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Prediction of MAX phases, $V_{N+1}SiC_N$ ($N=1,2$), from first-principles theory

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We have investigated the phase stability of two MAX phases, $V_3SiC_2$ and $V_2SiC$, by means of first-principles total-energy calculations within the generalized-gradient approximation and the projector-augmented wave method. The theoretical bulk modulus of $V_3SiC_2$ is 219 GPa, which is $\sim 17\%$ larger than that of $Ti_3SiC_2$ (187 GPa). The total-energy calculations show that $V_2SiC$ is stable with a formation energy of about 0.27 eV/f.u. and that $V_3SiC_2$ is metastable (only 0.02 eV/f.u. is required to stabilize this phase from its competing phases). We suggest that both these two MAX compounds should be possible to synthesize as stable (or metastable) phases using, e.g., thin-film deposition. © 2007 American Institute of Physics. [DOI: 10.1063/1.2405721]

INTRODUCTION

In recent years a group of inorganic nanolayered compounds with chemical formula $M_{N+1}AX_N$ (hence named MAX phases), where $N=1,2,3$, $M$ is an early transition metal, $A$ an A-group element, and $X=C$ or $N$, has become the subject of intensive studies. The MAX phases have remarkable physical properties, such as good electrical conductivity, exceptional shock resistance and damage tolerance, high loss factor, fully reversible plasticity, negligible thermopower, and high thermal conductivity. These unique properties make them potentially interesting for applications. Until now most MAX compounds have composition of $M_2AX$ (211, in short). Although much attention has been paid to the prototype Ti$_3$SiC$_2$, more MAX phases with formula $M_3AX_2$ (312, in short) with superior physical properties remain to be explored. Our recent theoretical simulations have shown that the mechanical properties of $M_3SiC_2$ crystals are determined primarily by the MC layers. The hardness of the MC component largely determines the stiffness of the MAX crystal. Since VC is much harder than TiC, $V_3SiC_2$ is expected to be a stiffer material than Ti$_3$SiC$_2$. However, until now there is little known about compounds in the V-Si-C system.

The phase diagram of the V-Si-C system was investigated by Schuster and co-workers. The ternary V-based MAX phases are competing with the binary compounds VC, SiC, and $V_3Si_3$, as shown in Fig. 1. Here we report the results of the first-principles calculations for the two ternary compounds, $V_3SiC_2$ and $V_2SiC$. The stability of the ternary compounds with respect to their competing binary phases is investigated by means of first principles total energy calculations. The crystal structures and the mechanical and electronic properties are also presented here.

DETAILS OF CALCULATIONS

Theoretical calculations were carried out using the first-principles molecular-dynamics code VASP (Vienna $ab$ initio simulation program) with the generalized-gradient approximation (GGA) and projector-augmented wave (PAW) potentials. The electronic wave functions were sampled on a $12 \times 12 \times 4$ mesh or 69 (57) $k$ points in the Brillouin zone (BZ) for $V_3SiC_2$ ($V_2SiC$), a $24 \times 24 \times 16$ mesh or 549 $k$ points for SiC, and on a $24 \times 24 \times 24$ mesh or 413 $k$ points for VC (with the NaCl-type structure). For $V_3Si_3$ an $8 \times 8 \times 6$ mesh with 40 $k$ points was employed in the BZ. For all the calculations the kinetic energy cutoff on the wave functions was 500 eV. The cutoff energy for the augmentation wave functions was 604 eV. Convergence of the total energy with the number of $k$ points and the plane-wave cutoff has been checked. Full relaxation of both lattice parameters and coordinates of atoms is performed for fixed volumes. The equilibrium volume and bulk modulus were calculated by a fit of the volume-energy curves using Murnaghan's equation of state.

CALCULATED RESULTS AND DISCUSSION

The calculated results involved the ratio of lattice parameters $c/a$, equilibrium volume, atomic coordinates, bulk modulus, and formation energy, and they are listed in Table I. We will return below to how the formation energy was calculated. In the table we also compare our results for $V_3SiC_2$ and $V_2SiC$ with the previously calculated values for Ti$_3$SiC$_2$ and Ti$_2$SiC. A schematic plot of the crystal structures of the two types of MAX phases (the 211 and 312 phases) is shown in Fig. 2. For Ti$_3$SiC$_2$ the calculated lattice parameters and atomic coordinates are found to be in good agreement with the experiments. The calculated volume is slightly larger.

![Fig. 1. The phase diagram of the V-Si-C ternary at 1573 K [after Fukai et al. (Ref. 12)].](image-url)
TABLE I. The calculated results for the $M_2SiC_3$ and $M_5SiC_2$ ($M=Ti$, V) compounds using the DFT-GGA method. All the phases have the same space group P6$_3$/mmc (No. 194). In the structure of (a) $-M_2SiC_3$, $M_1$ at 2a (0,0,0), $M_2$ at 4f (1/3,2/3,z$_d$), Si at 2b (0,0,1/4), and C at 4f (1/3,2/3,z$_d$). $\beta$-$M_5SiC_2$, with Si at 2d (1/3,2/3,1/4). In the structure of $M_5SiC_2$, $M$ at 4f (1/3,2/3,z$_d$), Si at 2d (1/3,2/3,1/4), and C at 2a (0,0,0).

<table>
<thead>
<tr>
<th></th>
<th>c/a</th>
<th>$z_M$</th>
<th>$z_C$</th>
<th>V ($\text{Å}^3$)</th>
<th>B (GPa)</th>
<th>$\delta E$ (eV/f.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_3$SiC$_2$</td>
<td>5.7823</td>
<td>0.1340</td>
<td>0.9279</td>
<td>145.80</td>
<td>187</td>
<td>0.03</td>
</tr>
<tr>
<td>V$_2$SiC$_2$</td>
<td>5.7811</td>
<td>0.1340</td>
<td>0.9279</td>
<td>143.50</td>
<td>190</td>
<td>0.03</td>
</tr>
<tr>
<td>$\beta$-Ti$_5$SiC$_2$</td>
<td>6.1641</td>
<td>0.1243</td>
<td>0.9312</td>
<td>155.50</td>
<td>219</td>
<td>0.02</td>
</tr>
<tr>
<td>V$_5$SiC$_2$</td>
<td>6.0150</td>
<td>0.1318</td>
<td>0.9295</td>
<td>129.06</td>
<td>219</td>
<td>0.02</td>
</tr>
<tr>
<td>$\beta$-V$_5$SiC$_2$</td>
<td>6.2093</td>
<td>0.1245</td>
<td>0.9309</td>
<td>134.77</td>
<td>219</td>
<td>0.02</td>
</tr>
<tr>
<td>Ti$_3$SiC</td>
<td>3.9420</td>
<td>0.0919</td>
<td>103.81</td>
<td>180</td>
<td>-0.20</td>
<td></td>
</tr>
<tr>
<td>V$_3$SiC</td>
<td>4.0553</td>
<td>0.0929</td>
<td>90.62</td>
<td>-0.27</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Reference 7.*

*Reference 19.

*Reference 20.

Then the experimental data, which is not atypical for this kind of first principles calculations, using GGA. The volume of $V_3SiC_2$ is calculated to be smaller than that of Ti$_3$SiC$_2$. A slightly larger c/a is found for V$_2$SiC$_2$ as compared to that of Ti$_3$SiC$_2$. Correspondingly V$_3$SiC$_2$ also has a smaller volume and larger c/a ratio than the corresponding values of Ti$_3$SiC$_2$. The bulk modulus for Ti$_3$SiC$_2$ is calculated to be 187 GPa, which is close to the somewhat scattered experimental data, shown in Table I. The bulk modulus is calculated to be about 219 GPa for V$_3$SiC$_2$, which is about 17% larger than that of Ti$_3$SiC$_2$. This trend agrees with the calculated trend of the bulk modulus for the parent compounds, i.e., TiC (~260 GPa) and VC (~310 GPa).

Structural optimizations have been performed for the binary components V$_5$Si$_3$, SiC, and VC. V$_5$Si$_3$ has a hexagonal structure with optimized lattice parameter $a=7.1258$ Å, $c=4.8180$ Å, and $V=211.87$ Å$^3$. The lattice parameters are slightly smaller than the experimental values $a=7.161$ Å and $c=4.762$ Å for V$_5$Si$_3$C. It should be noted here that experimentally the latter phase is always found to be substoichiometric and the true chemical formula should read V$_5$Si$_3$C$_x$ (with $x<1$). The small disagreement between theory and experiment for this phase is most likely due to the calculation for simplicity is made for a stoichiometric sample. The layered hexagonal structure of SiC is calculated to have lattice parameters of $a=3.0910$ Å and $c=5.0759$ Å, in good agreement with the experimental data. For VC the lattice parameter is calculated to be 4.1579 Å, in good agreement with the experiment and previous theoretical calculations.

The phase stability of the different MAX phases was calculated using the following formula:

$$\delta E_{V_5SiC_2} = E_{V_5SiC_2} - [7E_{VC} + (E_{V_3Si_3} + E_{SiC})]/4,$$

(1)

$$\delta E_{V_3SiC_2} = E_{V_3SiC_2} - [3E_{VC} + (E_{V_3Si_3} + E_{SiC})]/4.$$

(2)

If the calculated value is negative, the corresponding MAX phase has a lower total energy than the competing phases in the ternary phase diagram [as can be seen in Eqs. (1) and (2) these phases are VC, V$_3$Si$_3$, and SiC] and one would expect the MAX phase to be a stable phase. From our theoretical calculations we obtain $\delta E_{V_5SiC_2} = -0.02$ eV/f.u. and $\delta E_{V_3SiC} = -0.27$ eV/f.u. From this we draw the conclusion that the 211 phase is stable and that the 312 phase is unstable, but only with a very small energy. Hence, it is unlikely that also the 312 phase should be possible to stabilize as a meta-stable compound.

Since there is some ambiguity concerning what phases to treat as competing phases in the ternary phase diagram we also investigated the phase stability of the 211 and 312 phases with respect to VC, V$_5$Si$_3$, and V$_3$Si$_3$. From the formulas

$$\delta E_{V_5SiC_2} = E_{V_5SiC_2} - [2E_{VC} + (E_{V_3Si_3} + 2E_{SiC})]/7,$$

(3)

$$\delta E_{V_3SiC_2} = E_{V_3SiC_2} - [E_{VC} + (E_{V_3Si_3} + 2E_{SiC})]/7,$$

(4)

we obtained $\delta E_{V_5SiC_2} = -0.01$ eV/f.u., and $\delta E_{V_3SiC} = -0.27$ eV/f.u., i.e., values which are very close to the results from Eqs. (1) and (2). For reason of comparison, similar calculations have been performed for the ternary MAX phases in the Ti–Si–C system, in which the ternary compounds are competing with TiC, Ti$_3$Si$_3$, and Ti$_5$Si$_5$. The differences of the cohesive energies of these ternary MAX phases relative to their competing phases are listed in Table I. The present calculations show that Ti$_5$SiC$_2$ is stable compared with the competing binaries TiC, Ti$_3$Si$_3$, and Ti$_5$Si$_5$, by about 0.20 eV/f.u., and compared to the competing phases Ti$_3$SiC$_2$ and TiC, by about 0.23 eV/f.u. This finding is in agreement with the former theoretical results by Palmquist et al. who concluded that Ti$_5$SiC$_2$ is more stable (about 0.008 eV/at.) than the competing binary phases (Ti$_3$SiC$_2$, Ti$_5$Si$_3$, TiC, and Ti$_5$Si$_5$). Table I also shows that Ti$_5$SiC$_2$ is unstable, but only with a small energy, 0.02 eV/f.u., compared to the competing phases. It is notable that experimentally Ti$_3$SiC$_2$ bulk samples have been prepared, while Ti$_5$SiC bulk remains to be prepared. Based on this fact, and that the phase stabilities of the Ti-based and V-based systems are rather similar, we conclude that it is not unlikely that V-based MAX phases with 211 and 312 compositions should be possible to stabilize.

Another polymorphic ($\beta$-) Ti$_{n+1}AX_n$ ($n \geq 2$) phases with a previous structure being named ($\alpha$-) form were suggested by Farber et al. and later confirmed by other groups. The difference between the $\alpha$- and $\beta$- Ti$_{n+1}AX_n$ is that the A atoms occupy the 2b Wyckoff sites with the fractional coordinates (0,0,1/4) in the $\alpha$ form while in the $\beta$ phase the A atoms...
The calculated results are included in Table I. The calculations show that \( \beta \)-Ti3SiC2 has a slightly shorter \( a \) axis, longer \( c \) axis, and larger \( c/a \) ratio, the same as found in the previous work.\(^{25}\) \( \alpha \)-Ti3SiC2 is much more stable than \( \beta \)-Ti3SiC2, in line with the former theoretical work.\(^{25-27}\) The length of the \( a \) axis of \( \beta \)-V3SiC2 is calculated to be about 2.9266 \( \text{Å} \), which is slightly larger than that (2.9158 \( \text{Å} \)) of the \( \alpha \) form while the \( c \) axis (18.1717 \( \text{Å} \)) of \( \beta \)-V3SiC2 is much longer than that (17.5248 \( \text{Å} \)) of the \( \alpha \) phase. The calculations also show that \( \alpha \)-V3SiC2 is much more stable. Similar to the case of Ti3SiC2, if \( \beta \)-V3SiC2 is to be found it is probably a high-temperature or high-pressure phase.

Figure 3 shows for completion the partial and total densities of state (DOSs) for V3SiC2 and V2SiC. A similarity between the DOSs of the ternary carbides can be easily recognized. The DOS curves form continuous states from about—13.5 (−13.0) to about 3.5 (4.5) eV for V3SiC2 (V2SiC). It is easily recognized that the V 3d partial DOS in V3SiC2 is quite similar to that of the 3d projected V1 atoms in V3SiC2, i.e., the V atoms in the 312 compound that have similar chemical environment to the V atoms in the 211 compound. In both compounds, the semicore (C 2s and Si 3s) electrons have rather broad bands. In the middle of the energy band, the Si 3s states are located with a band that is rather broad (about 5.0 eV) for both compounds. The covalent chemical bonding in the ternary carbides originates mainly from the interaction (hybridization) between the V 3d and the \( p \) states of C and Si.

In summary first-principles calculations have been performed for the stability and physical properties of V3SiC2 and V2SiC. It is predicted that V3SiC2 is stable at ambient conditions and V2SiC2 is close to being stable. V3SiC2 is predicted to have a bulk modulus of \( \sim 17\% \) larger than the well-known Ti3SiC2 compound. It is likely that V3SiC2 and V2SiC2 are possible to be prepared by techniques such as thin-film deposition.

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