Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

First-principles study of Zr-N crystalline phases: phase stability, electronic and mechanical properties

CONTENTS

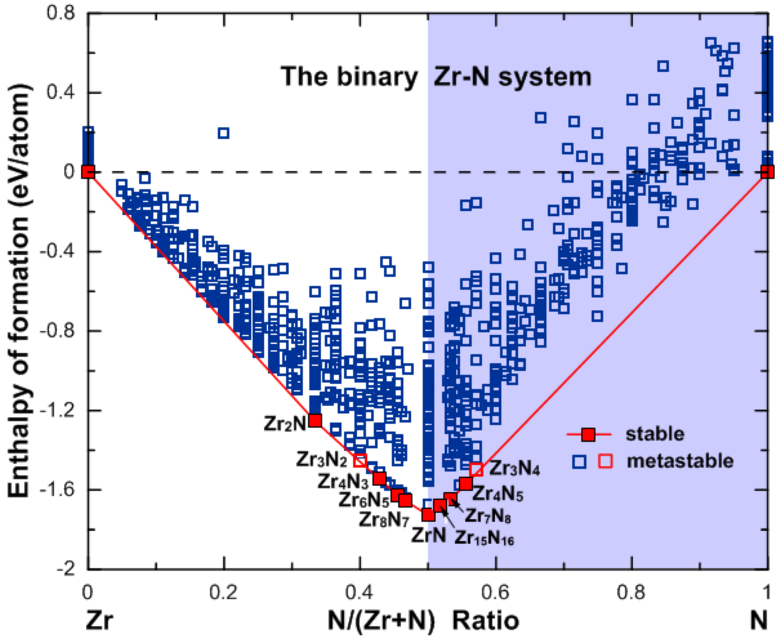


Figure S1 The convex hull diagram of the Zr-N system at 0 GPa.

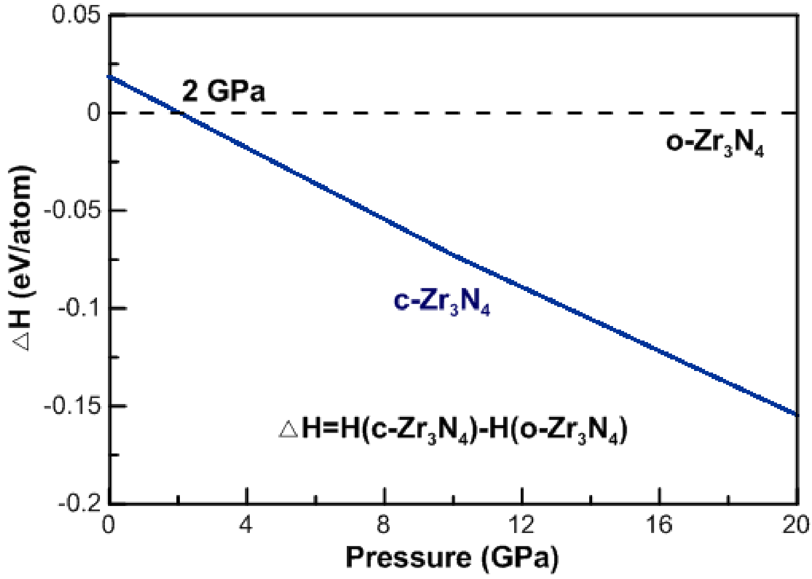
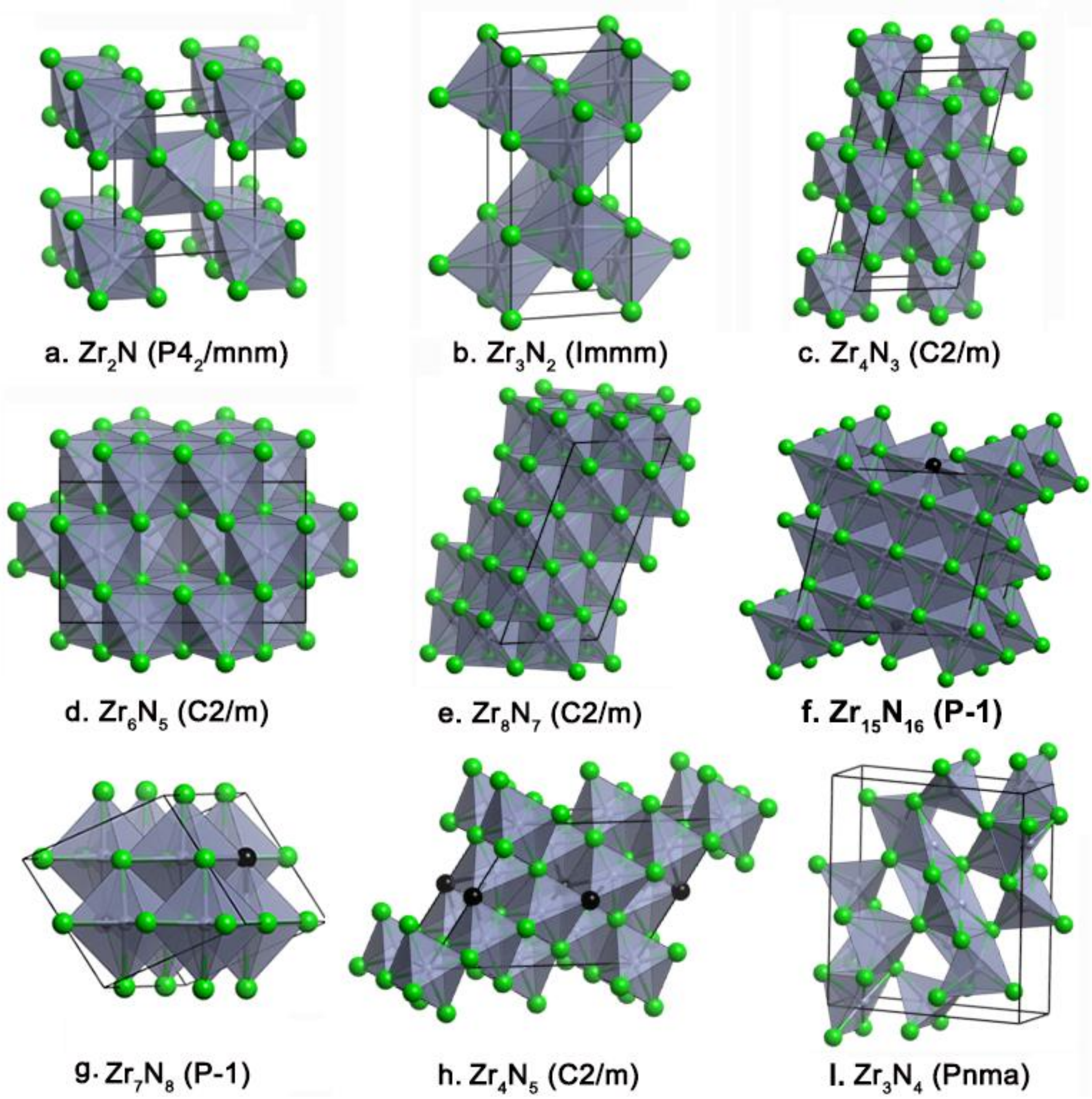


Figure S2 Pressure-driven phase transition in Zr_3N_4.



a. Zr_2N ($P4_2/mnm$)

b. Zr_3N_2 (Immm)

c. Zr_4N_3 (C2/m)

d. Zr_6N_5 (C2/m)

e. Zr_8N_7 (C2/m)

f. $Zr_{15}N_{16}$ (P-1)

g. Zr_7N_8 (P-1)

h. Zr_4N_5 (C2/m)

I. Zr_3N_4 (Pnma)

Figure S3 Crystal structures of the zirconium nitrides. The green spheres denote Zr atoms, while the black ones represent Zr vacancies. Nitrogen atoms are in the centers of the grey octahedra.

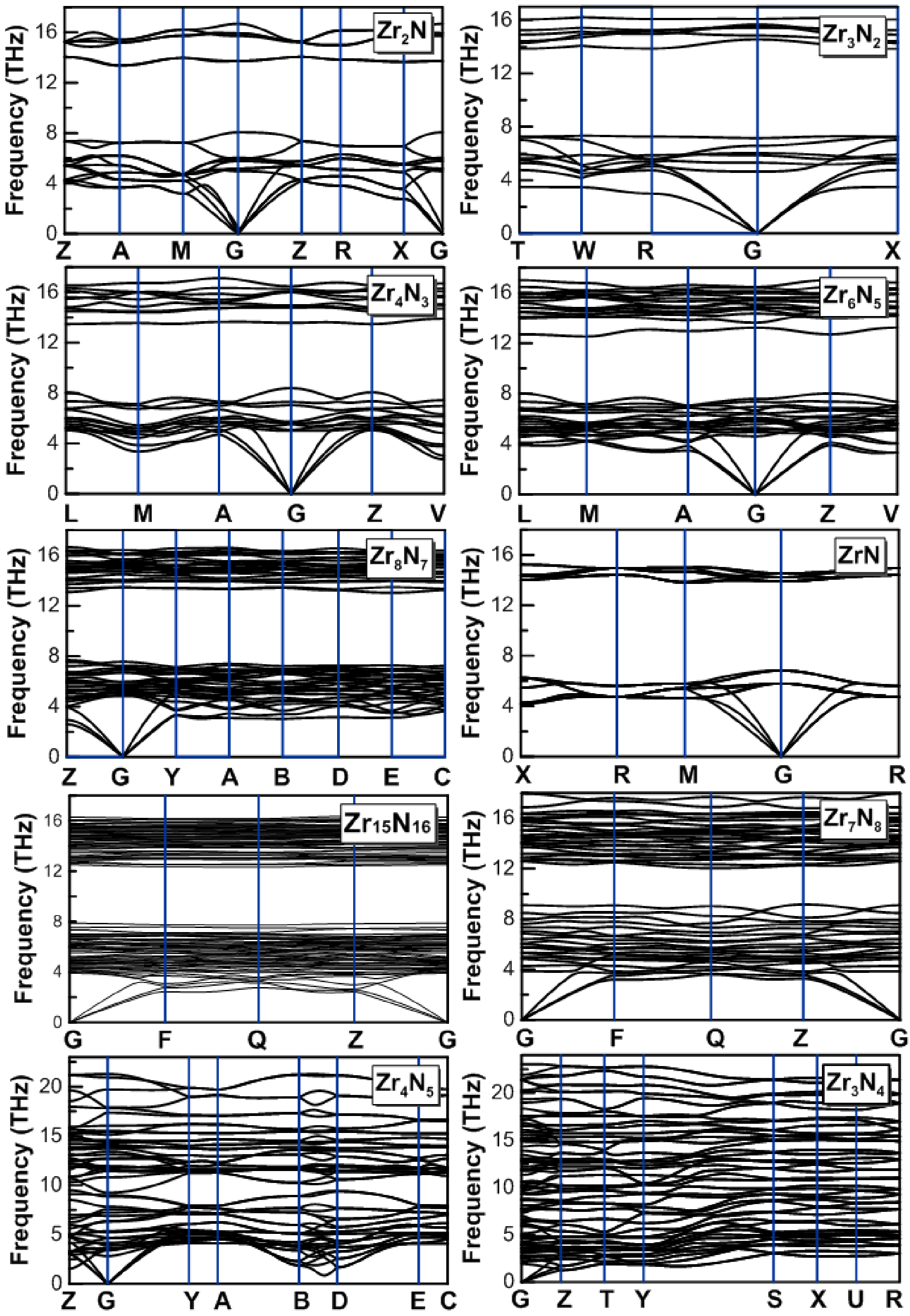


Figure S4 Calculated phonon dispersion curves of Zr_xN_Y compounds at ambient pressure. All of the dispersion curves have no imaginary phonon frequencies, indicating that they are all dynamically stable.

Vibrations and thermodynamics of Zr_xN_y compounds at ambient pressure

A. Free energies of Zr_xN_y solids

The free energy of a solid, can be expressed as:

$$G = E_0 + pV + F_{vib} + F_c \qquad (1)$$

where E_0 is the internal lattice energy, p is the external pressure, V is the volume, F_{vib} is the vibrational free energy, and F_{conf} denotes configurational entropy contribution. Vibrational contributions represent the phonon energy, which can be treated in the harmonic approximation, by summing over the normal modes frequencies,

$$F_{vib} = \frac{1}{2}\sum_{i=1}^{n} h\nu_i [\frac{1}{2} + \frac{1}{\exp(-h\nu_i / kT) - 1}] \qquad (2)$$

where k is Boltzmann constant, h is Planck constant.

$$F_{conf} = TS_{conf} = T \cdot k \ln \frac{N!}{n!(N-n)!} \qquad (3)$$

where S_{conf} is the configuration entropy, k is Boltzmann's constant

B. Free energies of N_2 gas

The free energy of diatomic N_2 gas molecule can be expressed as:

$$G(N_2) = U(N_2) + \frac{7}{2}k_B T - TS(N_2) \qquad (4)$$

where the entropy S can be divided into three parts, namely, translation entropy S_{trans}, rotational entropy S_{rot}, vibrational entropy S_{vib} and electronic entropy S_{elec}. Again, S_{elec} is neglected, while the other terms can be defined as,

$$S_{trans} = \frac{5}{2}Nk + Nk \ln[\frac{V}{N}(\frac{2\pi mkT}{h^2})^{3/2}] \qquad (5)$$

$$S_{rot} = Nk + Nk \ln \frac{T}{2\Theta_{rot}} \qquad (6)$$

$$S_{vib} = \frac{Nk\Theta_{vib}(\frac{1}{2} + \frac{1}{\exp(\Theta_{vib}/T) - 1})}{T} + Nk \ln(\frac{\exp(-\Theta_{vib}/T)}{1 - \exp(-\Theta_{vib}/T)}) \qquad (7)$$

Here, Θ_{rot} and Θ_{vib} are the characteristic rotational and vibrational temperatures, respectively. To be consistent with the free energy calculation of solids, here we calculated the entropy of N_2 within the same functional.

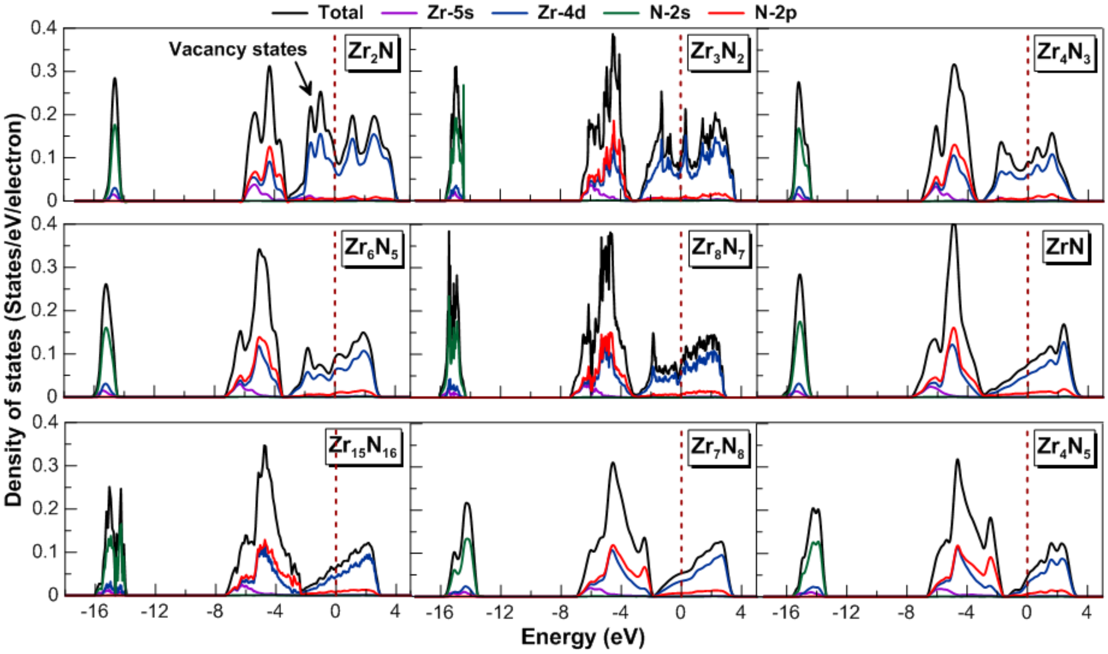


Figure S5 Calculated electronic density of states of zirconium nitrides at ambient conditions.

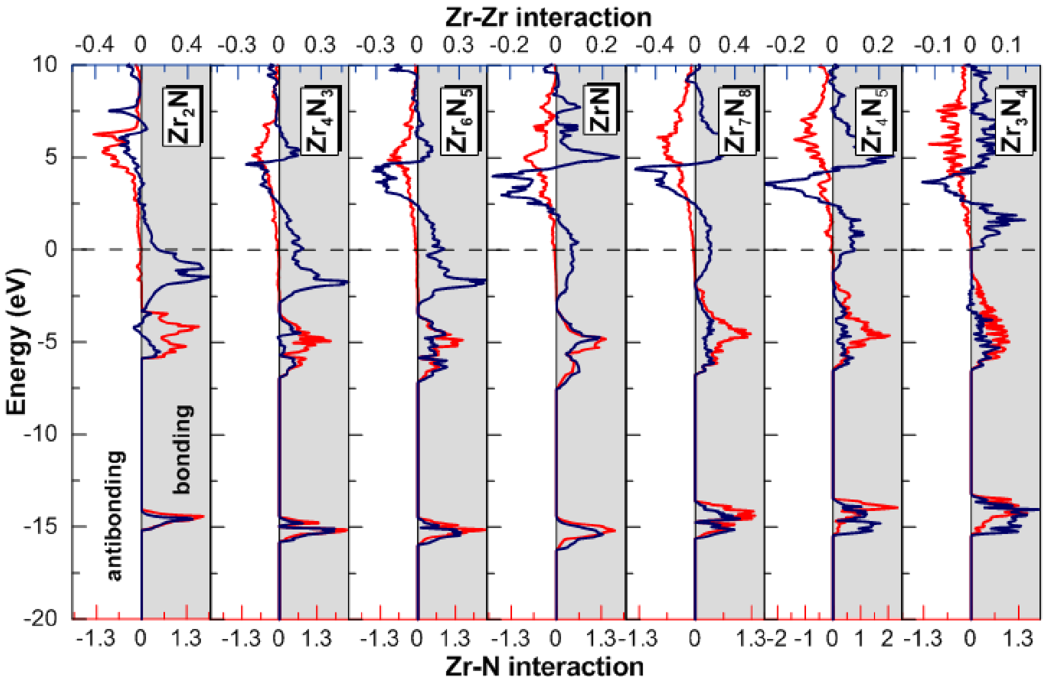


Figure S6 Calculated crystal orbital Hamilton population (-COHP) of zirconium nitrides at ambient conditions.

Supplementary Information

Table S1 Lattice parameters (Å,°), space groups, atomic coordinates, enthalpies and zero-point energies (ZPE, eV/atom) of Zr_xN_y compounds at 0 GPa.

Phase	Space group	Lattice parameter	Wyckoff position	H ZPE
Zr_2N	*$P4_2/mnm$*	a=5.426, c=3.319	Zr (0.704, 0.296, 1) N (0.5, 0.5, 0.5)	-9.681 0.052
Zr_3N_2	*Immm*	a=9.921, b=3.292, c=4.542	Zr (0.319, 0, 1); (0, 0, 1) N (0.337, 0, 0.5)	-9.872 0.057
Zr_4N_3	*C2/m*	a=10.836,b=3.267 c=5.645, β=100.7	Zr (0.127, 0, 0.883); (0.132, 0.5, 0.368) N (0.751, 0.5, 0.249); (0, 0.5, 0)	-9.962 0.061
Zr_6N_5	*C2/m*	a=5.659, b=9.763 c=5.654, β=109.5	Zr (0.756, 0.673, 0.253); (0.759, 0.5, 0.742) N (0.5, 0.165, 0); (0.5, 0.334, 0.5); (0, 0.5, 0.5)	-10.037 0.062
Zr_8N_7	*C2/m*	a=11.302,b=6.534 c=5.639, β=109.8	Zr (0.372, 0.256, 0.243); (0.628, 0, 0.241); (0.875, 0, 0.751) N (0.249, 0, 0.999); (0.25, 0.25, 0.5); (0, 0, 0.5); (0, 0.249, 1)	-10.064 0.062
ZrN	*Fm-3m*	a=4.608 *4.58*[1,2], *4.57*[3]	Zr (0, 0, 0) N (0.5, 0.5, 0.5)	-10.132 0.061
$Zr_{15}N_{16}$	*P-1*	a=5.640,b=8.590 c=8.584, α=106.3 β=90.0, γ=77.3	Zr (0.189, 0.439, 0.126);(0.685, 0.938, 0.133); (0.622, 0.635, 0.257); (0.144, 0.124, 0.256); (0.569, 0.306, 0.378); (0.06, 0.82, 0.378); (0, 0.5, 0.5); (0.246, 0.749, 0.994); N (0.370, 0.871, 0.241); (0.442, 0.188, 0.123); (0.311, 0.563, 0.375); (0.174, 0.935, 0.63); (0.246, 0.254, 0.5); (0, 1, 0);(0.5, 0.5, 0); (0.062, 0.312, 0.874); (0.122, 0.624, 0.747)	-10.092 0.063
Zr_7N_8	*P-1*	a=6.499, b=5.617 c=5.601, α=80.3 β=73.1, γ=90.0	Zr (0.867, 0.749, 0.520); (0.258, 0.999, 0.996); (0.377, 0.736, 0.507); (0, 0.5, 0) N (0.065, 0.877, 0.751); (0.563, 0.891, 0.742); (0.305, 0.365, 0.741); (0.174, 0.630, 0.262)	-10.046 0.065
Zr_4N_5	*C2/m*	a=10.820, b=3.239 c=8.158, β=122.2	Zr (0.771, 0, 0.684); (0.913, 0.5, 0.115) N (0.121, 0.5, 0.379); (0.302, 0.5, 0.189); (0, 0, 0)	-9.969 0.064
Zr_3N_4	*Pnma*	a=9.875, b=3.297 c=10.904 *9.79,3.30,10.88*[2] *9.73,3.28,10.82*[4]	Zr (0.772, 0.75, 0.648); (0.892, 0.75, 0.907); (0.930, 0.75, 0.377) N (0.103, 0.75, 0.970); (0.494, 0.75, 0.775); (0.643, 0.75, 0.018); (0.764, 0.25, 0.787)	-9.893 0.068
Zr_3N_4	*I-43d*	a=6.784 *6.740*[5], *6.786*[6]	Zr (0.375, 0, 0.25) N (0.063, 0.063, 0.063)	-9.875 0.063

The directional dependence of the Young's modulus

$$\begin{aligned}\frac{1}{E} = {} & l_1^4 s_{11} + 2l_1^2 l_2^2 s_{12} + 2l_1^2 l_3^2 s_{13} + 2l_1^2 l_2 l_3 s_{14} + 2l_1^3 l_3 s_{15} + 2l_1^3 l_2 s_{16} \\ & + l_2^4 s_{22} + 2l_2^2 l_3^2 s_{23} + 2l_2^3 l_3 s_{24} + 2l_1 l_2^2 l_3 s_{25} + 2l_1 l_2^3 s_{26} \\ & + l_3^4 s_{33} + 2l_2 l_3^3 s_{34} + 2l_1 l_3^3 s_{35} + 2l_1 l_2 l_3^2 s_{36} \\ & + l_2^2 l_3^2 s_{44} + 2l_1 l_2 l_3^2 s_{45} + 2l_1 l_2^2 l_3 s_{46} \\ & + l_1^2 l_3^2 s_{55} + 2l_1^2 l_2 l_3 s_{56} \\ & + l_1^2 l_2^2 s_{66}\end{aligned} \tag{8}$$

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

Using Šimůnek model to calculate the crystal hardness

The Vickers hardness was further estimated by Šimůnek's method for the vacancy-ordered Zr_xN_y phases within the following forms:

$$H = \frac{C}{\Omega} n \left[\prod_{i,j=1}^{n} b_{ij} s_{ij} \right]^{1/n} e^{-\sigma f_e} \tag{9}$$

$$f_e = 1 - \left[\frac{k(\prod_{i=1}^{k} e_i)^{1/k}}{\sum_{i=1}^{k} e_i} \right]^2 \tag{10}$$

$$s_{ij} = \frac{\sqrt{e_i e_j}}{n_i n_j d_{ij}} \tag{11}$$

where n_i and n_j are coordination numbers of atoms i and j, respectively; d_{ij} is the interatomic distance of atoms i and j; the reference energy e_i=Z_i/R_i , which represents the potential of the individual atom i to attract crystal valence charge; Z_i is the valence electron number of the atom i, and R_i is the ionic radius of the atom, here R(N)=0.99[7] and R(Zr)=1.21; k corresponds to the number of different atoms in the system; S_{ij} is the strength of the individual bond between atoms i and j; b_{ij} is the number of interatomic bonds between atoms i and j in the unit cell; Ω is the volume of the cell; The semi-empirical constant C equals to 1450; $e^{-\sigma fe}$ modifies the effect of the difference between reference energies (e_i , e_j) and σ equals to 2.8.

References

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