High-Pressure Chemistry

The First High-Pressure Chromium Oxonitridoborate CrB₄O₆N—an Unexpected Link to Nitridosilicate Chemistry

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Abstract: *CrB_4O_6N crystallizes in the non-centrosymmetric space group $P6_3mc$ (no. 186) with the lattice parameters $a = 5.1036(1)$, $c = 8.3519(3)$ Å, and a volume of $188.40(1)$ Å³. It was synthesized in a high-pressure/high-temperature experiment at 7 GPa and 1673 K and represents the first high-pressure oxonitridoborate. It is built up of starlike-shaped entities of four BO_3N tetrahedra, connected via one common nitrogen atom that resembles the fourfold-coordinated nitrogen atoms in the homeotypic nitridosilicates $MYbSi_4N_7$ ($M = Sr, Ba$). Building up a network with channels that contain the Cr^{3+} ions, CrB_4O_6N contains for the first time a tetrahedral building unit in contrast to trigonal planar $B(O/N)_3$ entities in all other known oxonitridoborates. The structural relations as well as the results of spectroscopic measurements and calculations on the chromium oxonitridoborate are discussed.*

Introduction

Through the application of high-pressure conditions during the syntheses of solid state materials, it is possible to accomplish new crystal structures and structural motifs that are often unknown and in most cases not accessible under ambient pressure conditions. Over the past two decades, a main aspect of our research has been the high-pressure synthesis of new borate materials. Astounding results in this field could be discovered, for example, the structural motif of edge-sharing BO_4 tetrahedra in centrosymmetric $Dy_4B_6O_{15}$[1] and non-centrosymmetric $La_3B_6O_{13}(OH)$,[2] the discovery of an synthetic access to the substance class of

ammine borates ($Cd(NH_3)_2[B_3O_5(NH_3)]_2$),[3] or unexpected Mo_4-clusters in the borate framework of $Mo_2B_4O_9$.[4]

Especially in the field of transition metal borates, a broad variety of new structures could be achieved. An excellent review of the newest developments with a special view on optical properties can be found in ref. [5]. Concerning the transition metal borates of the fourth period of the periodic table, there is only one element, from which no high-pressure borate is known up to now: chromium. There exist two ambient pressure chromium borates, the orthoborate $CrBO_3$[6] with calcite type structure and Cr_3BO_6[7] with norbergite structure. Herein, we report the synthesis of the new chromium oxonitridoborate CrB_4O_6N, which represents only the fourth existing oxonitridoborate and the first one synthesized under high pressure. The other known oxonitridoborates to date are $Sr_3(B_3O_3N_3)$,[8] $Eu_5(BO_{2.51}N_{0.49})_4$,[9] and $La_3(OBN_2)O_2$,[10] containing $[B_3O_3N_3]^{6-}$ rings, mixed O/N sites, and BON_2 units, respectively. All of these compounds require relatively complex starting materials such as imides and amides, and reaction times of several days. Additionally, an intricate setup is necessary, to ensure the exclusion of water or air during the syntheses of these oxonitridoborates. In contrast, the here presented chromium oxonitridoborate CrB_4O_6N can be obtained by using simple starting materials, such as nitrates, nitrides, and oxides like $Cr(NO_3)_3 \cdot 9H_2O$, h-BN, and B_2O_3 that can be handled under ambient conditions. In combination with a high-pressure/high-temperature approach, this synthetic strategy enables the introduction of nitrogen into a boron oxygen network.

In the past, the application of extreme synthetic conditions on borate systems already showed that new compositions homeotypic to silicate minerals could be enabled through the application of extreme high-pressure/high-temperature conditions in the sense of the boron/silicon diagonal relationship. E.g., the compounds $M_3B_5O_{12}$ ($M = Sc$, In, Er–Lu) crystallize in the structure type of the beryllosilicate semenovite,[11] the compounds β-MB_2O_5 ($M = Zr$, Hf) exhibit structures analogous to the gadolinite-group,[12] and $Sc_{1.67}B_3O_7$ represents the first ternary melilite-type compound.[13] For the new oxonitridoborate CrB_4O_6N, we found that it is homeotypic to the ambient pressure nitridosilicates $MYbSi_4N_7$ ($M =$ Ba, Sr, Eu),[14] which crystallize in the $NaBe_4SbO_7$ (swendenborgite)[15] structure type. In the literature, these nitridosilicates constitute the first representatives of a central fourfold coordinated nitrogen atom $N^{[4]}$, bridging four silicon atoms. The Si-N-network forms six-membered rings along [100] in which the respective alkaline earth cations (Sr^{2+}/Ba^{2+}) and Yb^{3+} cations are located. In contrast to $MYbSi_4N_7$ ($M = Sr$, Ba, Eu), the new oxonitridoborate only features chromium

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cations that occupy the ytterbium position, thus leaving the position of Sr^{2+}/Ba^{2+} vacant. Later on, additional nitridosilicate representatives of this structure type were found.[16] A fourfold connected carbon atom $C^{[4]}$, similar to the central nitrogen atom of the starlike-shaped entities, can be found in the isostructural phases $RE_2Si_4N_6C$ (RE = Y, La, Tb, Ho)[17] and $YScSi_4N_6C$.[18] Examples of oxonitridosilicates of this structure type could not be found up to now. Porob et al.[19] claimed the existence of both oxygen and nitrogen in $SrScSi_4(O,N)_7$ due to the blue shift of the Eu^{2+} activated material in comparison to the isostructural nitride phosphor. However, the successful insertion of oxygen into this framework is possible with simultaneous substitution of silicon by aluminum, as presented for example in the sialons (oxonitridoalumosilicates) $MLnSi_{4-x}Al_xO_xN_{1-x}$ (M = Sr, Ba, Eu; Ln = Ho-Yb)[20] and $SrYSi_{4-x}Al_xO_xN_{1-x}$.[21] Within these compounds, the Al atoms are distributed statistically on the Si sites, while O atoms are only found on the twofold bridging sites, not on the fourfold connected position. In the following work, we will present a detailed structural description of the new chromium oxonitridoborate, also in comparison to the aforementioned nitridosilicates, and the results of vibrational spectroscopy, second-harmonic generation measurements as well as band structure calculations.

Results and Discussion

The title compound CrB_4O_6N crystallizes in the hexagonal space group $P6_3mc$ (no. 186) with the lattice parameters a = 5.1036(1) and c = 8.3519(3) Å with two formula units per cell (Z = 2). All relevant data on the structure refinement is presented in Table 1, the positional and the displacement parameters can be seen in Tables S1 and S2, respectively.[22]

The structure is built up of starlike-shaped entities of four BO_3N tetrahedra that are connected via the common nitrogen atom N1 (Figure 1a). In detail, the nitrogen atom links three tetrahedra with the central boron atom B1 and one tetrahedron with the central boron atom B2 (dark and light blue tetrahedra in Figures 1 to 4, respectively). Through the connection of these $[N(BO_3)_4]$ building blocks, the $B1O_3N$ tetrahedra form layers of three- and six-membered rings (Figure 1b,c) in the ab-plane.

The chromium cations Cr^{3+} are located in these six-membered rings being octahedrally coordinated by oxygen atoms (Figure 2). The Cr-O distances are 1.948(2) and 1.947(2) Å to the oxygen atoms O1 and O2, respectively, with an average value of 1.9475 Å. This is in good agreement with the other two known chromium borates $CrBO_3$ (Cr-O: 1.996 Å)[6] and Cr_3BO_6 (Cr-O: 1.867–2.083 Å),[7] where the chromium cations are also coordinated by six oxygen atoms. The mean octahedral angles of 90.0° and 179.5° are in agreement with the expected ideal values.

The B−N bond lengths are significantly longer (1.608(3) Å and 1.570(6) Å) than in the other known oxonitridoborates,[8–10] but CrB_4O_6N also has an increased coordination number of the boron atoms in comparison to these compounds. A better comparison of these BO_3N tetrahedra can be drawn to B-N distances for also tetrahedrally coordinated

Table 1: Crystal data and structure refinement of CrB_4O_6N.

| Empirical formula	CrB_4O_6N
Molar mass, $g\,mol^{-1}$	205.25
Crystal system	hexagonal
Space group	$P6_3mc$ (no. 186)
Single-crystal data	
T, K	276(2)
Radiation	Mo-K_α (λ = 0.7107 Å)
a, Å	5.1036(1)
c, Å	8.3519(3)
V, Å^3	188.40(1)
Z	2
Calculated density, $g\,cm^{-3}$	3.618
Absorption coeff., mm^{-1}	2.995
$F(000)$, e	198
Crystal size, mm^3	$0.030 \times 0.030 \times 0.020$
θ range, deg	4.61–39.32
Index ranges	$-9 \leq h \leq 9, -9 \leq k \leq 9, -14 \leq l \leq 14$
Reflections collected	16397
Independent reflections	470
R_{int}/ R_σ	0.0502/ 0.0142
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	470/0/28
Goodness-of-fit on F^2	1.286
Final $R1$/ $wR2$ indices [$I \geq 2\sigma(I)$]	0.0168/ 0.0479
Final $R1$/ $wR2$ indices (all data)	0.0192/ 0.0488
Largest diff. peak/ hole, $e\text{Å}^{-3}$	0.37/ −0.61
Flack parameter	0.003(11)
Powder-diffraction data	
Radiation; wavelength λ, Å	Mo-$K_{\alpha1}$; 0.7093
a, Å	5.1068(2)
c, Å	8.3575(5)
V, Å^3	188.76(2)
2θ range, deg	2.0–42.0
2θ step width, deg	0.015
R_{exp}, %	3.23
R_{wp}, %	7.93
R_p, %	4.83
Goodness-of-fit	2.46

boron in cubic BN (1.565 Å),[23] and the ammine borate $Cd(NH_3)_2[B_3O_5(NH_3)]_2$ (1.605 Å).[3]

To further verify the crystal structure solution and the oxidation states, BL/BS (bond-length/bond-strength; ΣV)[24] and CHARDI (Charge distribution; ΣQ)[25] calculations have been performed. The results are listed in Table 2 and correspond well with the expected values of + 3 for chromium and boron, −2 for oxygen, and −3 for nitrogen. Especially the results of the CHARDI concept fit very well, with a deviation for the cations of only 0.2 % and 0.5 % for the anions. Furthermore, MAPLE calculations (*Ma*delung *P*art of *L*attice *E*nergy)[26] were performed on CrB_4O_6N, and compared to the result from the theoretical values of the binary starting materials CrN[27] and the high-pressure modification B_2O_3-II.[28]

Due to the additive potential of MAPLE values, a hypothetical value for CrB_4O_6N can be calculated. As a result, a lattice energy of 54701 $kJ\,mol^{-1}$ was obtained for the product in comparison to the calculated value of 54362 $kJ\,mol^{-1}$ starting from the binary components (CrN
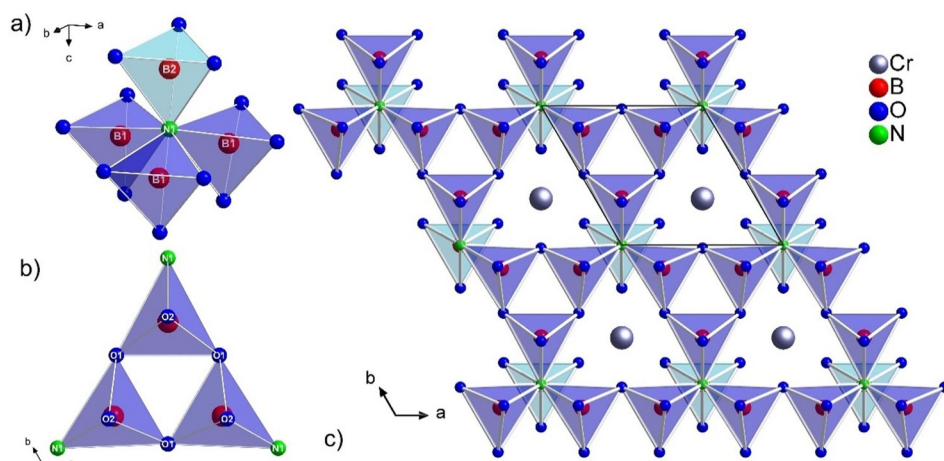
Figure 1. a) Fourfold connection of the N1 atoms. b) Three-membered ring of BO$_3$N tetrahedra, all pointing towards the direction [00$\bar{1}$]. c) The anionic oxonitridoborate structure of CrB$_4$O$_6$N consists of layers of three- and six-membered rings, that are formed by three [N(BO$_3$)$_4$] building blocks each. One layer is pictured here onto the *ab*-plane.
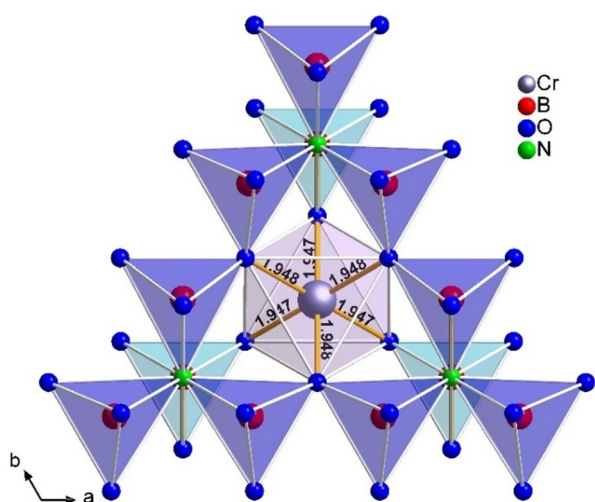
Figure 2. Octahedrally coordinated chromium cation Cr^{3+} in the middle of a six-membered ring of BO$_3$N tetrahedra. Cr-O distances in Å.

Table 2: Bond valence sums and charge distribution according to the bond-length/bond-strength (ΣV) as well as the CHARDI (ΣQ) concept, respectively.

	Cr1	B1	B2	O1	O2	N1
ΣV	+3.28	+2.94	+3.09	−2.06	−2.08	−2.83
ΣQ	+3.00	+3.00	+3.01	−2.01	−1.99	−3.00

(10486 kJ mol^{-1}) + 2 B$_2$O$_3$-II (2 × 21938 kJ mol^{-1}); deviation: 0.62 %).

The elucidation of the source of the nitrogen atoms in CrB$_4$O$_6$N was a real challenge. The first option is the chromium nitrate used as starting material, the second option is the crucible material h-BN. Up to this point, all contributions in the literature and our own work shows that the application of nitrates in combination with boron exclusively leads to borate nitrates in which isolated NO$_3$

groups exist next to a varying borate framework.[29] Most of these compounds were synthesized in autoclaves under slightly increased pressure conditions. In this context, a new borate nitrate was recently synthesized at a reasonably low pressure of 3 GPa.[30] Thus, from our experimental experience the reaction of nitrates and borates results exclusively in borate nitrates. Further experiments showed that it was not possible to reproduce CrB$_4$O$_6$N by only using Cr(NO$_3$)$_3$·9 H$_2$O and B$_2$O$_3$ in a platinum capsule, where no contact to h-BN was given. The initial experiment and seven reproduction experiments were only successful by using Cr(NO$_3$)$_3$·9 H$_2$O and B$_2$O$_3$ as starting materials inside a crucible made of h-BN. This leads to the conclusion that the contact to the crucible material h-BN is crucial for the formation of the title compound CrB$_4$O$_6$N, so the nitrogen atoms definitely stem from the h-BN. Self-evidently, experiments were performed in which h-BN was added to the educt mixture inside of a platinum capsule. Interestingly, these experiments led to a completely different product mixture consisting of CrO$_2$ and a yet unidentified new byproduct.

Surprisingly, the structure of the new chromium oxonitridoborate CrB$_4$O$_6$N is closely related to the nitridosilicates *M*YbSi$_4$N$_7$ (*M* = Sr, Ba, Eu),[14] which were synthesized at ambient pressure in a HF-furnace. These nitridosilicates are built up of [N(SiN$_3$)$_4$] building blocks, similar to the [N(BO$_3$)$_4$] entities in CrB$_4$O$_6$N and were the first compounds to feature nitrogen atoms coordinated to four silicon atoms. The linkage of these building blocks leads to a network of three- and six-membered rings where, in comparison to CrB$_4$O$_6$N, the silicon and nitrogen atoms occupy the positions of the boron and oxygen atoms, respectively. The ytterbium cations are octahedrally coordinated by nitrogen and located in the six-membered rings along [001] on the same positions as the chromium cations. As there is no analog to the alkaline earth cations Sr^{2+}/Ba^{2+}, these positions remain vacant in the oxonitridoborate (see Figure 3 and Table S5 for the comparison with BaYbSi$_4$N$_7$). The structure type of the nitridosilicates, NaBe$_4$SbO$_7$ (swendenborgite),[15] also occurs as other substitution variants like BaLuAlZn$_3$O$_7$,[31] where the silicon position is statistically occupied by Al^{3+} and Zn^{2+}. In all these compounds, there are two metal cations incorporated into the anionic network. In contrast, there is only one species (Cr^{3+}) inside the six-membered rings of the presented CrB$_4$O$_6$N, leaving the other 2*b* site vacant for the first time in this structure family.

Figure 4 shows the Rietveld refinement of a CrB$_4$O$_6$N sample. The experimental powder diffraction data is in good agreement with the values derived from the single-crystal structure refinement (see Table 1). Additional reflections
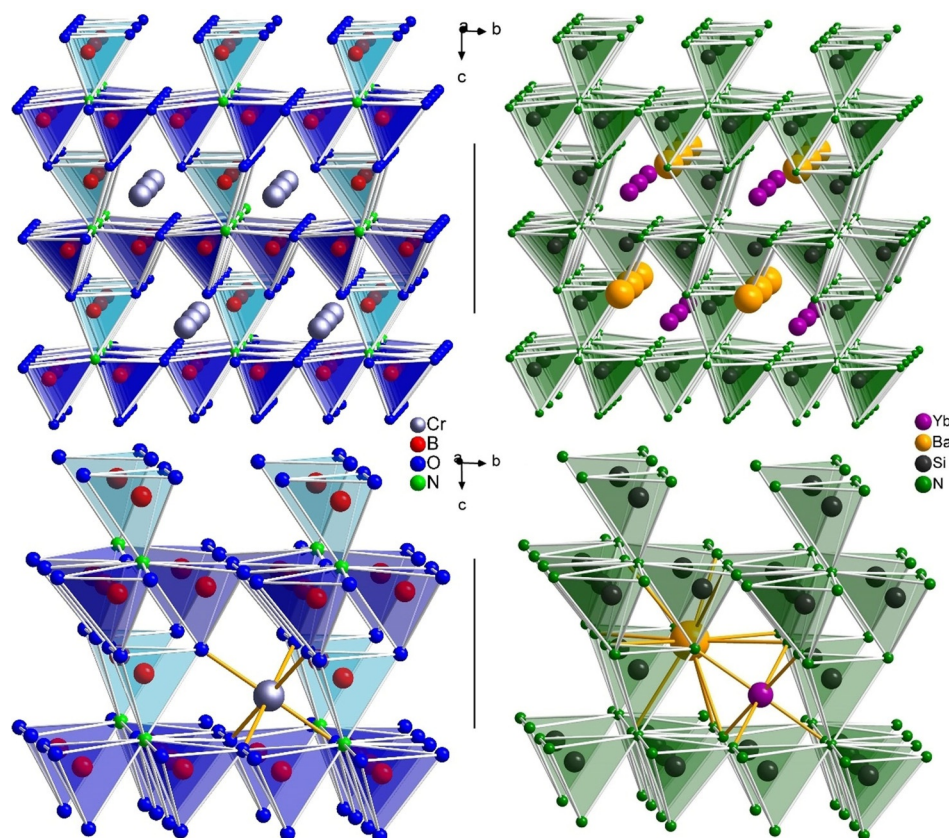
Figure 3. Comparison of CrB₄O₆N (left) and BaYbSi₄N₇ (right). Top: Structures with channels running along [1̄00]. Bottom: Coordination of the different cations inside the channels.
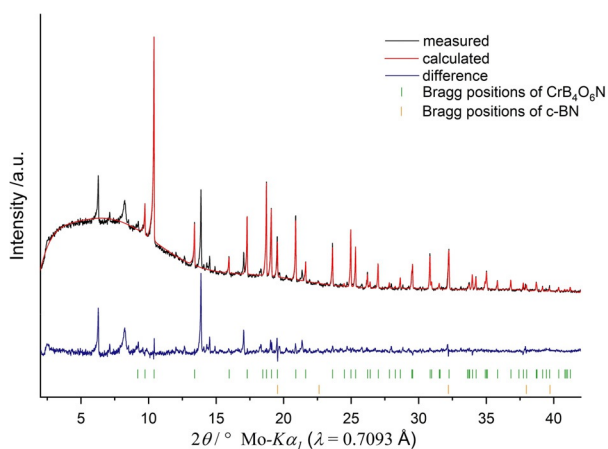
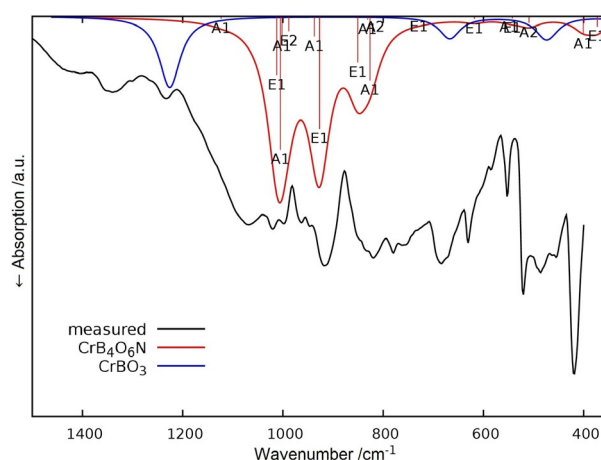***Figure 4.*** Rietveld refinement of a CrB₄O₆N sample containing a small amount of c-BN and an unknown side phase.

Figure 5. FTIR-ATR spectrum of a CrB₄O₆N powder-sample with CrBO₃ as a by-product in comparison with the calculated spectra.

could be assigned to residual c-BN (fraction of 12.5%) from the crucible and a not yet identified byproduct. The halo at low 2θ angles most likely originates from excess B_2O_3.

SHG (second-harmonic generation) measurements were performed on a powder-sample to prove the non-centrosymmetric space group. CrB_4O_6N yielded a SHG intensity of 41.2(20.1) mV, approximately 82% of the intensity of the quartz reference (see Table S6).

The IR spectrum of a powder-sample containing CrB_4O_6N as well as $CrBO_3$ in the spectral range of 400 to 1500 cm^{-1} is

shown in Figure 5. The measured spectrum is in good agreement with the calculated signals for the two compounds. Like in the homeotypic nitridosilicates $M\mathrm{YbSi_4N_7}$ ($M = \mathrm{Ba}$, Sr, Eu),[32] the most prominent signals can be found in the range between 800 and 1000 cm^{-1} with the strongest A1-Mode at ≈ 1000 cm^{-1}.

The electronic and phonon band structures of CrB_4O_6N were calculated using DFT methods. Structure relaxations with the PBEsol functional gives the best agreement with the

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experimental parameters with deviations as small as 0.2% (Table S7). Calculated band gaps are ≈2 eV using PBE and ≈1.65 eV using SCAN functionals. Magnetism reduces the total energy significantly by about 160 kJ mol⁻¹, while the difference between the ferro- and antiferromagnetic magnetic models is very small. The magnetic moments integrated in the Wigner-Seitz sphere are 2.8–2.9 μ_B/Cr in agreement with the expected 3 μ_B for Cr^{3+} (Table S8). Figure 6 shows the electronic band structure and the atom-projected density-of-states. Direct and indirect band gaps are almost identical (Table S7) and occur between the occupied and unoccupied parts of the Cr 3*d*-bands (Figure 6) with small contributions of oxygen and boron states. The phonon dispersions (Figure S4) reveal neither anomalies nor any imaginary modes, which confirms the mechanical stability of CrB_4O_6N.
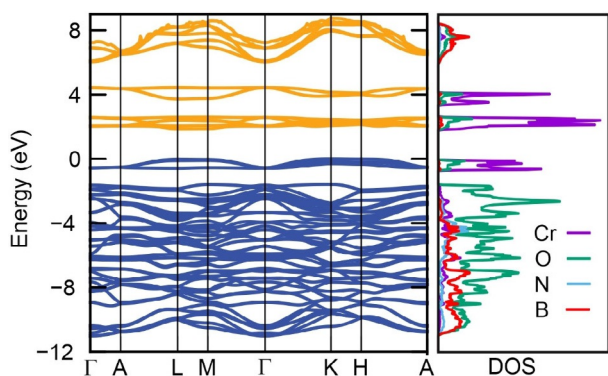
Figure 6. Electronic band structure of CrB_4O_6N with atom-projected DOS.

Conclusion

CrB_4O_6N represents the first high-pressure oxonitridoborate to date. Synthesized at 7 GPa and 1623 K, it comprises building blocks of four BO_3N tetrahedra that share one common corner, leading to a fourfold coordinated nitrogen atom. This structural unit is found in this class of compounds for the first time, the other three known oxonitridoborates only feature trigonal planar BON_2 groups that occur as isolated units or as $B_3O_3N_3$ rings. Additionally, CrB_4O_6N is homeotypic to MYbSi$_4$N$_7$ (M = Sr, Ba, Eu), the first nitridosilicates to feature fourfold coordinated nitrogen atoms.

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Conflict of Interest

The authors declare no conflict of interest.

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