# **Supporting Information**

## Accurate Mechanical and Electronic Properties of Spinel Nitrides

# from Density-Functional Theory

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### **Table of contents**

Figure S1. Convergence of crystal properties. Calculated energy vs. real space mesh cutoff parame γ-spinel nitrides	ter for 2
Figure S2. Mechanical properties. Calculated stress vs. strain for γ-spinel nitrides	3
Figure S3. Mechanical properties. Calculated pressure vs. volume for γ-spinel nitrides	4
Table S1. Calculated average bond lengths in γ-spinel nitrides	5
Table S2. Optimal anion cutoff radius for γ-spinel nitrides	5
Table S3. Enthalpies of formation of γ-spinel nitrides	5
Computational details of shDFT-1/2 bandgap calculations	5
Table S4. DFT (PBE/PP-NAO) Group 14 γ-spinel nitrides properties	6
Figure S4. Parameterization of DFT-1/2 and shDFT-1/2 calculations for $\gamma$ -Ge <sub>3</sub> N <sub>4</sub> .	7
Table S5. Summary of search conditions, maximum bandgap and optimal radii for shDFT-1/2	
calculations	8
References	8



Figure S1. Convergence of crystal properties. Calculated energy vs. real space mesh cutoff parameter for for (a)  $\gamma$ -Si<sub>3</sub>N<sub>4</sub>, (b)  $\gamma$ -Ge<sub>3</sub>N<sub>4</sub>, (c)  $\gamma$ -Sn<sub>3</sub>N<sub>4</sub>. The total energy of the system at 100 Ry cutoff serves as reference. For DFT calculations of periodic systems involving inverse space sampling, determining a real space mesh energy cutoff is a methodical approach to select the inverse space sampling grid (k-point grid). As the real space mesh energy cutoff energy increases, the number of k points will also increase. The mesh cutoff value was determined by a series of calculations with increasing cutoff value from 100 Ry to 350 Ry and comparing the resulting total system energy.



Figure S2. Mechanical properties. Calculated stress vs. strain for (a)  $\gamma$ -Si<sub>3</sub>N<sub>4</sub>, (b)  $\gamma$ -Ge<sub>3</sub>N<sub>4</sub>, (c)  $\gamma$ -Sn<sub>3</sub>N<sub>4</sub>, (d)  $\gamma$ -Ti<sub>3</sub>N<sub>4</sub> and (e)  $\gamma$ -Zr<sub>3</sub>N<sub>4</sub>. The data were obtained by applying a hydrostatic pressure to the system. All calculations were performed with DFT implementing full-potential numerical atomic orbital basis sets (FP-NAO).



Figure S3. Mechanical properties. Calculated pressure vs. volume for (a)  $\gamma$ -Si<sub>3</sub>N<sub>4</sub>, (b)  $\gamma$ -Ge<sub>3</sub>N<sub>4</sub>, (c)  $\gamma$ -Sn<sub>3</sub>N<sub>4</sub>, (d)  $\gamma$ -Ti<sub>3</sub>N<sub>4</sub> and (e)  $\gamma$ -Zr<sub>3</sub>N<sub>4</sub>. The data were obtained by applying a hydrostatic pressure to the full system. All calculations were performed with DFT implementing full-potential numerical atomic orbital basis sets (FP-NAO).

M3N4	FP-NAO r <sub>M-N</sub> ª (Å)	FP-LAPW r <sub>M-N<sup>b</sup></sub> (Å)
γ-Si₃N₄	1.803	1.852
γ-Ge₃N₄	1.989	1.987
γ-Sn₃N₄	2.201	2.199
γ-Ti <sub>3</sub> N <sub>4</sub>	1.957	2.023
γ-Zr₃N₄	2.052	2.083

Table S1. Calculated average bond lengths in y-spinel nitrides.

a. Calculated average M-N bond length, where M=Si, Ge, Sn, Ti and Zr with DFT (PBE/FP-NAO)

b. Calculated average M-N bond length, where M=Si, Ge, Sn, Ti and Zr with DFT (PBE/FP-LAPW)

Table S2.	Optimal anion	cutoff radius	for <b>γ</b> -spinel	nitrides
(	determined vari	ationally usin	g DFT-1/2	

M3N4	r <sub>cut</sub> (Å) <sup>a</sup>
γ-Si₃N₄	1.46
γ-Ge₃N₄	1.46
γ-Sn₃N₄	1.46
γ-Ti <sub>3</sub> N4	1.32
γ-Zr₃N₄	1.32

a. The calculated bandgap for all nitrides increases monotonically with  $\Gamma_{cut}$  up to a maximum value before it starts decreasing, as shown in Figure S4a for  $\gamma$ -Ge<sub>3</sub>N<sub>4</sub>

$M_3N_4$	Total enthalpy [eV/f.u]ª	Relative enthalpy of formation wrt binary 1:1 nitride [eV/f.u]
γ-Si₃N₄	-1513.4	b
γ-Ge₃N₄	-1465.4	b
γ-Sn₃N₄	-1465.1	b
γ-Ti₃N₄	-1474.4	0.96 <sup>c</sup>
γ-Zr₃N₄	-1452.5	0.35 <sup>d</sup>

Table S3. Enthalpies of formation of γ-spinel nitrides

a. The total enthalpy is the electronic energy augmented by the pressure\*volume term

b. 1:1 binary Group IV nitrides are not stable

c. Evaluated as the enthalpy difference between  $\gamma$ -Ti<sub>3</sub>N<sub>4</sub> and 3 c-TiN + 1/2N<sub>2</sub> (TiN: 398.5 eV/f.u; N<sub>2</sub>: -600.0 eV/f.u).

d. Evaluated as the enthalpy difference between  $\gamma$ -Zr<sub>3</sub>N<sub>4</sub> and 3 c-ZrN + 1/2N<sub>2</sub> (ZrN: 390.9 eV/f.u; N<sub>2</sub>: -600.0 eV/f.u).

### Computational details of shDFT-1/2 bandgap calculations

The current implementation of  $shDFT-1/2^1$  is only available for restricted density functional theory (DFT) with pseudo-potentials (PPs), where the SIC atomic self-energy potential can easily be added as an extra term to the pseudo-potential without requiring modification of the source code. All shDFT-1/2 calculation were thus completed using DFT with the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) exchange-correlation functional and the Troullier-Martins pseudo-potential-numerical atomic orbital (NAO) basis set implemented in

the SIESTA simulation package.<sup>2-4</sup> We note that the full-potential (FP) basis set approach was adopted for this work in the first place because PP methods introduce an extra possible source of uncertainty in calculated results,<sup>5</sup> and the cost of both computational approaches is similar for nitrides. As discussed below, both approaches using distinct software packages yield very similar DFT geometrical and bandgap results for Group 14 nitrides, which validates the use of PP-NAO to estimate bandgaps corrected for self-interaction with shDFT-1/2. Structure optimization was assumed complete with a  $6 \times 6 \times 6$  k-point grid and atomic forces falling all below a 0.008 eV/Å value.

	Lattice parameters (Å)	Bulk modulus (GPa)	Average bond length (Å)	Bandgap [eV]
γ-Si₃N₄	a=b=c=7.83	260.3	1.799	4.07
γ-Ge₃N₄	a=b=c=8.31	232.5	1.942	1.87
γ-Sn <sub>3</sub> N₄	a=b=c=8.90	188.1	2.165	0.65

Table S4. DFT (PBE/PP-NAO) Group 14 y-spinel nitrides properties

The standard PP provided as part of the SIESTA package tends to overestimate bond lengths while significantly underestimating the bulk moduli,<sup>6</sup> so a new PP set optimized to reproduce bulk electronic and structural properties for Group 14 elements was adopted.<sup>5</sup> The resulting lattice parameters, bulk modulus and average bond length for Group 14 nitrides calculated with PP-NAO agree with FP-NAO and FP-LAPW results (using the same k-point grid) within 6.0% and 5.8% respectively. For  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> and  $\gamma$ -Sn<sub>3</sub>N<sub>4</sub>, the calculated bandgap using PP-NAO with the new PP set is 20% larger than its FP-LAPW counterparts, 4.07 eV vs 3.23 eV and 0.58 eV vs 0.65 eV, respectively, while  $\gamma$ -Ge<sub>3</sub>N<sub>4</sub> stands out with a PP-NAO calculated bandgap 30% larger than its FP-LAPW counterpart, 1.87 eV vs 1.44 eV. Band structure calculation are very sensitive to geometry differences, and earlier simulation work showed that a 3% deviation in geometrical features can cause a bandgap change by 25%.<sup>7</sup> The larger bandgap difference between FP-LAPW and PP-NAO for  $\gamma$ -Ge<sub>3</sub>N<sub>4</sub> may be due to the smaller lattice parameters and average bond length of the PP-NAO optimized structure for Ge<sub>3</sub>N<sub>4</sub>. For the latter, the PP-NAO average bond length (1.942 Å) is closer to the experimental result (1.938 Å) than its FP-LAPW counterpart (1.987 Å).<sup>8</sup> Upon adjusting the FP crystal structure with experimental bond lengths, the FP-LAPW bandgap becomes 2.01 eV, quite comparable to the PP-NAO value of 1.87 eV (within 10% - and certainly much less than the magnitude of the self-interaction correction). Therefore, give or take subtle differences in crystal structures, both PP-NAO and FP-LAPW yield very similar uncorrected bandgap values, which validates the use of either approach to estimate bandgaps with shDFT-1/2. We note that Ge<sub>3</sub>N<sub>4</sub> is the Group 14 nitride for which FP-LAPW geometrical parameters deviate the most significantly from experimental data but, if adjusting the crystal structure with experimental bond lengths improves the DFT-1/2 bandgap (3.88 eV), the latter now overestimates its experimental counterpart by 0.38 eV, which indicates that obtaining accurate bandgaps for γ-Ge<sub>3</sub>N<sub>4</sub> likely does not rely on the crystal structure as much as on the approach used to refine the bandgap calculation, such as the proposed shDFT-1/2 of reference 1.



Figure S4. Parameterization of DFT-1/2 and shDFT-1/2 calculations for  $\gamma$ -Ge<sub>3</sub>N<sub>4</sub>: calculated bandgaps vs. nitrogen cutoff parameters (a) r<sub>cut</sub> for DFT-1/2, and b) outer (r<sub>out</sub>) and inner (r<sub>in</sub>) shell radii for shDFT-1/2, The vertical lines represent the r<sub>in</sub>=0.53 Å used for the outer radius scan and the r<sub>out</sub>=1.32 Å used for the inner shell radius scan.

For shDFT-1/2 calculations of the  $\gamma$ -Ge<sub>3</sub>N<sub>4</sub> bandgap, we performed 3 optimization sets of the r<sub>in</sub> and r<sub>out</sub> parameters in a stepwise fashion. For the first set, we fixed r<sub>in</sub> to 0.05 Å and scanned r<sub>out</sub> from 0.05 to 1.27 Å (with 0.0529 Å increments). The maximum bandgap is found to be 2.04 eV at a r<sub>out</sub> value of 1.22 Å. The minimum inner radius was chosen to afford comparison between shDFT-1/2 and DFT-1/2 (for which an optimal r<sub>cut</sub> of 1.46 Å was obtained, as shown in Figure S4a). For the second set, we increased r<sub>in</sub> to 0.53 Å and calculated the bandgap by scanning r<sub>out</sub> from 1.05 to 2.65 Å (with 0.0529 Å increments). The maximum bandgap is found to be 3.34 eV at a r<sub>out</sub> value of 1.32 Å. For the third set, we thus fixed r<sub>out</sub> at 1.32 Å and scanned r<sub>in</sub> from 0.25 to 1.2 Å (with 0.0529 Å increments). The calculated bandgap vs cutoff radius for the second optimization set (r<sub>out</sub>) and the third (r<sub>in</sub>) are shown in Figure S4b. The maximum bandgap is found to be 3.57 eV at a r<sub>in</sub> value of 0.31 Å.

Table S5. Summary of search conditions, maximum bandgap and optimal radii for shDFT-1/2 calculations<sup>a</sup>

Radius Search	r <sub>in</sub> [Å]	r <sub>out</sub> [Å]	Maximum bandgap [eV]	Optimal radius [Å]
1	0.05	0.05—1.27	2.04	r <sub>out</sub> =1.22
2	0.53	1.05-2.65	3.34	r <sub>out</sub> =1.32
3	0.25—1.22	1.32	3.57	r <sub>in</sub> =0.31

a. Calculated with DFT(PBE/Troullier Martins PP-NAO) as implemented in the SIESTA package<sup>1-3</sup>

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