkowski¹⁰⁰ did report some typical morphologies of the three phases. The natural crystal form is likely to be more relevant to compare to our calculations because they are more likely grown near thermodynamic conditions. In contrast, the experimentally grown morphology is presumably to be kinetically controlled and hence varies with the synthesis conditions. Thus the nanoparticles may not be at thermodynamic equilibrium. Most of the surfaces have similar surface energies, which might explain why various morphologies have been observed; the morphology depends strongly on the external conditions. However, the prediction of the morphology of the particle at the thermodynamic equilibrium under vacuum gives some insight in order to understand some experimental morphologies. In particular, atomistic simulations enable to calculate a wide range of surfaces and some surfaces not calculated with DFT appear clearly in the morphology. The {101} facet is one of the most stable surface, appearing in the morphology (see Figure 7b) and experimentally observed²¹ while the exposed {110} facet (see Figure 7b) having the same surface energy order is observed by Ohno *et al.*²³

For a direct comparison with different polymorphs, it is crucial to use the same method (for example, on rutile (110), surface energies calculated with different methods vary from 0.3 up to 1.8 J m⁻²).^{29,31,32,34,37,51} It is interesting to note that the (110) surface of rutile is slightly less stable

than the (101) surface of anatase. This result is surprisingly the opposite of the trend obtained by Lazzeri *et al.*²⁹ (anatase (101): 0.44 J m⁻², rutile (110): 0.31 J m⁻²) who have used a PBE functional, whereas their results on anatase surfaces are in complete agreement with a previous study with PW91.²⁶ The surface energy of the rutile (110) oscillates with the number of layers as it has been demonstrated by other studies.⁴⁰ We have calculated the surface energy for different numbers of layers with a large supercell with a surface area of 77.88 Å², k-point meshes: 4 × 3 × 1. The number of Lewis sites is: 8.5 μmol m⁻² μ₂O and 8.5 μmol m⁻² Ti_v. The number of broken bonds is 16.0 μmol m⁻². For 5 and 6 layers, the surface energy Γ₁₁₀⁰ is, respectively, 0.57 and 0.44 J m⁻². On increasing the number of layers, we know that the limit should be between those two values. In reducing the surface area at 19.48 Å² in order to be able to increase the number of layers, the surface energy is similar for 5 and 6 layers (respectively, 0.59 and 0.44 J m⁻²). For 7, 8 and 9 layers, it becomes, respectively, 0.53, 0.45 and 0.52 J m⁻². From Arrouel *et al.*,²⁶ the surface energy of anatase with 3 layers is Γ₁₀₁⁰ = 0.43 J m⁻² (k-point meshes 2 × 2 × 1), the number of Lewis sites are 8.4 μmol m⁻² μ₂O, 8.4 μmol m⁻² Ti_v and the number of broken bonds is 16.8 μmol m⁻². This slab is good enough to have a good description of the energetics and allows us to study the adsorption of small molecules.^{58,60} Effectively, for 4 layers, the surface energy is 0.44 J m⁻², so the surface with 3 layers is well converged. This is supported by the experimental observation that the anatase phase is more stable below 14 nm because of the higher surface energy of rutile than anatase.^{101,102}

The order of the number of Lewis sites might help to rationalize the crystal growth on brookite under different pH and PZC tendency. The order is as following (B = brookite, A = anatase, R = rutile):

Order based on the basic Lewis sites μ₂O *per* surface on brookite: (210) < (111) < (100) < (301) < (010).

And in general: (101) A < (110) R < (210) B < (100) A < (111) B < (001) A < (100) B < (110) A < (301) B < (010) B.

This order is then the same for the number of broken bonds. Following the idea from Hu *et al.*,⁸⁰ the most acidic (with lower PZC) should be the anatase (101) surface but with the same order of acidity strength than the rutile (110) surface. If we consider that the anatase phase has an increase of the (001) surface area, in that case, the anatase should have a higher PZC. However, the evaluation of the PZC through a simple relationship with the number of broken bonds does not take into account the hydroxylation state of the surfaces which is the basis of the MUSIC (Multisite Complexation) model.¹⁰³ The determination of the hydroxylation can help the interpretation of the

PZC of oxides as a function of the shape as described by Jolivet *et al.*¹⁰⁴ The authors have found a PZC of 5.3 for the anatase but the range of PZC from the literature¹⁰⁵ is wide and is highly dependent on the methodology (titration, electrokinetics), the temperature, the shape of crystal. Globally, it is reported that the PZC values of anatase and rutile are similar which should be true if rutile and anatase crystals are respectively dominated by the (110) and (101) surfaces.

Order based on the acid Lewis sites Ti_{IV} per surface on brookite: (010) < (301) < (111) < (210) < (100).

And in general: (110) A < (010) B < (301) B ca. (101) A < (110) R < (111) B < (210) B < (100) A < (001) A < (100) B.

Even if the number of acid sites is low compared to the (100) and (210) surfaces, the acid properties remain stronger. However, the (100) and (210) surfaces are less acidic (Lewis sense) than the (301) surface.

The brookite nanoparticles from Pottier *et al.*¹⁹ have been synthesized at low temperature using a $TiCl_4$ precursor with HCl and low pH (pH = 1). The morphology is a lozenge tablet. To obtain this morphology using the Gibbs-Curie-Wulff construction, we suggest that the basal surface is the (001) plane. The lateral surfaces perpendiculars to basal surface are the (210) surfaces (Figure 9 confirming the experimental morphology from Pottier *et al.*)¹⁹ In addition, it is possible to construct a morphology respecting Pottier *et al.*¹⁹ and Ohno *et al.*²³ morphologies with the following relative surface energies: (001) 1.2, (210) 0.72, (111) 1.08 and (201) 1.08.

Another interesting property derived from electronic structure calculations is the smallest band gap of the different surfaces. With the decrease of the band gap, it becomes easier to form an exciton which is required in dye sensitized solar cell devices. Brookite nanoparticles synthesized by Pottier *et al.*¹⁹ seem in fact to have the ideal morphology for lithium batteries, exposing mainly the (001) surface giving the best access for lithium diffusion. Indeed, this surface gives a direct access to the open channels for Li intercalation and diffusion along the [001] direction. Similar observations with force field methods have been made on the cathode material, $LiFePO_4$ where the authors demonstrate that flat particles exposing the (010) surfaces favor the reversible intercalation of Li and diffusion along the [010] open channels.¹⁰⁶ While regarding syntheses of anatase exposing mainly (001) surfaces, such morphologies should be better candidates for photovoltaic systems, exhibiting the most conducting surfaces.

Also, the brookite phase has been found to be a potential photocatalyst,^{7,78} which may be explained by the high Lewis acidity of the (010) surface (e.g., 4-fold Ti atoms). However,

the OH groups can be unfavorable for catalysis reactions, such as photocatalytic oxidation of trichloroethylene,¹⁰⁷ whereas they will be ideal for photomineralization of toluene.¹⁰⁸

Conclusions

This study describes various surfaces of brookite- TiO_2 which have been experimentally observed where the acid synthesis conditions seem to represent an excellent approach for generating highly reactive surfaces. DFT simulations indicate that the brookite phase is a potential catalyst because the main exposed surfaces have acid sites Ti_{IV} (i.e., (111) surface). The (010) surface of brookite exhibits a high concentration of Ti_{IV} and therefore is expected to be a reactive surface. This surface participates at the good photochemical properties as photoinduced hydrophilicity.²⁰ In contrast, the main traditional surfaces of rutile and anatase have Ti_V surface atoms. However, the number of Lewis sites is not a unique index to describe the acido-basic properties of oxides. The quality of the site also plays a key role. The brookite is more hydrophilic and reactive due to exposed surfaces with Ti_{IV} sites.

The understanding of the crystal growth is crucial to be able to select the best surface for a chosen purpose. Regarding our calculations, in comparing morphologies of brookite nanoparticles, those exhibiting a higher surface area of (001) surfaces are predicted to be more efficient for the anode in lithium batteries. Further experimental investigations should be able to confirm our predictions. In addition, another significant result is that the (001) surface of the anatase phase has the lowest calculated band gap and then we suggest that this surface should be more effective for photocatalysis.

Supplementary Information

Supplementary information on surfaces energies using force fields and DFT+U calculations is available free of charge at <http://jbcs.sbg.org.br> as PDF file.

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Additions and Corrections

Graphical abstract image:
Where it reads

Should be read

Figure 9:
Where it reads

Should be read

On page 60 where it reads:

We note also that the edges are perpendicular to the basal surfaces, which correspond to the $\{1\bar{1}\bar{1}\}$, $\{\bar{1}11\}$ and $\{11\bar{1}\}$, $\{\bar{1}\bar{1}1\}$ planes perpendicular to the $\{301\}$ and $\{\bar{3}1\bar{1}\}$.

Should be read:

We note also that the edges are perpendicular to the basal surfaces, which correspond to the $(1\bar{1}\bar{1})$, $(\bar{1}11)$ and $(11\bar{1})$, $(\bar{1}\bar{1}1)$ planes perpendicular to the (301) and $(\bar{3}0\bar{1})$.