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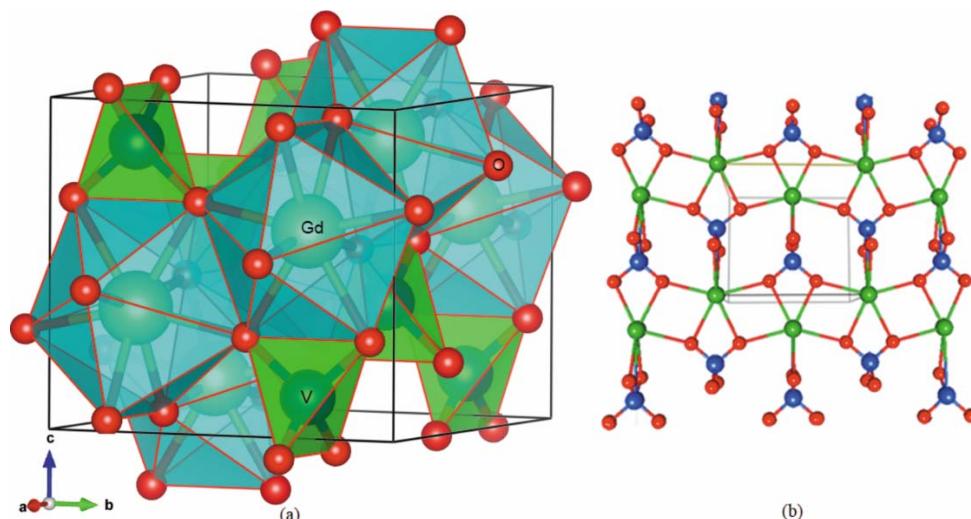
Supporting information for article:

**Morphology of GdVO<sub>4</sub> crystal: first-principles studies**

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## §1. Geometry of GdVO<sub>4</sub>

The geometry of GdVO<sub>4</sub> from X-rays crystallography has the lattice constants  $a = b = 7.223 \text{ \AA}$ ,  $c = 6.373(6) \text{ \AA}$  (Szczeszak *et al.*, 2014). The overall GdVO<sub>4</sub> structure is formed by GdO<sub>8</sub> polyhedrons and VO<sub>4</sub> tetrahedrons as shown in Fig. S1(a). Additionally, based on translations, the crystal structure of the GdVO<sub>4</sub> is presented in Fig. S1(b) as autostereogram (Katrusiak, 2011).



**Figure S1.** (a) Unit cell of GdVO<sub>4</sub> crystal - drawn by Vesta (Momma & Izumi, 2011); (b). Autostereogram of the crystal packing of GdVO<sub>4</sub> drawn with MoProViewer (Guillot *et al.*, 2014). The unit cell is shown,  $b$  is horizontal,  $c$  is vertical; legend: red color - oxygen, blue color - vanadium and green color - gadolinium.

In [VO<sub>4</sub>]<sup>3-</sup> tetrahedron, each V<sup>5+</sup> ion has four oxygen ion neighbors at a V-O distance of 1.4558 Å. The Gd<sup>3+</sup> ions (with point symmetry  $D_{2d}$ ) are arranged within a distorted eight fold coordination polyhedron of neighboring O<sup>2-</sup> ions. The Gd-O ionic bonds in the dodecahedra groups [GdO<sub>8</sub>]<sup>13-</sup> are divided into four short lengths at 2.5034 Å and four long ones at 2.5853 Å.

**Table S1.** Results of calculated (optimization) and experimental (X-Ray) bulk geometry for GdVO<sub>4</sub>.

Structural parameters	SOGGAXC	<b>B3LYP</b>	B3PW	WC1LYP	B3LYP-D3	Experimental (Szczeszak <i>et.al</i> , 2014).
$a = b$ (Å)	7.1337	7.2454	7.2012	7.1969	7.1410	7.2230
$c$ (Å)	6.2599	6.3746	6.3237	6.3356	6.3314	6.3736
$V$ (Å <sup>3</sup> )	318.56	334.64	327.93	328.15	322.86	332.52
$\delta$ ( $V$ )/ $V_0$	4.19%	0.6%	1.37%	1.31%	2.9%	-
$d$ (V–O <sub>1-4</sub> ), Å	1.7101	1.7136	1.7052	1.7106	1.7046	1.4558
$d$ (Gd–O <sub>1-4</sub> ), Å	2.3131	2.3683	2.3516	2.3461	2.3228	2.5034
$d$ (Gd-O <sub>5-8</sub> ), Å	2.3988	2.4510	2.4306	2.4332	2.4343	2.5853

As shown in Table S1, after the geometry optimization, cell parameters, coordinates of atoms and bond lengths changed, as normal. Regarding the V–O and Gd–O bond lengths it is seen that the Gd–O distances are smaller than the experimental values up to 0.18 Å, while the V–O distances have become larger than the experimental values up to 0.25 Å, for all the tested functionals.

The threshold on the SCF energy was set to 10<sup>-9</sup> hartree, a pruned (75,974)  $p$  grid was adopted (XLGRID) and the percentage of Fock/Kohn–Sham mixing matrices was set to 30 (IPMIX = 30). The values used in the present study for the five tolerances that evaluate Coulomb and exchange integrals were set to 10<sup>-7</sup> (ITOL1 to ITOL4) and 10<sup>-14</sup> (ITOL5), respectively. The shrinking factor of the reciprocal

space net is set to 8, 8, 8, corresponding to 59  $k$ -points in the irreducible Brillouin Zone (IBZ). To accelerate convergence in self-consistent calculation, we choose the Broyden scheme (Broyden, 1965).

## §2. DFT computed energy for bulk crystal and ions

**Table S2.** DFT energy (Hartree) for bulk and ions in GdVO<sub>4</sub>.

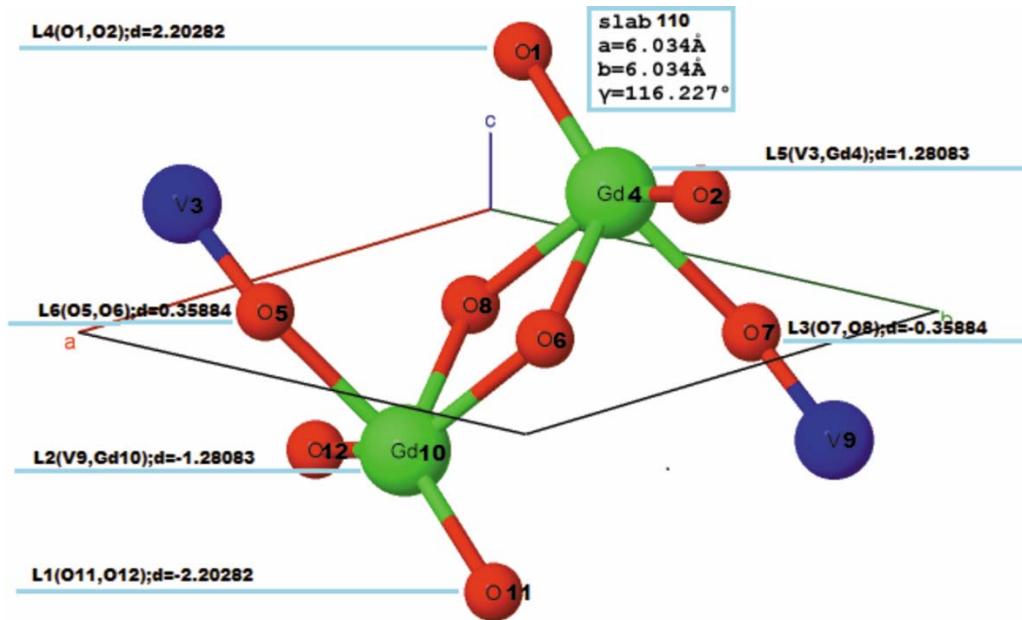
$E_{\text{bulk}}$	-4021.542514
$E_{\text{Gd}^{3+}}$	-763.984342
$E_{\text{V}^{5+}}$	-937.760389
$E_{\text{O}^{2-}}$	-74.703144

## §3. ( $hkl$ ) Faces of GdVO<sub>4</sub> crystal

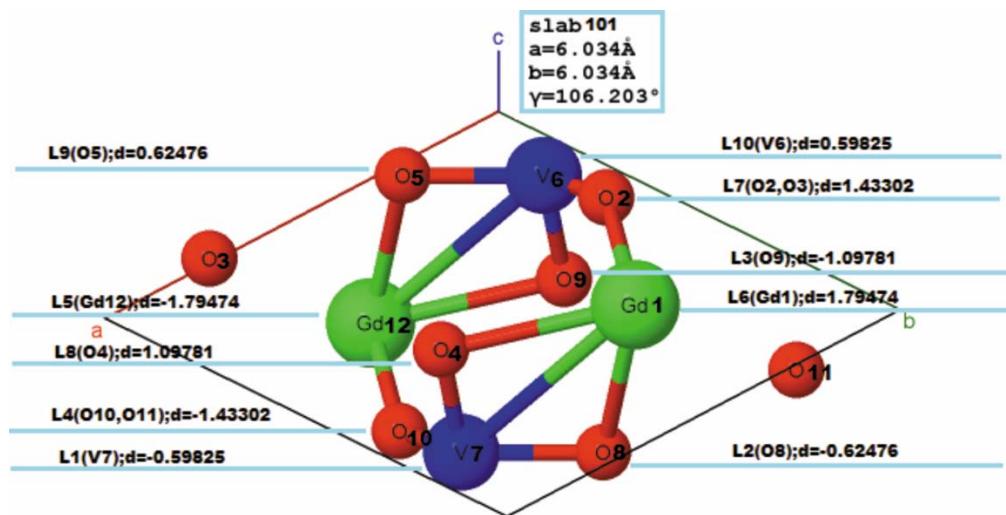
**Table S3.** The most important forms and faces of GdVO<sub>4</sub> crystal obtained from Crystal 17 analysis.

Faces ( $hkl$ )	Multiplicity	$d_{hkl}$ (Å)
110	$4 \rightarrow \{ 110, 1-10, -110, -1-10 \}$	5.1233
101	$8 \rightarrow \{ 101, 10-1, 011, 01-1, 0-11, 0-1-1, -101, -10-1 \}$	4.7860
200	$4 \rightarrow \{ 200, 020, 0-20, -200 \}$	3.6227

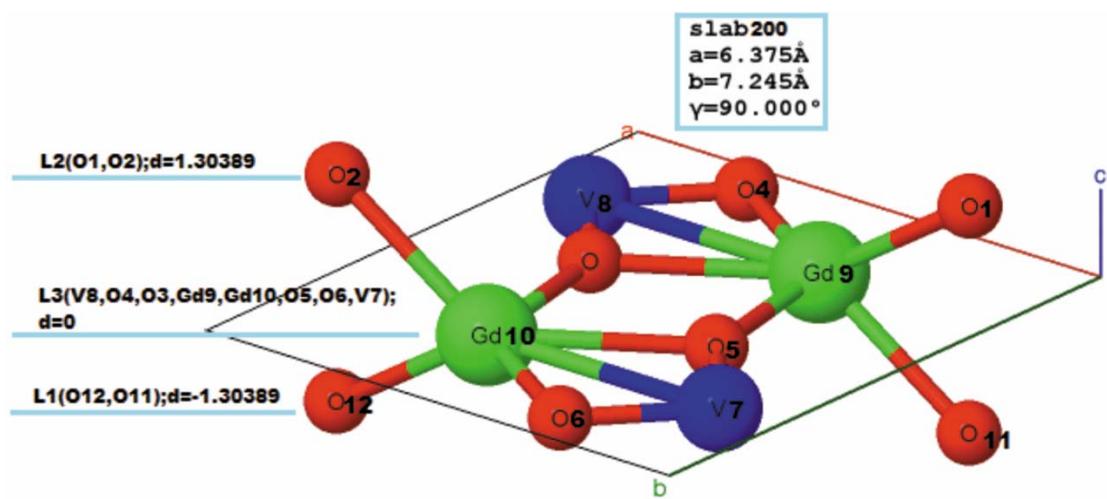
#### §4. Slabs's structure of GdVO<sub>4</sub>



**Figure S2.** View of the 110 slab structure of GdVO<sub>4</sub>; O-terminated.



**Figure S3.** View of the 101 slab structure of GdVO<sub>4</sub>; Gd-terminated.



**Figure S4.** View of the 200 slab structure of  $\text{GdVO}_4$ ; O-terminated.

## §5. Unrelaxed/relaxed geometrical parametres and energies of the slabs

**Table S4.** Unrelaxed/relaxed slab parameters for the main faces of  $\text{GdVO}_4$ .

Slabs hkl	Unrelaxed slab parameters				Relaxed slab parameters			
	$a$ (Å)	$b$ (Å)	$\gamma$ (degrees)	$A$ ( $\text{\AA}^2$ )	$a$ (Å)	$b$ (Å)	$\gamma$ (degrees)	$A$ ( $\text{\AA}^2$ )
110	6.0338	6.0338	116.2	32.659	6.3637	6.0208	121.2	33.291
101	6.0338	6.0338	106.2	34.961	5.9675	5.9675	116.6	33.014
200	6.3746	7.2454	90	46.187	6.2008	7.2155	90	44.743

**Table S5.** The computed unrelaxed and relaxed  $E_{\text{slice}}^{\text{hkl}}$  of different shape faces.

Faces (hkl)	Unrelaxed $E_{\text{slice}}^{\text{hkl}}$ (kJ mol <sup>-1</sup> )	Relaxed $E_{\text{slice}}^{\text{hkl}}$ (kJ mol <sup>-1</sup> )
(110)	-26596.8613	-26665.6258
(101)	-26423.6230	-26660.0400
(200)	-26586.4683	-26628.5918

**References**

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