A DIFFUSIONLESS TRANSFORMATION PATH RELATING Th$_3$P$_4$ AND SPINEL STRUCTURE
OPPORTUNITIES TO SYNTHESIZE CERAMIC MATERIALS AT HIGH PRESSURES

by

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ABSTRACT

A DIFFUSIONLESS TRANSFORMATION PATH RELATING Th₃P₄ AND SPINEL STRUCTURE: OPPORTUNITIES TO SYNTHESIZE METASTABLE CERAMIC MATERIALS AT HIGH PRESSURES

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This thesis investigates a transformation path between the Th₃P₄-type and the spinel-type structures of hafnium (IV) and titanium (IV) nitride, M₃N₄ (M = Hf, Ti) with computational methods. For both compounds, the Th₃P₄-type was synthesized experimentally at high-pressure conditions and was quenched to ambient conditions. Computations reveal that while at high pressure Th₃P₄-type structures are favored by enthalpy, at low pressure the Th₃P₄-type is only meta-stable. The spinel-type is energetically more favorable at zero pressure than the Th₃P₄-type in both systems. However, even the spinel-type is surpassed by another ground state modification for both Hf₃N₄ and Ti₃N₄.

The research presented in this thesis then addresses (i) thermal stability of the Th₃P₄ polymorphs and (ii) the conditions necessary to synthesize spinel-type structures of both compounds. The foundation for the study is a simple structural relation between Th₃P₄-type and the spinel-type structures: while the Th₃P₄-type is based on a body-centered cubic arrangement of anions with cations in interstitial sites, the spinel-type is best described by a face-centered...
cubic arrangement of anions with cations in interstitial sites. With anions following the Bain path of the bcc-fcc transformation, and cations undergoing a minor shuffle distortion, the Th$_3$P$_4$ to spinel transformation parallels the martensitic transformation known in many metal systems – only with additional cations in the structure.

Following the Bain correspondence, transformation paths between Th$_3$P$_4$-type and the spinel-type structures of Hf$_3$N$_4$ and Ti$_3$N$_4$ are constructed at different pressures. Along the proposed reaction coordinates total energies in both systems are computed. The obtained energy profiles yield activation barriers and, using an Arrhenius approach, corresponding temperatures. Assuming that the diffusionless Th$_3$P$_4$ to spinel path will yield the lowest activation barrier for a transformation process of the Th$_3$P$_4$-type, we can hypothesize on a rate of decomposition of the Th$_3$P$_4$-type at zero pressure and on a rate of transformation from Th$_3$P$_4$-type to spinel-type at high pressure.

From the results it is estimated that a thermal stability of the Th$_3$P$_4$-type of hafnium (IV) nitride is limited to 1200 K at zero pressure. The Th$_3$P$_4$-type of titanium (IV) nitride exhibits lower thermal stability, the estimation is 950 K. With increasing pressure, both system show increasing barrier height for the transformation process. Accordingly, at the pressure at which Th$_3$P$_4$-type and spinel-type are in equilibrium – as judged by equal enthalpy – temperatures needed to convert Th$_3$P$_4$-type into spinel-type are higher. The calculations lead to the proposal that a hitherto unknown spinel modification of Hf$_3$N$_4$ can be realized by first synthesizing the Th$_3$P$_4$-type at high pressure, then quenching the system to 3.9 GPa, and at this pressure activating the Th$_3$P$_4$ to spinel conversion by heating to 1300 K. A similar proposal is made for Ti$_3$N$_4$. Here a spinel-modification can be synthesized from the Th$_3$P$_4$-type at 3.9 GPa at a temperature of 1000 K.
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CHAPTER 1

INTRODUCTION

1.1 High Pressure Chemistry of Novel Compounds

Under high-pressure conditions, chemical reactivity of atoms and molecules increases manifold, significant shift in chemical equilibria observed and reaction rates get affected. On compression of any substance, distances between constituting atoms decrease and its electronic structure deforms. This leads to increase of the internal energy of the substance, and formation of denser structures could become energetically favorable on further compression [KOS01], [YAO08]. Shorter interatomic distances and/or higher coordination numbers of the constituent atoms characterize such structures when compared with the lower pressure phases. At high-pressure conditions, formation of compounds with elements in unusual oxidation states can take place. In many cases, these high-pressure phases can be quenched to ambient conditions where they may persist metastably due to slow kinetics of a reverse transformation [BOL09]. Such metastable products can have a number of unique physical and chemical properties, from high hardness and corrosion stability to interesting optoelectronic, magnetic or superconducting properties. Therefore, they can be of potential interest for various industrial applications.

1.2 Nitrides

Nitrides have found extensive use in industry because of their unique physical, chemical, electrical, optical or mechanical properties. The high pressure cubic phase of boron nitride, c-BN is the second hardest material after diamond. AlN, GaN and InN all have interesting semiconductor properties, and each one of them possesses a NaCl-type high pressure phase. Nitrides are used for different applications as refractory ceramics (hexagonal BN, α- and β-Si₃N₄, AlN, TiN), hard grinding materials (cubic BN, α- and β-Si₃N₄), in light
emitting diodes (GaN, InN), as catalysts (Mo₂N, W₂N), sintering additives, and as electrolyte in lithium batteries (Li₃N) [DZI09]. Recent progress in the study of nitrides is mainly due to development of new synthetic routes, which allows large production of compounds and also leads to the discovery of novel compounds [MON07].

Discovery of a new family of high-pressure group 14 cubic spinel nitrides, γ-A₃N₄ (A=Si, Ge or Sn) [ZER99] is partially responsible for the upsurge in the interest in the high-pressure nitrides during the last decade. γ-Si₃N₄, in particular, has unique combination of hardness and stability (both thermal as well as oxidation) and also a wide band gap semiconductor, which can be used in fabrication of blue LEDs.

Another particular family of ceramics are nitrides of the group 4 elements. High-pressure and high-temperature experiments with transition metals of group 4 resulted in the discovery of exotic family of high-pressure nitrides, c-Zr₃N₄ and c-Hf₃N₄, with cubic Th3P4-type structure [ZER03].

Since this thesis deals and investigates structural relations among high pressure phases of group 4 elements, we briefly discuss synthesis methods, structure, and experimental and theoretical studies of recently discovered high-pressure zirconium (IV)- and hafnium (IV) nitrides in the following section.

1.2.1 Group 4 transition metal nitrides
At ambient pressure conditions, mononitrides of group 4 transition metals having a cubic rocksalt structure type exist. These mononitrides can also be specified as δ-MN (M= Ti, Zr or Hf). They are used as refractory materials, and as coatings over tools as wear resistant layers. Although they are brittle and hard in comparison to other transition metals, they still exhibit metallic character. All the three mononitrides show superconducting properties with relatively high critical temperatures of 5.8, 10.5 and 6.9 K for TiN, ZrN and HfN, respectively [LEN00]. One more interesting property of these nitrides is their defect structure. They can form several non-stoichiometric structures by creating vacancies on the corresponding lattice sites while still
maintaining NaCl-type structure. As for example, in δ-HfN$_x$, x can have values from 0.74 to 1.7 and in δ-ZrN$_x$, x can vary from 0.54 to 1.35 [KRA98]. Presence of vacancies affect their properties significantly. When $x > 1$, δ-HfN$_x$ and δ-ZrN$_x$ can transform to insulating phases from metallic phases with an increase in nitrogen content. δ-TiN$_x$ maintains its metallic character for all the known compositions [AND97].

Out of all the stoichiometric M$_3$N$_4$ compounds of group 4 transition metals, only orthorhombic zirconium (IV) nitride, o-Zr$_3$N$_4$ was known for long [LER96]. The o-Zr$_3$N$_4$ was found to be insulating and diamagnetic. It decomposes above 1100 K on heating in presence of nitrogen yielding δ-ZrN and N$_2$. It oxidizes in air at 800 K [LER97]. The high-pressure investigation of group 4 transition metal nitrides of the type A$_3$N$_4$ was an extension of study of spinel nitrides. Discovery of novel γ-A$_3$N$_4$ (A=Si, Ge or Sn) has set the trend of investigation of possible existence of stable spinel nitrides of similar tetravalent elements like group 4 transition metals. On performing experiment at high temperature and pressure, treating Ti, Zr and Hf (or their mononitrides) with molecular nitrogen in a LH-DAC, Zr$_3$N$_4$ and Hf$_3$N$_4$ with cubic Th$_3$P$_4$ structure type results (for Zr-N system at 15.8-18 GPa and 2500-3000 K and for Hf-N system at 18 GPa and 2800 K) [ZER03]. However, for Ti-N systems no other phase besides δ-TiN was observed in the pressure range 17.5-25 GPa and temperature ranging from 1500 to 3000 K.

Examining the structure and surface morphology using XRD and EDX proved that the resulting structures are Zr$_3$N$_4$ and Hf$_3$N$_4$ with cubic Th$_3$P$_4$ structure type [ZER03]. The cubic Th$_3$P$_4$ structure type has cations eight-fold coordinated by nitrogen atoms, while nitrogens are six-fold coordinated by metal atoms (discussed in chapter 3). As the cation coordination number is higher (eight-fold) than NaCl-type mononitrides and o- Zr$_3$N$_4$ (six-fold) as well as in the hypothetical spinel nitrides (four- and six-fold), the density of c- Zr$_3$N$_4$ is 13% higher than o-Zr$_3$N$_4$. c-Zr$_3$N$_4$ and o- Hf$_3$N$_4$ are binary nitrides, first of its kind, with such high coordination number [ZER03]. Theoretical studies on their electronic properties followed after, which also supported structural assignment and low compressibility of c-M$_3$N$_4$ [KRO03b] as suggested by
experiments. Theoretical work on nitrogen rich part of Ti-N, Zr-N and Hf-N P-T phase diagrams provides equilibria conditions between $\delta$-MN + N$_2$ and c-M$_3$N$_4$ phases [KRO04]. Interest on these materials increased rapidly with the recent finding that thin films made of c-Zr$_3$N$_4$ are significantly harder than those of $\delta$-ZrN. Also, it functions as a better wear resistance tool in low-carbon steel manufacturing machine compared to $\delta$-TiN [CHH05], which is a well-known wear resistant material. To sum up, the recently discovered cubic Zr$_3$N$_4$ and Hf$_3$N$_4$ are of utmost interest for use in industry for their microelectronics and wear-resistant applications.

1.3 Goal of this work

This work exploits a structural relation between the Th$_3$P$_4$-type, the structure type of novel high-pressure Hf$_3$N$_4$ and Zr$_3$N$_4$ and the spinel type. We will construct a transition path from Th$_3$P$_4$ to spinel phase. While the spinel type has not been observed among the group 4 transition metal nitrides, it is the target of this work to investigate under which conditions it may form from the existing Th$_3$P$_4$–type. We, thus, will follow in two directions, which mark the goals of this work.

![Figure 1: Goal of this work](image)
First, we will compute the energy along the path from Th$_3$P$_4$ to spinel at ambient pressure. The resulting energy profile with its activation barrier will yield information about the thermal stability of the Th$_3$P$_4$ type at ambient pressure. Second, we will repeat these calculations along the path at the transition pressure of the Th$_3$P$_4$-spinel transition. Since the enthalpy of both structures at this pressure is equivalent, a transformation will not yield excess energy. Therefore, the activation barrier will yield information about the temperature needed to activate the Th$_3$P$_4$-spinel transition.
CHAPTER 2
METHODOLOGY

2.1 Density Functional Theory (DFT)

Electrons and atomic nuclei constitute any solid material. The laws of quantum mechanics govern their properties. In principle, physical properties in a solid can be calculated by solving the many-body Schrödinger equation. Density functional theory (DFT) is the quantum mechanical approach used to solve the many-body Schrödinger equation. Electron density is the fundamental quantity in DFT. Electronic density replaces the complicated many-electron wave function, $\Psi$ for efficient calculation of the Schrödinger equation, made possible by DFT.

Density functional theory (DFT) was introduced in 1960’s by Hohenberg and Kohn [HOH64] and Kohn and Sham [KOH65]. The major breakthrough that came out from these two approaches are: a) ground-state energy can be written as a unique functional of the electron density [Hohenberg-Kohn] and b) introduction of an energy functional for the total energy of the electronic system to derive Schrödinger-like single-particle equations [Kohn-Sham]. DFT is very effective in computing electronic structure of materials. DFT is used to make predictions of several material properties such as structure, vibrational frequencies, elasticity coefficients, electronic and magnetic properties, paths in catalytic reactions, etc [CUE03]. Out of the many programs available for solid state calculations we have chosen the VASP (Vienna Ab-initio Simulation Package)-code, since it allows efficient and fast calculations.

2.1.1. VASP (Vienna Ab-initio Simulation Package)

VASP is used to perform first-principles electronic calculations. VASP implements the DFT combining a plane-wave basis set with the total energy pseudopotential approach. The pseudopotentials used are based on the Projector-Augmented-Wave (PAW) method
The PAW potential, in principle, is an all-electron potential and therefore allows the calculation all-electron properties. The Generalized-Gradient Approximation (GGA) is used to treat the exchange-correlation energy of the electrons. Preferring the GGA over the Local Density Approximation (LDA) is based on the fact that gradient corrections yield more accurate results for the energy when comparing atoms in different environment. GGA reproduces experimental transition pressures while LDA artificially favors higher coordinated structures. All our results are obtained from well-converged structures with respect to cutoff energy (500 eV for nitrides and oxides) and k-point sampling.

2.2 Computational approach

While searching for new high-pressure modifications, the approach involves computations for structures from crystal database library. In a first step, a selected structure type is optimized in atomic positions and lattice parameters. Comparing the energies of various candidate structures the lowest energy modification for a compound is determined and, its energy and volume can be compared with all the other structure types [HOR06]. In a second step, the energy E is calculated for a series of volumes around the minimum energy structure for each candidate. The resulting energy-volume (E-V) data is used to calculate the enthalpy-pressure state function. The pressure p can be extracted from the E-V data by numerical differentiation. Using $p = - \frac{\delta E}{\delta V}$ the enthalpy $H = E + pV$ is obtained. Though it is the Gibbs energy, which determines thermodynamic stability, we neglect entropy contribution $-T\Delta S$ to the enthalpy. This approach is justified for compact compounds without sources of significant disorder, since entropy contributions $-T\Delta S$ are typically small in comparison to changes in relative enthalpy $\Delta H$ within a few GPa of pressure. Thus, comparing the enthalpy-pressure state functions for different structure types provides the structure with lowest enthalpy at a given p. The best way to extract the transformation pressure is to plot the enthalpy difference with reference to a reference state, usually the ground state.
CHAPTER 3

INTRODUCTION TO THE TRANSFORMATION PATH

3.1 The Bain Correspondence

bcc and fcc structures are related to each other by a tetragonal strain, either compression or extension. The mechanism governing the relation between these two structures is known as the Bain Correspondence. The bcc structure has a c/a ratio equal to 1. There is compression along the z-axis and a uniform expansion along the x and y axes resulting in change in c/a ratio to $\sqrt{2}$ in the resulting fcc structure [KRO03], [KIB07].

Figure 2: (Left) two unit fcc cells with a smaller body centered tetragonal cell marked in the center. By a homogeneous compression in the direction of arrows and an expansion in the plane normal to it, the bcc structure (right) is obtained.

No shuffle is required in this transformation, meaning, the atoms remain in their crystallographic positions. The Bain correspondence, which related the fcc to bcc arrangement in metal structures, is now used to connect the anion arrangement in the spinel structure, which is approximately fcc, to the arrangements of anions in the Th$_3$P$_4$ structure, which is approximately bcc. It will turn out that some cations will undergo additional shuffle. This shuffle, however, is surprisingly small and corresponds only to a change in the coordination environment, but not to a significant diffusion. The transformation from spinel to Th$_3$P$_4$, or vice versa, will proceed through an energy barrier with height $\Delta E_a$. Similar to conventional chemical kinetics, the rate of
transformation can now be described by an Arrhenius-type law. While the barrier must be overcome, the activation energy $\Delta E_a$ will correspond to a specific temperature. According to $T_a = \Delta E_a/K$ (or $T_a = \Delta E_a/R$, if one mole of particles is referenced). $T_a$ is about the temperature at which the rate becomes significant. Depending on the direction of the process and the overall reaction enthalpy, $T_a$ can be interpreted differently. If the reaction proceeds from a state with higher enthalpy to a state with lower enthalpy, $T_a$ provides a measure for the (maximum) thermal stability of the initial state. If the initial and final state are equal in enthalpy, $T_a$ may indicate the temperature above which equilibrium can be reached within a reasonable time.

3.2 Description of the structures: The spinel structure (fcc) and its bcc counterpart Th3P4 type

The spinel structure ($A_2BX_4$) adopts space group symmetry Fd-3m. In spinel the cations exist in two different environments: cations (A) in $\frac{1}{2}$ of the octahedral sites and cations (B) in $\frac{1}{8}$ of the tetrahedral sites. Anions are located in position 32e ($x,x,x$) with the free positional parameter $x = 3/8 + x_{sp}$. If $x_{sp} = 0$, the anions are at the points of a face centered cubic lattice (fcc). For all spinel structures the parameter $x_{sp}$ is very close to zero. Note that the spinel structure has two parameters only: the lattice parameter and the positional parameter of the anions.

Figure 3: Spinel structure

The Th$_3$P$_4$ structure ($A_3X_4$) adopts space group symmetry I-43d [OKE96]. Cations (A) fill sites in 12a and anions (X) fill sites in 16c ($x_0, x_0, x_0$). Similar to the spinel structure, the Th$_3$P$_4$ structure
has only two parameters: the lattice parameter and the positional parameter of the anions. With \( x_b = 0 \), the anion structure becomes ideal bcc. In the \( \text{Th}_3\text{P}_4 \)-type, \( x_b \) is close to -1/12. In this case, the coordination polyhedron around each cation is a bisdisphenoid. This 8-fold coordination is composed of two interpenetrating tetrahedral, one stretched and the other one flattened. Anions are coordinated 6-fold in \( \text{Th}_3\text{P}_4 \) and the environment is described by a metaprism, which is between a trigonal prism and a trigonal anti-prism which ideally equals an octahedron.

![Figure 4: Th₃P₄ structure. (left) cation position, \( \{A\}X_8 \)-bisdisphenoids and (right) anion position, \( \{X\}A_6 \)-metaprisms](image)

### 3.3 Crystallographic description of the transformation path

As pointed out before, spinel and \( \text{Th}_3\text{P}_4 \) structures adopt Fd-3m and I-43d space group symmetries respectively. To describe a path between the two structures, we choose the subgroup/super-group approach. A common subgroup for both structures is I-42d. Description of these two structures using subgroup I-42d is given below:
Table 1: Crystallographic description of the transformation path

| Atom | Wy | x   | y   | z         | x   | y   | z         |
|------|----|-----|-----|-----------|-----|-----|-----------|
| A    | 4a | 0   | 0   | 0         | 0   | 0   | 0         |
| B    | 8d | ½   | ¼   | 1/8       | 5/8 | ¼   | 1/8       |
| X    | 16e| 0   | ¼-2x_{sp} | 3/8+x_{sp} | x_{b} | ¼+2x_{b} | 3/8+x_{b} |

Here, a_{sp} and a_{b} are lattice parameters of spinel and Th_{3}P_{4} respectively, and x_{sp} and x_{b} are the anion positional parameter of the conventional settings of spinel and Th_{3}P_{4} structures, respectively. Wy stands for Wyckoff position.

Inspecting the table above, one observes that the cations in A position remain in their sites. Cation in B position change only in their x-coordinate. Anions change x, y, and z. However, given the fact that the anion structure parameter of spinel and Th_{3}P_{4}, x_{sp} and x_{b}, are of small values, their move is very limited. Thus, as in the standard Bain transformation, the dominant change in structure is made by varying the lattice parameter a and changing the ratio c/a. Overall, we have 6 parameters to describe the transition. However, exploring the complete 6-dimensional potential energy (or enthalpy) surface is impossible.

As an approximation of the transformation path, a one-dimensional reaction coordinate has been constructed applying linear interpolation of all structural parameters. Static calculation performed on the intermediate structures yield an activation barrier, ΔE_{a}. Next, we did calculations at the transition pressure, which yields the temperature of synthesis for this phase transformation.
CHAPTER 4

RESULTS

4.1 Variation of energy and enthalpy under pressure

All hard materials, including diamond and c-BN, derived at high pressure are metastable at ambient pressure. These materials can withstand high temperatures during compaction treatments necessary to form a tool from the powdery source material as well as during actual performance as a tool. Therefore, the importance of high “metastability” or thermal stability cannot be ignored. The term thermal stability refers to the temperature at which decomposition or back transformation to the low-pressure polymorphs occurs [SCH03]. In order to access thermal stability (our first goal, as stated before), we need to follow a definite regime as stated previously in section 2.2.

First, taking the internal energy E as a function of the volume V for both Hf$_3$N$_4$ and Ti$_3$N$_4$ energy-volume (E-V) diagrams are constructed, considering three structure types –spinel, Th$_3$P$_4$ and lowest energy form α-Zr$_3$N$_4$ (in case of Hf$_3$N$_4$) and CaTi$_2$O$_4$ (for Ti$_3$N$_4$) in each case. Next, enthalpy difference-pressure (dH-p) diagrams constructed for Hf$_3$N$_4$ and Ti$_3$N$_4$ with reference to lowest energy state. The dH-p diagrams for Hf$_3$N$_4$ and Ti$_3$N$_4$ shows that, cubic Th$_3$P$_4$ will be adopted at high pressures, although it will be metastable at 0 GPa. Also from the diagram, the synthesized cubic Hf$_3$N$_4$ is a metastable compound having appreciable difference in energy (0.5 eV/f.u.) to the lowest energy Zr$_3$N$_4$-type (not yet synthesized) modification of Hf$_3$N$_4$. Spinel phase is metastable for any pressure-temperature condition. Similarly, cubic Ti$_3$N$_4$ (yet to synthesized) is a metastable compound with energy difference ~0.75 eV/f.u. to the lowest energy CaTi$_2$O$_4$-type (also not yet synthesized) [KRO04]. Also from the diagrams, the spinel modification is always lower than Th$_3$P$_4$ in energy but close to the Zr$_3$N$_4$ type at zero pressure, and is unfavorable towards compression at high pressure. For spinel -> Th$_3$P$_4$ type phase
transitions the transition pressures calculated are 3.9 and 4.9 for Hf$_3$N$_4$ and Ti$_3$N$_4$ respectively. Cubic Hf$_3$N$_4$ was synthesized around 18 GPa and can be quenched to 0 GPa. Thus, it may be possible to attain a phase that is thermodynamically metastable at zero pressure. If we can provide the temperature corresponding to spinel $\rightarrow$ Th$_3$P$_4$ transition pressure (which was 3.9 and 4.87 for Hf$_3$N$_4$ and Ti$_3$N$_4$ respectively), it is possible to attain the spinel structure type on quenching. We want to predict an estimate of that temperature in this work.

Figure 5: Energy-volume (E-V) (left) and enthalpy-pressure ($\Delta$H-p) diagrams (right) of Hf$_3$N$_4$.

Table 2: Structure type, energy $E_0$ and volume $V_0$ calculated at zero pressure, relative energy $\Delta E$ with respect to the ground state configuration for the three polymorphs of interest of Hf$_3$N$_4$

| Structure type | $E_0$  | $V_0$  | $\Delta E$ |
|---------------|--------|--------|------------|
| o-Zr$_3$N$_4$ | -74.908| 85.28  | 0          |
| Th$_3$P$_4$   | -74.392| 75.66  | 0.516      |
| Spinel        | -74.806| 93.15  | 0.102      |
Table 3: Structure type, energy $E_0$ and volume $V_0$ calculated at zero pressure, relative energy $\Delta E$ with respect to the ground state configuration for the three polymorphs of interest of Ti$_3$N$_4$

| Structure type | $E_0$  | $V_0$  | $\Delta E$ |
|---------------|-------|-------|------------|
| CaTi$_2$O$_4$ | -65.804 | 69.41 | 0          |
| Th$_3$P$_4$   | -65.097 | 62.75 | 0.707      |
| Spinel        | -65.550 | 77.56 | 0.254      |

4.2 Energy profile calculation along the reaction coordinate

A transformation scheme between spinel and Th$_3$P$_4$ retaining the symmetry of their common subgroup I-42d, was given at table 1 (page 13) before. As it implies, the transformation can be defined within six-dimensional configuration space as there are six parameters, which are changing during the transformation. A reaction coordinate was constructed by simultaneous linear interpolation of all the six structural parameters. Static calculations of these intermediate geometries yield an upper boundary of the activation barrier. The results of these calculations for Hf$_3$N$_4$ are shown below. The same regime was followed for Ti$_3$N$_4$ too.
Figure 7: Energy profile diagram along the reaction coordinate for Hf₃N₄ (at 0 GPa). The linear interpolation was done for 9 points between Hf₃N₄ with spinel and Th₃P₄ structure types. All the six parameters were interpolated simultaneously. The activation energy Ea is about 0.63 eV per Hf₃N₄, the excess energy is equal to the energy difference between the spinel and the Th₃P₄ structure types, 0.4 eV per Hf₃N₄. In the x-axis 0 represents the spinel type while 10 is the Th₃P₄ type. (same notation is followed in the subsequent graphs).

Figure 8: Energy profile diagram along the reaction coordinate for Ti₃N₄ (at 0 GPa). (Followed the same procedure as for Hf₃N₄). Here, the activation energy Ea is about 0.4 eV per Ti₃N₄, the
excess energy is equal to the energy difference between the spinel and the Th$_3$P$_4$ structure types, 0.48 eV per Ti$_3$N$_4$.

4.2.1 Results of energy profile calculation

Activation barrier can be calculated along a continuous path following a continuous path of structural transformation [figure 6 and 7]. From these static energy profile calculations at 0 GPa, barriers of 0.63 eV/f.u. and 0.4 eV/f.u. were estimated for the spinel->Th$_3$P$_4$ transformation for Hf$_3$N$_4$ and Ti$_3$N$_4$ respectively. On translating these energies per atom into temperature it gives 1125 K and around 800 K for Hf$_3$N$_4$ and Ti$_3$N$_4$ respectively, which corresponds to the thermal barrier. On comparing to typical bond-energies necessary to break during a reconstructive process of Hf-N and Ti-N bonds, these are significantly smaller barriers.

Now to achieve our second goal, that is to estimate the temperature of synthesis of still hypothetical spinel modification from cubic Th$_3$P$_4$ type on quenching, linear interpolation were done at the transition pressure (same procedure as before but previous calculations were done at 0 GPa). The results of these calculations are shown below:

![Figure 9: Enthalpy profile diagram along the reaction coordinate for Ti$_3$N$_4$. Calculations were done at transition pressure (P$_t$=4.9 GPa).](image-url)
Figure 10: Enthalpy profile diagram along the reaction coordinate for Hf$_3$N$_4$ ($P_t = 4.9$ GPa).

The same formalism was applied as before and calculations were carried out for the transformation at the transition pressure to access the temperature of synthesis. Barriers of 0.7 eV/f.u. and 0.48 eV/f.u. were estimated for Hf$_3$N$_4$ and Ti$_3$N$_4$ respectively. These energies corresponds temperatures of around 1200 K and 900 K respectively.
CHAPTER 5
SUMMARY AND CONCLUSION

Using a simple structural relation paralleling martensitic transformations, energy profiles along a transformation path from Th$_3$P$_4$-type to spinel-type structures have been computed for hafnium (IV) and titanium (IV) nitride, M$_3$N$_4$ (M = Hf, Ti). At zero pressure, where a spinel modification is energetically more favorable than a Th$_3$P$_4$ modification, the activation barriers for the Th$_3$P$_4$ to spinel transformations are 0.63 eV/f.u. and 0.4 eV/f.u. for Hf$_3$N$_4$ and Ti$_3$N$_4$, respectively. It is estimated, therefore, that at temperatures of 1120 and 800 K, respectively, this transformation will play a significant role in the decomposition of Th$_3$P$_4$-type Hf$_3$N$_4$ and Ti$_3$N$_4$. The same transformation path is used to predict the conditions necessary to synthesize a (meta-stable) spinel modification from the Th$_3$P$_4$-type at elevated pressures, when both modifications are assumed to be in equilibrium. A barrier of 0.7 eV/f.u. at 3.9 GPa for Hf$_3$N$_4$ indicate that annealing of the Th$_3$P$_4$-type at this pressure may yield a spinel modification. The conditions for synthesizing a spinel modification of Ti$_3$N$_4$ from a Th$_3$P$_4$-type are computed from the barrier obtained at 4.9 GPa. 0.48 eV/f.u. correspond to 900 K.
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BIOGRAPHICAL INFORMATION

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