Electronic Supporting Information for:

First-principle and experimental characterization of the electronic properties of $CaGaSiN_3$ and $CaAlSiN_3$: The Impact of chemical disorder

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Supporting calculations on $CaGaSiN_3$:

Formulas used for the calculation of mechanical properties

Stability criteria for orthorhombic crystals:

$$C_{11}C_{22} > C_{12}^2, C_{22}C_{33} > C_{23}^2, C_{11}C_{33} > C_{13}^2$$

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

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

Bulk and shear modulus according to Voigt (B_v, G_v) and Reuss (B_R, G_R):

$$B_V = \frac{C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{23} + C_{31})}{9}$$

$$B_R = \frac{1}{S_{11} + S_{22} + S_{33} + 2(S_{12} + S_{23} + S_{31})}$$

$$G_V = \frac{(C_{11} + C_{22} + C_{33}) - (C_{12} + C_{23} + C_{31})}{15} + \frac{3(C_{44} + C_{55} + C_{66})}{15}$$

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

* 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:

$$B_{VRH} = \frac{B_V + B_R}{2} \qquad G_{VRH} = \frac{G_V + G_R}{2}$$

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

$$Y_{VRH} = \frac{9BG}{3B + G} \qquad v = \frac{3B - 2G}{6B + 2G}$$

Debye temperature:

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

$$\text{with } \Delta = \sqrt{\frac{B}{M}}\left[3\left[2\left(\frac{2}{3}\frac{1+\nu}{1-2\nu}\right)^{3/2} + \left(\frac{1}{3}\frac{1+\nu}{1-\nu}\right)^{3/2}\right]^{-1}\right]^{1/3}$$

where, k_B and $\hbar$ are the Boltzmann and Plank's constant respectively, ν 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:

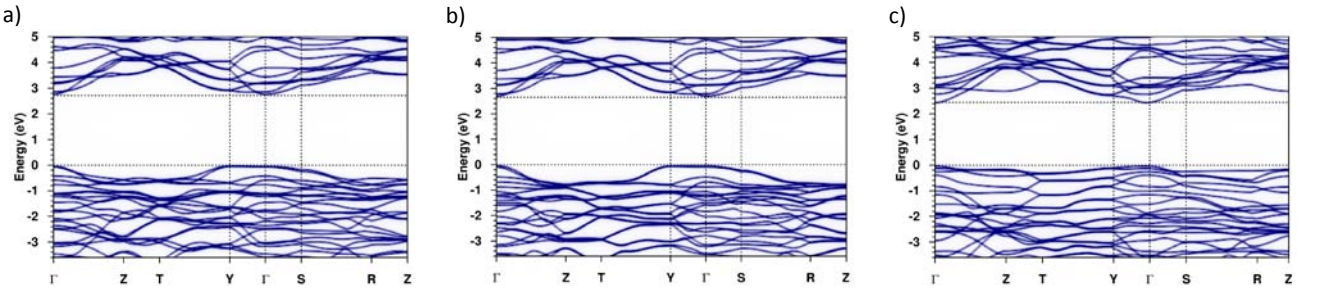


Fig. S 1 Bloch spectral function (a-c) calculated along high symmetry directions in the first Brillouin zone within the MUNICH SPR-KKR program package for the three $CaGaSiN_3$ ordering models based on the unrelaxed experimental crystal parameters where (a-c) represent the Si/Ga-ordering variants A, B and C, respectively.

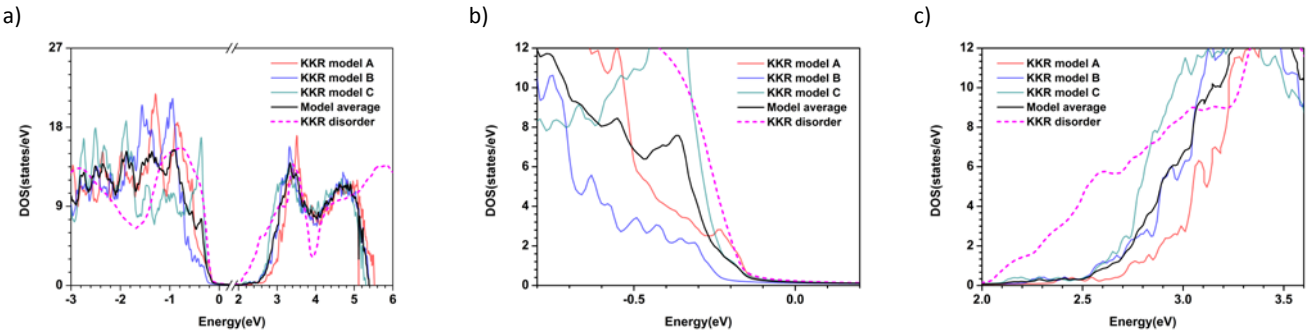


Fig. S 2 Colored: Interpolated total density of states near the valence and conduction band edge for the unrelaxed experimental $CaGaSiN_3$ ordering models as calculated from SPRKKR-CPA approach (a-c) including the Ga/Si disorder. Black: Average DOS of the three ordering models.

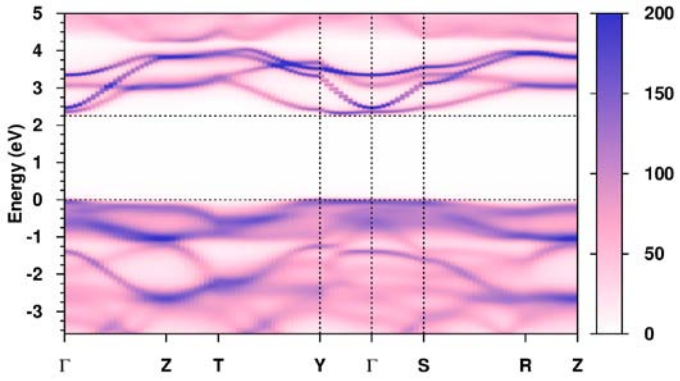


Fig. S 3 Bloch spectral functions along high symmetry directions in the first Brillouin zone for the fully disordered structure of $CaGaSiN_3$ as based on the experimental crystal structure refinement, calculated within the KKR approach based on the CPA.

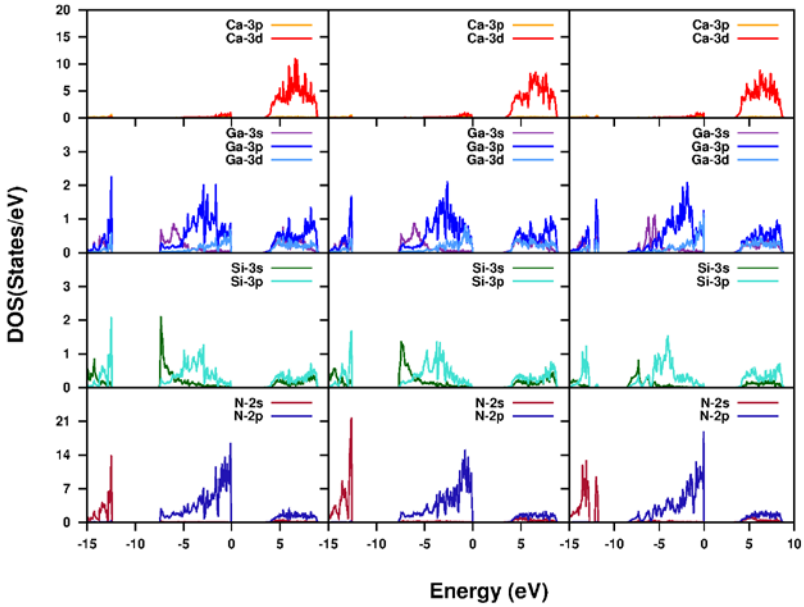


Fig. S 4 Partial density of states of the VASP relaxed ordering models of $CaGaSiN_3$. Left to Right: Ordering Models A, B and C.

The respective parts of the dielectric function ε, extinction coefficient *k*, 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

$$\mathrm{Im}\frac{1}{\varepsilon} = \frac{\epsilon_1^2}{\epsilon_1^2 + \epsilon_2^2 +}$$

taking large values for $\varepsilon_1 \rightarrow 0$ and $\varepsilon_2 < 1$.[49] 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 ε_1 and ε_2 are sufficiently close to zero.

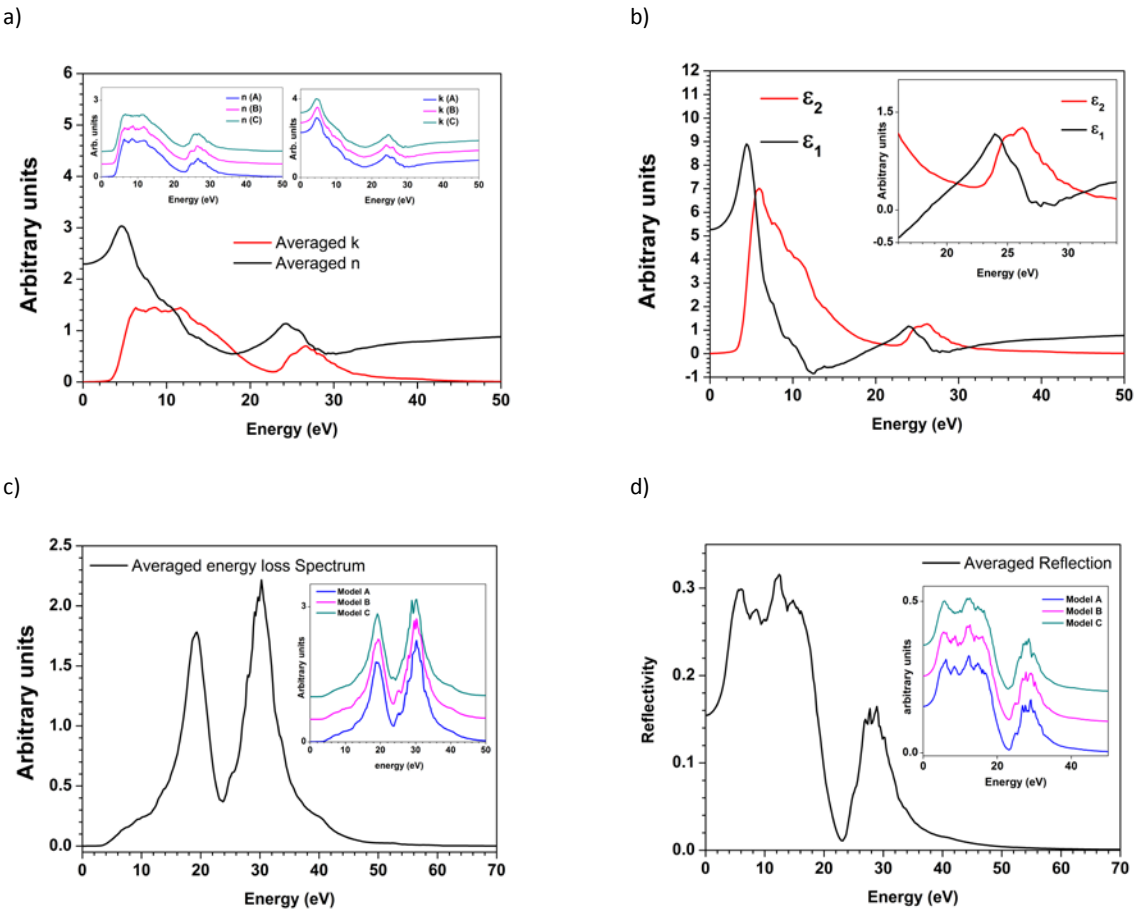


Fig. S 5 a) Calculated extinction coefficient k and refractive index *n*, b) imaginary (ε_2) and real (ε_1) part of the dielectric function, c) energy loss spectrum and d) reflectivity, for $CaGaSiN_3$ as an average of the ordering models A, B and C calculated from VASP. The differently colored inset (a,c,d) depicts the different contributions to the shape of the averaged spectrum.

Supporting calculations on $CaAlSiN_3$:

Total energies (eV/formula unit) for the relaxed ordering structures of $CaGaSiN_3$ and $CaAlSiN_3$

Table S 1 Total energy after structural relaxation for both $CaAlSiN_3$ and $CaGaSiN_3$ in eV / formula unit as calculated by VASP

Ordering variant	A	B	C
Total energy (eV/f.u. of $CaAlSiN_3$)	−43.982	−43.980	−43.803
Total energy (eV/f.u. of $CaGaSiN_3$)	−41.132	−41.140	−40.885

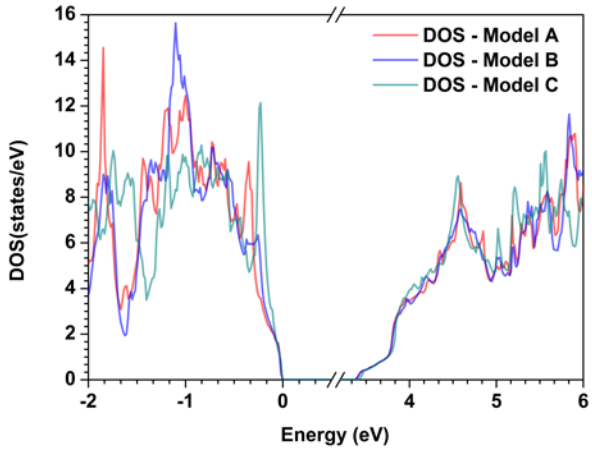


Fig. S 6 Density of states of $CaAlSiN_3$ for the relaxed $CaGaSiN_3$ analogue (Al/Si) ordering variants A, B and C as calculated by VASP.

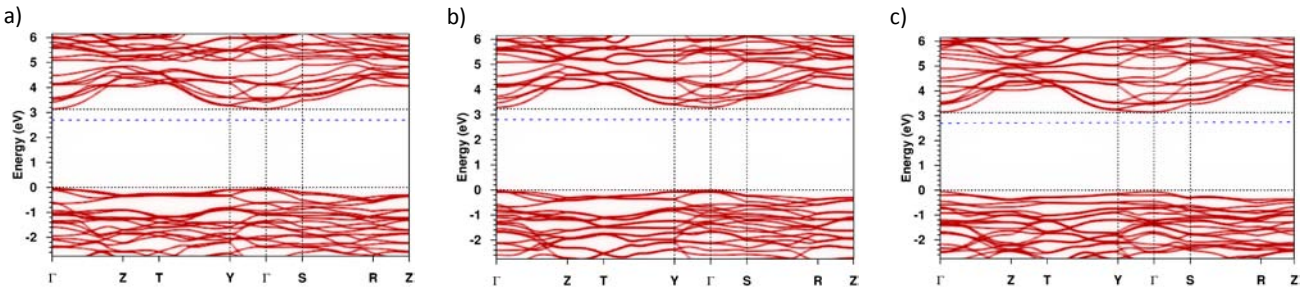


Fig. S 7 Bloch spectral function (a-c) calculated along high symmetry directions in the first Brillouin zone within the MUNICH SPR-KKR program package for the three relaxed $CaAlSiN_3$ ordering models, where (a-c) represent the Si/Al-ordering variants A, B and C, respectively. Blue lines indicate the relative conduction band minimum for the calculations of the respective $CaGaSiN_3$ models.

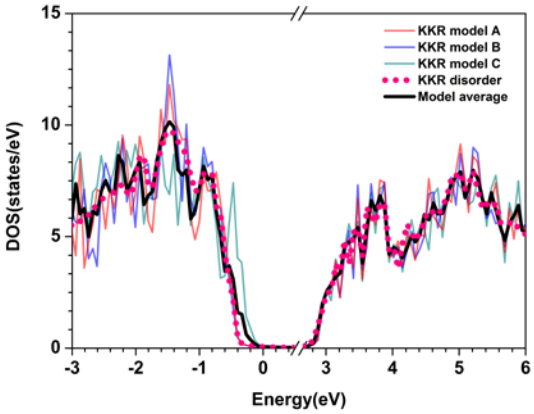
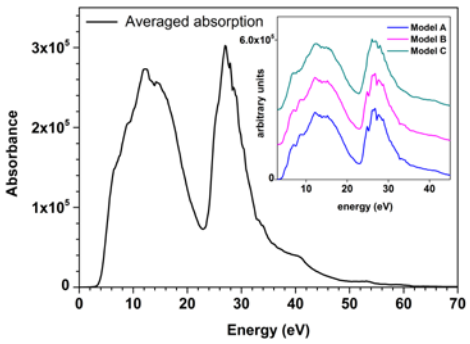


Fig. S 8 Unrelaxed calculated density of states of $CaAlSiN_3$ for the $CaGaSiN_3$ analogue (Al/Si) ordering variants A, B and C calculated with KKR. Black: Average density of states of the combined models.

a)



b)

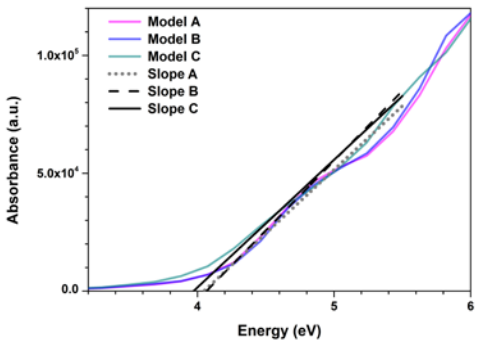


Fig. S 9 Calculated absorption (a) and intersecting slopes, corresponding to the optical band gap estimate, of the first steep ascend in absorption (b) for $CaAlSiN_3$ for the $CaGaSiN_3$ analogous (Al/Si) ordering variants A, B and C.