Puzzle of c-WN phase stabilization.

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Abstract—**In this paper, we present first-principles calculations that compare structural and electronic properties of WN in the NaCl and NbO phases. Our results predict that the NbO structure of WN is more stable than the NaCl structure without defects, where the enthalpy of formation per formula unit Hf = -0.872eV and 0.616eV for NbO and NaCl structures, respectively. Moreover, the calculated lattice parameters of c-WN are a=4.35Å and a=4.11Å for NaCl and NbO phases, respectively. It is very clear that the lattice parameter obtained for c-WN in NbO is in very good concordance with that reported experimentally of a = 4.14Å. Although the formation energy calculations support the hypothesis of the stability of the NbO phase, the experimental x-ray photoelectron spectroscopy (XPS) electron density of states for valence band spectra corresponds to that density of states calculated for c-WN in NaCl phase. Based on this comparison, more consideration must be taken into account to elucidate this issue.**

Index Terms—**Cubic Tungsten nitride ceramics, First-principles calculations, Formation energy.**

I. INTRODUCTION

In recent years, great focus has been given to investigate the structural and electronic properties of transition-metal nitrides and carbides. This interest arose due to their promising functional materials with high hardness, high melting point, and wear resistance such as the technological application to cutting tools and hard coatings. It is observed that the hardness of carbides such as NbC_x and TaC_x increases as the vacancy concentration (1-x) increases [1], [2]. In contrast, for transition metal nitrides the hardness is increased as the concentration of the N-vacancy is decreased, such as TiN_x, ZrN_x and HfN_x [2]–[4]. Due to that, the great effort was directed to the synthesis and characterization of transition metal mononitride with cubic sodium chloride structure. Recently, The cubic Tungsten nitride (c-WN) was found to be the hardest transition metal nitride with the highest Bulk modulus which is comparable to diamond [5]. Tungsten nitride is crystallized in large number of phases with various nonmetal ratios, including cubic WN, WN1/2, and a stoichiometric hexagonal WN phase, which form depending on the chosen process parameters including temperature and N2 flow rate [6]–[11]. The tungsten mononitride exists in hexagonal structure at low-temperature and metastable cubic NaCl-type structure at high temperature [1], [12] Most of transition-metal nitrides can be crystallized in a cubic structure with octahedral symmetry due to the hybridization of metals d valence electrons with the 2p electrons of nitrogen [13]–[16]. The excellent mechanical properties of c-WN could be ascribed to strengthen p-d bonding, which was proved by X-ray photoelectron spectroscopy (XPS) [5], [17]. In addition, theoretical works based on First-principles calculations have predicted that WN in NaCl-type structure is mechanically unstable unless there is at least 5% of vacancies which make its formation enthalpy negative [18], such that the most predicted stable phase for stoichiometric WN is the cubic NbO phase with 25% of vacancies, where only three sites of Tungsten and three sites of Nitrogen occupied per cubic unit cell in comparison to the NaCl structure [18]–[20]. Although the NbO phase has never been observed experimentally, the c-WN in the NaCl-type was successfully synthesized at high pressure and high temperature [5]. Moreover, X-Ray diffraction (XRD) results suggest that cubic stoichiometric WN exhibits a NaCl phase which is expected to contain both W and N vacancies [5], [6], [21].

In order to gain more insight about the phase stabilization of c-WN compound, it is very interested to compare stoichiometric c-WN in the NaCl and NbO structures. In this paper, we present first-principles calculations that compare structural and electronic properties of WN in the NaCl and NbO phases. Our results predict that the NbO structure of WN is more stable than the NaCl structure without defects, where the enthalpy of formation per formula unit Hf = -0.872eV and 0.616eV for NbO and NaCl structures, respectively. Moreover, the calculated lattice parameters of c-WN are a=4.35Å and a=4.11Å for NaCl and NbO phases, respectively. It is very clear that the lattice parameter obtained for c-WN in NbO is in very good concordance with that reported experimentally of a = 4.14Å [5]. Although the formation energy calculations support the hypothesis of the stability of the NbO phase, the experimental XPS-electron density of states corresponds to that of NaCl phase. Based on this comparison, more consideration must be taken into account to elucidate this issue.

II. COMPUTATIONAL DETAILS

In the present work, first-principles density functional theory(DFT) [22], [23] total energy calculations with fully structure optimization are performed with the projector-augmented wave (PAW) method as it is implemented in Quantum Espresso

code [24]. The interactions between transition metal W and nonmetal N atoms are included using PAW pseudo-potential technique [[25]]. The valence states used for W and N are $5d^4$ $6s^2$ and $2s^2$ $2p^3$, respectively, moreover the semi-core states $4f^{14}$ $5s^2$ $5p^6$ for W are treated as a valence states. An energy cutoff of 1229 eV is used for the plane wave basis set and the ion positions are always relaxed until the quantum mechanical forces acting on them become 0.010 eV/Å, while keeping the unit-cell shape fixed. The generalized gradient approximation was used to describe the exchange correlation interactions in the parametrization of Perdew, Burke, and Ernzerhof (PBE) [26]. An energy cutoff of 1229 eV is used for the plane wave basis set, and Brillouin zone sampling was performed using the MonkhorstPack grid of $13 \times 13 \times 13$ meshes. This dense k-point mesh were used to guarantee that the total energy was less than 10 meV/atom. The structures were optimized with the conjugate gradient algorithm method and the ionic positions of atoms were relaxed at a fixed volume that was varied for different of calculations to get a set of volume vs energy data. Subsequently, this data was fitted to a second order Birch-Murnaghan equation of state [27] to determine the equilibrium lattice parameter(a0), corresponding minimum energy (E0), and the Bulk modulus (B0) of the compound.

The energy of formation E^{form} of a given phase X (X : NaCl or NbO phases) is determined using Ef = ($E^{phase\ X}$ /n) (EW + EN), where Ephase is the total energy calculated for the phase X, n is the number of tungsten or nitrogen atoms, where n=4 for NaCl n=3 for NbO phase. In addition to this, EW is the eqilibrium energy of tungsten in bcc phase and EN is the minimum energy of nitrogen molecule gaz. It is worth to not that the pseudo potentials used in these calculations were taken from BURAI package [28], which is a GUI systemfor Quantum ESPRESSO code, and they used throughout the calculation. The electronic density of states (DOS) is calculated using conventional unit cells with four or three atoms for the NaCl or NbO structures, respectively, using the tetrahedron method for energy smearing in a dense mesh of 20 20 20 k points.

NaCl phase belongs to the space group 225 (F m-3m) with W and N atoms occupying the Wyckoff positions 4a (0,0,0) and 4b (0.5,0.5,0.5). NbO phase belongs to the space groupe 221 (pm-3m) with Wyckoff position W 3c(0, 1/2,) and N 3d (0, 1/2, 0). Both crystal structures are cubic and exhibit anion and cation sites on the same fcc sublattices. However, while all sites of the two fcc sublattices are occupied in the conventional cubic unit cell of the NaCl structure, the NbO structure has only three cations and three anions per cubic unit cell, exhibiting a regular array of both cation and anion vacancies that represent 25% of sites in comparison to the NaCl structure.

III. CONCLUSION

Based on this comparison, more theoritical considerations must be taken into account to elucidate this issue.

Phase	a(Å)	B(GPa)	E_{form}(eV)
NaCl	4.342	355	0.616
NbO	4.113	349	-0.872
exp.	4.145[a], 4.12[b]	423[a]	

[a]Ref [5], [b]Ref [29].

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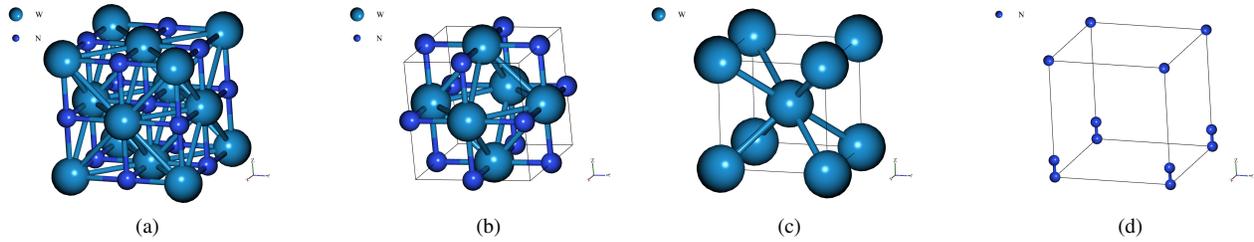
Fig. 1. Crystal structure of the conventional unit cells used in the simulation to calculate the total energies of elements. (a) c-WN in NaCl-type, (b) c-WN in NbO-type structure, (c) W bcc, and in (d) we depicted the box used to simulate the isolated N2-molecule.
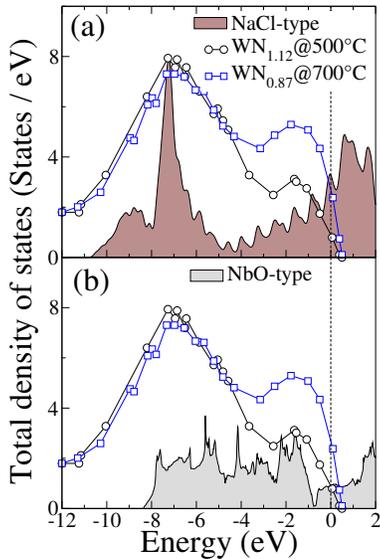

Fig. 2. Calculated total density of states for c-WN compared to the experimental XPS valence band spectra for (a) NaCl-type structure and (b) NbO-type structure. The symbols represent XPS-DOS of c-WN at 500°C(circles) and 700°C(squares) with exposed surface to lab atmosphere, taken from Ref.[Metaxa]. The vertical dashed-line represents the fermi energy shifted to zero eV.

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