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ScienceDirect
Scripta Materialia 58 (2008) 1043–1046
Scripta MATERIALIA
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# Ab initio study of polymorphism in layered ternary carbide $M_4AlC_3$ (M = V, Nb and Ta)

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Received 25 September 2007; revised 10 January 2008; accepted 14 January 2008
Available online 16 February 2008

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The mechanical and thermodynamic stabilities of $M_4AlC_3$ (M = V, Nb and Ta) and $Ti_4AlN_3$ polymorphs were investigated by means of the first-principles pseudopotential total energy method. All compounds satisfied the Born criteria for mechanical stability, but had different thermodynamic stabilities. Only $Ta_4AlC_3$ showed a possible polymorphic phase transformation driven by thermodynamic competition. The present theoretical results support the polymorphism of $Ta_4AlC_3$ in experimental synthesis and explain the underlying thermodynamic mechanism. Polymorphism was excluded from $V_4AlC_3$, $Nb_4AlC_3$ and $Ti_4AlN_3$.

*Keywords:* Carbides; Phase stability; Density functional calculation; Thermodynamic

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Layered ternary $M_{n+1}AX_n$ (where M is an early transition metal, A is an A-group element and X is carbon and/or nitrogen) ceramics are promising candidates for high-temperature structural applications. These ceramics crystallize in the space group $P6_3/mmc$ and contain two structural units alternately stacking along the *c* direction: the NaCl-type non-stoichiometric transition metal carbide or nitride slab, and the close-packed A-group atomic plane. Due to this layered crystal structure, these compounds exhibit an unusual combination of the properties of both carbides/nitrides and metals, such as low density, high elastic moduli, good high-temperature stability, high thermal and electrical conductivities, excellent thermal shock resistance, damage tolerance and micro-scale ductility at room temperature [1]. $M_{n+1}AX_n$ ceramics are classified into three groups with respect to the value of *n*, e.g. $M_2AX$ for $n = 1$, $M_3AX_2$ for $n = 2$, and $M_4AX_3$ for $n = 3$. To date, approximately 50 $M_2AX$ phases [2] and five $M_3AX_2$ compounds ($Ti_3SiC_2$, $Ti_3GeC_2$, $Ti_3AlC_2$, $Ti_3SnC_2$ and $Ta_3AlC_2$) have been identified experimentally [3–7]. For $M_4AX_3$ phases, $Ti_4AlN_3$, $V_4AlC_{3-x}$ ($x \approx 0.31$), $Nb_4AlC_3$ and $Ta_4AlC_3$ have been synthesized [8–12] in bulk form; and $Ti_4SiC_3$ and $Ti_4GeC_3$ have appeared in thin films synthesized by magnetron sputtering [13–15].

$M_{n+1}AX_n$ compounds show interesting polymorphism, which has been actively investigated in recent years [16–22]. For $M_2AX$ and $M_3AX_2$ ceramics, polymorphism was traced to the A-group atom occupying different internal positions in the unit cell; the transition metal carbide or nitride slabs remained unchanged [16–21]. Polymorphic phase transformation was reported to involve the A-group atom sliding along the (0001) basal plane between two local minimum positions on the energy surface. For the $M_4AX_3$ compounds, on the other hand, polymorphism was only reported for $Ta_4AlC_3$. Structural differences mainly reside within the $Ta_4C_3$ slab [12,21], as shown in Figure 1. The crystal structure of α-$Ta_4AlC_3$ shows a stacking sequence AB$\underline{A}$BACB$\underline{C}$BC for transition metal Ta and Al atoms along the [0001] direction [21]; β-$Ta_4AlC_3$ has a stacking sequence AB$\underline{A}$BABA$\underline{B}$AB [12]. Other experimentally identified $M_4AX_3$ compounds, such as $Ti_4AlN_3$, $V_4AlC_3$, $Nb_4AlC_3$, $Ti_4SiC_3$ and $Ti_4GeC_3$, only show the α-type crystal structure.

Since transition metal atoms V and Nb have the same valence electrons as Ta, polymorphism would be expected for $V_4AlC_3$ and $Nb_4AlC_3$ too. However, $Ta_4AlC_3$ distinguished itself from the other compounds. The reason for this discrepancy is not clear and needs to be

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doi:10.1016/j.scriptamat.2008.01.058

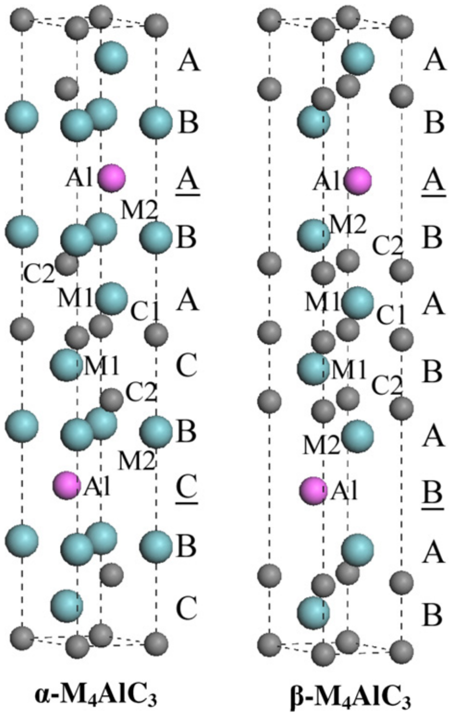

**Figure 1.** Crystal structures of $M_4AlC_3$ polymorphs.

explained. The results may contribute to a better understanding of the crystal structure and phase stability of ternary $M_4AX_3$ compounds. In the present paper, we studied the mechanical and thermodynamic stabilities of $V_4AlC_3$, $Nb_4AlC_3$, $Ta_4AlC_3$ and $Ti_4AlN_3$ polymorphs. The hypothetical crystal structures of β-type $V_4AlC_3$, $Nb_4AlC_3$ and $Ti_4AlN_3$ were constructed with respect to that of β-$Ta_4AlC_3$. Elastic coefficients and Gibbs free energy were calculated to study the mechanical and thermodynamic stabilities of the two possible polymorphic structures. The results showed that only $Ta_4AlC_3$ displayed a possible polymorphic phase transformation driven by thermodynamic competition.

Calculations were accomplished using the CASTEP code, in which the plane-wave pseudopotential total energy calculation was employed [23]. The plane-wave energy cutoff and the Brillouin zone sampling were fixed to 450 eV and $9 \times 9 \times 2$ special $k$-point meshes [24], respectively. Interactions of electrons with ion cores were represented by the Vanderbilt-type ultrasoft pseudopotential [25]. The electronic exchange-correlation energy was treated under the generalized gradient approximation (GGA-RPBE) [26]. The equilibrium crystal structures were fully optimized by independently modifying lattice parameters and internal atomic coordinates. The Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization scheme [27] was used to minimize the total energy and interatomic forces. The second-order elastic coefficients were determined by means of the linear fitting of the stress–strain relationship. The computational strategies can be referenced in our previous works, wherein crystal structure, elastic stiffness and interatomic force constants of layered ternary carbides and complex oxides such as $LaPO_4$ monazite, $Y_2Si_2O_7$ and $La_2Zr_2O_7$ pyrochlore were investigated [28–33].

The thermodynamic stabilities were investigated by comparing the free energy difference of the corresponding polymorphs. The most stable structure of any compound at a given temperature is the one with the lower Gibbs free energy, $G$, given by

$$G(p,T) = F(V,T) + pV, \tag{1}$$

where $F$ is the Helmholtz free energy, and is the summation of vibrational free energy $F_{\text{vib}}$ and perfect lattice energy $F_{\text{perfect}}$ ($F_{\text{perfect}} = U_0 + U_{\text{el}} - TS_{\text{el}}$). The $U_0$ and $U_{\text{el}}$-$TS_{\text{el}}$ are contributions from the lattice and electronic excitations, respectively. The vibrational free energy $F_{\text{vib}}$ is calculated within the harmonic approximation:

$$F_{\text{vib}} = k_B T \sum_i \left( \frac{h\omega_i}{2k_B T} + \ln\left(1 - e^{\frac{h\omega_i}{k_B T}}\right)\right), \tag{2}$$

where $\omega_i$ is the phonon frequency, $T$ the absolute temperature, $h$ the Planck constant and $k_B$ the Boltzmann constant. If the electronic excitations and pressure changes are neglected, the Gibbs free energy is given by $G = U_0 + F_{\text{vib}}$. Phonon frequencies were calculated via a direct force constant approach [34,35].

The mechanical stability of the polymorphs was investigated first. The fundamental basis for the study of the mechanical stability of a crystal lies on the formulation of stability criteria, a set of conditions that specify the critical internal strain or external stress under which the homogeneous crystal lattice becomes structurally unstable. Born and Huang systematically studied the lattice mechanical stability and formulated stability criteria in terms of the elastic constants $c_{ij}$. The Born criterion for a lattice to be mechanically stable is that the elastic energy density must be a positive definite quadratic function of strain. For a hexagonal crystal, only five elastic constants are independent, and in this case the mechanical stability criterion is [36]:

$$c_{11} + c_{12} - \frac{2c_{13}^2}{c_{33}} > 0, \quad c_{44} > 0, \quad \text{and}$$
$$c_{66} = \frac{c_{11} - c_{12}}{2} > 0. \tag{3}$$

The theoretical second-order elastic coefficients of studied $M_4AX_3$ compounds are listed in Table 1. All investigated polymorphs satisfy the mechanical stability conditions presented in Eq. (3). The results suggest that all phases are stable from the point of view of mechanical stability. Therefore, thermodynamic stability is considered in order to explain the absence of some polymorphic phases in experimental synthesis.

**Table 1.** Theoretical second-order elastic coefficients $c_{ij}$ (in GPa) of $Ti_4AlN_3$ and $M_4AlC_3$ (M = V, Nb and Ta) polymorphs

| Compound | $c_{11}$ | $c_{12}$ | $c_{13}$ | $c_{33}$ | $c_{44}$ | $c_{66}$ |
|---|---|---|---|---|---|---|
| α-$V_4AlC_3$ | 435 | 121 | 105 | 384 | 168 | 157 |
| β-$V_4AlC_3$ | 381 | 85 | 129 | 350 | 130 | 148 |
| α-$Nb_4AlC_3$ | 413 | 124 | 135 | 328 | 161 | 144 |
| β-$Nb_4AlC_3$ | 420 | 110 | 122 | 381 | 124 | 155 |
| α-$Ta_4AlC_3$ | 496 | 154 | 181 | 417 | 200 | 171 |
| β-$Ta_4AlC_3$ | 509 | 143 | 156 | 440 | 147 | 183 |
| α-$Ti_4AlN_3$ | 387 | 96 | 96 | 352 | 153 | 145 |
| β-$Ti_4AlN_3$ | 389 | 90 | 85 | 380 | 112 | 149 |