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High-pressure phase transitions of TiN: an *ab initio* constant pressure study

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An *ab initio* constant pressure molecular dynamics technique is carried out to explore the behaviour of rock salt-structured titanium nitride (TiN) under pressure. Two successive phase transformations are successfully observed in the dynamical simulations. The first one is an isostructural phase transition accompanied by an anomalous volume compression without any symmetry breaking. The second one is a reconstructive phase transformation into a CsCl-type structure. For the first time, the previously proposed two-phase transformations for TiN are confirmed through the simulations.

Keywords: phase transitions; nitride; *ab initio*; ceramic

1. Introduction

Titanium nitride (TiN) is one of the new classes of high technology engineering materials and possesses various fascinating properties [1,2]. Exceptional hardness, high melting point, biocompatibility and good electrical and thermal conductivity are a few unique characteristics of this ceramic. Therefore, TiN is a promising engineering compound for a wide range of important technological applications, for example, wear protective coatings, biomaterial coatings and microelectronics, etc. [3–7].

The ground state of TiN is the six-fold coordinated rock salt (RS) structure. Its response to extreme temperature and pressure conditions is of particular importance [8–13] when its high-tech applications are deliberated. High-pressure X-ray diffraction experiment [8] on polycrystalline powder TiN suggested the existence of a phase transition with a first-order nature at 7.0 GPa. Interestingly, no modification was observed in the XRD patterns at this pressure, but the volume showed an anomalous behaviour between 7.0 and 11.0 GPa. The authors interpreted the irregular volume modification as a first-order isostructural phase transition and speculated that this phase change might be due to electron collapse as seen in EuO [14].

The high-pressure behaviour of TiN has been investigated by different theoretical approaches using the thermodynamic theorem [9–13,15,16] as well. All these theoretical calculations focused on the stability of the RS and CsCl-type crystals since the RS-structured materials typically transform into a CsCl-type crystal with the application of pressure though there are some exceptional cases. For example BaO, MgSe

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and PbTe convert to a hexagonal NiAs-type, a FeSi-type and an orthorhombic $Pnma$ structures, respectively [17–19]. The RS-to-CsCl phase modification for TiN was predicted to occur at more than 300 GPa in these theoretical studies except Ref. [15] in which the transition pressure was estimated to be about 126 GPa. Under the nonhydrostatic compressions, the critical pressure was drastically reduced to around 100 GPa [10].

To our knowledge, these two-phase transformations suggested for TiN have not been confirmed in other experiments or dynamical simulations yet. Also as mentioned above, the RS-structured materials do not always follow a typical transformation path and can adapt a crystal structure different from the CsCl-type phase at high pressure. Therefore, additional studies are unquestionably desirable to fully uncover the behaviour of TiN under pressure.

The key purpose of this study is to shed some light on the response of TiN to pressure using a well-tested constant pressure *ab initio* technique that can provide significant evidence about the dynamics and does not depend on any guess on high-pressure phases unlike the thermodynamic theorem. Two successive phase transformations are predicted for TiN through the simulations. The first one is correlated with a volume collapse with no modification of the symmetry. The second one is a reconstructive phase transition from the RS crystal to a CsCl-type structure.

2. Methods

First-principles pseudopotential method based upon density functional theory, as employed in the SIESTA *ab initio* program [20], was used to investigate the stability of TiN under pressure. The method uses a linear combination of numerical atomic orbitals as a basis set. A double- ζ plus polarized basis set was employed for the valence electrons. The exchange-correlation energy was computed using the Perdew et al. [21] generalized gradient approximation. The pseudopotentials were generated within the Troullier and Martins scheme [22]. A cut-off of 150 Ry is used for a real space grid. Our prior investigations [23,24] reveal that the SIESTA code is successful in exploring materials under different stress conditions. The simulation supercell consists of 216 atoms (108 Ti and 108 N atoms) with periodic boundary conditions. Γ -point was applied solely for the Brillouin zone sampling. The molecular dynamics (MD) simulations were done within the isenthalpic–isobaric ensemble that held constant number of atoms, constant pressure and constant enthalpy. External hydrostatic pressure was controlled by the Parrinello and Rahman method [25] and increased progressively. A period of 3,000 MD step was found to be long enough to reach the equilibrium volume at each applied pressure. A time step of one femtosecond (fs) was used for the MD simulations. Additionally during the MD simulations, we adopted the power quenching technique, in which the velocity components for atoms or supercell were set to zero when the velocities and forces had opposite signs. The total energy–volume calculations were performed using a conjugate gradient technique for the unit cell of the RS- and CsCl-type crystal. The Brillouin zone sampling was achieved by automatically built $8 \times 8 \times 8$ (RS phase) and $12 \times 12 \times 12$ (CsCl phase) k -point mesh using the Monkhorst and Pack scheme [26].

3. Results

We plot the variation of volume under pressure in Figure 1. At the low-pressure regime, the volume decreases slowly and then it shows a fast modification between 35 and 57.5 GPa. Above 57.5 GPa, the volume presents a gradual decrease again up to 1,100 GPa at which point it exhibits a clear discontinuous change. The first volume reduction is about 2%. The second one is quite sharp and about 10%. According to the thermodynamic classification, both volume modifications can be categorized as a first-order phase transformation.

With the aim of the KPLOT program [27], we determine the symmetry of the structure at each applied pressure. Surprisingly no new symmetry adaption is detected up to 1,100 GPa in spite of the apparent change in the volume between 35 and 57.5 GPa. On the other hand, a CsCl-type crystal is identified at 1,100 GPa as shown in Figure 2.

The observation of the first volume reduction without any symmetry breaking in the simulation is rather surprising but offers for the first time supportive evidence for an isostructural phase transformation in TiN as reported in the experiment [8]. Yet to ensure that the first volume decline is not associated with the simulation conditions such as the number of k -points or the pressure controlling technique, we performed additional simulations to study the variation of volume under pressure. We used a unit cell

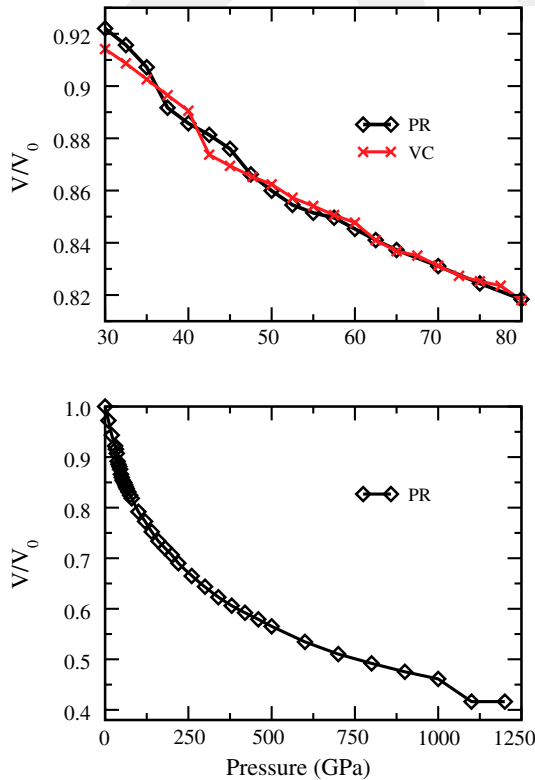


Figure 1. (colour online) Variation of volume with the application of pressure. PR: Parrinello and Rahman technique and VC: variable-cell shape conjugate gradient technique.

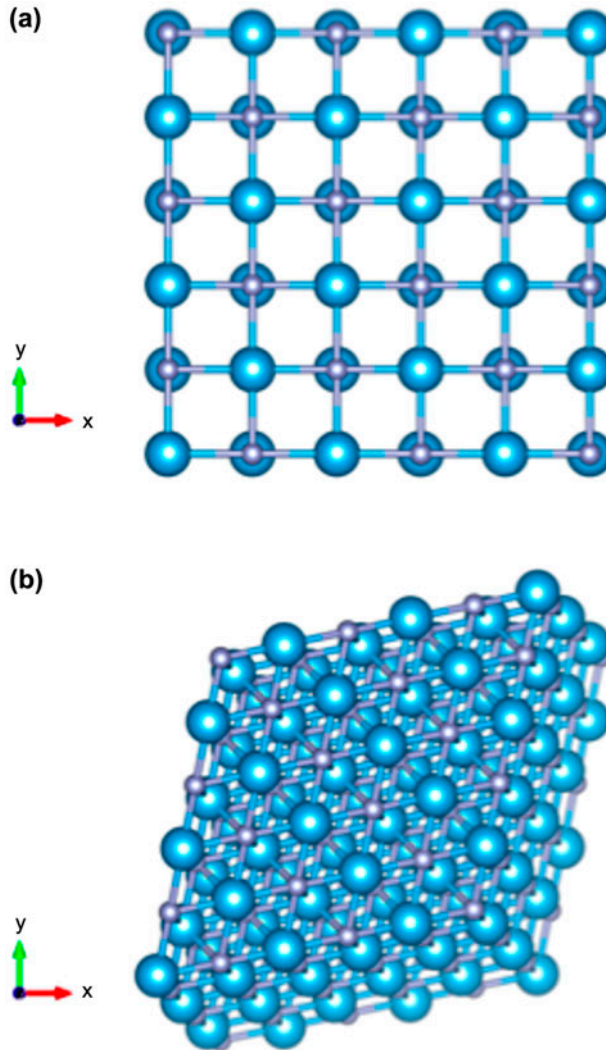


Figure 2. (colour online) (a) RS structure at zero pressure and (b) CsCl structure obtained 1,100 GPa.

with 256-special k -points and the variable-cell shape conjugate gradient method. At each applied pressure, we relaxed both the lattice vectors and atomic positions until the maximum force was less than 0.01 eV/\AA . The stress tolerance was set to 0.5 GPa . The volume obtained using this technique given in Figure 1 also exhibits a sharp volume modification similar to what has been found in the Parrinello and Rahman method. Yet the unusual volume change occurs at slightly different pressure ranges in these two different techniques, which is probably related to the lack of thermal effect in the variable-cell shape conjugate gradient method. Nonetheless, these findings suggest that the volume collapse is the nature of TiN and is independent of with the number of k -points or the pressure controlling technique.

On the basis of symmetry evaluations and the variation of the volume using two different pressure controlling techniques, we propose two-phase transformations for TiN: isostructural phase transformation in which the symmetry does not change and a reconstructive phase transformation in which the NaCl state convert into a CsCl-type crystal. Our predictions are particularly important because they support for the first time the existence of the previously proposed experimental and theoretical phase transformations for TiN.

The interpretation of a small volume change (about 2–3%) as a first-order isostructural phase transition in the simulation might be questionable. The fraction of volume modification for the isostructural phase change in TiN was not provided in the experiment [8], but it was reported to be quite small in different materials that undergo an isostructural phase transformation with the application of pressure. For example, it is about 4% for EuO [14], 1% for Zr [28] and 0.7% for Ti_2O_3 [29], which are comparable with our result. Therefore the first volume reduction might be interpreted as a first-order isostructural phase transformation in TiN.

Additionally, it should be emphasized here that the comparison of critical pressures obtained in the dynamical Parrinello and Rahman simulations with experiments or thermodynamic theorem is definitely impracticable because transition pressures in the dynamical simulations are generally overstated. This is a well-known restriction of this technique [30] and can be attributed to simulation environments, for example, the absence of surface effects because of the use of periodic boundary conditions, perfect structure (no defects) in contrast to samples used experiments, very fast pressurizing conditions relative to experiments, etc.

On the other hand, the thermodynamic theorem commonly offers an accurate transition pressure, and hence, the RS-to-CsCl phase modification is further evaluated using the thermodynamic principle of equal Gibbs free energies ($G = H - ST$). At zero temperature, the free energy is equal to enthalpy given by $H = E + PV$, where E , V and P are the energy, volume and external pressure, respectively. In order to determine the enthalpy of both phases, we first estimate their energy at different volumes by scaling equivalently the lattice parameters and atomic positions (constant volume simulation) and demonstrate our data in Figure 3. From the figure, one can notice the abnormal

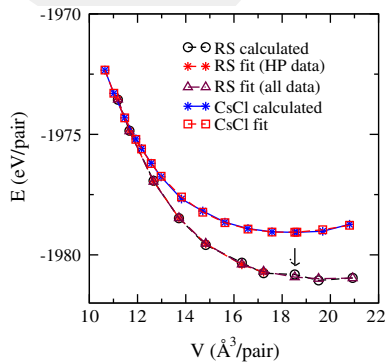


Figure 3. (colour online) Energy–volume relation.

dispersion of the data at the low-pressure region for the RS structure, which also supports the exceptional behaviour of TiN at low-pressure range. In the second step, we fit the data to the third-order Birch–Murnaghan equation of state. Since the energy–volume data scatter slightly around the equilibrium volume for the RS crystal and it undergoes an isostructural phase transition around 7 GPa in experiment, we fit only high-pressure data to the equation of state. In the third step, we obtain pressure ($P = -dE/dV$) from the energy–volume curve and finally compute the enthalpy as a function of pressure. We should underline here that fitting all data to the equation of state does not considerably change the computed pressure or enthalpy values. The enthalpy curve of the RS and CsCl phases illustrated in Figure 4 crosses approximately 385 GPa, denoting a phase transition between them. The critical pressure computed from the thermodynamic theorem agrees reasonably with 310–350 GPa predicted in other theoretical studies.

One can see that the transition pressure predicted in the constant pressure simulation is overestimated by a factor of about 2.6–2.8, relative to one obtained from the thermodynamic conditions, and thus, the critical pressure for the isostructural phase transformation for TiN is estimated to be about 13–20 GPa, which is slightly larger than the experimental result of 7 GPa. This controversy might be due the nonhydrostatic effects or the sample properties. It should be noted here that polycrystalline powder was used in the experiments, and thus, the stress distribution is not uniform for polycrystalline samples because of the existence of grains. Additionally, TiN has a roughly 1:1 stoichiometry [31]. In other words, TiN is normally not perfectly stoichiometric, but contains N vacancies. Such vacancies will accelerate the phase transition in experiments and result to a low transition pressure relative to the present theoretical calculation in which a perfect crystalline phase having exactly 1:1 stoichiometry is considered.

From the energy–volume relations, we also find the equilibrium parameters of both phases and provide them in Table 1. In general, our data are accord with the previous theoretical estimations [10–16] except that the bulk modulus of the RS phase is predicted to be quite less relative to them.

Finally, the electronic structure of TiN is investigated, in particular, just before and after the isostructural phase transition. We used the variable-cell shape conjugate gradient technique data because of enormous number of k -points used in the simulation. The

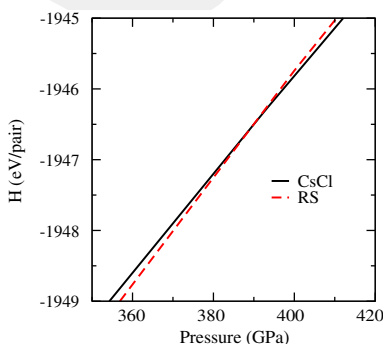


Figure 4. (colour online) Enthalpy curve of the RS- and CsCl-type phases.

Table 1. The calculated equilibrium parameters (lattice constant a and the bulk modulus B) of the RS-type and CsCl-type phases.

	a (Å)	B (GPa)	
RS	4.27	208	Present study
	4.25	277	Ref. [10]
	4.24	277	Ref. [11]
	4.1	320	Ref. [12]
CsCl		271	Ref. [16]
	2.6	300	Present study
	2.64	262	Ref. [10]
	2.63	253	Ref. [11]
	2.5	298	Ref. [12]
		247	Ref. [16]

calculated partial density of states (PDOS) at 0, 40 and 42.5 GPa are illustrated in Figure 5. As seen from the figure, there are no apparent drastic changes in the electronic states accompanied by the phase transformation. The Mulliken charge population analysis is also performed to determine whether the phase transition is related to any

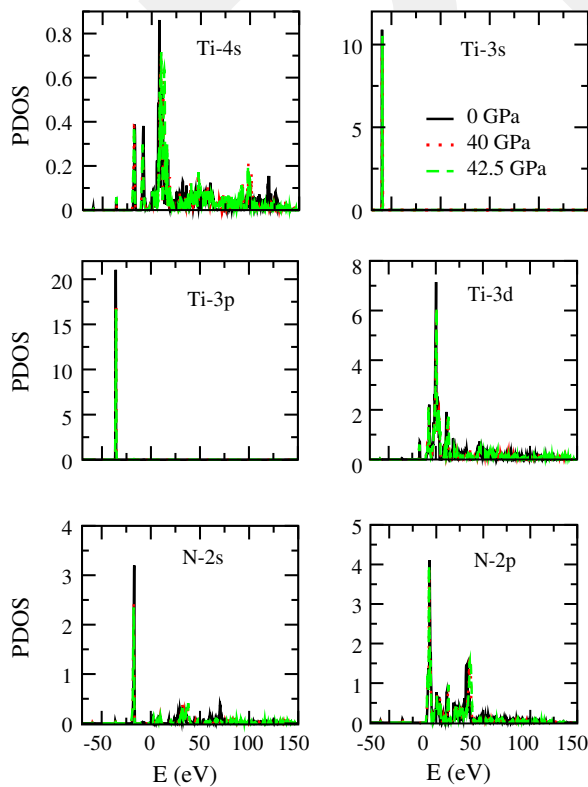


Figure 5. (colour online) PDOS at 0, 40 and 42.5 GPa.

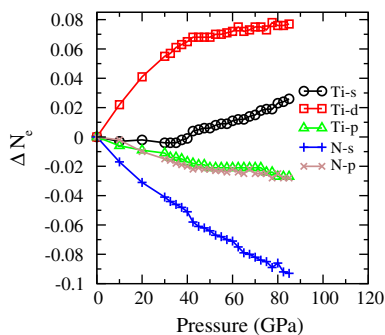


Figure 6. (colour online) Variation of number of electrons on s, p and d orbitals under pressure, relative to zero pressure values.

electron transfer. The variation of the number of electrons on s, p and d orbitals with the application of pressure is given in Figure 6. d electrons of Ti increase whereas its p electrons decreases slightly under pressure. Both N-s and N-p electrons have a tendency to decrease with increasing pressure. The number of Ti-s electrons, on the other hand, decreases ($\Delta N_{\text{Ti-s}} < 0$) until the first volume reduction occurs at 42.5 GPa, and at which point, Ti-s electrons start to increase ($\Delta N_{\text{Ti-s}} > 0$). The general trend of Ti-s, p and d electrons of TiN under pressure is surprisingly similar to what has been reported for pure Ti [32] but the quantity of transferred charge in TiN is roughly a factor of ten smaller than that in Ti. The charge transfer in TiN with increasing pressure is indeed too small, and hence, it is rather hard to conclude that it is responsible for the isostructural phase change in TiN.

4. Conclusions

We have applied an *ab initio* constant pressure MD technique to investigate the high-pressure behaviour of TiN and characterized two-phase transformations. The first one is an isostructural phase change and associated with a small volume collapse as seen in the experiment. The second one is a reconstructive phase transformation into a CsCl-type phase as proposed in the theoretical studies. Regrettably, we are not able to describe the nature of the isostructural phase change, and thus, additional experimental studies are certainly desirable to understand this phase transformation in details.

Disclosure statement

No potential conflict of interest was reported by the author.

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