Crystal Structure Prediction of the Novel Cr$_2$SiN$_4$ Compound via Global Optimization, Data Mining, and the PCAE Method

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Abstract: A number of studies have indicated that the implementation of Si in CrN can significantly improve its performance as a protective coating. As has been shown, the Cr-Si-N coating is comprised of two phases, where nanocrystalline CrN is embedded in a Si$_x$N$_y$ amorphous matrix. However, these earlier experimental studies reported only Cr-Si-N in thin films. Here, we present the first investigation of possible bulk Cr-Si-N phases of composition Cr$_2$SiN$_4$. To identify the possible modifications, we performed global explorations of the energy landscape combined with data mining and the Primitive Cell approach for Atom Exchange (PCAE) method. After ab initio structural refinement, several promising low energy structure candidates were confirmed on both the GGA-PBE and the LDA-PZ levels of calculation. Global optimization yielded six energetically favorable structures and five modifications possible to be observed in extreme conditions. Data mining based searches produced nine candidates selected as the most relevant ones, with one of them representing the global minimum in the Cr$_2$SiN$_4$. Additionally, employing the Primitive Cell approach for Atom Exchange (PCAE) method, we found three more promising candidates in this system, two of which are monoclinic structures, which is in good agreement with results from the closely related Si$_x$N$_y$ system, where some novel monoclinic phases have been predicted in the past.

Keywords: Cr-Si-N compounds; structure prediction; global optimization; computational studies

1. Introduction

Tools and equipment used in metal and wood machining frequently experience severe damage during their usage, which leads to the urgent need for protective coatings to extend the lifetime of the machinery [1,2]. This particularly applies to marine equipment, where certain parts have to operate in challenging marine environments. Additionally, past nuclear accidents have led to an increase in research regarding nuclear materials and the development of coatings that can be used under such extreme conditions.

Transition metal nitrides are widely used as hard coatings, and, among them, CrN is one with many desired properties—high hardness, toughness, and corrosion resistance, good oxidation resistance, good adhesion strength, and excellent wear resistance [3–10]. However, due to its high friction coefficient, it does not perform well in some extreme conditions [2]. Delamination is considered to be critical to the wear failure of CrN coatings in seawater where microcracks play an important role in the evolution of delamination [11].

Even though CrN is a well-established and very stable coating in wide use, the addition of alloying elements, such as Si, has been actively investigated to further improve its properties as a hard coating material [5,6,12–18]. Compared to CrN thin films, Cr-Si-N
coatings exhibit lower friction coefficients and wear rates due to their low surface roughness. In general, their tribological and mechanical characteristics show significant improvement under different environments and conditions (dry, humid, or aqueous; dynamic or static; ambient or high temperature; etc.) compared to CrN [3,19–27]. Due to the finer crystal structure, the addition of Si can also lead to the elimination of large flake pits, which were previously found on the wear trace of CrN coatings [26]. This increase in silicon content also leads to a change in the crystal structure of the coating, and the particle shape changes from triangular to circular with a distribution that tends to be uniform, while the density of the coating increases [28].

Four kinds of Cr-Si-N coatings are known that are considered to be harder than the CrN coating [28]. Nanocomposite Cr-Si-N thin films (usually in the form of nanoclusters or nanoclusters of CrN embedded in an amorphous Si3N4 matrix) also have higher hardness and oxidation resistance compared with CrN thin films [5,6,15–18,29]—their hardness can be increased by up to ~9 GPa [2,3,30,31], while their oxidation resistance is significantly improved at temperatures well above the oxidation limit of ~600–700°C of CrN [6,32,33]. Epitaxially grown Cr-Si-N thin films that appear to constitute solid solutions of Si in CrN exhibit even higher hardness than less homogeneous nanocomposite Cr-Si-N thin films—a maximum hardness value of 51 GPa was obtained for 10 mol% Si in Cr-Si-N [34]. The increased hardness of Cr-Si-N is obtained due to the formation of a fine nanocomposite structure and the refinement of CrN crystallites [18,24] as well as to the dissolution of Si in CrN [34]. The decrease of friction is attributed to the formation of SiOx or Si(OH) layers in a humid environment, which plays a role as a self-lubricant, and by a smoother surface due to the Cr-Si-N amorphous phase [18,27]. Improved oxidation resistance can be explained by the formation of amorphous silicon oxide, which retards the diffusion of O as well as of Cr, Si, and N [29].

As its Si content increases, the structure of the Cr-Si-N coating changes from a crystalline to an amorphous state [35,36], and while the corrosion resistance constantly improves and the friction coefficient decreases, wear-resistance and hardness also improve until a certain Si content limit is reached beyond which the coatings start to deteriorate [25,34,37]. The electronic properties of Cr-Si-N thin films also change significantly depending on their chemical composition. While fcc-CrN exhibits metallic-like behavior, an increase of N or Si content leads to a more non-metallic character of the material [37].

Furthermore, investigations of the friction and wear properties of CrSi based coatings led to the conclusion that Cr-Si-N coatings showed better properties in comparison to the CrSi coatings [38]. Increasing the silicon content in these coatings led to the best friction and wear performance, which, in the case of an ATF system in a water environment, can reduce the wear volume by three orders of magnitude [38]. In summary, the Cr-Si-N coatings exhibit superior tribological performance due to their excellent toughness, high hardness, preferable adhesion, and good corrosion resistance [2], which all lead to the possibility of wide applications.

Gaining deeper insight into the structure–property relationship of the Cr-Si-N coating on the atomic level would greatly support the optimization of such coatings. As a first step, we focus on the possible existence of crystalline phases in the Cr/Si/N system. Considering the large hardness of Si3N4, we chose the analogous composition CrSiN4, where we would expect similarly high hardness as for Si3N4 itself. Thus, in this study, we identify feasible structure candidates of the composition CrSiN4 using global optimization techniques, data-mining, and the Primitive Cell approach for Atom Exchange (PCAE) method, followed by careful re-optimizations of the candidates on the ab initio level.

2. Materials and Methods

To perform structure prediction and gain insight into the structural stability of the possible phases existing in the Cr:SiN4 system, a combination of global optimization (GO),
data mining (DM), and the PCAE method has been used [39,40]. First, we performed global optimizations on the energy landscape of CrSiN using simulated annealing [41], within the G42+ code [42]. A fast computable robust empirical two-body potential consisting of Lennard-Jones and exponentially damped Coulomb terms was employed to perform the GO searches with a reasonable computational effort [43]. Next, we have performed DM-based searches of the ICSD database [44,45] in order to find possible structure candidates for the unknown CrSiN compound.

We used the well-known KDD (knowledge discovery in databases) process, which involves selection, preprocessing, transformation, and interpretation/evaluation (or post-processing), and has been successfully used in previous studies [46–48]. Finally, the Primitive Cell approach for Atom Exchange (PCAE) method was employed for generating alternative structure candidates in the CrSiN compound. The PCAE method is simple, fast, and computationally inexpensive compared to the supercell approach [40].

In the current study, the starting modifications were taken from the related Si3N4 chemical system by first transforming the crystallographic (conventional) cell to the primitive cell, while keeping the symmetry and multiplicity of the atom positions (for more information, c.f. ref [40]). In the next stage, we replaced the number of atoms needed to obtain a certain stoichiometry ($2 \times$ Si by $2 \times$ Cr atoms) on the symmetry-related Wyckoff positions. Subsequently, an ab initio full structure optimization without symmetry constraints was performed.

After the structure candidates have been identified using the GO, DM and PCAE methods, each structure candidate has been subjected to local optimization on the ab initio level. Density functional theory (DFT) calculations of the total energy, and local optimizations (including volume, cell parameters, and atomic positions), were performed using the CRYSTAL17 code [49,50] based on linear combinations of atomic orbitals (LCAO). For the local optimization runs, we employed analytical gradients [51,52], and equation of state (EOS) calculations using polynomial fitting [49,50].

Local optimizations were performed on the DFT level employing two different functionals: the Local Density Approximation (LDA) with the Perdew–Zunger (PZ) correlation functional [53] and the Generalized Gradient Approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional [54] for comparison. It is reasonable to choose at least two different ab initio methods, to gain better insight into the quantitative validity of the results since no compounds of the composition CrSiN4 are available for comparison with the experiment [55–57].

An all-electron basis set based on Gaussian-type orbitals was employed in the case of chromium (Cr_86-411d41G_catti_1995) [58,59], silicon (Si_86-311G**_pascale_2005) [60,61], and nitrogen (N_6-21G*_dovesi_1990) [62,63]. The symmetries of the analyzed structures were determined using the SFND [64] and RGS [65] algorithms, and duplicate structures were removed using the CMPZ algorithm [66]; these three algorithms were implemented in the KPLOT code [67]. The optimized structures of various modifications were visualized using the Vesta3 program [68].

3. Results and Discussion

3.1. Global and Local Optimization Using Empirical and Ab Initio Energy Functions

Global optimizations were performed on the energy landscapes using empirical potentials for various numbers of formula units per simulation cell and for slightly varying ionic radii, yielding a total of 5000 structure candidates. Most of these global searches resulted in low-symmetry structure candidates (triclinic and monoclinic symmetry). After detailed statistical, structural, and crystallographic analysis, the most promising ones were submitted for local optimization on ab initio level. With further local optimization on the ab initio level, we have obtained the 11 most-relevant structure candidates from global optimization (GO).
Table 1 presents the energetic ranking of these new Cr$_2$SiN$_4$ phases using the GGA-PBE functional, where the α-Cr$_2$SiN$_4$-type is the lowest in calculated total energy, and the nf5-Cr$_2$SiN$_4$-type the highest one. Moreover, we grouped the resulting GO structures into energetically favorable ones, ranging from the α- to the λ'-Cr$_2$SiN$_4$ phase, and non-favorable Cr$_2$SiN$_4$ modifications marked nf1- to nf5, which might be observed under extreme conditions. In addition, each favorable structure candidate has been subjected to a DFT-LDA optimization with similar results in the energetic ranking (Table A2).

| Modification | Total Energy (Eh) | Relative Energy (kcal/mol) |
|--------------|------------------|----------------------------|
| α-Cr$_2$SiN$_4$-type | -5193.474 | 20.708 |
| β-Cr$_2$SiN$_4$-type | -5193.438 | 43.298 |
| δ-Cr$_2$SiN$_4$-type | -5193.419 | 55.221 |
| ε-Cr$_2$SiN$_4$-type | -5193.413 | 58.986 |
| λ-Cr$_2$SiN$_4$-type | -5193.407 | 62.750 |
| λ'-Cr$_2$SiN$_4$-type | -5193.404 | 64.634 |
| nf1-Cr$_2$SiN$_4$-type | -5193.398 | 68.399 |
| nf2-Cr$_2$SiN$_4$-type | -5193.388 | 74.674 |
| nf3-Cr$_2$SiN$_4$-type | -5193.385 | 76.556 |
| nf4-Cr$_2$SiN$_4$-type | -5193.364 | 89.734 |
| nf5-Cr$_2$SiN$_4$-type | -5193.364 | 89.734 |

3.1.1. Structural Analysis of the Most Promising Modifications Found after Global Optimization (GO)

The energetically most favorable modification after global optimization is denoted as α-Cr$_2$SiN$_4$-type and appears in the orthorhombic space group $Pma2$ (no. 28) with unit cell parameters of $a = 5.54$, $b = 7.91$, and $c = 2.81$ Å on the GGA-PBE level of calculation. The α-Cr$_2$SiN$_4$ phase is visualized in Figure 1a, while full structural data of all favorable candidates are presented in Table 2 for calculations with the PBE functional, and in Table A1 for those computed with the LDA functional, respectively.

In the α-modification, chromium is six-fold coordinated by nitrogen, forming two different CrN$_6$ octahedra (with atom–atom distances of Cr(1) $2 \times 1.82$ Å-N, $1 \times 1.89$ Å-N, $1 \times 1.97$ Å-N, $2 \times 2.13$ Å-N, $2 \times 1.91$ Å-N, $2 \times 1.95$ Å-N, and $2 \times 2.04$ Å-N), while silicon is four-fold coordinated by nitrogen (with atom–atom distances of $2 \times 1.77$ Å-N and $2 \times 1.71$ Å-N) forming a tetrahedron. Moreover, the octahedra are connected by edges, while the tetrahedra are corner connected to them; additionally, the tetrahedra fall into two groups with opposite orientations.
A second energetically favorable candidate obtained from GO is denoted as $\beta$-Cr$_2$SiN$_4$-type. This triclinic structure appears in space group $P\overline{1}$ (no. 2), with cell parameters $a = 7.28$, $b = 7.79$, $c = 2.74$ Å, $\alpha = 93.66$, $\beta = 82.48$, and $\gamma = 120.64$ calculated with GGA-PBE, and is visualized in Figure 1b. In this structure, chromium has a six-fold coordination by nitrogen forming two different CrN$_6$ octahedra similar to the $\alpha$-modification, while silicon is four-fold coordinated by nitrogen with interatomic distances for chromium (Cr(1) $2 \times 1.88$ Å, $1 \times 1.93$ Å, $1 \times 1.99$ Å, $1 \times 2.00$ Å, $1 \times 2.12$ Å, Cr(2) $1 \times 1.86$ Å, $1 \times 1.90$ Å, $1 \times 1.94$ Å, $1 \times 1.96$ Å, $1 \times 2.02$ Å, and $2 \times 2.05$ Å) and silicon ($2 \times 1.70$ Å, $1 \times 1.78$ Å, and $1 \times 1.81$ Å).

As in the $\alpha$-Cr$_2$SiN$_4$-type modification, SiN$_4$ tetrahedra are oriented in different directions; however, in this modification, the CrN$_6$ octahedra are face-connected and lean against each other, thus, forming a void in the center of the structure that is reminiscent of zeolite formation.

Table 2. The modifications, space groups, unit cell parameters, and atomic positions for favorable Cr$_2$SiN$_4$ modifications found after global optimization and later locally optimized on the ab initio level using the GGA-PBE functional.

| Modifications and Space Group | Cell Parameters | Position of Atoms |
|------------------------------|----------------|------------------|
| $\alpha$-Cr$_2$SiN$_4$-type  |                |                  |
| $Pma2$ No 28                 | $a = 5.54 \ b = 7.91 \ c = 2.81$ | Cr 0.750000 0.245688 0.560883  |  |
|                              |                | Si 0.750000 0.616760 0.000000  |  |
|                              |                | N 0.750000 0.011076 0.423540  |  |
|                              |                | N 0.750000 0.493745 0.499960  |  |
| $\beta$-Cr$_2$SiN$_4$-type   |                |                  |
| $P\overline{1}$ No 2         | $a = 7.28 \ b = 7.79 \ c = 2.74$ | Cr 0.347419 0.861114 0.730714  |  |
|                              |                | Si 0.627078 0.740684 0.913120  |  |
|                              |                | N 0.050229 0.677562 0.759435  |  |
|                              |                | N 0.333428 0.666353 0.160724  |  |
|                              |                | N 0.660109 0.973354 0.749444  |  |
| $\delta$-Cr$_2$SiN$_4$-type  |                |                  |
| $P21/m$                      | $a = 6.21 \ b = 3.82 \ c = 5.54$ | Cr 0.088537 0.750000 0.660564  |  |
|                              |                | Cr 0.155145 0.750000 0.253988  |  |

Figure 1. Visualization of favorable Cr$_2$SiN$_4$ modifications: (a) $\alpha$-Cr$_2$SiN$_4$-type in space group $Pma2$ (no. 28); (b) $\beta$-Cr$_2$SiN$_4$-type in space group $P\overline{1}$ (no. 2). Green, red, and yellow spheres denote Cr, Si, and N atoms, respectively.
The next energetically favorable candidate found using global optimization is a monoclinic structure denoted as the δ-Cr$_2$SiN$_4$-type that crystallizes in space group $P2_1/m$ (no. 11). This structure is presented in Figure 2a with unit cell parameters $a = 6.21$, $b = 3.82$, $c = 5.54$ Å, and $\beta = 116.24$, computed using the PBE functional (Table 2). Interestingly, in the δ-phase both, chromium and silicon are six-fold coordinated by nitrogen, with the octahedra being edge-connected, indicating that this candidate might be a high-pressure phase.

Additionally, the interatomic distances in the two different CrN$_6$ octahedra are Cr(1) $1 \times 1.91$ Å-N, $2 \times 1.94$ Å-N, $1 \times 1.95$ Å-N, $1 \times 1.97$ Å-N, $1 \times 2.06$ Å-N, Cr(2) $1 \times 1.71$ Å-N, $1 \times 1.88$ Å-N, $2 \times 1.95$ Å-N, $1 \times 2.12$ Å-N, and $1 \times 2.27$ Å-N, and the atom–atom distances in the SiN$_6$ octahedra are $1 \times 1.81$ Å-N, $1 \times 1.93$ Å-N, $2 \times 1.92$ Å-N, $1 \times 1.85$ Å-N, and $1 \times 1.91$ Å-N, respectively.
Figure 2. Visualization of favorable CrSiN₄ modifications: (a) δ-CrSiN₄-type in space group P21/m (no. 11). (b) ε-CrSiN₄-type in space group P21/m (no. 11). Green, red, and yellow spheres denote Cr, Si, and N atoms, respectively.

One more energetically favorable candidate is a monoclinic structure, denoted as ε-CrSiN₄-type, which appears in space group P21/m (no. 11). It is visualized in Figure 2b with the unit cell parameters a = 5.09 Å, b = 2.89 Å, c = 8.90 Å, and β = 90.20. However, the ε-CrSiN₄-type is composed of SiN₄ tetrahedra (with interatomic distances 1 × 1.77 Å, 2 × 1.72 Å, and 1 × 1.73 Å), while chromium is four-fold and six-fold coordinated by nitrogen, thus, forming CrN₁ tetrahedra and CrN₂ octahedra (interatomic distances are Cr(1) 1 × 1.90 Å, 4 × 2.00 Å, 1 × 2.07 Å, Cr(2) 1 × 1.75 Å, 2 × 1.78 Å, and 1 × 1.82 Å). Apart from being the same space group as the δ-phase, the monoclinic ε-modification resembles more the α- and β-CrSiN₄-types (Tables 1 and 2 and Figure 2).

Two other interesting favorable structure candidates are monoclinic modifications belonging to space group Pm (no. 6) and are visualized in Figure 3a,b, respectively. The first one (a) is denoted the λ-CrSiN₄-type with unit cell parameters a = 5.07 Å, b = 2.88 Å, c = 9.27 Å, and β = 99.77, while the other one (b) is called the λ’-CrSiN₄-type and has the unit cell parameters a = 5.06 Å, b = 2.87 Å, c = 9.18 Å, and β = 90.97. These two structures are structurally and energetically very similar, and both of them are composed of CrN₁ and SiN₄ tetrahedra, with CrN₂ octahedra between them.

The CrN₂ octahedra are edge-connected, with corner-connected tetrahedra. Similar to the previous structures of the α-, β-, ε-CrSiN₄-type of modifications, these tetrahedra have the opposite orientations in different layers of the structure. In the λ-CrSiN₄-type of structure, chromium is connected to nitrogen with atom-atom distances Cr(1) 1 × 1.70 Å, 2 × 1.79 Å, 1 × 1.89 Å, Cr(2) 1 × 1.91 Å, 2 × 1.93 Å, 2 × 2.02 Å, 1 × 2.19 Å, Cr(3) 1 × 1.91 Å, 2 × 1.93 Å, 3 × 2.09 Å, Cr(4) 2 × 1.75 Å, 1 × 1.79 Å, 1 × 1.81 Å, and 1 × 2.64 Å, while there are also two different types of SiN₄ tetrahedra (with interatomic distances Si(1) 1 × 1.72 Å, 1 × 1.76 Å, 2 × 1.73 Å, Si(2) 3 × 1.74 Å, and 1 × 1.75 Å).

The modification referred to as λ’-CrSiN₄-type has a similar structure, with chromium being tetrahedrally and octahedrally coordinated by nitrogen in four different ways (with atom-atom distances Cr(1) 2 × 1.75 Å, 1 × 1.80 Å, 1 × 1.81 Å, Cr(2) 1 × 1.92 Å, 2 × 1.94 Å, 2 × 2.01 Å, 1 × 2.23 Å, Cr(3) 1 × 1.92 Å, 2 × 1.97 Å, 2 × 2.01 Å, 1 × 2.08 Å, Cr(4) 1 × 1.71 Å, 2 × 1.78 Å, and 1 × 1.88 Å) and two types of SiN₄ tetrahedra (interatomic distances Si(1) 1 × 1.73 Å, 2 × 1.74 Å, 1 × 1.75 Å, Si(2) 2 × 1.74 Å, and 2 × 1.73 Å).

We note that, after optimization on the ab-initio level with the LDA-PZ functional and with the GGA-PBE functional, both structures remain distinct but stay in the same space group.
3.1.2. Structural Details of Non-Favorable Structures Found after a Global Search

At extreme conditions of temperature and/or pressure, the global optimization (GO) yielded several additional candidate structures, and Table 3 presents the structural data for the five energetically non-favorable yet structurally promising GO modifications. The first modification, lowest in the energy compared to the other structures within this group is denoted as nfini-CrSiN4-type and appears in space group P21/m (no. 11). It is visualized in Figure 4a with the unit cell parameters a = 5.03 Å, b = 2.89 Å, c = 9.25 Å, and β = 100.34°. It is composed of CrN6 octahedra positioned between two layers of nitrogen tetrahedra coordinating silicon and chromium. Hence, chromium in this structure has a four-fold coordination (with interatomic distances Cr(1) 1 × 1.94 Å, 2 × 1.98 Å, 2 × 2.00 Å, 1 × 2.08 Å, 1 × 1.80 Å, and 1 × 2.72 Å) while silicon still remains in four-fold coordination (with the interatomic distances 1 × 1.76 Å and 3 × 1.74 Å). Both CrN6 and SiN4 tetrahedra in the upper and lower part of the structure are oriented in the opposite directions.

The next modification according to the total energy ranking is referred to as nf2-CrSiN4-type and crystallizes in space group Cc (no. 9). It is visualized in Figure 4b with the unit cell parameters a = 5.06 Å, b = 14.14 Å, c = 4.77 Å, and β = 121.05°. Within this structure, chromium is five-fold coordinated by nitrogen and forms two types of polyhedra (with atom–atom distances Cr(1) 1 × 1.84 Å, 1 × 1.87 Å, 1 × 1.88 Å, 1 × 1.91 Å, 1 × 1.93 Å, Cr(2) 1 × 1.78 Å, 1 × 1.79 Å, 1 × 1.84 Å, 1 × 2.00 Å, and 1 × 2.11 Å) while silicon is four-fold coordinated by nitrogen (interatomic distances are 1 × 1.71 Å, 1 × 1.77 Å, 1 × 1.75 Å, and 1 × 1.76 Å).

Other relevant modifications are denoted as nf3-CrSiN4-type, nf4-CrSiN4-type, and nf5-CrSiN4-type with the first two structures appearing in the space group Pm (no. 6) and the last one showing space group P-1 (no. 2), respectively. The total energies of these five modifications on ab initio level (GGA-PBE functional) are listed in Table 1. Furthermore, we note that most of the energetically favorable and non-favorable structures found after global optimization exhibit low symmetry, mostly orthorhombic and monoclinic symmetry (Tables 2 and 3). This is in agreement with previous theoretical reports in the closely related Si3N4 chemical system, where orthorhombic and monoclinic structures have been proposed [69].
Table 3. The modifications, space groups, unit cell parameters, and atomic positions for non-favorable CrSiN₄ modifications found using global optimization and later optimized at the GGA-PBE level of calculation.

| Modifications and Space Group | Cell Parameters | Position of Atoms |
|------------------------------|----------------|------------------|
| nf1-CrSiN₄-type P21/m No 11 | a = 5.03 b = 2.89 c = 9.25 β = 100.34 | Cr 0.780740 0.750000 0.501443 |
|                              |               | Cr 0.025858 0.250000 0.824580 |
|                              |               | Si 0.517842 0.750000 0.797882 |
|                              |               | N 0.959527 0.250000 0.630184 |
|                              |               | N 0.552291 0.250000 0.393501 |
|                              |               | N 0.609701 0.750000 0.135709 |
|                              |               | N 0.136923 0.250000 0.122932 |
| nf2-CrSiN₄-type Cc No 9     | a = 5.06 b = 14.14 c = 4.77 β = 121.05 | Cr 0.622331 0.095134 0.360180 |
|                              |               | Cr 0.380879 0.098904 0.725602 |
|                              |               | Si 0.000000 0.191719 0.000000 |
|                              |               | N 0.487148 0.004091 0.555289 |
|                              |               | N 0.511786 0.374204 0.196387 |
|                              |               | N 0.720274 0.147401 0.064041 |
|                              |               | N 0.358846 0.192090 0.368624 |
| nf3-CrSiN₄-type Pm No 6     | a = 6.79 b = 3.09 c = 6.88 β = 109.29 | Cr 0.779088 0.000000 0.218259 |
|                              |               | Cr 0.459516 0.500000 0.327876 |
|                              |               | Cr 0.253478 0.000000 0.544973 |
|                              |               | Cr 0.396471 0.500000 0.935322 |
|                              |               | Si 0.000000 0.500000 0.000000 |
|                              |               | Si 0.852505 0.000000 0.603621 |
|                              |               | N 0.330961 0.500000 0.474928 |
|                              |               | N 0.889506 0.500000 0.738026 |
|                              |               | N 0.613308 0.000000 0.401256 |
|                              |               | N 0.355218 0.000000 0.802744 |
|                              |               | N 0.932400 0.000000 0.070113 |
|                              |               | N 0.262965 0.500000 0.082041 |
|                              |               | N 0.643042 0.500000 0.129399 |
|                              |               | N 0.988794 0.000000 0.464379 |
| nf4-CrSiN₄-type Pm No 6     | a = 7.37 b = 3.05 c = 7.56 β = 115.96 | Cr 0.654478 0.292004 0.523373 |
|                              |               | Cr 0.288987 0.742844 0.838266 |
|                              |               | Si 0.865354 0.748679 0.767528 |
|                              |               | N 0.255163 0.244316 0.972502 |
| nf5-CrSiN₄-type P-1 No 2    | a = 7.17 b = 3.06 c = 7.41 α = 89.69 β = 66.68 γ = 88.06 | Cr 0.654478 0.292004 0.523373 |
|                              |               | Cr 0.288987 0.742844 0.838266 |
|                              |               | Si 0.865354 0.748679 0.767528 |
|                              |               | N 0.255163 0.244316 0.972502 |
3.2. Data Mining (DM) Based Searches Using the ICSD Database

The DM-based searches were performed within the ICSD database, which, in the latest release contains 242,828 inorganic structures, out of which more than 80% have already been assigned to distinct structure types (up to now, 9724 structure types are listed in the ICSD) [44,45]. Using the final prototype criterion as part of the KDD approach [46–48] to eliminate quasi-duplicate structures, the number of structures was reduced to 66 unique structure candidates in the \(\text{A1B2C4}\) chemical system. After performing full structural optimization on the ab initio level, the number of structure candidates was further reduced. Table 4 shows the total energy ranking of the DM-based structure candidates in the \(\text{CrSiN}_4\) system using the GGA-PBE functional.

Full structural data for all \(\text{CrSiN}_4\) modifications found from the DM-based searches are presented in Table 5, while their corresponding total energies are listed in Table 4. The data-mining-based searches of the ICSD database resulted in many possible modifications, among which the four structures presented here are distinguished as being the energetically most favorable ones, while the others corresponded to non-favorable DM structure candidates.

Table 4. The total energy and relative energy values compared to the global minimum (spinel structure taken as the zero of energy) of \(\text{CrSiN}_4\) modifications obtained from DM-based searches and calculated using GGA-PBE.

| Modification          | Total Energy (Eh) | Relative Energy (kcal/mol) |
|-----------------------|-------------------|-----------------------------|
| \(\text{Al}_2\text{MgO}_2\)-spinel-type | -5193.507         | 0.0                         |
| \(\text{Na}_2\text{MnCl}_3\)-type         | -5193.436         | 44.553                      |
| \(\text{TiMnO}_4\)-type                  | -5193.414         | 58.358                      |
| \(\text{Mg}_2\text{SiO}_4\)-type         | -5193.403         | 65.261                      |
| \(\text{Ca}_2\text{RuO}_4\)-type         | -5193.402         | 65.889                      |
| \(\text{HgCuO}_4\)-like                 | -5193.400         | 67.144                      |
| \(\text{Ca}_2\text{IrO}_4\)-type        | -5193.349         | 99.147                      |
| \(\text{Ca}_2\text{CuO}_4\)-like        | -5193.347         | 100.402                     |
| \(\text{Mn}_2\text{SnS}_4\)-type        | -5193.342         | 103.539                     |
Table 5. The modifications, space groups, unit cell parameters, and atomic positions for CrSiN\(_4\) modifications obtained from data-mining-based searches and local optimization at the GGA-PBE level.

| Modifications and Space Group | Cell Parameters | Position of Atoms |
|------------------------------|-----------------|-------------------|
| Al2MgO4-spinel-type          |                 |                   |
| \(Fd-3m\)                    | \(a = 7.88\)    | Cr 0.000000       |
| No 227                       |                 | 0.000000          |
|                              |                 | Si 0.625000       |
|                              |                 | 0.625000          |
|                              |                 | N 0.752483        |
|                              |                 | 0.752483          |
|                              |                 | 0.752483          |
| Na2MnCl2-type                |                 | Cr 0.433387       |
| \(Pbam\)                     | \(a = 4.74\) b = 8.70 c = 2.73 | 0.175989          |
| No 55                        |                 | 0.500000          |
|                              |                 | Si 0.000000       |
|                              |                 | 0.000000          |
|                              |                 | 0.000000          |
|                              |                 | N 0.133667        |
|                              |                 | 0.203146          |
|                              |                 | 0.000000          |
| TiMn2O4-type                 |                 | Cr 0.500000       |
| \(P 43 2 2\)                 | \(a = 5.64\) c = 7.74 | 0.288490          |
| No 95                        |                 | 0.500000          |
|                              |                 | Cr 0.234522       |
|                              |                 | 0.234522          |
|                              |                 | 0.625000          |
| Mg2SiO4-type                 |                 | Cr 0.911733       |
| \(Pnma\)                     | \(a = 9.42\) b = 5.45 c = 4.82 | 0.750000          |
| No 62                        |                 | 0.580414          |
|                              |                 | Si 0.915086       |
|                              |                 | 0.750000          |
|                              |                 | 0.227101          |
|                              |                 | N 0.579248        |
|                              |                 | 0.750000          |
|                              |                 | 0.754925          |
| Ta2RuO4-type                 |                 | Cr 0.951271       |
| \(Pbca\)                     | \(a = 4.55\) b = 4.88 c = 10.32 | 0.883328          |
| No 61                        |                 | 0.314395          |
|                              |                 | Si 0.000000       |
|                              |                 | 0.000000          |
|                              |                 | 0.000000          |
|                              |                 | N 0.189814        |
|                              |                 | 0.299961          |
|                              |                 | 0.071415          |
|                              |                 | N 0.821277        |
|                              |                 | 0.910789          |
|                              |                 | 0.170556          |
| Hg2O-like                    |                 | Cr 0.009785       |
| \(P 21\)                     | \(a = 5.34\) b = 5.09 c = 5.36 \(\beta = 115.62\) | 0.463302          |
| No 4                         |                 | 0.266681          |
|                              |                 | Cr 0.242643       |
|                              |                 | 0.853311          |
|                              |                 | 0.472408          |
|                              |                 | Si 0.651871       |
|                              |                 | 0.000000          |
|                              |                 | 0.959796          |
|                              |                 | N 0.021251        |
|                              |                 | 0.353294          |
|                              |                 | 0.916553          |
|                              |                 | N 0.626651        |
|                              |                 | 0.296871          |
|                              |                 | 0.103741          |
|                              |                 | N 0.597719        |
|                              |                 | 0.030584          |
|                              |                 | 0.610720          |
|                              |                 | N 0.079595        |
|                              |                 | 0.179181          |
|                              |                 | 0.498154          |
| Ca2IrO4-type                 |                 | Cr 0.000000       |
| \(P-62m\)                    | \(a = 8.33\) c = 2.70 | 0.000000          |
| No 189                       |                 | 0.000000          |
|                              |                 | Cr 0.333333       |
|                              |                 | 0.666667          |
|                              |                 | 0.500000          |
|                              |                 | Cr 0.699230       |
|                              |                 | 0.000000          |
|                              |                 | 0.500000          |
|                              |                 | Si 0.337748       |
|                              |                 | 0.000000          |
|                              |                 | 0.000000          |
|                              |                 | N 0.173727        |
|                              |                 | 0.000000          |
|                              |                 | 0.500000          |
|                              |                 | N 0.473996        |
|                              |                 | 0.000000          |
|                              |                 | 0.500000          |
|                              |                 | N 0.448912        |
|                              |                 | 0.247641          |
|                              |                 | 0.000000          |
| Ca2B2O4-like                 |                 | Cr 0.931376       |
| \(P c c n\)                   | \(a = 7.98\) b = 14.42 c = 4.85 | 0.565538          |
| No 56                        |                 | 0.393557          |
|                              |                 | Cr 0.170647       |
|                              |                 | 0.535703          |
|                              |                 | 0.989804          |
|                              |                 | Si 0.857355       |
|                              |                 | 0.679567          |
|                              |                 | 0.867484          |
|                              |                 | N 0.864237        |
|                              |                 | 0.698217          |
|                              |                 | 0.499220          |
|                              |                 | N 0.303715        |
|                              |                 | 0.441717          |
|                              |                 | 0.754883          |
|                              |                 | N 0.009972        |
|                              |                 | 0.618966          |
|                              |                 | 0.076401          |
|                              |                 | N 0.377123        |
|                              |                 | 0.568169          |
|                              |                 | 0.113939          |
| Mn2SnS4-type                 |                 | Cr 0.750000       |
| \(C m m m\)                   | \(a = 5.58\) b = 7.82 c = 2.76 | 0.750000          |
| No 65                        |                 | 0.500000          |
|                              |                 | Si 0.000000       |
|                              |                 | 0.000000          |
|                              |                 | 0.000000          |
|                              |                 | N 0.000000        |
|                              |                 | 0.247324          |
|                              |                 | 0.000000          |
|                              |                 | N 0.220861        |
|                              |                 | 0.000000          |
|                              |                 | 0.500000          |
3.2.1. Structural Analysis of Low-Energy Candidates from the DM-Based Searches

The Al$_3$MgO$_4$-spinel-type modification [70,71], generated from the DM-based searches and visualized in Figure 5a, is the lowest one in the calculated total energy at both the GGA-PBE and the LDA-PZ level, for the whole energy landscape including the structures obtained from the GO and the PCAE method calculations. It exhibits space group Fd-3m (no. 227) with unit cell parameters $a = 7.88$ Å at the GGA-PBE level of calculation with all structural data presented in Table 5.

In the Al$_3$MgO$_4$-type modification, chromium is six-fold coordinated forming a CrN$_6$ octahedron with the interatomic distance Cr 6 $\times$ 1.95 Å, while silicon is four-fold coordinated forming a SiN$_4$ tetrahedron with the atom–atom distance 4 $\times$ 1.74 Å. In this cubic modification, the CrN$_6$ octahedra are connected by edges while the SiN$_4$ tetrahedra are corner-connected. When performing structure optimizations of the candidates on the DFT-LDA level, the Al$_3$MgO$_4$-spinel-type modification remains the global minimum (Tables A1 and A2). We note that the Al$_3$MgO$_4$-spinel-type of the structure appears in more than 4000 compounds (4250) with the chemical formula Al$_2$B$_2$C$_4$ indicating the importance of this structure-type on the energy landscape of ternary systems [44,45].

The next favorable modification found after DM is in the Na$_2$MnCl$_4$-type [72], which is an orthorhombic structure that appears in space group Pbam (no. 55) with unit cell parameters $a = 4.73$, $b = 8.70$, and $c = 2.73$ Å and is visualized in Figure 5b. In this modification, both chromium and silicon are six-fold coordinated by nitrogen, thus, forming distorted octahedra that are quite different from each other.

The CrN$_6$ octahedra are quite similar to those in the WC structure-type, while the SiN$_4$ octahedra are “NaCl-type” octahedra. Interatomic distances in the CrN$_6$ octahedra are longer ($1 \times 1.92$ Å–N, $2 \times 1.97$ Å–N, $2 \times 1.98$ Å–N, and $1 \times 2.01$ Å–N) than in the SiN$_4$ octahedra ($4 \times 1.85$ Å–N, $2 \times 1.88$ Å–N). The SiN$_4$ octahedra are positioned in the center and at the edges of the cell, with the CrN$_6$ octahedra connecting them. Both edge and corner connections are observed.

![Visualization of favorable CrSiN4 modifications](image1)

**Figure 5.** Visualization of favorable CrSiN4 modifications: (a) Al$_2$MgO$_4$-spinel-type in space group Fd-3m (no. 227); (b) Na$_2$MnCl$_4$-type that appears in space group Pbam (no. 55). Green, red, and yellow spheres denote Cr, Si, and N atoms, respectively.

The next favorable modification obtained via DM is denoted as TiMnO$_4$-type [73]. It is a tetragonal structure in space group $P$ 4322 (no.95) with unit cell parameters $a = 5.64$ and $c = 7.74$ Å and is visualized in Figure 6a. In the TiMnO$_4$ phase, chromium is both four-fold and six-fold coordinated by nitrogen, thus, forming CrN$_6$ tetrahedra (with atom–atom distances $2 \times 1.78$ Å–N and $2 \times 1.81$ Å–N) and CrN$_6$ octahedra (with atom–atom distances $2 \times 1.89$ Å–N, $2 \times 1.97$ Å–N, and $2 \times 2.05$ Å–N). Silicon is six-fold coordinated by
nitr

togen with interatomic distances \((2 \times 1.86 \text{ Å-N} \text{ and } 4 \times 1.91 \text{ Å-N})\). The octahedra are edge-connected, while the CrN\(_6\) tetrahedra are corner-connected.

The next modification obtained from the data mining search is a structure denoted as Mg\(_2\)SiO\(_4\) (Forsterite) type of structure \([74]\), and it crystallizes in space group Pnma (no. 62) with unit cell parameters \(a = 9.42\), \(b = 5.45\), and \(c = 4.82\) Å. Within this modification, two types of CrN\(_6\) octahedra are connected by edges and oriented in the structure in two directions with interatomic distances (Cr(1) \(2 \times 1.92\) Å-N, \(2 \times 1.98\) Å-N, \(2 \times 2.00\) Å-N, Cr(2) \(1 \times 1.88\) Å-N, \(2 \times 1.95\) Å-N, \(2 \times 2.00\) Å-N, and \(1 \times 2.02\) Å-N). Silicon is four-fold coordinated by nitrogen (with atom–atom distances \(1 \times 1.70\) Å-N, \(2 \times 1.76\) Å-N, and \(1 \times 1.77\) Å-N) connected by the edges; the structure is visualized in Figure 6b.

![Figure 6](image)

**Figure 6.** Visualization of favorable CrSiN\(_4\) modifications: (a) TiMn\(_2\)O\(_4\)-type in space group \(P4322\) (no. 95); (b) Mg\(_2\)SiO\(_4\)-type in space group \(Pnma\) (no. 62). Green, red, and yellow spheres denote Cr, Si, and N atoms, respectively.

### 3.2.2. Structural Analysis of Non-Favorable Candidates Found after Data Mining

The first non-favorable energy minimum found after data mining appears in the CaRuO\(_4\)-type \([75]\) and is visualized in Figure 7a. This is an orthorhombic structure that appears in space group \(Pbca\) (no. 61) with the unit cell parameters \(a = 4.55\), \(b = 4.88\), and \(c = 10.31\) Å. Chromium and silicon are both six-fold coordinated by nitrogen but form different octahedra. Similar to the energetically favorable Na\(_2\)MnCl\(_4\)-type modification, within this modification, the CrN\(_6\) octahedra resemble those in the WC-type of structure with the interatomic distances \(1 \times 1.82\) Å-N, \(1 \times 1.89\) Å-N, \(1 \times 1.90\) Å-N, \(1 \times 1.94\) Å-N, \(1 \times 1.97\) Å-N, and \(1 \times 2.49\) Å-N.

These octahedra are connected by edges to each other; however, the connection to the SiN\(_6\) octahedra is via edges and corners as well. The whole structure consists of layers of different octahedra, where the SiN\(_6\) ones are located on the faces and in the center of the cell with the CrN\(_6\) octahedra situated in-between.
The next non-favorable modification found after data mining is denoted as a HgC\textsubscript{4}O\textsubscript{4}-like type of structure and crystallizes in space group P2\textsubscript{1} (no. 4). We note that the starting HgC\textsubscript{4}O\textsubscript{4} structure [76] after DFT optimization has been structurally modified, however, within the same space group (no.4), thus, resulting in a HgC\textsubscript{4}O\textsubscript{4}-like structure. This is a monoclinic structure with the unit cell parameters \(a = 5.34\), \(b = 5.09\), \(c = 5.36\), and \(\beta = 115.62\), with the structural parameters with corresponding energies given in Tables 4 and 5.

Within this structure, chromium is six-fold coordinated by nitrogen forming CrN\textsubscript{6} octahedra (atom–atom distance Cr(1) 1 × 1.83 Å-N, 1 × 1.88 Å-N, 1 × 1.94 Å-N, 1 × 1.98 Å-N, 1 × 2.03 Å-N, 1 × 2.19 Å-N, Cr(2) 1 × 1.91 Å-N, 1 × 1.94 Å-N, 1 × 1.95 Å-N, 1 × 1.99 Å-N, 1 × 2.00 Å-N, and 1 × 2.09 Å-N), connected by faces and corners among each other. Silicon is four-fold coordinated forming edge- and corner-connected SiN\textsubscript{4} tetrahedra with the interatomic distances 1 × 1.72 Å-N, 1 × 1.73 Å-N, 1 × 1.75 Å-N, and 1 × 1.77 Å-N. The structure is visualized in Figure 7b.

The next modification by energy shows a CaIrO\textsubscript{4}-type [77] structure; it exhibits the space group \(P\overline{6}2m\) (no. 189) with the unit cell parameters \(a = 8.33\) and \(c = 2.70\) and is visualized in Figure 8a. Within the structure, chromium is six-fold and seven-fold coordinated by nitrogen with the interatomic distances Cr(1) 6 × 1.98 Å-N, Cr(2) 6 × 2.08 Å-N, 3 × 2.42 Å-N, Cr(3) 1 × 1.88 Å-N, 4 × 2.02 Å-N, and 2 × 2.18 Å-N. The CrN\textsubscript{6} octahedra are face-connected resembling the ones in the WC-type of a structure, while the CrN\textsubscript{7} polyhedra are edge- and corner-connected. Similarly, the SiN\textsubscript{4} octahedra are edge- and corner-connected, with the atom–atom distances 2 × 1.76 Å-N, 2 × 1.79 Å-N, and 2 × 1.92 Å-N.

Another interesting modification obtained from the data mining search is the orthorhombic structure denoted as a CaB\textsubscript{4}O\textsubscript{4}-like structure, visualized in Figure 8b. This modification crystallizes in space group \(Pccn\) (no. 56) with the unit cell parameters \(a = 7.98\), \(b = 14.42\), and \(c = 4.85\). Similarly, as with the HgC\textsubscript{4}O\textsubscript{4}-like modification, the CaB\textsubscript{4}O\textsubscript{4}-like structure is modified during the local optimization from the original prototypic CaB\textsubscript{4}O\textsubscript{4} structure [78] but still within the same space group (no. 56).

In this structure, chromium is five-fold and six-fold coordinated by nitrogen forming two different polyhedra with the atom–atom distances Cr(1) 1 × 1.83 Å-N, 1 × 1.87 Å-N, 1 × 1.98 Å-N, 1 × 1.99 Å-N, 1 × 2.01 Å-N, 1 × 2.05 Å-N, Cr(2) 1 × 1.81 Å-N, 1 × 1.82 Å-N, 1 × 1.88 Å-N, 1 × 1.92 Å-N, and 1 × 2.07 Å-N, and one has a SiN\textsubscript{4} polyhedron with the interaction distances 2 × 1.81 Å-N, 1 × 1.88 Å-N, and 2 × 1.90 Å-N.
Figure 8. Visualization of non-favorable CrSiN$_4$ modifications obtained from data-mining: (a) CaIrO$_4$-type in space group P-62m (no. 189); (b) CaB$_2$O$_4$-type in space group Pccn (no. 56). Green, red, and yellow spheres denote Cr, Si, and N atoms, respectively.

A final interesting modification from the data mining search is denoted as Mn$_2$SnS$_4$-type [79] and is visualized in Figure 9. This orthorhombic structure appears in the space group Cmmm (no. 65) with the unit cell parameters $a = 5.58$, $b = 7.82$, and $c = 2.76$. In this structure, both chromium and silicon are six-fold coordinated by nitrogen with edge-connected octahedra and the interatomic distances Cr $6 \times 1.96$ Å-N, Si $4 \times 1.85$ Å-N, and $2 \times 1.93$ Å-N.

Figure 9. Visualization of non-favorable CrSiN$_4$ modification obtained from data-mining referred to as Mn$_2$SnSi-type in space group Cmmm (no 65).

We note that most of the structure candidates found using DM-based searches show orthorhombic symmetry (Table 5), in some cases reminiscent of the structurally related Si$_3$N$_4$ chemical system where orthorhombic structures have also been found [69]. In this context, we would like to remark on the Cu$_2$HgI$_4$ type of structure [80]. This structure type has been recently predicted to exist as a modification in a study of novel hard phases of Si$_3$N$_4$ [69].

The same Cu$_2$HgI$_4$ type has also been found in our DM-based searches; however, it is energetically much worse than most of the other DM or GO/CAE-based structure candidates ($E_{\text{tot}} = -5193.312$ Eh calculated using the GGA-PBE functional). Full structural optimization resulted in the original prototypic structure in tetragonal space group I-42m.
(no. 121) with unit cell parameters a = 4.34 and c = 8.09 Å, at the GGA-PBE level of computation (both chromium and silicon are fourfold coordinated by nitrogen forming tetrahedra with interatomic distances of Cr 4 × 1.80 Å-N and Si 4 × 1.75 Å-N).

3.3. Structural Searches Using the PCAE Method

Finally, the Primitive Cell approach for Atom Exchange (PCAE) method was employed for generating alternative structure candidates in the CrSiN₄ compound, starting from typical structures in the related SiN₄ system, the γ-, β-, and α-phase of SiN₄. Ranking the ab initio minimized structures according to the calculated total energy using the GGA-PBE functional, the most promising candidates generated using the PCAE method are presented in Table 6.

Table 6. The total energy and relative energy values compared to the global minimum (spinel structure taken as the zero of the energy) of CrSiN₄ modifications found using the PCAE method and locally optimized using the GGA-PBE functional.

| Modification        | Total Energy (Eh) | Relative Energy (kcal/mol) |
|---------------------|-------------------|----------------------------|
| γ-CrSiN₄-type       | −5193.435         | 45.181                     |
| CrSiN₄-PCAE-1-type  | −5193.385         | 76.556                     |
| CrSiN₄-PCAE-2-type  | −5193.374         | 83.459                     |

Structural Details of Candidates Found Using the PCAE Method

The lowest energy minimum found using the PCAE method was denoted the γ-CrSiN₄-type modification. Figure 10a shows a prototypic γ-phase in the SiN₄ system [71], which was used as starting structure for generating the γ-CrSiN₄-type. The SiN₄ γ-phase crystallizes in the cubic space group I-43d (no. 220), [71] forming corner connected tetrahedra of silicon atoms (Figure 10a). However, after local optimization in the CrSiN₄ system using both GGA-PBE and LDA-PZ functionals, it converts to the γ-CrSiN₄-type modification. It is a low-energy candidate in the CrSiN₄ system; however, it is structurally completely different from the starting γ-phase in the SiN₄ system (compare Figure 10a,b).

The γ-CrSiN₄-type modification crystallizes in the monoclinic space group Cc (no. 9) with unit cell parameters a = 5.62, b = 8.96, c = 5.36 Å, and β = 117.93, with both cations—chromium and silicon—being six-fold coordinated by nitrogen where these octahedra are edge- and face-connected (Figure 10b). We deal with two different types of CrN₆ octahedra with the interatomic distances Cr(1) 1 × 1.84 Å-N, 1 × 1.85 Å-N, 1 × 1.92 Å-N, 1 × 1.96 Å-N, 1 × 2.01 Å-N, 1 × 2.13 Å-N, Cr(2) 1 × 1.83 Å-N, 1 × 1.90 Å-N, 1 × 1.92 Å-N, 1 × 1.96 Å-N, 1 × 2.01 Å-N, and 1 × 2.03 Å-N; the atom–atom distances in the SiN₄ octahedra are 1 × 1.74 Å-N, 1 × 1.75 Å-N, 1 × 1.81 Å-N, 1 × 2.08 Å-N, 1 × 2.20 Å-N, and 1 × 2.34 Å-N). In the closely related SiN₄ compound, there has been a prediction of novel monoclinic phases from first-principles calculations [69].
Figure 10. Visualization of: (a) the Si$_3$N$_4$ $\gamma$-phase in space group $I-43d$ (no. 220); (b) $\gamma$-CrSiN$_4$-type in space group $Cc$ (no. 9). Green, red, and yellow spheres denote Cr, Si, and N atoms, respectively. The next minimum found using the PCAE method is marked as Cr$_2$SiN$_4$-PCAE-1 phase, which is energetically less favorable than the $\gamma$-phase (Table 6). The Cr$_2$SiN$_4$-PCAE-1 type has been generated similarly to the previous one, starting from the $\beta$-phase of Si$_3$N$_4$ in the hexagonal $P63/m$ (no. 176) space group [81,82]. After ab initio structural optimization in the Cr$_2$SiN$_4$ system, the structure converted to a monoclinic modification denoted Cr$_2$SiN$_4$-PCAE-1 that crystallizes in space group $Pm$ (no. 6) with unit cell parameters $a = 7.04465$, $b = 3.03610$, $c = 7.03270$, $\beta = 110.7203$ (Table 7).

In this structure type, both chromium and silicon are four-fold and five-fold coordinated by nitrogen forming different types of polyhedra (Figure 11a). There are two different CrN$_4$ tetrahedra and two different CrN$_5$ polyhedra, with the atom–atom distances Cr(1) 2 $\times$ 1.86 Å-N, 1 $\times$ 1.89 Å-N, 1 $\times$ 1.95 Å-N, 1 $\times$ 2.01 Å-N, Cr(2) 2 $\times$ 1.81 Å-N, 1 $\times$ 1.88 Å-N, 1 $\times$ 1.92 Å-N, 1 $\times$ 1.93 Å-N, Cr(3) 2 $\times$ 1.74 Å-N, 1 $\times$ 1.75 Å-N, 1 $\times$ 1.99 Å-N, 1 $\times$ 2.18 Å-N, Cr(4) 2 $\times$ 1.77 Å-N, and 2 $\times$ 1.78 Å-N.

In the corners of the cell, there are four Si$_3$N$_4$ tetrahedra with interatomic distances of 1 $\times$ 1.74 Å-N, 2 $\times$ 1.76 Å-N, and 1 $\times$ 1.83 Å-N. Additionally, there is one Si$_3$N$_4$ polyhedron corner connected to one of the tetrahedra (atom–atom distances of 1 $\times$ 1.72 Å-N, 1 $\times$ 1.77 Å-N, 2 $\times$ 1.78 Å-N, and 1 $\times$ 2.49 Å-N), where chromium is completely located in the inner part of the unit cell, and the connection between polyhedra is formed via edges and corners (Figure 11a).

Figure 11. Visualization of the non-favorable PCAE structures: (a) Cr$_3$SiN$_4$-PCAE-1-type in space group $Pm$ (no 6); (b) Cr$_3$SiN$_4$-PCAE-2-type in space group $P1$ (no. 1). Green, red, and yellow spheres denote Cr, Si, and N atoms, respectively.
Structurally and energetically related is the CrSiN₄-PCAE-2-type of structure presented as a final non-favorable structure candidate generated using the PCAE method. In this case, the α-type structure of SiN₄ with trigonal P31c (no. 159) space group [82,83] was used as starting point. However, after full structural optimization on the GGA-PBE level, the symmetry of the CrSiN₄-PCAE-2-type is completely reduced to space group P1 (no. 1) with unit cell parameters of a = 7.87856, b = 7.96102, c = 5.78635, α = 89.9706, β = 89.8616, and γ = 120.2646 (Table 7).

Within this triclinic modification, both chromium and silicon are four-fold coordinated by nitrogen thus forming tetrahedra (Figure 11b). In this modification there are eight different CrN₄ tetrahedra, with the atom–atom distances Cr(1) 1 × 1.77 Å, Cr(2) 2 × 1.78 Å, Cr(3) 2 × 1.79 Å, Cr(4) 1 × 1.76 Å, Cr(5) 1 × 1.77 Å, Cr(6) 1 × 1.78 Å, Cr(7) 1 × 1.78 Å, Cr(8) 1 × 1.8 Å, and Cr(9) 1 × 1.8 Å.

Silicon is also four-fold coordinated by nitrogen resulting in two different SiN₄ tetrahedra with the interatomic distances Si1 1 × 1.74 Å, Si2 1 × 1.75 Å, Si3 2 × 1.74 Å, and Si4 2 × 1.75 Å. The SiN₄ tetrahedra are mostly positioned at the corners of the cell with three tetrahedra located inside along with CrN₄ tetrahedra located entirely inside the cell. Nevertheless, all tetrahedra within this phase are corner-connected (Figure 11b). A summary of the structural data of the presented PCAE structures is shown in Table 7; other structure candidates generated using the PCAE method were energetically much less favorable and, thus, have not been included.

**Table 7.** The modifications, space groups, unit cell parameters, and atomic positions for favorable CrSiN₄ modifications found using the PCAE method and the GGA-PBE functional.

| Modification and Space Group | Cell Parameters | Position of Atoms |
|-----------------------------|-----------------|------------------|
| γ-CrSiN₄-type Cc (no. 9)    | a = 5.62 b = 8.96 c = 5.36 Å, β = 117.93 | Cr 0.505134 0.354319 0.539894 |
|                            |                 | Cr 0.490988 0.640587 0.506788 |
|                            |                 | Si 0.000000 0.574728 0.000000 |
|                            |                 | N 0.820626 0.494637 0.668512 |
|                            |                 | N 0.339534 0.498028 0.687817 |
|                            |                 | N 0.683793 0.745757 0.858424 |
|                            |                 | N 0.673275 0.237591 0.860703 |
| CrSiN₄-PCAE-1-type Pm (no. 6) | a = 7.04 b = 3.04 c = 7.03 β = 110.72 | Cr 0.338406 0.500000 0.381358 |
|                            |                 | Cr 0.068281 0.000000 0.404484 |
|                            |                 | Cr 0.778353 0.500000 0.589017 |
|                            |                 | Cr 0.381419 0.500000 0.771064 |
|                            |                 | Si 0.000000 0.000000 0.000000 |
|                            |                 | Si 0.613136 0.000000 0.165992 |
|                            |                 | N 0.569205 0.500000 0.274738 |
|                            |                 | N 0.859037 0.000000 0.522005 |
|                            |                 | N 0.985060 0.500000 0.869495 |
|                            |                 | N 0.164949 0.500000 0.544984 |
|                            |                 | N 0.227376 0.000000 0.231306 |
|                            |                 | N 0.437810 0.000000 0.912940 |
|                            |                 | N 0.551129 0.500000 0.653619 |
|                            |                 | N 0.853139 0.000000 0.153320 |
| CrSiN₄-PCAE-2-type P1 (no. 1) | a = 7.88 b = 7.96 c = 5.79 α = 89.97 β = 120.26 | Cr 0.179061 0.774468 0.214657 |
|                            |                 | Cr 0.576899 0.834251 0.216822 |
|                            |                 | Cr 0.514893 0.179271 0.214657 |
3.4. Energy Landscape of Cr$_2$SiN$_4$ on the Ab Initio Level

The global optimization, data mining, and PCAE based searches resulted in structure candidates that were, after detailed structural and crystallographic analysis, reduced to the eleven energetically most favorable Cr$_2$SiN$_4$ modifications. Table 8 presents the energetic ranking of these modifications, where the Al$_2$MgO$_4$-spinel-type appears lowest in calculated total energy with the value of $-5193.507 \text{ E}_h$, thus, representing the global minimum among the candidates obtained in the various searches. If the calculations are performed using DFT-LDA (Table A2), the spinel structure remains the global minimum, and the energetic ranking of the other modifications is very similar, with few exceptions.

Table 8. The total energies and relative energy values compared to the global minimum (spinel structure taken as the zero of energy) of the energetically most favorable Cr$_2$SiN$_4$ modifications found using various search methods and later locally optimized on the ab initio level using the GGA-PBE functional. DM stands for data mining, GO stands for global optimization, and PCAE stands for Primitive Cell approach for Atom Exchange method.

| Modification         | Search Method | Total Energy (E$_h$) | Relative Energy (kcal/mol) |
|----------------------|---------------|----------------------|-----------------------------|
| Al$_2$MgO$_4$-spinel-type | DM            | −5.193.507           | 0.0                         |
| α-Cr$_2$SiN$_4$-type  | GO            | −5193.474            | 20.708                      |
| β-Cr$_2$SiN$_4$-type  | GO            | −5193.438            | 43.298                      |
| Na$_2$MnCl$_2$-type   | DM            | −5193.436            | 44.553                      |
| γ-Cr$_2$SiN$_4$-type  | PCAE          | −5193.435            | 45.181                      |
| δ-Cr$_2$SiN$_4$-type  | GO            | −5193.419            | 55.221                      |
| TiMn$_2$O$_4$-type    | DM            | −5193.414            | 58.358                      |
| ε-Cr$_2$SiN$_4$-type  | GO            | −5193.413            | 58.986                      |
| λ-Cr$_2$SiN$_4$-type  | GO            | −5193.407            | 62.750                      |
Figure 12 presents the energy versus volume (E(V)) curves on the ab initio level using the GGA-PBE functional for the energetically most favorable Cr$_2$SiN$_4$ modifications. We note that the global minimum in the Cr$_2$SiN$_4$ system is the Al:MgO$_2$-spinel phase. This prominence of the Al:MgO$_2$-type candidate on the energy landscape of Cr$_2$SiN$_4$ is not unreasonable, since several earlier calculations in the related (binary) Si$_3$N$_4$ system have also found a Al:MgO$_2$-spinel-like phase [71,84,85].

At high-temperature conditions, one might expect structures, like the β-, ε-, λ-, and λ'-Cr$_2$SiN$_4$-type to possibly become competitive, as well as the TiMnO$_4$-type and Mg$_2$SiO$_4$-type modifications from the DM-based searches. Similarly, the most relevant modifications that might appear in the high-pressure region are the Na$_2$MnCl$_4$-type, and the α-, γ-, and δ-Cr$_2$SiN$_4$-types. Therefore, enthalpy vs. pressure, H(p), curves were computed for these five modifications (Figure 13).

A high-pressure phase transition was predicted between the spinel and the Na$_2$MnCl$_4$-type at a pressure of ~33 GPa (Figure 13). In addition, there was a phase transition between the Na$_2$MnCl$_4$-type and the metastable α-Cr$_2$SiN$_4$-type modifications at ~15 GPa (Figure 13), i.e., the α-phase was more stable than the Na$_2$MnCl$_4$-type modification below 15 GPa in the Cr$_2$SiN$_4$ system.

| Modification Type | Abbreviation | Energy (E$_h$) | Pressure (GPa) |
|-------------------|--------------|---------------|----------------|
| λ'-Cr$_2$SiN$_4$-type | GO           | -5193.404     | 64.634         |
| Mg$_2$SiO$_4$-type  | DM           | -5193.403     | 65.261         |

Figure 12. Energy vs. volume, E(V), curves for the most favorable Cr$_2$SiN$_4$ modifications calculated using the GGA-PBE functional. Energies per formula unit are given in Hartree (E$_h$).
In summary, the energy landscape of Cr$_2$SiN$_4$ is highly complex with a wide range of structurally different modifications possible. On the ab initio level, the global minimum corresponds to the AlMg$_2$O$_4$-type of structure. This modification is also known as a spinel structure, formulated as AB$_2$X$_4$ with a fcc close-packed array of anions X, and A and B cations occupying some or all of the octahedral and tetrahedral sites in the lattice, respectively. The structural features found in this structure type are the most dominant ones in the low-energy region of the landscape of Cr$_2$SiN$_4$ at standard pressure, where most of the structures are found to exhibit an octahedral coordination of chromium by nitrogen and a tetrahedral one for silicon, respectively.

However, some of the structure candidates observed exhibit six-fold coordination with an octahedral environment for both Cr and Si atoms (e.g., the γ- and the δ-Cr$_2$SiN$_4$-type, the Na$_2$MnCl$_4$-type, and the Mn$_2$SnS$_4$-type), while there is only one stable modification (Cr$_2$SiN$_4$-PCAE-2-type) exhibiting tetrahedral coordination by nitrogen for both cations. In addition, a few structures show unusual five-fold and seven-fold coordination, but these are energetically non-favorable.

The appearance of spinel as a global minimum in Cr$_2$SiN$_4$ and the observation of analogous coordination environments of Cr and Si in most of the structures found as low-energy minima on the landscape are strong indications that this compound should be synthetically accessible. Furthermore, a spinel-type modification of Cr$_2$SiN$_4$ could be of great importance, since ferrite spinels and related structures are of technological interest.
due to their magnetic ordering, which can be ferrimagnetic or antiferromagnetic depending on the structure and the nature of the metal ions.

Similarly, the results of recent investigations demonstrating that spinel coatings can be used to protect metals, such as chromium, from oxidation or corrosion, serve as another indication for the possible technological and industrial usefulness of the proposed Cr$_2$SiN$_4$ structure candidates [86–88]. Another interesting point is that the global minimum AlMg$_2$O$_4$-spinel-type of the structure shows the highest cubic Fd-3m symmetry, while most of the predicted structure candidates show much lower symmetry.

Here, we note that the spinel structure contains so many atoms that it was not feasible to be realized in the periodic simulation cell employed for the global optimizations; as a consequence, the closely related α-Cr$_2$SiN$_4$-type structure was obtained instead. Quite generally, data-mining-based searches produced high-symmetry candidates (except for the HgC$_2$O$_4$-type, which is monoclinic), while global optimization and the PCAE method mostly produced structures with lower symmetry, with the orthorhombic space group Pma$2_1$ (no. 28) of the α-Cr$_2$SiN$_4$-type as the highest symmetry space group.

We note that each of the methods used brought us a new perspective: data mining found the global minimum and suggested known structure types that can be stable in the Cr$_2$SiN$_4$ system, the global optimization resulted in a large number of new unknown but kinetically stable low-energy structures and provided a general overview over the broad structural variety present in the system at low energies, while the PCAE method generated the most diverse modifications, ranging from structures consisting of networks with only tetrahedral coordination polyhedra of the cations by nitrogen to modifications with only octahedral coordination environments.

4. Conclusions

A combination of global optimization, data mining, and the PCAE method was used to explore the energy landscape of Cr$_2$SiN$_4$ and to perform structure prediction in the Cr$_2$SiN$_4$ system. Global optimization was performed using simulated annealing and a fast computable robust empirical two-body potential. Data-mining-based searches reduced a large number of crystal structures from the ICSD database to four energetically favorable structures and five structure candidates that might be feasible modifications at extreme conditions for the not-yet-synthesized Cr$_2$SiN$_4$ compound.

Additionally, the Primitive Cell approach for Atom Exchange (PCAE) method was employed for generating alternative structure candidates in the Cr$_2$SiN$_4$ system with starting modifications taken from the related Si$_2$N$_4$ chemical system. Every structure candidate found in these searches was subjected to crystallographic analysis and all the promising ones to a local optimization on the ab initio level.

The local optimizations were performed on the DFT level employing the LDA-PZ and the GGA-PBE functional, for comparison, since there exists no experimental data that one could compare the results with. There was good agreement between the results from the two chosen functionals regarding the total energy ranking, space group symmetry, and other structural data of the various structure candidates after relaxation, which strongly supports the plausibility of the proposed candidates to correspond to actual (meta)stable modifications in the Cr$_2$SiN$_4$ system.

The explorations of the energy landscape of the Cr$_2$SiN$_4$ system resulted in numerous predicted new structures/modifications not yet observed in the experiment. Within each method used in this study, we grouped our results into energetically favorable and non-favorable Cr$_2$SiN$_4$ modifications, with the latter ones perhaps accessible for extreme thermodynamic conditions. Among the eleven energetically most favorable candidates, the global minimum was the AlMg$_2$O$_4$-spinel-type exhibiting the cubic Fd-3m symmetry.

At high pressures of ca. ~33 GPa, a phase transition between the spinel-type and the Na$_2$MnCl$_4$-type modifications should take place. Thus, we present a large number of feasible structures for modifications in the synthetically not-yet-explored Cr$_2$SiN$_4$ system, which might be suitable for many technological applications, such as high-speed cutting,
wood machining applications, hydraulic piston pumps, valves, gears, shafts, and propellers, as corrosion-resistant coatings and low-cost water-based lubricating systems.

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### Appendix A

**Table A1.** The modifications, space groups, unit cell parameters, and atomic positions for the most favorable Cr$_2$SiN$_4$ modifications after structural optimization on the DFT-LDA level.

| Modifications and Space Groups | Cell Parameters | Position of Atoms |
|-------------------------------|----------------|------------------|
| Al$_2$MgO$_4$-spinel-type LDA  | a = 7.76       | Cr 0.000000, 0.000000, 0.000000 |
| Fd-3m                         |                | Si 0.625000, 0.625000, 0.625000 |
| No 227                        |                | N 0.752556, 0.752556, 0.752556 |
| α-Cr$_2$SiN$_4$-type LDA      | a = 5.45 b = 7.80 c = 2.76 | Cr 0.750000, 0.241721, 0.552936 |
| Pma2                          |                | Cr 0.500000, 0.000000, 0.898141 |
| No 28                         |                | Si 0.750000, 0.614777, 0.000000 |
|                               |                | N 0.750000, 0.006165, 0.421951 |
|                               |                | N 0.750000, 0.489793, 0.499478 |
|                               |                | N 0.501351, 0.244258, 0.983987 |
| Na$_2$MnCl$_4$-type LDA       | a = 4.67 b = 8.58 c = 2.69 | Cr 0.432611, 0.175929, 0.500000 |
| Pbam                          |                | Cr 0.490863, 0.639616, 0.502192 |
| No 55                         |                | Si 0.000000, 0.000000, 0.000000 |
|                               |                | N 0.133271, 0.203741, 0.000000 |
|                               |                | N 0.257704, 0.966687, 0.500000 |
| γ-Cr$_2$SiN$_4$-type LDA      | a = 5.56 b = 8.82 c = 5.25 β = 117.96 | Cr 0.499339, 0.356416, 0.521849 |
| Cc                            |                | Cr 0.350127, 0.864148, 0.734578 |
| No 9                          |                | Cr 0.863665, 0.518329, 0.302902 |
|                               |                | Si 0.000000, 0.578114, 0.000000 |
|                               |                | N 0.817340, 0.495466, 0.665199 |
|                               |                | N 0.336682, 0.499101, 0.681972 |
|                               |                | N 0.677149, 0.750383, 0.851076 |
|                               |                | N 0.670732, 0.238989, 0.855745 |
| β-Cr$_2$SiN$_4$-type LDA      | a = 7.18 b = 7.69 c = 2.70 α = 94.01 β = 82.69 γ = 121.02 | Cr 0.352905, 0.668370, 0.167669 |
| P-1                           |                | Cr 0.662487, 0.971411, 0.739846 |
| No 2                          |                | Cr 0.713401, 0.667644, 0.365727 |
|                               |                | N 0.350127, 0.864148, 0.734578 |
|                               |                | N 0.863665, 0.518329, 0.302902 |
| δ-Cr$_2$SiN$_4$-type LDA      | a = 6.14 b = 3.76 c = 5.41 β = 115.88 | Cr 0.148173, 0.750000, 0.246670 |
| P21/m                         |                | Cr 0.610570, 0.750000, 0.913336 |
| No 11                         |                | N 0.638880, 0.250000, 0.419381 |
|                               |                | N 0.142755, 0.250000, 0.721438 |
| Crystal Structure | Space Group | A | B | C | \(a\) | \(b\) | \(c\) | \(\alpha\) | \(\beta\) | \(\gamma\) |
|-------------------|-------------|---|---|---|------|------|------|------|------|------|
| TiMn\(_2\)O\(_4\)-type LDA | P 43 2 2 | N | Cr | Cr | 5.56 | 5.35 | 7.61 | a = 5.56 | c = 7.61 |
| Mg\(_2\)SiO\(_4\)-type LDA | Pnma | Cr | Cr | Si | 9.23 | 5.35 | 4.77 | a = 9.23 | b = 5.35 | c = 4.77 |
| \(\varepsilon\)-Cr\(_2\)SiN\(_4\)-type LDA | P21/m | Cr | Cr | Cr | 5.07 | 2.86 | 8.45 | \(a = 5.07\) | \(b = 2.86\) | \(c = 8.45\) |
| \(\lambda\)-Cr\(_2\)SiN\(_4\)-type LDA | Pm | Cr | Cr | Cr | 4.96 | 2.84 | 8.88 | \(a = 4.96\) | \(b = 2.84\) | \(c = 8.88\) |
| \(\lambda^\prime\)-Cr\(_2\)SiN\(_4\)-type LDA | Pm | Cr | Cr | Cr | 4.99 | 2.82 | 8.84 | \(a = 4.99\) | \(b = 2.82\) | \(c = 8.84\) |
Table A2. The total energy and relative energy values compared to the global minimum (spinel structure taken as the zero of energy) of the energetically most favorable CrSiN modifications found using various search methods and later locally optimized on the ab initio level using the LDA–PZ functional. DM stands for data mining, GO stands for global optimization, and PCAE stands for primitive cell approach for atom exchange methods.

| Modification and Space Group | Search Method | Total Energy (Eh) | Relative Energy (kcal/mol) |
|-----------------------------|---------------|-------------------|----------------------------|
| Al:MgO-spinel-type_LDA      | DM            | −5180.729         | 0.0                        |
| α-CrSiN-type_LDA            | GO            | −5180.694         | 21.963                     |
| Na₂MnCl₂-type_LDA           | DM            | −5180.672         | 35.768                     |
| γ-CrSiN-type_LDA            | PCAE          | −5180.667         | 38.906                     |
| β-CrSiN-type_LDA            | GO            | −5180.653         | 47.691                     |
| δ-CrSiN-type_LDA            | GO            | −5180.653         | 47.691                     |
| TiMnO₂-type_LDA             | DM            | −5180.621         | 67.771                     |
| Mg:SiO₂-type_LDA            | DM            | −5180.620         | 68.399                     |
| ε-CrSiN-type_LDA            | GO            | −5180.615         | 71.536                     |
| λ-CrSiN-type_LDA            | GO            | −5180.606         | 77.184                     |
| λ'-CrSiN-type_LDA           | GO            | −5180.604         | 78.439                     |

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