

Compression of $\text{Ti}_3\text{Si}_{0.5}\text{Ge}_{0.5}\text{C}_2$ to 53 GPa

Bouchaib Manoun,^{a)} H. P. Liermann, R. P. Gulve, and S. K. Saxena

Center for Study of Matter at Extreme Conditions (CeSMEC), Florida International University, VH-140, University Park, Miami, Florida 33199

A. Ganguly and M. W. Barsoum

Dept. of Materials Scienc and Engin., Drexel University, Philadelphia, Pennsylvania 19104

C. S. Zha

Cornell High Energy Synchrotron Source (CHESS), Wilson Laboratory, Cornell University, Ithaca, New York 14853

(Received 27 October 2003; accepted 13 February 2004)

Using a synchrotron radiation source and a diamond anvil cell, we measured the pressure dependence of the lattice parameters of a polycrystalline $\text{Ti}_3\text{Si}_{0.5}\text{Ge}_{0.5}\text{C}_2$ sample. Up to a pressure of 53 GPa, no phase transformations were observed. As for the isostructural hexagonal Ti_3SiC_2 , the compressibility along the c axis was greater than along a . The bulk modulus is 183 ± 4 GPa with a pressure derivative of 3.4 ± 0.2 . This work shows that the replacement of Si by Ge in Ti_3SiC_2 results in a systematic decrease in the bulk moduli. © 2004 American Institute of Physics. [DOI: 10.1063/1.1699477]

Layered ternary carbides, such as Ti_3SiC_2 , are of significant interest because they are elastically stiff, electrically and thermally conductive, and similar to the *stoichiometric* carbides, but in contrast, are readily machinable, relatively soft, resistant to thermal shock and show unusual damage tolerance.^{1–12} To date, Ti_3SiC_2 has been the most extensively studied phase in the $\text{M}_{n+1}\text{AX}_n$ (MAX) phase group, 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 and/or N. In particular, Ti_3SiC_2 has a relatively low coefficient of thermal expansion.^{1,5,13,14} This carbide adopts a hexagonal crystal structure that consists of a double layer of edge-sharing TiC_6 octahedra and a square-planar Si layer. With a structure similar to Ti_3SiC_2 , $\text{Ti}_3\text{Si}_{0.5}\text{Ge}_{0.5}\text{C}_2$ has near-close-packed layers with Ti layers interleaved with layers of Si/Ge atoms, the C atoms filling the octahedral sites between the former. The Si/Ge atoms are located at the center of trigonal prisms that are larger than the octahedral sites and are thus better able to accommodate the larger Si/Ge atoms. The edge-sharing TiC_6 octahedra are identical to those found in the rocksalt structure of the corresponding binary carbides, MX.

The only paper dealing with the compressibility of these type of materials is a recent study on Ti_3SiC_2 .¹⁵ No phase transitions were observed up to a pressure of 61 GPa. The isothermal bulk modulus, calculated by fitting the PV data with the Birch–Murnaghan equation,¹⁶ K_o (206 GPa) is lower than that of TiC (220 GPa)¹⁷ but $\approx 10\%$ – 15% larger than the values calculated from the highest Young's moduli reported (326–334 GPa)¹⁸ and Poisson's ratio (0.2).¹⁹

The pressure (P) dependencies of the relative shrinkage of the a and c lattice parameters were reported to be, respectively,

$$a/a_o = 1 - 9.15 \times 10^{-4} (P/P_o), \quad (1)$$

$$c/c_o = 1 - 2.02 \times 10^{-3} (P/P_o) + 1.28 \times 10^{-5} (P/P_o)^2, \quad (2)$$

where $P_o = 1$ GPa.

In this letter, we report the data on the compressibility of the solid solution $\text{Ti}_3\text{Si}_{0.5}\text{Ge}_{0.5}\text{C}_2$ in an attempt to understand the effect of Ge substitutions on the bulk modulus. We also explore the stability of this phase at higher pressures.

This work is part of a larger effort aiming to understand the chemistry–structure–property relationships of the MAX phases. In order to do so, a database needs to be created and one of the more intriguing and important questions that this and related work try to answer is: What effects do substitutions on the A sites have on properties in general? Ultimately, this understanding will allow us to tailor the properties of these potentially important compounds for any given application.

Bulk polycrystalline samples of $\text{Ti}_3\text{Si}_{0.5}\text{Ge}_{0.5}\text{C}_2$ were synthesized by mixing Ti, C, SiC, and Ge powders in the appropriate stoichiometric composition, followed by presintering in vacuum-sealed glass tubes. The tubes were, in turn, hot isostatically pressed at 1600 °C for 8 h. The chamber was pressurized with Ar to ~ 172 MPa. The main impurity was TiC ~ 2 vol %. However a Si-Ti rich liquid phase was observed (~ 3 vol %) with a Si:Ti:Ge ratio determined by energy-dispersive x-ray (EDX) analysis to be $\sim 48 \pm 4:40 \pm 3.5:12 \pm 1.4$. The grains were plate-like, with an average diameter of 40 ± 30 μm and an aspect ratio of 2.3. At 5.0 ± 0.1 Mg/m^3 , the measured density was $\sim 99\%$ of theoretical (5.035 Mg/m^3).

A powdered sample was pressurized using a gasketed diamond anvil cell with 400 μm culet. The gasket, made of rhenium was 250 μm in initial thickness, indented to 40 μm , and had a 150- μm -diameter hole. The sample, placed between two pieces of aluminum foil (15 μm thick), was packed in the hole. In the past, solid pressure transmitting media have been used (e.g., Refs. 20 and 21), here, we used high-purity aluminum, which acts as a pressure marker

^{a)}Author to whom correspondence should be addressed; electronic mail: manounb@fiu.edu

TABLE I. Unit cell parameters and volume of $\text{Ti}_3\text{Si}_{0.5}\text{Ge}_{0.5}\text{C}_2$ at various pressures.

P (GPa)	a (\AA) \pm 0.001	c (\AA) \pm ± 0.01	V (\AA^3) \pm ± 0.1	V/V_o	a/a_o	c/c_o
0	3.079	17.77	145.9	1	1	1
4.65	3.062	17.56	142.6	0.977	0.994	0.988
6.00	3.054	17.56	141.8	0.972	0.992	0.988
8.94	3.038	17.45	139.4	0.955	0.986	0.982
13.16	3.020	17.33	136.9	0.939	0.981	0.976
18.79	2.996	17.13	133.1	0.912	0.973	0.964
23.61	2.983	17.00	131.0	0.898	0.969	0.957
29.64	2.960	16.85	127.8	0.876	0.961	0.949
40.20	2.933	16.68	124.2	0.851	0.952	0.939
43.45	2.922	16.49	122.0	0.836	0.949	0.928
47.42	2.910	16.43	120.5	0.826	0.945	0.925
50.74	2.900	16.44	119.7	0.821	0.942	0.925
53.53	2.897	16.29	118.4	0.812	0.941	0.917
38.23	2.947	16.50	124.1	0.850	0.957	0.929
0	3.077	17.79	145.9	1.000	0.999	1.001

and also a pressure medium by virtue of its low shear strength. Measurements were conducted at room temperature; pressure was determined from the equation of state of Al.²² EDX diffraction spectra were collected with a fixed 2θ ($=11^\circ$). The cell parameters were determined using least-squares refinement on individually fitted peaks. The peaks were assigned to the hexagonal structure with the space group $P6_3/mmc$.

A summary of the lattice parameters, their relative change, the unit cell volumes, V , and their relative changes with pressure are listed in Table I. As the pressure increased, the peaks broadened and some merged due to differences in the compressibility along the a and c axes. A least-squares fit of the changes in the relative unit cell volume V/V_o as a function of P (Fig. 1) yields

$$V/V_o = 1 - 0.005P/P_o + 3 \times 10^{-5}(P/P_o)^2, \quad (3)$$

where $V_o = 145.9 \pm 0.1 \text{ \AA}^3$.

Fitting the same results to the Birch–Murnaghan equation¹⁶ yields

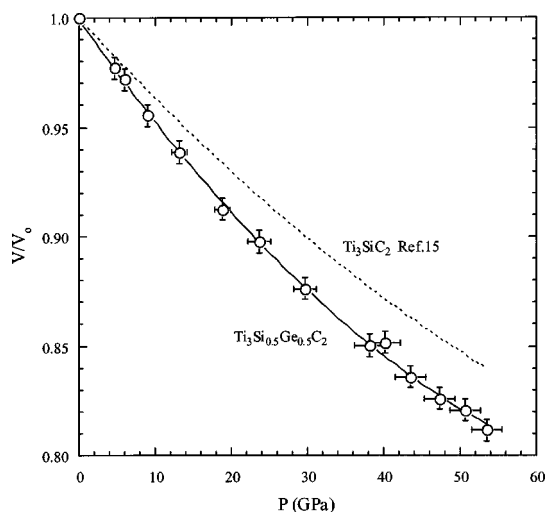


FIG. 1. Relative unit cell volume of $\text{Ti}_3\text{Si}_{0.5}\text{Ge}_{0.5}\text{C}_2$ as a function of pressure. Also shown are the results for Ti_3SiC_2 (see Ref. 15).

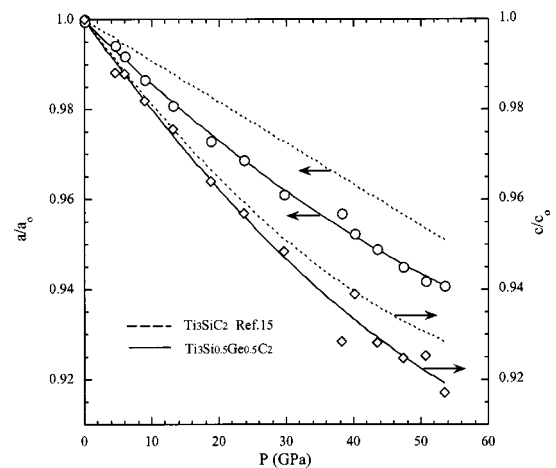


FIG. 2. a/a_o (upper curves) and c/c_o (lower curves) of $\text{Ti}_3\text{Si}_{0.5}\text{Ge}_{0.5}\text{C}_2$ and Ti_3SiC_2 as a function of pressure (see Ref. 15).

$$P = (3/2)K_o[(V/V_o)^{-7/3} - (V/V_o)^{-5/3}]\{1 + 3/4(K'_o - 4) \times [(V/V_o)^{-2/3} - 1]\}, \quad (4)$$

where K_o is the isothermal bulk modulus and K'_o its pressure derivative. Based on these results, K_o and K'_o were calculated to be 183 ± 4 GPa and 3.4 ± 0.2 , respectively. This value of K_o is $\approx 10\%$ higher than the same value measured by ultrasound on bulk samples of $\text{Ti}_3\text{Si}_{0.5}\text{Ge}_{0.5}\text{C}_2$.²³ This value is also lower than the corresponding values for Ti_3SiC_2 (see Ref. 15) and TiC ,¹⁷ but slightly higher than Ti_3GeC_2 (168 GPa).²³ Based on the totality of the evidence, there is little doubt that the substitution of Si by Ge in Ti_3SiC_2 results in a general reduction of the bulk moduli. Interestingly, this conclusion is not in accord with recent *ab initio* calculations that have shown that at 198 GPa, the bulk modulus of Ti_3GeC_2 is almost identical to that of Ti_3SiC_2 at 202 GPa.²⁴

While the crystal structure is stable to pressures of ≈ 53 GPa, the compressibility is anisotropic. As shown in Fig. 2, the relative reduction along the c axis is given by

$$c/c_o = 1 - 0.0021(P/P_o) + 10^{-5}(P/P_o)^2, \quad (5)$$

and is higher than along the a axis, given by:

$$a/a_o = 1 - 0.0015(P/P_o) + 7 \times 10^{-6}(P/P_o)^2. \quad (6)$$

The corresponding values for Ti_3SiC_2 are also plotted in Fig. 2; the close similarity between the two sets of results is obvious, and not too surprising. Interestingly, the effect of Ge substitutions on the compressibility of the a axis is greater than along the c axis. Based on these results, it is fair to assume that thermal expansion anisotropy in $\text{Ti}_3\text{Ge}_{0.5}\text{Si}_{0.5}\text{C}_2$ is similar to that in Ti_3SiC_2 , with expansion along the c axis slightly larger than along the a axis.^{13,14}

This work was financially supported by the Division of Sponsored Research at FIU and grants from the National Science Foundation (EAR-00769641, EAR-0132270, DMR 0231291) and (DMR 0072067 to Drexel U.).

¹M. W. Barsoum and T. El-Raghy, *J. Am. Ceram. Soc.* **79**, 1953 (1996).

²M. W. Barsoum, D. Brodtkin, and T. El-Raghy, *Scr. Metall. Mater.* **36**, 535 (1997).

- ³T. El-Raghy, A. Zavalangos, M. W. Barsoum, and S. Kalidini, *J. Am. Ceram. Soc.* **80**, 513 (1997).
- ⁴M. W. Barsoum, T. El-Raghy, and L. Ogbuji, *J. Electrochem. Soc.* **144**, 2508 (1997).
- ⁵M. W. Barsoum and T. El-Raghy, *J. Mater. Synth. Process.* **5**, 197 (1997).
- ⁶M. W. Barsoum, G. Yaroshuck, and S. Tyagi, *Scr. Mater.* **37**, 1583 (1997).
- ⁷M. W. Barsoum, *Prog. Solid State Chem.* **28**, 201 (2000).
- ⁸I. M. Low, S. K. Lee, B. Lawn, and M. W. Barsoum, *J. Am. Ceram. Soc.* **81**, 225 (1998).
- ⁹L. Farber, M. W. Barsoum, A. Zavalangos, T. El-Raghy, and I. Levin, *J. Am. Ceram. Soc.* **81**, 1677 (1998).
- ¹⁰E. H. Kisi, J. A. A. Crossley, S. Myhra, and M. W. Barsoum, *J. Phys. Chem. Solids* **59**, 1437 (1998).
- ¹¹M. Amer, M. W. Barsoum, T. El-Raghy, I. Wiess, S. Leclair, and D. Liptak, *J. Appl. Phys.* **84**, 5817 (1998).
- ¹²Y. Du, J. C. Schuster, H. Seifert, and F. Aldinger, *J. Am. Ceram. Soc.* **83**, 197 (2000).
- ¹³M. W. Barsoum, T. El-Raghy, C. J. Rawn, W. D. Porter, A. Payzant, and C. Hubbard, *J. Phys. Chem. Solids* **60**, 429 (1999).
- ¹⁴B. Manoun, S. K. Saxena, H.-P. Liermann, and M. W. Barsoum (unpublished).
- ¹⁵A. Onodera, H. Hirano, T. Yuasa, N. F. Gao, and Y. Miyamoto, *Appl. Phys. Lett.* **74**, 3782 (1999).
- ¹⁶F. Birch, *J. Geophys. Res.* **83**, 1257 (1978).
- ¹⁷H. G. Drikamer, R. W. Lynch, R. L. Clendenen, and E. A. Perez-Alubuerne, in *Solid State Physics* Vol. 19, edited by F. Seitz and D. Turnbull (Academic, New York, 1996), p. 135.
- ¹⁸R. Pampuch, J. Lis, J. Piekarczyk, and L. Stobierski, *J. Mater. Synth. Process.* **1**, 93 (1993).
- ¹⁹P. Finkl, M. W. Barsoum, and T. El-Raghy, *J. Appl. Phys.* **87**, 1701 (2000).
- ²⁰A. K. Singh and G. C. Kennedy, *J. Appl. Phys.* **48**, 3362 (1977).
- ²¹W. A. Passett, M. S. Weathers, T. C. Wu, and T. Holmquist, *J. Appl. Phys.* **74**, 3824 (1993).
- ²²R. G. Greene, H. Luo, and A. L. Ruoff, *Phys. Rev. Lett.* **73**, 2075 (1994).
- ²³P. Finkel, PhD thesis, Drexel University, 2003.
- ²⁴Y. C. Zhou, Z. Sun, X. Wang, and S. Chen, *J. Phys.: Condens. Matter* **13**, 10001 (2001).