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Phase stability, chemical bonding and mechanical properties of titanium nitrides: A first-principles study

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Tab. 1s Space group, lattice parameters, Wyckoff position, enthalpy of formation (ΔH, eV/atom) of Ti-N compounds

Compounds	P (GPa)	Lattice parameters					Wyckoff position				ΔH (eV/atom)	
		a	b	c	β	Z	Atom	Site	x	y	z	
Ti_2N *$P4_2/mnm$*	0	4.958 4.945[2]		3.037 3.034[2]		2	Ti	4g	0.703	0.703	0.5	-1.286
							N	2b	0	0	0.5	
Ti_3N_2 *Immm*	0	4.156	3.035	9.160		2	Ti	2d	0.5	0	0.5	-1.465
							Ti	4j	0	0.5	0.316	
							N	4i	0	0	0.162	
Ti_4N_3 *C2/m*	0	9.934	3.018	10.302	150.3	2	Ti	4i	0.266	0.5	0.633	-1.549
							Ti	4i	0.258	0	0.885	
							N	4i	0.001	0.5	0.749	
							N	2a	0	1	1	
Ti_6N_5 *C2/m*	0	5.214	9.015	8.517	144.8	2	Ti	8j	0.487	0.824	0.746	-1.621
							Ti	4i	0.001	1	0.738	
							N	4h	1	0.335	0.5	
							N	4g	0.5	0.166	0	
							N	2c	1	0	0.5	
TiN *Fm-3m*	0	4.255 4.246[1],4.25[3]				4	Ti	4a	0	0	0	-1.671
							N	4b	0	0.5	1	
Ti_2N *Cmcm*	60	2.78	10.545	4.027		4	Ti	4c	0.5	0.318	0.25	-2.103
							Ti	4c	1	0.452	0.75	

							N	4c	0.5	0.317	0.75	
TiN_2 *I4/mcm*	60	4.148	5.033			4	Ti	4a	0.5	0.5	0.75	-2.347
							N	8h	0.615	0.885	1	

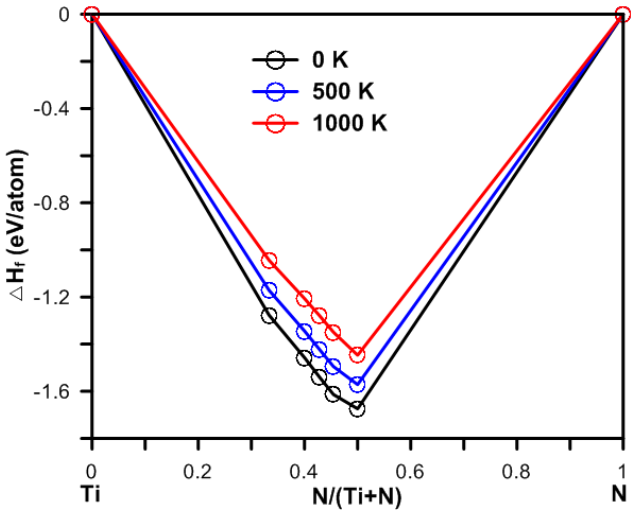

Fig. 1s (Color online). Convex hull of Ti-N system at finite temperatures (0 GPa). The effects of temperature on the structural stability of the ground-state Ti-N compounds are estimated by the quasi-harmonic approximation. Using the phonon calculations, we calculated the zero point energy (ZPE) and vibrational entropy, and together with configurational entropy of ideal disorder. The results yield a conclusion that none of the Ti-N compounds will lose their thermodynamic stability up to 1000 K.

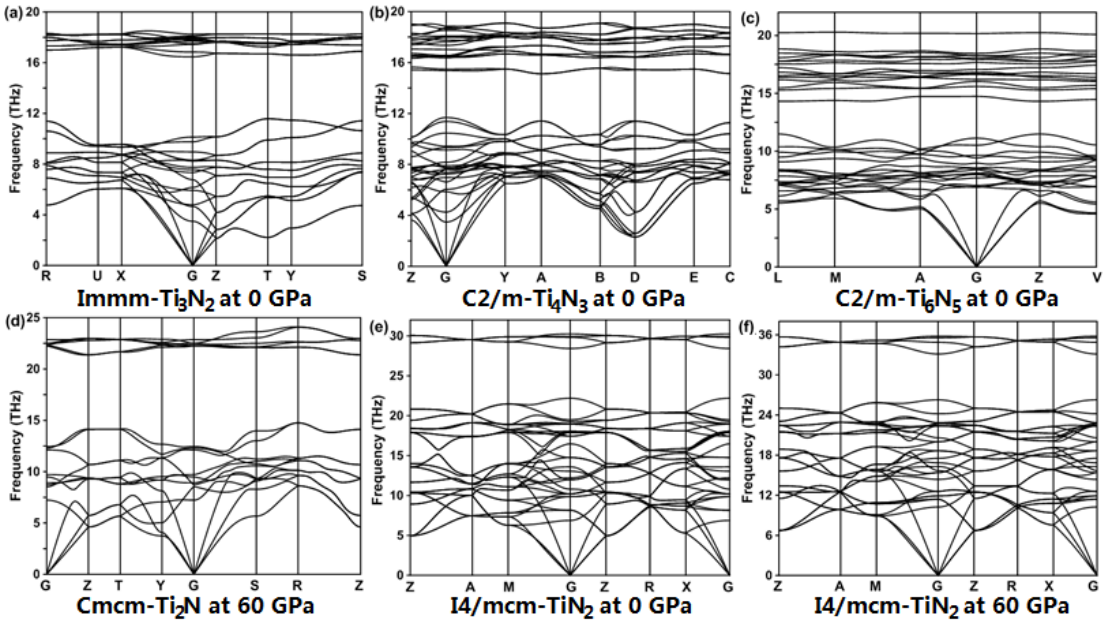

Fig. 2s (Color online). Calculated phonon dispersion curves for the Ti-N polymorphs.

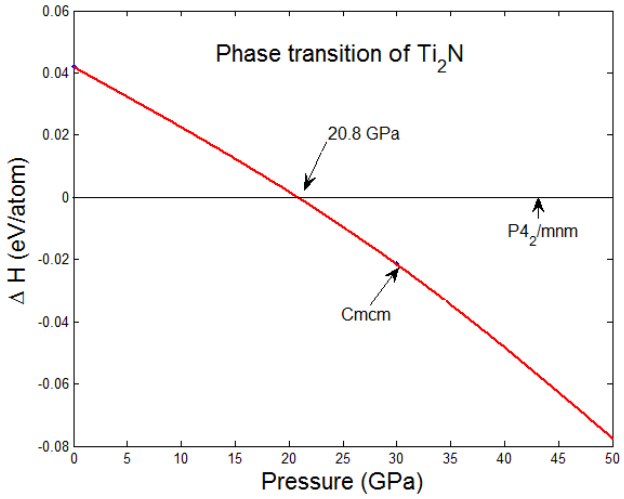

Fig. 3s (Color online). Phase transition from *P4₂/mnm* to *Cmcm* of Ti_2N with increasing pressure

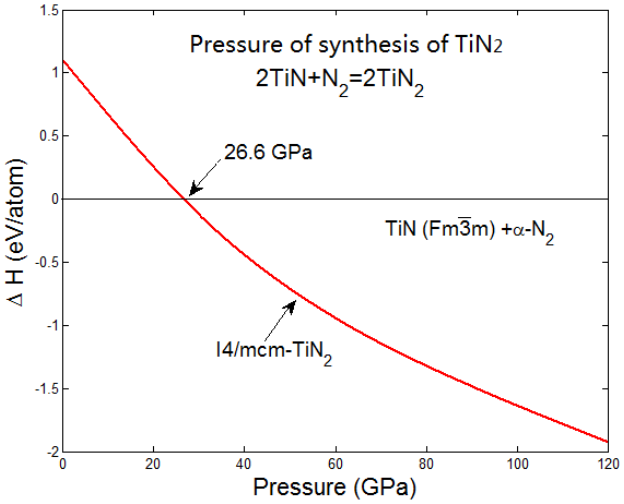

Fig. 4s (Color online). The pressure of synthesis of *I4/mcm*-TiN_2. The Fm-3m-TiN and α-N_2 are selected as reference states.

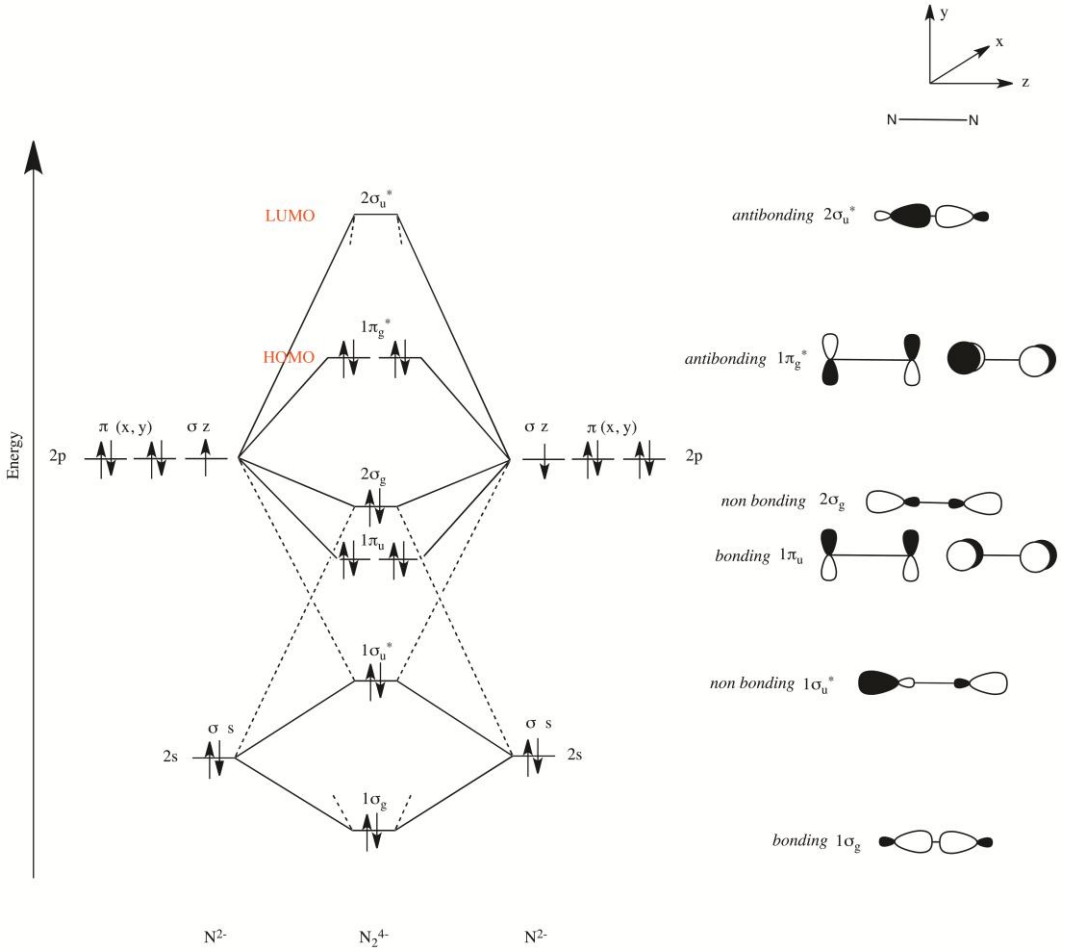

Fig. 5s (Color online). Schematic molecular orbital diagram of N_2^{4-}. The plain and dashed lines indicated the primary and secondary parentages of the orbitals, respectively (2s-2p$_z$ mixing). Only the valence orbitals are shown. N_2^{4-} anion has 14 valence electrons and a bond order of 1.

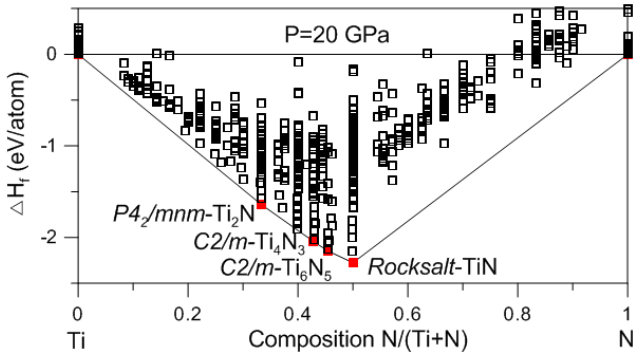

Fig. 6s (Color online). Convex hull diagram of the Ti-N system at 20 GPa.

Equations: The directional dependence of the Young's modulus for crystals of different symmetries

$$\frac{1}{E_{Cubic}} = s_{11} - 2(s_{11} - s_{12} - \frac{1}{2}s_{44})(l_1^2 l_2^2 + l_2^2 l_3^2 + l_3^2 l_2^2)$$

$$\frac{1}{E_{Tetra}} = (l_1^4 + l_2^4)s_{11} + l_3^4 s_{33} + l_1^2 l_2^2 (2s_{12} + s_{66}) + l_3^2 (1 - l_3^2)(2s_{13} + s_{44})$$

$$\frac{1}{E_{Orth}} = l_1^4 s_{11} + l_2^4 s_{22} + l_3^4 s_{33} + l_1^2 l_2^2 (2s_{12} + s_{66}) + l_2^2 l_3^2 (2s_{23} + s_{44}) + l_1^2 l_3^2 (2s_{13} + s_{55})$$

$$\frac{1}{E_{Orth}} = l_1^4 s_{11} + l_2^4 s_{22} + l_3^4 s_{33} + 2(l_1^2 l_2^2 s_{12} + l_2^2 l_3^2 s_{23} + l_1^2 l_3^2 s_{13}) + l_2^2 l_3^2 s_{44} + l_1^2 l_3^2 s_{55}$$

$$l_1^2 l_2^2 s_{66} + 2l_1 l_2 (l_1^2 s_{16} + l_2^2 s_{26} + l_3^2 (s_{36} + s_{45}))$$

where S_{ij} are the elastic compliance tensor components constants and l_1, l_2 and l_3 are the direction cosines.

References

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2. Holmberg B. Structural studies on the titanium-nitrogen system [J]. Acta Chemica Scandinavica, 1962, 16(5): 13.
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