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Hardness characterization parameters of Niobium Carbide and Niobium Nitride: A first principles study

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HIGHLIGHTS

- Rocksalt, zincblende, and wurtzite phases of NbC and NbN are mechanically stable.
- NbC in rocksalt phase had higher Vickers hardness and other mechanical properties.
- A correlation between toughness and Vickers hardness (H_v) was established.
- Compounds with $H_v > 20$ GPa were brittle, and ductile for those with $H_v < 20$ GPa.

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ABSTRACT

Niobium carbides and nitrides have been proposed as potential candidates for hardness and related applications, however, comprehensive studies are still needed for better understanding that may pave way for their re-engineering for the ultra hard industry. Here we present *ab initio* Density Functional Theory calculations that provide a comprehensive description of various hardness characterization parameters. Our results show that NbC in rocksalt (RS) had a higher shear modulus, Young's modulus, and Voigt-Reuss-Hill shear modulus compared to other phases of NbC and NbN considered in this work. Further, it was noted that NbC in RS had a higher value of Vickers hardness amongst the various phases NbC and NbN studied, thus identified as a potential candidate for hardness and related application. Finally, we showed that compounds with Vickers hardness (H_v) > 20 GPa were found to be brittle while those with $H_v < 20$ GPa were ductile.

1. Introduction

In recent years, there has been a renewed interest in the search of novel materials with unique properties that include hardness, high incompressibility, chemical inertness and thermal [1]stability. In this respect, a number of materials have been considered such as diamond, derivatives of boron, nitrides and carbides of ternary metals [1–4]. These efforts have been focused on understanding, developing and optimizing materials for hardness related applications. Previously, characterization of such materials has been achieved primarily via indentation tests such as the Rockwell and Brinell, among others [5]. However, with recent advancements in computing, theoretical simulations are becoming an indispensable tool for material design. In most theoretical studies, hardness is routinely expressed in terms of bulk modulus, which measures the isotropic compressive stress while other parameters such as elastic constants, shear and Young's modulus are largely ignored yet are essential for comprehensive characterization of such materials. This is particularly relevant in applications that involve twisting and turning. Conventional hard materials, such as diamond and c-BN have previously been used almost exclusively for such applications, however, these materials have drawbacks that limit their usage. For example, diamond is not suitable for machining ferrous alloys, especially at high temperature because under such conditions carbon dissolves into iron, thus rendering the tip ineffective [5]. Furthermore, natural diamond usage in industrial applications is an expensive venture thus there is a need for cheaper alternative material. In addition, development of synthetic diamond has not been able to significantly lower the cost of such tools. On the other hand, c-BN has a relatively low hardness value compared to diamond, thus may only be used in a limited number of applications [5]. Thus this has necessitated

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[1] In the case of c-BN, norm-conserving pseudopotential was used, thus higher cutoff energy was obtained compared to those of ultra-soft potential.

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the search for alternative materials, which are robust, versatile and cost effective compared to existing materials.

Silicon Carbide (SiC) and other Transition Metal Carbides and Nitrides (TMCNs) such as Niobium Carbide (NbC) and Niobium Nitride (NbN) have been identified as potential alternatives to c-BN and diamond. In particular, these materials have been shown to possess, amongst other properties, ultra high hardness, high melting point, high thermal and electrical conductivities [6–8]. However, there is need for a more comprehensive characterization, which may provide insights essential for their optimization that may pave way for broader utilization. Previous studies on SiC, NbC, and NbN have focused on electronic properties with little attention being given to mechanical properties, yet it is critical for their application in industry. For example, Klein et al. [9] calculated the electronic densities of states and spatial Blochl functions of NbC_x, TaC_x and HfC_x, and showed that charge transfer occurs from transition metal to non-metal. Similarly, electronic properties of group-V and VI nitrides (VN, NbN, TaN, CrN, MoN, WN) based on self-consistent augmented plane wave method have been reported [10,11]. Chadi and coworkers [12] studied the electronic band structure and charge densities of NbC and NbN, and showed that C/N 2p states contributed significantly to states occurring near the Fermi level. While Chen et al. [13], used the X-ray diffraction technique to investigate the equation of state parameters for NbN in rocksalt phase.

Recently, Korir et al. [14] predicted hardness across the group 4d TMCNs based on the magnitude of their bulk modulus, where it was found that NbC and NbN had higher values of bulk modulus when compared to other transitional metals in series, thus were identified as a potential candidates for hardness related applications. It would be helpful if comprehensive studies that consider other parameters such as elastic constants, shear modulus, Vickers hardness are investigated to confirm the viability of these materials in hardness related applications, particularly where turning, twisting, and shearing is envisaged.

Besides the materials mentioned above, SiC has also been studied by several groups using both experimental and theoretical techniques. In particular, Chang et al. [15] using *ab initio* electronic structure approaches, showed that the band gap of SiC with cubic phase decreases with increasing pressure while the zinc-blende phase transforms to rocksalt structure at 660 Kbar under hydrostatic pressure. In addition, molecular dynamics studies have also shown that the zinc-blende phase of SiC is the most stable at ambient conditions [16], while other studies have shown an existence of temperature dependent electron mobility [17]. Similar to NbC and NbN, SiC has not been studied exhaustively, particularly the mechanical properties essential for understanding its potential application in ultra-hard industry. Therefore, the current study seeks to investigate the mechanical properties such as parameters Vickers hardness, Young's modulus, bulk modulus, ductility and brittleness of NbC, and NbN in Rocksalt (RS), Zincblende (ZB), and Wurtzite (WZ) phases, while SiC is studied in ZB phase. The results obtained are compared to those of c-BN and diamond, which are considered standard industrial materials for ultra-hard applications.

2. Computational details

In this work, all calculations were performed within the density functional theory approach by solving the Kohn-Sham equations [18] as implemented in the Quantum Espresso suite [19]. The generalized gradient approximation of the exchange and correlation potential was employed in the form proposed by Perdew, Burke and Ernzerhof (PBE) [20]. The core-electrons were replaced with ultra-soft pseudopotentials as described in Vanderbilt's formulation [21], and the electronic wave functions were expanded in a plane wave basis set with an energy cutoff of 60 Ry (NbC, NbN), 90 Ry (SiC), and 120 Ry (c-BN). Unless stated otherwise, all calculations reported in this work relates to bulk systems, where it is considered relaxed only when the forces on all atoms are smaller than 0.02 eV/Å. Integration over the Brillouin zone was performed using Monkhorst and Pack [22] mesh, and for all systems considered a grid of $11 \times 11 \times 11$ was used for RS and ZB phases, while for WZ phase a grid of $10 \times 10 \times 5$ was used for both NbC and NbN. Only for SiC (ZB phase) an optimum k-point grid of $8 \times 8 \times 8$ was obtained. Elastic constants were determined by introducing a small distorting (δ) in the crystal, and the corresponding energy change ($\Delta E/V$) computed. For each system, 21 sets of $\Delta E/V$ data were acquired from DFT calculations with the range of δ being -0.02 to 0.02 in steps of 0.002. This range is considered sufficient to induce the desired deformation without disrupting the structure of the materials. The obtained $\Delta E/V$ data were then fitted to the respective equation for each elastic constant as described in Ref. [23]. Other parameters critical in hardness characterization that include the Voigt-Reuss-Hill approximation, Young's modulus, shear modulus, Pugh's ratio, and Vickers hardness were determined as described in Ref. [24].

3. Results and discussions

3.1. Structural properties

The intrinsic hardness of a material is determined by a number of factors such as the strength of interatomic forces and the crystal structure. Materials exhibiting high intrinsic hardness are generally characterization by a high cohesive energy, short bond-length, and high degree of covalent bonding [25]. The strength of the interatomic forces and the bonding lengths play an important role in determining elastic properties as well as hardness. Fig. 1(a–c) shows the optimized crystal structures of NbC and NbN in the phases considered in this study. Values of optimized bond angles and bond lengths are shown in Table 1. Bond length is an important indicator of material hardness i.e., shorter bond lengths suggest a strong bonding between the atoms and vice versa.

Shown in Table 1, the bond-length of NbC/N for NbC and NbN in the same crystal structure were observed to be almost similar in magnitude (with a variance of between 1.4% and 2.8%), which can be attributed to negligible difference in atomic radii of carbon and nitrogen atoms. It was further noted that for both carbides and nitrides, the RS phase had the longer bond-length, followed by ZB, and WZ had the shortest. A comparison of c-BN and SiC indicated that c-BN had shorter bond-length, but still longer by about 9% compared to that of diamond [26]. The bond-angles of both NbC and NbN of the same phase were found to be comparable. In particular, the bond-angles of C/N—Nb—C/N for RS, ZB, and WZ were found to be 90.0, 109.5 and 108.7, respectively.

The lattice parameters were obtained by fitting the energy-volume data to the Murnaghan equation of state [27] and the results presented

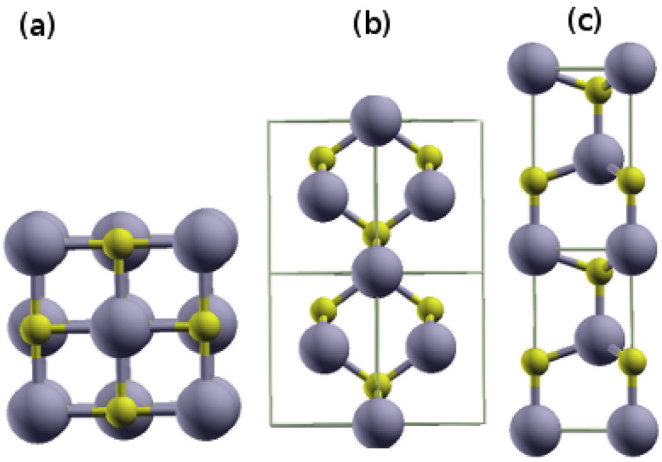

Fig. 1. Ball and stick representation of crystal structures of NbN and NbC studied in this work: (a) rocksalt, (b) zinc-blende and (c) wurtzite. The bigger balls represent Nb atoms while the small balls represent either C or N atoms.

Table 1
Calculated DFT-GGA bond lengths (Nb—C, Nb—N, Si—C, B—N) and lattice parameters for NbC, NbN, SiC, and c-BN in different phases.

Structure	Bond Length (Å)	Lattice Constants (Å)	c/a
NbC (RS)	2.25	4.49	
Other works	2.24[g]	4.48[a]	
Experimental works		4.47[b]	
NbC (ZB)	2.09	4.82	
Other works	2.09[g]	4.84[a]	
NbC (WZ)	1.76	3.70	1.10
Other works	2.22[g]	3.71[a]	1.20[a]
NbN (RS)	2.20	4.38	
Other works	2.01[g]	4.44[g], 3.11[i]	
Experimental works		4.39[c], 4.21[h]	
NbN (ZB)	2.06	4.76	
Other works		4.76[g], 3.35[i]	
NbN (WZ)	1.71	3.01	1.85
Other works		2.96[g], 2.94[i]	1.87[d]
SiC (ZB)	1.90	4.37	
Experimental works		4.36[f]	
c-BN (ZB)	1.55	3.63	
Experimental works		3.63[e]	

[a] Ref [28].
[b] Ref [29].
[c] Ref [6].
[d] Ref [31].
[e] Ref [32].
[f] Ref [33].
[g] Ref [14].
[h] Ref [1].
[i] Ref [30].

in Table 1. It was observed that NbC reported higher values of lattice constants for all the phases considered in this work compared to NbN, for example, by as much as 1.2% in ZB phase. The findings of this study which included $a = c$ values were also found to be in good agreement with the available experimental and theoretical studies [1,6,28–33] as shown in Table 1.

3.2. Elastic properties

Elasticity describes a material's response to external forces via a mechanism such as deformation and subsequent recovery of original shape [34]. DFT calculations employed in this work have been shown to provide reliable results consistent with experimental data, thus can provide complementary information whenever such data are inaccessible [35]. Calculated elastic constants for various systems studied in this work are presented in Table 2.

From the results presented in Table 2, it is noted that elastic constants C_{11} and C_{44} of NbC in RS are overestimated compared to experimental values by as much as 7% and 17%, respectively. In spite of this, for those systems where experimental values were available, acceptable agreement with our calculated values is established. It is of importance to note that computational studies such as the current work considers perfect crystal under ideal conditions, while in experiments such structures and conditions are almost unattainable, thus this may attributed to the observed variance.

Fig. 2(a and b) shows the elastic constants trends for different phases considered, with the solid line used only as a guide to the eye. With the exception of ZB phase, C_{11} was found to be higher compared to other calculated elastic constants for all phases considered. Furthermore, as can be seen from these data, all the independent elastic constants obey Born criterion [45,46], where for cubic phase (RS, ZB) $C_{44} > 0$, $C_{11} > C_{12}$ and $C_{11} + C_{12} > 0$, while in the hexagonal phase (WZ) $C_{33} > 0$, $C_{44} > 0$, $C_{12} > 0$, $C_{11} > C_{12}$, $(C_{11} + 2C_{12})C_{33} > 2C_{13}^2$. This is a confirmation that these phases are mechanically stable.

Table 2
Calculated DFT-GGA elastic properties of NbC, NbN, SiC and c-BN in different structures.

Structure	C_{11} (GPa)	C_{12} (GPa)	C_{13} (GPa)	C_{33} (GPa)	C_{44} (GPa)
NbC (RS)	666.90	115.90			180.50
Other Works	667.00[j]	121.00[f]			164.30[d]
	627.10[d]	134.60[d]			151.00[f]
Expt Work	620.00[e]	200.00[e]			150.00[e]
NbC (ZB)	282.00	168.00			71.00
Other Works					
NbC (WZ)	589.77	192.28	92.33	815.02	216.34
SiC (ZB)	363.60	136.50			241.50
Other Works	390.00[i]	134.00[i]			253.30[i]
	390.00[h]	142.00[h]			256.30[h]
NbN (RS)	603.50	152.00			66.30
Other Works	718.00[a]	134.00[a]			101.80[a]
Expt Work	739.00[b]	161.00[b]			76.00[b]
	608.00[e]	122.90[b]			117.00[b]
NbN (ZB)	277.70	189.80			35.30
Other Works	287.80[a]	217.20[a]			23.90[a]
NbN (WZ)	520.52	222.17	144.58	808.21	206.83
Other Works	560.00[g]	220.00[g]	132.00[g]	770.00[g]	216.30[g]
	544.90[c]	217.40[c]	140.40[c]	739.10[c]	241.40[a]
c-BN (ZB)	761.10	162.70			454.20
Experimental work	820[h]	190[h]			480[h]

[a] Ref [36].
[b] Ref [13].
[c] Ref [35].
[d] Ref [37].
[e] Ref [38].
[f] Ref [39].
[g] Ref [40].
[h] Ref [41].
[i] Ref [42].
[j] Ref [43].

NbC was found to have higher values of C_{11}, C_{33}, and C_{44} in all its phases compared to NbN. On the other hand, NbN had the highest values of C_{12} in all its phases compared to NbC. Finally, the calculated C_{33} values were the largest amongst all the other elastic constants observed in NbC and NbN, thus these systems are predicted to offer high resistance to compressive stress as shown in Fig. 2ab and Table 2. C_{13} and C_{33} are not plotted in Fig. 2ab since they are only relevant in the case of WZ structure only. Compared to other carbides, SiC reported higher C_{44} while other elastic constants (C_{11} and C_{12}) were generally lower compared to those of other systems studies in work. Based on the high elastic constants observed in RS and WZ phases, compounds in such phases are anticipated to exceed those in ZB in relevance to hardness related application.

3.3. Other mechanical properties

The bulk modulus is a measure of the resistance against volume change imposed by the applied pressure, as shown in Eq. (1) below,

$$B_0 = \frac{2}{9}C_{11} + C_{12} + 2C_{13} + \frac{C_{33}}{2}. \quad (1)$$

Based on calculated bulk moduli, our study revealed that both NbC and NbN in the same phase have comparable resistance to volume change as shown in Table 3. While the shear modulus denotes the resistance against reversible deformation upon shear stress [47] and calculated using Eq. (2) below,

$$\frac{\Delta E}{V} = 6G\delta + 0(\delta^3). \quad (2)$$

The calculated shear moduli revealed that NbC had higher shear modulus compared to NbN in all the phases considered (with range between 57 and 276 GPa), thus suggesting it is better suited for

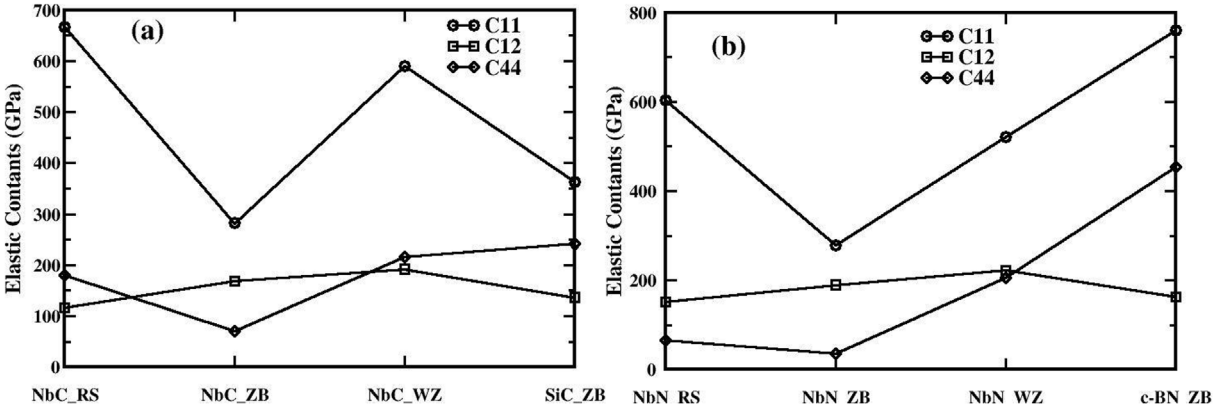

Fig. 2. Elastic constants of phases NbC (left panel) and NbN (right panel), respectively, in RS, ZB and WZ phases.

Table 3
Calculated Bulk modulus (B_0), shear modulus (G), Young's modulus (E), Poisson ratio (ν), shear Voigt-Reuss- Hill moduli (G_{VRH}), and Vickers hardness (H_v) of NbC, NbN, SiC, and c-BN.

Structure	B_0 (GPa)	G (GPa)	E (GPa)	ν	G_{VRH} (GPa)	H_v
NbC (RS)	300.0	275.5	518.0	0.21	214.0	28.0
Other Works	293.0[x]					
	300.2[p]					
Expt Work	302.0[h]					
NbC (ZB)	206.1	56.9	177.0	0.35	65.0	5.0
Other Works	204.9[p]					
NbC (WZ)	305.4	196.6	511.0	0.22	209.0	26.0
SiC (ZB)	212.2	113.5	418.0	0.17	178.0	30.0
Other Works	219.0[m]					34.0[p]
	224.0[n]					
NbN (RS)	302.5	225.7	297.0	0.33	111.0	8.0
Other Works	349.5[b]					
	304.8[p]					
Expt Work	292.0[d]					
NbN (ZB)	219.1	44.0	109.0	0.41	38.0	2.0
Other Works	224.9[p]					
NbN (WZ)	332.0	173.5	461.0	0.26	182.0	18.0
Other Works	308.0[j]	211.0[j]				
	312.1[e]	199.0[f]				
c-BN (ZB)	362.2	299.2	853.0	0.11	384.0	66.0
	364.6[g]					66.0[p]

[b] Ref [36].
[d] Ref [13].
[e] Ref [35].
[h] Ref [38].
[j] Ref [40],
[n] Ref [41].
[f] Ref [33].
[m] Ref [42].
[x] Ref [43].
[p] Ref [14].
[g] Ref [3].

hardness applications that entail twisting, turning, and shearing. It is worth noting that ZB phase in both NbC and NbN reported lower shear modulus of 57 GPa and 44 Gpa, respectively, thus this phase may not be ideal for shear related application, as shown in Table 3.

Further, it is observed that WZ phase of in both NbC and NbN had lower shear modulus of 197 GPa and 173 GPa, respectively compared to those of RS phase 275 GPa (NbC) and 226 GPa (NbN). Therefore, it is expected that NbC in RS would offer maximum resistance to the mobility of dislocations within its structure, hence it is conceivable that this phase may be ideal for shear related application [49]. In the case of SiC, its bulk modulus was found to be comparable to that of NbC in ZB phase, while the shear modulus was lower than that of NbC in RS phase, thus predicted to be a poor candidate for shear related application, in agreement with previous studies [13,38]. We also calculated Young's modulus (E), which measures the stiffness and stability of crystal, and is using Eq. (3) below,

$$E = \frac{9G}{3 + k}, \tag{3}$$

were G and k denotes shear modulus and Pugh's ratio, respectively.

High values of Young modulus indicate the rigidity of materials as it represents the ratio of linear stress to linear strain. The results obtained are shown in Table 3, where it is observed that NbC in all its phases considered has higher values of Young's modulus compared to similar phases of NbN. It is further noted that NbC in RS phase has the highest Young's modulus amongst all the phases of NbC and NbC considered in this work. Generally, Young's modulus of a material for hardness related applications is normally extremely high, as shown by data in Table 3 in the case of c-BN. It is therefore expected that NbC in RS phase would perform comparatively in such application due to its high Young's modulus as compared to other phases studied in this work.

Reuss and Voigt bounds on the shear modulus [24] are given by:

$$G_R = \frac{5C_{44}(C_{11} - C_{12})}{4C_{44} + (C_{11} - C_{12})}, \tag{4}$$

$$G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5}. \tag{5}$$

Finally, G_{VRH} mean value is obtained as shown in Eq. (6) below,

$$G_{VRH} = \frac{1}{2}(G_V + G_R). \tag{6}$$

We calculated Voigt-Reuss-Hill shear moduli (G_{VRH}) and the are results presented in Table 3. G_{VRH} relates to the actual magnitude of elastic anisotropy possessed by the crystal [25]. Results obtained were found to be consistent to those of elastic properties, where NbC reported higher values compared NbN in all the phases. Additionally, it was noted that NbC in RS phase had the highest values of G_{VRH} amongst Carbide in all phases studied, though slightly lower than that of c-BN.

Materials for hardness and related applications are normally associated with high bulk and shear modulus. However, these are not the only mechanical parameters that determine their applicability. Toughness is another critical property, which measures the degree of plastic deformation (ductility) of the solids under mechanical loading. Ductility of our materials of interest were analyzed using Pettifor criterion [24], which states that for a metallic non-directional bonding compounds, the Cauchy pressure ($C_{12}-C_{22}$) values are typically positive, and this region is considered ductile. The other criterion that was considered is the Pugh's modulus ratio (B/G) [47], where materials with B/G > 0.57 are considered brittle. Using both Pettifor's and Pugh's criteria, we have mapped the ductile and brittle behaviour of our materials of interest as shown in Fig. 3. It is shown that NbC in RS, NbC

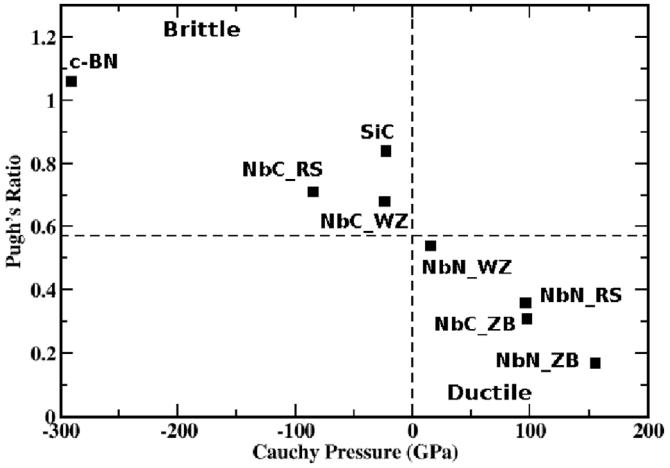

Fig. 3. Map of brittleness and ductility trends of NbC and NbN in different phases, SiC, and c-BN.

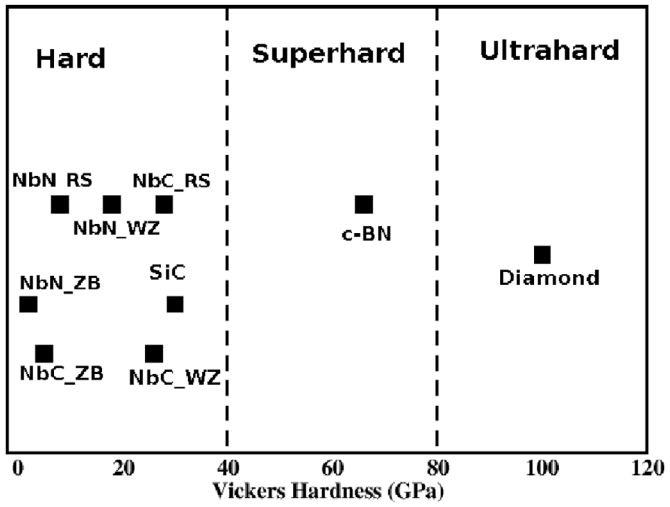

Fig. 4. Hardness classification of NbC and NbN in different phases, SiC, and c-BN.

in WZ, SiC, and c-BN are brittle, while NbC in ZB, NbN in WZ, NbN in ZB, and NbN in RS are ductile, as shown in Fig. 3. In addition, the Poisson ratio is used to predict either the ductility or brittleness of any material. Ductility and brittleness, in this case, are separated by a value of about 0.26. A value of Poisson ratio of more than (less than) 0.26 corresponds to ductility (brittleness) of the material [5]. As indicated in Table 3, these values range from 0.11 to 0.41. Based on this data, NbN in all its phases and NbC in ZB have Poisson ratio above 0.26 thus ductile while NbC in RS and WZ, SiC and c-BN have values below 0.26 hence brittle. This is consistent with the Pettifor's criterion presented above.

Furthermore, the Pugh's ratio (k) is associated with ductility and it gives a trend similar to that of Poisson's ratio and B/G for the material considered in this work. Specifically, NbC in ZB and all phases of NbN are ductile. Vickers hardness (H_v) is another property considered in the study as it is influenced by the elastic moduli G and B. From the data in Table 3, the brittle systems have high values of H_v compared to the ductile materials identified in the earlier analysis. The hardness of materials tends to increase with increasing shear moduli [50]. This study has not considered the stability of the hard materials under extreme conditions and shall be a subject for future work.

Finally, we analyzed the hardness of different phases considered in this work by adopting the empirical scheme [48], which correlates the Vickers hardness and Pugh's modulus ratio as shown in Eq. (7) below,

$$H_V = 2(k^2G^{0.585}) - 3, \quad (7)$$

where $k = G/B$ is the pugh's ratio with G and B being shear and bulk modulus, respectively. Using Eq. (7), the obtained Vickers hardness are presented in Table 3. It was observed that c-BN had the highest hardness value of 65 GPa, thus categorized as super-hard ($H_v \simeq 40$–80 GPa). Amongst NbC and NbN in different phases studied in this work, NbC in RS had the highest H_v of about 28 GPa, which is comparable to that SiC of 30 GPa. Also, it was noted that NbC in WZ had H_v of 26 GPa, which is close to that of NbC in RS and SiC, thus comparable performance in terms of hardness related application as anticipated amongst these compounds. Other compounds, namely, NbN in ZB, NbC in ZB, and NbN in RS had $H_v < 10$, while NbN in WZ reported a higher H_v value of 18 GPa, as shown in Table 3. Using the calculated Vickers hardness, we have classified the various materials studied in this work based on the H_v magnitude, as shown Fig. 4, where it is noted that the various phases of NbC and NbN and c-SiC were found to be hard, while c-BN was classified as super-hard.

4. Conclusion

In summary, by means of *ab initio* DFT simulations, we have investigated hardness characterization parameters for NbC, NbN, SiC, and c-BN with particular emphasis on elastic constants, bulk, shear modulus and Young's modulus, toughness as well as Vickers hardness. Based on this work, it is noted that all the phases considered conform to the Born stability criterion, thus predicted to be mechanically stable. In addition, high C_{13} and C_{33} observed in RS phase of NbC and NbN means such systems would offer high resistance to compressive stress. Amongst the NbC and NbN in different phases, NbC in RS phase consistently reported high shear modulus, Young's modulus, and shear Voigt-Reuss-Hill modulus, thus predicted to be a potential candidate for hardness related application. Finally, a correlation of toughness and Vickers hardness is noted amongst the systems studied, where compounds with $H_V > 20GPa$ were found to be brittle while those with $H_V < 20GPa$ were ductile. These findings may assist in identifying the appropriate hardness related application for the systems studied, and also may provide pathways for engineering intrinsic hardness in such systems to improve performance.

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