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Effects of high pressure on ScMN$_2$-type (M = V, Nb, Ta) phases studied by density functional theory

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ABSTRACT

ScMN$_2$-type (M = V, Nb, Ta) phases are layered materials that have been experimentally reported for M = Ta and Nb, but their high-pressure properties have not been studied. Here, we have used first-principles calculations to study their thermodynamic stability, elastic and electronic properties at high-pressure. We have used density functional theory to calculate the formation enthalpy relative to the competing binary phases, electronic density of states and elastic constants ($c_{ij}$), bulk ($B$), shear ($G$) and Young’s ($E$) modulus as the pressure is varied from 0 to 150 GPa. Our results show that when the pressure increases from 0 to 150 GPa, elastic constants, bulk, shear and elastic moduli increase in the range 53–216% for ScTaN$_2$, 72–286% for ScNbN$_2$, and 61–317% for ScVN$_2$.

Introduction

High-pressure studies on materials are important in contributing to increased fundamental understanding of the behavior of materials. For example, high pressure-studies allow explanations of the properties of materials at the Earth’s core [1–3], high-temperature superconductivity occurring at high pressure [4] or in technological applications at high pressure. Thus, ab initio studies of material stability at high pressure are important to determine stability and can lead to prediction of new phases.

The MAX phases are a family of ternary carbides and nitrides described with the general formula $M_{n+1}AX_n$, where $M$ is a transition metal, $A$ is an A-group element, $X$ is carbon or nitrogen and $n = 1,2$ or 3. In the case of $n = 1$ a MAX phase is referred to as a “211” MAX phase, for $n = 2$, “312” and for $n = 3”, “413” ” [5,6]. Their high-pressure properties have been investigated both theoretically and experimentally and these have concerned phase transformations and their mechanical properties [7–13]. For example, MAX phases exhibit polymorphism; one type occurs because of shearing of the A-layer at high pressure in Ti$_2$Ge$_2$ [12,14]. A second type of polymorphism is due to different stacking sequences in Ta$_3$AlC$_6$, where the transition between the two different stacking sequences is induced by high pressure [10]. The MAX phases have relatively low densities at the same time as they are quite stiff but relatively stiff, and they are damage and thermal shock resistant. This unusual combination of properties makes the MAX phases good candidates for high pressure applications, especially taking into account that they are readily machinable [8,10].

The ScMN$_2$-type structure is a closely related structure to a 211 MAX phase. These structures have been experimentally observed in the ScTaN$_2$ and ScNbN$_2$ systems [15–17], but has been relatively little studied. As determined by Niewa at al. using Rietveld refinement of X-rays and neutron diffraction results [17], the structure of ScMN$_2$ belongs to the space group P6$_3$/mmc (#194). In the archetypical case of ScTaN$_2$, it is comprised of alternating layers of ScN$_6$/3 octahedra and TaN$_6$/3 prisms. Sc occupies 2a Wyckoff positions, Ta the 2d positions and N the 4f positions.[17,18] The structure can be termed “inverse MAX phase”, because the Wyckoff positions are the inverted positions of a 211 MAX phase [19]. The structure of ScTaN$_2$ is visualized in Fig. 1. We have previously [20] shown from density functional theory (DFT) calculations that ScTaN$_2$, ScNbN$_2$ and ScVN$_2$ are thermodynamically stable at 0 K and 0 GPa [18,20]. Our previous results also suggest that these materials could be interesting for thermoelectric applications and the thermoelectric properties could be tuned by doping. Thus, there is an interest to synthesize these materials and this motivates that the fundamental understanding of these materials needs to be increased. So far, no information on either thermodynamic stability or elastic properties at high pressure of these materials is available. Here, we here present a high-pressure study on physical properties of ScTaN$_2$, ScNbN$_2$ and ScVN$_2$ to investigate if any phase decomposition occurs and how the elastic properties change with pressure.
In order to determine the phase stability of ScMN₂ (where M is Ta, Nb or V) at different pressures, P, and the volume, V, corresponding to each pressure, the formation enthalpy relative to the competing binary phases in each state was calculated according to

\[ \Delta H = H_{\text{ScMN}} - H_\text{ScN} - H_\text{MN}, \]  

where the enthalpy, H, of each phase with the internal energy, U, is calculated according to

\[ H = U + PV \]  

For relaxation the energy and force tolerance was 0.0001 eV and 0.001 eV/Å, respectively. It is well known that NaCl structured ScN, or here referred as c-ScN, is the ground state stable phase and that the binary remains in this phase up to a pressure about 366 GPa [21], which motivates using only this phase for ScN in the calculation of formation enthalpy relative to the competing binary phases. For the MN binary, we choose in first instance the NaCl structure for TaN, NbN and VN as they have been used in calculations of formation enthalpy relative to the competing binary phases [18,20]. We also considered hexagonal TaN. In this system there are two binary phases, ε-TaN and π-TaN that only differ by a shift in N position, with the consequence that the two phases cannot be readily distinguished with x-ray diffraction. They can, however, be distinguished by neutron diffraction [22]. For this reason, there are some discrepancies in the descriptions of the structure of the ε-TaN phase in literature [22–24]. π-TaN (P-62m, #189) is the most stable phase of the two [22], which we therefore use in the calculations. It is here referred as h-TaN. For NbN the most stable phase has the anti-TIP structure (P6₃/mmc, #194) [25], which here is referred as h-NbN. For VN at 0 K, the most stable phase has the WC structure [26,27], here referred as h-VN and at low temperatures also a tetragonal phase can exist [28,29], here referred as t-VN. However, for VN, the cubic phase is known to be stabilized by atomic vibration at higher temperatures [22,29], which implies that h-VN and t-VN are stable only at low temperature. For discussion about properties near room temperature, it is therefore more accurate to consider ε-VN as the competing phase. We have included all of these phases.

Density functional theory (DFT) calculations were performed with the help of the Vienna Ab initio Simulation Package (VASP) [30–34]. The cutoff energy was set to 650 eV, projector augmented wave (PAW) basis sets [35] were used and the exchange-correlation potential was modeled with the generalized gradient approximation according to Perdew, Burke and Ernzerhof (PBE-GGA) [36]. The unit cells of the considered systems consisted of 8 atoms each and an 8 × 8 × 8 k-point mesh was used for the energy calculations. The elastic tensor for each pressure was determined in VASP by first introducing finite distortions in the lattice followed by calculations on strain-stress relationships [37]. For these calculations 25 × 25 × 11 k-point mesh was used. The magnitude of the strains was in the order of 0.015 Å. Furthermore, density of states (DOS) was calculated for selected pressures with a plane wave cutoff of 650 eV and with a 25 × 25 × 11 k-point mesh. The PBE-GGA functional was used together with the tetrahedron method with Blöchl correction [38]. The value of the level broadening was 0.2 eV.

Results and discussion

Eqs. (3)-(9) define the formation enthalpies relative to the competing binary phases \( \Delta H_i \) (i = 1, 2,...7) that were calculated with the enthalpies \( H \) of the previously defined phases, \( H \) at a given pressure. The chosen pressure values were 0, 30, 50, 100, and 150 GPa. \( V \) is the volume, corresponding to each \( P \), per formula unit and was obtained by first fitting energies and volumes to the Birch-Murnaghan equation of state (EOS) [39].

\[ \Delta H_1 = H(\text{ScTaN}) - H(c - \text{ScN}) - H(c - \text{TaN}) \]  

\[ \Delta H_2 = H(\text{ScTaN}) - H(c - \text{ScN}) - H(h - \text{TaN}) \]  

\[ \Delta H_3 = H(\text{ScNbN}) - H(c - \text{ScN}) - H(c - \text{NbN}) \]  

\[ \Delta H_4 = H(\text{ScVN}) - H(c - \text{ScN}) - H(c - \text{VN}) \]  

\[ \Delta H_5 = H(\text{ScTaN}) - H(c - \text{ScN}) - H(h - \text{VN}) \]  

\[ \Delta H_6 = H(\text{ScVN}) - H(c - \text{ScN}) - H(h - \text{VN}) \]  

\[ \Delta H_7 = H(\text{ScVN}) - H(c - \text{ScN}) - H(t - \text{VN}) \]  

Fig. 2a–c shows the calculated formation enthalpies relative to the competing binary phases as a function of pressure for the three different material systems. The formation enthalpy relative to the competing binary phases of each pressure is shown with markers. The continuous lines are cubic spline interpolations. Fig. 2a shows the enthalpies of formation for ScTaN₂ as defined in Eqs. (3) and (4). At 0 GPa, ScTaN₂ is stable. Pressure increases the thermodynamic stability of this phase, as can be seen by comparing the enthalpies of formation with those of c-TaN as well as h-TaN. For pressures in the range 0–90 GPa, the enthalpy of formation relative to c-TaN tends to be lower than relative to h-TaN. At pressures > 90 GPa there is an intersection between the two,
indicating that $h$-TaN is more stable than $c$-TaN at high pressure.

Fig. 2b shows the formation enthalpies relative to the competing binary phases of ScNbN$_2$ as a function of pressure as defined in Eq. (5) and (6). Similarly to ScTaN$_2$, ScNbN$_2$ is stable at 0 GPa and the effect of pressure is to increase the thermodynamic stability of this phase. It can be noted that the two curves in Fig. 2b are similar and have almost the same slope for all pressures. The curves do not intersect, in contrast to the case of ScTaN$_2$.

Fig. 2c shows the formation enthalpies relative to the competing binary phases as a function of pressure for ScVN$_2$ as defined in Eqs. (7)–(9). It can first be noted that ScVN$_2$ exhibits a positive formation enthalpy at 0 relative to $c$-ScN and $h$-VN. For VN, the cubic phase is known to be stabilized by atomic vibration at higher temperatures [22,29], which implies that $h$-VN is stable only at very low temperatures. It is therefore more reasonable to consider $c$-VN as the competing phase. Relative to $c$-VN, the ScVN$_2$ phase is stable at 0 GPa. Thus, it is reasonable to conclude that ScVN$_2$ is thermodynamically stable at room temperature and pressure, even though the formation enthalpy relative to $h$-VN at 0 K is positive. However, even when considering $h$-VN as competing phase, ScVN$_2$ is thermodynamically stable at pressures higher than 40 GPa this phase becomes thermodynamically stable.

Tables 1–3 show the calculated elastic constants, the bulk modulus ($B$), shear modulus ($G$) and elastic modulus ($E$) of each material system. $B$ and $G$ are calculated with the Voigt approximation ($B_v$ and $G_v$) [40] and the Reuss approximation ($B_r$ and $G_r$) [40,41]. The Voigt approximation is based on the assumption that the strain throughout the polycrystalline aggregate is uniform, while the Reuss approximation is based on the assumption that the stress in uniform [40]. For a hexagonal lattice, the Voigt shear modulus, $G_v$, and the Voigt bulk modulus, $B_v$, are:

\[
G_v = \frac{1}{15} (2c_{11} + c_{13} - c_{12} - 2c_{13}) + \frac{1}{5} (2c_{44} + (c_{11} - c_{12})/2) \\
B_v = \frac{2}{9} (c_{11} + c_{12} + 2c_{13} + c_{13}/2)
\]

(10)

(11)

The Reuss shear modulus, $G_r$ and Reuss bulk modulus, $B_r$ for a hexagonal lattice are:

\[
G_r = \frac{1}{15} \left( \frac{4(2s_{11} + s_{13}) - 4(s_{12} + 2s_{13}) + 3(2s_{44} + s_{66})}{4s_{11} + 2s_{13} + 2s_{11}} \right) \\
B_r = \frac{1}{(2s_{11} + s_{13}) + 2(s_{12} + 2s_{11})}
\]

(12)

(13)

For the calculation of the Young’s modulus in both cases, i.e., $E_v$ and $E_r$, the following relation was used [40]:

\[
E = \frac{9BG}{3B+G}
\]

(14)

In order to determine if the systems are elastically anisotropic the universal elastic anisotropy index, $A''$, was calculated [42]:

\[
A'' = \frac{5G_v}{B_v} + \frac{E_v}{E_r} - 6
\]

(15)

At each pressure, it is valid for the elastic constants in Tables 1–3 that $c_{11} > |c_{12}|$, $2c_{13} < c_{44}(c_{11} + c_{12})$, $c_{44} > 0$ and $c_{11} - c_{12} > 0$, which are the necessary and sufficient conditions for elastic stability (Born criteria) in the case of a hexagonal crystal structure [43]. This means that all three phases are elastically stable at higher pressure. ScTaN$_2$ and ScNbN$_2$ are stable at ambient pressures and their stability increases with increasing pressure. No other ternary phases are known to exist in these systems. It is thus likely that these phases that will be stable at higher pressures. The case of ScVN$_2$ is
somewhat more complicated since $\Delta H > 0$ at 0 GPa; however, that is assuming the 0 K h-VN is the most competing phase. Assuming instead that c-VN is the competing phase, since this is the stable form of VN at room temperature, $\Delta H < 0$ already at 0 GPa. This means that the elastic constants also for pressures below 40 GPa are of interest.

For all three material systems (Tables 1–3), it can be noted that the elastic constants $C_{ij}$ for all indices $i,j$ increase with pressure. That is, increased pressure makes the materials stiffer. The change is largest for ScTaN$_2$ in Table 1. The changes in elastic constants also results in increase of the bulk, shear and elastic moduli as can be noted in Tables 1–3. The universal anisotropy indices in Tables 1–3 for 0 GPa are very low, which is comparable to the indices of other hexagonal systems and indicate that the anisotropy in elastic properties in these materials is limited [42]. It can furthermore be noted in Tables 1–3 that the universal anisotropy indices increase as the pressure increases. The change is most pronounced increase, when the pressure is increased from 0 GPa to 150 GPa in ScTaN$_2$, but it can be seen that ScVN$_2$ has the highest universal anisotropy index at 150 GPa.

Fig. 3 shows the calculated total and partial DOS of ScTaN$_2$. The figure shows two cases, 0 GPa (Fig. 3a) and 150 GPa (Fig. 3b). The basic structure of the DOS does not change significantly, but it can be noted when the two figures are compared that peaks in the high-pressure graphs are shifted towards lower energies and that the states of each energy value are lower. All bands in the DOS have also become broader.

Fig. 4 shows the calculated total and partial DOS of ScNbN$_2$ of the case 0 GPa (Fig. 4a) and 150 GPa (Fig. 4b). Fig. 5 shows the calculated total and partial DOS of ScVN$_2$ and at 0 GPa (Fig. 5a) and 150 GPa (Fig. 5b). In both cases, it can be noted that the peaks in the high-pressure case have shifted towards lower energies that the number of states of each energy value is lower and that each band has become broader, just like for ScTaN$_2$. When the high-pressure effects between Figs. 3–5 are compared, the shift of the bands are most pronounced in Fig. 5 and least in Fig. 3. This means that broadening of the bands and the shift of bands are largest in the ScVN$_2$ case and lowest in the ScTaN$_2$ case. The general trends are that with increasing pressure, the interatomic distances decrease, which in turn lead to an overlap of the electronic wave functions. The total number of electronic states does not change with pressure. Therefore, the number of states of each energy level is decreased, but the energy bands are broader.

Conclusions

We have used DFT calculations to investigate the formation enthalpies relative to the competing binary phases, elastic properties and DOS ScTaN$_2$, ScNbN$_2$ and ScVN$_2$ under high pressure. Increased pressure has a stabilizing effect of the thermodynamics of the three phases relative to their competing phases. The elastic constants and, bulk, shear, and elastic moduli increase in the range 53–216 % for ScTaN$_2$, 72–286% for ScNbN$_2$, and 61–317% for ScVN$_2$, when pressure increases from 0 to 150 GPa the elastic anisotropy is relatively limited but increases in all three phases for increasing pressure. This study suggests that these phases are interesting to study further experimentally at high-pressure conditions.
Fig. 3. Total DOS and DOS projections for ScTaN$_2$ at a) 0 GPa b) 150 GPa.
Fig. 4. Total DOS and DOS projections for ScNbN$_2$ at a) 0 GPa b) 150 GPa.
Fig. 5. Total DOS and DOS projections for ScVN$_2$ at a) 0 GPa b) 150 GPa.
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