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First-principles prediction of metastable niobium and tantalium nitrides M_4N_5 and M_5N_6 stoichiometry

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ABSTRACT

A first-principles plane-wave pseudopotential method based on the density functional theory is used to investigate the structural, elastic and electronic properties of M_4N_5 and M_5N_6 (M = a transition metal (TM) Nb, Ta). C_{33} elastic constant for all compounds is found to be much larger than C_{11}, indicating that *a*-axis is more compressible than *c*-axis. Interestingly, we find that C_{33} and C_{11} are significantly larger than other elastic constants, resulting in a pronounced elastic anisotropy.

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1. Introduction

TaN_x, NbN_x transition metal nitrides are refractory metals that possess technologically useful properties including superconductivity and ultra high hardness, comparable to diamond (experimental bulk modulus = 443 GPa). Also, they combine various physical and chemical, such as high melting points (around 3000 °C). While the Ta–N and Nb–N equilibrium phase diagrams are extremely rich and relatively unexplored both experimentally and theoretically. It exhibits a remarkable richness with regard to that can form and is used, for example, in coatings for cutting tools and wear-resistant layers, as well as for thin-film resistors and diffusion barriers in integrated circuits. In addition to the equilibrium phases, a variety of metastable phases have been reported. As far as tantalum mononitride (TaN) is concerned, owing to its outstanding mechanical and chemical stability [1], it is widely used in many technological applications, for example as a hard coating material. Niobium nitrides are very interesting materials because of their high hardness [2,3], high wear resistance [4], high melting point [1], good temperature stability, good chemical stability at high temperature [5] and superconducting properties [6]. Focusing on superconducting properties, Papaconstantopoulos et al. [7] studied V and VI groups of transition metal mononitrides, whereas on one hand Stampfl et al. [8] investigated electronic structure and physical properties of early transition metal mononitrides. On the other hand Stampfl et al. [9] studied stable and metastable structures of the multiphase tantalum nitride system, using the density functional theory (DFT) calculations and the Full-potential Linearized Augmented Plane-Wave (FLAPW) method. S. Nagao et al. [10] studied anisotropic elasticity in group IVB of transition-metal mononitrides., Chen et al. [11] investigated pressure effects on niobium nitride while Ojha et al. [12] explored pressure-induced structural phase transformations and elastic properties in transition metal mononitrides. Also, Joelsson and Hultman [13] analysed phase stability of $Nb_xZr_{1-x}N$ thin films [14]. Obtained the nitrides Ta_4N_5 and Ta_5N_6 by heating Ta_3N_5 in an atmosphere of Ar or NH_3 [15]. Observed that when thin films of Ta are evaporated in an O free NH_3 atmosphere, Ta_5N_6 forms at 1100 °C. Ta_4N_5 and Ta_5N_6 also form when Ta_3N_5 is heated in vacuum.

Here we perform first-principles density functional calculations to investigate the crystal structures and electronic characteristics of a bulk of Niobium and Tantalum nitrides M_4N_5 and M_5N_6. Many of these nitrides can be described as close-packed metal lattices (f.c.c. or h.c.p.), with a nitrogen atom at the center of an octahedral

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structure. Hexagonal (composition, at.% N ~ 54.5 for Ta_5N_6, Pearson symbol *hP*22) M_5N_6 present an Nb_5N_6 prototype structure with a space group *P6₃/mcm*, N°193 [14–16], while tetragonal (composition, at. % N ~ 55 for Ta_4N_5, Pearson symbol *tI*18) M_4N_5 present a H_4Li_4Rh prototype structure with a space group *I4/m*, N°87 [14,15,17]. This article is organized as follows: The computational method is described in Section 2. In Section 3, the results of the calculations are presented and compared with available experimental and theoretical data. Conclusion is given in Section 4.

2. Computational method

Computer simulation techniques are becoming more and more important in understanding of physical properties of materials. Our first-principles calculations are performed within a Plane Wave Pseudo Potential (PWPP) method which has been implemented in a CASTEP (Cambridge Serial Total Energy Package) simulation program [18]. It is based on the Density Functional Theory (DFT) [19,20] which is, in principle, an exact theory of the ground state. In our calculations, using the Perdew-Burke-Ernzerhof scheme, known as PBE scheme [21], a Generalized Gradient Approximation (GGA) is made for the electronic exchange-correlation potential energy. Coulomb potential energy caused by electron–ion interaction is described within an ultrasoft scheme, in which the Nb ($4d^4\ 5s^1$), Ta ($4f^{14}\ 5d^3\ 6s^2$), and N ($2s^2\ 2p^3$) orbitals are treated as valence electrons. According to an ultrasoft condition, the pseudo-wave function which is related to the pseudo potential matches the plane-wave function expanded with Kohn-Sham beyond cut-off energy. Using high cut-off energy, at the price of spending long computational time, can actually provide accurate results. The cut-off energy for the plane-wave expansion was set at 380 eV and the Brillouin zone sampling was carried out using the $6 \times 6 \times 6$ set of Monkhorst-Pack mesh [22]. Atomic positions are relaxed and optimized with a density mixing scheme using the Conjugate Gradient (CG) method for eigenvalues minimization. The equilibrium lattice parameter is then computed from a structural optimization, using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization technique. This technique provides a fast way of finding out the lowest energy structure out of all the converged strustures, with the following thresholds: energy change per atom less than 2×10^{-5} eV, residual force less than 0.05 eV/Å, displacement of atoms during the geometry optimization less than 0.002Å, and maximum stress within 0.1 GPa. The crystal structures are reported (Table 1). The large and small balls represent M and N atoms Fig. 1.

Table 1
Calculated M_4N_5 and M_5N_6 (composition, at.% N ~ 55 and 54.5 respectively) structures: lattice parameter in Å; ratio c/a; volumes per formula unit (f.u.) in Å^3, and the space group and compared with experimental data. The notation $N_{f.u.}$ represents the number of f.u. in the unit cell.

Space group	*a*	*c*	*c/a*	V	$N_{f.u}$
		Tetragonal prototypes			
Nb_4N_5					
$I_{4/M}$	7.254	4.557	0.628	239.81	2
	6.873[a]	4.298[a]	0.625[a]		
	6.853[e]	4.270[e]	0.623[e]		
Ta_4N_5					
$I_{4/M}$	6.875	4.230	0.615	200.00	2
	6.831[a]	4.269[a]	0.624[a]		
	6.835[c]	4.272[c]	0.625[c]		
		Hexagonal prototypes			
Nb_5N_6					
$P6_3/mcm$	5.335	10.603	1.987	261.349	2
	5.193[a]	10.380[a]	1.998[a]		
	5.195[f]	10.382[f]	1.998[f]		
Ta_5N_6					
$P6_3/mcm$	5.170	10.299	1.992	238.42	2
	5.181[b]	10.361[b]	1.999[b]		
	5.175[c]	10.307[c]	1.991[c]		
	5.160[d]	10.270[d]	1.990[d]		

[a] [24].
[b] [25].
[c] [15].
[d] [16].
[e] [26].
[f] [27].

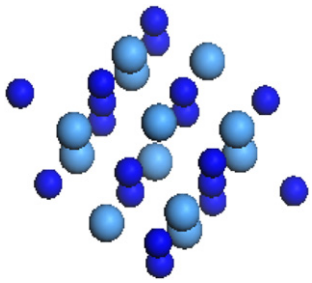

Fig. 1. M_4N_5 (M = Nb, Ta) structure: perspective view. The large and small balls represent M and N atoms.

3. Results and discussion

3.1. Structural properties

M_4N_5 (M = a transition metal (TM) Nb, Ta) compounds structures belong to the same tetragonal I4/m space group (No: 87, Pearson symbol *tI18*, prototype H_4Li_4Rh), with two formula units per unit cell, for Ta_4N_5 and Nb_4N_5 the compositions at.%N are 55 [14] and 15.9 [23] respectively, while M_5N_6 (M = (TM) Nb, Ta) compounds structures belong to the same hexagonal $P6_3/mcm$ space group (No: 193, Pearson symbol *hP22*, prototype Nb_5N_6), with two formula units per unit cell, the composition at.%N for Ta_5N_6 and Nb_5N_6 are 54.5 [14] and 15.3 [23], M_4N_5 has 18 atoms in the unit cell, while M_5N_6 has 22 atoms as shown in Figs. 1 and 2. Results for the lattice parameter *a*, *c* and *c/a* are reported (Table 1) and compared with experimental and theoretical calculations. Our calculated GGA values for (*a*) are in rather good agreement with available experimental data [24] for M_4N_5 and M_5N_6 [24,25]. More precisely, our computed lattice constants (*a*) are bigger than the measured ones, within 5.5% and 0.6% [24] for Nb_4N_5 and Ta_4N_5 respectively, and within 2.7% [24] for Nb_5N_6 and 0.2% [25] for Ta_5N_6. Also, for both structures, the calculated lattice parameter ratio *c/a* (0.628 and 0.615 for M_4N_5 (M = (TM) Nb, Ta) respectively) is in

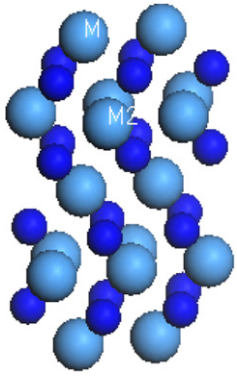

Fig. 2. M_5N_6 (M = Nb, Ta) structure: perspective view. The large and small balls represent M and N atoms.

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