Prediction of Polynitrogen Species in Materials

Gilles FRAPPER

Applied Quantum Chemistry group @ IC2MP

19th ONLINE USPEX workshop (19th Lyakhov School) Supported by the Russian Scientific Foundation grant No. 19072-30043 "Computational materials design laboratory", Moscow, 11-13 november 2020

outline

- *Ba – N binary phase under pressure*

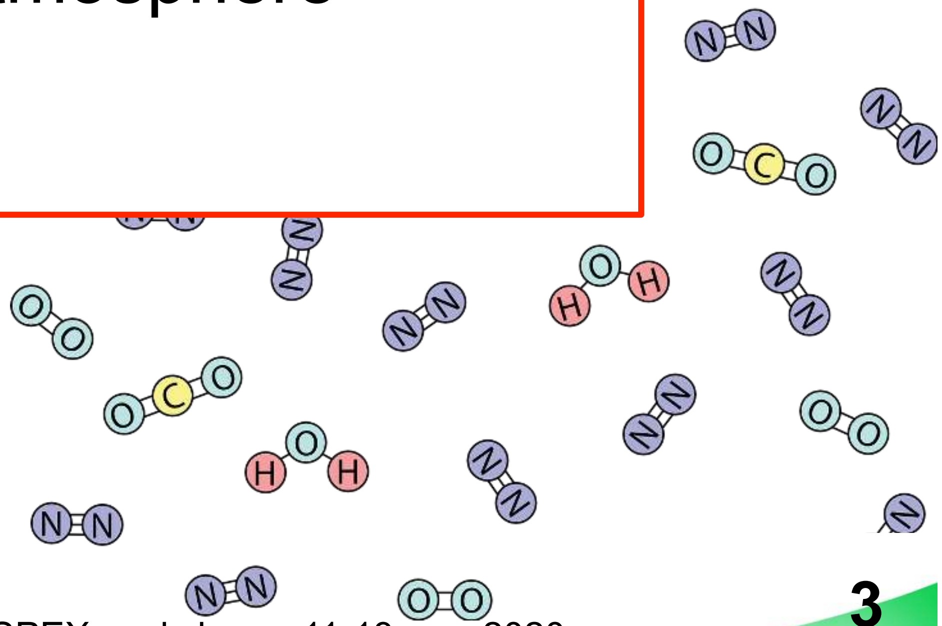
- *M – N_5 pentazolates*

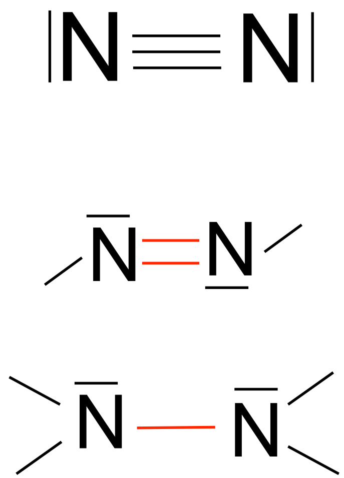
Nitrogen element: $\mathbf{N_{2}}_{(g)}$

- potential natural resource in chemistry

~78% of the Earth's atmosphere

- inert gas



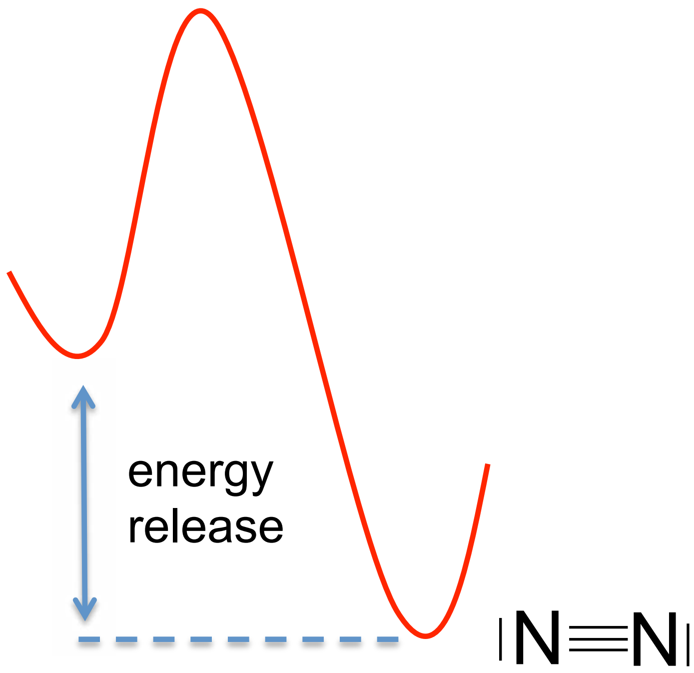


945 kJ/mol

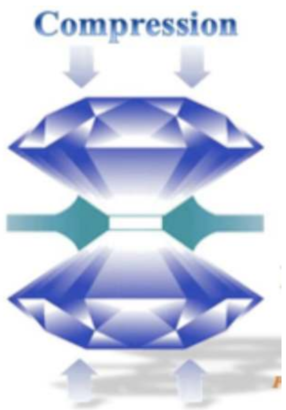
418 kJ/mol

160 kJ/mol

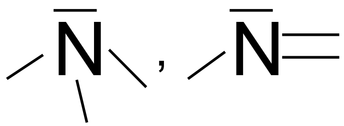
N-rich compounds: HEDM



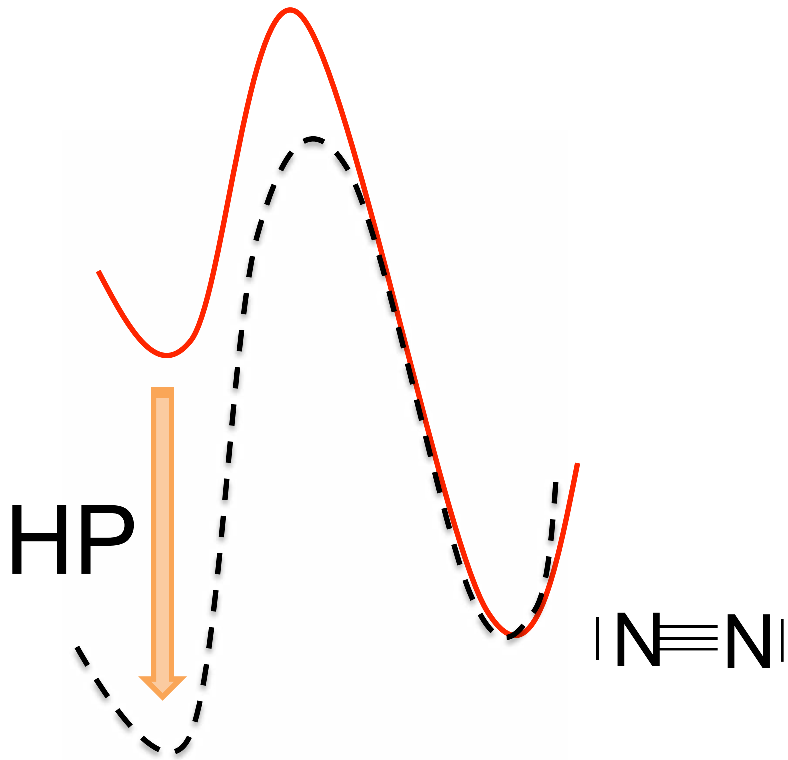
Pressure-Induced Polymerisation



based on building blocks

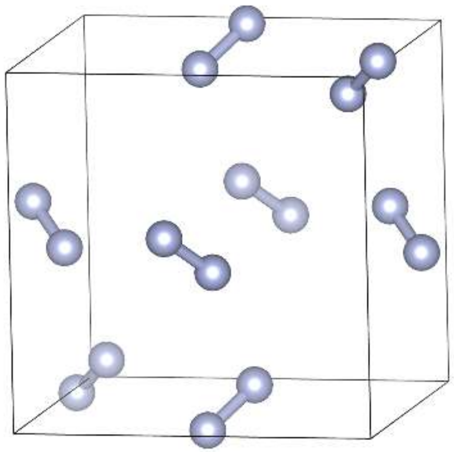
e.g. 

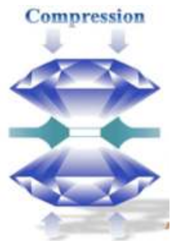
stable



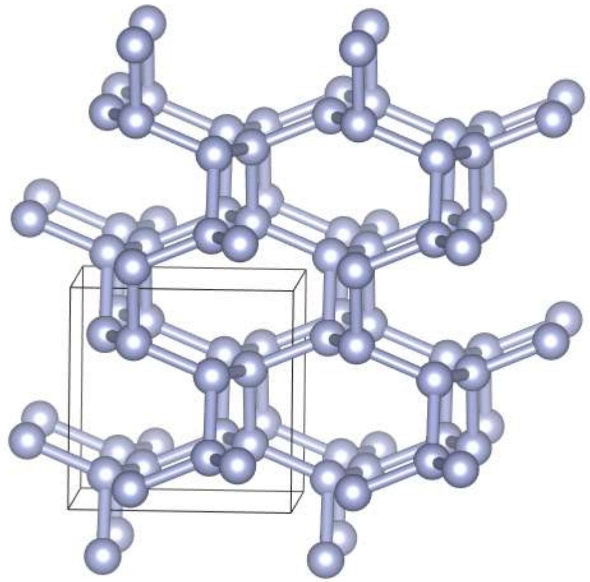
Pressure-Induced Polymerisation

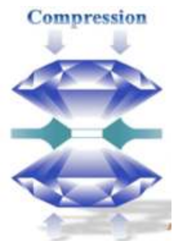
1 atm



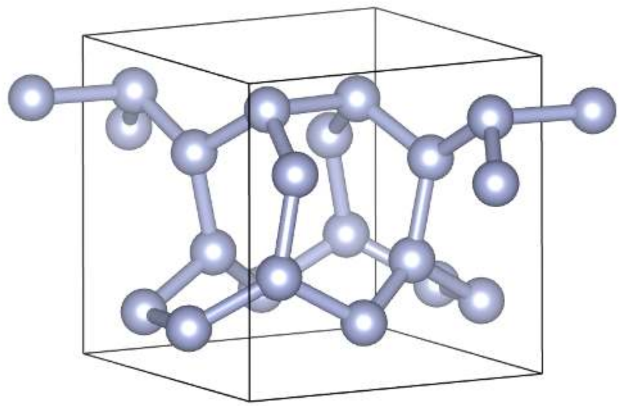


>56 GPa





>188 GPa



Pa-3

I$2_1$3

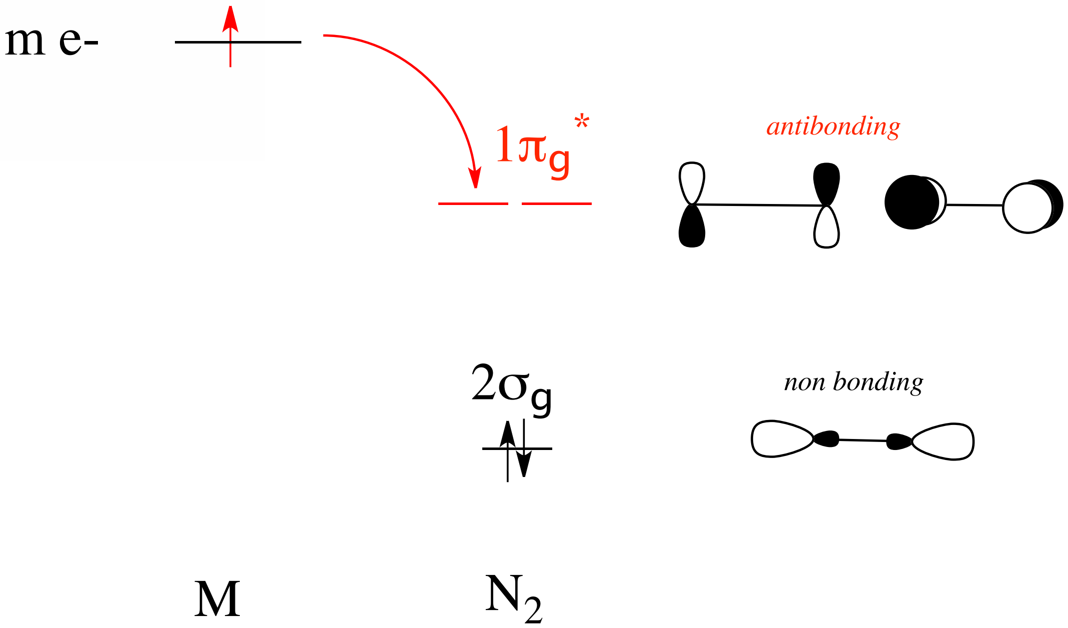
*Pba*2

HP phases from CSP searches

Mailhot&McMahan 1992, sg-N - Ma&Oganov PRL 2009)

Electropositive Metal–Nitrogen Mixing

$$xM + y/2N_2 \longrightarrow [M^{m+}]_x[N^{(x/y)m-}]_y$$



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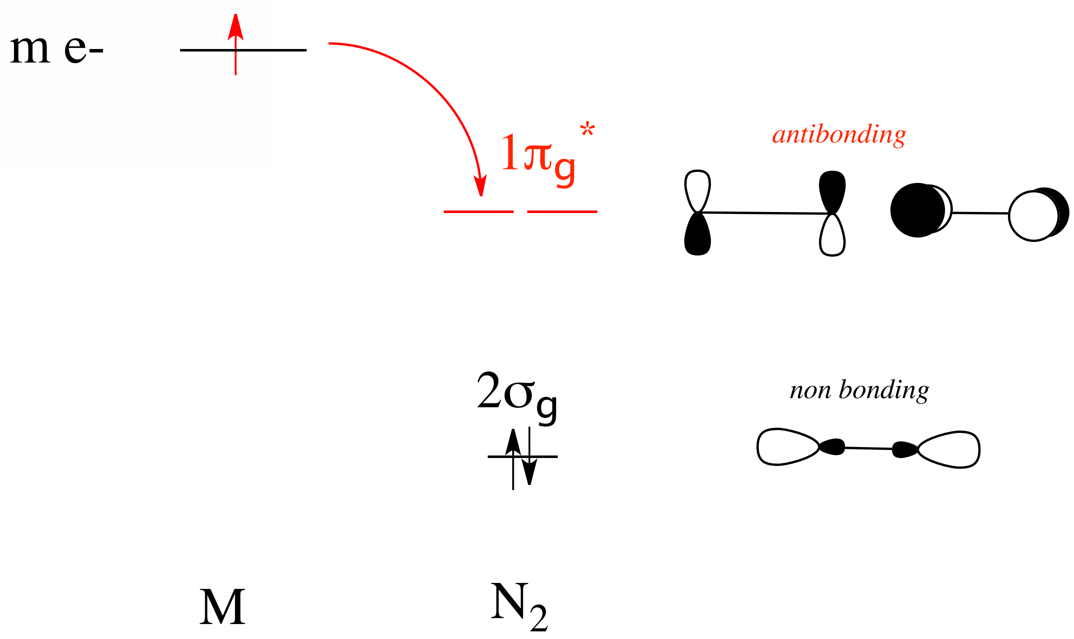

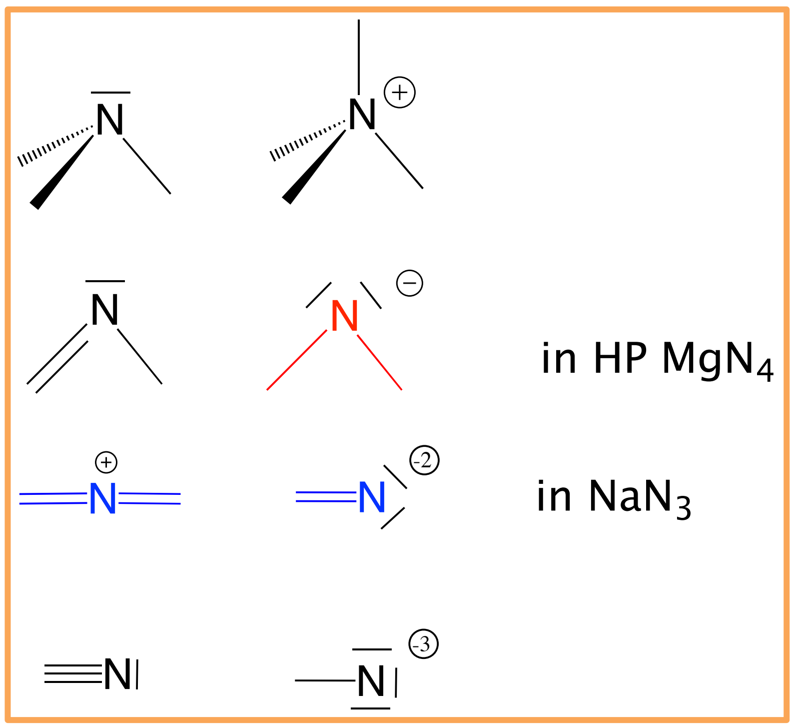

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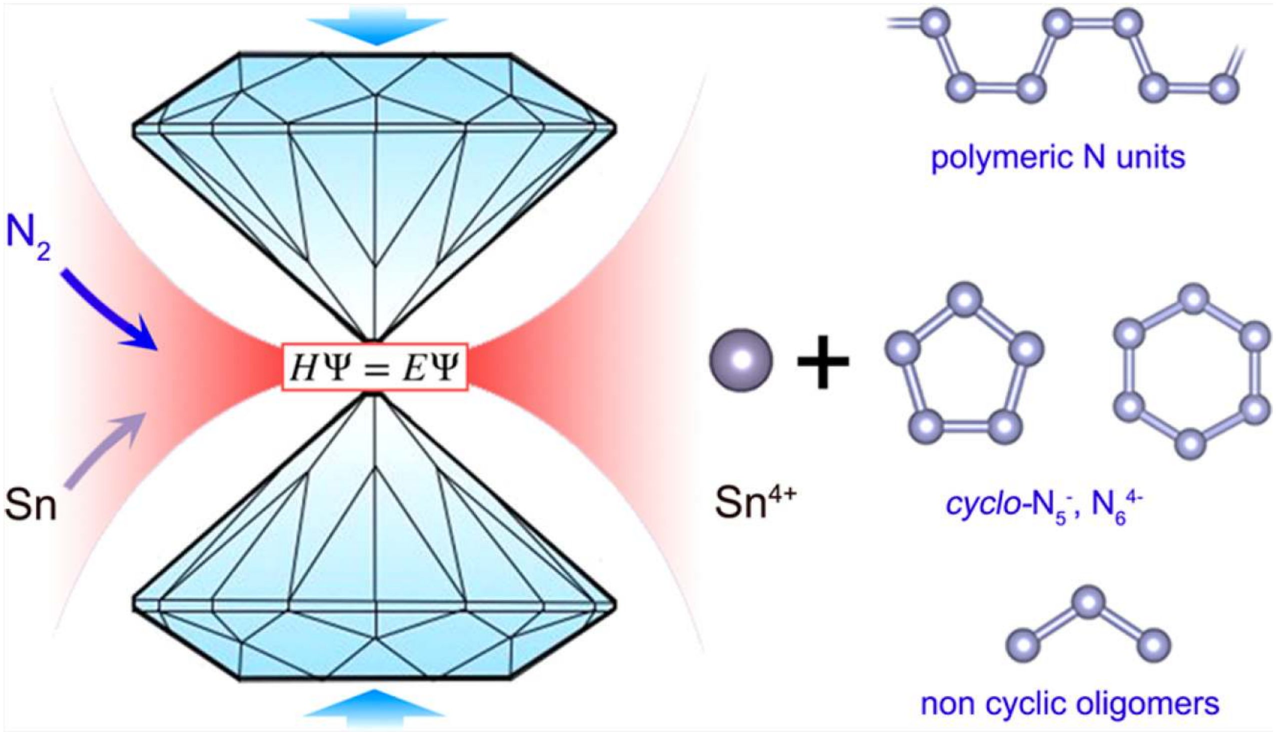
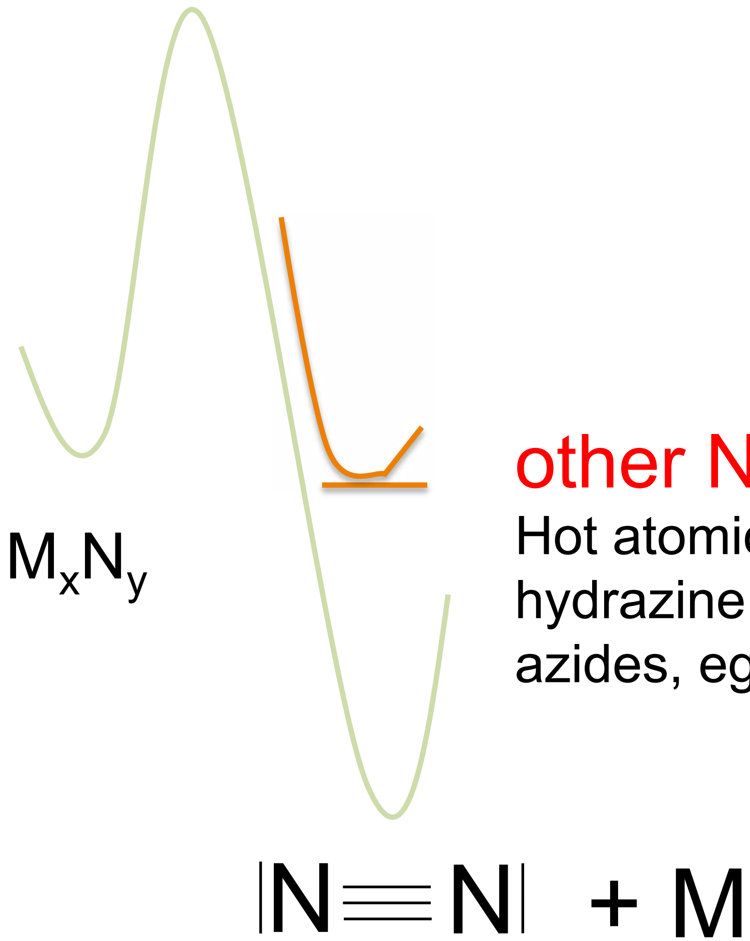


Sn-N: B. Huang *et al* J. Phys. Chem. C **2020**, 124, 8080−8093; DOI 10.1021/acs.jpcc.9b11404

Pressure-induced polymerisation



(+ MN_z)

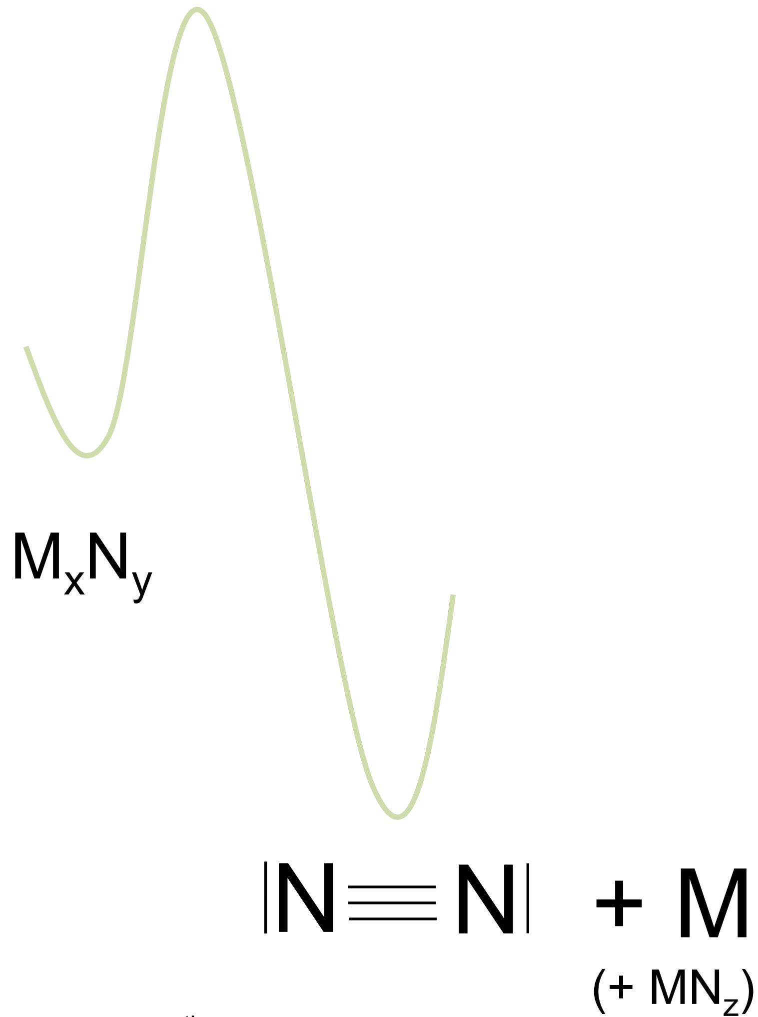
other N precursor

Hot atomic nitrogen,
hydrazine N_2H_4,
azides, eg CsN_3, ...

Pressure-induced polymerisation

metastable M_xN_y

but viable?

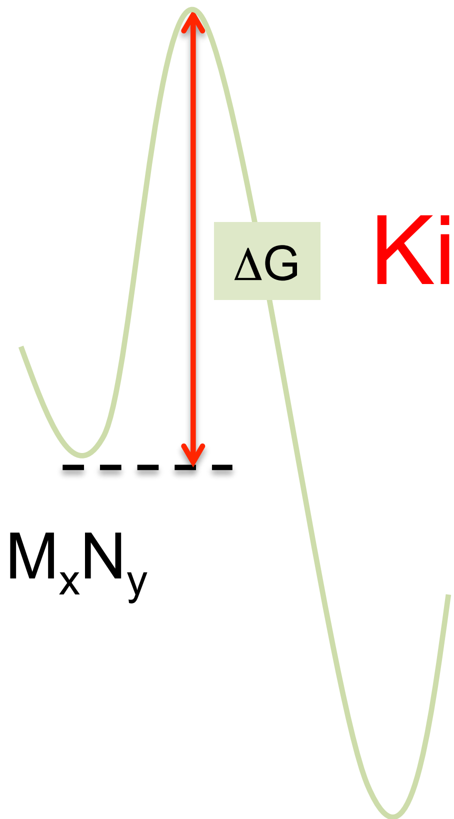


Pressure-induced polymerisation

metastable
M_xN_y

but viable?

metal cations – polynitrogen anions stabilizing interactions



Kinetic, thermal (AIMD)

Dynamical (phonons)
Mechanical (tensors)

Chemical (OH, O, H… absorption)

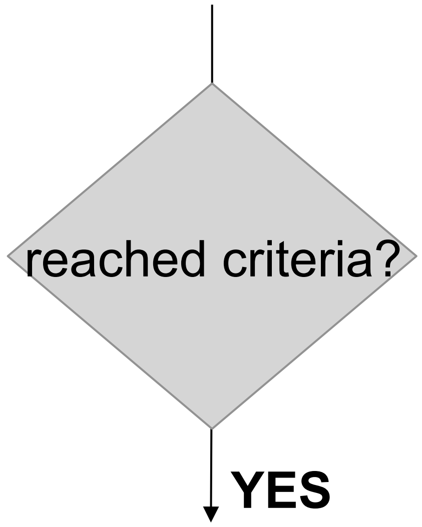
$|N \equiv N|$ + M
(+ MN_z)

Predicting new polynitrogen materials

- *Ba – N*
- *M – N_5 pentazolates*

Knowledges: chemical composition, (P, T) conditions

USPEX Computational Materials Discovery



ie, same lowest structure during 10-15 generations

END of USPEX
We got our "ground state structure"

Our work can start!

Chemical bonding analysis
(DOS, COHP, ELF, QTAIM, Manz bond order, orbital interactions,…),

Relation between electronic structure and structural arrangement

Properties calculations: energies (T, P), electrical conductivity, superconductivity, thermoelectric, elasticity, hardness, etc.

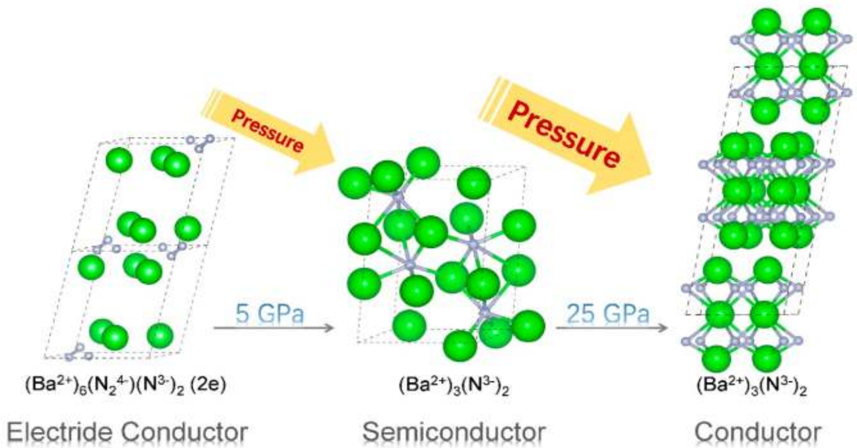
• *Ba – N binary system*

Methodology: DFT GGA-PBE, SCAN;
~1 meV/atom accuracy

Tools: PHONOPY ; LOBSTER ; eHT ; VESTA ; …

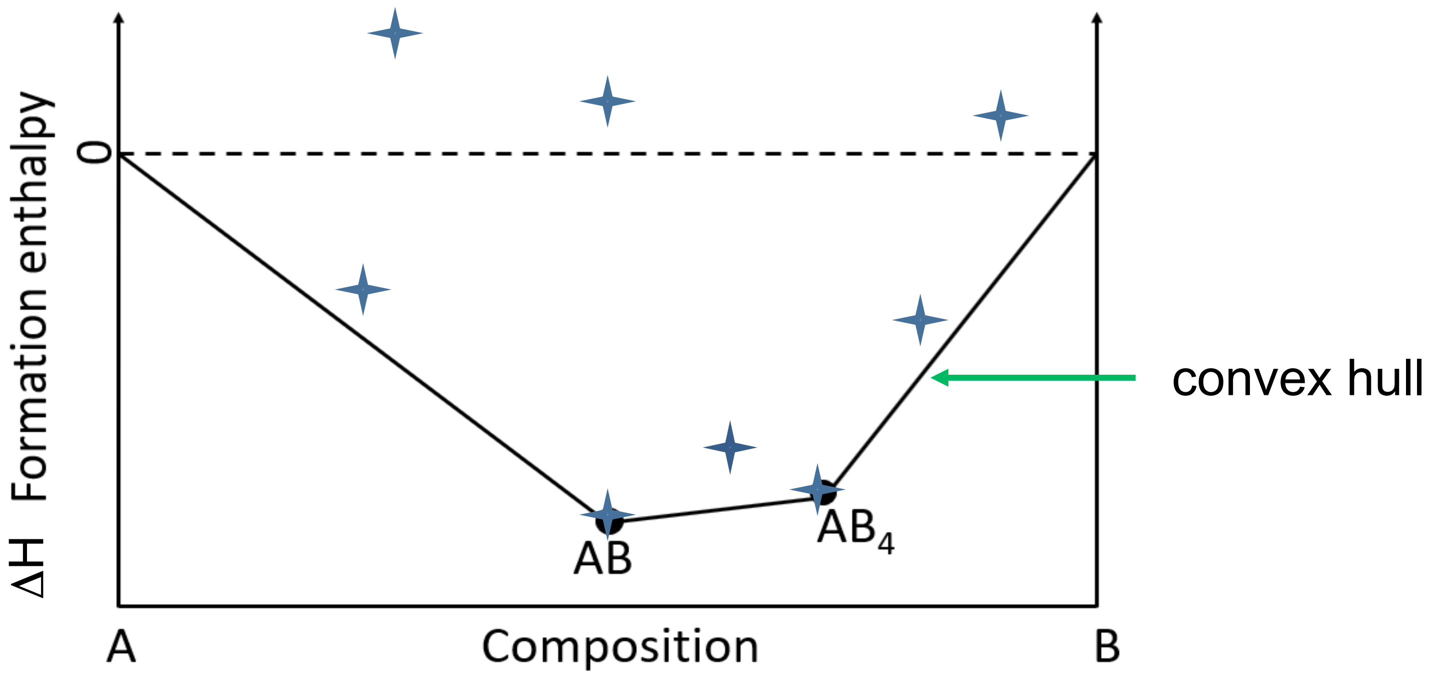
Barium-Nitrogen Phases Under Pressure: Emergence of Structural Diversity and Nitrogen-Rich Compounds

Bowen Huang[†,‡] and Gilles Frapper[*,‡]



B. Huang, G. Frapper – Chemistry of Materials (ACS) 2018

variable composition search

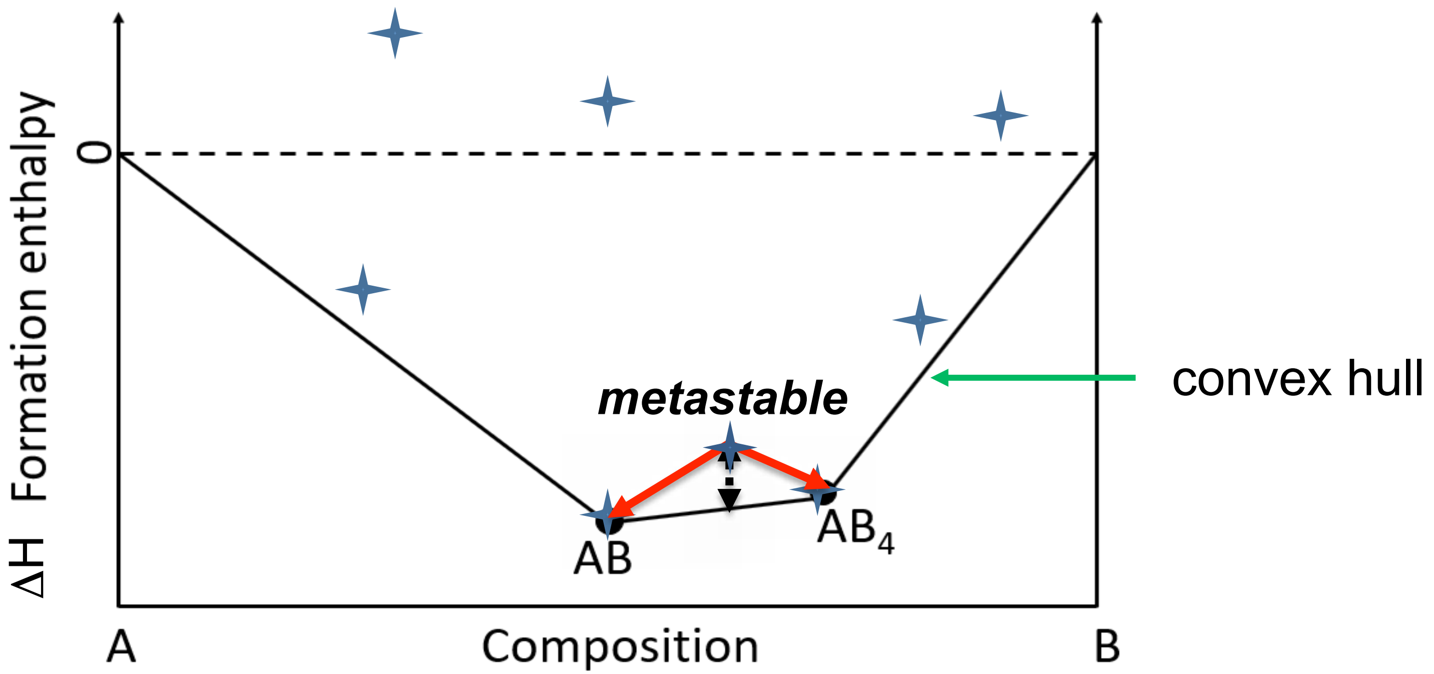


A, B: elements (*eg*, Ba, N_2) or compounds (N_5)

Stationary point on the PES; lowest energy structure for a given stoichiometry

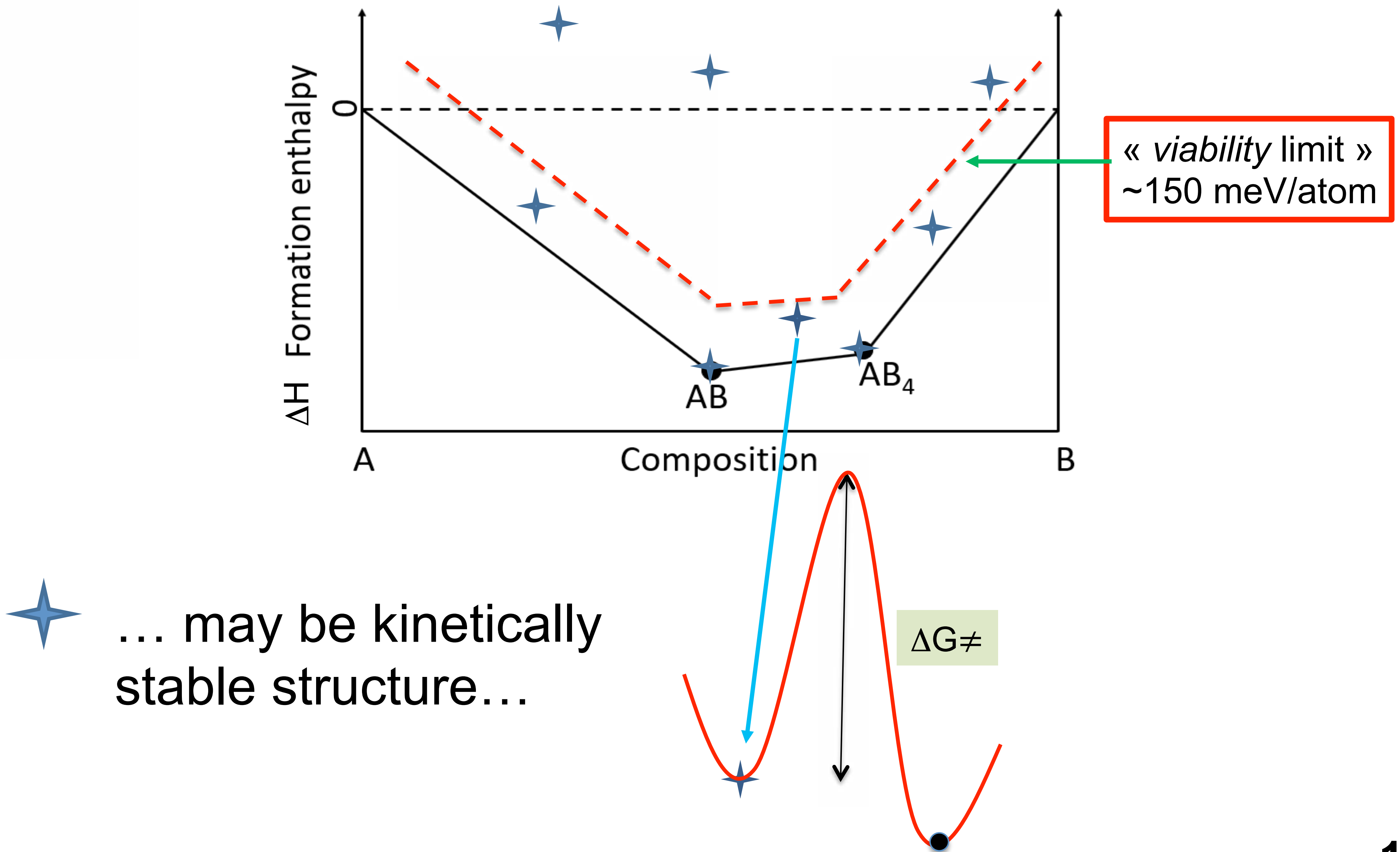
$\Delta H = [H(A_xB_y) - xH(A) - yH(B)]/(x+y)$, **fitness**

variable composition search



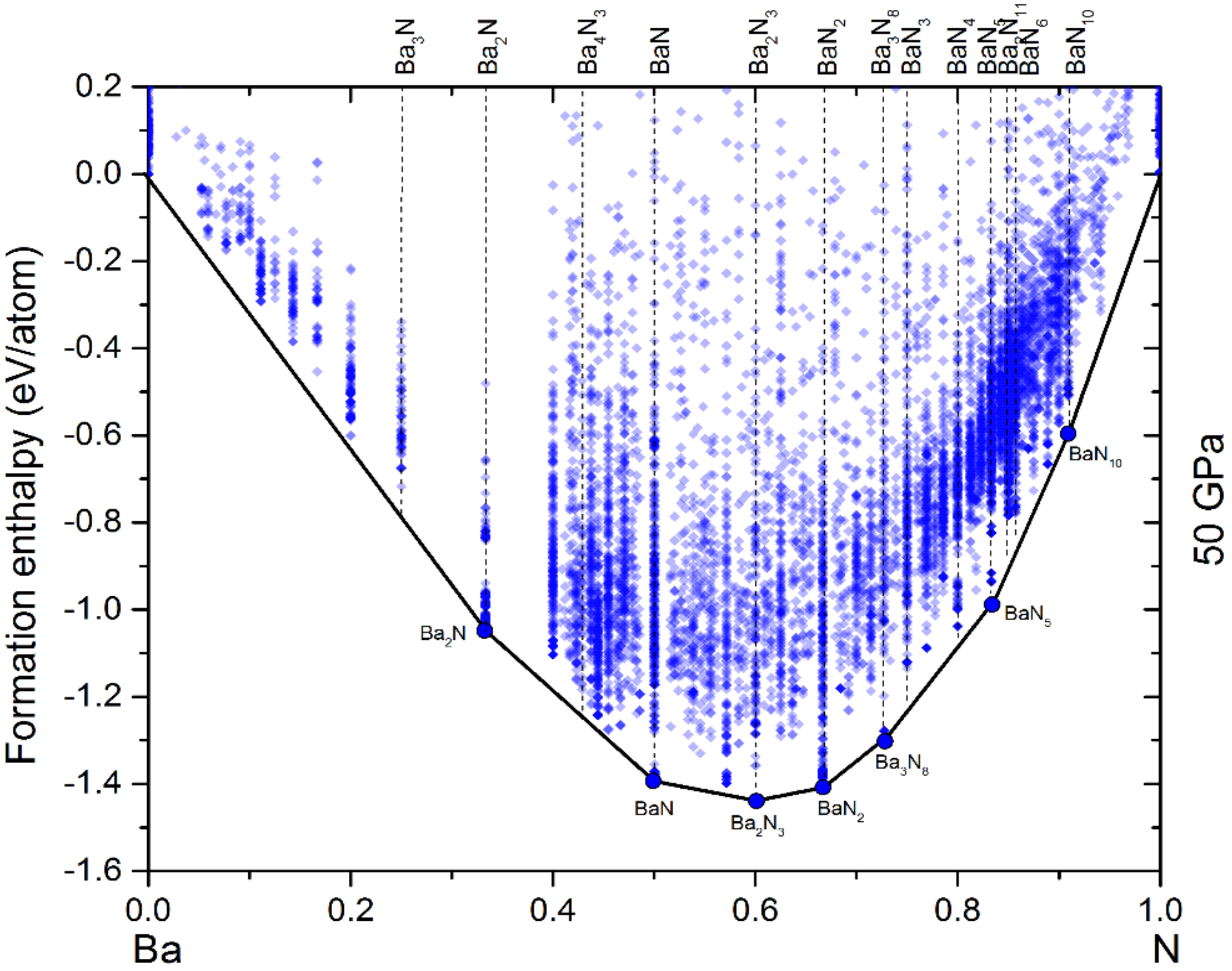
above the convex hull, ***thermodynamically*** metastable structure

variable composition search



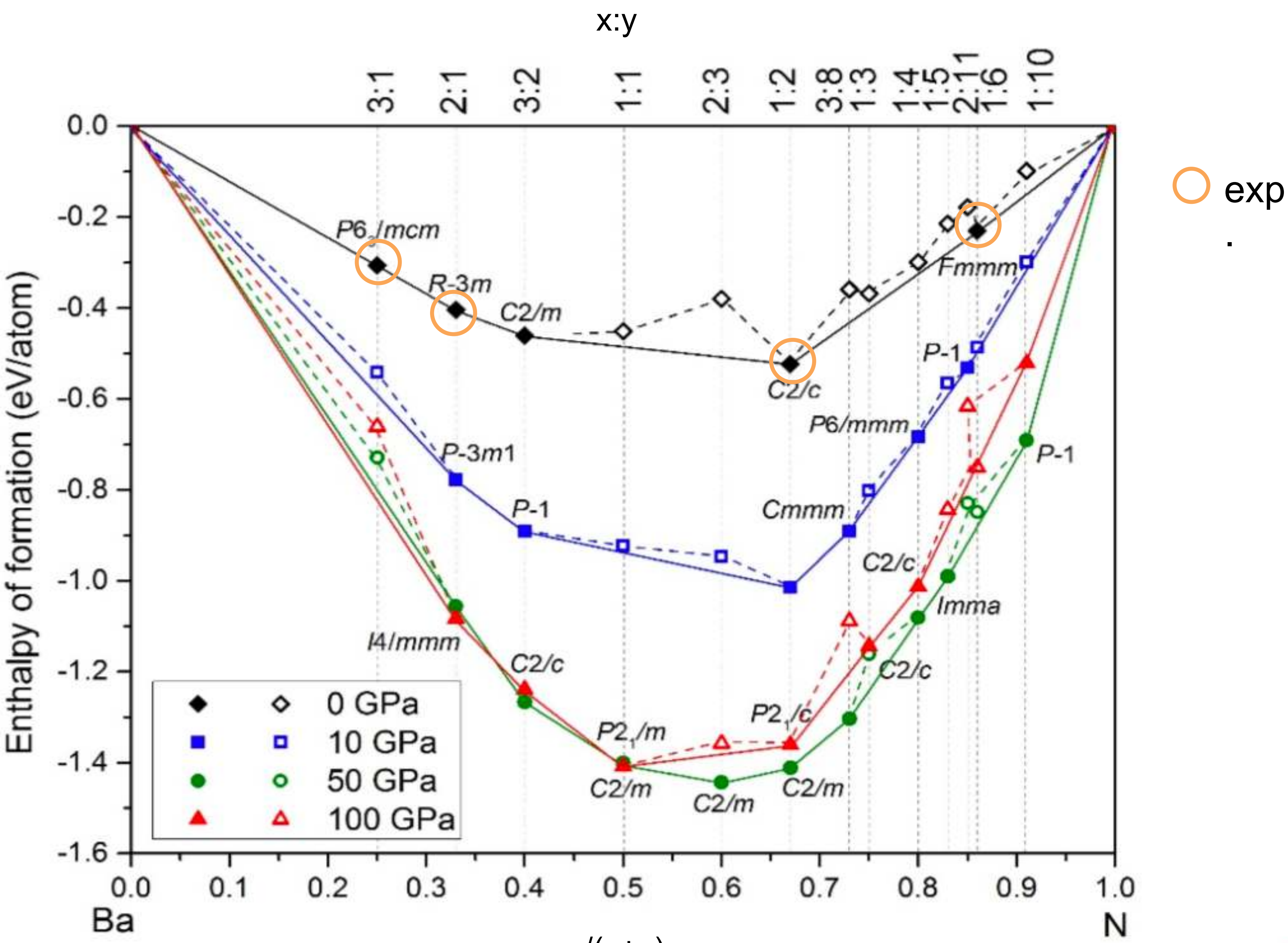
… may be kinetically stable structure…

2a. Ba-N

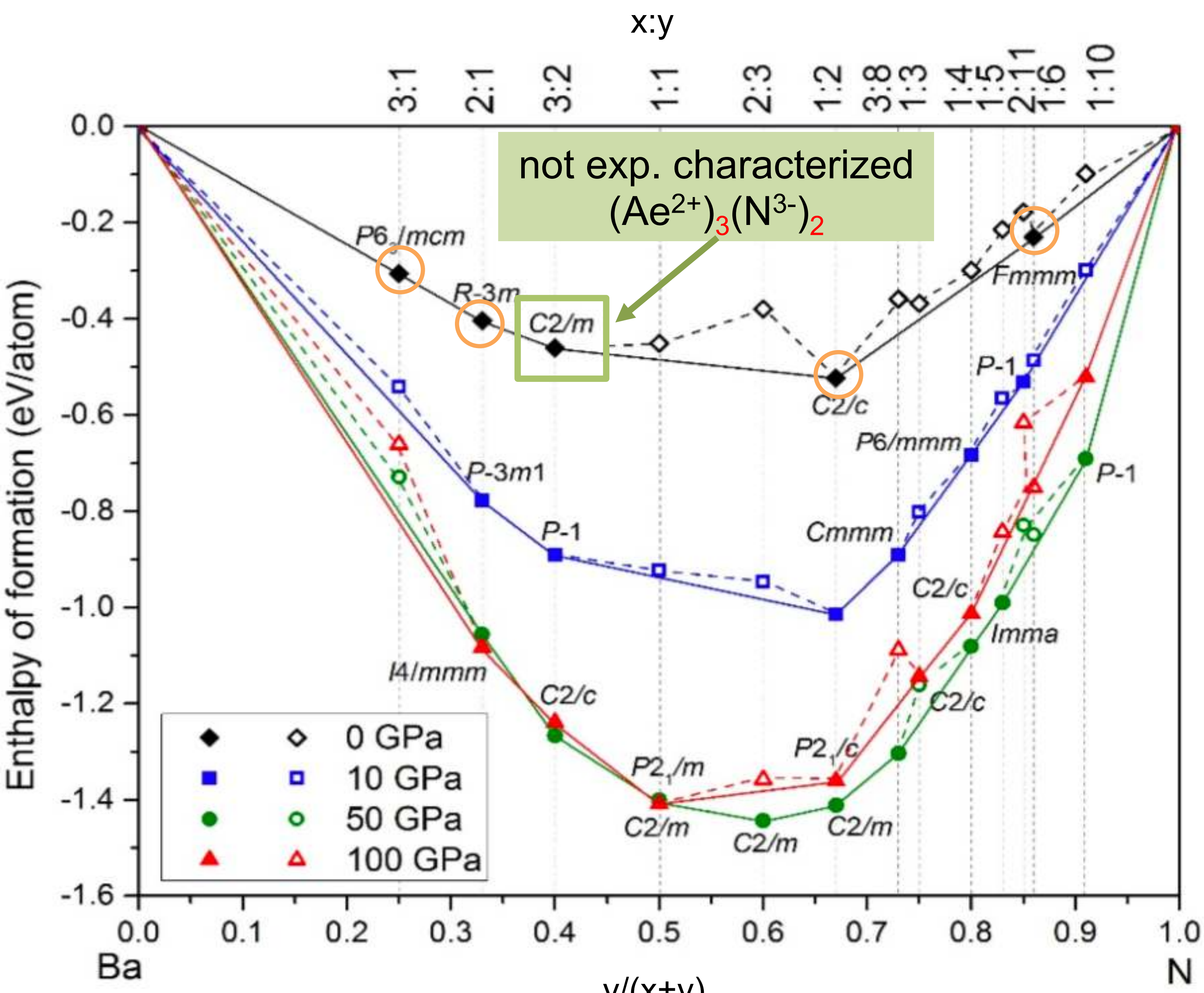


+ At each composition:
Run fixed-composition USPEX jobs
to locate low-lying ground-state structures

Results Ba_xN_y



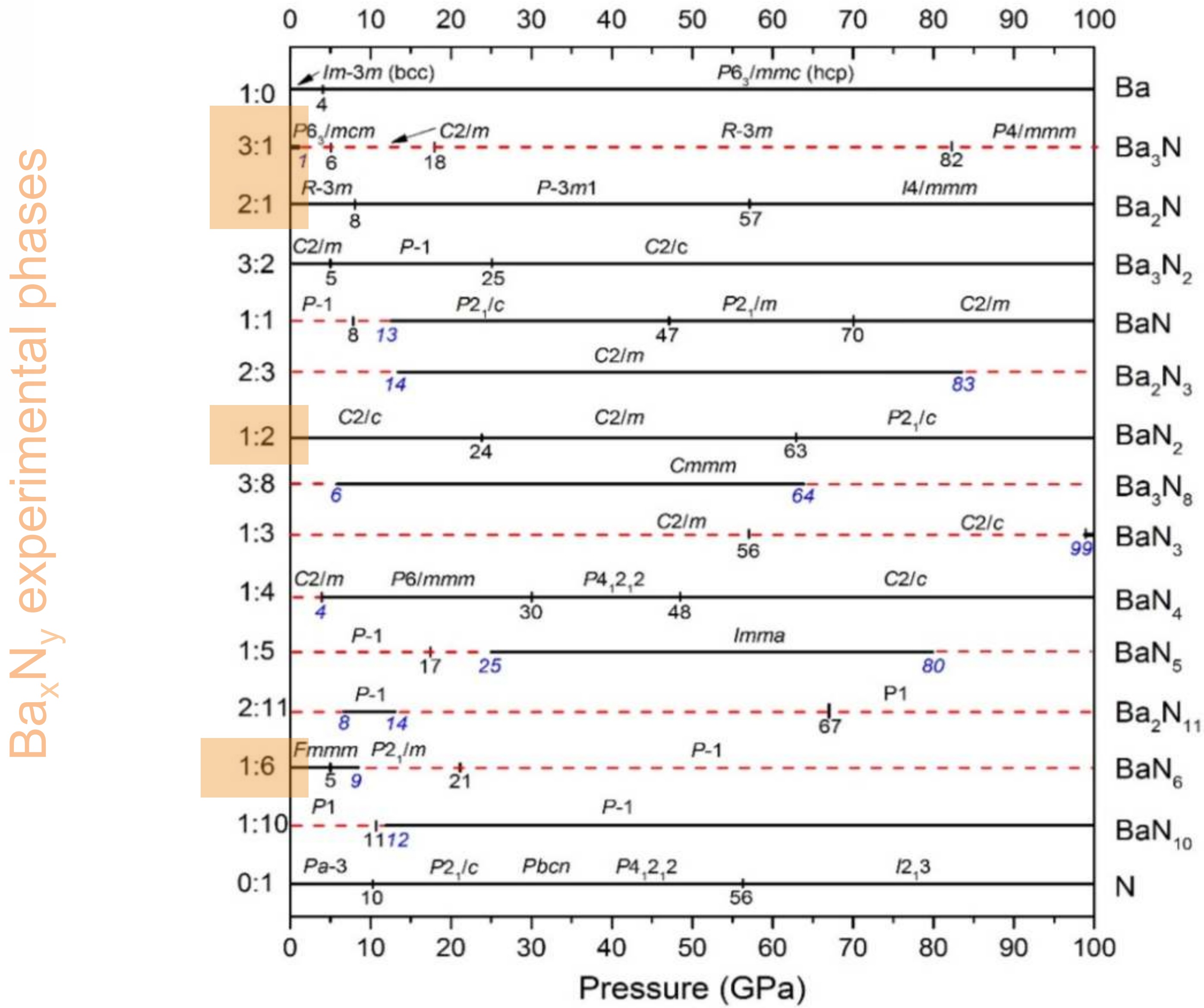
Results Ba_xN_y



○ exp
.

2a. Ba-N

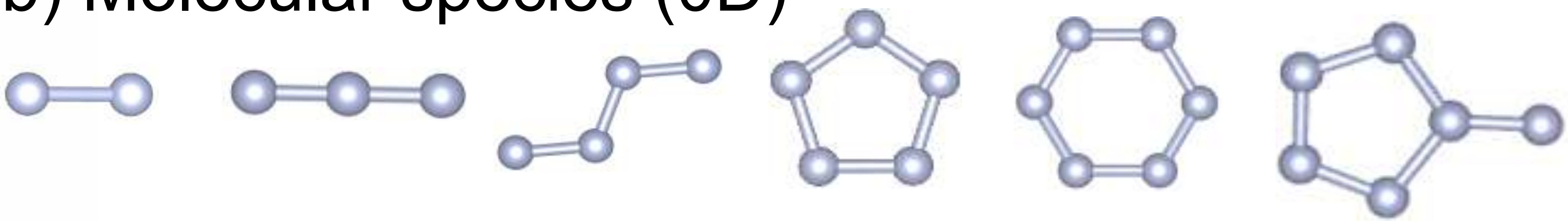
Ba-N from 0 to 100 GPa:
13 compositions and 24 stable phases



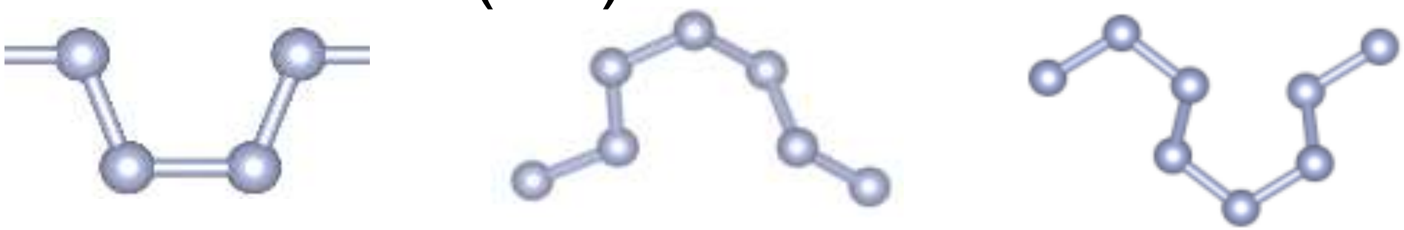
2a. Ba-N

(a) Isolated atom

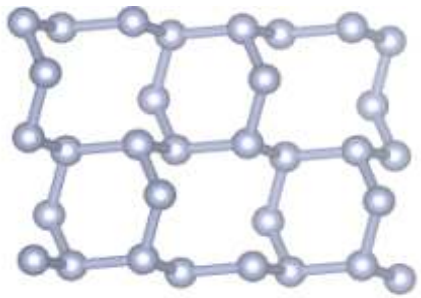
(b) Molecular species (0D)



(c) Infinite chains (1D)



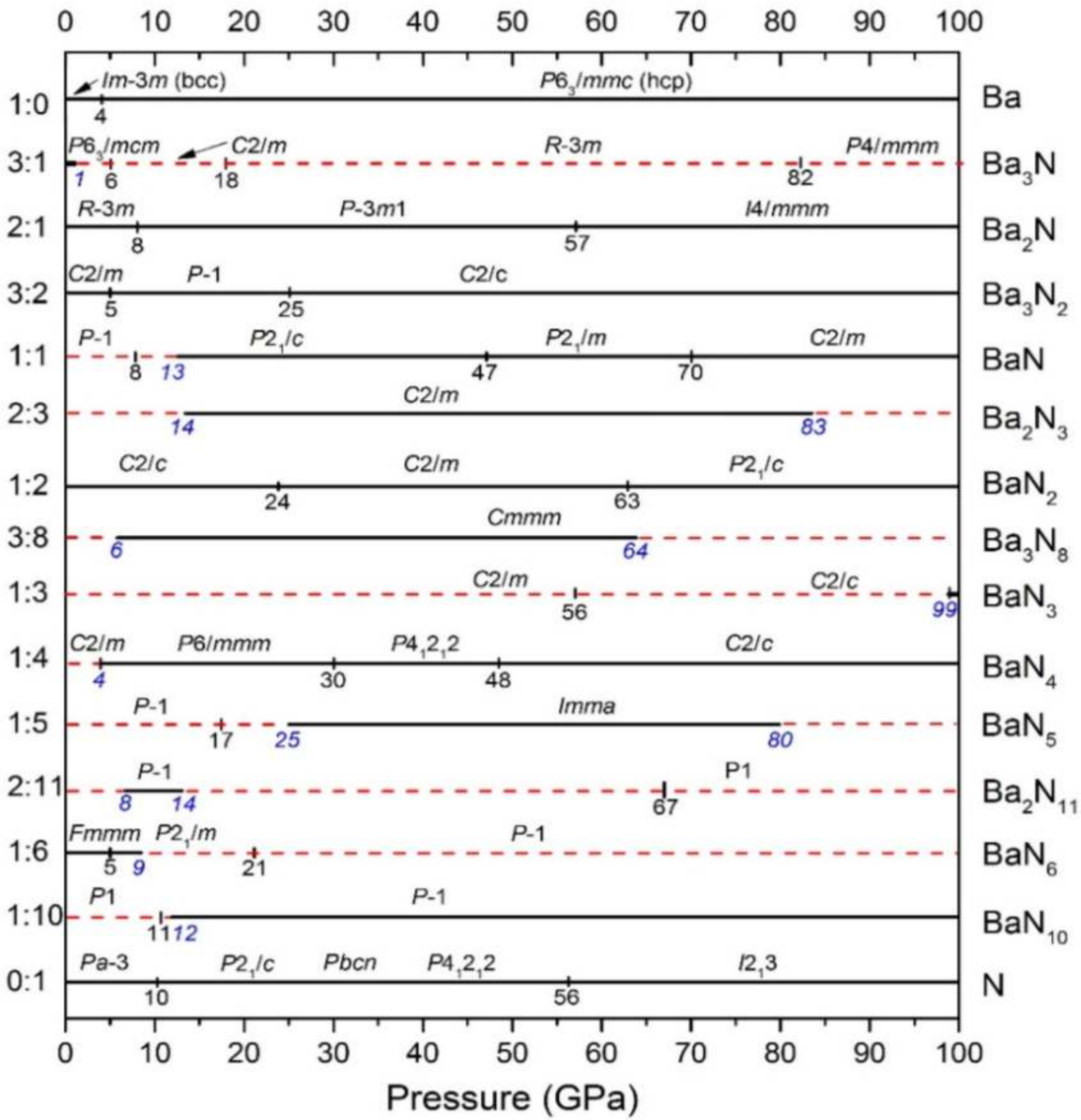
(d) Layer (2D)



2a. Ba-N

Ba-N from 0 to 100 GPa:
13 compositions and 24 stable phases

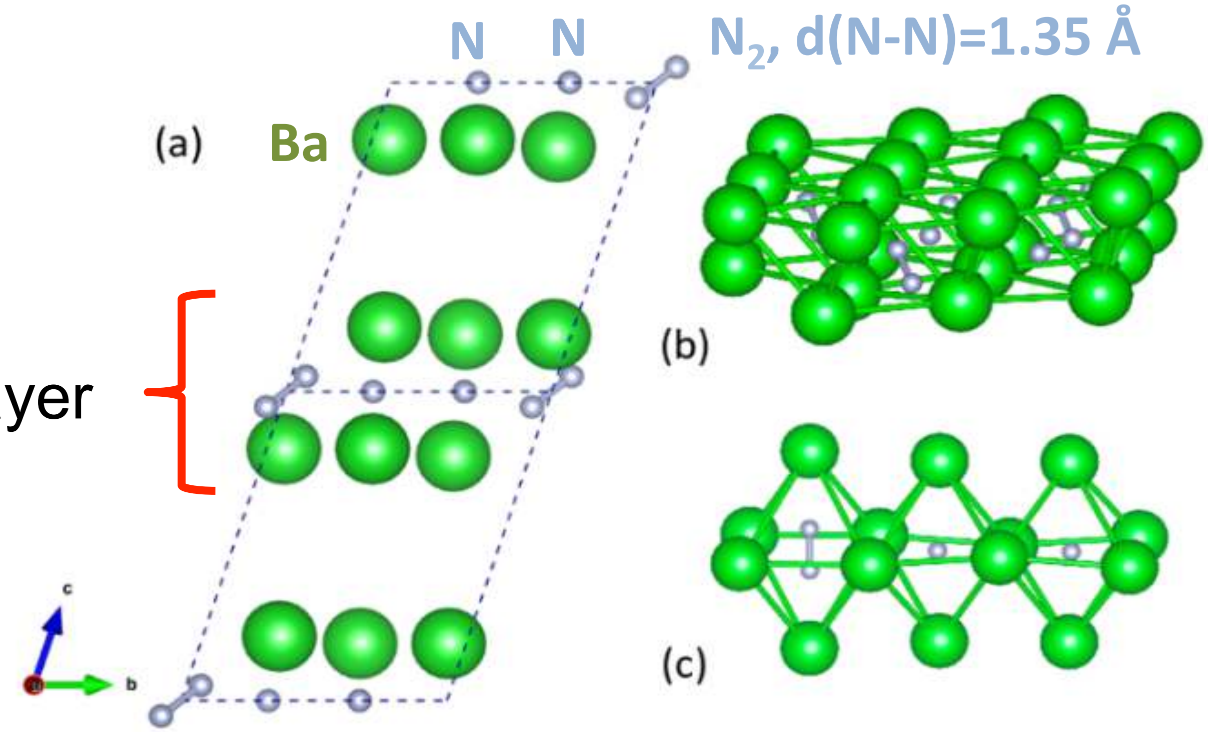
expected stoichiometry → 3:2



← $(Ba^{2+})_3(N^{3-})_2$

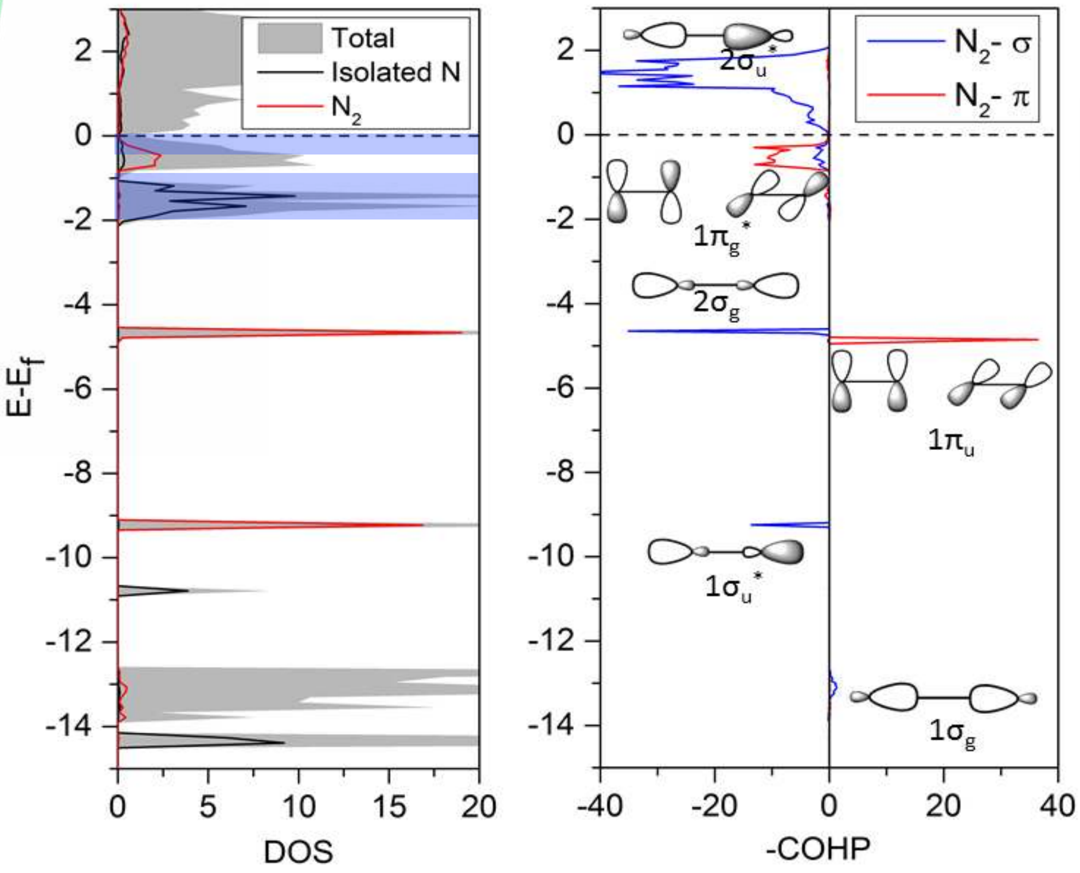
$C2/m$ Ba_3N_2

$Ba_6(N_2)(N)_2$ layer



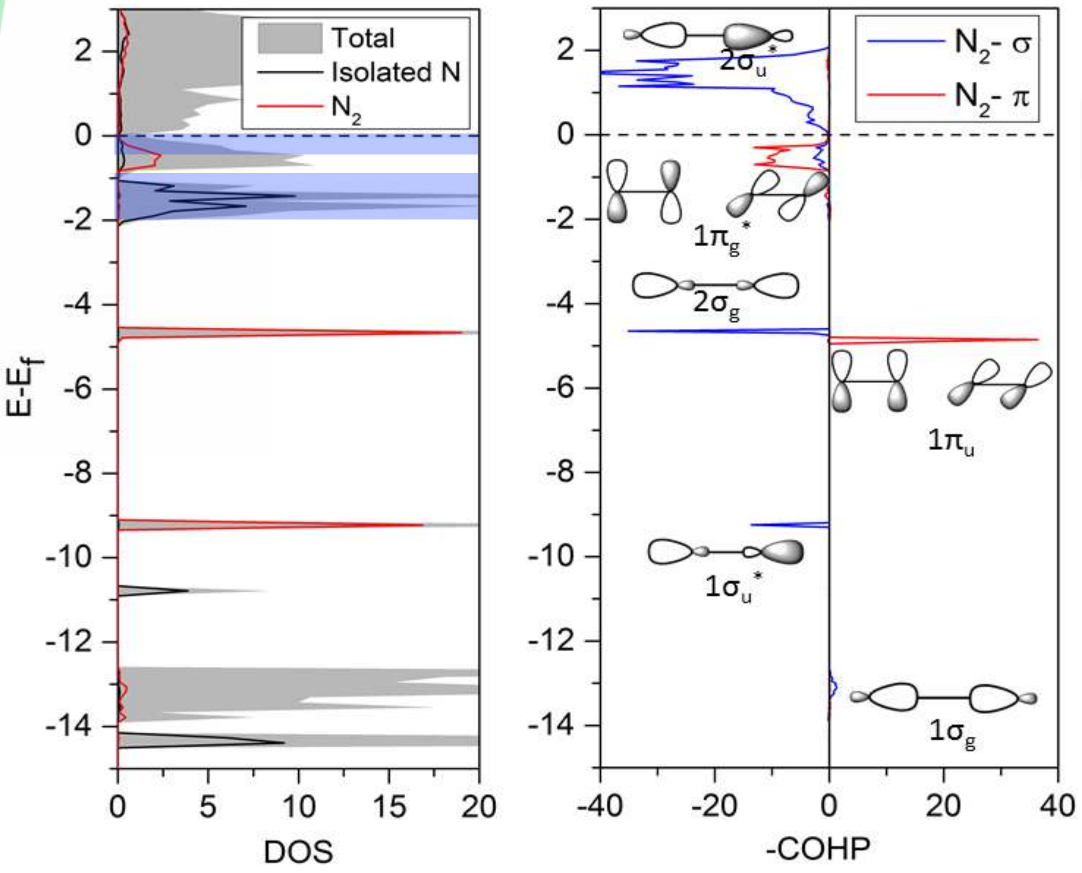
Stable: 0-5 GPa

C2/m Ba_3N_2



N_2^{4-}, isoelectronic to F_2

C2/m Ba_3N_2

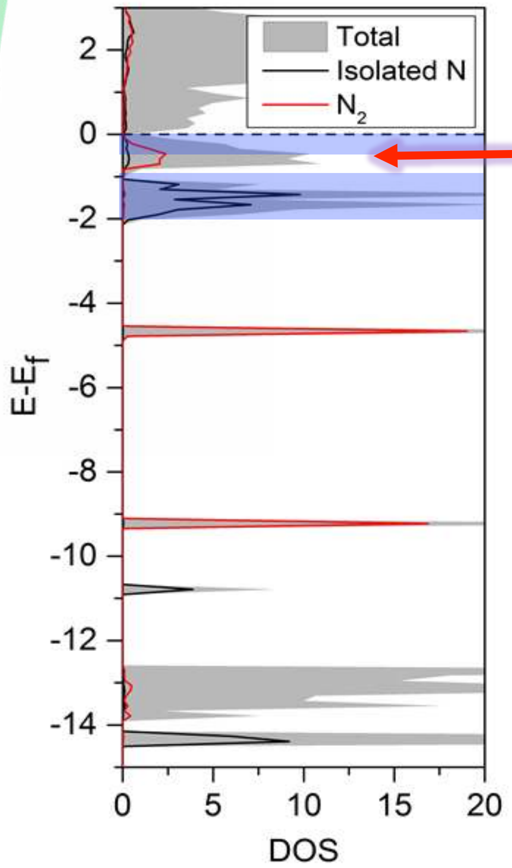


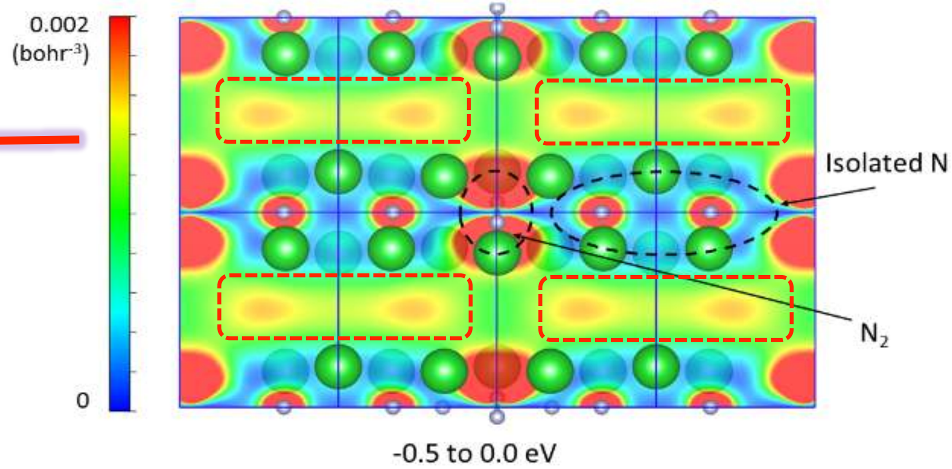
N_2^{4-}

$(Ba^{2+})_6(N_2^{4-})(N^{3-})_2$**$(2e^-)$**

C2/m Ba_3N_2, an electride

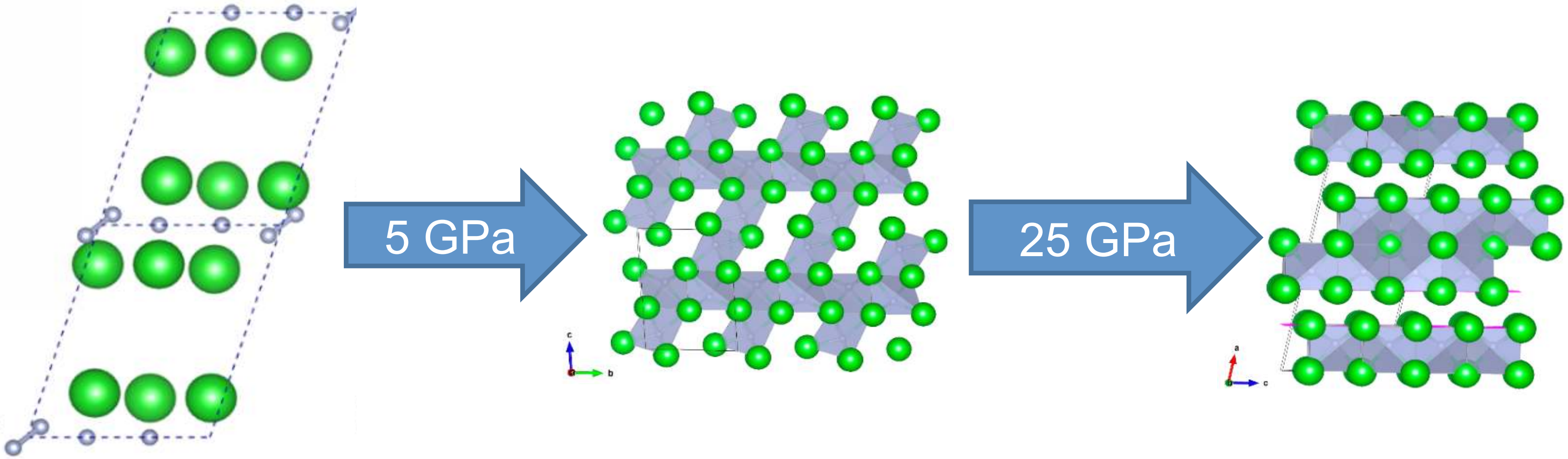
Partial density of charge
(010) plane





$(Ba^{2+})_6(N_2^{4-})(N^{3-})_2(\mathbf{2e^-})$

Ba_3N_2: phase transition & conducting properties

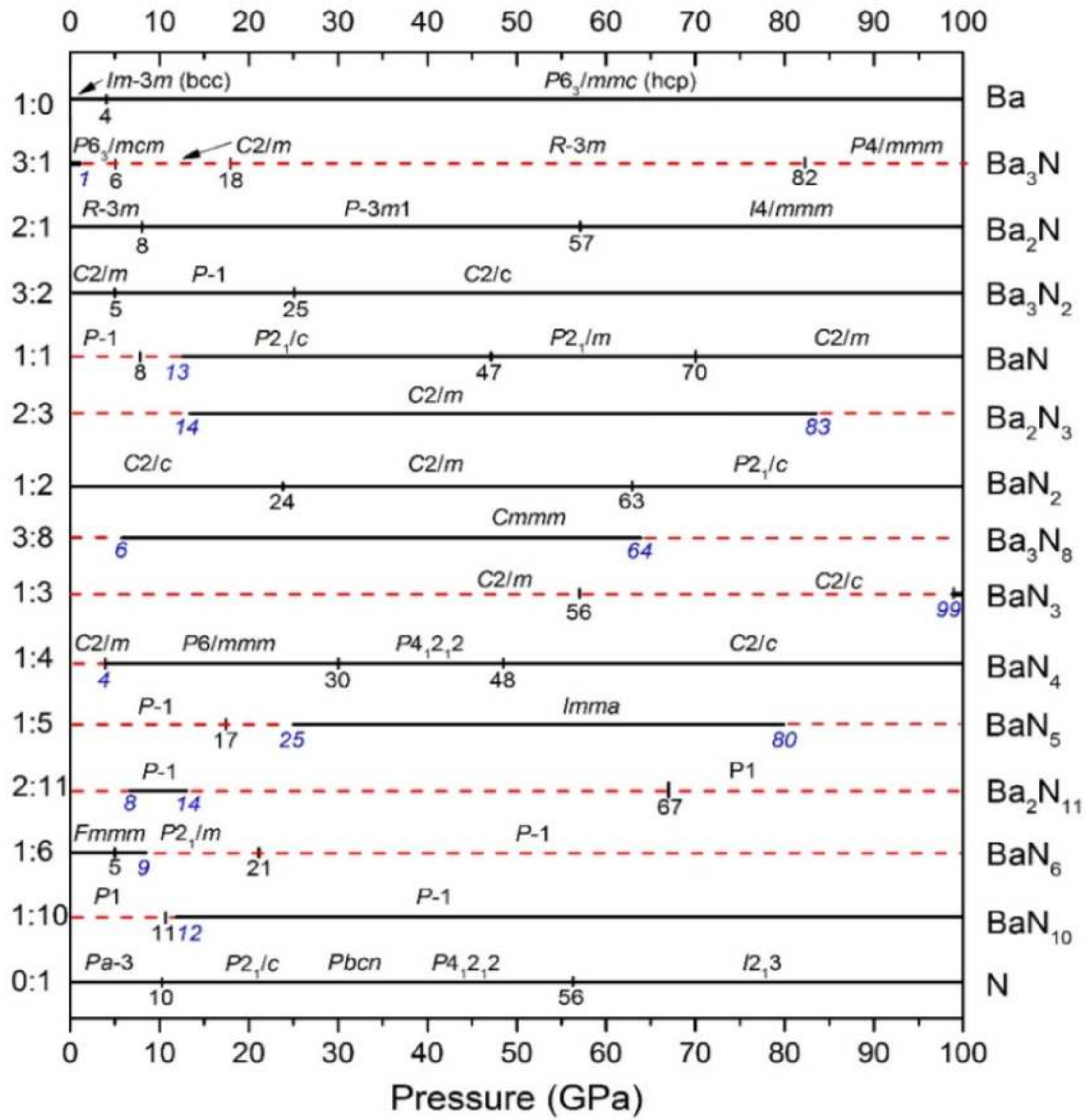


N_2 dumbbell + N^{3-} nitride	**N^{3-} nitride**	**N^{3-} nitride**
C2/m	*P-1*	*C2/c*
$(Ba^{2+})_6(N_2^{4-})(N^{3-})_2(2e^-)$	$3Ba^{2+}$, $2N^{3-}$	6s→5d (Ba) transition

metallic electride → semiconductor → metal

2a. Ba-N

Ba-N from 0 to 100 GPa:
13 compositions and 24 stable phases



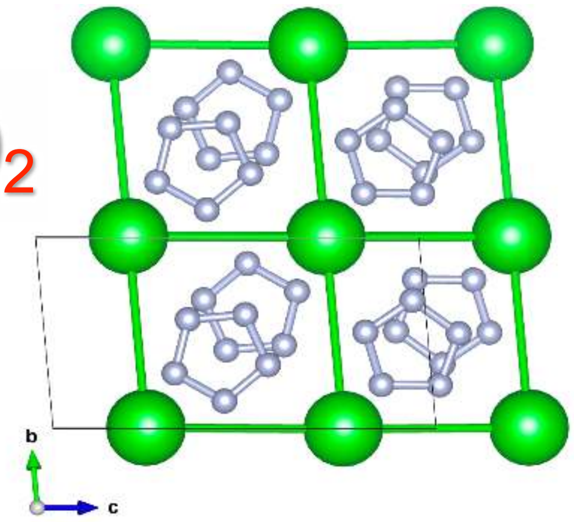
10 nitrogen atom per Ba: HEDM

Pentazolate N_5^-

$Ba(N_5)_2$

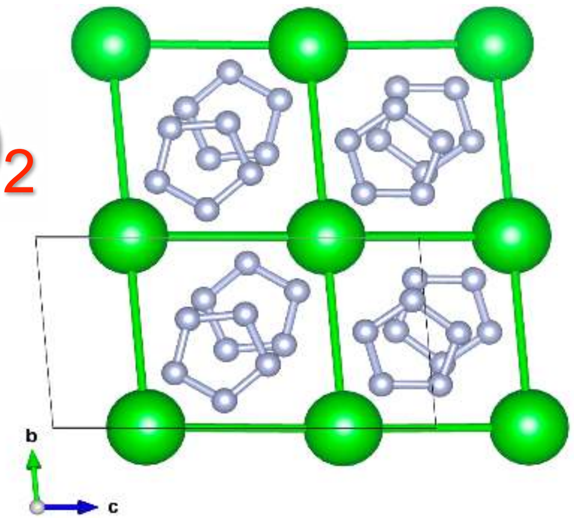
P-1

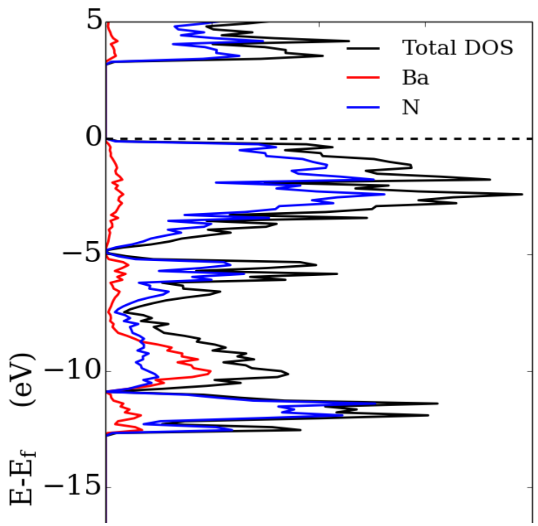
50 GPa



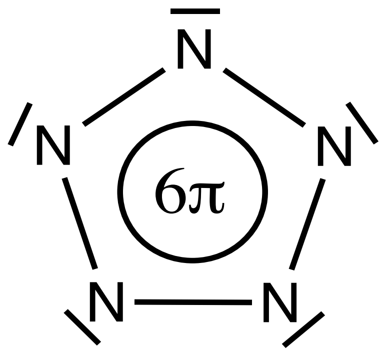
Pentazolate N_5^-

$Ba(N_5)_2$
P-1
50 GPa





$Ba^{2+}(N_5^-)_2$



Potential High Energy Density Materials?

Explosive Properties* for Potential HEDMs

	phase space group	energy density, kJ/g	VoD, km/s	detonation pressure, kPa
quenchable	BaN_4 $P4_12_12$	0.623	5.9	234
	BaN_4 $C2/c$	0.626	5.7	213
	BaN_{10} $I\bar{4}2d$	0.577	6.1	204

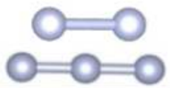
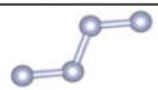
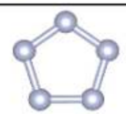
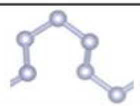
lead azide $Pb(N_3)_2$ ~ 3.8 km/s

2,4,6-trinitrotoluene (TNT) ~ 6.9 km/s

detonation velocity (VoD)

Kamlet−Jacobs empirical equation

Ba-N under pressure: a summary

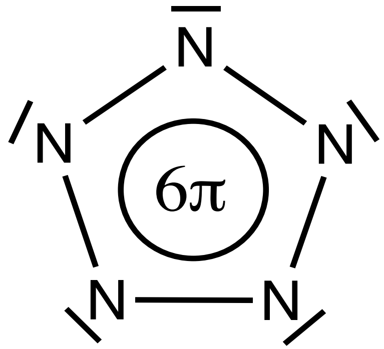
Structure information	Nitrogen network	Composition	VEC[a]	Space group and associated pressure stability range[b]
Isolated nuclei		Ba_3N Ba_2N Ba_3N_2	11 9 8	*P*6₃/*mcm*, 0-1 *R*-3*m*, 0-8; *P*-3*m*1, 1-57; *I*4/*mmm*, >57 *P*-1, 5-25; *C*2/*c*, >25
Isolated nuclei and N_2 dumbbells		Ba_3N_2	8	*C*2/*m*, 0-5
N_2 dumbbells		BaN Ba_2N_3 BaN_2 Ba_3N_8 BaN_4 BaN_6	7 6.3 6 5.8 5.5 5.3	$P2_1/c$, 13-47; $P2_1/m$, 47-70; *C*2/*m*, >70 *C*2/*m*, 14-83 *C*2/*c*, 0-24; *C*2/*m*, 24-63 *Cmmm*, 6-64 *P*6/*mmm*, 4-30 *Fmmm*, 0-5
N_2 dumbbells and linear N_3 azides		Ba_2N_{11}	5.4	*P*-1, 6-14
Linear N_3 azides		BaN_6	5.3	$P2_1/m$, 5-9
Finite N_4 chains		BaN_2	6	$P2_1/c$, >63
Five-membered rings		BaN_5 BaN_{10}	5.4 5.2	*Imma*, 25-80 *P*-1, >12
1D armchair chains; 1D chains linked by non-planar *cis*-bent N_4 units		BaN_4	5.5	$P4_12_12$, 30-48; *C*2/*c*, > 48
1D infinite helical chains		BaN_3	5.7	*C*2/*c*, 99-100

[a]Valence electron concentration of Ba_xN_y is given in brackets; VEC = (2*x*+5*y*)/(*y*).

[b]Pressure in GPa. The pressure range corresponds to the domain of thermodynamic stability.

Studied pressure range: [0 to 100 GPa]

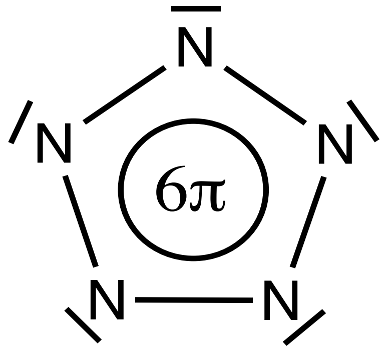
Pentazolates $M(N_5)_x$

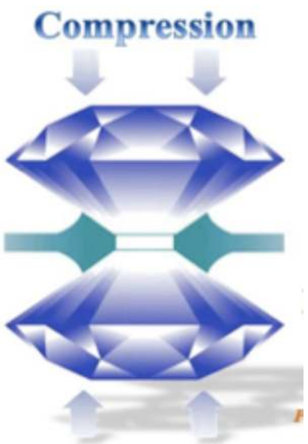


N_5^-

- Alkaline earth elements– pentazolates: B. Huang, PhD thesis 2014-2017 (Poitiers U.)
http://theses.univ-poitiers.fr/59262/2017-Huang-Bowen-These
- Transition metals-N_5: B. Huang, B. Wang, F. Guégan, W. Hu, G. Frapper - *coming soon*
- $Sn(N_5)_4$: B. Wang, R. Larhlimi, H. Valencia, F. Guégan, G. Frapper - JPC C (ACS), 2020

Pentazolates $M(N_5)_x$

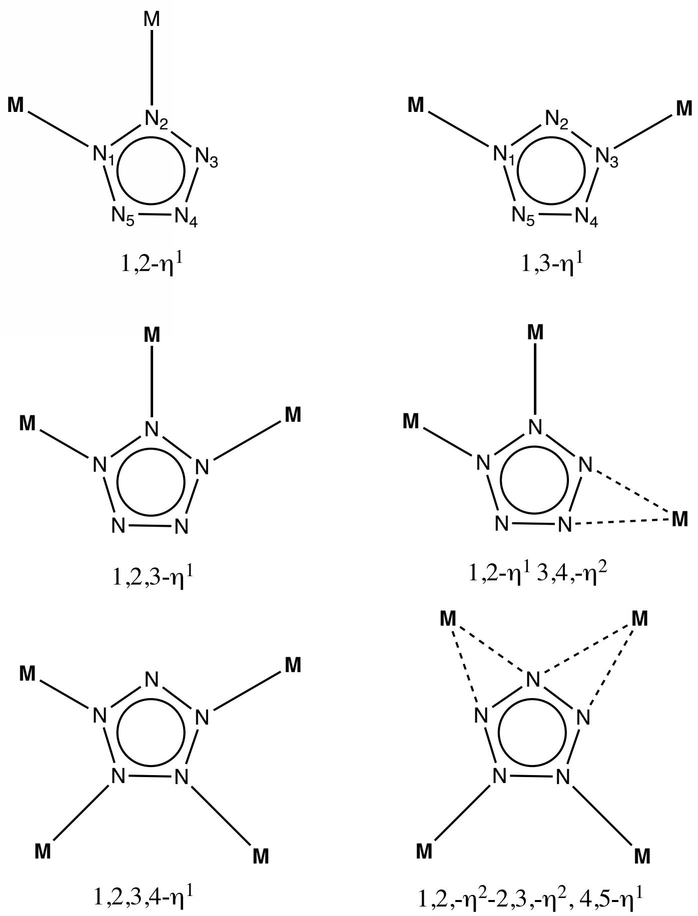




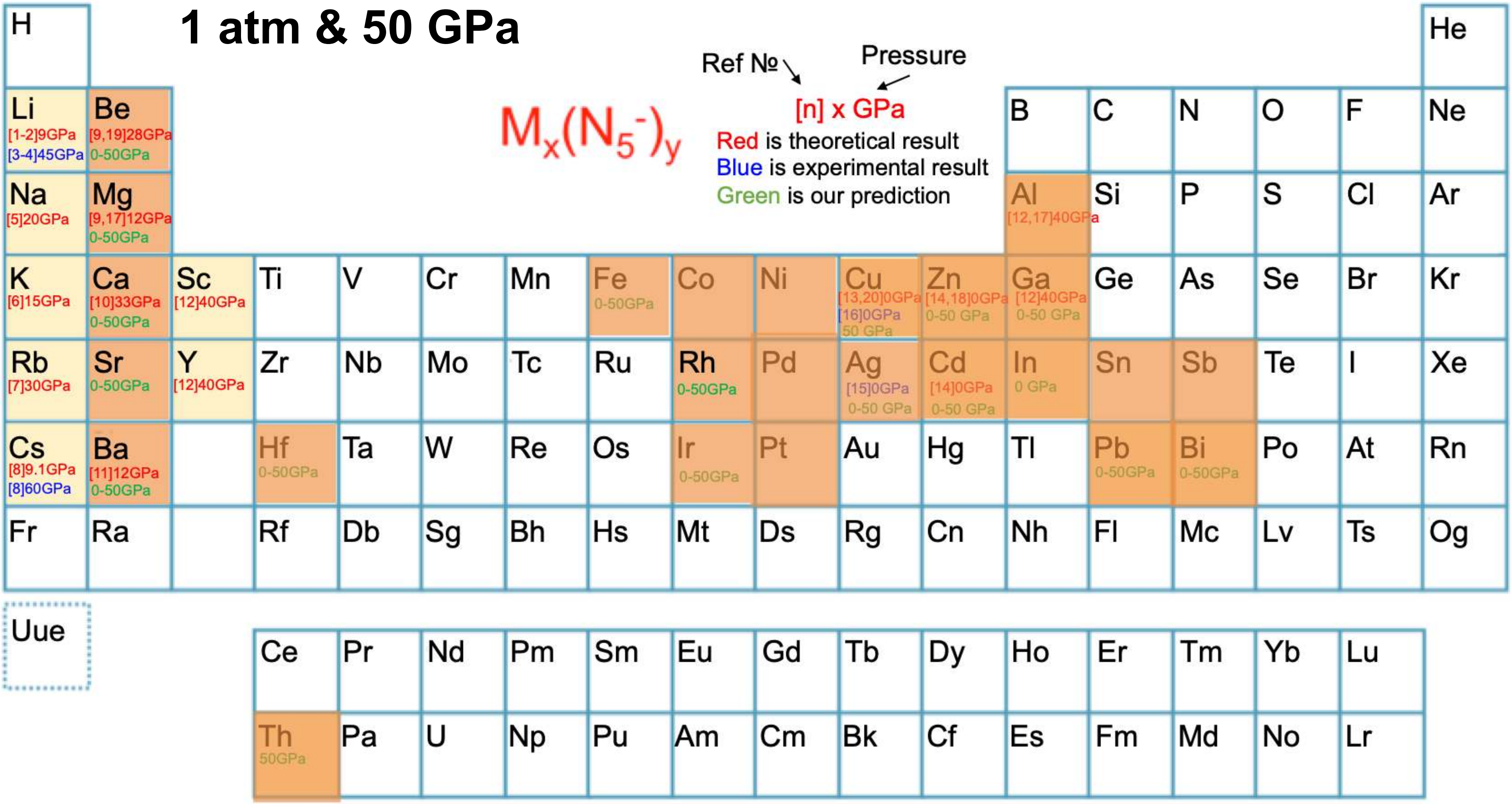
CsN_5 : Steele, B. A, Oleynik, I. *et al Chem. Mater.* **2017**, *29*, 735.
LiN_5 : Laniel, D. *et al J. Phys. Chem. Lett.* **2018**, *9*, 1600.

+ **hydrated pentazolates salts**

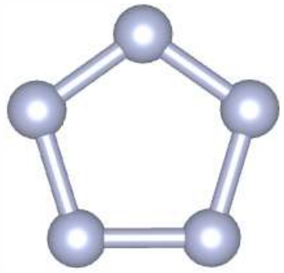
Pentazolates $M(N_5)_x$



- Structural diversity
- 1D, 2D, 3D nets in bulk crystals?


1 atm & 50 GPa
$M_x(N_5^-)_y$
Ref №
Pressure
[n] x GPa
Red is theoretical result
Blue is experimental result
Green is our prediction
H
He
Li [1-2]9GPa [3-4]45GPa
Be [9,19]28GPa 0-50GPa
B C N O F Ne
Na [5]20GPa
Mg [9,17]12GPa 0-50GPa
Al [12,17]40GPa
Si P S Cl Ar
K [6]15GPa
Ca [10]33GPa 0-50GPa
Sc [12]40GPa
Ti V Cr Mn
Fe 0-50GPa
Co Ni
Cu [13,20]0GPa [16]0GPa 50 GPa
Zn [14,18]0GPa 0-50 GPa
Ga [12]40GPa 0-50 GPa
Ge As Se Br Kr
Rb [7]30GPa
Sr 0-50GPa
Y [12]40GPa
Zr Nb Mo Tc Ru
Rh 0-50GPa
Pd
Ag [15]0GPa 0-50 GPa
Cd [14]0GPa 0-50 GPa
In 0 GPa
Sn Sb Te I Xe
Cs [8]9.1GPa [8]60GPa
Ba [11]12GPa 0-50GPa
Hf 0-50GPa
Ta W Re Os
Ir 0-50GPa
Pt Au Hg Tl
Pb 0-50GPa
Bi 0-50GPa
Po At Rn
Fr Ra Rf Db Sg Bh Hs Mt Ds Rg Cn Nh Fl Mc Lv Ts Og
Uue
Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Th 50GPa
Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

2b. Pentazolates



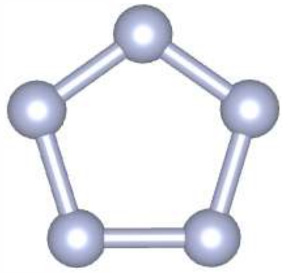
structural constraint

USPEX *9.4.4*: molecular crystal EA

```
PARAMETERS EVOLUTIONARY ALGORITHM
***************************************
***************************************
*        TYPE OF RUN AND SYSTEM       *
***************************************
***************************************
USPEX      : calculationMethod
310        : calculationType
1          : optType

% symmetries
2-230
% endSymmetries

% atomType
Ni N
% EndAtomType


% numSpecies
1 2
% EndNumSpecies
```

$Ni(N_5)_2$ →

INPUT.txt



structural constraint

USPEX 9.4.4: molecular crystal EA

MOL_1: Ni

MOL_1
```
MOL_Ni
Number of atoms:   1
  Ni     0.0000    0.0000    0.0000    0  0  0  1
```

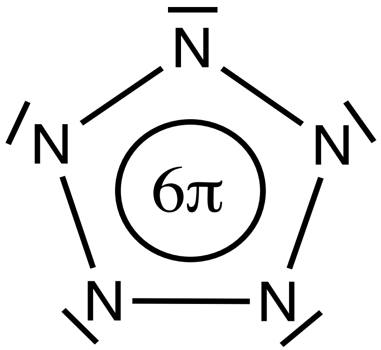
MOL_2: N_5

MOL_2
```
MOL_N5
Number of atoms:   5
   N    0.0018  -1.1107    0.0069   0 0 0  0
   N    1.0433  -0.3377   -0.0070   1 0 0  0
   N    0.6474   0.8873    0.0043   2 1 0  0
   N   -0.6432   0.9080    0.0000   3 2 1  0
   N   -1.0494  -0.3468   -0.0043   4 3 2  0
```

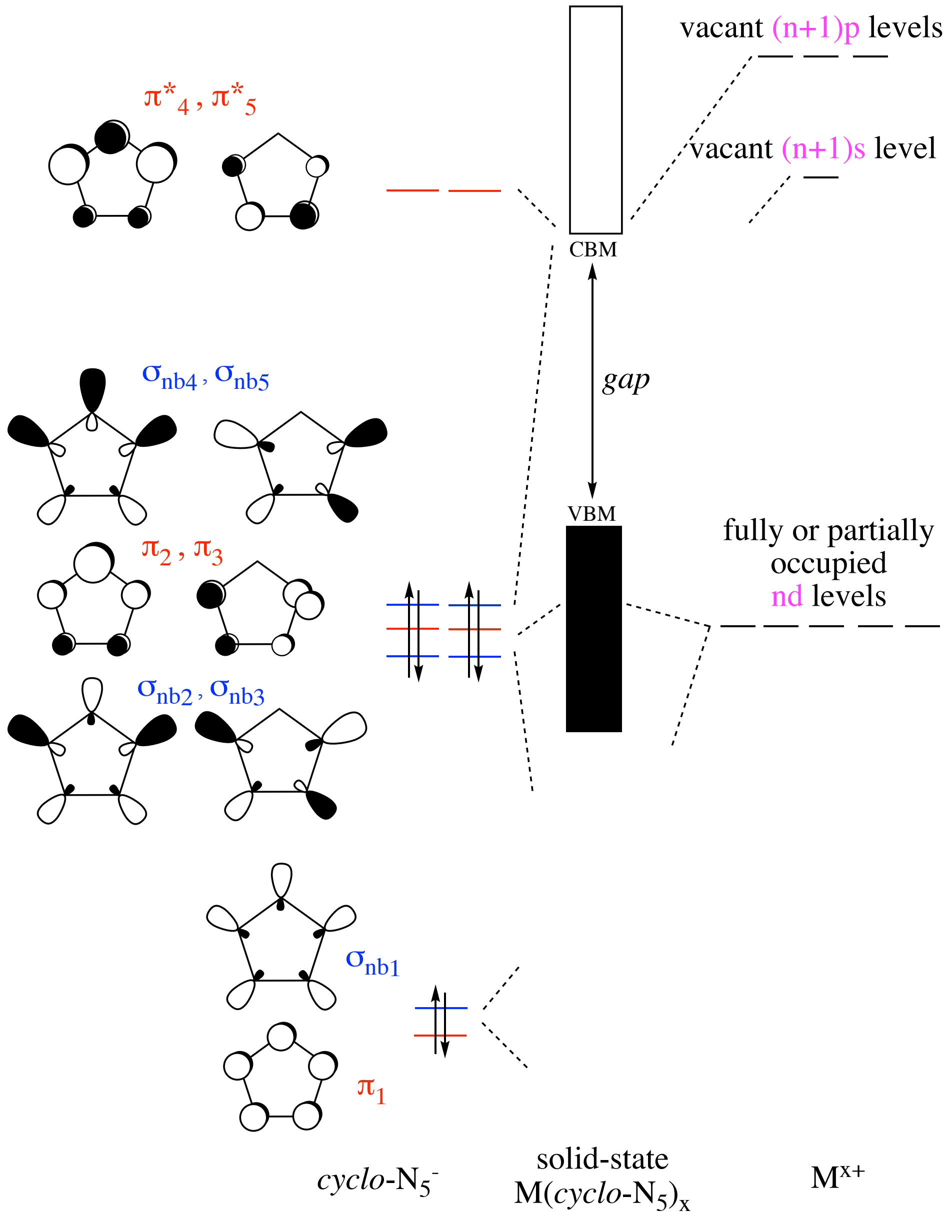
Z-matrix

Pentazolates $M(N_5)_x$

N-N: 1.30-1.35 Å
(single-double bonds)

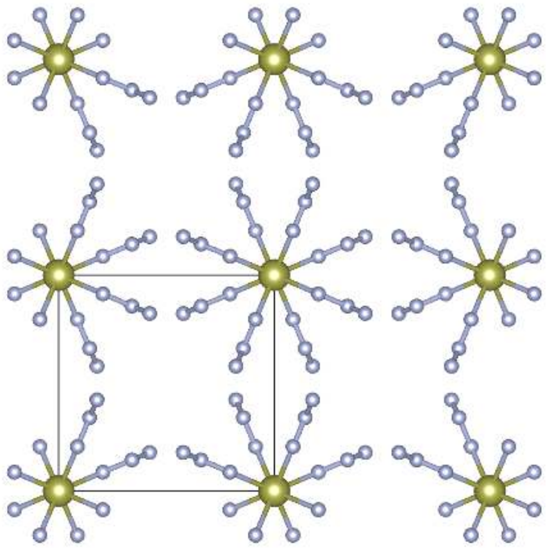


Hückel rule 4n+2

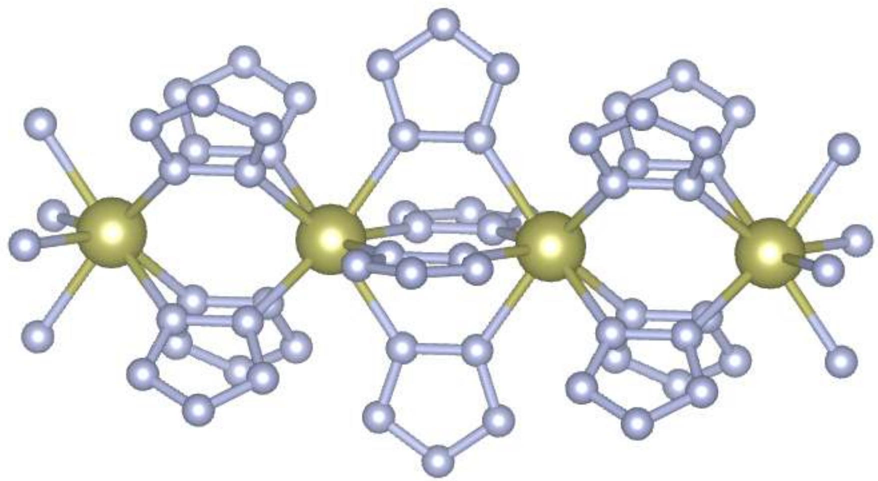


Hf^{4+}

Up to twenty nitrogen per metal: Hf(*cyclo*-N_5)$_4$



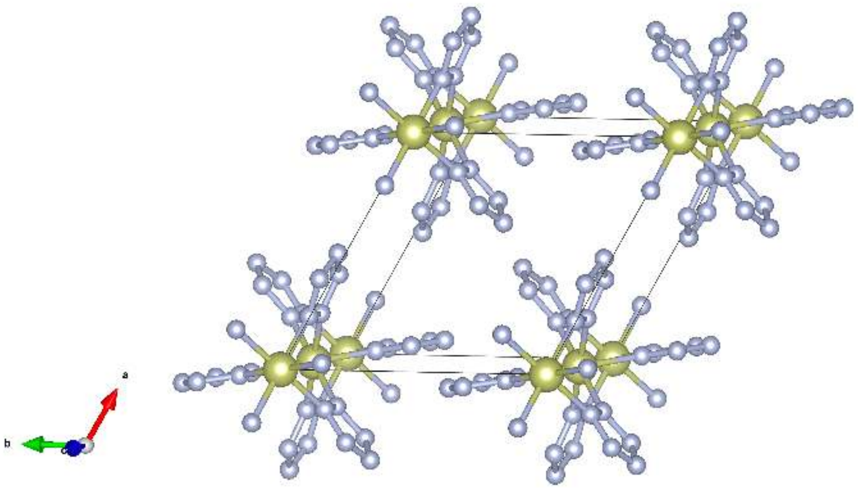
P4/mcc



1 atm: 1D, Hf^{4+} in square antiprism site, 16e ML_8 d^0

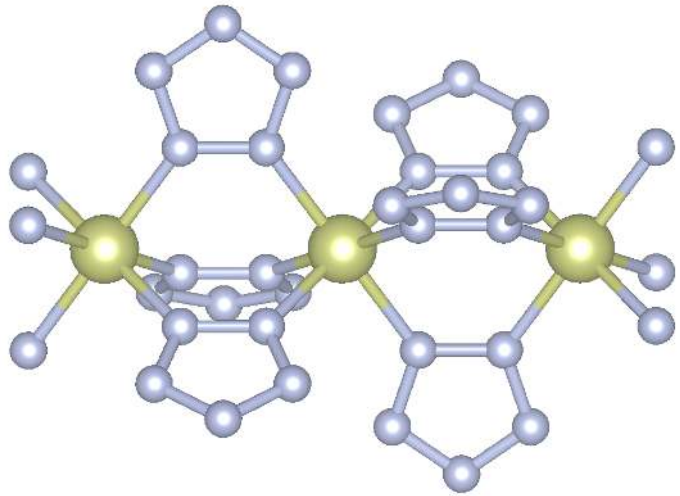
Ir^{3+}

1D Ir(*cyclo*-N_5)$_3$ at 1 atm



P6_3/m at 1 atm

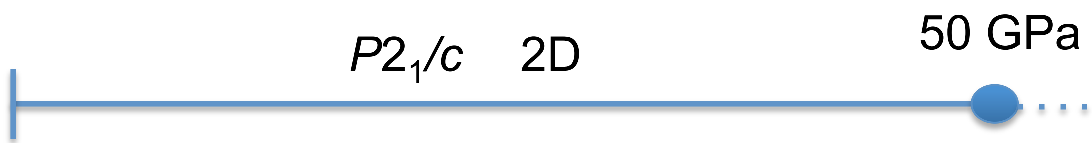
1,2-N_5



Ir-N:1.85 Å

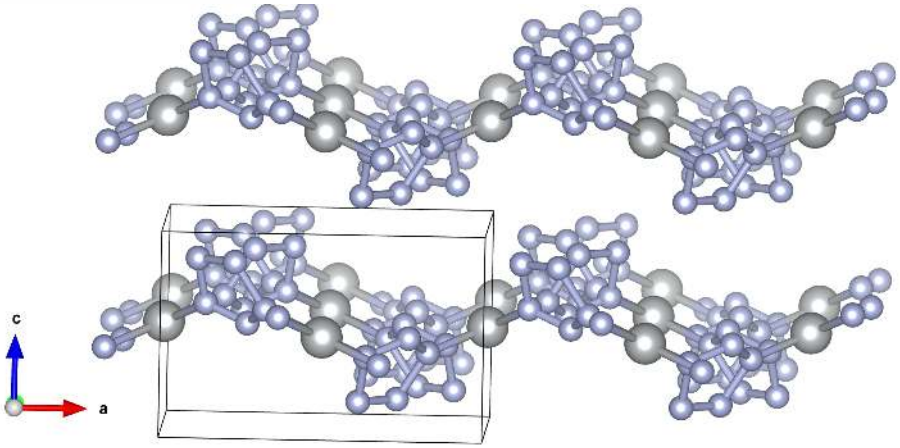
1 atm: 1D, Ir^{3+} in octa site, 18e ML_6 d^6

Ni^{2+}

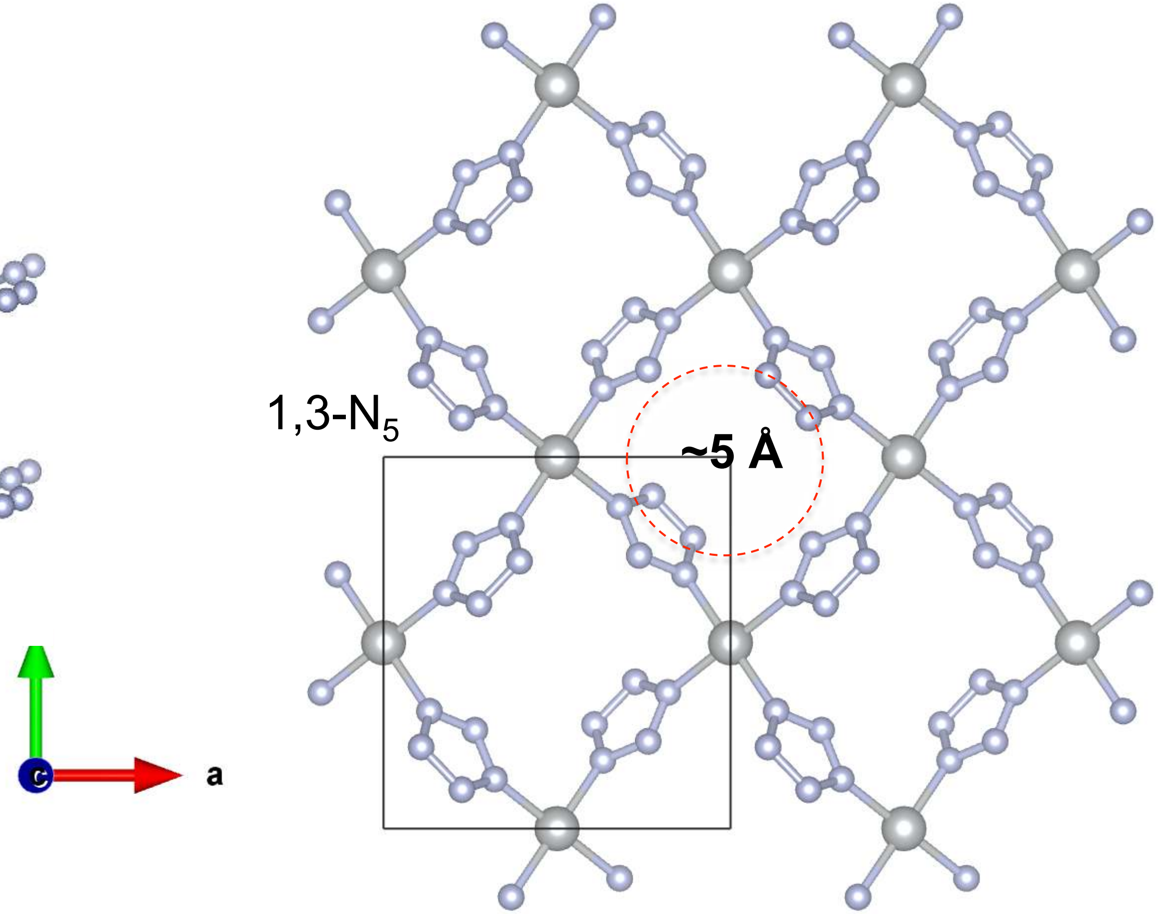


2D Ni(*cyclo*-N_5)$_2$

Ni-N: 1.92-2.02 Å



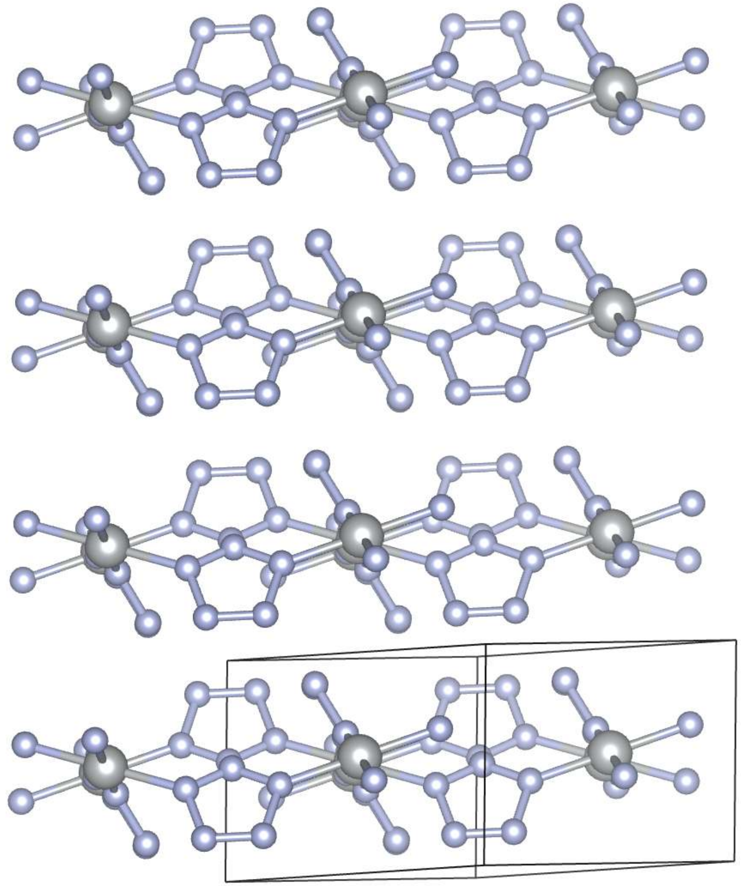
*P*2$_1$/*c* at 1 atm



1 atm: 2D, Ni^{2+} in square planar 16e ML_4 d^8

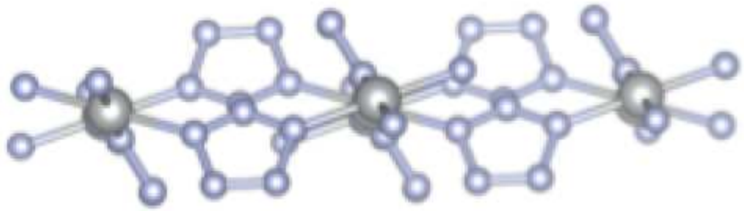
Ni^{2+}

$Ni(\textit{cyclo}\text{-}N_5)_2$: From bulk layered phase to 2D structure



$P2_1/c$ at 1 atm

exfoliation →



2D $Ni(\textit{cyclo}\text{-}N_5)_2$

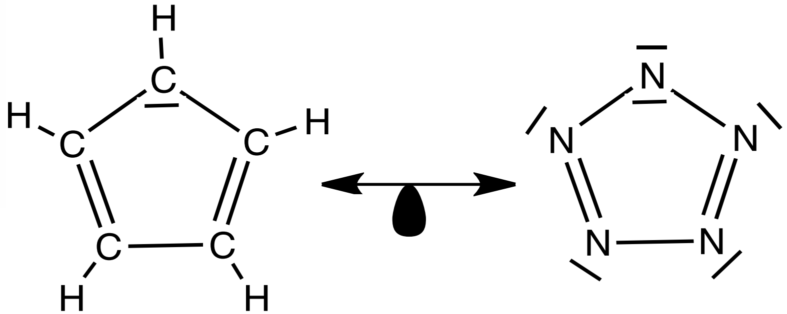
- Dynamically stable
- Thermally stable up to 900 K

Cleavage energy: 0.180 kJ/m^2

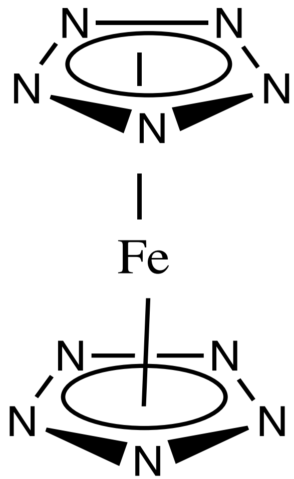
(Graphite to graphene: 0.371 kJ/m^2 @ SCAN-rVV10)

Fe^{2+}

solid-state Fe(*cyclo*-N_5)$_2$?



$C_5H_5^- = N_5^-$



Isolobal to ferrocene Fe(η^5-C_5H_5)$_2$

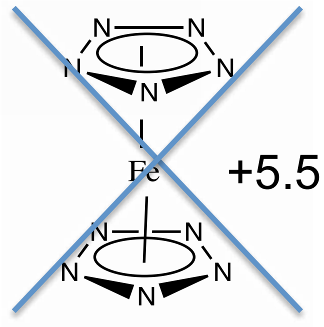
Lein M1, Frunzke J, Timoshkin A, **Frenking G.**
Chemistry. 2001 Oct 1;7(19):4155-63. Iron bispentazole Fe(eta5-N_5)$_2$,
a theoretically predicted high-energy compound:
structure, bonding analysis, metal-ligand bond strength
and a comparison with the isoelectronic ferrocene.

Fe^{2+}

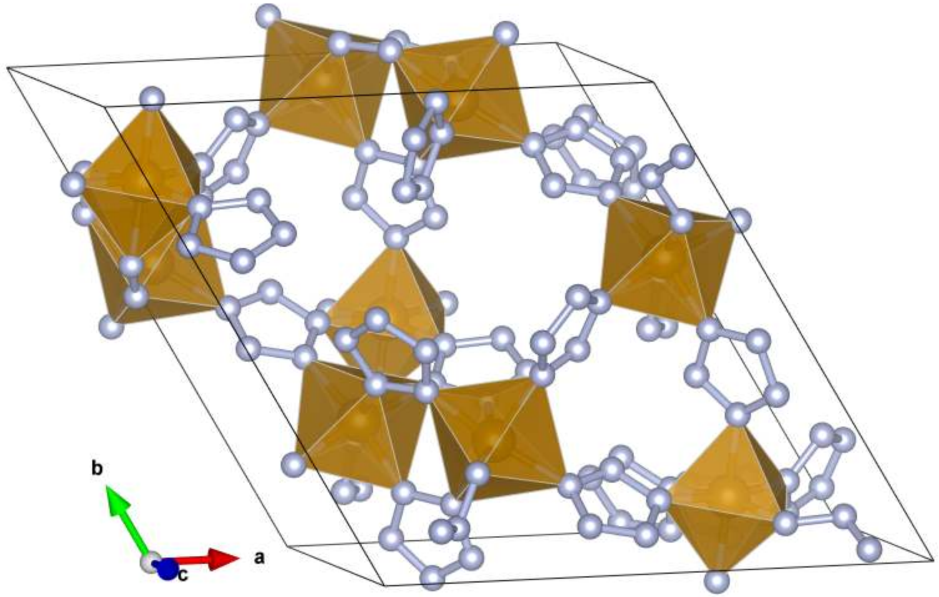
50 GPa

***R*3** 3D

3D Fe(*cyclo*-N_5)$_2$



+5.5 eV/mol



*R*3 at 1 atm
MIF

1 atm: 3D, Fe^{2+} in octa site, 18e ML_6 d^6

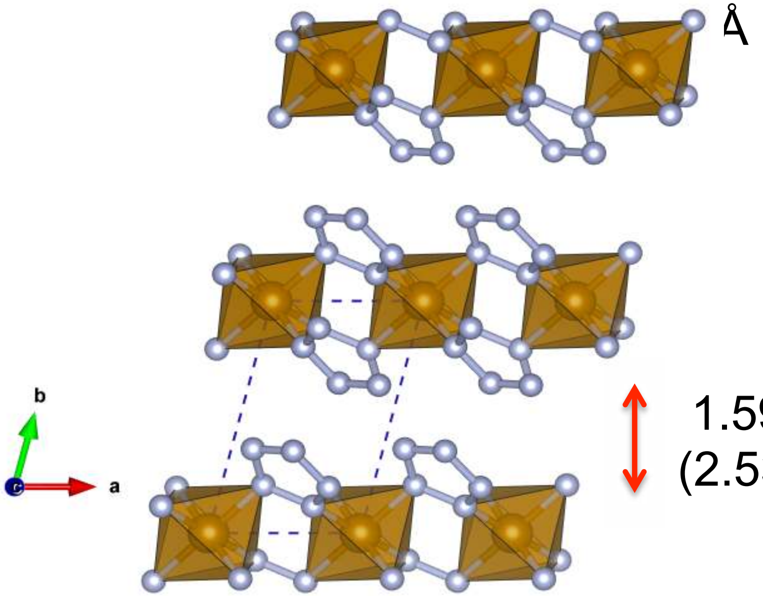
2b. Pentazolates

Fe^{2+}

14 GPa 50 GPa

*R*3 3D *P*-1 2D

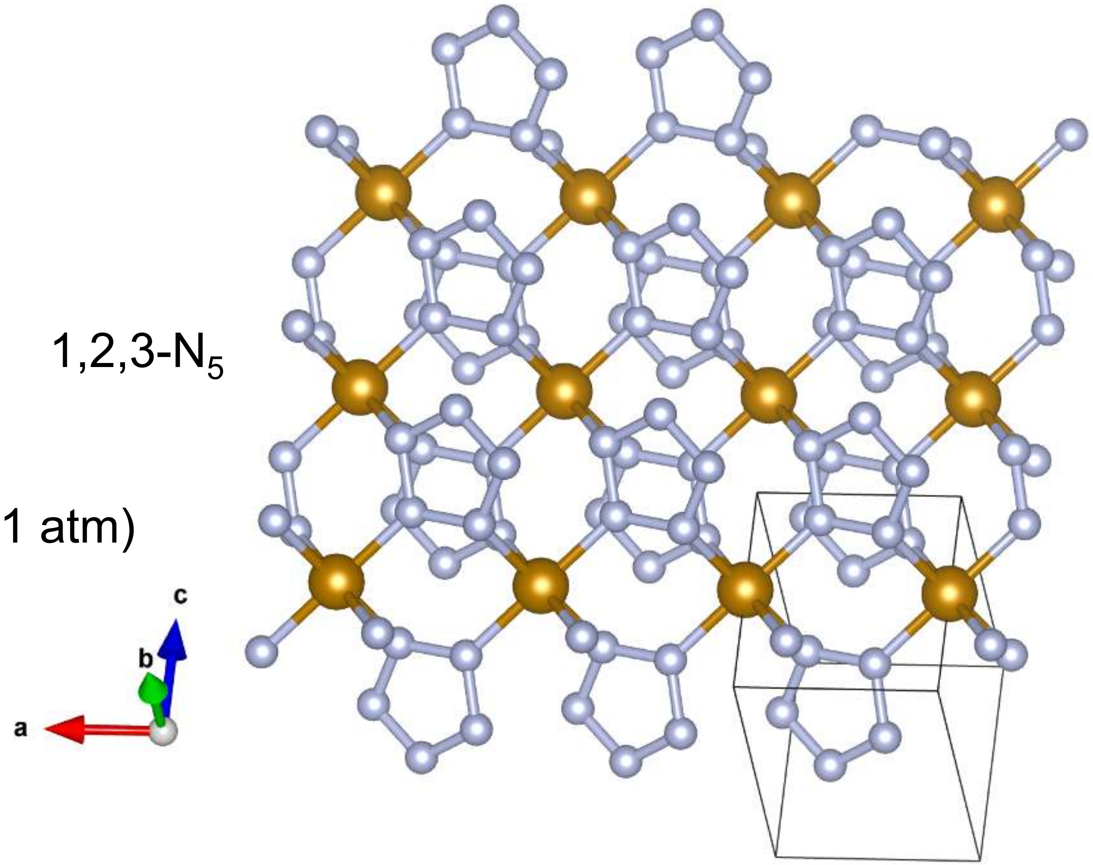
2D Fe(*cyclo*-N_5)$_2$



1.59 Å
(2.53 Å @1 atm)

P-1 at 50 GPa

1,2,3-N_5



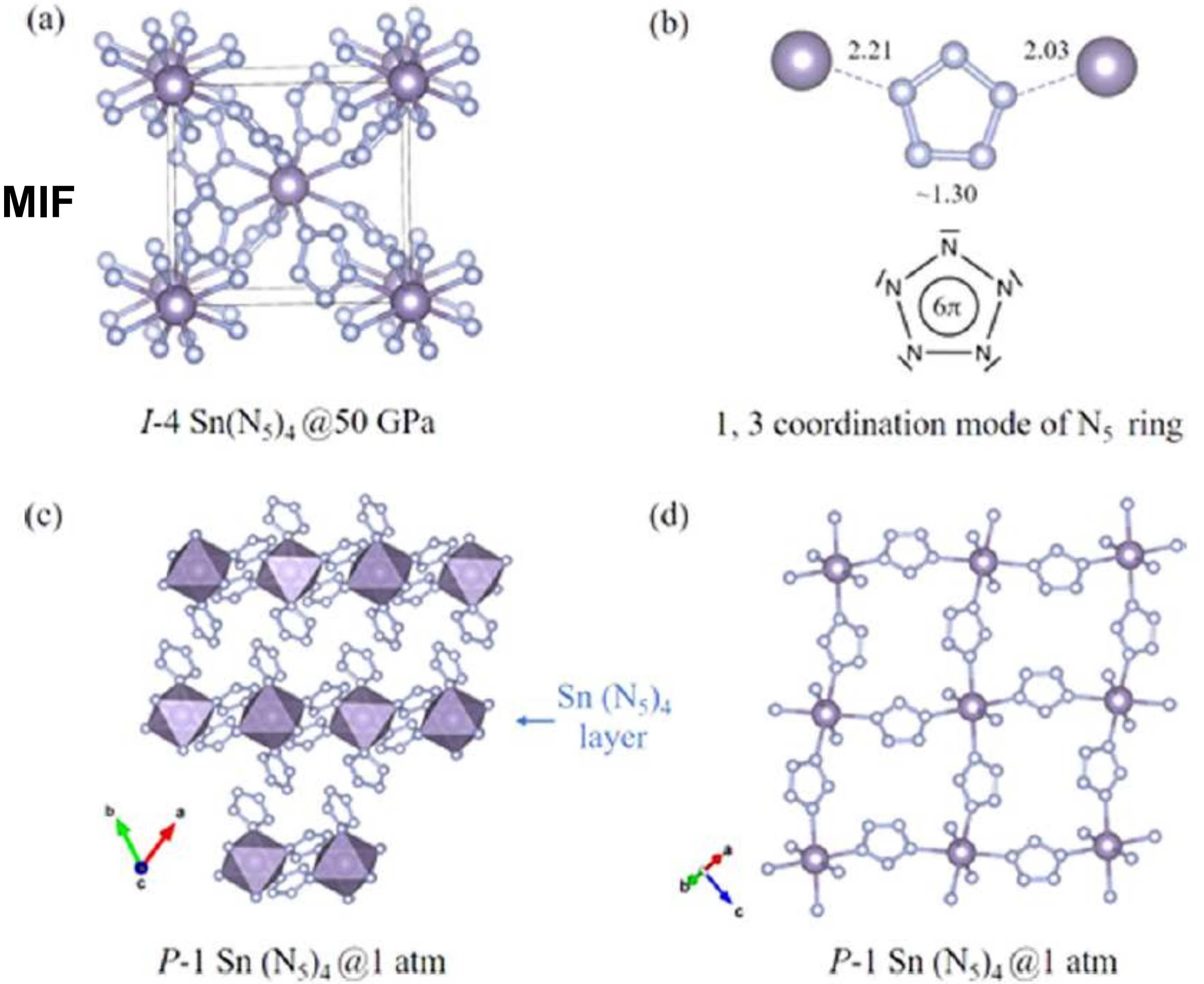
HP: 2D, Fe^{2+} in octa site, 18e ML_6 d^6

Quenchable : +60 meV/atom above *R*3 phase

Sn^{4+}

3D&2D Sn(*cyclo*-N_5)$_4$

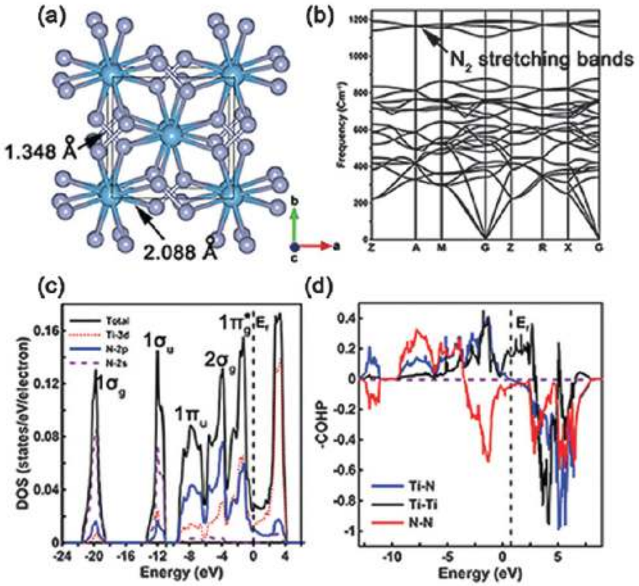
MIF

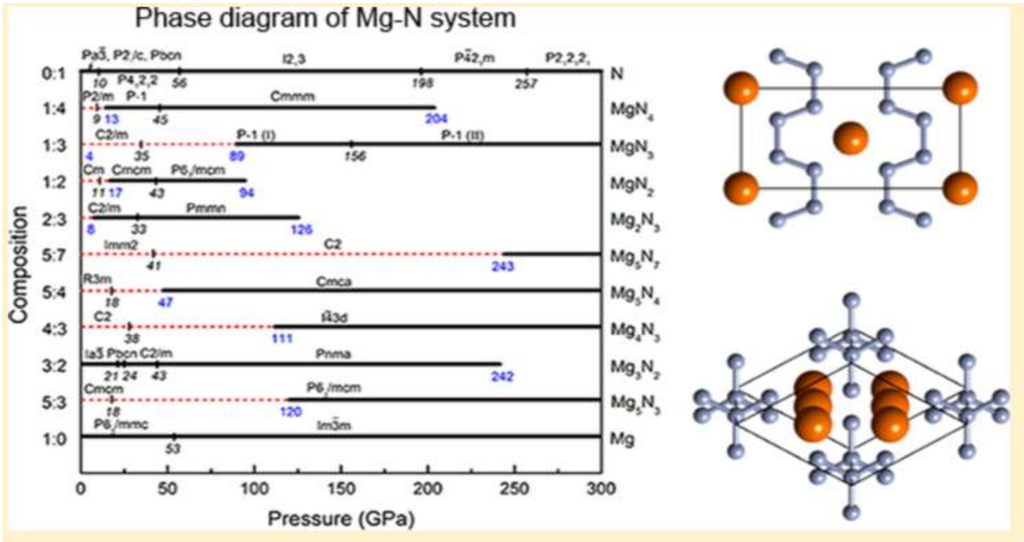


1,,2,3,4-N_5

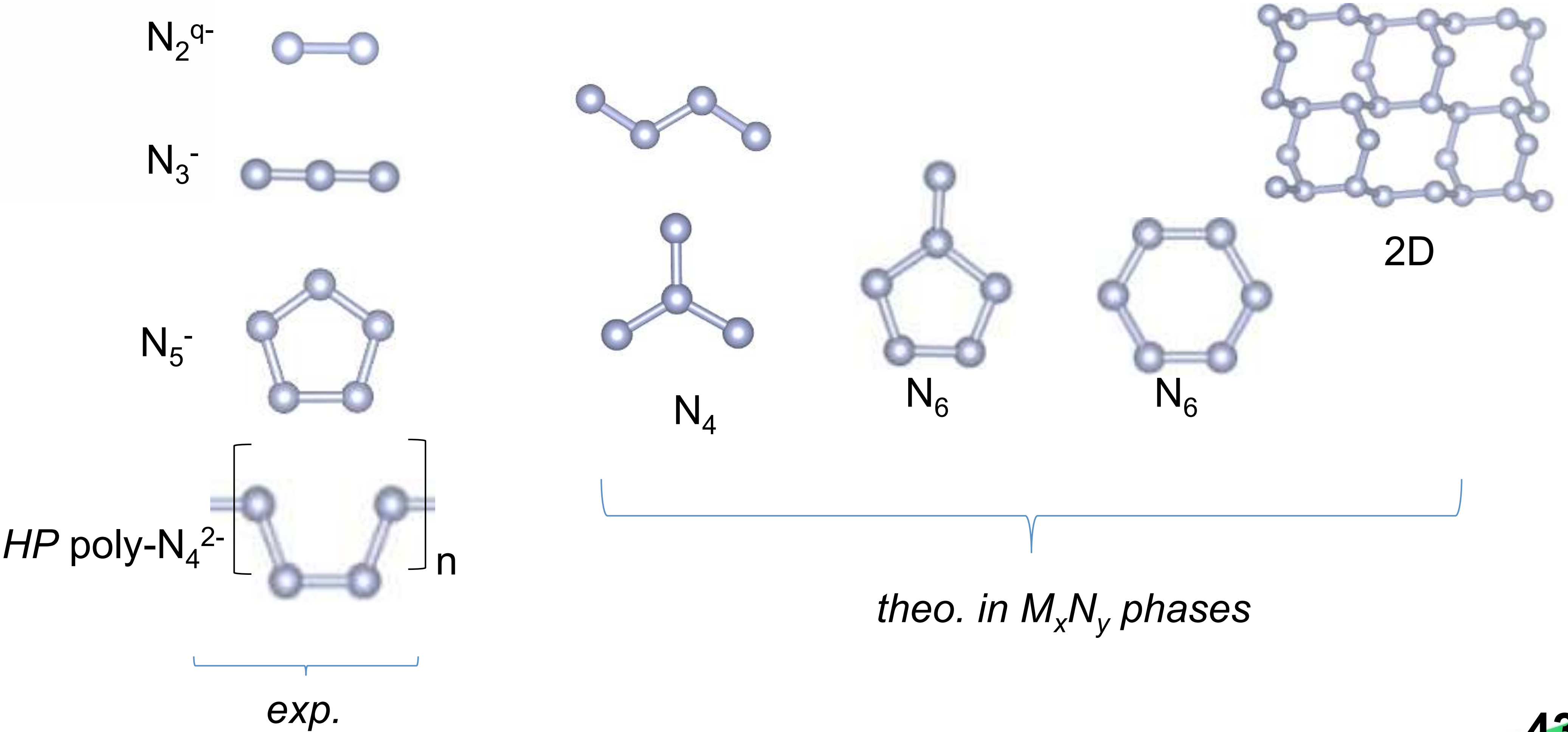
Predicting polynitrogen materials

HP TiN_2 & MgN_4 compositions
have been experimentally characterized

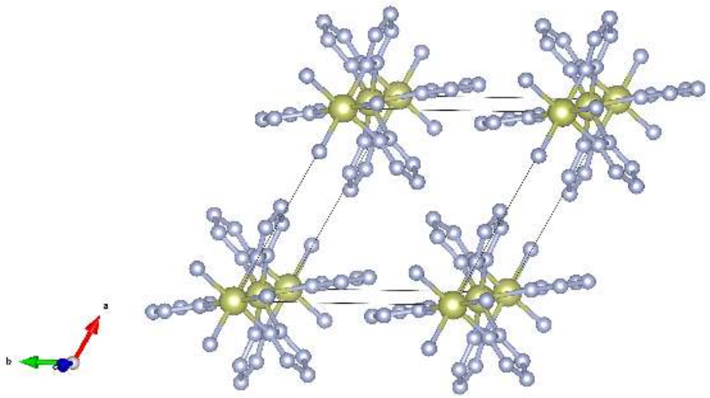




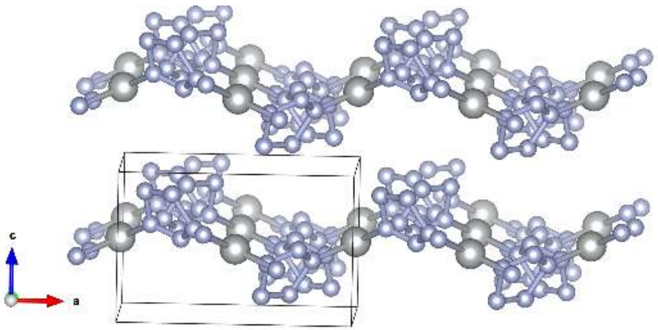
To summarize… ***aesthetic motivation…***



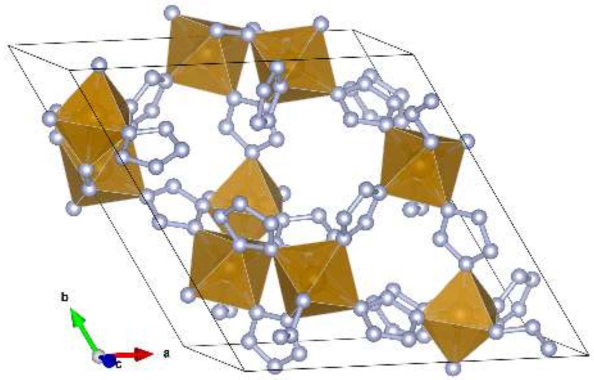
To summarize… ***aesthetic motivation…***



1D



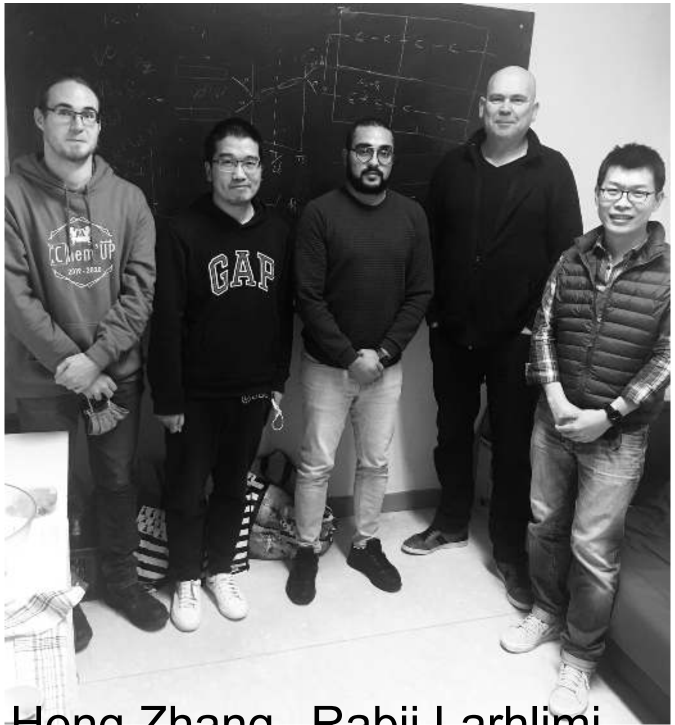
2D



3D

Acknowledgements

Pr Frédéric Guégan



Dr Busheng Wang

Heng Zhang   Rabii Larhlimi

Post-docs: Dr. Dongho Nguimbo (MOPGA) - Dr. Somayeh Faraji Nafchi (ANR)

Collaborators : Dr B. Huang (Hunan University, Changsha), Dr Shuyin Yu (Particle Cloud)
Dr H. Valencia (Nagoya U., Japan, OVHPA
Pr. Q. Zeng, K. Yu, J. Wang (NPU Xi'an - ANR)
Pr. A.R. Oganov (Skoltech & MIPT Moscow, NPU Xi'an)

- High Performance Applications

IC2MP

€€€

HPC – computational ressources

GENCI TGCC – Curie / GENCI CINES
Meso-centre SPIN – THOR U. Poitiers
FEDER + Nouvelle Aquitaine + UFR SFA (cluster local : 240 coeurs)

Grants (time to time…)

ANR PRCI China-France *Predict_2D_NanoMat* 2018-2021;

Région Nouvelle Aquitaine / Feder (PhD fellowship B. Huang/R. Larhlimi)
CNRS – Université de Poitiers

PHC Cai Yuanpei 2018 – CSC (PhD fellowship H. Zhang)
PHC Sakura France-Japan 2020 – Nagoya U. Pr. Ken Niwa

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cnrs dépasser les frontières

In a real space (not virtual), future ML-CSP workshop in Poitiers (Fr) ?!

Any comments, questions?