# PHASE STABILITY OF TiN AND $Ti_2N$ UNDER PRESSURE: A FIRST-PRINCIPLES INVESTIGATION

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Titanium nitrides TiN and $Ti_2N$ are widely used as the main layers in ultrahard nanocomposite coatings. Despite the broad experience stored on the properties of these materials, the investigation of pressure-induced structural changes in them is an infant stage.

In this work we present the results of investigations of various phases of TiN and $Ti_2N$ under pressure within a first-principles puseudopotential method. We used the "Quantum EXPRESSO" code. For the exchange-correlation potential, the generalized gradient approximation (GGA) was employed.

For the stoichiometric TiN, the B1→B2 structural transformation at P=342 GPa was revealed. Below we will accent on the substoichiometric ordered phase of $TiN_x$, x=0.5 ($Ti_2N$). In Fig. 1 we show the total energy ($E_T$) for various phases of $Ti_2N$ as functions of cell volume. The phonon spectrum (FS) of the δ'-phase ($I4_1/amd$) is presented in Fig. 2. It follows from Fig. 1 that the δ'-phase $TiN_x$ is stable for x>0.5 (larger cell volumes) and at high temperature, since the FS has the soft modes. At low temperature, the ε-phase (P4/mnm) is most stable in accordance with an experiment.

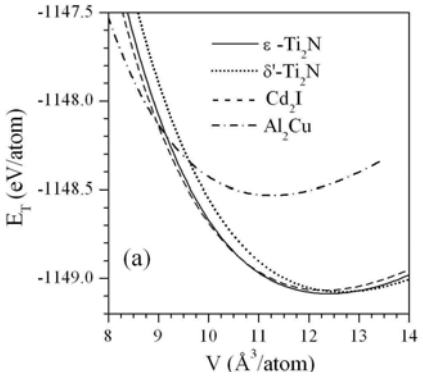


Fig. 1. Total energy ($E_T$) vs cell volume (V) for various phases of $Ti_2N$.

Given the results of the total-energy and phonon spectrum calculations of different phases of $Ti_2N$ under pressure we arrived ad the following conclusion. At low temperature, the sequence ε-$Ti_2N$ (P4/mnm) P=77.7 GPa → $Au_2Te$ (C2/m) P=86.8 → $Al_2Cu$ (I4/mcm) is supposed to take place. At high temperature, the sequence ε-$Ti_2N$ (P4/mnm) P=39.8 GPa → $Cd_2I$ (P-3m1) P=92.4 → $Al_2Cu$ (I4/mcm) is supposed to take place. The $Cd_2I$-type $Ti_2N$ can be stable only at high temperature owing to the availability of the condensed acoustic phonon modes (not shown here).

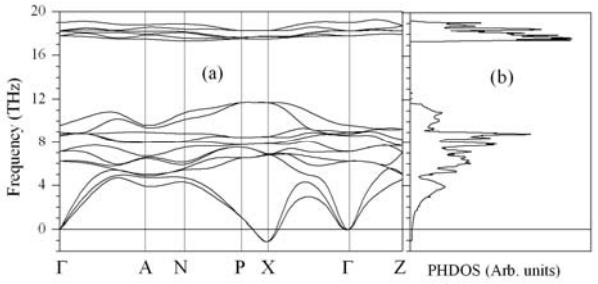


Fig. 2. Phonon spectrum (a) and phonon density of states (PHDOS) (b) for δ'-$Ti_2N$.

In Fig. 3 we show the densities of states (DOS) of some computed phases of $Ti_2N$. For all the stable phases, the Fermi level falls on the DOS minimum, except for the $Cd_2I$-$Ti_2N$ phase, where $E_F$ is located at the peak of the DOS. The condensation of the phonon modes at low temperature leads to the second-order $Cd_2I$ → $Au_2Te$ phase transformation and to splitting the DOS peak (cf. Fig. 3).

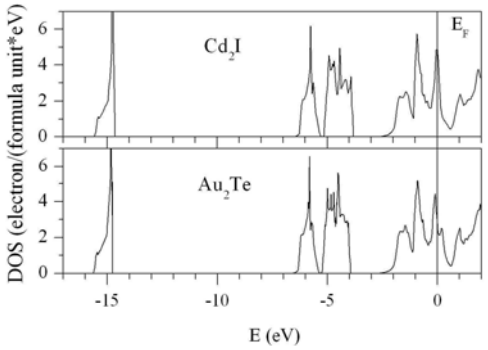


Fig. 3. Densities of states (DOS) of the $Cd_2I$- and $Au_2Te$-type $Ti_2N$.

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