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# Mechanical and electronic properties of transition metal hexa-nitrides in hexagonal structure from density functional theory calculations



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Keywords: Transition Metal Nitrides Density Functional Theory Vickers Hardness Electronic properties Vibrational properties	We investigated structural, vibrational, mechanical, electronic, and magnetic properties of all 29 nitrogen-rich transition metal nitrides (TMNs) with a stoichiometric 1:6 (M:N) ratio in the hexagonal phase (space group: $R\overline{3}m$ with Wyckoff positions M (3a) and N (18 h)) by utilizing density functional theory-based calculations. Only 13 of these compounds are found to be both mechanically and vibrationally stable. Among them, FeN <sub>6</sub> is predicted to be the hardest compound with a Vickers hardness of 22 GPa. Compounds from group 8 elements which have a valence electron concentration of 38 (FeN <sub>6</sub> , RuN <sub>6</sub> , and OsN <sub>6</sub> ) are predicted to be the hardest and they also possess the highest densities. In general, hardness increases with decreasing M–M or M–N bond lengths. The calculation of local density of states and electronic band structures further suggests that all 13 stable MN <sub>6</sub> compounds have metallic bonding character. Three compounds from group 4 elements are semiconductors,

### 1. Introduction

Transition metal nitrides (TMNs) have shown broad areas of applications ranging from hard coating to semiconducting devices as well as the energy harvesting materials in the past decade [1-4]. They are also known to have excellent mechanical properties, high hardness, and chemical inertness [5-11]. Although experimental synthesis of such TMNs is challenging for various reasons such as positive formation energies and inertness of nitrogen, some experimentally synthesized TMNs have shown their importance as a suitable hard coating material [4,12,13] and routes of synthesis for some TMNs have been discovered [14,15]. Along with experimental methods, researchers are utilizing theoretical as well as computational techniques for example, the density function theory-based first principles calculations to predict and study properties of such novel TMNs [16-19]. Also, good agreement of available experimental data with the predicted values from theoretical and computational methods validates such approaches [20-23]. Moreover, the systematic studies done with theoretical and computational methods can save significant amount of time, effort, and expense that might occur while searching for novel TMNs solely with experimental methods.

Recently, the search for harder binary TMNs phases which involves the investigation with various metal to nitrogen ratios by using the machine learning techniques and first principles-based calculations have been reported [16,24-27]. The predicted TMNs crystal structures are found to be mechanically as well as dynamically stable. Some of these have even shown exceptionally high Vickers hardness higher than 40 GPa as reported by Kandel et. al [16] in the prediction of WN<sub>6</sub> (59 GPa),  $\mathrm{MoN}_{6}$  (52 GPa), and  $\mathrm{TaN}_{6}$  (43 GPa) and others [25,26]. Thus these are considered to be potential super-hard materials [28]. Besides these, Wei et. al [27] have predicted a nitrogen rich hexagonal phase of MoN<sub>6</sub> and ReN<sub>6</sub> structures, containing a hexagonal ring of nitrogen atoms, in space group  $R\overline{3}m$  by utilizing the intelligence-based Crystal Structure AnaLYsis by the Particle Swarm Optimization (CALYPSO) algorithm. This hexagonal phase of MN<sub>6</sub> will be called MN<sub>6</sub> hereafter. The predicted MoN<sub>6</sub> showed the phase transition from  $R\overline{3}m$  to  $Pm\overline{3}$  at predicted applied pressure of 54 GPa while the ReN<sub>6</sub> did not show any phase change for predicted pressure range of 50 GPa to 100 GPa [27]. Besides the prediction of hard and stable phases, the comprehensive study of stability, mechanical, energetic, and electronic properties as well as the possible explanation for the predicted values of hardness and origin behind these observed values for these MN6 compounds are needed. This article tries

however, they are only mechanically stable. The bonding analysis reveals that hardness is primarily attributed to

M-N and M-M interactions. Eight of the investigated MN<sub>6</sub> compounds have a magnetic moment.

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Fig. 1. Hexagonal MN6 structure prepared by using VESTA [66]. Crystallographic directions are given by a, b, and c.

### to present the answers to some of these questions.

In this study, the density function theory-based calculations were performed to predict the structural, mechanical, energetic, electronic, magnetic, and vibrational properties for nitrogen rich hexagonal phases of all 29 MN<sub>6</sub> structures. Our calculations showed that 13 MN<sub>6</sub> compounds are both dynamically and mechanically stable. The highest hardness is observed for compounds of group 8 elements of each row for all mechanically stable compounds. For both mechanically as well as vibrationally stable compounds, highest Vickers hardness is predicted for FeN<sub>6</sub> (22 GPa) and softest compound is being TaN<sub>6</sub> (11 GPa). All hardest compounds are predicted to have metallic character as can be seen in the study of Local Density Of States (LDOS) and band structure calculations. We also found there is no direct relationship between the observed hardness and N–N bond length, however, there is anticorrelation between M–M and M–N bond lengths with hardness. The anti-bonding nature of N–N interactions also suggests that contribution to the hardness could be mainly coming from M–M and M–N bonding. The study of magnetic properties reveals that only 3 vibrationally and mechanically stable compounds have magnetic nature, the highest magnetic moment is seen in FeN<sub>6</sub> with 4.821  $\mu_{\rm B}$  in unit cell.

# 2. Computational methods

We performed the first principles calculation based on Density Functional Theory (DFT) by utilizing Vienna Ab initio Simulation Package (VASP) [21,22,29-37]. Perdew-Burke-Ernzerhof (PBE) functional within Generalized Gradient Approximation (GGA) was utilized, where the Projector Augmented Wave (PAW) method was implemented for the electron density approximation [21,22,29,30,37-42]. VASP pseudopotentials with the inner core electrons for all 29-transition metals where available and the standard N pseudopotential for nitrogen were considered [20,43-46]. The kinetic energy cut-off for the plane wave basis set for electrons was set at 600 eV and  $\Gamma$ -centered k-mesh of spacing  $2\pi \times 0.03$  Å<sup>-1</sup> were used. Conjugate-gradient algorithm with a force criterion of 0.01 eV/Å was used for the ionic relaxation while the electronic minimization was achieved through the convergence criterion of 10<sup>-6</sup> eV/atom and Gaussian smearing of smearing width 0.1 eV [42,45,46]. The initial structure of MN<sub>6</sub> was obtained from the theoretical work of Wei et. al [27].

The geometry of the crystal structures was optimized by allowing change in ionic positions, cell shape, and cell volume during the relaxation process. The formation energy ( $E_f$ ) of the relaxed cell per formula

#### Table 1

Group number, lattice constants (a, c), elastic constants ( $C_{11}$ ,  $C_{12}$ ,  $C_{13}$ ,  $C_{33}$ , and  $C_{44}$ ), charge transfer from metal to nitrogen ( $Q_t$ ) in units of elementary charge e, and total magnetic moment (Mag.) in Bohr magneton ( $\mu_B$ ) per transition metal atom of MN<sub>6</sub> compounds. "S" and "U" respectively denote the mechanically stable and unstable compounds.

Group No.	М	a (Å)	c (Å)	<i>C</i> <sub>11</sub> (GPa)	<i>C</i> <sub>12</sub> (GPa)	C <sub>13</sub> (GPa)	C <sub>33</sub> (GPa)	C <sub>44</sub> (GPa)	$Q_t(e)$	Mech. Stability	Mag. $(\mu_B)$
3	Sc	5.51	8.27	306	124	102	200	28	1.95	"S"	0.024
4	Ti	5.31	7.92	420	154	135	258	91	1.98	"S"	0
5	v	5.26	7.68	426	140	119	270	91	1.77	"S"	1.473
6	Cr	5.21	7.66	459	117	95	262	98	1.62	"S"	2.323
7	Mn	5.13	7.31	578	150	132	330	121	1.40	"S"	0.029
8	Fe	5.13	7.44	467	100	74	290	110	1.23	"S"	1.301
9	Со	5.13	7.51	431	84	81	301	94	1.11	"S"	0.83
10	Ni	5.17	7.67	377	104	75	267	74	1.02	"S"	0
11	Cu	5.35	7.82	236	86	61	210	49	0.98	"S"	0
12	Zn	5.44	7.76	256	110	73	199	61	1.23	"S"	0
3	Y	5.70	8.88	244	115	97	156	-24	2.13	"U"	0.032
4	Zr	5.50	8.41	384	163	148	221	74	2.35	"S"	0
5	Nb	5.44	7.84	470	227	167	241	109	2.19	"S"	0
6	Mo	5.36	7.65	555	216	181	261	125	1.89	"S"	0
		5.322 <sup>a</sup>	6.403 <sup>a</sup>	974 <sup>a</sup>	417 <sup>a</sup>	276 <sup>a</sup>	392 <sup>a</sup>	193 <sup>a</sup>			
7	Tc	5.30	7.52	590	195	178	286	129	1.56	"S"	0
8	Ru	5.27	7.52	591	169	150	294	128	1.31	"S"	0
9	Rh	5.25	7.82	472	128	108	274	101	1.10	"S"	0
10	Pd	5.36	8.12	271	79	69	202	59	0.87	"S"	0
11	Ag	5.79	8.27	118	55	50	115	32	0.76	"S"	0.032
12	Cd	5.77	8.14	197	95	68	144	51	1.20	"S"	0
4	Hf	5.45	8.34	428	168	155	241	85	2.38	"S"	0
5	Та	5.41	7.88	537	244	190	253	123	2.38	"S"	0
6	W	5.33	7.77	620	247	210	278	152	2.17	"S"	0
7	Re	5.29	7.64	658	242	209	306	146	1.70	"S"	0
		5.255 <sup>a</sup>	6.485 <sup>ª</sup>	1057 <sup>a</sup>	439 <sup>a</sup>	308 <sup>a</sup>	453 <sup>a</sup>	252 <sup>a</sup>			
		5.215 <sup>a</sup>	5.917 <sup>a</sup>	1397 <sup>a</sup>	641 <sup>a</sup>	453 <sup>a</sup>	617 <sup>a</sup>	239 <sup>a</sup>			
8	Os	5.28	7.53	680	213	190	317	150	1.45	"S"	0
9	Ir	5.24	7.75	596	183	152	300	129	1.25	"S"	0
10	Pt	5.27	8.09	382	111	101	250	85	1.02	"S"	0
11	Au	5.55	8.50	130	102	56	142	4	0.80	"S"	0
12	Hg	5.92	8.40	102	70	43	101	28	0.88	"S"	0

<sup>a</sup> Theoretical Ref. [27].

#### Table 2

Bulk modulus (*B*), shear modulus (*G*), Young's modulus (*E*), Vickers hardness ( $H_V$ ), Pugh's ratio (k), Poisson's ratio ( $\nu$ ), Debye temperature ( $\theta_D$ ), formation energy per atom ( $E_f$ ), and mass density ( $\rho$ ) for all mechanically stable MN<sub>6</sub> compounds.

Group No.	М	B(GPa)	G(GPa)	E(GPa)	H <sub>V</sub> (GPa)	k	ν	$\theta_D(K)$	$E_f(eV)$	$\rho$ (kg/m <sup>3</sup> )
3	Sc	159	54	145	5	0.34	0.35	655	0.18	2958
4	Ti	210	105	271	11	0.50	0.28	882	0.29	3396
5	v	203	112	283	13	0.55	0.27	888	0.47	3651
6	Cr	192	127	311	18	0.66	0.23	934	0.60	3769
7	Mn	248	156	387	19	0.63	0.24	1015	0.67	4155
8	Fe	186	141	338	22	0.76	0.20	960	0.69	4118
9	Со	181	128	312	19	0.71	0.21	908	0.78	4171
10	Ni	167	104	257	14	0.62	0.24	824	0.83	4004
11	Cu	121	64	164	9	0.53	0.27	651	0.90	3797
12	Zn	134	69	176	9	0.51	0.28	672	0.74	3737
4	Zr	203	84	222	8	0.41	0.32	701	0.21	3969
5	Nb	238	106	277	10	0.45	0.31	771	0.46	4387
6	Mo	260	131	335	13	0.50	0.28	838	0.65	4709
		414 <sup>a</sup>	195 <sup>a</sup>	507 <sup>a</sup>		0.47 <sup>a</sup>	0.29 <sup>a</sup>			
7	Tc	268	145	368	16	0.54	0.27	871	0.70	4952
8	Ru	253	154	383	18	0.61	0.25	885	0.77	5091
9	Rh	204	128	318	17	0.63	0.24	808	0.81	4987
10	Pd	129	76	191	11	0.59	0.25	625	0.89	4693
11	Ag	73	32	84	4	0.44	0.31	420	0.95	3977
12	Cd	109	51	132	6	0.47	0.30	519	0.79	4174
4	Hf	218	98	255	9	0.45	0.31	613	0.18	6102
5	Та	262	120	312	11	0.46	0.30	669	0.45	6623
6	W	290	146	376	14	0.51	0.28	727	0.68	6985
7	Re	303	156	400	15	0.52	0.28	744	0.76	7260
		457 <sup>a</sup>	244 <sup>a</sup>	621 <sup>a</sup>		0.53 <sup>a</sup>	$0.27^{a}$			
		639 <sup>a</sup>	255 <sup>a</sup>	676 <sup>a</sup>		0.40 <sup>a</sup>	0.32 <sup>a</sup>			
8	Os	297	170	429	19	0.57	0.26	767	0.84	7518
9	Ir	259	154	385	18	0.59	0.25	727	0.87	7456
10	Pt	178	105	263	14	0.59	0.25	604	0.93	7139
11	Au	92	12	35	1	0.13	0.44	216	1.08	6186
12	Hg	68	23	63	3	0.34	0.35	297	1.04	5558

<sup>a</sup> Theoretical Ref. [27].

unit of MN<sub>6</sub>, is then calculated by using the following formula as:

$$E_f = E(MN_6) - E(M) - 3E(N_2)$$
(1)

Here,  $E(MN_6)$ , E(M), and  $E(N_2)$  represent ground state energies of MN<sub>6</sub>, transition metal, and nitrogen dimer respectively [20,47]. All ground state energies were obtained from the full relaxation of relevant MN<sub>6</sub> (space group:  $R\overline{3}m$ ), transition metals with lowest  $E_f$  as obtained from Materials Project [47], and a nitrogen dimer placed in a large cubic cell of length 10 Å.

The calculation of elastic constants was achieved by calculating the Hessian matrix, which is obtained by employing six finite distortions of the lattice followed by stress–strain relationship. Bulk modulus (*B*) and shear modulus (*G*) were calculated by using the components of stiffness ( $C_{ij}$ ) and compliance ( $S_{ij}$ ) tensors as suggested by Voigt-Reuss-Hill approximations [27,48,49] with following sets of equations:

$$B_V = [(C_{11} + C_{22} + C_{33}) + 2(C_{12} + C_{23} + C_{31})]/9$$
(2)

$$G_V = [(C_{11} + C_{22} + C_{33}) - (C_{12} + C_{23} + C_{31}) + 3(C_{44} + C_{55} + C_{66})]/15$$
(3)

$$B_R = \left[ (S_{11} + S_{22} + S_{33}) + 2(S_{12} + S_{23} + S_{31}) \right]^{-1}$$
(4)

$$G_R = 15[4(S_{11} + S_{22} + S_{33}) - 4(S_{12} + S_{23} + S_{31}) + 3(S_{44} + S_{55} + S_{66})]^{-1}$$
(5)

 $B = (B_V + B_R)/2$  and  $G = (G_V + G_R)/2(6)$ Here, the subscripts *V* and *R* are used to denote Voigt and Reuss approximations respectively. Thus, obtained *B* and *G* were used for further calculations of Pugh's ratio (k = G/B), Poisson's ratio ( $\nu = (3 - 2k)/(6 + 2k)$ ), and Young's modulus (E = 9G/(3 + k)). Vickers hardness was calculated by using macroscopic properties as suggested by Tian et. al ( $H_V = 0.92k^{1.137}G^{0.708}$ ) as discussed in references [16,20–22,24,29,38,45,49–53].

Debye temperature ( $\theta_D$ ) of a material with *n* atoms in a unit cell is calculated by using the following equation [16,20,24,42]:

$$\theta_D = \frac{h}{k_B} \left[ \frac{3n}{4\pi} \left( \frac{\rho N_A}{M} \right) \right]^{1/3} \left[ \frac{1}{3} \left( \frac{2}{v_l^3} + \frac{1}{v_l^3} \right) \right]^{-1/3}$$
(7)

where, *h* is Plank's constant,  $k_B$  is Boltzmann's constant, and  $N_A$  is Avogadro's number.  $v_t = \sqrt{G/\rho}$ , and  $v_l = \sqrt{(3B + 4G)/3\rho}$  are the transverse and longitudinal components of speed of sound. Thus the  $\theta_D$  calculated from formula above purely depends on the mechanical properties.

The electronic properties were studied by performing electronic LDOS and band structure analysis [21,22,25,29,42,54]. The study of charge transfer ( $Q_t$ ) from metal to nitrogen was studied by employing Bader charge analysis [55–58]. The vibrational stability of the material was checked by the calculation of Phonon Density Of States (DOS) by employing the Phonopy code, which is based on the Density Functional Perturbation Theory (DPFT) [21,29,42,50,59,60]. For the study of bonding relationship between atoms, Crystal Orbital Hamilton Population (COHP) was calculated by applying Local-Orbital Basis Suite Towards Electric-structure Reconstruction (LOBSTER) package [61–65].

# 3. Results and discussions

### 3.1. Structural properties

The optimized crystal structure of  $MN_6$  (space group:  $R\overline{3}m$ ) is shown in Fig. 1 [66]. The Wyckoff positions of M atoms are occupying 3a sites and N atoms are occupying 18 h sites as it can be seen in Supplementary Table S1. Moreover, the structure has octahedral symmetry with each M atom surrounded by 6 nearest N atoms. Table 1 presents calculated values of lattice constants (*a* and *c* in Å) for all  $MN_6$  compounds whereas Table 2 gives the predicted values of density of all mechanically stable



**Fig. 2.** Study of variation of  $E_f$ ,  $Q_t$ , and volume (*V*) with group number for all mechanically stable MN<sub>6</sub> compounds.

 $MN_6$  materials with the values ranging from lowest 2958 kg/m<sup>3</sup> to highest 7518 kg/m<sup>3</sup>. It is evident from Table 2 that the materials with higher density will have higher Vickers hardness in general for 3d, 4d and 5d compounds, which agrees with the result presented by Kandel et. al [24] in case of cubic  $MN_6$  materials. To understand how bond length is related to hardness, we studied the variation of N–N, M–N, and M–M bond lengths with predicted hardness and the result is shown in Supplementary Fig. S1. For all mechanically stable 3d, 4d, and 5d compounds, the dependence of hardness on N–N bond length is hard to predict (Supplementary Fig. S1 (a)), however, the harder materials have tendency of having shorter M–N or M–M bond lengths compared to the softer materials (Supplementary Figs. S1 (b) and (c)) in general. This could be an indication that the smaller sized crystals are harder than bigger sized crystals and it is consistent with the previously discussed result that harder materials have higher densities.

We calculated the formation energy per atom  $(E_f)$  for all mechanically stable MN<sub>6</sub> compounds, and the result is presented in Table 2. The predicted values of  $E_f$  are all positive indicating the challenging nature of synthesis of such MN<sub>6</sub> materials. However, synthesis of similar nitride materials is possible by applying high pressure and temperature as revealed by Gregoryanz et. al [14] for the synthesis of PtN and by Crowhurst et. al [15] for the synthesis of PtN<sub>2</sub>, where they have used a high pressure of 50 GPa and temperature of 2000 K. Moreover, the

materials thus synthesized were stable even at ambient. To further understand the variation of  $E_f$  and volume of each unit cell (*V*), we plotted their predicted values against the group number and the result is shown in Fig. 2 (a) and (c). For all mechanically stable 3d, 4d, and 5d MN<sub>6</sub> compounds,  $E_f$  is found to be increasing up to group number 11 and then it slightly decreases (Fig. 2 (a)). Similarly, the volume of these compounds decreases with the group number at first, reaches its minimum value and then increases again with group number in general as in Fig. 2 (c). Such variation of volume with group number may be understood by the fact that the size of transition metal decreases first up to the intermediate elements and then start increasing after that as proposed by Khatri et. al [67].

#### 3.2. Vibrational properties

The study of phonon frequencies can provide an insight for the vibrational properties and consequently the dynamical stability of a material. A material is considered stable when it is dynamically as well as mechanically stable and only such materials can be quenched back to ambient conditions [68]. We have performed the phonon DOS calculation for all mechanically stable 3d, 4d, and 5d MN<sub>6</sub> compounds and the results are shown in Supplementary Figs. S2- S4. The presence of population of phonon DOS in the imaginary frequency region signifies the

4



Fig. 3. Phonon DOS for 3d, 4d, and 5d compounds of group 8 elements having high hardness.

dynamic instability of compound. From these figures we observe that out of all 28 mechanically stable 3d, 4d, and 5d MN<sub>6</sub> compounds, only 13 (MnN<sub>6</sub>, FeN<sub>6</sub>, CoN<sub>6</sub>, NiN<sub>6</sub>, NbN<sub>6</sub>, MoN<sub>6</sub>, TcN<sub>6</sub>, TaN<sub>6</sub>, WN<sub>6</sub>, ReN<sub>6</sub>, OsN<sub>6</sub>, IrN<sub>6</sub>, and PtN<sub>6</sub>) have not shown any population of phonon DOS in imaginary frequency region and hence they are dynamically stable. Remaining all 15 MN<sub>6</sub> compounds have shown the presence of population of phonon DOS in the imaginary region and thus, they are dynamically unstable. The phonon DOS calculations for the 3 hardest compounds of 3d, 4d, and 5d MN<sub>6</sub> materials are presented in Fig. 3. Although being the hardest and mechanically stable compound from 4d row elements, RuN6, is dynamically unstable having population of phonon DOS in the imaginary frequency region. For all dynamically stable compounds, the distribution of phonon DOS does not have wide gaps, instead phonon DOS population is zero for discrete small frequency gaps between 15 and 25 THz region. The gap in the phonon frequency signifies the material's ability to block sound frequencies falling in the gap region and potential of its application as sound filter [69]. Thus, these materials may not be useful for the application as sound filters for wide frequency range but still be useful for small frequency range selective sound blocker.

#### 3.3. Mechanical and magnetic properties

The MN<sub>6</sub> crystal structure we have studied is of hexagonal type. Symmetry of such crystal requires only five independent elastic constants ( $C_{11}$ ,  $C_{12}$ ,  $C_{13}$ ,  $C_{33}$ , and  $C_{44}$ ) to describe the stiffness tensor  $C_{ii}$ . Table 1 presents the calculated values of these independent elastic constants. The mechanical stability of all 29 MN<sub>6</sub> structures were checked by using the following conditions in terms of calculated elastic constants [16,27,49,70]:  $C_{44} > 0$ ,  $C_{11} > |C_{12}|,$ and  $(C_{11}+2C_{12})C_{33} > 2C_{13}^2$ . All the MN<sub>6</sub> compounds that satisfy those conditions are mechanically stable, the letter "S" denotes mechanically stable compounds as shown in Table 1 and the unstable one is denoted by letter "U". Our calculations showed that except YN<sub>6</sub> all other nitrides mechanically stable. The components of compliance tensor  $(S_{ii})$  can be obtained by taking the inverse of stiffness tensor. To calculate the values of bulk modulus (B) and shear modulus (G), we used Eqs. (2) – (6)described in section 2. These calculated values of B and G were further used to predict E,  $H_V$ ,  $\nu$ , and k by using the relations described in section 2. All these predicted values of elastic moduli for mechanically stable 3d, 4d, and 5d compounds of MN<sub>6</sub> are presented in Table 2. It shows the predicted values of Vickers hardness are increasing up to group 8, where



B, G, k and H<sub>V</sub> vs Group Number

Fig. 4. Study of variation of B, G, k, and  $H_V$  with group number for all mechanically stable MN<sub>6</sub> compounds.

they have the maximum value (22 GPa for 3d, 18 GPa for 4d, and 19 GPa for 5d compounds), and then decreasing. The differences in our calculated values of elastic constants and moduli as compared with the literature values (Table 1 and Table 2) could be due to the fact that their values were obtained at high pressures of 50 GPa and 100 GPa [27]. We also did the study of variation of B, G, k, and  $H_V$  with group number for all mechanically stable MN<sub>6</sub> compounds and the result is shown in Fig. 4. In general, the overall trend for these quantities is increasing with the group number at first, reaching its maximum value in intermediate group number and then decreasing. For example, Fig. 4 (b) and (d) shows G and  $H_V$  reaches their maximum values corresponding to group number 8 while for *B*, the maximum values are seen at group number 7 (Fig. 4 (a)) for all mechanically stable 3d, 4d, and 5d  $MN_6$  compounds. However, the group number corresponding to maximum value of k is not unique as it is seen from Fig. 4 (c). The calculated values of k can be used to predict if the material is brittle (k > 0.57) or ductile ( $k \le 0.57$ ) [16,24,27,71–73]. Our investigation shows that most of the mechanically stable 3d, 4d, and 5d MN6 materials having  $H_V > 16$  GPa are





**Fig. 5.** Relationship between Debye temperature  $(\theta_D)$  and hardness for all mechanically stable MN<sub>6</sub> compounds.

brittle in nature which can be seen in Table 2 and in Supplementary Fig. S5. As material's ability to deform against the external forces could be related to the elastic constant  $C_{44}$  and hence *G*, we studied the variation of *B*, *G*, *E*, and  $H_V$  for all mechanically stable MN<sub>6</sub> with the corresponding  $C_{44}$  and the result is presented in Supplementary Fig. S6. The overall trend for these elastic moduli is found to be increasing for increasing values of  $C_{44}$ , which is expected.

We have also calculated the Debye temperature ( $\theta_D$ ) by using the  $C_{ij}$  as shown in Eq. (7) discussed earlier for all mechanically stable MN<sub>6</sub> compounds and the result is presented in Table 2. Majority of the mechanically stable MN<sub>6</sub> compounds are predicted to have  $\theta_D$  higher than 600 K and harder materials have higher  $\theta_D$ . As proposed by Deus et. al [74] and Miao et. al [75], relationship between  $\theta_D$  and  $H_V$  can also be described by the equation:  $\theta_D = aH_V^{1/2}\rho^{-1/6}M^{-1/3} + b$ , where *a* and *b* are linear fitting constants, *M* is molecular weight of TMN and  $\rho$  is its density. We fitted this equation by using our calculated values of  $H_V$  and the result is shown in Fig. 5, the estimated values of *a* and *b* are found to be 5810.09 GPa<sup>-1/2</sup> (kg/m<sup>3</sup>)<sup>1/6</sup> (g/mol)<sup>1/3</sup>K and 134.53 K respectively. We also compared our calculated values of  $\theta_D$  obtained by using equation of Deus et. al and Miao et. al [74,75] in the same plot (blue dots in Fig. 5) and found that calculated values are well matched with the equation above.

We studied the magnetic properties of these TMNs by calculating the magnetic moments in terms of Bohr magneton ( $\mu_B$ ). Only 8 of the compounds have shown the presence of magnetic moment with its predicted values per transition metal are shown in Table 1. Out of these 8 magnetic compounds YN6 is mechanically unstable, whereas only 3 (MnN<sub>6</sub>, FeN<sub>6</sub>, and CoN<sub>6</sub>) are both vibrationally as well as mechanically stable. Among these both vibrationally and mechanically stable compounds, FeN<sub>6</sub> has the highest magnetic moment of 1.301  $\mu_B$  per Fe atom or 4.821  $\mu_B$  per unit cell and MnN<sub>6</sub> has the lowest magnetic moment of 0.029  $\mu_B$  per Mn atom or 0.087  $\mu_B$  per unit cell as presented in Supplementary Table S2. We can also see from Supplementary Table S2 that the contribution to the total magnetic moment for M atoms is mainly coming from the d-orbital as compared to s- and p-orbitals, whereas the contribution from p-orbital is dominating for N atoms except for MnN<sub>6</sub> where s- and p-orbitals of N atoms do not contribute any magnetic moment.

#### 3.4. Electronic properties

We performed the Bader charge analysis as described in section 2 for all 29 MN<sub>6</sub> compounds to predict the amount of charge transfer  $(Q_t)$ from metal to nitrogen. The study of charge transfer could be helpful to predict the nature of chemical bonding between atoms which can be related to the mechanical properties [76]. The calculated values of  $Q_t$  in the units of elementary charge e for all 29 MN<sub>6</sub> compounds are presented in Table 1. The study of variation of  $Q_t$  with group number is presented in Fig. 2 (b),  $Q_t$  is found to be decreasing for increasing group number, this result is similar to the one described in reference [24] in case of cubic MN<sub>6</sub> compounds. Table 1 also shows that the values of  $Q_t$  are more than 1 for most of the compounds showing the ionic nature of MN<sub>6</sub> compounds. Supplementary Table S3 represents the values for electronegativity ( $\chi$ ) for transition metals taken from reference [77]. Our calculated values of  $Q_t$  are found to have positive correlation with the absolute value of difference of electronegativities between M and N, however, any direct relationship between hardness with  $\chi$  or  $Q_t$  could not be predicted. Supplementary Fig. S7 shows the variation of  $H_V$  and  $Q_t$  with valence electron concentration (VEC) where the hardest MN<sub>6</sub> compounds are corresponding to VEC = 38.

The computed result of LDOS per atom for 3d, 4d, and 5d mechanically stable  $MN_6$  compounds are presented in Supplementary Figs. S8 – S10. In all these figures we can see that as we go from top to bottom the population of nitrogen LDOS (blue solid line) stays the same, whereas the population of metallic LDOS (red dashed line) shifts towards left from right and the hardness goes on increasing (see Table 2). The hardness reaches its maximum value when the population of metallic LDOS is maximum around the Fermi level set at zero eV in these figures. The hardness then decreases with increasing group number while the shifting of population of metallic LDOS towards left is continuous. Fig. 6 shows the LDOS for 3d, 4d, and 5d compounds of group 8 elements having high hardness. The population of LDOS for all these hardest compounds signifies the metallic nature of these  $MN_6$  compounds.

To understand the bonding and anti-bonding states of metal and nitrogen atoms we performed the -pCOHP calculations for all mechanically stable MN<sub>6</sub> compounds. The result of our calculations is presented in Supplementary Figs. S11 - S13 respectively for 3d, 4d, and 5d mechanically stable MN<sub>6</sub> compounds. In these plots, the bonding states are represented by -pCOHP population above baseline and anti-bonding states are represented by -pCOHP population below baseline, where the baseline has -pCOHP population equal to zero. We can also observe from these figures that the bonding and anti-bonding states for N-N (red line) and M-N (blue line) are consistent for all mechanically stable MN<sub>6</sub> compounds. For example, the N-N and M-N interactions are in bonding states deep below the Fermi level, whereas anti-bonding states are found near the Fermi level. Also, Total interactions which represents the -pCOHP averaged over all atom pairs specified, are in bonding states throughout. The anti-bonding states below the Fermi energy for N-N and M-N could be the reason for predicted positive formation energies. We also found that higher number of the M-N interactions than N-N interactions below Fermi level. This could be an indication of having the ionic bonding between M and N atoms which can be understood via the presence of charge transfer from M to N atoms as presented in Table 1.

The electronic band structure calculation was performed for all mechanically stable  $MN_6$  compounds using GGA functional. The results of this calculation are presented in Supplementary Figs. S14 – S16 for 3d, 4d, and 5d mechanically stable  $MN_6$  compounds respectively. Our calculation indicates that one compound of group 4 from each 3d, 4d, and 5d rows are predicted to have band gaps (TiN<sub>6</sub>: 1.461 eV, ZrN<sub>6</sub>: 1.469 eV, and HfN<sub>6</sub>: 1.404 eV) and remaining all 25 compounds have zero band gaps. Since these band gaps were predicted by using GGA functional, the actual band gap could be even higher than these values as it is found that GGA functional tends to underestimate the band gap [42]. To further study the observed band gaps, we performed band gap calculations by utilizing the Heyd-Scuseria-Ernzerhof (HSE06) hybrid



Fig. 6. LDOS for 3d, 4d, and 5d compounds of group 8 elements having high hardness. The Fermi energy is set to 0 eV.

functional. The calculated values of band gaps using HSE06 are TiN<sub>6</sub>: 2.512 eV, ZrN<sub>6</sub>: 2.458 eV, and HfN<sub>6</sub>: 2.329 eV. These are higher than the values calculated form GGA, which is expected [42]. These band gaps provide an opportunity to use these materials as absorber layers in solar cells. Also, these compounds which possess band gaps are only mechanically stable and are vibrationally unstable which can be inferred from Table 1 and Supplementary Figs. S2 – S4. Thus, all the compounds which are both mechanically as well as vibrationally stable have zero band gap indicating their metallic character. Fig. 7 represents the electronic band dispersion curves for the three hardest 3d, 4d, and 5d compounds of group 8 elements and shows there is no band gap for them

which can be confirmed from Fig. 6 as well. Although being metallic in nature, the highest predicted hardness of 22 GPa for FeN<sub>6</sub> falls around the lower edge for other materials used in hard-coating industries such as ZrC (27 GPa), TaC (26 GPa), TiN (25 GPa), and HfN (20 GPa) [42,78–80] indicating the potential application of FeN<sub>6</sub> as hard coating material.

#### 4. Conclusion

In conclusion, we have used DFT based first principles calculations to study all 29 MN<sub>6</sub> materials in hexagonal phase (space group:  $R\overline{3}m$ ). Our



Fig. 7. Electronic band structure for three hardest 3d, 4d, and 5d compounds of group 8 elements. Fermi energy is set at 0 eV.

study reveals that 28 of such materials are mechanically stable and only 13 of them (MnN<sub>6</sub>, FeN<sub>6</sub>, CoN<sub>6</sub>, NiN<sub>6</sub>, NbN<sub>6</sub>, MoN<sub>6</sub>, TcN<sub>6</sub>, TaN<sub>6</sub>, WN<sub>6</sub>, ReN<sub>6</sub>, OsN<sub>6</sub>, IrN<sub>6</sub>, and PtN<sub>6</sub>) are vibrationally stable as well. Of these 13 both mechanically and dynamically stable compounds, the predicted hardest compound has Vickers hardness of 22 GPa (FeN<sub>6</sub>) and the softest one has Vickers hardness of 11 GPa (TaN<sub>6</sub>). We can conclude from Table 2 that compounds from group 8 elements of 3d, 4d, and 5d rows are the hardest and these compounds have the highest densities as well in general. We believe the predicted hardness of 22 GPa for FeN<sub>6</sub> could make it potential candidate as a hard coating material. We found that the Vickers hardness value does not depend on N–N bond length while it is increasing for decreasing values of M–M and M–N bond lengths in general for all mechanically stable MN<sub>6</sub> materials. We also observed that all the harder materials with hardness greater than 16 GPa are brittle in nature which is expected. Moreover, these materials meet our

expectation that the harder material will have higher Debye temperature thereby showing its applicability in applications where tolerance of high temperature is sought for. Our study on magnetic property for both mechanically and vibrationally stable compounds shows that only 3 (MnN<sub>6</sub>, FeN<sub>6</sub>, and CoN<sub>6</sub>) are predicted to have magnetic moment with FeN<sub>6</sub> possessing highest magnetic moment of 1.301  $\mu_B$  per Fe atom (4.821  $\mu_B$  in unit cell). Further analyses on charge transfer from metal to nitrogen and the LDOS reveal that these compounds possess ionic bonding as well as they are metallic in nature and hence most of the contribution to hardness is coming from these bonding states. This can be verified by the -pCOHP analysis showing N–N interactions are in antibonding states while more M–N interactions are in bonding states below Fermi level. We also noticed that the charge transfer decreases with the increasing group number and this is expected. The electronic band structure analysis also confirmed that all mechanically as well as vibrationally stable compounds have zero band gaps indicating the metallic nature. Three compounds from group 4 elements of each 3d, 4d, and 5d rows have positive band gaps, however, they are only mechanically stable but vibrationally unstable.

#### **CRediT** authorship contribution statement

S.R. Kandel: Investigation, Software, Writing - original draft. B.B. Dumre: Software, Validation, Writing - review & editing. D. Gall: Writing - review & editing, Funding acquisition. S.V. Khare: Writing review & editing, Supervision, Funding acquisition.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

No data was used for the research described in the article.

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#### Appendix A. Supplementary data

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#### References

- [1] P. Eklund, S. Kerdsongpanya, B. Alling, Transition-metal-nitride-based thin films as novel energy harvesting materials, J. Mater. Chem. C 4 (18) (2016) 3905-3914.
- [2] A. Kobayashi, Formation of TiN coatings by gas tunnel type plasma reactivespraying, Surf. Coat. Technol. 132 (2000) 152-157.
- [3] J. Bareño, et al., TiN surface dynamics role of surface and bulk mass transport processes, Am. Inst. Phys. 885 (2007) 205-224.
- [4] C. Haihua, et al., Strength and elastic moduli of TiN from radial x-ray diffraction under nonhydrostatic compression up to 45 GPa, J. Appl. Phys. 107 (11) (2010), 113503.
- [5] D. Gall, et al., Growth of poly- and single-crystal ScN on MgO (001): role of lowenergy N<sub>2</sub><sup>+</sup> irradiation in determining texture, microstructure evolution, and mechanical properties, J. Appl. Phys. 84 (1998) 6034-6041.
- [6] Z.T.Y. Liu, et al., First-principles investigation of the structural, mechanical and electronic properties of the NbO-structured 3d, 4d and 5d transition metal nitrides, Comput. Mater. Sci 84 (2014) 365-373.
- [7] Amy Y. Liu, Marvin L. Cohen, Prediction of New Low Compressibility Solids, Science 245 (4920) (1989) 841-8420.
- [8] S. Kodambaka, et al., Absolute orientation-dependent anisotropic TiN(111) island step energies and stiffnesses from shape fluctuation analyses, Phys. Rev. B 67 (3) (2003), 035409.
- [9] H. Holleck, Material selection for hard coatings, J. Vac. Sci. Technol. A 4 (1986) 2661
- [10] S.H. Jhi, et al., Electronic mechanism of hardness enhancement in transition-metal carbonitrides, Nature 399 (1999) 132-134.
- [11] S.H. Jhi, et al., Vacancy hardening and softening in transition metal carbides and nitrides, Phys. Rev. Lett 86 (15) (2001) 3348-3351.
- C.S. Shin, et al., Vacancy hardening in single-crystal TiN<sub>x</sub>(001) layers, J. Appl. [12] Phys. 93 (10) (2003) 6025-6028.
- S. Kodambaka, et al., Size-dependent detachment-limited decay kinetics of two-[13] dimensional TiN islands on TiN(111), Phys Rev Lett 89 (17) (2002), 176102.
- [14] E. Gregoryanz, et al., Synthesis and characterization of a binary noble metal nitride, Nat. Mater. 3 (2004) 294-297.
- [15] J.C. Crowhurst, et al., Synthesis and Characterization of the Nitrides of Platinum and Iridium, Science 311 (5765) (2006) 1275-1278.
- S.R. Kandel, et al., Prediction of super hardness in transition metal hexa-nitrides [16] from density functional theory computations, Materialia 25 (2022), 101550.
- S.V. Khare, T.L. Einstein, Energetics of steps and kinks on Ag and Pt using [17] equivalent crystal therory (ECT), Surf. Sci. 314 (1994) L857-L865.

- Computational Materials Science 221 (2023) 112084
- [18] I. Efthimiopoulos, et al., Pressure-induced transition in the multiferroic CoCr2O4 spinel, Phys. Rev. B 92 (6) (2015), 064108.
- [19] N.J. Szymanski, et al., Electronic and optical properties of vanadium oxides from first principles, Comput. Mater. Sci 146 (2018) 310-318.
- [20] V. Adhikari, et al., First-principles study of mechanical and magnetic properties of transition metal (M) nitrides in the cubic M<sub>4</sub>N structure, J. Phys. Chem. Solid 120 (2018) 197-206.
- [21] B.B. Dumre, D. Gall, S.V. Khare, Stability, and electronic and optical properties of ternary nitride phases of MgSnN<sub>2</sub>: A first-principles study, J. Phys. Chem. Solid 153 (2021), 110011.
- [22] V. Adhikari, et al., First principles investigation into the phase stability and enhanced hardness of TiN-ScN and TiN-YN alloys, Thin Solid Films 688 (2019), 137284.
- [23] N.J. Szymanski, et al., Dynamical stabilization in delafossite nitrides for solar energy conversion, J. Mater. Chem. A 6 (42) (2018) 20852-20860.
- [24] S.R. Kandel, et al., Investigation of hardness in transition metal hexa-nitrides in cubic structure: A first-principles study, J. Phys. Chem. Solid 171 (2022), 111022.
- [25] X. Kang, et al., A novel superhard tungsten nitride predicted by machine-learning ccelerated crystal structure search, Sci. Bull. 63 (13) (2018) 817-824.
- [26] Li Qian, et al., New multifunctional tungsten nitride with energetic N6 and extreme hardness predicted from first principles, EPL (Europhysics Letters) 118 (4) (2017), p. 46001p1-p5.
- [27] W. Qun, et al., High-pressure phases and pressure-induced phase transition of MoN<sub>6</sub> and ReN<sub>6</sub>, Phys. Lett. A 383 (20) (2019) 2429–2435.
- [28] H.J. McSkimin, W.L. Bond, Elastic Moduli of Diamond, Phys. Rev. 105 (1) (1957) 116-121
- [29] B.B. Dumre, et al., Improved optoelectronic properties in CdSe<sub>x</sub>Te<sub>1-x</sub> through controlled composition and short-range order, Sol. Energy 194 (2019) 742-750.
- [30] N.J. Szymanski, et al., Unconventional superconductivity in 3d rocksalt transition metal carbides, J. Mater. Chem. C 7 (40) (2019) 12619-12632.
- [31] S.K.R. Patil, et al., Mechanical stability of possible structures of PtN investigated using first-principles calculations, Phys. Rev. B 73 (10) (2006), 104118.
- [32] P.P. Gunaicha, et al., Structural, energetic and elastic properties of Cu2ZnSn (SxSe1-x)4 (x=1, 0.75, 0.5, 0.25, 0) alloys from first-principles computations, Solar Energy 102 (2014) 276–281.
- [33] W. Yuejian, et al., Thermal equation of state of silicon carbide, Appl. Phys. Lett. 108 (6) (2016), 061906.
- [34] G. Kresse, J. Furthmuller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, Comput. Mater. Sci 6 (1996) 15-50.
- [35] G. Kresse, J. Furthmuller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Phys. Rev. B 54 (1996) 11169.
- [36] G. Kresse, J. Hafner, Ab initio molecular dynamics for liquid metals, Phys Rev B Condens Matter 47 (1) (1993) 558-561.
- [37] G. Kresse, J. Hafner, Ab initio molecular-dynamics simulation of the liquid-metalamorphous-semiconductor transition in germanium, Phys Rev B Condens Matter 49 (20) (1994) 14251–14269.
- [38] T.R. Stefan, K. Mania, First Principles Density Functional Theory Prediction of the Crystal Structure and the Elastic Properties of Mo<sub>2</sub>ZrB<sub>2</sub> and Mo<sub>2</sub>HfB<sub>2</sub>, Crystals 10 (10) (2020) 865
- [39] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmentedwave method, Phys. Rev. B 59 (1999) 1758-1775.
- [40] P.E. Blochl, O. Jepsen, O.K. Andersen, Improved tetrahedron method for Brillouinzone integrations, Phys Rev B Condens Matter 49 (23) (1994) 16223-16233.
- [41] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple, Phys. Rev. Lett. 77 (1996) 3865-3868.
- [42] B.B. Dumre, S.V. Khare, Interrelationship of bonding strength with structural stability of ternary oxide phases of MgSnO3: A first-principles study, Phys. B Condens. Matter 637 (2022), 413896.
- [43] J.A. Warner, et al., Ab initio calculations for properties of MAX phases Ti<sub>2</sub>TlC, Zr<sub>2</sub>TlC, and Hf<sub>2</sub>TlC, Appl. Phys. Lett. 88 (10) (2006), 101911.
- [44] J.L. Roehl, et al., Binding sites and diffusion barriers of a Ga adatom on the GaAs  $(001)-c(4\times4)$  surface from first-principles computations, Phys. Rev. B 82 (16) (2010), 165335.
- [45] Z. Xiuquan, G. Daniel, S.V. Khare, Mechanical properties and electronic structure of anti-ReO3 structured cubic nitrides, M3N, of d block transition metals M: An ab initio study, J. Alloy. Compd. 595 (2014) 80-86.
- J. Nanke, et al., An ab initio computational study of pure Zn<sub>3</sub>N<sub>2</sub> and its native point [46] defects and dopants Cu Ag and Au, Thin Solid Films 564 (2014) 331-338.
- [47] J. Anubhav, et al., Commentary: The Materials Project: A materials genome approach to accelerating materials innovation, APL Mater. 1 (1) (2013), 011002.
- [48] R. Hill, The Elastic Behaviour of a Crystalline Aggregate, Proc. Phys. Soc. 65 (1952) 349-354.
- [49] W.u. Zhi-jian, et al., Crystal structures and elastic properties of superhard IrN2 and IrN<sub>3</sub> from first principles, Phys. Rev. B 76 (5) (2007), 054115.
- [50] V.T. Barone, et al., Optoelectronic and mechanical properties of the orthogonal and tetragonal  $Cu_2CdGe(S_xSe_{1-x})_4$  semiconducting system via first principles methods, J. Appl. Phys. 131 (20) (2022), 205701.
- [51] Z.T. Liu, et al., Structural, mechanical and electronic properties of 3d transition metal nitrides in cubic zincblende, rocksalt and cesium chloride structures: a firstprinciples investigation, J Phys Condens Matter 26 (2) (2014), 025404.
- [52] Tian Yongjun, Xu Bo, Zhao Zhisheng, Microscopic theory of hardness and design of novel superhard crystals, Int. J. Refr. Metals Hard Mater. 33 (2012) 93-106.
- [53] W. Bao, D. Liu, Y. Duan, A first-principles prediction of anisotropic elasticity and thermal properties of potential superhard WB<sub>3</sub>, Ceram. Int. 44 (12) (2018) 14053-14062.

#### S.R. Kandel et al.

- [54] D. Ruopeng, et al., Optical and transport measurement and first-principles determination of the ScN band gap, Phys. Rev. B 91 (4) (2015), 045104.
- [55] W. Tang, E. Sanville, G. Henkelman, A grid-based Bader analysis algorithm without lattice bias, J Phys Condens Matter 21 (8) (2009), 084204.
- [56] H. Graeme, A. Andri, J. Hannes, A fast and robust algorithm for Bader decomposition of charge density, Comput. Mater. Sci 36 (3) (2006) 354–360.
- [57] E. Sanville, et al., Improved adjoint for Bader charge allocation, J Comput Chem 28 (5) (2007) 899–908.
- [58] M. Yu, D.R. Trinkle, Accurate and efficient algorithm for Bader charge integration, J Chem Phys 134 (6) (2011), 064111.
- [59] T. Atsushi, T. Isao, First principles phonon calculations in materials science, Scr. Mater. 108 (2015) 1–5.
- [60] Z.T.Y. Liu, D. Gall, S.V. Khare, Electronic and bonding analysis of hardness in pyrite-type transition-metal pernitrides, Phys. Rev. B 90 (13) (2014), 134102.
- [61] S. Maintz, M. Esser, R. Dronskowski, Efficient Rotation of Local Basis Functions Using Real Spherical Harmonics, Acta Phys. Pol. B 47 (4) (2016) 1165–1175.
- [62] S. Maintz, et al., LOBSTER: A tool to extract chemical bonding from plane-wave based DFT, J Comput Chem 37 (11) (2016) 1030–1035.
- [63] R. Dronskowski, P.E. Bloch, Crystal Orbital Hamilton Populations (COHP). Energy-Resolved Visualization of Chemical Bonding in Solids Based on Density-Functional Calculations, J. Phys. Chem. 97 (33) (1993) 8617–8624.
- [64] N.J. Szymanski, et al., Prediction of improved magnetization and stability in  $Fe_{16}N_2$  through alloying, J. Appl. Phys. 126 (9) (2019), 093903.
- [65] V.L. Deringer, A.L. Tchougreeff, R. Dronskowski, Crystal orbital Hamilton population (COHP) analysis as projected from plane-wave basis sets, J Phys Chem A 115 (21) (2011) 5461–5466.
- [66] M. Koichi, I. Fujio, VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data, J. Appl. Cryst. 44 (6) (2011) 1272–1276.
- [67] I. Khatri, et al., Correlating structure and orbital occupation with the stability and mechanical properties of 3d transition metal carbides, J. Alloy. Compd. 891 (2022), 161866.

- [68] Z. Zhonglong, et al., Potentially superhard hcp CrN<sub>2</sub> compound studied at high pressure, Phys. Rev. B 93 (21) (2016), 214104.
- [69] R.M. Hornreich, et al., Phonon Band Gaps, J. Phys. I 7 (3) (1997) 509–519.
- [70] C.M. Kube, M. de Jong, Elastic constants of polycrystals with generally anisotropic crystals, J. Appl. Phys. 120 (16) (2016).
- [71] X. Jiang, J. Zhao, X. Jiang, Correlation between hardness and elastic moduli of the covalent crystals, Comput. Mater. Sci 50 (7) (2011) 2287–2290.
- [72] S.F. Pugh, Relations between the elastic moduli and the plasctic properties of polycrystaline pure metals, Philos. Mag. J. Sci. 45 (1954) 823–843.
- [73] A. Mansouri Tehrani, J. Brgoch, Hard and superhard materials: A computational perspective, J. Solid State Chem. 271 (2019) 47–58.
- [74] P. Deus, H.A. Schneider, Estimation of the debye temperature of diamond-like semiconducting compounds from bulk modul and microhardness, Cryst. Res. Technol. 18 (1983) 491–500.
- [75] N.H. Miao, et al., Theoretical investigation on the transition metal borides with Ta<sub>3</sub>B<sub>4</sub>-type structure a class of hard and refractory material, Comput. Mater. Sci 50 (2011) 1559–1566.
- [76] F. Gao, et al., Hardness of covalent crystals, Phys Rev Lett 91 (1) (2003), 015502.
- [77] A.L. Allred, E.G. Rochow, A scale of electronegativity based on electrostatic force, J. Inorg. Nucl. Chem. 5 (1958) 264–268.
- [78] K. Balasubramanian, S.V. Khare, D. Gall, Valence electron concentration as an indicator for mechanical properties in rocksalt structure nitrides, carbides and carbonitrides, Acta Mater. 152 (2018) 175–185.
- [79] B.D. Ozsdolay, et al., Cubic β-WN layers: Growth and properties vs N-to-W ratio, Surf. Coat. Technol. 304 (2016) 98–107.
- [80] J. Bareño, et al., Orientation-dependent mobilities from analyses of twodimensional TiN(111) island decay kinetics, Thin Solid Films 510 (1–2) (2006) 339–345.