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Abstract
Using a synchrotron x-ray radiation source and a diamond anvil cell we measured the functional dependences of the lattice parameters of Cr_2GeC and V_2GeC to quasi-hydrostatic pressures of the order of 50 GPa. Like other solids in this family of layered ternary carbides and nitrides, the bulk moduli are high and no phase transformations were observed. The bulk modulus of V_2GeC (165 ± 2 GPa) is lower than that of Cr_2GeC (182 ± 2 GPa). Replacing Ge by Al in V_2GeC to form V_2AlC leads to a 22% increase in bulk modulus. In contradistinction, the same substitution in Cr_2GeC results in a 10% decrease in bulk modulus.

1. Introduction

The MAX phases are thermodynamically stable nanolaminates that display unusual and sometimes unique properties [1–4]. The $M_{n+1}AX_n$ (MAX) compounds, where $n = 1$, 2 or 3, M is an early transition metal, A is an A-group (mostly IIIA and IVA) element, and X is C or N, have been studied extensively over the past decade [1–9]. These ceramics adopt a hexagonal crystal structure consisting of layers of edge-sharing MC_6 octahedra interleaved with square-planar A layers. The edge-sharing TiC_6 octahedra are identical to those found in the rock salt structure of the corresponding binary carbides, MX [10].

These phases are highly damage tolerant, thermal shock resistant, readily machinable, and with Vickers hardness values of 2–8 GPa, are anomalously soft for transition metal carbides

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and nitrides [1–4]. Some of them display a ductile–brittle transition at temperatures $>1000\,^\circ\mathrm{C}$, while retaining reasonable mechanical properties at these elevated temperatures [5–9].

Over the last few years a concerted effort has been made to try to understand the relationship between MAX-phase chemistries and their elastic properties in general and their response to pressure in particular. Recently Manoun *et al* [11–17] reported on the quasi-hydrostatic compression behavior of M_2AlC (M = Ti, V, Cr, Nb and Ta) [11], TiMAlC (M = V, Nb) [12], Ti_3AlCN [13], $Ti_3Si_{0.5}Ge_{0.5}C_2$ [14], Zr_2InC [15], Ti_4AlN_3 [16] and Ta_4AlC_3 [17]. In all cases, and like in Ti_3SiC_2 [18], no phase transitions were observed up to pressures of the order of 55 GPa. The isothermal bulk moduli, K_0, of these compounds, varied from a high of 261 GPa for Ta_4AlC_3 [17] to a low of 127 GPa for Zr_2InC [15]. For the most part, the relative shrinkage along the c-direction with pressure was greater than that along the a-direction. The exceptions were for Cr_2AlC [11], Nb_2AsC [19] and Nb_2AlC [11]. The Ta-containing phases were unique in that the shrinkages along the two directions were quite similar [11, 17].

Recently we have also explored the effects of solid solutions on the M-, X- and A-sites. For example, we have shown that replacing the C by N in Ti_2AlC results in a decrease in bulk moduli, despite a decrease in lattice parameters [20]. This behavior was attributed to the formation on vacancies in the nitrides. Replacing Si by Ge in Ti_3SiC_2, on the other hand, does not affect K_0 greatly [21]. Interestingly, the substitution of Nb by Ti in Nb_2AlC led to a solid solution softening effect, attributed to atomic corrugation of the Ti–Nb planes [12].

The combination of easy machinability, relatively low densities (of some of the phases) and high elastic constants, together with the possibility of high damping (the attenuation of sound waves in Ti_2AlC was higher than in many woods and comparable to that in some polymers [22–24]), is one that to date had not been possible. Thus one motivation for this work was to identify compositions of potential technological interest. The second motivation was to directly measure, for the first time, K_0 for Cr_2GeC and V_2GeC and compare the results to the bulk moduli of Cr_2AlC and V_2AlC measured previously [11]. We were also interested in exploring the stability of these phases at high pressures.

2. Experimental details

To synthesize Cr_2GeC, powders of Cr (99% pure, -325 mesh, Alfa Aesar, Ward Hill, MA), Ge (99% pure, -325 mesh, Cerac, Milwaukee, WI) and C (99.0% pure, -300 mesh, Alfa Aesar, Ward Hill, MA) were stoichiometrically weighed, ball milled for 24 h and dried in vacuum for 24 h at $180\,^\circ\mathrm{C}$. The powder mixture was then poured onto and sealed in graphite foil, placed in a graphite die and heated, under vacuum, at $10\,^\circ\mathrm{C}\,\mathrm{min}^{-1}$—in a graphite-heated hot press, HP (Series 3600, Centorr Vacuum Industries, Somerville, MA)—up to $1350\,^\circ\mathrm{C}$ and held at temperature for 6 h. A load, corresponding to a stress of $\sim$45 MPa, was applied at $600\,^\circ\mathrm{C}$ and maintained throughout the entire process.

To fabricate the V_2GeC samples, powders of V (Alfa Aesar, MA; -325 mesh, 99.5%), Ge (Advanced Technology Inc., NJ; -200 mesh, 99%) and C (Alfa Aesar, MA; -300 mesh, 99%) were weighed in the stoichiometric ratio and mixed. The mixed powders were sealed in borosilicate glass tubes under a mechanical vacuum. The sealed tubes were heated to $650\,^\circ\mathrm{C}$ for 10 h, which resulted in their collapse. The collapsed tubes were subsequently placed in a hot isostatic press, that was heated at $10\,^\circ\mathrm{C}\,\mathrm{min}^{-1}$ to $650\,^\circ\mathrm{C}$, and then at $2\,^\circ\mathrm{C}\,\mathrm{min}^{-1}$ to $750\,^\circ\mathrm{C}$. The heating chamber was then pressurized to $\approx$70 MPa, before further heating at $10\,^\circ\mathrm{C}\,\mathrm{min}^{-1}$ to $1600\,^\circ\mathrm{C}$ under pressure. The samples were held at that temperature for 8 h.

An online image plate recorded the angle-dispersive diffraction patterns of V_2GeC; the measurements were conducted at room temperature using synchrotron radiation at the

Table 1. Ambient pressure lattice parameters and unit cell volumes of M_2AC compounds measured herein. Also listed are previous results taken from various sources; note that the data taken from [31] are theoretical. The space group adopted for all phases is $P6_3/mmc$.

M_2AC	V_2AlC	V_2GeC	Cr_2GeC	Cr_2AlC
a (Å)	2.914 ± 0.003	3.038 ± 0.005	2.950 ± 0.006	2.857 ± 0.002
	2.909[a]	2.999[c]	2.931[c]	2.854[a]
	2.925[b]			2.848[b]
c (Å)	13.19 ± 0.03	12.112 ± 0.009	12.086 ± 0.008	12.81 ± 0.02
	13.127[a]	12.255[c]	12.066[c]	12.82[a]
	13.105[b]			12.72[b]
V_0 (Å)^3	97.0 ± 0.7	96.6 ± 0.9	91.1 ± 0.8	90.6 ± 0.5

[a] Reference [30].
[b] Reference [31].
[c] Reference [32].

High Pressure Collaborating Access Team (HPCAT) beam line at the Advanced Photon Source (Chicago). A monochromatic beam—with wavelength $\lambda = 0.4066$ Å—was focused to a 10 μm spot size on the sample.

The x-ray diffraction, XRD, patterns for Cr_2GeC were collected using a wavelength $\lambda = 0.496$ Å of a monochromatic beam focused down to a 35 μm spot size, collected at CHESS (Cornell University, Ithaca, NY). Diffraction rings were recorded between $2\theta = 1°$ and $35°$.

Measurements were conducted at room temperature; powdered samples were pressurized using a gasketed diamond anvil cell (DAC) with a 300–400 μm culet. A 250 μm initial thickness rhenium gasket was indented to about 50–70 μm. The stress state of a sample compressed in a DAC can become highly non-hydrostatic if the material is hard and has low compressibility like the MAX phases. However, it has been shown that the sample pressure can be rendered nearly hydrostatic by using a large volume of a low shear strength material as the pressure-transmitting medium. We have repeatedly shown that Al—with its low shear modulus and lack of phase transitions—was a good pressure-transmitting medium [11–17, 20, 21, 25, 26]. Another advantage of Al is the fact that its pressure–volume relationship is well established [27]. In this work, powdered samples were placed between two 15 μm thick Al foils, before packing them in the 100–150 μm hole in the Re gasket.

The FIT2D software [28, 29] was employed to convert the image plate records into 2θs and intensities. The a and c lattice cell parameters were determined using least squares refinement on individually fitted peaks.

3. Results and discussion

All the major peaks in the XRD patterns were assigned to the hexagonal structure with the space group $P6_3/mmc$. The agreement between the unit cell parameters measured herein, those previously reported [30–32] and those predicted from *ab initio* calculations is good (table 1).

Upon compression, and for both compositions, most peaks remain visible up to the highest pressures reached (figure 1). With increasing pressure, P, the peaks become broader, lose intensity, and some merge together. No extra peaks appear in the patterns up to about 47 GPa, which indicates the stability of these phases under quasi-hydrostatic pressure and is in line with previous work. As noted above, to date all MAX phases examined have been stable up to $\approx$50 GPa.
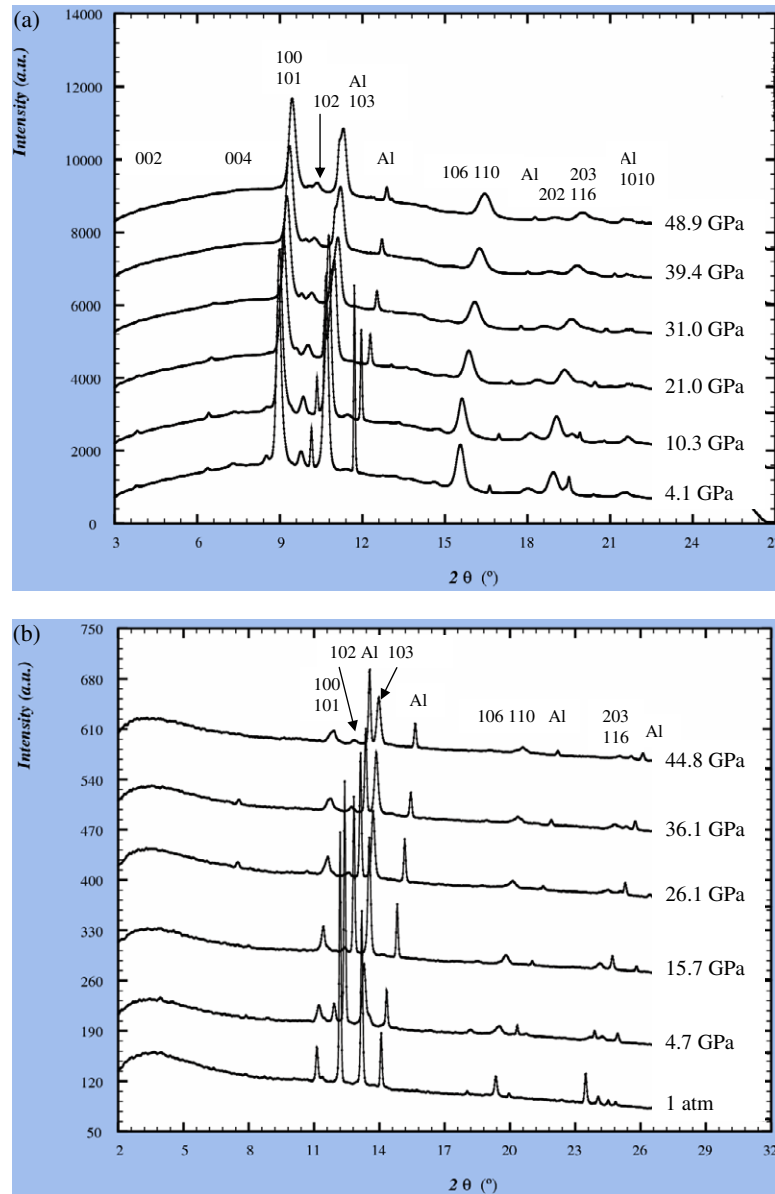
Figure 1. Functional dependence of XRD spectra of (a) V_2GeC and (b) Cr_2GeC on quasi-hydrostatic pressure, P. Upon compression, most peaks remain visible up to the highest pressures reached. With increasing P, the peaks become broader, lose intensity, and some merge together. No extra peaks appear in the patterns up to about 50 GPa.

From relative unit cell volumes, V/V_0 (where V_0 is the unit cell volume when $P = 1$ atm), versus P plots (figure 2(a)), it is clear that the bulk modulus of V_2GeC is lower than that of Cr_2GeC. Least squares fits of these data yield the results listed in table 2. Fitting the same results to the Birch–Murnaghan equation [33]:

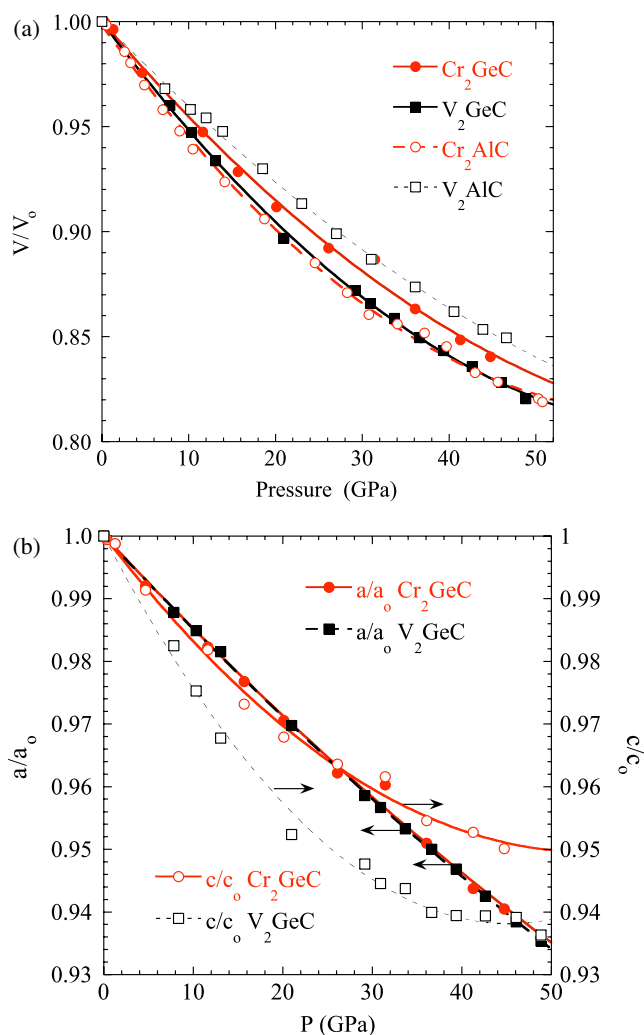$$P = \tfrac{3}{2}K_0[(V/V_0)^{-7/3} - (V/V_0)^{-5/3}][1 + \tfrac{3}{4}(K_0' - 4)[(V/V_0)^{-2/3} - 1]]$$

Figure 2. Pressure dependences of (a) V/V_0 and (b) a/a_0 and c/c_0 for Cr_2GeC and V_2GeC. The lines are least squares fits of the data points. Also included in (a) are the results for Cr_2AlC and V_2AlC taken from [11].

(This figure is in colour only in the electronic version)

yields K_0 values of 182 ± 2 GPa for Cr_2GeC and 165 ± 2 GPa for V_2GeC. The pressure derivative values, K_0', were fixed at 4.

The K_0 values reported herein are in line with previous MAX-phase results in that these solids are elastically quite stiff [11–21]. The bulk modulus of Cr_2GeC (182 ± 2 GPa) is higher than that of Cr_2AlC (165 ± 2 GPa). Conversely, the bulk modulus of V_2GeC (165 ± 2 GPa) is lower than that of V_2AlC (201 ± 2 GPa).

To gain further insight into the response of these solids to pressure we plot, in figure 2(b), the variations in a/a_0 and c/c_0—where the subscripts refer to the values of a and c when $P = 1$ atm—versus P. Second-order polynomial least squares fits resulted in the coefficients listed in table 3. Interestingly, the compressibilities along the a-axes, for both compositions, have

Table 2. Relative unit cell volume changes, V/V_0, with pressure and summary of experimental bulk moduli. The pressure derivatives, K_0', were fixed to 4. Data for the Al-containing ternaries were taken from [11]. All correlation coefficient values were >0.99.

Solid	$V/V_0 = \alpha + \beta P/P_0 + \gamma(P/P_0)^2$	K_0 (GPa)	K_0'
V_2AlC	$1 - 0.0043P/P_0 + 2 \times 10^{-5}(P/P_0)^2$	201 ± 3	4.05 ± 0.13
V_2GeC	$1 - 0.0056P/P_0 + 4 \times 10^{-5}(P/P_0)^2$	165 ± 2	4
Cr_2GeC	$1 - 0.0049P/P_0 + 3 \times 10^{-5}(P/P_0)^2$	182 ± 2	4
Cr_2AlC	$1 - 0.0058P/P_0 + 4 \times 10^{-5}(P/P_0)^2$	165 ± 2	4.1 ± 0.1

Table 3. Relative lattice parameter changes with pressure, P. P_0 defines the units used and is equal to 1 GPa. Data for the Al-containing ternaries were taken from [11]. The correlation coefficient values in all cases were >0.99.

M_2AC	Max pressure (GPa)	$a/a_0 = 1 + \beta P/P_0 + \gamma(P/P_0)^2$	$c/c_0 = 1 + \beta P/P_0 + \gamma(P/P_0)^2$
V_2AlC	47	$1 - 0.0010P/P_0 + 7 \times 10^{-7}(P/P_0)^2$	$1 - 0.0022P/P_0 + 2 \times 10^{-5}(P/P_0)^2$
V_2GeC	49	$1 - 0.0015P/P_0 + 4.1 \times 10^{-6}(P/P_0)^2$	$1 - 0.0027P/P_0 + 3 \times 10^{-5}(P/P_0)^2$
Cr_2GeC	45	$1 - 0.0015P/P_0 + 4.6 \times 10^{-6}(P/P_0)^2$	$1 - 0.0019P/P_0 + 1.7 \times 10^{-5}(P/P_0)^2$
Cr_2AlC	51	$1 - 0.0021P/P_0 + 2 \times 10^{-5}(P/P_0)^2$	$1 - 0.0017P/P_0 + 1 \times 10^{-5}(P/P_0)^2$

little curvature and are almost identical. The differences in K_0 between the two compositions must thus be traced to the different compressibilities along the c-axes, which are greater in the case of in V_2GeC. In contrast to a/a_0, the curvature of c/c_0—again for both compositions—is quite pronounced, especially at the higher pressures. The higher curvature causes c/c_0 to cross over the a/a_0 lines at higher pressures. This crossover behavior has not been observed to date in any of the MAX phases explored. The exact reason for this state of affairs is not clear at this time, but must ultimately be related to the intricacies of bonding in these phases and/or non-stoichiometric effects. For example we have recently shown that the most likely reason for K_0 of Ti_2AlN being smaller than Ti_2AlC was the presence of N and/or Al vacancies in the former [13].

4. Conclusions

Using a synchrotron x-ray radiation source and a diamond anvil cell we measured the pressure dependences of the lattice parameters of Cr_2GeC and V_2GeC up to quasi-hydrostatic pressures of the order of 50 GPa. Like for other solids in this family of layered ternary carbides and nitrides, the bulk moduli, K_0, are high and no phase transformations were observed. The bulk modulus of V_2GeC (165 ± 2 GPa) was lower than that of Cr_2GeC (182 ± 2 GPa). The effects of replacing Ge by Al in V_2GeC lead to a 22% increase in K_0; conversely, replacing Ge by Al in Cr_2GeC results in a 10% decrease in K_0.

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