Electronic Supporting Information for:

First-principle and experimental characterization of the electronic properties of CaGaSiN₃ and CaAlSiN₃: The Impact of chemical disorder

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Supporting calculations on CaGaSiN₃:

Formulas used for the calculation of mechanical properties

Stability criteria for orthorhombic crystals:

\[ C_{11}C_{22} > C_{12}^2, C_{22}C_{33} > C_{23}^2, C_{11}C_{33} > C_{13}^2 \]

\[ C_{ii} > 0 \ (i=1; 4-6) \]

and \[ C_{11}C_{22}C_{33} + 2C_{12}C_{23}C_{13} - C_{11}C_{23}^2 - C_{22}C_{33} - C_{11}C_{33} > 0 \]

Bulk and shear modulus according to Voigt (Bᵥ, Gᵥ) and Reuss (Bᵣ, Gᵣ):

\[ Bᵥ = \frac{C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{23} + C_{31})}{9} \]

\[ Bᵣ = \frac{1}{S_{11} + S_{22} + S_{33} + 2(S_{12} + S_{23} + S_{31})} \]

\[ Gᵥ = \frac{(C_{11} + C_{22} + C_{33}) - (C_{12} + C_{23} + C_{31})}{15} \]

\[ + \frac{3(C_{44} + C_{55} + C_{66})}{15} \]

\[ Gᵣ = \frac{4(S_{11} + S_{22} + S_{33} - S_{12} - S_{23} - S_{31} + 3(S_{44} + S_{55} + S_{66}))}{15} \]

* Subscripts \( C_{nm} \) obtained from \( C_{ijkl} \) according to the Voigt notation
  \( xx \rightarrow 1, yy \rightarrow 2, zz \rightarrow 3, yz \rightarrow 4, zx \rightarrow 5, xy \rightarrow 6 \).

** Compliance constants \( S_{nm} \) are obtained from the inversion of elastic constant matrix \( S=C^{-1} \).

Voigt-Reuss-Hill approximation:

\[ B_{VRH} = \frac{Bᵥ + Bᵣ}{2} \]
\[ G_{VRH} = \frac{Gᵥ + Gᵣ}{2} \]

Young’s modulus (\( Y \)) and the Poisson ratio (\( v \)) are obtained by the relations:

\[ Y_{VRH} = \frac{9BG}{3B + G} \]
\[ v = \frac{3B - 2G}{6B + 2G} \]
Debye temperature:

\[ \theta_D = \frac{\hbar}{k_B} \left[ 6 \pi^2 V^{1/2} N \right]^{1/3} \]

with \( \Delta = \frac{\hbar}{\sqrt{2}} \left[ 3 \left( \frac{1}{2} \left( \frac{3}{2} \right) \frac{1}{2} \right)^{3/2} + \left( \frac{1}{2} \left( \frac{3}{2} \right) \frac{1}{2} \right) \right]^{-1/3} \)

where, \( k_B \) and \( \hbar \) are the Boltzmann and Plank’s constant respectively, \( \nu \) is the Poisson ratio, \( V [m^3] \) is the volume of the unit cell, \( N \) is the number of atoms in the cell. \( B \) [Pa] represents the bulk modulus and \( M \) [a.u.] the molar mass of the unit cell.

Band structure/DOS calculations for the unrelaxed experimental structure models:

Fig. S 1 Bloch spectral function (a-c) calculated along high symmetry directions in the first Brillouin zone within the MUNICH SPR-KKR program package for the three CaGaSiN3 ordering models based on the unrelaxed experimental crystal parameters where (a-c) represent the Si/Ga-ordering variants A, B and C, respectively.

Fig. S 2 Colored: Interpolated total density of states near the valence and conduction band edge for the unrelaxed experimental CaGaSiN3 ordering models as calculated from SPRKKR CPA approach (a-c) including the Ga/Si disorder. Black: Average DOS of the three ordering models.
The respective parts of the dielectric function $\varepsilon$, extinction coefficient $\kappa$, refractive index $n$, reflectivity and energy loss spectra from the VASP calculations are depicted in Fig. S 5 (a-d). The static refractive index is found to be 2.29 and the overall refractive index reaches its maximum at 4.6 eV with a value of 3.03. The energy loss function is defined as

$$\text{Im} \frac{1}{\varepsilon} = \frac{\varepsilon_2^2}{\varepsilon_1^2 + \varepsilon_2^2}$$

taking large values for $\varepsilon_1 \to 0$ and $\varepsilon_2 < 1$. The peaks of the plasma frequency can, therefore, be identified as the maxima of the average energy loss function, with values of 19.5 and 30.25 eV, where $\varepsilon_1$ and $\varepsilon_2$ are sufficiently close to zero.

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Fig. S 3 Bloch spectral functions along high symmetry directions in the first Brillouin zone for the fully disordered structure of CaGaSiN$_3$ as based on the experimental crystal structure refinement, calculated within the KKR approach based on the CPA.

Fig. S 4 Partial density of states of the VASP relaxed ordering models of CaGaSiN$_3$. Left to Right: Ordering Models A, B and C.
Supporting calculations on CaAlSiN₃:

Total energies (eV/formula unit) for the relaxed ordering structures of CaGaSiN₃ and CaAlSiN₃

Table S 1 Total energy after structural relaxation for both CaAlSiN₃ and CaGaSiN₃ in eV / formula unit as calculated by VASP

<table>
<thead>
<tr>
<th>Ordering variant</th>
<th>A</th>
<th>B</th>
<th>C</th>
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</thead>
<tbody>
<tr>
<td>Total energy</td>
<td>−43.982</td>
<td>−43.980</td>
<td>−43.803</td>
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<tr>
<td>(eV/f.u. of CaAlSiN₃)</td>
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<td></td>
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<tr>
<td>Total energy</td>
<td>−41.132</td>
<td>−41.140</td>
<td>−40.885</td>
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<tr>
<td>(eV/f.u. of CaGaSiN₃)</td>
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Fig. S 5: a) Calculated extinction coefficient k and refractive index n, b) imaginary (ε₂) and real (ε₁) part of the dielectric function, c) energy loss spectrum and d) reflectivity, for CaGaSiN₃ as an average of the ordering models A, B and C calculated from VASP. The differently colored inset (a,c,d) depicts the different contributions to the shape of the averaged spectrum.
Fig. S 6 Density of states of CaAlSiN₃ for the relaxed CaGaSiN₃ analogue (Al/Si) ordering variants A, B and C as calculated by VASP.

Fig. S 7 Bloch spectral function (a-c) calculated along high symmetry directions in the first Brillouin zone within the MUNICH SPR-KKR program package for the three relaxed CaAlSiN₃ ordering models, where (a-c) represent the Si/Al ordering variants A, B and C, respectively. Blue lines indicate the relative conduction band minimum for the calculations of the respective CaGaSiN₃ models.

Fig. S 8 Unrelaxed calculated density of states of CaAlSiN₃ for the CaGaSiN₃ analogue (Al/Si) ordering variants A, B and C calculated with KKR. Black: Average density of states of the combined models.
Fig. S9 Calculated absorption (a) and intersecting slopes, corresponding to the optical band gap estimate, of the first steep ascend in absorption (b) for CaAlSiN₃ for the CaGaSiN₃ analogous (Al/Si) ordering variants A, B and C.