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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$_3$SiC$_2$ and V$_2$SiC, 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$_3$SiC$_2$ is 219 GPa, which is ~17% larger than that of Ti$_3$SiC$_2$ (187 GPa). The total-energy calculations show that V$_2$SiC is stable with a formation energy of about 0.27 eV/f.u. and that V$_3$SiC$_2$ 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$_3$SiC$_2$ 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$_3Si$, as shown in Fig. 1. Here we report the results of the first-principles calculations for the two ternary compounds, V$_3$SiC$_2$ and V$_2$SiC. 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$_3$SiC$_2$ (V$_2$SiC), 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$_3$Si$_3$ 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$_3$SiC$_2$ and V$_2$SiC 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...
TABLE I. The calculated results for the $M_2SiC_2$ and $M_3SiC$ ($M$=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) $M_2SiC_2$, M1 at 2a (0,0,0), M2 at 4f (1/3,2/3,z$_M$), Si at 2b (0,0,1/4), and C at 4f (1/3,2/3,z$_C$). $\beta$-$M_2SiC_2$ with Si at 2d (1/3,2/3,1/4). In the structure of $M_3SiC$, M at 4f (1/3,2/3,z$_M$), Si at 2d (1/3,2/3,1/4), and C at 2a (0,0,0).

<table>
<thead>
<tr>
<th>$c/a$</th>
<th>$z_M$</th>
<th>$z_C$</th>
<th>$V$ (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>
</tr>
<tr>
<td>Ti$_2$SiC$_2$</td>
<td>5.7811</td>
<td>0.1348</td>
<td>0.9328</td>
<td>143.50</td>
<td>190</td>
</tr>
<tr>
<td>V$_3$SiC$_2$</td>
<td>6.1464</td>
<td>0.1243</td>
<td>0.9312</td>
<td>155.50</td>
<td>210</td>
</tr>
<tr>
<td>V$_2$SiC$_2$</td>
<td>6.0150</td>
<td>0.1318</td>
<td>0.9295</td>
<td>129.06</td>
<td>219</td>
</tr>
<tr>
<td>V$\beta$V$_2$SiC$_2$</td>
<td>6.2093</td>
<td>0.1245</td>
<td>0.9309</td>
<td>134.77</td>
<td>211</td>
</tr>
<tr>
<td>Ti$_3$SiC</td>
<td>3.9420</td>
<td>0.0919</td>
<td>0.1038</td>
<td>180</td>
<td>0.20</td>
</tr>
<tr>
<td>V$_2$SiC</td>
<td>4.0553</td>
<td>0.0929</td>
<td>0.9620</td>
<td>0.20</td>
<td></td>
</tr>
</tbody>
</table>


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 $\delta E_{V_3SiC_2} = 0.02$ eV/f.u. and $\delta E_{V_2SiC} = -0.27$ 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 not 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$_3$Si$_3$, and V$_2$Si$_2$. From the formulas

$$\delta E_{V_3SiC_2} = E_{V_3SiC_2} - [2E_{VC} + (E_{V_3Si_3} + E_{SiC})]/4,$$

$$\delta E_{V_2SiC} = E_{V_2SiC} - [E_{VC} + (E_{V_3Si_3} + E_{V_2Si_2})]/4,$$

we obtained $\delta E_{V_3SiC_2} = 0.01$ eV/f.u., and $\delta E_{V_2SiC} = -0.27$ 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$_2$Si$_2$. 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$_3$SiC$_2$ is stable compared with the competing binaries TiC, Ti$_3$Si$_3$, and Ti$_2$Si$_2$, by about 0.20 eV/f.u., and compared to the competing phases Ti$_3$Si$_2$ 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$_3$SiC is more stable (about 0.008 eV/atom) than the competing binary phases (Ti$_3$Si$_2$, Ti$_3$Si$_3$, TiC, and Ti$_2$Si$_2$). Table I also shows that Ti$_2$SiC$_3$ 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$_3$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

FIG. 2. Crystal structure of $M_2SiC$ [(a) left] and $M_3SiC_2$ [(b) right]. The big black balls represent the Si atoms, the small black balls the C atoms, and the light small balls the M atoms.
atoms occupy the 2d sites with the fractional coordinates (1/3, 2/3, 1/4). Theoretical analysis found that the $\beta$-Ti$_3$SiC$_2$ structures are less favored than the $\alpha$ form. $\beta$-Ti$_{n+1}$AX$_n$ structures might be stabilized at high pressure or high temperature.

Total-energy calculations have been performed for $\beta$-V$_3$SiC$_2$, as well as $\beta$-Ti$_3$SiC$_2$ for the sake of comparison. The calculated results are included in Table I. The calculations show that $\beta$-Ti$_3$SiC$_2$ has a slightly shorter $a$ axis, longer $c$ axis, and larger $c/a$ ratio, the same as found in the previous work. $\alpha$-Ti$_3$SiC$_2$ is much more stable than $\beta$-Ti$_3$SiC$_2$, in line with the former theoretical work.

The length of the $a$ axis of $\beta$-V$_3$SiC$_2$ is calculated to be about 2.9266 Å, which is slightly larger than that (2.9158 Å) of the $\alpha$ form while the $c$ axis (18.1717 Å) of $\beta$-V$_3$SiC$_2$ is much longer than that (17.5248 Å) of the $\alpha$ phase. The calculations also show that $\alpha$-V$_3$SiC$_2$ is much more stable. Similar to the case of Ti$_3$SiC$_2$, if $\beta$-V$_3$SiC$_2$ 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 V$_3$SiC$_2$ and V$_3$SiC$_2$. A similarity between the DOSs of the two ternary compounds can be easily recognized. The DOS curves form continuous states of C and Si.

In summary first-principles calculations have been performed for the stability and physical properties of V$_3$SiC$_2$ and V$_3$SiC$_2$. It is predicted that V$_2$SiC is stable at ambient conditions and V$_3$SiC$_2$ is close to being stable. V$_3$SiC$_2$ is predicted to have a bulk modulus of $\sim$17% larger than the well-known Ti$_3$SiC$_2$ compound. It is likely that V$_2$SiC and V$_3$SiC$_2$ are possible to be prepared by techniques such as thin-film deposition.

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