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Assessment of the Hf–N, Zr–N and Ti–N phase diagrams at high pressures and temperatures: balancing between MN and M_3N_4 (M = Hf, Zr, Ti)

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Abstract

We study the nitrogen-rich part of the phase diagram Hf–N, Zr–N and Ti–N, employing first-principle calculations for an assessment of energy and enthalpy as a function of pressure. At zero pressure the novel cubic Th_3P_4 -type structures are metastable modifications of M_3N_4 (M = Hf, Zr). The lowest energy configuration of both compounds is an orthorhombic Zr_3N_4 -type. This orthorhombic structure will transform into the Th_3P_4 -type at 9 and 6 GPa, for Hf_3N_4 and Zr_3N_4 , respectively. The lowest energy configuration of Ti_3N_4 is a $CaTi_2O_4$ -type structure. It will first transform into the orthorhombic Zr_3N_4 -type at 3.8 GPa, then further transform into the cubic Th_3P_4 -type at 15 GPa. The spinel type is metastable throughout the phase diagram for all three systems.

The phase boundary between mononitrides MN and the M_3N_4 -phases is accessed as a function of pressure. We include the entropy of gaseous nitrogen from tabulated data to estimate the free enthalpy ΔG of the nitride phases. The orthorhombic modification of Hf_3N_4 turns out to be thermodynamically stable with respect to a decomposition into the mononitrides and nitrogen for temperatures up to about 1000 °C. The stability of Zr_3N_4 is in question; within the estimated error no final conclusion can be drawn. Ti_3N_4 , on the other hand, will only be metastable. At higher pressures, however, the free energy of nitrogen is substantially reduced and the 3:4 compositions become more stable. We reproduce the experimental requirements (18 GPa and 2800 K) for the synthesis of the novel Hf_3N_4 . At 2800 K the pressures needed to synthesize cubic phases of Zr_3N_4 and Ti_3N_4 are estimated to be 40 and 100 GPa, respectively.

1. Introduction

Recently, Zerr *et al* [1] succeeded in the high pressure synthesis of two novel binary nitrides of hafnium and zirconium with the cubic thorium phosphide (Th_3P_4) structure. c- Hf_3N_4 formed

at 18 GPa and 2800 K in the diamond-anvil cell from elemental Hf and nitrogen. Experiments on the synthesis of zirconium nitride were analogous and yielded the isostructural c-Zr₃N₄ at 15.6–18 GPa and 2500–3000 K. Both compounds are the first binary nitrides with eightfold coordinated cations. c-Hf₃N₄ appears transparent, while c-Zr₃N₄ is opaque to visible light. The only stoichiometric 3:4 nitride compound of Ti, Zr or Hf previously known is the orthorhombic Zr₃N₄, which has a brownish colour [2, 3]. Following the characterization of γ -Si₃N₄ with spinel structure, which was also synthesized at high pressures by Zerr *et al*, Ching *et al* [5] made predictions on hypothetical spinel-type structures of Ti₃N₄, Zr₃N₄ and Hf₃N₄. They also investigated the system Zr₃N₄ in more detail, including the orthorhombic, the spinel and a defect-NaCl modification [6]. Zerr *et al* had outlined already, however, that the suggested spinel compound would be less dense than the orthorhombic Zr₃N₄, which then of course will be favoured at high pressures according to LeChatelier's principle.

In contrast to the 3:4 compounds c-Hf₃N₄ and c-Zr₃N₄, mononitrides of all fourth-column transition metals, TiN, ZrN and HfN, have been known for a much longer time [7]. They adopt the rock salt (NaCl) structure type. They all show, however, significant variation in composition, both towards cation- and anion-rich. The mononitrides are well-known as refractory and hard materials and used for cutting tools and wear-protection. Due to their golden colour, which is as bright as 24-carat gold, TiN and ZrN are also used as decorative coatings.

In a recent letter we have investigated the physical and electronic properties of the novel phase c-Hf₃N₄ [8]. Based on the calculated elastic moduli, namely the aggregate shear modulus G , we proposed that c-Hf₃N₄ will be harder than the mononitride HfN. We furthermore calculated electronic and vibrational properties of the novel phases. The previous work included a preliminary calculation of the reaction $3MN + \frac{1}{2}N_2 \rightarrow M_3N_4$, which governs the thermodynamics of formation and decomposition of the novel nitrides. The goal of this work is to concentrate on the phase boundary between the mononitrides MN on the one hand, and the nitrogen-richer 3:4 compounds M₃N₄ on the other.

In this contribution we will first give a report on the energetics of different hypothetical polymorphs with composition M₃N₄, and will derive a phase diagram for the phase development under pressure based on our assessment of the enthalpy (ΔH) of each phase. We then will repeat the procedure for the mononitrides, which, however, will turn out to be very simple within our approximation. The phase boundary between MN and M₃N₄ is, finally, calculated by augmenting the enthalpy with the entropy contributions of gaseous nitrogen.

2. Computational method

Our calculations of the total energies, atomic structures and atomic dynamics are within density functional theory (DFT) [9]. The implementation of the DFT employed here combines a plane-wave basis set with the total energy pseudopotential method. In particular we used the Vienna *ab initio* simulation package (VASP) [11, 11, 12]. The pseudopotentials we have used are based on the projector-augmented-wave (PAW) method [13]. For the exchange-correlation energy of the electrons we chose the generalized-gradient approximation (GGA) of Perdew and Wang [14]. All results rely on well-converged structures with respect to cut-off energy (500 eV) and \mathbf{k} -point sampling.

The choice of the GGA is motivated by our previous experiences with both the LDA and the GGA for simulating phase transitions under pressure. For example, the LDA fails to compute the relative energies of phases with different coordination correctly; a good example for this is the system SiO₂ and the quartz to stishovite transition [15]. Gradient corrections, on the other hand, offer significant improvements when structures with different environments for the atoms

Table 1. Structure type, average coordination of cations n_c , energy E_0 and volume V_0 calculated at zero pressure, relative energy ΔE and relative volume ΔV with respect to the ground state configuration for several hypothetical polymorphs of Hf_3N_4 . The last column contains the zeroth order approximation to the transition pressure between ground state structure and the respective hypothetical polymorph for those structure types, which are more dense than the lowest energy configuration. Energies are given in eV and volumes in \AA^3 per formula unit Hf_3N_4 , p^* in GPa.

Structure type	n_c	E_0	V_0	ΔE	ΔV	p^*
Orthorhombic	6	-74.912	85.48	0	0	
Spinel	5.33	-74.803	93.13	0.109	7.65	
CaTi_2O_4	6	-74.795	83.66	0.117	-1.82	10.3
Yb_3N_4	6.33	-74.745	83.58	0.167	-1.90	14.1
$\text{Sr}_2\text{Pb}_2\text{O}_4$	6	-74.666	83.71	0.246	-1.77	22.2
CaFe_2O_4	6.33	-74.411	81.00	0.501	-4.48	17.9
Th_3P_4	8	-74.397	75.70	0.515	-9.78	8.4
Th_3N_4	6.66	-74.389	84.57	0.523	-0.91	92.1
Ni_3Se_4	6	-74.300	90.96	0.612	5.48	
Nb_3N_4	6	-74.183	102.94	0.729	17.46	
Ca_2SiO_4	5.16	-73.855	102.69	1.057	17.21	
def-NaCl	6	-72.789	87.92	2.123	2.44	

are compared with each other. However, even though some results obtained within the GGA are very close to experimental values (e.g. the transition pressure for $\beta\text{-Si}_3\text{N}_4 \rightarrow \gamma\text{-Si}_3\text{N}_4$; experiment: 13 GPa, calculated: 12.1 GPa [4]), we encountered situations for which the deviation is still significant (e.g. the transition pressure for $\alpha\text{-P}_3\text{N}_5 \rightarrow \gamma\text{-P}_3\text{N}_5$; experiment: 11 GPa, calculated: 6.2 GPa (LDA: 1.9 GPa) [16]). It should, therefore, be kept in mind that such calculations refer to idealized crystalline systems calculated at 0 K and both carry the errors of the theoretical method and the underlying computational model. Experimental conditions, especially the influence of temperature combined with imperfect structures, cannot be handled in fully (yet), and may cause further discrepancies between calculated and observed properties.

3. Results

3.1. The 3:4 compounds, M_3N_4 ($M = \text{Hf}, \text{Zr}, \text{Ti}$)

We began to search for possible polymorphs with composition M_3N_4 by scanning the database on binary and ternary structure types that comprise three cations and four anions. This approach is quite similar to our previous study on post-spinel phases of Si_3N_4 [17]. After mapping the elements—Hf, Zr or Ti as cations, N as the anion—onto the structure type, we completely optimized all crystallographic parameters, atomic positions and cell geometry. In some cases we observed a distortion of the initial geometry towards lower or higher symmetrical arrangements, combined with a change in the local coordination of the atoms.

Results of this scanning procedure are presented in tables 1–3, for Hf_3N_4 , Zr_3N_4 and Ti_3N_4 , respectively. The tables contain structure type, average coordination number n_c of the cations, energy and volume calculated for the optimized geometry at zero pressure, and energy and volume relative to the lowest energy configuration for several hypothetical polymorphs of M_3N_4 . The last column in every table shows the quantity p^* , which is calculated by dividing the relative energy by the relative volume ($p^* = -\Delta E/\Delta V$). To zeroth order, p^* approximates the transition pressure p_t between the ground state with lower density and this particular structure type with higher density. Although a crude approximation (assuming

Table 2. Same as table 1, but for Zr_3N_4 .

Structure type	E_0	V_0	ΔE	ΔV	p^*
Orthorhombic	-69.385	89.18	0	0	
CaTi ₂ O ₄	-69.236	87.69	0.149	-1.49	16.0
Yb ₃ N ₄	-69.190	87.54	0.195	-1.64	19.0
Spinel	-69.143	97.82	0.242	8.64	
Th ₃ P ₄	-69.048	79.01	0.337	-10.17	5.3
Ni ₃ Se ₄	-68.730	95.11	0.655	5.93	
Nb ₃ N ₄	-68.643	107.72	0.742	18.54	
def-NaCl	-67.377	92.32	2.008	3.14	

Table 3. Same as table 1, but for Ti_3N_4 .

Structure type	E_0	V_0	ΔE	ΔV	p^*
CaTi ₂ O ₄	-66.395	69.23	0	0	
Yb ₃ N ₄	-66.313	69.14	0.082	-0.09	146
Orthorhombic	-66.272	70.92	0.123	1.69	
Spinel	-66.211	77.20	0.184	7.97	
Nb ₃ N ₄	-65.978	79.67	0.417	10.44	
Ni ₃ Se ₄	-65.977	74.96	0.418	5.73	
Th ₃ P ₄	-65.631	64.50	0.764	-4.73	25.9
def-NaCl	-65.400	71.95	0.995	2.72	
Sr ₂ Pb ₂ O ₄	-64.820	80.80	1.575	11.57	

equal compression behaviour and a bulk modulus much larger than the transition pressure), p^* , nevertheless, gives a reasonable estimate of p_t . It can, therefore, be taken as a good indicator to identify a possible high pressure phase.

The ground state structures we find for Hf_3N_4 are neither the synthesized cubic Th_3P_4 -type modification, nor the spinel-type investigated by Ching *et al* [5]. Instead, not less than half a dozen structure types come out lower in energy than the novel cubic polymorph of Hf_3N_4 . The calculated energy differences to the lowest energy configuration, an orthorhombic modification which is isotypic to the known orthorhombic modification of Zr_3N_4 [3], is quite large, more than 0.5 eV/ Hf_3N_4 , indicating that the cubic polymorph indeed is metastable at zero pressure. The cubic Th_3P_4 -type of Hf_3N_4 , nevertheless, comes out as a possible high pressure modification of Hf_3N_4 ; judging from p^* it will be the first (and only) to appear under equilibrium conditions.

The structure with lowest energy we find for Zr_3N_4 is the orthorhombic modification which was identified experimentally some time ago [2, 3]. Recent calculations, however, had indicated that a defective NaCl type structure with composition Zr_3N_4 should have a much lower total energy [6]. Obviously in disagreement with our pseudopotential calculations, we set out and performed all-electron calculations using the Wien2K code [18]. The results we obtained corroborate not only our relative ordering of orthorhombic, spinel and defective NaCl structure, but also agreed with the relative energies we found. We attribute the differences between our results and that of [6] to the choice of local basis sets in [6], which may lead to an improper description of the vacancy, as well as to the applied functional (the LDA in [6], while we use the GGA). Taken together with the experimental findings, we are thus confident, that the orthorhombic structure is indeed the ground state of Zr_3N_4 . An assessment of the configurational (mixing) entropy for the defective NaCl type, for which we calculate $S = 18.7 \text{ J K}^{-1}/Zr_3N_4$, shows that even at 2000 K entropy effects will not overcome the large

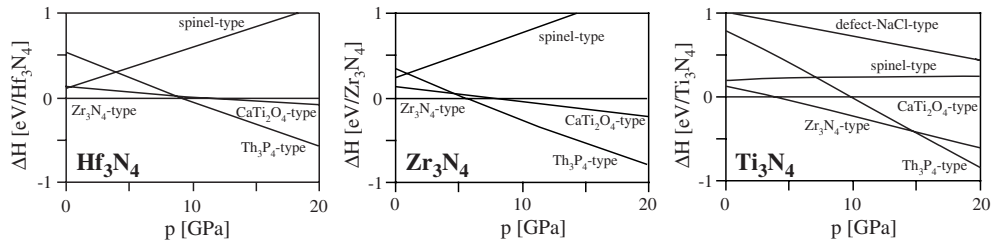


Figure 1. Enthalpy–pressure (ΔH – p) diagrams of Hf_3N_4 (left), Zr_3N_4 (middle), and Ti_3N_4 (right). The enthalpy is given relative to the orthorhombic Zr_3N_4 -type structure for Hf_3N_4 and Zr_3N_4 , and relative to the CaTi_2O_4 -type modification for Ti_3N_4 .

energy difference we calculate. Similar to Hf_3N_4 , the cubic Th_3P_4 -type of Zr_3N_4 comes out as the most likely high pressure modification as indicated by p^* .

The ground state structures we find for Ti_3N_4 are neither the orthorhombic Zr_3N_4 -type we suggested earlier [8], nor the spinel-type proposed by Ching *et al* [6]. Instead, we find a CaTi_2O_4 -type modification to be slightly lower in energy than the orthorhombic Zr_3N_4 -type, which in turn is somewhat lower in energy in comparison to a spinel modification. The CaTi_2O_4 -type also comes out more dense than both modifications suggested previously, making them unlikely as candidates obtainable at high pressures. The defective NaCl-type comes out about 1 eV/ Ti_3N_4 higher in energy, the smallest energy difference we found for all three phase systems. Again, a cubic Th_3P_4 -type modification of Ti_3N_4 is proposed as a high pressure phase.

To derive a high pressure phase diagram for the 3:4 compounds, we have to access the energetics of every structure at high pressures. We therefore calculated the energy E of every structure as a function of volume V , compressing the unit cell to higher densities. In every step, atomic positions and lattice parameters were optimized under the constraint of constant volume. The pressure p is extracted from the E – V graph by a simple numerical differentiation of a spline fit to the E – V data: $p = -\partial E/\partial V$. Murnaghan's fit can also be used for structures as dense as those we encounter in this study. Having calculated p and H it is good practice to plot the enthalpy with reference to a given phase, for which we usually choose the ground state structure. In the experiment, where pressure p and temperature T are varied, the thermodynamical variable which governs the transition between phases under equilibrium conditions is the free energy $G = E + pV - TS$. The difference ΔG between two phases constitutes the driving force for a structural transformation. The entropy contribution to ΔG is commonly neglected, due to the small difference in entropy between solid state crystal structures and the large enthalpy differences ΔH we obtain at high pressures. Thus, ΔG can be replaced by ΔH , which we can calculate within the theoretical method. The resulting enthalpy–pressure (ΔH – p) diagrams for Hf_3N_4 , Zr_3N_4 and Ti_3N_4 , are shown in figure 1.

The essence of the (ΔH – p) diagrams is very simple. In the phase systems of Hf_3N_4 and Zr_3N_4 we find only one transition from the ground state into the cubic Th_3P_4 -type modification. The calculated transition pressures p_t are 9 and 6 GPa, respectively. We see that indeed p_t corresponds very well with p^* . In the phase systems of Ti_3N_4 we find two transitions. First the CaTi_2O_4 -type \rightarrow orthorhombic transition at about 3.8 GPa. This transition was not indicated by p^* , since the orthorhombic modification has a slightly larger volume at zero pressures. Its compression behaviour, nevertheless, is more favourable. Interestingly, this holds only for Ti_3N_4 , but not for Hf_3N_4 , see figure 1. The orthorhombic \rightarrow Th_3P_4 -type transition in Ti_3N_4 is found at 15 GPa. The approach pursued above, however, constrains the composition and,

Table 4. Structure type, coordination number of cations n_c , energy E_0 and volume V_0 calculated at zero pressure, relative energy ΔE and relative volume ΔV with respect to the ground state configuration for several hypothetical polymorphs of HfN. Energies are given in eV and volumes in \AA^3 per formula unit Hf_3N_4 , p^* in GPa.

Structure type	n_c	E_0	V_0	ΔE	ΔV	p^*
NaCl	6	-21.773	23.33	0.000	0.00	0
Anti-NiAs	6	-21.702	23.40	0.071	0.07	
ε	6	-21.253	25.67	0.520	2.34	
NiAs	6	-21.074	24.30	0.699	0.97	
θ	6	-20.987	24.07	0.786	0.74	
CsCl	8	-19.799	22.29	1.974	-1.04	304

Table 5. Same as table 4, but for ZrN.

Structure type	E_0	V_0	ΔE	ΔV	p^*
NaCl	-20.240	24.60	0.000	0.00	
anti-NiAs	-20.137	24.57	0.103	-0.03	550
ε	-19.630	26.91	0.610	2.31	
NiAs	-19.569	25.59	0.671	0.99	
θ	-19.493	25.22	0.747	0.62	
CsCl	-18.471	23.24	1.769	-1.36	208

Table 6. Same as table 4, but for TiN.

Structure type	E_0	V_0	ΔE	ΔV	p^*
NaCl	-19.652	19.22	0.000	0.00	
anti-NiAs	-19.429	19.22	0.223	0.00	
θ	-18.968	19.72	0.684	0.50	
ε	-18.869	21.24	0.783	2.02	
CsCl	-17.863	18.35	1.789	-0.87	330

thus, neglects a possible decomposition into the mononitrides and nitrogen. Such a process requires an investigation of the phase boundary between MN and M_3N_4 , a situation we will address further below.

3.2. The mononitrides, MN ($M = \text{Hf}, \text{Zr}, \text{Ti}$)

The results we found for mononitrides of HfN, ZrN and TiN are given in tables 4–6, respectively. As it turns out, only the NaCl-type and the CsCl-type are of relevance. The appearance of different crystal polymorphs in some cases can only be explained by the influence of entropy for non-stoichiometric compounds, or by some non-equilibrium routes in the process of their synthesis. The transition between NaCl- and CsCl-type structures (B1 \rightarrow B2 transition), however, appears at exceedingly high pressures. Since this regime, beyond 150 GPa, is not important for our study, we can take the NaCl as the reference state of our mononitride phases for all pressures we consider.

3.3. Enthalpy and free enthalpy of nitrogen

The enthalpy difference ΔH between solid state compounds is a good measure to derive a phase diagram for constant composition. This argument holds because the entropy differences

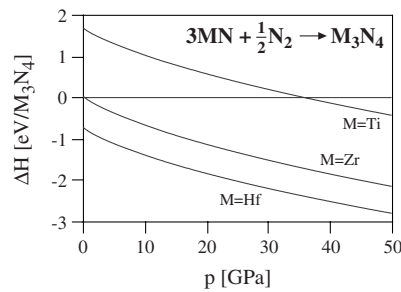
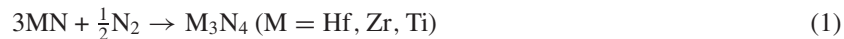


Figure 2. ΔH of the reactions $3MN + \frac{1}{2}N_2 \rightarrow M_3N_4$ ($M = \text{Hf, Zr, Ti}$) at zero temperature as a function of pressure.

that contribute to the free enthalpy ΔG are typically small in comparison to the much larger variation of ΔH within a few gigapascal of pressure. The situation, however, is inherently more complicated if we are to consider a decomposition reaction in which gaseous products occur. In such a case, it is mandatory to include the effects of entropy.

In this study, which focuses on the phase boundary between MN and M_3N_4 at elevated temperatures, the nitridation reaction



comprises molecular nitrogen gas. We therefore first need to calculate the enthalpy of nitrogen as a function of pressure and, further, augment the calculated enthalpy to yield the free enthalpy ΔG of nitrogen as a function of temperature and pressure.

Our approach is based on a combination of quantum-chemical and empirical, thermodynamical calculations. In a first step, we calculate the enthalpy of molecular nitrogen as a function of pressure. As reference state, we choose the ϵ -phase that comprises N_2 molecules. At 0 K, we find a transformation into a polymeric polymorph at about 45 GPa. However, we do not take this transformation into account, since the formation of the latter modification is unlikely to occur at temperatures above 1000 K within the pressure range of interest. In a second step, we acquire the tabulated thermochemical data of nitrogen from standard reference data [19]. The thermochemical data is, however, given only for zero pressure. Unfortunately, no reference data exists for the free energy of nitrogen for pressures over 1 GPa. We therefore calculate the residual pressure dependence of ΔG according to the standard formula $\Delta G(p, T) = \Delta G(p = 0, T) + RT \ln p$. This procedure should yield, at least to first order, the dominant temperature effects on the reaction (1).

3.4. The phase boundary between MN and M_3N_4 ($M = \text{Hf, Zr, Ti}$)

Collecting the data we calculated for M_3N_4 , MN and nitrogen we can now plot a phase diagram that reflects the equilibrium, $\Delta G = 0$, of the formation reaction (1). Without the effects of temperature, $\Delta G = \Delta H$ holds and the ΔH – p diagrams of every reaction are shown in figure 2.

Apparently, without temperature effects, the formation of the Hf_3N_4 compounds is exothermic at any pressure. Zr_3N_4 shows $\Delta H \approx 0$ at $p = 0$, but an increasing driving force for the formation of the higher nitrated compound with increasing pressure. In the case of titanium nitride, however, we find that it needs about 35 GPa to form Ti_3N_4 from TiN and N_2 already at 0 K. Thus, at zero pressure the equilibrium of reaction (1) is on the side of the mononitride and the gas. Given the accuracy of the method, it thus seems unlikely that a Ti_3N_4 will form within the reaction conditions used for the synthesis of the cubic polymorphs of

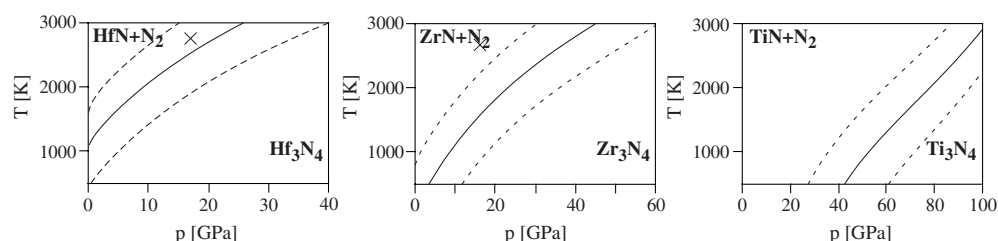


Figure 3. p, T -diagrams of the reactions $3MN + \frac{1}{2}N_2 \rightarrow M_3N_4$ ($M = \text{Hf, Zr, Ti}$). The solid curves correspond to phase equilibria ($\Delta G = 0$); the dashed curves to $\Delta G = +0.5$ and -0.5 . The crosses in the Hf–N and Zr–N phase diagrams indicate the experimental conditions of Zerr *et al* [1].

Hf_3N_4 and Zr_3N_4 . The trend for 3:4 nitrides of Hf and Zr, however, is that the former will have a larger driving force for formation than the latter. We would thus expect c- Hf_3N_4 to form at lower pressure than needed to synthesize c- Zr_3N_4 .

Including the effects of the free energy of nitrogen then leads to the phase diagrams outlined in figure 3. We have included a rather generous error bar (± 0.5 eV to account for the uncertainties of the procedure). The orthorhombic ground state of Hf_3N_4 is apparently stable at zero pressure with regard to a decomposition into HfN and N_2 for temperatures approximately up to 1000 K. The diagram for hafnium nitride, moreover, shows that within the outlined approximation we are able to reproduce the experimental conditions of Zerr *et al* [1]. Though we tend to slightly higher pressures and/or lower temperatures within the calculations, the difference—either 200 K or 5 GPa—is rather small. Zr_3N_4 , on the other hand, comes out unstable at zero pressure and 1000 K. It should decompose into ZrN and N_2 . For the formation of Zr_3N_4 from the mononitride ZrN and nitrogen we obtain a significantly higher pressure than for Hf_3N_4 , 40 GPa at 2800 K. Obviously, this does not reproduce the experimental conditions of approximately 18 GPa at 2800 K. Synthesis of a cubic Th_3P_4 -type Ti_3N_4 will, finally, require about 100 GPa at 2800 K. Hence, much more drastic conditions are needed than proposed before [5].

4. Discussion

In view of the experiments of Zerr *et al* [1], our results presented here are encouraging. We reproduce the experimental requirements for the synthesis of Hf_3N_4 fairly well, and can also explain why a Ti_3N_4 did not form at similar conditions. For Zr_3N_4 , however, the transition pressure we predict is too high. Given the existence of orthorhombic Zr_3N_4 and its decomposition at about 1000 K [3], our complete curve for the Zr–N phase diagram seems to be shifted by 1000 K and/or 10 GPa. The exact reason for this is unclear. A general trend to estimate the phase boundary at pressures too high, or temperatures too low, within our approach can be understood. Even with the inclusion of entropic effects of nitrogen gas, we still neglect any entropy contributions of the solid state phases MN and M_3N_4 in reaction (1). Obviously, M_3N_4 contains more atoms than 3 MN, and most likely will also have the larger entropy contribution to the free energy. Therefore, the error we introduce by neglecting such contributions will favour the mononitride side and will shift the phase boundary to higher pressures. While a correction may lead to much better results in the case of hafnium nitride, it will presumably not be enough to reproduce the experimental conditions for Zr_3N_4 as well. Whether the disagreement stems from the pseudopotentials used (the lattice constants for

c-Zr₃N₄ or the orthorhombic structure came out fine, see [8]), or other imperfections of the computational model, however, remains undecided at this moment.

Some criticism on the described assessment of the free enthalpy of nitrogen gas is certainly justified. First of all, the procedure is merely a semi-empirical treatment and not a rigorous calculation from *first principles*. Secondly, the application of the formula to derive the pressure dependence may no longer be valid for the regime of high pressures we are interested in. Thirdly, the activity or fugacity of nitrogen, which is most important for the reaction (1), might be very different under the conditions of high pressure synthesis. Consequently, the data we derive incorporates a substantial error bar. At the bottom line there is still room for improvement.

5. Summary

In summary, we investigated nitrogen-rich compounds of hafnium, zirconium and titanium. We found the lowest energy configuration of Hf₃N₄ and Zr₃N₄ to be the orthorhombic Zr₃N₄-type structure. The novel cubic compounds of Hf₃N₄ and Zr₃N₄ with Th₃P₄-type structure are metastable at zero pressure. They become more favourable in enthalpy with increasing pressure, the transition pressure from the ground state structure being 9 and 6 GPa for Hf₃N₄ and Zr₃N₄, respectively. Since the orthorhombic Zr₃N₄ can be synthesized via ammonolysis of ZrCl₄ [3], we propose that this phase be used as precursor for the synthesis of cubic Zr₃N₄ at about 6 GPa. The lowest energy configuration of Ti₃N₄ adopts a CaTi₂O₄-type structure. It first transforms at 3.8 GPa into the orthorhombic-type, and then further into the cubic Th₃P₄-type at 15 GPa. In all three systems the spinel modification has a lower density than the ground state structure and remains metastable throughout the enthalpy–pressure phase diagram.

Using a combination of quantum-chemical calculations and thermodynamical data, we accessed the phase boundary between the mononitrides MN and M₃N₄ compounds (M = Hf, Zr, Ti). We find that the orthorhombic modifications of Hf₃N₄ are stable at zero pressure with regard to a decomposition into the mononitrides and nitrogen gas for temperatures up to 1000 K. The stability of Zr₃N₄ is in question, given the estimated error of our procedure. Ti₃N₄, on the other hand, is unstable for pressures up to about 40 GPa. At 2800 K, we find the pressures necessary to synthesize cubic M₃N₄ compounds to be 22, 40 and 100 GPa for Hf₃N₄, Zr₃N₄ and Ti₃N₄, respectively. While a discrepancy between calculations and experimental results is apparent for Zr₃N₄, we reproduce the experimental conditions of the synthesis of Hf₃N₄ reasonably well.

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