Energetic Order of Nb$_2$O$_5$ and Ta$_2$O$_5$ Polymorphs

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Nb$_2$O$_5$ and Ta$_2$O$_5$ are materials with important technical applications, e.g., in electrochemistry as anode materials for Li or Na storage, or as selective oxidation catalysts. The properties of both oxides largely depend on their various polymorphs with different crystal structures. So far, the literature does not agree on which polymorphs of Nb$_2$O$_5$ and Ta$_2$O$_5$ are most stable under standard conditions. Herein, the relative stability of all relevant polymorphs of Nb$_2$O$_5$ and Ta$_2$O$_5$ is calculated using density-functional theory and the recently developed RSHXLDA without dispersion correction proves to be the method of choice for the systems under investigation. For this reason, the stability order obtained with RSHXLDA is considered as most reliable.

1. Introduction

In the past years, Nb$_2$O$_5$ and Ta$_2$O$_5$ have been considered materials with important technical applications, Nb$_2$O$_5$, e.g., as anode material for Na- or Li-ion batteries, as a catalyst for aldol condensation, as a catalyst for methanol oxidation, or as an electrocatalyst for the oxygen reduction reaction. It has been frequently reported that the properties of both oxides largely depend on their various polymorphs with different crystal structures. However, the literature so far does neither agree on the most stable polymorphs of the two solids, nor on the order of stability. Numerous phases of Nb$_2$O$_5$ and Ta$_2$O$_5$ were found, but only a few studies on their stabilities are available.

Kato et al. obtained H-Nb$_2$O$_5$ in a crystalline growth experiment at room temperature. Andersson produced N-Nb$_2$O$_5$ at 900 °C in a sealed Pt tube with 10–20 weight percent of water. R-Nb$_2$O$_5$ was reported by Gruehn after heating H$_2$NbO$_4$ at 550–650 °C. Schäfer et al. obtained B-Nb$_2$O$_5$ and F-Nb$_2$O$_5$ from NbOCl$_4$. The crystal structures of B-Nb$_2$O$_5$ and F-Nb$_2$O$_5$ were analyzed by Ercit et al. and Martin et al. A high-pressure form of Z-Nb$_2$O$_5$ was obtained by Zibrov et al. by compressing H-Nb$_2$O$_5$ at 1050 °C.

B-Ta$_2$O$_5$ was found by Izumi et al. after cooling TaOCl$_3$ from 620 to 570 °C. Holleweger et al. synthesized β-Ta$_2$O$_5$ by deposition of tantalum oxide films at 500 °C on silicon substrates. Another high-pressure form of Z-Ta$_2$O$_5$ was obtained by Zibrov et al. via compressing of B-Ta$_2$O$_5$ at 1200 °C. Jacob et al. measured the formation enthalpy for H-Nb$_2$O$_5$ depending on the temperature. Khan et al. reported a theoretical and experimental study on the optoelectronic properties of Nb$_2$O$_5$ and H-Nb$_2$O$_5$. They used plane waves and generalized gradient approximation (GGA) functionals for structure optimization, and the TB-mBJ approach was used for electronic structure calculations. They could reproduce their experimental value for the optical bandgap of 3.2 eV with a deviation of 0.2 eV, but did not study the relative stability of polymorphs. Pinto et al. calculated the structural, electronic, and thermodynamic properties of T-Nb$_2$O$_5$ and B-Nb$_2$O$_5$ at the GGA + U level using plane waves. B-Nb$_2$O$_5$ is reported to be more stable than T-Nb$_2$O$_5$.

In this work, the relative stability of relevant Nb$_2$O$_5$ and Ta$_2$O$_5$ polymorphs was calculated at the density functional theory (DFT) level, to identify the thermodynamically most stable phases under standard conditions. Structures with more than two partially occupied atom positions (T-Nb$_2$O$_5$, HT-Ta$_2$O$_5$, T-Ta$_2$O$_5$, L-Ta$_2$O$_3$) were not taken into account. Such partial occupancies require an elaborate configuration analysis in theoretical model calculations. Ignoring these structures is justified because all of these are high-temperature phases that are not candidates...
for the most stable polymorph. The high-pressure phases Z-Nb₂O₅ and Z-Ta₂O₅ were ignored because preliminary calculations on hybrid DFT levels showed that they are more than 200 kJ mol⁻¹ less stable than the other structures without external pressure. The structure of the low-temperature phase TT-Ta₂O₅ is higher by more than 300 kJ mol⁻¹ and is ignored as well.

Additional to the experimentally reported structures of Nb₂O₅ and Ta₂O₅, the set of polymorphs was extended by some hypothetical polymorphs. These were constructed using experimental VₐO₄[24,25] and A₈O₃[26] structures and substituting V or As by Nb/Ta. Also, some Nb₂O₅ polymorphs were added to the Ta₂O₅ set by substituting Ta with Nb and vice versa.

As a preliminary step, an assessment of selected GGA and hybrid functionals was performed to identify the most suitable functional for the energetic properties of Nb₂O₅ and Ta₂O₅. We also investigated the effect of London dispersion on the calculated thermodynamic properties. The atomization free enthalpy of H-Nb₂O₅ was benchmarked against the study of Jacob et al.[21] since this is the only available experimental reference data on thermodynamical properties of the two oxides to our knowledge. Using the best functionality of this benchmark test, the relative energies and free enthalpies of all relevant Nb₂O₅ and Ta₂O₅ polymorphs were calculated.

2. Computational Details

All calculations were performed with CRYSTAL17 (version 1.0.2),[27] a quantum-chemical program that uses linear combinations of Gaussian-type atomic orbitals as basis functions of the crystal orbitals. This is advantageous for efficient hybrid DFT calculations compared to plane-wave methods. For all calculations, the optimized rev2-POB-TZVP basis sets[28] were used which reduce the basis set superposition error and provide improved structural properties of solids. The integration truncation parameters TOLINTEG were set to 7 7 7 7 14. Monkhorst–Pack grids for integration in reciprocal space were converged individually for every unit cell (see below).

First, a benchmark of selected density functionals for the calculation of the atomization free enthalpy of H-Nb₂O₅ was performed. For this purpose, the standard GGA functional PBE[29] (with and without D3(BJ) correction)[30], the global hybrid functionals B1WC[31] B97H,[32,33] PBE0[34] (with and without D3(BJ) correction), PW1PW[35] (with and without D3(BJ) correction), M06[36] (with and without D3(BJ) correction), WC1LYP,[37] and the range-separated (RS) hybrid functionals HSE06[38] HISS,[39,40] and RSHXLA[41,42] were used. This selection was in most cases based on the performance of the functionals in the benchmark test of Tran et al.[43] for simple cubic solids. It has to be noted that the results of our benchmark test for Nb₂O₅ and Ta₂O₅ do not coincide with the previous study,[43] due to the higher electronic and structural complexity of the transition metal oxides. In the following, we use the shorthand notation D3 for the D3(BJ) correction.

The Monkhorst–Pack grids were converged for each unit cell of the individual polymorphs. For space groups 12 (N-Nb₂O₅), 15, 19, 53, 59, 62, 72, and 139 a 4 × 4 × 4, for space group 3 a 2 × 2 × 2 and for space group 12 (R-Nb₂O₅) a 4 × 4 × 8 k-point-mesh was used.

Thermodynamic corrections to the electronic DFT energy were calculated from harmonic frequency calculations using the standard GGA functional PBE-D3. The free enthalpy \( G_{M,O} \) was calculated from the enthalpy \( H_{M,O} \) and entropy \( S_{M,O} \)

\[
G_{M,O} = H_{M,O} - TS_{M,O}
\]  

(1)

The thermodynamic correction \( \Delta_{\text{therm}} \) (see the following) is the difference between the polymorph DFT energy and the polymorph-free enthalpy.

\[
\Delta_{\text{therm}} = G_{M,O} - E_{M,O}
\]  

(2)

\( H_{M,O} \) and \( S_{M,O} \) were calculated as the sum of the individual components for translation, rotation, vibration, and electronic excitation. Translation and rotation contributions are not present in solids, and electronic excitations were neglected because the electronic band gaps were larger than the thermal energy \( RT \) (all bandgaps are larger than 3.5 eV on the hybrid DFT level). The vibrational enthalpy and entropy were calculated from the Boltzmann distribution of the vibrational frequencies \( \nu_i \), the temperature \( T \), the pressure \( P \), and the cell volume \( V \) (using the ideal gas constant \( R \) and the Planck constant \( h \))

\[
H_{\text{vib}} = \sum_i \frac{1}{2} h\nu_i + \sum_i \frac{h\nu_i}{e^{\nu_i/kT} - 1} + pV
\]  

(3)

\[
S_{\text{vib}} = \frac{1}{T} \left( \sum_i \frac{1}{2} h\nu_i + \sum_i \frac{h\nu_i}{e^{\nu_i/kT} - 1} \right) + R \cdot \ln \left( \sum_i \frac{h\nu_i}{e^{\nu_i/kT} - 1} \right)
\]  

(4)

Exemplarily, the phonon densities of states of the most stable polymorph H-Nb₂O₅ for Nb and Ta are shown in the Supporting Information.

The translational enthalpy for gas-phase Nb, Ta, and O was calculated from the ideal gas law

\[
H_{\text{trans}} = \frac{3}{2} RT + pV
\]  

(5)

The translational entropy is available from the NIST chemical webbook[44] (161.059 J (K mol⁻¹) for O, 185.22 J (K mol⁻¹) for Ta, and 186.29 J (K mol⁻¹) for Nb). The atomization free enthalpy of M₂O₅ was calculated as

\[
E_{\text{at}} = 2E_M + 5E_O - E_{M,O}
\]  

(6)

\[
H_{\text{at}} = E_{\text{at}} + 2H_{\text{trans,M}} + 5H_{\text{trans,O}} - H_{\text{vib}}
\]  

(7)

\[
S_{\text{at}} = 2S_{\text{trans,M}} + 5S_{\text{trans,O}} - S_{\text{vib}}
\]  

(8)

\[
G_{\text{at}} = H_{\text{at}} - TS_{\text{at}}
\]  

(9)

The calculated \( G_{\text{at}} \) values were compared with formation free enthalpies of Nb₂O₅ from Jacob et al.[21] using

\[
G_{\text{ref}}^{\text{at}} = -\Delta_f G_{\text{Nb}_2O_5} + 2\Delta_f G_{\text{Nb}^{8+}} + 5\Delta_f G_{O^{8-}}
\]  

(10)

The gas-phase formation enthalpies in (677.5 kJ mol⁻¹ for Nb, 726.8 kJ mol⁻¹ for Ta, and 201.2 kJ mol⁻¹ for O) were also taken from NIST chemical webbook[44]
3. Results and Discussion

3.1. Structures of the Selected Polymorphs

Experimental structural data of the selected polymorphs are collected in Table 1. ICSD numbers are provided where available.

Table 1 contains five Nb2O5 polymorphs (space groups 3, 12 (2 structures), 15, and 139), 3 Ta2O5 polymorphs (space groups 15, 53, and 139), 2 V2O5 polymorphs (space groups 59 and 62), and 1 As2O5 polymorph (space group 19). To increase the number of studied Nb2O5 and Ta2O5 structures, hypothetical polymorphs were calculated in addition to the experimentally known polymorphs. For Nb2O5, the remaining M2O5 polymorphs were added to the six Nb2O5 polymorphs by M/Ta substitution. Similarly, the remaining M2O5 polymorphs were added to the three Ta2O5 polymorphs by M/Ta substitution.

3.2. Atomization-Free Enthalpies of H-Nb2O5

In Table 2, the calculated atomization enthalpies, entropies, and free enthalpies of H-Nb2O5 are compared to available experimental data from Ref. [21].

The atomization energies, enthalpies, and free enthalpies of the different methods differ by up to 500 kJ mol⁻¹, which corresponds to 10% of the experimental values. For \( H_\text{at} \), the smallest \( \Delta \) is obtained with RSHXLDA, WC1LYP, and PBE (2.5, -11.2, -22.7 kJ mol⁻¹). Since the atomization entropy (only calculated with PBE-D3) closely agrees with the experiment, the trends are the same for \( G_\text{at} \). The global hybrid functionals (PW1PW, M06, PB0, B1WC, and B97H), as well as the short-range and medium-range, corrected RS hybrids HSE06 and HISS strongly underestimate \( G_\text{at} \), ranging from -55.9 kJ mol⁻¹ (B1WC) to -384.0 kJ mol⁻¹ (HISS). This is not improved by D3 correction (\( \Delta = -199.4 \) kJ mol⁻¹ for PBE0-D3 and -113.5 kJ mol⁻¹ for PW1PW-D3). The long-range corrected RS hybrid functional RSHXLDA (\( \Delta = +5.2 \) kJ mol⁻¹), the global hybrid functional WC1LYP (-8.5 kJ mol⁻¹), and the standard GGA functional PBE (-20.0 kJ mol⁻¹) provide the most accurate values for \( \Delta G_\text{at} \). As expected, the D3 correction significantly increases the atomization energy in all cases (except M06 since dispersion is already included in its parameterization), which leads to a strong overestimation of \( G_\text{at} \) with PBE-D3, by +103.5 kJ mol⁻¹.

Table 2. Comparison of calculated and measured thermodynamic properties of H-Nb2O5 (in kJ mol⁻¹) at 298.15 K. Atomization energy \( E_\text{at} \), enthalpy \( H_\text{at} \), entropy \( S_\text{at} \), and free enthalpy \( G_\text{at} \). Experimental values from Ref. [21]. \( \Delta \) is the absolute deviation in kJ mol⁻¹.

| Functional      | \( E_\text{at} \) | \( H_\text{at} \) | \( \Delta \) | \( S_\text{at} \) | \( G_\text{at} \) | \( \Delta \) |
|-----------------|-----------------|-----------------|-------------|-----------------|-----------------|-------------|
| RSHXLDA         | 4636.7          | 4612.8          | 2.5         | 4305.2          | 5.2             |
| WC1LYP          | 4623.0          | 4599.1          | -11.2       | 4291.5          | -8.5            |
| PBE             | 4611.5          | 4587.6          | -22.7       | 4280.0          | -20.0           |
| B1WC            | 4575.6          | 4551.7          | -58.6       | 4244.1          | -55.9           |
| M06-D3          | 4569.3          | 4545.4          | -64.9       | 4237.8          | -62.2           |
| M06             | 4542.0          | 4518.1          | -92.2       | 4210.5          | -89.5           |
| PBE-D3          | 4735.0          | 4711.1          | 100.8       | 4403.5          | 103.5           |
| PW1PW-D3        | 4518.0          | 4494.1          | -116.2      | 4186.5          | -113.5          |
| B97H            | 4481.5          | 4457.6          | -152.7      | 4150.0          | -150.0          |
| PB0-D3          | 4432.1          | 4408.2          | -202.1      | 4100.6          | -199.4          |
| PW1PW           | 4378.7          | 4354.8          | -255.5      | 4047.2          | -252.8          |
| HSE06           | 4309.0          | 4285.1          | -325.2      | 3977.5          | -322.5          |
| HISS            | 4247.5          | 4223.6          | -386.7      | 3916.0          | -384.0          |
| Experiment      | 4610.3          | 1040.6          | 4300.0      |                 |                 |

Table 1. Experimental structure parameters of the selected M2O5 polymorphs (M = Nb, Ta).

| Name        | Space group | Number | \( a \) [Å] | \( b \) [Å] | \( c \) [Å] | \( \beta \) [°] | ICSD | References |
|-------------|-------------|--------|-------------|-------------|-------------|-------------|------|------------|
| H-Nb2O5     | P2          | 3      | 21.160      | 3.822       | 19.350      | 119.5       | 16 605 | [11]       |
| N-Nb2O5     | C2/m        | 12     | 28.510      | 3.830       | 17.48       | 120.8       |       | [7]        |
| R-Nb2O5     | C2/m        | 12     | 12.790      | 3.826       | 3.983       | 90.8        |       | [8]        |
| B-Nb2O5     | C2mm        | 15     | 12.740      | 4.883       | 5.561       | 105.0       | 71 317 | [10]       |
| M-Nb2O5     | C2mm        | 15     | 12.790      | 4.856       | 5.527       | 104.3       |       | [13]       |
| As2O5       | P2,2,2,1    | 19     | 4.632       | 8.505       | 8.640       |             |       | [26]       |
| \( \beta \)-Ta2O5 | Pnma      | 53     | 6.425       | 3.769       | 7.706       | 671 147     |       | [14]       |
| V2O5        | Pmmn        | 59     | 3.560       | 11.513      | 4.372       |             |       | [24]       |
| \( \gamma \)-Ta2O5 | Pnna    | 62     | 9.946       | 3.585       | 10.042      |             |       | [25]       |
| F-Ta2O5     | Ibam        | 72     | 10.455      | 7.349       | 6.958       | 250 052     |       | [15]       |
| M-Nb2O5     | I4/mmm     | 139    | 20.440      | 20.440      | 3.832       | 17 027      |       | [9]        |

3.3. Lattice Parameters and Atom Positions of B-Nb2O5

B-Nb2O5 (space group 15) is a simple polymorph with only 4 symmetry-independent atoms. That makes it a suitable candidate for benchmarking atom positions and lattice parameters. Table 3 shows a comparison of calculated and measured lattice parameters of B-Nb2O5.\(^{[10]}\)

Accurate results (\( \Delta < 0.4\% \)) were obtained with the RS hybrid functionals RSHXLDA (long-range corrected) and HSE06 (short-range corrected), the global hybrids PW1PW, PB0, M06-D3 and M06, and with the standard GGA-functional PBE-D3. Among these, M06-D3 is the most accurate (0.16%). PBE without D3 correction has a larger deviation \( \Delta \) of 1.29%, which is, however, in accordance with the benchmark test of Tran et al.\(^{[43]}\) London dispersion correction significantly improves the PBE structures (\( \Delta = 0.30\% \)). Table 4 shows the comparison of calculated and measured atom positions of B-Nb2O5.\(^{[10]}\)
The atomic positions can be calculated accurately with all functionals (Δ between 0.001 and 0.003). With the global hybrid functional B97H and the standard GGA functional PBE, the largest deviations are observed (0.0033 and 0.0032, respectively). The hybrid functional M06 (with and without D3) provides the smallest deviations (0.0008 and 0.0009, respectively).

### 3.4. Electronic Bandgaps of H-Nb2O5

Table 5 shows the comparison of calculated and measured electronic bandgaps of H-Nb2O5.[22]

| Functional   | Band Gap (eV) | Δ |
|--------------|---------------|---|
| HSE06        | 2.99          | −0.08 |
| PW1PW-D3     | 3.15          | 0.08  |
| PW1PW        | 3.20          | 0.13  |
| B1WC         | 2.75          | −0.32 |
| WCl1LYP      | 2.73          | −0.34 |
| B97H         | 3.43          | 0.36  |
| PBE0-D3      | 3.60          | 0.53  |
| PBE0         | 3.65          | 0.58  |
| HISS         | 3.65          | 0.58  |
| M06-D3       | 3.75          | 0.68  |
| M06          | 3.76          | 0.69  |
| PBE          | 1.60          | −1.47 |
| PBE-D3       | 1.58          | −1.49 |
| RSHXLDA      | 7.91          | 4.84  |
| Experiment   | 3.07          |      |

In the discussion of the deviation of the bandgaps, it must be taken into account that the literature value is an optical gap. Usually, fundamental band gaps are larger than optical gaps due to excitonic effects. The slight bandgap changes observed for the D3 corrected functionals are due to the different geometries. The hybrid functionals HSE06 and PW1PW provide the best agreement with experiment with Δ values of +0.08 and +0.13 eV, again in line with earlier studies. As expected, PBE strongly underestimates the experimental gap due to the well-known self-interaction error. The large deviation observed for RSHXLDA (Δ = +4.84 eV) is striking. This means that although

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Table 3. Comparison of calculated and measured lattice parameters of B-Nb2O5. Experimental values are taken from Ref. [10]. Δ is the relative absolute deviation of the lattice parameters in %.

| Functional | a [Å] | b [Å] | c [Å] | β [°] | Δ |
|------------|-------|-------|-------|------|---|
| M06-D3     | 12.748| 4.880 | 5.575 | 104.91| 0.12 |
| PBE0       | 12.736| 4.880 | 5.555 | 104.46| 0.19 |
| HSE06      | 12.746| 4.879 | 5.552 | 104.41| 0.21 |
| PW1PW      | 12.760| 4.886 | 5.558 | 104.38| 0.22 |
| PBE-D3     | 12.819| 4.886 | 5.534 | 104.94| 0.22 |
| M06        | 12.767| 4.888 | 5.584 | 104.74| 0.25 |
| RSHXLDA    | 12.695| 4.876 | 5.554 | 104.48| 0.29 |
| B1WC       | 12.725| 4.856 | 5.513 | 104.85| 0.42 |
| WCl1LYP    | 12.826| 4.901 | 5.571 | 104.18| 0.30 |
| HISS       | 12.69| 4.848 | 5.514 | 104.67| 0.57 |
| PW1PW-D3   | 12.700| 4.842 | 5.505 | 105.36| 0.62 |
| PBE0-D3    | 12.679| 4.835 | 5.502 | 105.44| 0.73 |
| B97H       | 12.799| 4.916 | 5.616 | 104.1 | 0.75 |
| PBE        | 12.879| 4.931 | 5.607 | 104.01| 0.97 |
| Experiment | 12.740| 4.883 | 5.561 | 105.02|      |

The atomic positions can be calculated accurately with all functionals (Δ between 0.001 and 0.003). With the global hybrid functional B97H and the standard GGA functional PBE, the largest deviations are observed (0.0033 and 0.0032, respectively). The hybrid functional M06 (with and without D3) provides the smallest deviations (0.0008 and 0.0009, respectively).

Table 5. Comparison of calculated and measured electronic band gaps (eV) of H-Nb2O5. The experimental value of the optical gap is taken from Ref. [22]. Δ is the absolute deviation in eV.

| Functional |
|------------|
| Band Gap |
| Δ |
| HSE06   |
| PW1PW-D3 |
| PW1PW |
| B1WC |
| WCl1LYP |
| B97H |
| PBE0-D3 |
| RSHXLDA |
| Experiment |

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Table 4. Comparison of calculated and measured atom positions of B-Nb2O5. Experimental values are taken from Ref. [10]. Δ is the absolute deviation in fractional units.

| Functional |
|------------|
| Nb   |
| O1   |
| O2   |
| O3 (y) |
| Δ |
| M06  |
| M06-D3 |
| B1WC |
| HISS |
| PBE-D3 |
| PBE0 |
| PW1PW-D3 |
| HSE06 |
| PBE0-D3 |
| PW1PW |
| WCl1LYP |
| RSHXLDA |
| PBE |
| B97H |
| Experiment |
RSHXLD provides accurate energetic and structural properties of Nb₂O₅, it is not well suited for the calculation of electronic properties.

3.5. Relative Energies of the Nb₂O₅ and Ta₂O₅ Polymorphs

In the following section, we present the relative energies of the selected Nb₂O₅ and Ta₂O₅ polymorphs, obtained with selected functionals RSHXLD, M06-D3, PBE, and PBE-D3. RSHXLD gives the most reliable results for free atomization enthalpies (see Table 2) and is therefore considered as most reliable. Both PBE and PBE-D3 were selected to investigate the effect of dispersion correction. M06-D3 was chosen since it gave good lattice parameters (Table 3) and was among the more accurate DFT functionals in previous benchmark tests. It is important to note that PBE, PBE-D3, and M06-D3 are only used to show the influence of the functional choice on the energetic order of the polymorphs. Figure 1 shows the calculated relative energies per formula unit in kJ mol⁻¹.

The polymorphs are sorted by the energetic order obtained with RSHXLD, which gave the most accurate results for the atomization-free enthalpies (Section 3.2). According to RSHXLD, R-Nb₂O₅ (12_2) is the most stable polymorph. However, the energies of the polymorphs with space groups 3 (0.5 kJ mol⁻¹), 12 (0.8 kJ mol⁻¹), 15 (1.8 kJ mol⁻¹), and 59 (2.0 kJ mol⁻¹) are only slightly higher with differences that are within the usual DFT error (all relative energies listed in Table 6). In most cases, PBE parallels the energetic order obtained with RSHXLD, although space group 3 is the most stable polymorph. The large difference between PBE and PBE-D3 shows that the D3 correction has a significant effect on the relative stability. In earlier studies, it was shown that the C₆ parameters of the D3 method are too large for solids (due to missing reference systems with high coordination numbers), and lead to inconsistent relative stabilities of titania polymorphs. Since also the atomization energy is overestimated with PBE-D3 (see Table 2), we conclude that the PBE-D3 is not appropriate for the present investigation. M06-D3 shows a similar trend as PBE-D3, both predicting space group 15 as the most stable polymorph for Nb₂O₅. The reason for this is a drawback in the D3 correction for large coordination numbers. Since the D3-correction is originally made for molecules, the reference compounds all have low coordination numbers. For solids with higher coordination numbers, the D3-correction just uses the highest available reference coordination number, which is much lower than the real coordination number (2.922 for Nb, see Table 7). This leads to an overestimation of the D3-energy. The polymorph with space group 15 has larger Nb coordination numbers (see Table 7), which increases this effect. The improved version D4 which diminishes this effect is not implemented in the present CRYSTAL code.

Table 6. Relative energies in kJ mol⁻¹ for M₂O₅ polymorphs (M = Nb, Ta) on RSHXLD-level. Only the space group numbers are given, see Table 1.

| Space group | Nb₂O₅ | Ta₂O₅ |
|-------------|-------|-------|
| 12_2        | 0.0   | 2.2   |
| 3           | 0.5   | 0.0   |
| 12          | 0.8   | 6.1   |
| 15          | 1.8   | 0.8   |
| 59          | 2.0   | 3.7   |
| 139         | 9.8   | 22.1  |
| 72          | 43.0  | –     |
| 62          | 54.2  | 68.7  |
| 19          | 60.1  | 67.6  |
| 53          | 74.9  | 62.5  |

Table 7. Average Nb coordination numbers (CN) for the energetic low Nb₂O₅ polymorphs. The reference CN (used by DFT-D3) is also given.

| SG  | 15  | 3   | 12  | 12_2 | 59  | 139 |
|-----|-----|-----|-----|------|-----|-----|
| Average CN | 9.051 | 8.194 | 8.212 | 8.380 | 8.387 | 8.129 |
| Ref CN | 2.922 | 2.922 | 2.922 | 2.922 | 2.922 | 2.922 |

Figure 1. Relative Energies of Nb₂O₅ (left) and Ta₂O₅ (right) polymorphs per formula unit in kJ mol⁻¹, calculated with RSHXLD, M06-D3, PBE, and PBE-D3. The two polymorphs of Space group 12 are called 12 (N-Nb₂O₅) and 12_2(R-Nb₂O₅).
For Ta$_2$O$_5$, PBE and RSHXLDA predict H-Nb$_2$O$_5$ as the most stable polymorph (both same energy). However, the energies of the polymorphs with space groups 12, 12, 12$_2$, 15, 19, 3, 12, 12$_2$, and 59 are only slightly higher with differences that are within the usual DFT error. M06-D3 and PBE-D3 again differ significantly from the other functionals and predict B-Ta$_2$O$_5$ as the most stable polymorph (for the same reason as for Nb$_2$O$_5$). For Ta$_2$O$_5$ no value for F-Ta$_2$O$_5$ (SG 72) could be calculated because of an SCF convergence failure in geometry optimization with RSHXLDA.

However, one has to keep in mind that these predictions are based on electronic energies. The presence of a particular polymorph in equilibrium at a given temperature is determined by the Gibbs free enthalpy $G(T)$. For this reason, we calculated the vibrational contributions to the thermodynamic functions under standard conditions from phonon calculations with PBE-D3. Here PBE-D3 was chosen as it is frequently used for the calculation of thermodynamic corrections, and also gave an accurate atomization entropy, see Table 2. Test calculations showed that PBE-D3 and PBE provide similar phonon frequencies and thus thermal contributions. Wherever possible, large supercells with lattice parameters >10 Å were used for the frequency calculations to obtain convergence with respect to long-wavelength phonons (supercell in Table 8). For comparison, we also present results for the primitive unit cell (normal in Table 8). Gas-phase thermodynamic data were taken from experimental databases (see Computational Details section).

### 3.6. Thermodynamic Corrections

The corrections at 298 K range from 20.8 to 33.1 kJ mol$^{-1}$ for Nb$_2$O$_5$, and from 14.6 to 31.3 kJ mol$^{-1}$ for Ta$_2$O$_5$ for the primitive unit cells. Due to computer time limitations, only for four systems with larger supercells could be used for frequency calculations. The effect was quite different: only 1–3 kJ mol$^{-1}$ for polymorphs with SG 12, 12, 15, and 62, but +8 kJ mol$^{-1}$ for SG 59 (Nb$_2$O$_5$), and +9 kJ mol$^{-1}$ for SG 12 and 59 (Ta$_2$O$_5$). In these cases, the primitive cell vectors were too small to allow the calculation of low-frequency modes in the Γ-point approximation.$^{[47]}$ The primitive cell vectors of the polymorphs with SG 12 and 139 are larger than 10 Å, thus we assume that the present values are close to convergence. For SG 3, the lattice parameters $a$ and $c$ is about 20 Å while $b$ is 3.8 Å. However, the primitive cell already contains 98 atoms, therefore the computational effort of the supercell frequency calculation is too high. For SG 19, 53, and 72, the supercell effects were ignored because the relative DFT energies are already higher than 40 kJ mol$^{-1}$ for Nb$_2$O$_5$ and Ta$_2$O$_5$ on the RSHXLDA level. The relative stability order of the polymorphs is only slightly changed by the vibration contributions obtained at 298 K. This is shown in the next section.

### 3.7. Relative Free Enthalpies of the Nb$_2$O$_5$ and Ta$_2$O$_5$ Polymorphs

Figure 2 shows the relative free enthalpies of the polymorphs of Nb$_2$O$_5$ and Ta$_2$O$_5$ per formula unit in kJ/mol calculated from the energies and the thermal corrections as previously.

The thermodynamic correction changes the order of polymorphs with SG 3, 12, 12, 59, and 15 which are energetically close to each other (also see Figure 3). The strong stabilization of the polymorph with SG 15 with M06-D3 and PBE-D3 compared to the other functionals remains. In the case of Nb$_2$O$_5$, H-Nb$_2$O$_5$ (SG 3) is the most stable polymorph. However, the free enthalpies of the polymorphs with SG 12 (0.9 kJ mol$^{-1}$), 12, 2 (3.7 kJ mol$^{-1}$), 59 (6.1 kJ mol$^{-1}$), 15 (8.6 kJ mol$^{-1}$), and 139 (11.1 kJ mol$^{-1}$) are only slightly higher with differences that are within the usual DFT error. For Ta$_2$O$_5$ the lowest free enthalpy is also obtained for H-Nb$_2$O$_5$ (SG 3). The polymorphs with SG 12 (3.6 kJ mol$^{-1}$), 59 (4.9 kJ mol$^{-1}$), 15 (7.2 kJ mol$^{-1}$), and 12 (8.7 kJ mol$^{-1}$) are only slightly higher and close to the DFT error. The energetic difference of the polymorphs remains very small (see Table 9), so the identification of the most stable polymorph is difficult at the DFT level.

It is therefore interesting to investigate if the order of stability changes with increasing temperature, Figure 4 shows the temperature dependence of the free enthalpy of the polymorphs. For Nb$_2$O$_5$, H-Nb$_2$O$_5$ (SG 3) is the most stable polymorph in the investigated temperature range. This is the only experimental structure that was prepared at room temperature.$^{[66]}$ So this is a clear indication that the most stable structure was correctly determined. For Ta$_2$O$_5$, H-Nb$_2$O$_5$ (SG 3) is also the most stable polymorph in the investigated temperature range. This is interesting because this structure has not yet been synthesized. It is still important to mention that the TT-Ta$_2$O$_5$ structure$^{[186]}$ was reported to be a low-temperature phase but was not studied here because of partial occupations. So it has to be taken into account that this structure might be more stable than the hypothetical H-Nb$_2$O$_5$ structure. The hypothetical polymorphs with SG 19, 62, 72, and 53 are significantly less stable than the others over the entire temperature range, so they are not shown in the plot. In addition, the change in free enthalpy with temperature is very different for some of the polymorphs. The polymorph with SG 15 is energetically similar to the stable polymorphs with space groups 3, 12, 12, 2, and 59 at room temperature. As $T$ increases, the SG 15 polymorph becomes increasingly unstable and is

![Table 8. Thermodynamic corrections Δ$^{\text{therm}}$ at 298 K in kJ mol$^{-1}$ for M$_2$O$_5$ polymorphs (M = Nb, Ta) obtained with PBE-D3.](image)
clearly set apart from the other stable polymorphs. This occurs for both Nb$_2$O$_5$ and Ta$_2$O$_5$.

4. Conclusion

We calculated the relative stability of selected Nb$_2$O$_5$ and Ta$_2$O$_5$ polymorphs at the GGA and hybrid DFT level. The most accurate functional for the calculation of Nb$_2$O$_5$ atomization energies, RSHXLDA, predicts the following order of stability at room temperature. For Nb$_2$O$_5$: H-Nb$_2$O$_5$ < N-Nb$_2$O$_5$ < R-Nb$_2$O$_5$ < V$_2$O$_5$ < B-Nb$_2$O$_5$ < M-Nb$_2$O$_5$ < F-Nb$_2$O$_5$ < γ-V$_2$O$_5$ < As$_2$O$_5$ < β-Ta$_2$O$_5$; for Ta$_2$O$_5$: H-Nb$_2$O$_5$ < R-Nb$_2$O$_5$ < V$_2$O$_5$ < B-Nb$_2$O$_5$ < M-Nb$_2$O$_5$ < β-Ta$_2$O$_5$ < γ-V$_2$O$_5$ < As$_2$O$_5$. The small energy differences between the first 5 to 6 polymorphs in this order are in line with the experimentally reported dependence of the resulting Nb$_2$O$_5$ and Ta$_2$O$_5$ phases from the synthesis conditions. From the temperature-dependent ΔG curves, we conclude that several phase transitions are possible at elevated temperatures.

For Nb our calculations confirm H-Nb$_2$O$_5$ as the most stable structure as found in the experiment. A quite interesting result is the high stability of the V$_2$O$_5$ structure for Ta$_2$O$_5$ and Nb$_2$O$_5$ at low temperatures, which was unanimously confirmed by all
functions. Even though this polymorph has not yet been produced experimentally, as far as we know, this appears possible. Furthermore, the polymorphs H-Nb$_{2}$O$_{5}$, R-Nb$_{2}$O$_{5}$, B-Nb$_{2}$O$_{5}$, and N-Nb$_{2}$O$_{5}$ have only been synthesized for Nb$_{2}$O$_{5}$ so far, although our calculations consistently predict their existence at room temperature for Ta$_{2}$O$_{5}$. The experimentally reported TT-Ta$_{2}$O$_{5$ low-temperature phase could not be studied here due to fractional occupation numbers.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

Research data are not shared.

**Keywords**

density functional theory, Nb$_{2}$O$_{5}$, polymorphs, Ta$_{2}$O$_{5}$, thermodynamic properties

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