RESEARCH ARTICLE

High-pressure Synthesis of Cobalt Polynitrides: Unveiling Intriguing Crystal Structures and Nitridation Behavior

Huawei Chen[a,b]*, Maxim Bykov[c], Iskander G. Batyrev[d], Lukas Brüning[e], Elena Bykova[f], Mohammad F. Mahmood[a], Stella Chariton[g], Vitali B. Prakapenka[g], Timofey Fedotenko[h], Hanns-Peter Liermann[h], Konstantin Glazyrin[h], Andrew Steele[b], Alexander F. Goncharov[b *)]

[a] Dr. H. Chen, Dr. M. Mahmood
Department of Mathematics
Howard University, Washington DC 20059 U.S.A.
E-mail: hchen10@carnegiescience.edu

[b] Dr. H. Chen, Dr. A. F. Goncharov, Dr. A. Steele
The Earth and Planets Laboratory
Carnegie Institution for Science. Washington DC, 20015, U.S.A.

[c] Dr. M. Bykov
Institute of Inorganic and Analytical Chemistry,
Goethe University Frankfurt, Max-von-Laue-Straße 7, 60438 Frankfurt am Main, Germany

[d] Dr. I. G. Batyrev
U.S. Army Research Laboratory
RDRLWML-B Aberdeen Proving Ground, Maryland, 21005 U.S.A.

[e] Dr. L. Brüning
Institute of Inorganic Chemistry
University of Cologne, Greinstrasse, 50939 Cologne, Germany.

[f] Dr. E. Bykova
Institute of Geosciences,
Goethe University Frankfurt, Altenhöferallee 1, 60438 Frankfurt am Main, Germany

[g] Dr. S. Chariton, Dr. V. B. Prakapenka
Center for Advanced Radiation Sources
University of Chicago, Argonne, IL 60439, U.S.A.

[h] Dr. T. Fedotenko, Dr. H. Liermann, Dr. K. Glazyrin.
Deutsches Elektronene-Synchrotron DESY
Notkestr. 85, 22607 Hamburg, Germany.

Supporting information for this article is given via a link at the end of the document.

*) Corresponding author (email: agoncharov@carnegiescience.edu)

Abstract In this study, we conduct extensive high-pressure experiments to investigate phase stability in the cobalt-nitrogen system. Through a combination of synthesis in a laser-heated diamond anvil cell, first-principles calculations, Raman spectroscopy, and single-crystal X-ray diffraction, we establish the stability fields of known high-pressure phases, hexagonal NiAs-type CoN, and marcasite-type CoN_2 within the pressure range of 50-90 GPa. We synthesize and characterize previously unknown nitrides, Co_3N_2, *Pnma*-CoN and two polynitrides, CoN_3 and CoN_5, within the pressure range of 90-120 GPa. Both polynitrides exhibit novel types of polymeric nitrogen chains and networks. CoN_3 feature branched-type nitrogen trimers (N_3) and CoN_5 show π-bonded nitrogen chain. As the nitrogen content in the cobalt nitride increases, the CoN_6 polyhedral frameworks transit from face-sharing (in CoN) to edge-sharing (in CoN_2 and CoN_3), and finally to isolated (in CoN_5). Our study provides insights into the intricate interplay between structure evolution, bonding arrangements, and high-pressure synthesis in polynitrides, expanding the knowledge for the development of advanced energy materials

Introduction

Polynitrides are a class of compounds containing structural units, exhibiting nitrogen-nitrogen bonds, including azides, diazenides, pentazolates, etc.[1–3] These compounds have recently undergone extensive investigation through high-pressure experiments, where they were synthesized in laser-heated diamond anvil cells.[1–7] Transition metal pernitrides (e.g. PtN_2, ReN_2, OsN_2) containing N-N dimers are recognized for their high bulk modulus and potential applications as superhard materials.[1,8,9] Polynitrides containing polymeric nitrogen chains (such as FeN_4,[2] TaN_5,[10] MgN_4,[11] WN_{10},[12] YN_6[13]) represent higher levels of nitridation. More recently, experimental studies have uncovered nitrogen rings including pentazolates (N_5^-), hexazine anions N_6^{x-} and N_{18}.[3,13,14,15]

The presence of dimers, chains, and rings in polynitrides can contribute to their potential usage as high-energy density material,[15,16] because converting singly or doubly bonded nitrogen to triple-bonded nitrogen can release a substantial

amount of energy. Therefore, there has been an active pursuit of the synthesis and prediction of polynitrides as prospective high-energy density materials.[2,3,6,16]

Cobalt nitrides have emerged as promising candidates for potential polynitride with higher energy density.[17] Several cobalt nitrides were experimentally identified, such as Co_2N,[18,19] Co_3N,[20] Co_4N,[20] CoN,[5] and CoN_2.[5] The cobalt nitrogen system had been investigated in comparison with the iron nitrogen system.[5] These two chemical systems share similarities, as both iron and cobalt pernitride exhibit a marcasite-type structure.[2,5,21] Additionally, both FeN and CoN undergo a transition from a ZnS-type structure to a NiAs-type structure at higher pressures.[5] Iron nitrides start to form polynitride anions $[N_4^{2-}]_n$ at 106 GPa.[2] However, it is currently unknown whether similar behavior occurred in cobalt nitrides at high pressure, approximately 100 GPa.

Understanding the nitridation path for transition metals might greatly help develop nitrogen-based materials at high pressure.[21,22] While there was not a single universal nitridation path applicable to all transition metals, first-principle calculation reported the progressive nitridation trend for transition metals.[17,23] Numerous experimental studies had demonstrated a wealth of polymorphs of transition metal nitrides at different pressure and temperature conditions.[4,6,21,22] However, to uncover the nitridation path, the nitridation behavior of transition metals at high-pressure needs to be explored.

Results and Discussion

We conducted the synthesis of cobalt nitride starting from metallic cobalt and nitrogen in diamond anvil cells. In our typical experimental procedure, we initially compressed the sample in the diamond anvil cell to the desired pressure. Subsequently, we employed an infrared laser, coupled with cobalt metal to heat the sample to temperatures ranging from 1700-2200 K. We investigated their structure and composition using synchrotron X-ray diffraction (XRD) and Raman spectroscopy. The experiments are summarized in Table 1.

Laser heating at pressures between 50-90 GPa resulted in the formation of two known high-pressure phases: hexagonal NiAs-type CoN and marcasite-type CoN_2[5] (Figure 1a, 1d, and S1). Additionally, we identified *Pnma*-Co_3N_2, *Pnma*-CoN, CoN_3, and CoN_5 in the Co-N system from 90-120 GPa (Figures 1b, 1c, 1e, 1f, S2, and S3). To obtain more comprehensive and detailed information on these crystals, we employed single-crystal XRD techniques (see Supporting information) together with powder diffraction and Raman spectroscopy to identify the crystal structures and composition of all phases.

Table 1. Experimental runs

P(GPa)[a]	T(K)[b]	Beamline	Results	Structures and Composition[c]
97(5)	2200(200)	Petra III	CoN_3+CoN_5+CoN+Co_3N_2	*Pnma*-CoN_3
				*C*2/*c*-CoN_5
58(3)	1850(150)	GSECARS	CoN_2+CoN	*P*6$_3$/*mmc*-CoN
67(4)	1760(200)	GSECARS	CoN_2+CoN	*Pnnm*-CoN_2
117(6)	2460(300)	Petra III	CoN+Co_3N_2+CoN_3+CoN_5	*Pnma*-CoN
				Pnma-Co_3N_2

[a] P (Pressure), [b] T (Temperature), Starting materials: Cobalt and Nitrogen. [c] We included the crystal structures deposited in CCDC (Cambridge Crystallographic Data Centre).[24] Deposition numbers are CSD 2325509 (for *Pnma*-Co_3N_2), 2325510 (*P*6$_3$/*mmc*-CoN), 2325511 (for *Pnma*-CoN), 2308801(Marcasite-type CoN_2), 2325513 (for *Pnma*-CoN_3), 2325514 (for *C2c*-CoN5).

The crystal structure of NiAs-type CoN is shown in Figure 2b, which can be described as a hexagonal cell with the space group *P*6$_3$/*mmc*. At a pressure of 55 GPa, the unit cell parameters are *a* = 2.726(2) Å and *c* = 4.713(2) Å. Detailed crystal information from single-crystal diffraction can be found in Table S1. In the NiAs-type CoN structure, the coordination number for cobalt is 6. The CoN_6 octahedra share faces in the NiAs-type structure. There is no close N-N bonding (typical bond lengths <1.5 Å) observed in the NiAs-type CoN. At higher pressure (110 GPa), we found *Pnma*-type CoN (Figure 2c), which is a distorted NiAs-type structure (see Table S2). The *Pnma*-type structure was documented in FeN as the higher pressure form.[23]

The marcasite-type structure of CoN_2, initially reported using powder diffraction[5], is depicted in Figure 2d. The peaks observed in single-crystal diffraction can be indexed to the *Pnnm* space group (Figure 1a). At a pressure of 67 GPa, the unit cell parameters are determined as *a*=4.307(6) Å, *b*=3.597(3) Å, and *c*=2.445(8) Å. Atomic parameters for CoN_2 can be found in Table S3. The crystal structure of CoN_2, shown in Figure 2d, exhibits a marcasite-type structure within the pressure range of 50-90 GPa. In this structure, the coordination number of cobalt is 6. Edge-sharing octahedra form infinite chains along the *z*-axis. Two adjacent octahedra between two chains are closely positioned. The nearest nitrogen-nitrogen distance in CoN_2 is 1.27(2) Å, which indicates a double nitrogen-nitrogen bond, as is known in diazenides.[25,26]

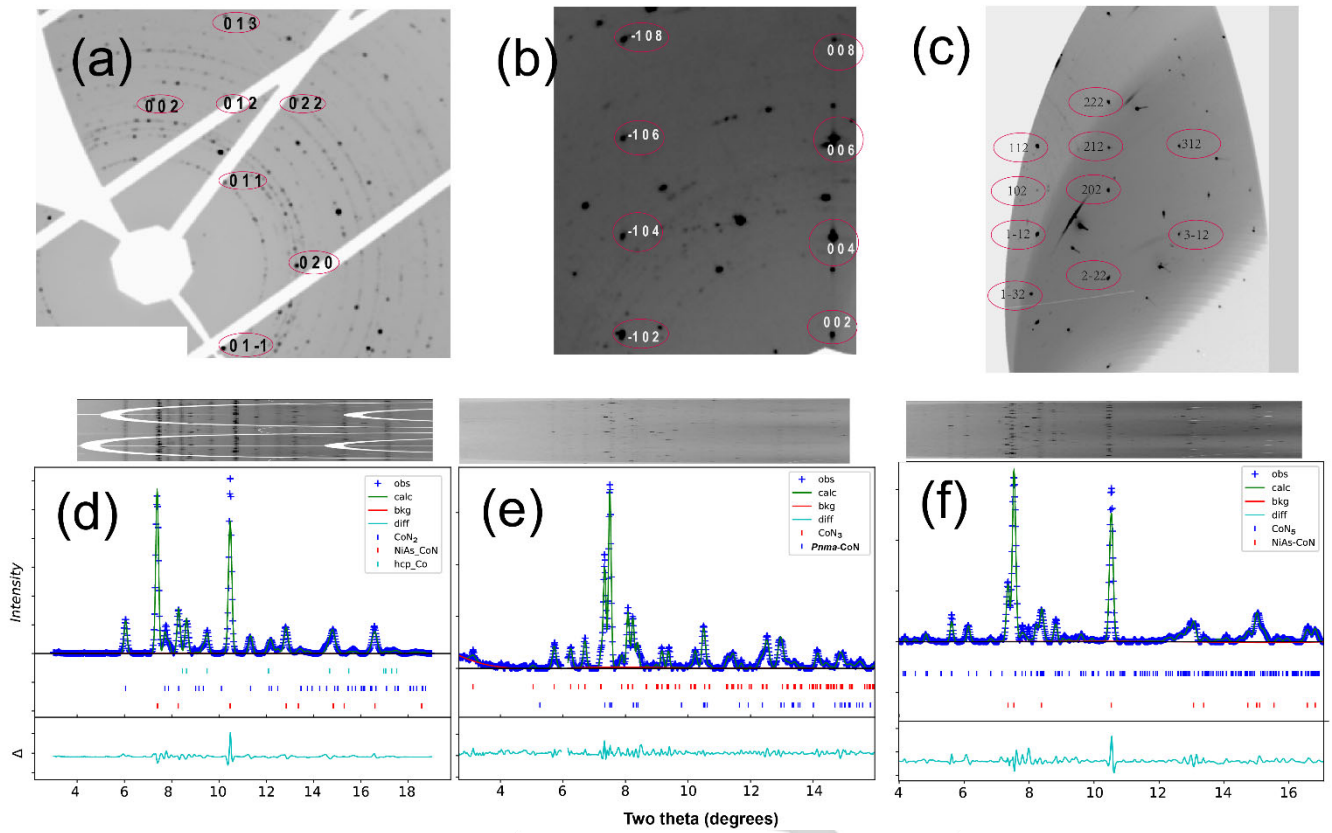

Figure 1. XRD data in the Co-N system at high pressures. (a) Indexation of marcasite-type CoN_2 from the unwarped single-crystal diffraction image at 67 GPa. (b) Indexation of CoN_3 from the unwarped single-crystal diffraction images at 120 GPa. (c) Indexation of CoN_5 from the unwarped single-crystal diffraction images at 120 GPa. (d) Rietveld refinements of powder diffraction patterns collected at 67 GPa, Calculated diffraction lines for the marcasite-type CoN_2 (blue ticks), NiAs-type CoN (red ticks), and *hcp*-Co are shown in figures. The X-ray wavelength λ=0.2952 Å, residue for refinement Rwp=9% (e) Rietveld refinements of powder diffraction patterns collected at 120 GPa, calculated diffraction lines for *Pnma*-type CoN (blue ticks) and CoN_3 (red ticks) are exhibited in the figure, The X-ray wavelength λ=0.2905 Å, Rwp=12%. (f) Rietveld refinements of powder diffraction patterns collected at 120 GPa, calculated diffraction lines for NiAs-type CoN (red ticks) and CoN_5 (blue ticks) are exhibited in the figure, X-ray wavelength λ=0.2900 Å, Rwp=15%. The Miller index for single crystal diffraction spots is shown in red circles in (a, b, and c) Unrolled projection for 2D powder diffraction images were shown on top of d, e and f.

We discovered Co_3N_2 at a pressure range from 90-120 GPa. The Co_3N_2 has an orthorhombic structure with the space group *Pnma*. The lattice parameters at 120 GPa for Co_3N_2 are *a*=5.228(2) Å, *b*=2.523(5) Å and *c*=9.972(5) Å (Table S4). The cobalt atoms in Co_3N_2 have a coordination number of 4-5. A similar Fe_3N_2 had been documented in Fe-N system.[2]

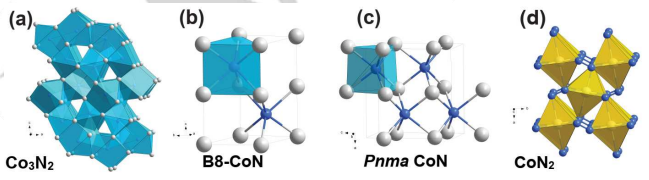

Figure 2. Crystal structures of Co_3N_2 (a), NiAs-type (B8) CoN (b), *Pnma*-CoN(c), marcasite-type CoN_2 (d). Yellow polyhedra represents Co-N framework. Blue polyhedral represent N-Co framework. The closely bonded nitrogen atoms are connected by blue lines in (d).

We discover two new cobalt polynitride compounds CoN_3 and CoN_5, within the pressure range of 90-120 GPa, the structures of which do not correspond to any existing cobalt nitride or known nitrogen phases at high pressure (Figures 3 and 4). The crystal structure of the new compound CoN_3 has an orthorhombic symmetry (space group *Pnma*), with the following unit cell parameters: *a* = 2.555(7) Å, *b* = 3.463(2) Å, and *c* = 10.655(5) Å at 100 GPa. Structure solution and refinement revealed the chemical formula CoN_3 (detailed crystal structure information is provided in the Table S5). Based on 2D- XRD images (Fig. 1b), the structure might contain certain amount of structure disorder at high pressure. One symmetry-independent Co as well as three N atoms occupy the Wyckoff sites 4*e*. Similar to CoN_2, the cobalt atom is octahedrally coordinated by six nitrogen atoms in a slightly distorted CoN_6 octahedron (Figure 3). The CoN_6 octahedra are interconnected by sharing edges along the *a*-axis, forming infinite chains. These chains are interconnected through vertices forming a zig-zag pattern along the *b*-axis. Nitrogen atoms form an unprecedented arrangement (Figure 3). N1, N2, N3 atoms form bent N_3 units (N2-N3-N1 angle of 110.5(9)°). These N_3 units are interconnected by longer N1-N1 bonds into infinite chains along the *a*-axis. The bond distances in the N_3 units are 1.284(17) Å (N1-N3) and 1.358(13) Å (N3-N2), which are typical for covalent N-N bonds. The inter-N_3 distances of 1.66(3)-1.70(2) Å are significantly longer than typical covalently bonded nitrogen atoms in polynitrides, manifesting that CoN_3 is a unique compound

featuring the intermediate state between a polynitride with oligomeric units (bent N_3) and a polymeric branched chain (like in TaN_5[10]). The calculated isosurfaces of electron localization function (ELF) in Figure S8, which support the N3-N3 bonding at 112 GPa. However, the unusual N-N bonding will disappear during decompression.

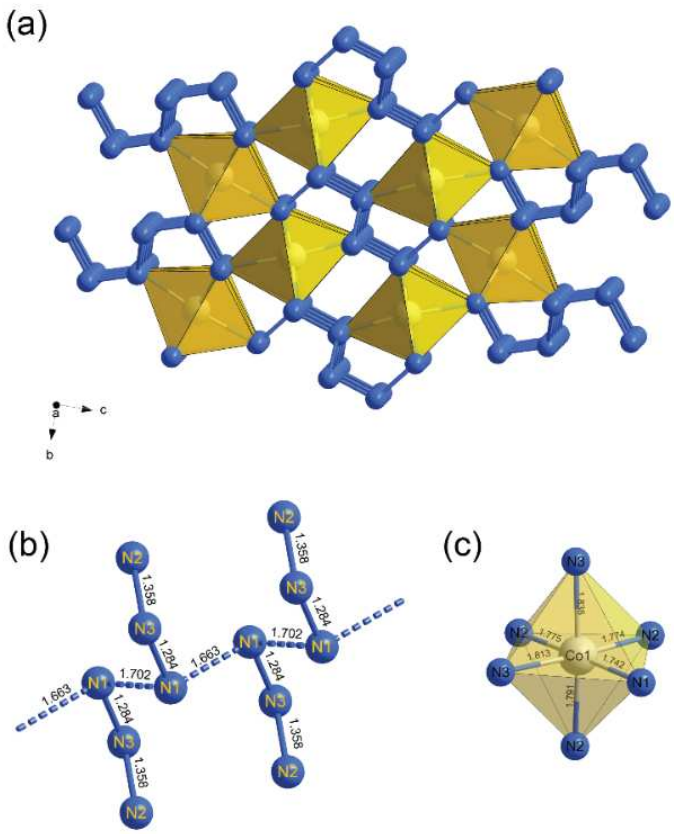

Figure 3. Crystal structure of CoN_3 at 100 GPa. CoN_6 polyhedra are shown by yellow octahedra in (a) and (c). N-N covalent bonds are depicted by solid blue lines while longer N-N bonds are shown by dotted lines in (b).

The crystal structure of CoN_5 has a monoclinic symmetry (space group *C*2/*c*), with the unit cell parameters: *a*=4.951(5) Å, *b*=6.910(8) Å, *c*=8.062(6) Å, *β*=95.77(5)°. Single-crystal diffraction is used to determine the crystal structure (Table S6). In the crystal structure (Figure 4), a single symmetry independent Co atom and five nitrogen atoms occupy Wyckoff sites 8*f*. The cobalt atom maintains its six-fold coordination, located in the distorted CoN_6 octahedra (Figure 4d). These octahedra do not share common vertices, edges or faces, but are interconnected through polymeric nitrogen chains (Figure 2e). Despite the apparent simplicity of the non-branched polymeric nitrogen chain, crystal chemical analysis shows that the shortest repeating unit consists of 10 nitrogen atoms [-N1-N2-N3-N4-N5-N5-N4-N3-N2-N1-] (Figure 4d). Within the chains, all atoms except N3 have three-fold coordination by one Co and two N atoms, manifesting sp^2 hybridization. The N3 atom is tetrahedrally coordinated by two Co and two N atoms, suggesting sp^3 hybridization of these atoms. Therefore, N3-N2 and N3-N4 bonds are of single character, which is in agreement with refined interatomic distances (1.366(2) and 1.372(4) Å, respectively). These distances are in good agreement with those in single-bonded N polymorphs (*bp*-N and *cg*-N).[27,28] The sp^2 hybridization of N1, N2, N4 and N5 atoms suggest that there exist an extended π-system in cis- and trans-tetrazene fragments (N4-N5-N5-N4 and N2-N1-N1-N2, respectively (Figure 4d)).

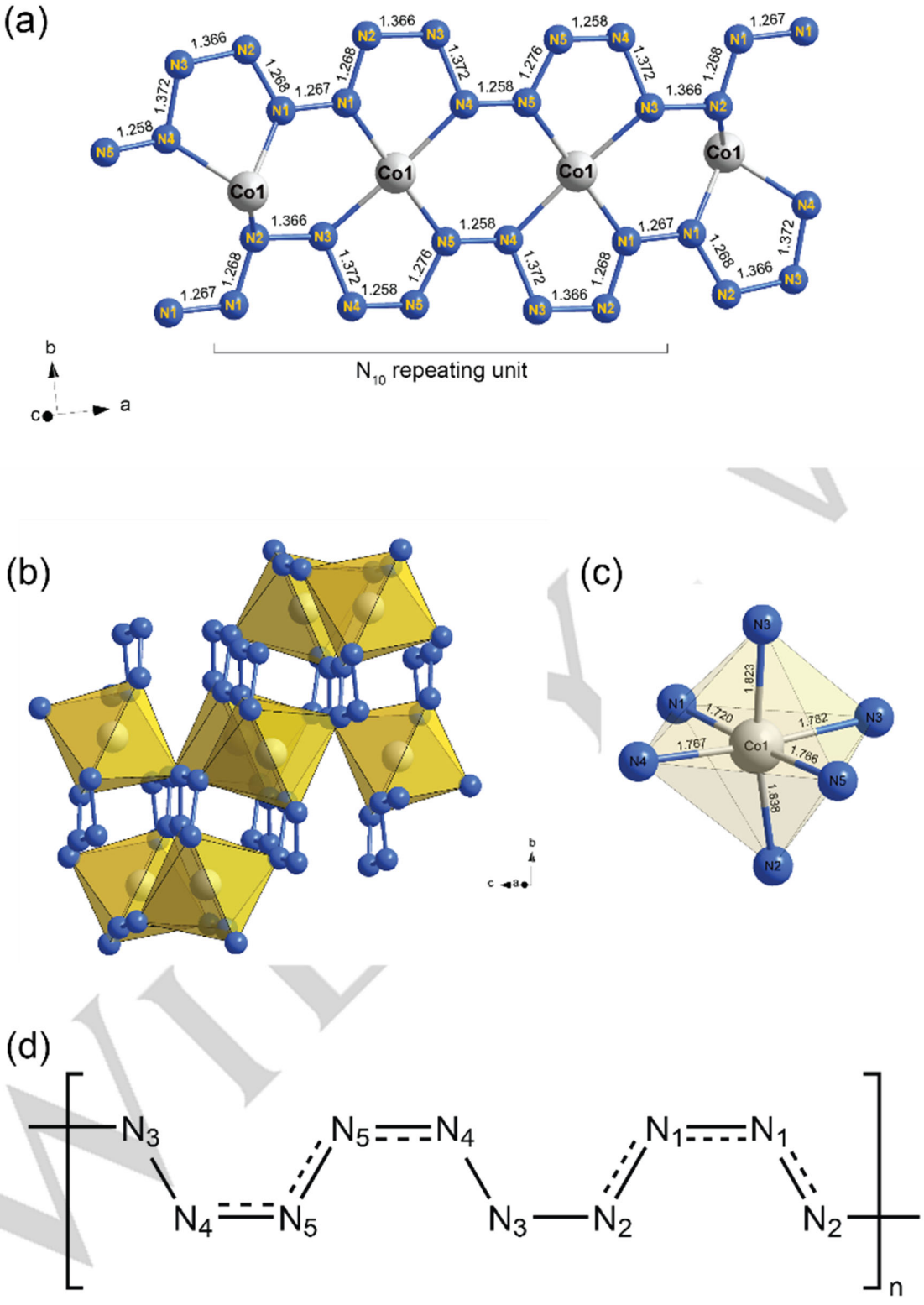

Figure 4. Crystal structure of CoN_5 at 100 GPa; (a) shows atomic arrangements of CoN_5; (b) shows the crystal structure of CoN_5; (c) shows the CoN_6 octahedra; (d) shows the repeated units of N_{10} fragments in CoN_5.

In our powder X-ray diffraction experiments, we consistently observe the co-existence of CoN+CoN_2 phases in the X-ray diffraction patterns within the pressure range of 50-90 GPa (Figures 1d and S1). Similarly, we observe the coexistence of Co_3N_2+CoN+CoN_3+CoN_5 in the diffraction patterns within the pressure range of 90-120 GPa (Figures 1 and S2). These observations indicate that these phases are close to thermodynamic stability within their respective pressure ranges as it will be discussed below. Specifically, NiAs-type CoN and CoN_2 are stable from 50-90 GPa, Co_3N_2+*Pnma*-CoN+CoN_3+CoN_5 phases are stable from 90-120 GPa. The coexistence of multiple stoichiometries of cobalt nitride at the same pressure can be due to a possible variation of nitrogen content in the diamond anvil cell cavity during the high-temperature synthesis. Multiple phases (with a low formation energy) that are stable or metastable form the phase assemblages on temperature quenching at nominally the same pressure. We calculated the unit cell volumes of all the phases per formula in comparison with the atomic volumes of cobalt and polymeric nitrogen (Figure S4). The agreements observed between these values support our crystal structure solutions including Co_3N_2, CoN, CoN_2, CoN_3, and CoN_5. It is worthwhile to note that CoN_3 and CoN_5 are not quenchable to ambient conditions (determined by Raman spectroscopy on unloading at 300 K) while NiAs-type CoN and CoN_2 can be recovered at ambient condition.[5]

In our research, we conducted Raman spectroscopy measurements of cobalt nitride samples under high-pressure conditions. `At a pressure of 80 GPa, we identify the Raman peaks at approximately 900 and 1280 cm^{-1} from the heated spots on the sample. These Raman frequencies do not correspond to any known molecular nitrogen Raman vibrational modes, which have lower frequencies (Figure 5b). To gain further insights into the observed Raman mode, we compare Raman spectra from this study with the Raman spectra of marcasite-type FeN_2.[21] The marcasite-type FeN_2 exhibit similar Raman peaks at 740 and 1100 cm^{-1}.[21] These peaks correspond to the symmetric deformation and stretching modes (A_g) within the marcasite-type structure.[21,29] Notably, previous studies[5] did not observe any Raman signals in recovered samples of marcasite-type CoN_2. This is because the Raman spectra of CoN_2 are weak, as this compound is likely metallic based on the results of our electronic band structure calculations (Figure S5).

After laser heating the sample at 120 GPa, we observe weak Raman peaks, which could be tentatively assigned to CoN_3 +CoN_5 (Figure 5a). These peaks are distinguished from the Raman signal from molecular θ-N_2[30] as well as polymeric *cg*-N and *bp*-N.[27,28,31] Group theory predicts 24 Raman modes ($8A_{1g}$+$4B_{1g}$+$8B_{2g}$+$4B_{3g}$) for the *Pnma*-CoN_3 structure, whereas 36 Raman active modes ($18A_g$+$18B_g$) are expected in *C*2/*c*-CoN_5. We also theoretically calculated the Raman modes for CoN_3 and CoN_5. We note that the Raman modes of CoN_3+CoN_5 can be divided into three major groups separated in the frequency ranges. The high-frequency group (two or more modes) correspond to the N-N stretching vibrations; their frequencies are consistent with single- and double bonded N-N atoms. The middle-frequency range (three modes at 650-800 cm^{-1}) corresponds to deformation modes of N_3 or N_5 units. The low-frequency range (one mode) corresponds to vibrations of N_3 or N_5 units (weakly bonded) with respect to each other. Due to the complexity of multiple phases (CoN+CoN_3+CoN_5), we are not able to assign all Raman modes (Figure 5). Most of the peaks can be explained by CoN_5 (Table S7). The differences in frequency between calculated and experimental Raman modes are within 10%, with most of them are being extremely close (less than 3%) (Table S7). The typical Raman shifts differences from calculations and experimental results for strong correlated electronic systems are about 10%.[32,33] The good fitness of calculated Raman suggests that our sample contains polynitride CoN_5 and CoN_3. Due to the metallicity of CoN_3 and CoN_5 (Figures. S6, S7), some of the predicted Raman peaks could not be observed in the spectra because they are too weak. In sum, our Raman spectra support the existence of polynitride compounds in Co-N system at 90-120 GPa.

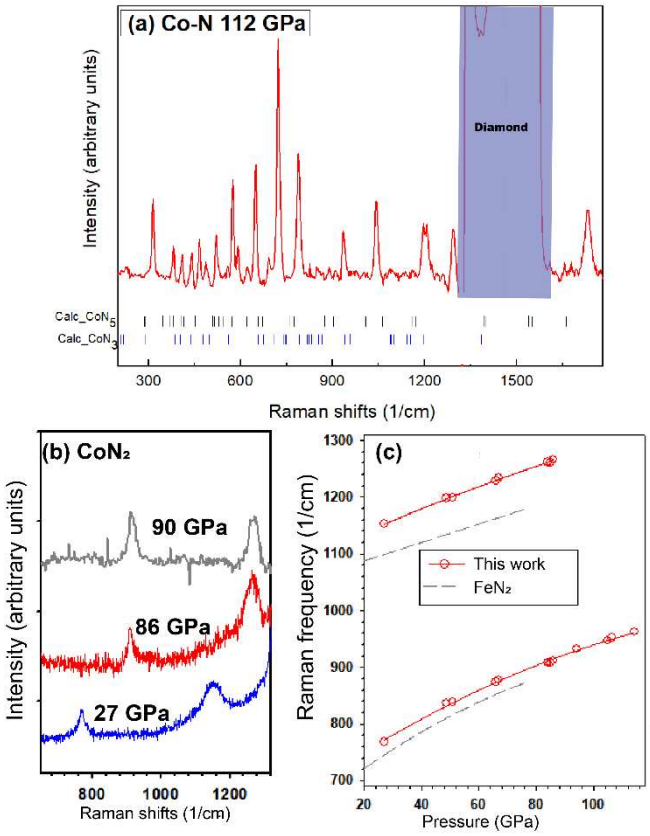

Figure 5. Raman spectra of CoN_3+CoN_5 at 120 GPa (a) and marcasite-type CoN_2 (b). (c) Pressure dependences of the Raman frequencies for the marcasite-type CoN_2 together with Raman data from FeN_2.[21]

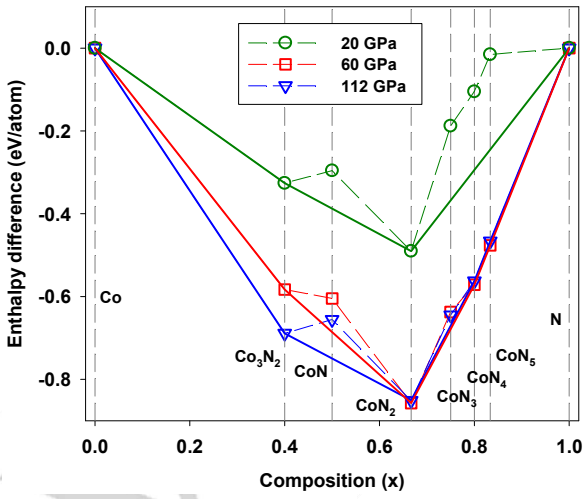

Figure 6. Convex hull diagram calculated from density functional theory of cobalt nitride systems at 20, 60, and 112 GPa. Stable phase include NiAs-type CoN, CoN_2, CoN_3, CoN_4[2] and CoN_5 (black triangle). The stable phases of nitrogen are assumed to be ε-N2 at 20 and 60 GPa and cg-N – at 112 GPa.

We calculated the convex hull diagram for Co-N nitrides (see the Supplementary Information) at 20, 60, and 112 GPa (Figure 6). The stability fields of cobalt nitride phases were determined by calculating the formation enthalpies at the pressure range 20-112 GPa. The points connected by the solid lines in Figure 6 correspond to the thermodynamically stable phases. We find that CoN, CoN_2, and Co_3N_2 are thermodynamically stable or metastable compounds at 20 GPa. At 60 and 112 GPa, CoN_4 and CoN_5 gradually become stable, and CoN_3 stays very close to thermodynamic stability line. The crystal structures obtained from calculations and experimental studies are consistent. We did not observe CoN_4, which is expected to form infinite nitrogen chains[2] similar to CoN_5.

Conclusion

The discovery of CoN_3 and CoN_5 phases represents a significant advancement in our understanding of polynitride structures. CoN_3

is observed where Co atoms are connected by nitrogen trimer bonds. This branched-type structure arrangement in CoN_3 can be considered as an intermediate state between octahedra connected by N-N bonds and the formation of branched or infinite -N-N- chains. At extremely high pressures, metal nitrides tend to form long chains or even ring structures. In this context, CoN_5 shows an infinite π bonded nitrogen chain at higher pressure in its crystal structure. Progressive nitridation is clearly observed in our study from CoN, CoN_2 to CoN_3, and CoN_5 with an increasing degree of nitrogen polymerization.

Another intriguing finding of our study is the correlation between CoN_6 octahedra and the increasing nitrogen content in the unit cell. The coordination number is based on the ionic radii between cation and anion in ionic crystals.[34] In the cobalt nitrogen system, Co atoms are preferentially coordinated with six nitrogen atoms within the pressure range of 50-120 GPa. Polynitrogen anions influence CoN_6 octahedral connectivity in these structures, leading to the formation of face sharing (CoN) to edge sharing (CoN_2 and CoN_3) octahedra. In order to accommodate more nitrogen in the crystal structure, the CoN_6 octahedra in CoN_5 become disconnected, leaving enough space for the polymerized nitrogen atoms. This finding adds to our understanding of the structure evolution and bonding behaviors of polynitrides under various pressure conditions, shedding light on the intricate interplay between CoN_6 octahedra arrangements and nitrogen polymerization of polynitride.

In sum, we experimentally and theoretically explored the cobalt nitride system at pressure up to 120 GPa. With the single-crystal XRD, we successfully solved several phases including NiAs-type CoN, marcasite-type CoN_2, *Pnma*-CoN, Co_3N_2, and the novel polynitrides CoN_3 and CoN_5. CoN_3 and CoN_5 are very different from iron polynitride FeN_4 observed in the Fe-N system. These observations emphasize the need for additional experimental studies and first-principles calculations to gain a deeper understanding of the nitridation processes and to facilitate the design of transition metal polynitride materials.

Supporting Information

The authors have cited additional references within the Supporting Information.[35–53] Experimental details, additional data are provided in the Supporting Information.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Polynitride • Cobalt • Crystal Structure • High-Pressure • Diamond-Anvil Cell.

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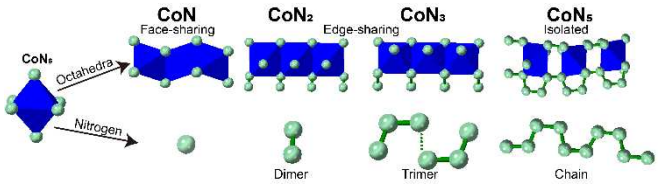
Entry for the Table of Contents



The nitridation behaviour of cobalt nitride unfolds along a progressive path under high-pressure conditions, as investigated using a laser-heated diamond anvil cell, combined with synchrotron XRD, Raman spectroscopy, and density funtional theory. Our observations reveal a sequence of CoN_6 octahedral framework transformations, including face-sharing (in CoN), edge-sharing (in CoN_2 and CoN_3), and isolated (in CoN_5) polyhedra. These changes align with the polymerization of nitrogen within the crystal.