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Morphology of the GdVO₄ crystal: first-principles studies

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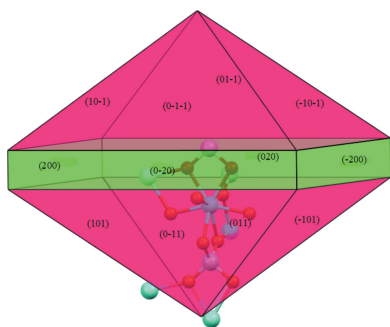
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The present paper reports a theoretical investigation based on first-principles density functional theory calculations to predict the external morphology of the tetragonal GdVO₄ crystal from its internal structure. The Bravais–Friedel–Donnay–Harker (BFDH) method, attachment energy (AE) method and surface energy (SE) method were used in this study. Slice energies (cohesive, attachment and specific surface) of the three main crystal faces having (110), (101) and (200) orientation and their d_{hkl} thicknesses were computed using *CRYSTAL17* code, in the frame of a 2D periodic slab model. The relative growth rate (R_{hkl}) and the morphological importance (MI_{hkl}) for each unrelaxed and relaxed (hkl) face of interest were determined. Consequently, the crystal shapes predicted based upon BFDH, AE and SE methods were represented by the Wulff construction. The results of the morphology crystal predictions, based on the above methods, were compared both against each other and against the experimentally observed morphologies. A quite satisfactory agreement between the predicted and observed crystal morphologies is noticed.

1. Introduction

Gadolinium orthovanadate (GdVO₄) belongs to the group of rare-earth orthovanadates (REVO₄), where RE are rare-earth elements, including lanthanoids from La to Lu and also Y and Sc. GdVO₄ has attracted worldwide attention as a multifunctional material due to the half-filled 4*f* shell of gadolinium, which plays an important role in the field of inorganic compounds. As a tetragonal crystal system, having *I*₄/*amd* space group and zircon-type structure, GdVO₄ exhibits chemical stability, high thermal conductivity, luminescent and magnetic properties (Szczeszak *et al.*, 2014). This material can be doped with trivalent lanthanide ions (Dy³⁺, Eu³⁺, Er³⁺, Nd³⁺, Yb³⁺, Tm³⁺, Ho³⁺, Sm³⁺...), due to the similar ionic radii between Gd³⁺ and other RE (RE³⁺) cations. Therefore, GdVO₄ could be used as a laser, phosphor or up-converter (Cho, 2013; Yu *et al.*, 2013; Yan & Gu, 2009; Shanta Singh *et al.*, 2012; Tang *et al.*, 2012; Cante *et al.*, 2018; Shimamura *et al.*, 1996; Rabasovic *et al.*, 2018; Qiao *et al.*, 2017; Min & Jung, 2019; Jovanović *et al.*, 2018; Zheng *et al.*, 2011; Gavrilović *et al.*, 2016). The Bi³⁺-doped GdVO₄ crystal is also of great importance in modern electronics because of unique luminescent characteristics that can be applied in white light emitting diodes (Vasylechko *et al.*, 2018; Krasnikov *et al.*, 2019). In addition, recent efforts show important implications of GdVO₄ for photocatalytic reactions since it possesses a strong ability to generate hydrogen from water or water/alcohol



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solutions (Oshikiri *et al.*, 2014*a,b*; Mazierski *et al.*, 2019). Many studies have demonstrated that downscaled systems of GdVO₄ exhibit multiple characteristics in the field of biomedical applications: photodynamic therapy, radiation therapy, drug delivery *etc.* (Teo *et al.*, 2016; Belkina *et al.*, 2016; Dong *et al.*, 2015). There are many preparation methods that have been reported in the literature for obtaining GdVO₄ such as sol–gel (Chumha *et al.*, 2014), edge-defined film-fed (EFG) (Epelbaum *et al.*, 1998), Czochralski (Loiko *et al.*, 2013), co-precipitation (Vosoughifar, 2017), hydrothermal (Szczechak *et al.*, 2014; Mahapatra & Ramanan, 2005), solvothermal (Liang *et al.*, 2011). Among all the processes mentioned above, hydrothermal growth is one of the most promising and widely employed methods, due to the possibility of producing large crystals and the advantage of being able to control the morphology and crystal size.

Various theoretical DFT (density functional theory) studies of GdVO₄ have been published regarding electronic structure, Fermi surface, optical properties as well as the elastic properties (Huang *et al.*, 2012; Reshak & Azam, 2013). Therefore, due to its excellent properties stated above, knowledge of the shape, size and crystal faces is critically important to many industrial processes. In order to obtain high-quality crystals by means of morphology predictions, experimental researchers most often need to visualize a crystal shape resulting from theoretical studies or from a set of experimental data, *e.g.* specific surface energies or growth rates. Many researchers, over the years, have reported in a series of theoretical and experimental papers the growth form and equilibrium morphology of some ionic solids and molecular crystals (Liu *et al.*, 2019; Zhu *et al.*, 2004; Wang *et al.*, 2010; Zhang, 2014; Singh *et al.*, 2012; Heo *et al.*, 2018; Barbosa *et al.*, 2017; Ribeiro *et al.*, 2019; Stirner *et al.*, 2018; Arrouvela & Eon, 2019; Goel *et al.*, 2019; Credendino *et al.*, 2009; Bittarello *et al.*, 2018; Nakayama *et al.*, 2013; Oliveira *et al.*, 2016). In all these works, a variety of methods have been employed for the morphology prediction. Here, we only mention those that are of interest to us: Bravais–Friedel–Donnay–Harker (BFDH) rules (Bravais, 1866; Friedel, 1907; Donnay & Harker, 1937), attachment energy (AE) method (Hartman & Perdok, 1955; Hartman, 1973; Bennema, 1993; Hartman & Bennema, 1980; Woensdregt, 1993), surface energy (SE) method and the Wulff construction method (Dovesi *et al.*, 2005; Wulff, 1901). It should be emphasized that all these theoretical methods, which are in continuous development versus a trial-and-error experimental approach, give, in advance, reliable morphology predictions for crystals. However, in spite of the fact that inorganic crystal growth has been intensively investigated, the theoretical predictions of morphology for these crystals are scarce (Dandekar *et al.*, 2013). So, our goal is to bring more insight into the field of theoretical morphology of inorganic crystals, based on the quantum-mechanical computer simulations and modern first-principles methods like DFT. There is a lot of literature on the crystal growth of GdVO₄, but there is no prediction using theoretical simulation for the growth and equilibrium form of this crystal. The clue, in these simulations, is related to the specific surface energies ($E_{\text{surf}}^{\text{hkl}}$), cohesive

energies (E_{coh}) and attachment energies ($E_{\text{att}}^{\text{hkl}}$). In the literature, there is one single result that deals with orthovanadate morphology predictions by a semi-empirical force-field method, based on the AE method of Hartman–Perdok theory (Hartman & Perdok, 1955), for monoclinic LaVO₄ and tetragonal YVO₄ single crystals (Cong *et al.*, 2010). Furthermore, two articles deal with $E_{\text{surf}}^{\text{hkl}}$ calculations and equilibrium shape related to the tetragonal phase of LaVO₄ by means of a DFT method (Li *et al.*, 2012; Gouveia *et al.*, 2016).

The aim of this paper is the first-principles calculation of the crystal growth morphology and equilibrium morphology of the GdVO₄ crystal *in vacuum*, based on DFT methodology and the above-mentioned methods. A detailed description of first-principles calculation of $E_{\text{surf}}^{\text{hkl}}$, E_{coh} and $E_{\text{att}}^{\text{hkl}}$ energies is presented and illustrated in this paper. The predicted morphologies from each method are discussed and compared both against each other and against the experimentally observed morphologies.

2. Theoretical methods

2.1. BFDH method

Bravais in 1866, Friedel in 1907, Donnay and Harker in 1937 founded the BFDH method (Bravais, 1866; Friedel, 1907; Donnay & Harker, 1937), based merely on the lattice parameters and the symmetry of the crystal. The BFDH method is based on two rules: the first allows us to generate a list of possible crystal growth faces (Donnay & Harker, 1937) and the second one shows how the growth rate R_{hkl} of a given (*hkl*) face is calculated (Bravais, 1866; Friedel, 1907). The R_{hkl} of a given face is proportional to the D_{hkl} distance from the center of the crystal to the (*hkl*) face, in the normal direction (Wulff, 1901) and inversely proportional to d_{hkl} interplanar spacing. An initial approach for R_{hkl} was as given by equation (1) (Friedel, 1907), where C is a rate constant:

$$R_{\text{hkl}} = 1/(Cd_{\text{hkl}}). \quad (1)$$

Later, two new equations [equations (2), (3)] were formulated for growth rates (Donnay & Harker, 1937):

$$R_{\text{hkl}} = \exp(-Cd_{\text{hkl}}) \quad (2)$$

$$R_{\text{hkl}} = d_{\text{hkl}} \exp(-Cd_{\text{hkl}}). \quad (3)$$

Besides the growth rate R_{hkl} , another parameter to characterize a crystal face is the morphological importance (MI_{hkl}) of a face. According to Friedel (1911), the MI_{hkl} of a crystal face is understood as its relative size in a given crystal shape. In the frame of the BFDH model, relation (4) shows that faces with the smaller D_{hkl} [distance from the center of the crystal to (*hkl*) face in the normal direction] have the lowest growth rate and most morphological importance:

$$R_{\text{hkl}} \sim D_{\text{hkl}} \sim (\text{MI}_{\text{hkl}})^{-1}. \quad (4)$$

In the BFDH approach, no consideration is given when predicting relative growth rates of faces to the atoms, to partial charges, to the bond types or to the interatomic forces. However, this method remains the simplest way to quickly

identify the possible crystal growth faces and to estimate, at first, the shape of a given crystal.

2.2. Attachment energy (AE) method

In the literature, in the field of growth theory, two contributions can be found for predicting the ideal crystal morphology:

(i) Periodic bond chain (PBC) theory of Hartman and Perdok (Hartman & Perdok, 1955), a method that reflects the morphological importance of various crystal faces.

(ii) Attachment energy (AE) method (Hartman & Bennema, 1980), a method that provides the relative growth rates of faces (R_{hkl}).

The attachment energy E_{att}^{hkl} , an important parameter used to understand the nature of chemical bonding in solids, is defined as the energy released upon the addition of a building unit (growth slice) to the growing crystal surface. Within this method, it is assumed that the growth rate R_{hkl} of a face (hkl) is proportional to the attachment energy E_{att}^{hkl} (Hartman & Bennema, 1980; Berkovitch-Yellin, 1985; Docherty *et al.*, 1991). The AE method predicts also that MI_{hkl} is inversely proportional to the E_{att}^{hkl} of a face. Therefore, this method assumes that faces with the lowest E_{att}^{hkl} will have the largest MI_{hkl} and are the slowest growing:

$$R_{hkl} \sim |E_{\text{att}}^{hkl}| \quad (5)$$

$$\text{MI}_{hkl} \sim \frac{1}{|E_{\text{att}}^{hkl}|}. \quad (6)$$

Unfortunately, E_{att}^{hkl} is not a directly measurable parameter; however, it is related to a measurable value by the determination of the cohesive energy E_{coh} for the bulk and slices. In turn, relative to any crystal face, E_{att}^{hkl} is calculated as follows (Hartman & Bennema, 1980; Berkovitch-Yellin, 1985; Docherty *et al.*, 1991):

$$E_{\text{att}}^{hkl} = E_{\text{latt}} - E_{\text{slice}}^{hkl} \quad (7)$$

where E_{latt} is the lattice energy of the crystal (often referred to as the binding or cohesive energy of the crystal) and E_{slice}^{hkl} is the slice energy, *i.e.* energy released per molecule on the formation of a new growth layer with a thickness of d_{hkl} (Hartman, 1973; Hartman & Bennema, 1980). The AE method is widely applied to organic and inorganic crystals and can successfully predict the crystal growth morphology, as it takes into account the energetic interactions of the system (Kevin *et al.*, 2018; Massaro *et al.*, 2011; Aquilano *et al.*, 2016).

2.3. Surface energy (SE) method

The SE method, known also as the equilibrium morphology method and very common in the field of inorganic compounds, especially when one is interested in the chemical processes occurring on a crystal surface, requires the knowledge of E_{surf}^{hkl} and the R_{hkl} , for all relevant crystal faces, at 0 K. The equilibrium crystal shape can be determined based on Wulff's theorem (Wulff, 1901). Under these conditions, the R_{hkl} , MI_{hkl} and E_{surf}^{hkl} values are connected as follows:

$$R_{hkl} \sim E_{\text{surf}}^{hkl} \quad (8)$$

$$\text{MI}_{hkl} \sim (E_{\text{surf}}^{hkl})^{-1}. \quad (9)$$

The formula to calculate the surface energy is given in equation (10):

$$E_{\text{surf}}^{hkl} = [E(n)_{\text{slab}}^{hkl} - N \times E_{\text{bulk}}] / 2 \times A. \quad (10)$$

Thus, the surface energy defined in equation (10) is the difference between two energy quantities, where $E(n)_{\text{slab}}^{hkl}$ is the energy of a slab with n layers. N represents the number of atoms in the surface slab, E_{bulk} is the bulk energy per atom and A is the surface area of the slab. Despite its importance, E_{surf}^{hkl} is difficult to obtain experimentally and cannot be directly measured. Surfaces are sensitive to many factors such as temperature, pressure and dielectric constant, for example. Hence, it is not surprising that experimental measurement of equilibrium shape for a wide range of materials has not yet been performed, probably because the true equilibrium is not reached.

3. Computational methodology

All calculations in this article were performed with the *ab initio* CRYSTAL17 code (Dovesi *et al.*, 2018). This software adopts atom-centered Gaussian-type functions as basis sets to represent crystalline orbitals and implements the Hartree–Fock and Kohn–Sham self-consistent field (SCF) methods for the treatment of periodic systems. Here, we focus on the assessment of current DFT methods explored on 3D and 2D geometrical structures of GdVO_4 to capture the effect of stability that arises from full relaxation of atomic positions and lattice constants.

3.1. Geometry optimization of the bulk (3D periodicity) and E_{latt} computed

GdVO_4 is a tetragonal crystal system with zircon-type structure having space group $I4_1/amd$ (No. 141 in the *International Tables of Crystallography*) and four chemical formulae per unit cell ($Z = 4$). The unit cell of GdVO_4 is presented in Fig. S1 of the supporting information (SI), beside its autostereogram.

Firstly, we have carried out full geometry optimization in order to obtain the ground-state energy of the crystal. The performance of different functionals like SOGAXC, B3LYP, B3PW, WC1LYP and B3LYP-D3 has been successfully tested. Further computational details and data (Table S1) for lattice parameters, volumes and distances, after the full optimization process, are collected and presented in the SI. The calculations show that, among all of these probed functionals, B3LYP (Becke, 1988; Becke, 1993; Lee *et al.*, 1988) emerged with an average absolute deviation of 0.6% on the unit-cell volume. Also, the Becke hybrid exchange correlation functional gives reasonable agreement between the calculated energy band gap 4.54 eV (this paper) and the experimental value 3.6 eV (Jovanović *et al.*, 2018). All calculations were carried out taking into account a polarization TZVP basis set (Vilela

Table 1

The two most important (*hkl*) faces of the GdVO₄ crystal, interplanar distances, growth rates and the morphological importance.

| Faces (<i>hkl</i>) [multiplicity] | d_{hkl} (Å) | R_{hkl}^\dagger | MI_{hkl} |
|-------------------------------------|---------------|-------------------|------------|
| (101) [4] | 4.7860 | 0.06 | 17.66 |
| (200) [8] | 3.6227 | 0.11 | 8.79 |

[†] Calculated with equation (2) and $C = 0.6$.

Oliveira *et al.*, 2019) for V⁵⁺ and O²⁻ ions (spin $S = 0$) and a quasi-relativistic ECP28MWB pseudopotential (Desmarais *et al.*, 2018) for Gd³⁺ ions (in the high-spin state with $S = 7/2$).

Because the morphology predictions are sensitive to the force field, it is necessary to verify if the calculated lattice energy value is relatively close to the experimental one and overall to confirm that the energetics of the crystal are captured. E_{latt} of a crystal can be defined as (Gavezzotti & Filippini, 1997)

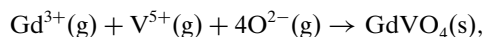
$$E_{latt} = E_{bulk} - \sum_i^N E_i \quad (11)$$

where E_{bulk} is the energy of the bulk crystal unit cell, E_i is the energy for each ion belonging to the crystal unit cell and N is the number of ions in the unit cell. From equation (11), one obtains $E_{latt} = -26816.7259$ kJ mol⁻¹ per unit formula and the remaining terms are given in Table S2 in the SI. This value cannot be compared with the experimental value of E_{latt} , because it cannot be empirically measured. That is why it is compared using its relation with the lattice enthalpy ΔH_{latt} (Jenkins, 2005),

$$\Delta H_{latt} = E_{latt} + 2RT, \quad (12)$$

where T is the temperature at which the lattice enthalpy is measured and R is the gas constant (the magnitude of RT is approximately 2.4789 kJ mol⁻¹; at $T = 0$ K, $\Delta H_{latt} = E_{latt}$). It is important to note that, in equation (12), both quantities ΔH_{latt} and E_{latt} are related by a correction term $2RT$, relatively small in magnitude.

According to the Born–Haber thermochemical cycle (Born, 1919; Haber, 1919),



the lattice enthalpy of GdVO₄, at 298.15 K and 760 torr (1 torr = 133.322 Pa) pressure, is 26080 ± 23 (kJ mol⁻¹) (Petrov, 2013). From equation (12), the corresponding value of E_{latt} is 26075.0422 ± 23 kJ mol⁻¹. The sign of the ΔH_{latt} must be reversed if the process takes place in the opposite direction. Frequently ΔH_{latt} and E_{latt} are assumed to be synonymous (Jenkins, 2005). So, one can deduce that the lattice energy from DFT calculation agrees well with the corresponding value deduced from equation (12), as the deviation is only 2.8%.

3.2. Geometry optimization of slabs (2D periodicity) and E_{slice}^{hkl} computed

To start, an analysis of the forms and planes of the GdVO₄ crystal was performed by means of the *CRYSTAL17* code (Dovesi *et al.*, 2018) and the results are summarized in Table S3 in the SI.

In the second step, the main objective was to construct the surfaces corresponding to forms from Table S3, starting from the new optimized geometry of the bulk. Naturally, we employed the procedure implemented in the *CRYSTAL17* code (Dovesi *et al.*, 2018) to build bidimensional slabs and to carry out again a new optimization of these slabs. For the slabs relaxation process, we have maintained the computational parameters as we discussed in Section 3.1, barring the shrinking factor along the reciprocal-lattice vectors, here set to 8, 8 and 34 k -points in the first Brillouin zone. The thickness of the 2D slab is associated with the number of atomic layers. Therefore, slab models containing six, ten and three atomic layers for the (110), (101) and (200) surfaces, respectively, were constructed. Special attention must be paid to the surface termination, because often more than one surface termination is possible. In that case, a slab must have a minimal total energy and surface energy. Representations of the main slabs before relaxation are shown in Figs. S2, S3 and S4 in the SI, drawn with *J-ice* (Canepa *et al.*, 2011), and the slab parameters before and after relaxation are compiled in Table S4 in the SI.

Based on the 2D periodic slab model, a DFT calculation has been performed to compute E_{slice}^{hkl} , *i.e.* the cohesion energy E_{coh} per mole of any slab *hkl* for the most stable faces of the GdVO₄ crystal, in accordance with Table S3. All computed results for E_{slice}^{hkl} , regarding the (110), (101) and (200) faces, are listed in Table S5 in the SI.

4. Results and discussion

In this section, the theoretical morphology of GdVO₄ crystals associated with several low-index faces is explored by means of BFDH, AE and SE methods.

4.1. Morphology prediction by the BFDH method

In spite of the fact that *CRYSTAL17 ab initio* code analysis (Dovesi *et al.*, 2018) shows that the first three most important faces are (110), (101) and (200), the BFDH method, implemented in *Mercury* software (Macrae *et al.*, 2008), reports only two major faces (101) and (200) which dominate the crystal habit. The (110) face is missing, because the BFDH method explains the morphology based on d_{hkl} values as reproduced in an X-ray diffraction pattern. Therefore, based on this consideration, only two faces are displayed in Table 1 together with d_{hkl} , R_{hkl} and MI_{hkl} .

According to BFDH rules, the larger the interplanar distance d_{hkl} is, the larger the morphological importance of the corresponding (*hkl*) face is. Thus, the BFDH theory predicts the (101) face to be of highest MI_{hkl} : $MI_{101} > MI_{200}$. The Donnay & Harker (1937) analysis suggests that the GdVO₄ crystal shape is built only from experimental observed forms.

Table 2

The calculated unrelaxed and relaxed $E_{\text{att}}^{\text{hkl}}$ per unit formula, R_{hkl} and MI_{hkl} of the different shape faces of the GdVO_4 crystal in the AE method.

R_{hkl} is $R_{(\text{hkl})}/R_{(110)}$.

| Faces (hkl) | d_{hkl} (Å) | Unrelaxed | | | Relaxed | | |
|----------------|-------------------------|--|------------------|--------------------------|--|------------------|--------------------------|
| | | $E_{\text{att}}^{\text{hkl}}$ (kJ mol ⁻¹) | R_{hkl} | MI_{hkl} | $E_{\text{att}}^{\text{hkl}}$ (kJ mol ⁻¹) | R_{hkl} | MI_{hkl} |
| (110) | 5.1233 | -54.9661 | 1.00 | 1.79 | -37.7750 | 1.00 | 1.25 |
| (101) | 4.7860 | -98.2757 | 1.79 | 1.00 | -39.1714 | 1.04 | 1.20 |
| (200) | 3.6227 | -57.5644 | 1.05 | 1.71 | -47.0335 | 1.25 | 1.00 |

The two forms are $\{101\}$, consisting of eight faces (101), (10 $\bar{1}$), (011), (01 $\bar{1}$), (0 $\bar{1}$ 1), (0 $\bar{1}$ $\bar{1}$), ($\bar{1}$ 01), ($\bar{1}$ 0 $\bar{1}$), and $\{200\}$ consisting of four faces (200), (020), (0 $\bar{2}$ 0), ($\bar{2}$ 00).

Crystal morphology predicted by this simple model (Fig. 1), strictly based on geometry and symmetry, shows the ideal shape of the GdVO_4 crystal as a combination of a short tetragonal prism with a square bipyramid. It was compared with the shape of the GdVO_4 synthesized crystals, presented in Fig. 2 (Yan *et al.*, 2013), and was found to be in favorable agreement.

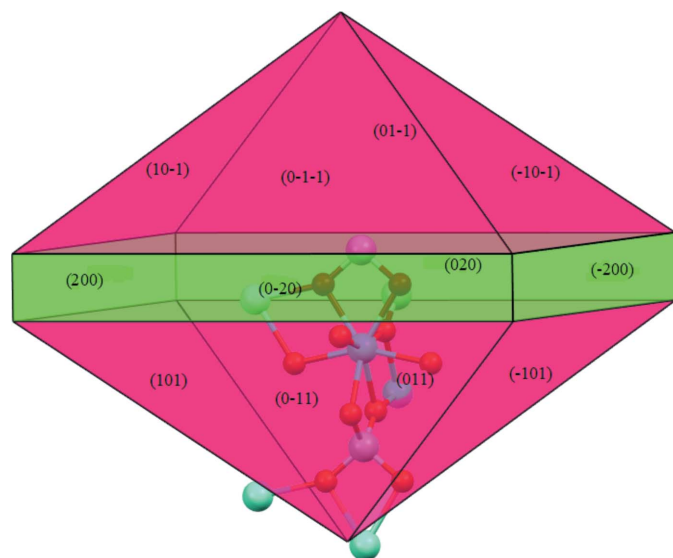


Figure 1
The indexed shape of GdVO_4 predicted by BFDH rules, drawn with Mercury software (Macrae *et al.*, 2008).

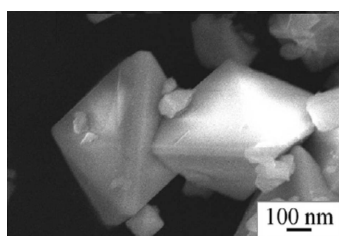


Figure 2
SEM (scanning electron microscopy) micrograph of $\text{GdVO}_4:\text{Eu}^{3+}$ crystals synthesized hydrothermally. [Reproduced with the permission of Elsevier from Yan *et al.* (2013).]

Like in the case of the GdVO_4 crystal, the BFDH method shows good agreement with experiment for many crystals (Docherty *et al.*, 1991; Kevin *et al.*, 2018) and can be used for initial prediction of the crystal shapes, before more sophisticated energy calculations. However, the BFDH approach may not always be accurate in predicting the crystal shape. This depends, especially for molecular crystals, on the bonding effect in the crystal. The stronger the bonding effect, the less accurate the method becomes. But in all cases the method is useful to identify the most morphologically important faces needed for shape building.

4.2. Growth morphology prediction by the AE method

The calculation of the parameters $E_{\text{att}}^{\text{hkl}}$, R_{hkl} and MI_{hkl} of the different faces of the GdVO_4 crystal, based on equations (6)–(8), both for unrelaxed and relaxed faces (110), (101) and (200), was performed and the results are collected in Table 2.

As can be seen from Table 2, the $E_{\text{att}}^{\text{hkl}}$ values decrease upon relaxation and induce a change in MI_{hkl} arrangement. Clearly, the crystal growth morphology calculated by the AE method predicts the MI_{hkl} pattern for the shape faces as follows:

- (a) Unrelaxed structure: $\text{MI}_{110} > \text{MI}_{200} > \text{MI}_{101}$.
- (b) Relaxed structure: $\text{MI}_{110} > \text{MI}_{101} > \text{MI}_{200}$.

On the basis of these results, it appears that the most stable face is (110) for both relaxed and unrelaxed structures, but the relative sequences found for the second and third most stable surfaces (200) and (101) are different in the two predictions.

A morphological sketch of the GdVO_4 crystal deduced from the AE model *in vacuum* can be seen in Fig. 3(a) for the unrelaxed case and Fig. 3(b) for the relaxed case.

From the AE theoretical growth morphology shown in Fig. 3, two different shapes with the same form can be seen: (a) a long bipyramid prism and (b) a short bipyramid prism. The unrelaxed AE theoretical predictions from Fig. 3(a) show good agreement with the experimental shape in Fig. 4(a) (Min

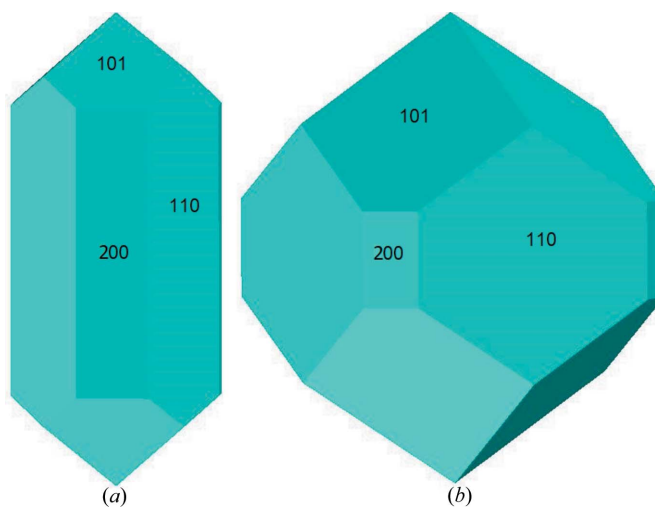


Figure 3
Growth morphology prediction by the AE method: (a) unrelaxed and (b) relaxed shape faces.

Table 3

The calculated unrelaxed and relaxed $E_{\text{surf}}^{\text{hkl}}$ per unit formula, R_{hkl} and MI_{hkl} of the different shape faces of the GdVO_4 crystal in the SE method.

R_{hkl} is $R_{(\text{hkl})}/R_{(200)}$.

| Faces (hkl) | d_{hkl} (Å) | Unrelaxed $E_{\text{surf}}^{\text{hkl}}$ (J m^{-2}) | R_{hkl} | MI_{hkl} | Relaxed $E_{\text{surf}}^{\text{hkl}}$ (J m^{-2}) | R_{hkl} | MI_{hkl} |
|-------------|----------------------|--|------------------|-------------------|--|------------------|-------------------|
| (110) | 5.1233 | 0.1397 | 1.35 | 1.67 | 0.0942 | 1.08 | 1.05 |
| (101) | 4.7860 | 0.2333 | 2.26 | 1.00 | 0.0985 | 1.13 | 1.00 |
| (200) | 3.6227 | 0.1034 | 1.00 | 2.26 | 0.0872 | 1.00 | 1.13 |

& Jung, 2019), and theoretical prediction from Fig. 3(b) is confirmed by the experimentally observed crystal shape in Fig. 4(b) (Gavrilović *et al.*, 2014).

It is surprising to find that an S (stepped) face (in the Hartman–Perdok theory) can have a smaller attachment energy than an F (flat) face. Therefore, it could be possible if external conditions (high temperature and pressure like in the hydrothermal growth method) are taken into account. Under these circumstances, the (110) face changes its S character into

F, and its contribution to the morphology prediction of the crystal becomes more important.

It can be concluded that the predicted morphologies compared favorably with the experimental morphologies. Compared with BFDH predicted morphology, the AE method shows the appearance of the (110) faces that become the most dominant in area, due to the fact that the energetic features of the crystal were taken into account. Despite the appearance of the (110) face by the AE method, the morphology predicted in the case of the relaxed structure has the same trend as the ranking provided by the BFDH method: $MI_{101} > MI_{200}$. As expected, the results gained from the *ab initio* DFT by the AE model help us to improve the understanding of GdVO_4 crystal growth mechanisms and to develop a more reliable and accurate morphology prediction than the BFDH model.

4.3. Equilibrium morphology predictions by the SE model

Based on equation (11), the calculated surface energies for (110), (101) and (200) faces, along with the corresponding values of R_{hkl} and MI_{hkl} are listed in Table 3.

As can be seen from Table 3, the order of stability for the most morphologically important surfaces, suggested by $E_{\text{surf}}^{\text{hkl}}$ values, is the same for relaxed and unrelaxed structures: $MI_{200} > MI_{110} > MI_{101}$.

The theoretical equilibrium crystal shapes were obtained from these surface energy values and from the Wulff construction method [see Figs. 5(a), 5(b)]. The Wulff shape of the unrelaxed structure, Fig. 5(a), indicates a long bipyramid prism, while the Wulff shape of the relaxed structure, Fig. 5(b), indicates a short bipyramid prism. Both calculated shapes of GdVO_4 , using the SE method, match well with the experimental morphology of crystals from the work of Calderón-Villajos *et al.* [2012, Fig. 6(a)] and Min & Jung [2019, Fig. 6(b)].

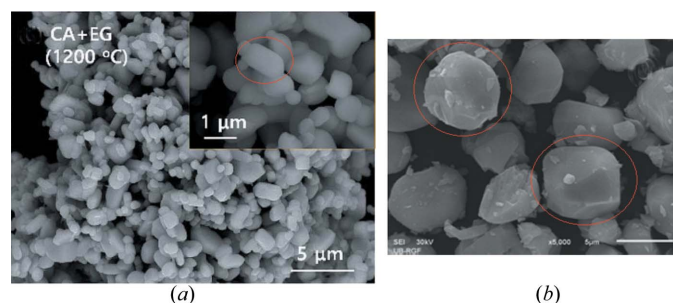


Figure 4
SEM images of GdVO_4 doped with $\text{Er}^{3+}/\text{Yb}^{3+}$. (a) Reproduced with the permission of the Royal Society of Chemistry from Min & Jung (2019); (b) reproduced with the permission of Elsevier from Gavrilović *et al.* (2014).

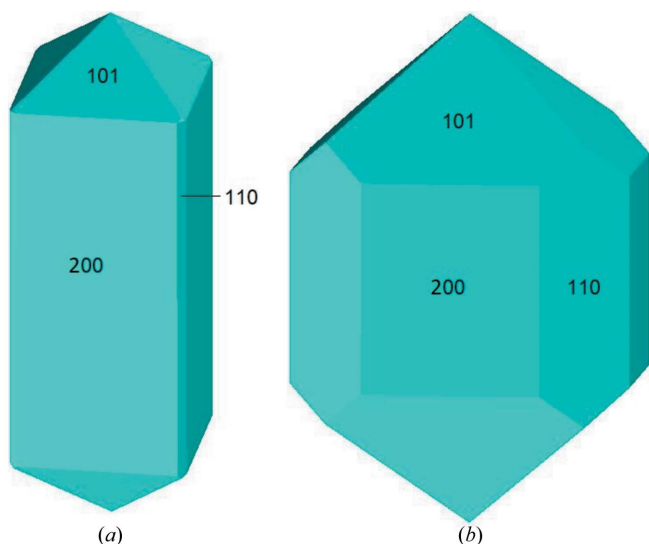


Figure 5
Equilibrium morphology prediction by the SE model: (a) unrelaxed and (b) relaxed shape faces.

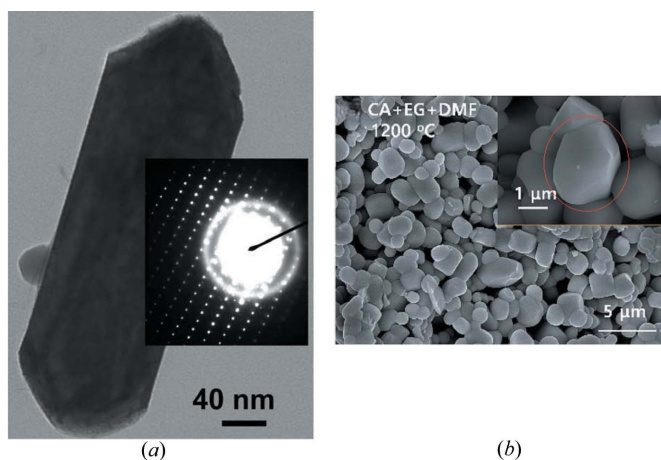


Figure 6
(a) TEM (transmission electron microscopy) image of synthetic crystal $\text{GdVO}_4:\text{Tm}^{3+}$ [reproduced with the permission of the Royal Society of Chemistry from Calderón-Villajos *et al.* (2012)]; (b) SEM microphotography of synthetic crystals $\text{GdVO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ [reproduced with the permission of the Royal Society of Chemistry from Min & Jung (2019)].

These morphologies show some similarity with that obtained with the AE method.

In light of these studies, based on first-principles DFT calculations, we have predicted several theoretical external morphologies of the GdVO₄ crystal, connected with its internal structure, symmetry and energetics. The predicted morphologies depend on the method used and the application of relaxation.

All methods discussed above yielded morphologies which correspond, in a reasonable manner, to experimental crystals observed in nature or synthesized. Although the order of MI_{hkl}'s is different, the AE and SE methods based on the energetics of the system present the (110), (101) and (200) as the three most stable surfaces.

The BFDH method is an approximate method only, based on the geometry of the crystal unit cell and its symmetry. In the case of BFDH, only two faces (101) and (200) are retrieved as the most stable, which corresponds to the morphology of some experimentally observed crystals. Both the AE and SE methods take into account the energetics of the crystal. Finally, it is important to note that the main difference between the attachment energy method and surface energy method is that the first one gives information on the growth morphology and the second one on the equilibrium morphology of the crystal.

5. Conclusions

In this article, first-principles DFT calculations were performed in order to investigate the growth shape and equilibrium morphology of the GdVO₄ crystal. The BFDH, AE and SE methods, in the frame of the 2D periodic slab model, were used. The slice energies, E_{coh} , $E_{\text{att}}^{\text{hkl}}$ and $E_{\text{surf}}^{\text{hkl}}$, of the main faces having (110), (101) and (200) orientation and their d_{hkl} thicknesses were computed using CRYSTAL17 code. The morphologies predicted by each of the three methods were presented, discussed and compared with each other as well as with the experimentally observed morphologies.

Our results show a good consistency and have the ability to describe, in a reasonable manner, several experimentally observed GdVO₄ crystal shapes.

The simplest, BFDH, theory predicts (101) and (200) faces to be of highest MI_{hkl}, with the order MI₁₀₁ > MI₂₀₀. The AE method gives a prediction of the crystal growth morphology with three MI_{hkl} faces (110), (101) and (200), for both unrelaxed and relaxed crystal geometries. The analysis of these three faces shows that the relaxation process of the crystal changes the order of MI_{hkl} for the faces (101) and (200). The SE method gives a prediction of the equilibrium crystal morphology, with MI_{hkl} faces (200), (110) and (101) and the unchanged order of MI_{hkl} for both unrelaxed and relaxed geometry.

Although the order of MI_{hkl} is different in AE and SE methods, they predict that the (110), (101) and (200) faces are the three most stable surface faces of the crystal. The agreement of the theoretical prediction from our study with experiment is quite satisfactory, in the sense that the broad

features of the observed morphologies are reproduced. This justifies this new attempt to use first-principles DFT methodology in combination with AE and SE methods in the frame of predicting morphology of orthovanadate crystals.

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