



# First-principles equation of state and phase stability of niobium pentoxide



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## ARTICLE INFO

### Article history:

Received 23 May 2013

Received in revised form 10 July 2013

Accepted 17 July 2013

Available online 18 September 2013

### Keywords:

First-principles calculations

Crystal structure

Phase stability

Semiconductor compounds, Nb<sub>2</sub>O<sub>5</sub>

## ABSTRACT

Niobium pentoxide is a polymorphic wide-gap semiconductor with good dielectric properties that make it an important material in technological applications. In spite of its significance, there are not theoretical studies of its phase stability and polymorphism. We have investigated the energetics and phase stability of several phases of Nb<sub>2</sub>O<sub>5</sub> under pressure. The equation of state, the isothermal bulk moduli and the equilibrium crystal structures have been calculated from first-principles density functional theory for pressures up to 100 kbar. The equation of state reveals that the stable crystalline structure at zero pressure is the H phase, then, a crystallographic phase transition takes place at 0.24 kbar to the B phase. Additionally, it is shown that in the pressure range studied the B phase remains as the sole high-pressure stable phase.

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## 1. Introduction

Niobium pentoxide (Nb<sub>2</sub>O<sub>5</sub>) is a wide-gap *n*-type semiconductor with a diversity of possible technological applications including dye-sensitized solar cells, catalysis and electrochromic devices [1–3]. This is due to its unique physical properties such as high dielectric permittivity [4–7], wide band gap [4,8,9], and good chemical and thermal stability [10]. Especially, due to its high dielectric permittivity and low dielectric loss, Nb<sub>2</sub>O<sub>5</sub> is a good material to use in capacitors and transparent optical devices. Niobium pentoxide has been intensively studied as a gate dielectric for complementary metal oxide semiconductor (CMOS) devices, and it is a very interesting candidate for nonvolatile memories based on resistive switching (memristors) [11].

Experimentally, it is well known that Nb<sub>2</sub>O<sub>5</sub> is a polymorphic ceramic that exists in several crystalline phases depending on the pressure and temperature at which this compound is subjected. Also, the synthesized crystal structures are considerably affected by the preparation methods and crystal growth [10,12–18]. The most common observed phases are: B (*C2/c*, monoclinic) [19,20], H (*P2/m*, monoclinic) [21,22], M (*I4/mmm*, tetragonal) [23], N (*C2/m*, monoclinic) [24,18], P (*I4<sub>1</sub>22*, tetragonal) [25], R (*C2/m*, monoclinic) [14,26], T (*Pbam*, orthorhombic) [27], TT (monoclinic or pseudo-hexagonal) [28,29] and Z (*C2*, monoclinic) [12].

Historically, the previous crystalline structures are classified into low, medium, and high-temperature phases [10,13,16]. T and TT are called the low-temperature phases (~700 to 900 K), one finds the B, M, N, P and R phases at medium-temperature (~900 to 1200 K), and above 1273 K the high-temperature H phase is observed. On the other hand, studies of Nb<sub>2</sub>O<sub>5</sub> under pressure were done by different experimental techniques such as piston-cylinder, belt and anvil cells for low, medium and high-pressures, respectively. It was established that at atmospheric pressure the stable phase is H [15–17], and then at high-pressure (~3 kbar) this phase underwent a crystallographic transition to either B or T, depending on the temperature range at which the crystals are heated [15–17]. Further compression, up to ~100 kbar, showed the coexistence of B and a new phase called Z [12].

Structurally, all the niobium pentoxide crystals are built up by distorted octahedra, where the degree of distortion depends on whether the crystal structure is formed of octahedra connected by the corners and (or) the edges. It is important to note that the T and Z phases present a fraction of Nb atoms with sevenfold coordination (pentagonal bipyramids and mono-capped trigonal prisms, respectively) [12,27], and the TT phase shows some Nb atoms with eightfold coordination (hexagonal bipyramids) [13,30].

Envisaging the possible technological applications of Nb<sub>2</sub>O<sub>5</sub>, a deep knowledge of the phase stability and formation energies is absolutely necessary. In this work we have investigated, by means of first-principles density functional theory calculations, the effects of pressure on several crystalline phases of Nb<sub>2</sub>O<sub>5</sub>. The crystal

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structures, equation of state, isothermal bulk modulus, formation energies and enthalpy have been evaluated up to pressures of 100 kbar for the B, H, M, N, P, R, T, TT and Z phases. The paper is organized as follows: Section 2 describes the computational methodology, Section 3.1 presents a description of the crystal structures and structural models used in this work and a brief discussion of their dynamical stability, Section 3.2 discusses the equation of state, formation energies, phase stability and crystallographic phase transitions of Nb<sub>2</sub>O<sub>5</sub> and Section 4 presents the conclusions of this work.

## 2. Computational methodology

To study the physical properties of Nb<sub>2</sub>O<sub>5</sub>, we have calculated the total energy as a function of the unit cell volume ( $E = E(\Omega)$ ), by fully relaxing the ionic positions and the lattice shape for each calculated volume. We have fitted the calculated data to a polynomial Eulerian strain Birch–Murnaghan equation of state (EOS) of  $n$  order and extracted the equilibrium volume ( $\Omega_0$ ), the bulk modulus ( $K$ ) and its derivatives [31,32]. All total energy, ionic forces and stress tensor components have been calculated via density functional theory (DFT). We have used for the exchange–correlation functional the generalized gradient approximation with a new parameterization specially targeted for solids (PBEsol) [33]. The Kohn–Sham equations are solved by the projector augmented wave (PAW) method [34] as implemented in the VASP code [35,36]. The PAW atomic reference configurations are:  $4p^6 4d^4 5s^1$  for Nb and  $2s^2 2p^4$  for O, where only electrons treated as valence electrons are explicitly enumerated. The energy cut-off in the plane waves expansion is 520 eV. All structural parameters for each calculated volume have been optimized by simultaneously minimizing all atomic forces and stress tensor components via a conjugate gradient algorithm. Brillouin-zone integration (for the body center, base center and hexagonal lattices) has been performed on a Monkhorst–Pack  $2 \times 2 \times 2$ - $\mathbf{k}$ -mesh with a Gaussian broadening of 0.01 eV for relaxation (ionic forces are converged to 1 meV/Å) and a  $\Gamma$ -centered- $6 \times 6 \times 6$ - $\mathbf{k}$ -mesh using the tetrahedron method including Blöchl corrections for the calculation of the total energy (this is converged to 1 meV/formula unit). For the H phase (T phase) we have used a  $\Gamma$ -centered- $2 \times 8 \times 2$  ( $6 \times 3 \times 3$ )- $\mathbf{k}$ -mesh with the same total energy convergence accuracy. Finally, zone centered ( $\Gamma$ -point) vibrational frequencies are calculated using density functional perturbation theory [37,38], we have used four symmetry inequivalent displacements for each direction and ion.

## 3. Results and discussion

### 3.1. Crystal structure

Niobium pentoxide is generally obtained by chemical transport methods and the resulting crystal structure depends strongly on the starting materials, level of impurities, interactions with other components, growth times, etc. Among these crystalline forms one encounters the low-temperature T and TT phases (shown in Fig. 1); the latter was indexed as a pseudo-hexagonal or monoclinic crystal structure [28,29], but its unit cell was never fully determined. It was also claimed that TT is a less crystalline form of T, which is only stabilized by impurities such as OH<sup>-</sup>, Cl<sup>-</sup> or vacancies [13,30]. The most distinctive feature of this phase is the presence of some pentagonal and hexagonal bipyramids (NbO<sub>7</sub> and NbO<sub>8</sub>), in addition to the distorted octahedra (NbO<sub>6</sub>) [30]. Recently, the dielectric properties of the TT phase have been calculated [6] assuming that it is isostructural to a model proposed for  $\delta$ -Ta<sub>2</sub>O<sub>5</sub> [39]. This model was constructed following experimental X-ray diffraction data, with a hexagonal crystal structure associated to

the space group  $P6/mmm$  and containing two formula units per unit cell. In this model there are two types of Nb atoms, one located at the Wyckoff position 1a with sevenfold coordination and another one placed at the Wyckoff position 3f with eightfold coordination (see Fig. 1(c)). Complementary, the O atoms are located at the Wyckoff positions 1b, 3g and 6l. Although strictly speaking the TT phase cannot be considered as Nb<sub>2</sub>O<sub>5</sub>, for the sake of completeness, we have also used this hexagonal model for the calculation of the crystallographic properties of this phase. We have found that the hexagonal lattice has been retained during the relaxation of the ionic positions and the lattice shape for all the calculated volumes. This result contrasts a previous work where the lattice vectors have experienced a considerable depart from the hexagonal symmetry to a monoclinic one [6]. The energetics and plausibility of this model is discussed in the next section.

On the other hand, the unit cell of the T phase was completely determined and refined [27]; it belongs to the orthorhombic crystal family with space group  $Pbam$ . The crystal structure has 16.8 Nb atoms and 42 O atoms in its unit cell. There are 16 Nb atoms located at four Wyckoff positions 8i with half occupancy, distributed in such way that the Nb atoms lie on a sheet parallel to the (001) plane. Six or seven O atoms forming distorted octahedra or pentagonal bipyramids, respectively, coordinate them. In Fig. 1(a) one can see that edge or corner sharing within the (001) plane and solely by corner sharing along the [001] direction connects these polyhedra. The remaining 0.8 Nb atoms are randomly distributed in three Wyckoff positions 4g (denoted by black dots in Fig. 1(a)) with occupancies of 0.08, 0.08 and 0.04, respectively; those Nb atoms are coordinated by nine anions. The O atoms are located at eleven Wyckoff positions: one 2b, four 4g and six 4h. In order to cope with the fractional occupancies of the unit cell of the T phase, we have constructed a minimal supercell that attains integer occupation of the 4g positions, in this case a  $1 \times 1 \times 5$  supercell (294 atoms). We have built this supercell by occupying 80 out of 160 available 8i positions and identifying that for each independent 8i position there will be half of the Nb atoms extremely close to the other ones ( $d_{\text{Nb-Nb}} \sim 0.4 \text{ \AA}$ ), then we have chosen the positions following the experimental nearest neighbor distances and discarding the superfluous ones. The remaining four Nb atoms are randomly placed on the sixty available 4g positions and checking that their distances with the surrounding O atoms are inside the range of minimum and maximum distances reported experimentally. We have not taken into consideration the issue of configurational disorder of the Nb atoms located in the 4g positions due to the huge size of the configurational space to be explored (about  $5 \times 10^5$  configurations for this supercell).

The dielectric properties of the T phase have also been calculated [6] assuming a very simple orthorhombic model based on the  $\beta$ -Ta<sub>2</sub>O<sub>5</sub> crystal structure [40]. We have calculated this model as well, but we will refer to it as T'. The crystal model was constructed in such a way that Nb atoms have pentagonal bipyramidal and octahedral coordination as observed in  $\beta$ -Ta<sub>2</sub>O<sub>5</sub> (see Fig. 1(b)).

We have found that the relaxed lattices of T and T', for all the calculated volumes, present a tiny deviation of the angle  $\gamma$  from 90°, thus a tendency toward a monoclinic crystal structure is manifested for this phase. We have also calculated the  $\Gamma$ -point vibrational frequencies for the TT and T' models. Unfortunately, it is not possible to calculate the vibrational frequencies for the T phase due to the supercell size. We have found that these models are dynamical unstable, i.e., imaginary frequencies, showing that they are not appropriate for the calculation of the physical properties of Nb<sub>2</sub>O<sub>5</sub>.

Continuing with the medium-temperature phases: B, M, N, P and R, they crystalize into base center monoclinic (B, N, R) or body center tetragonal (M, P) structures. All the crystal structures of the medium-temperature phases were entirely determined and

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