On the heat capacity of Ti$_3$GeC$_2$

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Abstract

In this paper, we report experimental data of the heat capacities, $c_p$, of bulk polycrystalline samples of Ti$_3$GeC$_2$ in the 3–260 K temperature range. The results obtained are compared with those on Ti$_3$SiC$_2$. The $c_p$ results are analyzed using the Debye and Einstein models and are compared to the heat capacities values calculated from first principles. At temperatures up to 10 K the main contributors to $c_p$ are electrons with $\gamma = 6.5$ (mJ/mol K$^2$) and phonons with a Debye temperature $\theta_D$ of 556 K. In that temperature range only four atoms of the six in a formula unit—most likely one Ge and three Ti atoms—contribute to $c_p$. In the 10–120 K temperature range excellent fits were obtained using a $\theta_D$ of 513 K and an optical mode with an Einstein temperature $\theta_E$ of 139 K. For $T > 120$ K, five additional optical modes with $\theta_E = 870$ K are required to properly fit the experimental results. The ab initio calculations throughout the temperature range (4–1500 K) show reasonably good agreement with the experimental data obtained particularly at low temperatures.

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1. Introduction

The ternary carbides with the general formula M$_{n+1}$AX$_n$, where $n = 1–3$, M is an A-group element (mostly IIIA and IVA), and X is C and/or N [1–4] form a large family of the layered hexagonal (space group $D_6h$-$P$6$_3$/mmc) compounds with two formula units per unit cell. By now it is fairly well established that these phases constitute a new class of solid best described as polycrystalline nanolaminates as a consequence of their layered structure and their propensity to kink and delaminate during deformation [2].

The M$_{n+1}$AX$_n$ phases combine an unusual, and sometimes unique, set of properties [2–12]. Like their corresponding binary carbides and nitrides, they are elastically stiff [5,6], have relatively low thermal expansion coefficients, good thermal and electrical conductivities, and are resistant to chemical attack [2]. They are relatively soft (1–5 GPa) and most readily machinable, thermal shock, and damage tolerant [2,4]. Moreover, some are fatigue [11], creep [12], and oxidation resistant [13]. At higher temperatures, they undergo a brittle to ductile transition [2]. At room temperature, they can be compressed to stresses up to 1 GPa and fully recover upon removal of the load, while dissipating 25% of mechanical energy [7]. The most studied of these phases is Ti$_3$SiC$_2$ compound [2]. Of special interest to this work is Ti$_3$GeC$_2$ and Ti$_3$SiC$_2$. The unit cell of both compounds consists of Ti$_3$X$_2$ layers interleaved with layers comprised of hexagonal nets of pure Si or Ge [14]. Because the Si to Si and Ge to Ge distances along $a$ (≈3.07 Å) in the ternaries are considerably longer than their covalent bonding in pure Si (2.35 Å) and Ge (2.44 Å) consequently, these atoms act as rattlers that tend to vibrate along the $a$-direction [2]. The bonding in these compounds is comparable to TiC, viz. a combination of ionic, covalent, and metallic characters [2,15]. However, the density of states (DOS) of 5 (eV unit cell)$^{-1}$ at the Fermi level for Ti$_3$SiC$_2$ [15] is considerably larger than in TiC. Ti$_3$SiC$_2$ is roughly twice as electrically and thermally conductive as Ti [16,17]. While currently the low temperature properties of Ti$_3$SiC$_2$ are

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reasonably well characterized [18–22], the same information for Ti3GeC2 does not exist. Recently, a number of papers have been published on the properties of Ti3GeC2 and its solid solutions with Ti3SiC2 [23,24]. In ref. 24 the room temperature elastic, and low (4–300 K) temperature transport properties of Ti3SiC2−xGeC2 were measured and found to be quite insensitive to x. Young’s modulus of Ti3GeC2 is 340 GPa and its thermal expansion coefficient in the 25–1200 °C temperature range is 7.8 × 10−6 °C−1. In another paper [23] it was shown that the mechanical properties are also quite insensitive to x.

The purpose of this paper is to report on and analyze the heat capacities, cp, for Ti3GeC2 over the 3–260 K temperature range. These results are compared with those of the isostructural Ti3SiC2, as well as ab initio calculations of cp.

2. Experiment

The synthesis procedure is described in detail in ref. [23]. In short, stoichiometric mixtures of Ti, C and Ge powders were hot pressed at 1600 °C for 48 h in an argon atmosphere to render the samples single phase. The polished samples were microstructurally characterized using an optical microscope (PMG3, Olympus, Tokyo, Japan) and a field emission scanning electron microscope, FESEM (XL-30, FEI-Philips, Hillsboro, OR) equipped with an energy dispersive spectroscope, EDS (Edax Inc., Mahwah, NJ). The predominantly single phase Ti3SiC2 samples contained ~3 vol% TiO2. All samples were >99% dense.

The cp measurements were carried out between 3 and 260 K, using two different adiabatic calorimeters. In the first, which operates in the 2–70 K temperature range, a small bulk sample (~1 g) is thermally anchored by Apiezon N grease to a sapphire plate, which, in turn, is suspended by threads inside the adiabatic shield. Also mounted on the plate are a resistance thermometer Cernox 1030-3C and a nichrome heater. The calorimeter is fully automated. In the second device, which operates in the 2–280 K temperature range, a larger bulk piece (~2.5 g) is thermally connected with a slope 45 MPa. The samples were then annealed in 1600 °C for 48 h in an argon atmosphere to render the samples single phase. The polished samples were microstructurally characterized using an optical microscope (PMG3, Olympus, Tokyo, Japan) and a field emission scanning electron microscope, FESEM (XL-30, FEI-Philips, Hillsboro, OR) equipped with an energy dispersive spectroscope, EDS (Edax Inc., Mahwah, NJ). The predominantly single phase Ti3SiC2 samples contained ~3 vol% TiO2. All samples were >99% dense.

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In both cases, a computer was used to control the set-up and acquire the data. The cp of each sample was obtained by subtracting the addenda contributions.

3. Results and discussion

The temperature dependence of cp for Ti3GeC2 is depicted in Fig. 1.

Table 1 list the cp values for Ti3GeC2 together with its relevant thermodynamic functions.

For metallic-like, three-dimensional materials at the lowest temperatures, cp can be approximated by the well-known relationship

\[ \epsilon_p = \gamma T + \beta T^3 \]

where \( \gamma \) and \( \beta \) are the coefficients of electronic and lattice heat capacities, respectively.

A plot of \( \epsilon_p/T \) versus \( T^2 \) in the 3.3–10 K temperature range for Ti3GeC2 yields a straight line (lower inset in Fig. 1) with a slope \( \beta = 4.5 \pm 0.1 \times 10^{-3} \text{ mJ/mol K}^4 \) and intercept \( \gamma = 6.5 \pm 0.1 \text{ mJ/mol K}^2 \). The DOS at the Fermi level is thus calculated to be 5.52 (eV unit cell)−1, which is not too different from the value of 5 (eV unit cell)−1 obtained for Ti3SiC2.
It is also in reasonable agreement with the value of 4.3 (eV unit cell)\(^{-1}\) obtained from recent ab initio calculations [24]. In contradistinction with Ti3SiC\(_2\) no evidence was found here for an anomaly in \(c_p\) at the lowest temperatures [22].

At low temperatures, \(\beta\) in Eq. (1) is related to the Debye temperature \(\theta_D\) by

\[
\beta = \left(\frac{12}{13}\right) \frac{N c_p \theta_D^4}{R} \left(\frac{\theta_D}{T}\right)^3
\]  

(2)

where \(N\) is the number of modes per formula unit, and \(R\) is the molar gas constant. For simple solids with atoms that are not too different in mass, \(N = 3\pi\), where \(\pi\) is the number of atoms per formula unit and the calculation of \(\theta_D\) from Eq. (2) is straightforward. However, in cases when atoms with different masses are involved, not all of which may be participating fully in the acoustic vibrations—the latter an implicit assumption in Debye’s theory—it is not obvious what the \(\theta_D\) values should be. Following the arguments described in detail in ref. [22], here we again conclude that only 12 modes, or four atoms—most likely three Ti and one Ge—effectively contribute to the Debye lattice part of \(c_p\) in the lowest temperature regime.

Assuming \(N = 12\) in Eq. (2) results in \(\theta_D = 556\) K. Note that \(\theta_D\), as a rule, only describes the temperature dependence of \(c_p\) for \(T < \theta_D/10\). To better understand the various terms that contribute (apart from Debye) to \(c_p\) at slightly higher temperatures, it is useful to plot the \(c_p\) data as a \(c_p T^γ\) versus \(T\) (upper inset in Fig. 1). When plotted thusly, a maximum at \(T_{max} = 28\) K for Ti3GeC\(_2\) is evident. Such maximum is indicative of the presence of low (20–150 cm\(^{-1}\)) Einstein-like modes that accompany the Debye-like terms and contribute to the low temperature specific heat of many substances [25].

Assuming such modes are operative here, their contribution to the heat capacity is described by the Einstein function,

\[
cv = \frac{N_1 c_p}{\theta_D^4} \frac{1}{\sinh^2 \left( \frac{T}{\theta_D} \right)}.
\]  

(3)

where \(\theta_E\) is the Einstein temperature. In the low temperature regime, \(c_p\) is thus the sum of the well-known Debye function:

\[
cp = \gamma T + \frac{NRT^\gamma}{\theta_D^4} \int_0^{\theta_D} \frac{x^4 e^x}{(e^x - 1)^2} \, dx,
\]  

(4)

and Eq. (3). Keeping \(\gamma = 6.5\) (m J/mol K\(^4\)), \(N = 12\) in Eq. (4) and \(N_1 = 1\) in Eq. (3), a least squares fit in the 30–80 K temperature range, yields \(\theta_D = 513\) K, \(\theta_E = 139\) K (95 cm\(^{-1}\)). These parameters thus describe the specific heat of Ti3GeC\(_2\) in the 3–120 K temperature range (dashed line in Fig. 2).

The mode with an energy of \(\theta_E = 139\) K (95 cm\(^{-1}\)) may be associated with a shear mode analogous to that of Ti3SiC\(_2\) at \(\theta_E = 219\) K (152 cm\(^{-1}\)) [22]. While \(\theta_E = 152\) cm\(^{-1}\) is very close to the frequency of \(\omega = 159\) cm\(^{-1}\) found in the Raman spectra of Ti3SiC\(_2\) [26], the value of \(\theta_E = 95\) cm\(^{-1}\) estimated in our heat capacity measurements is lower than the peak at \(\omega = 144\) cm\(^{-1}\) as measured in the Raman scattering from Ti3GeC\(_2\) [24]; this peak is attributed to the vibration of the Ge atoms along the \(\omega\)-direction.

To fit the experimental data at \(T > 120\) K, more optical modes in the phonon density of states must be taken into account. As noted previously for Ti3SiC\(_2\) [22] some optical vibration modes associated mainly with the Ti=C=Ti bonds in the Ti3C octahedra become active only at higher temperatures. This conclusion is bolstered by recent Raman spectra studies [26] and ab initio calculations made for this compound [27]. In our previous paper [22] we modelled the contribution of the C atoms to \(c_p\) in Ti3SiC\(_2\) for 120 \(\leq T \leq 260\) K taking \(\theta_E = 942\) K for the carbon modes as deduced from the Raman scattering analysis [26] and assuming \(N^C = 6\) (see Fig. 9 in ref. [22]). To be sure that our assumption (\(N^C = 6\)) is valid also in the highest temperature range we repeated this calculation, but over a wider temperature range 120 \(\leq T \leq 1500\) K to enable comparison with experimental high temperature (\(T > 500\) K) \(c_p\) results for Ti3SiC\(_2\) taken from ref. [17]. All previously calculated low temperature parameters (see ref. [22]) were fixed here and the only variable was the number of carbon atom modes, \(N^C\). As seen in Fig. 3, much better agreement between the calculated \(c_p\) and measured \(c_p\) is obtained for \(N^C = 5\) rather than for \(N^C = 6\), suggesting that one of the C atom modes is participating at lower temperatures. Note that at \(T > 500\) K the agreement between the experimental and calculated results is pretty good: the difference \((c_p - \text{calc})\) for \(N^C = 5\), does not exceed 2% (Fig. 3). We neglected the possible difference \(c_p - \text{calc}\) caused by thermal expansion at high temperatures, which is at 1500 K smaller than 1.5 J/mol K.

The fact that the ab initio calculations (see below) actually bridge the two sets of experimental results lends them even more credence.

Unfortunately, similar high temperature \(c_p\) data for Ti3GeC\(_2\) do not exist. Nevertheless, we calculated \(c_p\) of Ti3GeC\(_2\) up to 1500 K, assuming, per analogy to Ti3SiC\(_2\), that at high temperatures only five of six carbon modes con-
Table 2

Summary of parameters deduced in this and previous work

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$ (mJ/mol K$^{-2}$)</td>
<td>6.41</td>
</tr>
<tr>
<td>$\beta$ (mJ/mol K$^{-4}$)</td>
<td>0.041</td>
</tr>
<tr>
<td>$\theta_D$ (K)</td>
<td>575</td>
</tr>
<tr>
<td>$\theta_E$ (K)</td>
<td>552</td>
</tr>
<tr>
<td>$T_c$ (&lt;10 K), $N_C = 1$</td>
<td>218</td>
</tr>
<tr>
<td>$T_c$ (&gt;20 K), $N_C = 5$</td>
<td>942</td>
</tr>
</tbody>
</table>

$T_c$ Ref. [22].

4. Conclusions

Based on this work we surmise that the total phonon densities of states in Ti$_3$GeC$_2$ and Ti$_3$SiC$_2$ are comparable, as is expected from symmetry considerations and the fact that these compounds only differ in their A group element. In particular, we note differences in the energies of low temperature, shear-like modes. Furthermore, an improvement in the fit of $c_p$ at $T > 500$ K is obtained if $N_C = 5$ compared with $N_C = 6$. It suggests that, apart from the Si in Ti$_3$SiC$_2$ and Ge atoms in Ti$_3$GeC$_2$, at least one of the vibrational modes involving the C atoms is a low-temperature mode. Therefore, only five modes appear to participate in $c_p$ at higher temperatures.

Finally, the first principles calculations of the $c_v$ show excellent agreement with experiment, particularly in the low temperature region. Further investigation is underway.

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