Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for

Energy Density of High-pressure Nitrogen-Rich MN_x Compounds

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I. Crystal structures and energy densities of ternary nitrides ABN_x.

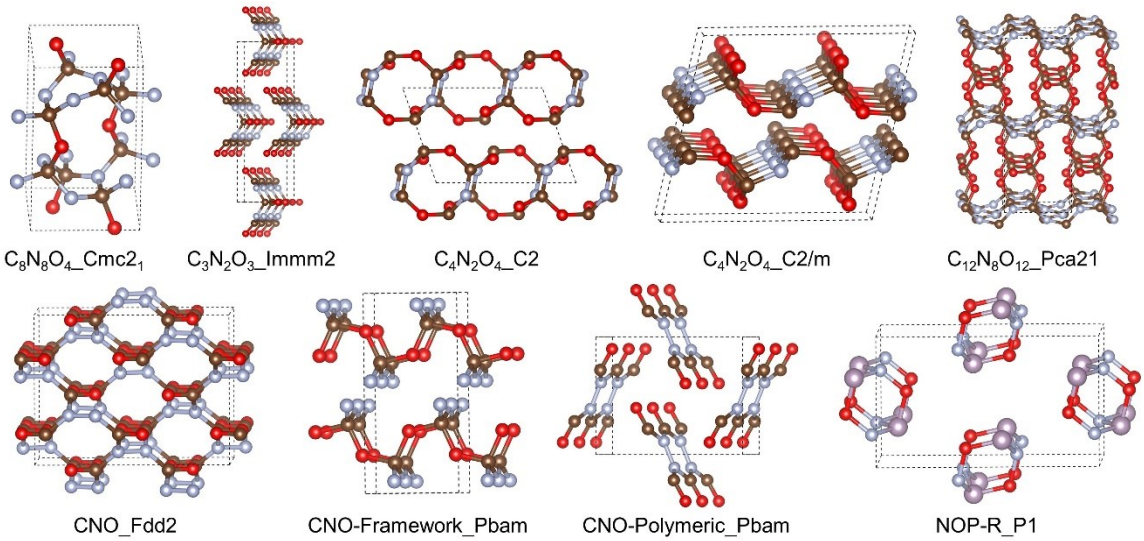

Figure S1. Crystal structures of 9 ternary nitrides ABN_x. N, C, O and P atoms are in silver, brown, red and pink colors, respectively.

Table S1. Decomposition reactions and chemical energy release per formula unit of ABN_x at 0 GPa.

$C_8N_8O_4$_Cmc2$_1$ = 2CO_2_$Pa\bar{3}$ + 4N_2_$Pa\bar{3}$ + 6C_$P6_3/mmc$ + 11.61 eV
$C_3N_2O_3$_Immm2 = 1.5CO_2_$Pa\bar{3}$ + N_2_$Pa\bar{3}$ + 1.5C_$P6_3/mmc$ + 4.19 eV
$C_4N_2O_4$_C2 = 2CO_2_$Pa\bar{3}$ + N_2_$Pa\bar{3}$ + 2C_$P6_3/mmc$ + 7.28 eV
$C_4N_2O_4$_C2/m = 2CO_2_$Pa\bar{3}$ + N_2_$Pa\bar{3}$ + 2C_$P6_3/mmc$ + 7.27 eV
$C_{12}N_8O_{12}$_Pca2$_1$ = 6CO_2_$Pa\bar{3}$ + 4N_2_$Pa\bar{3}$ + 6C_$P6_3/mmc$ + 22.00 eV
CNO_Fdd2 = 0.5CO_2_$Pa\bar{3}$ + 0.5N_2_$Pa\bar{3}$ + 0.5C_$P6_3/mmc$ + 2.15 eV
CNO-Framework_Pbam = 0.5CO_2_$Pa\bar{3}$ + 0.5N_2_$Pa\bar{3}$ + 0.5C_$P6_3/mmc$ + 3.03 eV
CNO-Polymeric_Pbam = 0.5CO_2_$Pa\bar{3}$ + 0.5N_2_$Pa\bar{3}$ + 0.5C_$P6_3/mmc$ + 1.94 eV
NOP-R_P1 = 0.2P_2O_5_Fdd2 + 0.6N_2_$Pa\bar{3}$ + P_$P\bar{1}$+ 2.85 eV

Table S2. Crystal density, type of N oligomer, synthesis pressure, recoverable pressure and energy density of ABN_x.

Compounds	Reference	Density at 0 GPa (g/cm^3)	N Oligomer	Synthesis Pressure (GPa)	Recoverable Pressure (GPa)	E_g(Ref) (kJ/g)	$E_g(N_s)$ (kJ/g)	$E_g(N_g)$ (kJ/g)
$C_8N_8O_4$_$Cmc2_1$	Cal[1]	3.35	N-C chains	10	-	2.91^{Ns}	3.01	4.12
$C_3N_2O_3$_Immm2	Cal[1]	2.56	N-C chains	3.8	-	-	2.45	3.61
$C_4N_2O_4$_C2	Cal[1]	3.36	N-C chains	20	-	-	3.89	6.56
$C_4N_2O_4$_C2/m	Cal[1]	3.15	N-C chains	93	-	-	3.89	4.12
$C_{12}N_8O_{12}$_$Pca2_1$	Cal[1]	3.34	N-C chains	17.3	-	-	3.58	4.74
CNO_Fdd2	Cal[2]	2.85	N-C chains	18	-	-	3.72	4.95
CNO-Framework_Pbam	Cal[2]	3.48	N-C chains	52	0	2.2*	5.74	6.96
CNO-Polymeric_Pbam	Cal[2]	2.57	N-C chains	40	30	-	3.24	4.46
NOP-R_P1	Cal[3]	2.46	N-P chains	-	0	10.6*	4.11	4.51

*Note: The reported energy densities of CNO_Pbam and NOP-R_P1 are noticeably different from our calculation results. For CNO_Pbam, our calculation would result in 2.3 kJ/g if cg-N was used as the decomposition product. Therefore, we think 2.2 kJ/g was obtained because cg-N was used as the decomposition product in the literature. For NOP-R_P1, the reference mistakenly used the reaction energy with external oxygen, instead of the decomposition energy which should be, in the definition of energy density for an energetic material.

Until now, stable high-pressure ternary nitrides[1-3] or quaternary nitrides[4] were scarcely reported. From the literature, we have selected the ternary nitrides ABN_x structures with both thermodynamic and dynamical stability (Figure S1). The energy densities were calculated using the same methods as described in the manuscript (Tables S1-2). The calculated $E_g(N_g)$ range from 3.61 to 6.96 kJ/g, comparable to the energy densities of the binary nitrides MN_x consisting of polymeric nitrogen chains. In particular, the energy densities of CNO-Framework_Pbam (6.96 kJ/g) and $C_4N_2O_4$_C2 (6.56 kJ/g) are relatively

high, which is potentially associated with the high crystal density and high oxygen density. It is interesting that in all reported stable ternary nitrides[1-3] and quaternary nitrides[4] ($C_2N_2H_2O_2$-Pn), the nitrogen atoms form [-N-C-N-]$_n$ or [-N-P-N-]$_n$ polymeric chains rather than [-N-O-N-]$_n$, whereas the reason is unclear yet. To achieve the best recipe in designing nitride compounds that balances the high-energy density and the moderate stability, more research efforts are still needed to understand the complex interplay between two or even more impurities and material properties.

References

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