

## High-Pressure Synthesis and Crystal Structure of $VGe_2$ and $Cr_4Ge_7$

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The new germanides,  $Cr_4Ge_7$  with the defect disilicide-type structure and  $VGe_2$  with the C40 structure, are synthesized at 4–5.5 GPa and 800–1100°C for 1–3 hr using the belt-type high-pressure apparatus. The relationship between the chemical composition and crystal structure in transition metal disilicides and digermanides is systematically discussed. The following chemical composition sequence accompanied with the change of crystal structure is proposed for the high-pressure synthesis of transition metal ( $T$ ) silicide ( $X$ ) and germanide ( $X$ ) systems:  $T_nX_m \xrightarrow{P} T_nX_{m'}, (n > n' \text{ and } m/n < m'/n' < 2) \xrightarrow{P} TX_2$ . © 1988 Academic Press, Inc.

### Introduction

Many studies have been carried out for the preparation of binary transition metal silicides and germanides. The atomic ratio of silicon/metal and germanium/metal in these compounds, except  $IrSi_3$ , is usually less than 2.

From the crystal structural point of view, disilicides and digermanides are classified in several groups.  $CoSi_2$  and  $NiSi_2$  have the C1 ( $CaF_2$ -type) structure and silicon in these compounds acts as an anion (1), while  $FeGe_2$  has the C16 ( $CuAl_2$ -type) structure and germanium behaves like a metalloid (2).

Various crystal structures such as C11b, C40, C54, and the defect disilicide-type structures are known as the intermediate structure between C1 and C16 structures. The C11b ( $MoSi_2$ -type), C40 ( $CrSi_2$ -type), and C54 ( $TiSi_2$ -type) structures are com-

posed of the close-packed layers of metal and metalloid atoms in different stacking sequences depending on the valence electron concentration of the transition metal atom (1, 3). Disilicides and digermanides of 4A group elements have the C54 structure, those of 5A group elements have the C40 structure and those of 6A group elements, except  $CrSi_2$ , have the C11b structure (4).

On the other hand, the defect disilicide-type structure, the so-called Nowotny chimney-ladder structure, is widely found in disilicides and digermanides of 5A–8 group elements. The defect disilicide-type compounds have the various chemical compositions represented by formulas such as  $T_4X_5$  ( $TX_{1.25}$ ),  $T_2X_3$  ( $TX_{1.5}$ ),  $T_3X_5$  ( $TX_{1.67}$ ),  $T_{11}X_{19}$  ( $TX_{1.73}$ ), and  $T_{17}X_{31}$  ( $TX_{1.82}$ ) (1, 4, 5).

Jeitschko and Parthé (6) reported that the chemical compositions of the defect disilicide-type compounds were controlled by the valency of the transition metal atom, in which silicon or germanium acted as an electron donor and the chemical composi-

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tion was controlled to maintain about 14 valence electrons per transition metal atom. Therefore, these compounds were regarded as electron compounds. These electron compounds are the narrow gap semiconductors (7–9), except for a few compounds such as  $\text{Cr}_{11}\text{Ge}_{19}$  (10), which have less than 14 valence electrons per transition metal atom (6).

The crystal structure of the defect disilicide-type compounds was widely investigated by Nowotny and co-workers (11–13). The unit cell in these compounds consisted of the long period superstructures, in which the  $\beta$ -Sn like transition metal subcells were stacked along the  $c$ -axis. The number of subcells stacked along the  $c$ -axis just corresponded to  $n$ , when the chemical formula of the compound was expressed as  $T_nX_m$ . The stacking number,  $n$ , is generally large, and the defect disilicide-type compound with very long  $c$ -axes of about 18 nm was synthesized (1).

Recently,  $\text{Mn}_3\text{Ge}_5$  (5),  $\text{Co}_2\text{Si}_3$  (14), and  $\text{Re}_4\text{Ge}_7$  (14) with the defect disilicide-type structure were synthesized under high-pressure temperature conditions. These compounds had small stacking numbers,  $n = 2$  for  $\text{Co}_2\text{Si}_3$ ,  $n = 3$  for  $\text{Mn}_3\text{Ge}_5$ , and  $n = 4$  for  $\text{Re}_4\text{Ge}_7$ . It is expected that the compound with the long period superstructure should be converted to that with short period superstructure under high-pressure conditions.

In the present study, vanadium germanide and chromium germanide were synthesized under high-pressure temperature conditions, and effects of pressure on the formation of the defect disilicide-type structure were determined.

## Experimental

Vanadium and chromium powders (>99.9% purity) and germanium powder (>99.99% purity) were mixed in the desired molar ratio using an agate mortar and uni-

TABLE I  
X-RAY POWDER DIFFRACTION DATA OF  $\text{Cr}_4\text{Ge}_7$

$h$	$k$	$l$	$I_{\text{obs.}}^a$	$d_{\text{obs.}}$ (nm)	$d_{\text{calc.}}$ (nm)
2	0	0	vw	0.2912	0.2910
2	1	3	s	0.2408	0.2408
2	1	4	vs	0.2285	0.2284
1	1	7	vs	0.2270	0.2271
1	1	8	m	0.2064	0.2062
2	2	0	m	0.2059	0.2058
3	1	1	vw	0.1832	0.1832
1	0	10	w	0.1809	0.1811
3	0	4	m	0.1797	0.1797
3	1	6	vw	0.1591	0.1592
3	2	3	vw	0.1564	0.1564
2	1	10	vw	0.1538	0.1538
3	2	4	vw	0.1529	0.1529
3	1	7	vw	0.1524	0.1525
2	1	11	w	0.1443	0.1442
4	1	3	vw	0.1378	0.1378
3	0	10	w	0.1360	0.1360

<sup>a</sup> v, very; w, weak; s, strong; m, medium.

axially pressed at 100 MPa at room temperature to form pellets, 5 mm in diameter and 3 mm in thickness. The pellets were put into a cylindrical BN capsule, which was placed in a carbon heater. The assemblage was put into a cell constructed with NaCl and subjected to high-pressure temperature conditions using a belt-type apparatus. The high-temperature pressure reactions were carried out at 4–5.5 GPa and 800–1100°C for 1–3 hr, and then the samples were quenched to room temperature prior to releasing the applied pressure. The detailed high-pressure experimental procedures were described in the previous paper (5). The phase of product was identified by X-ray powder diffraction analysis using Ni filtered  $\text{CuK}\alpha$  radiation. Lattice parameters were determined by a least-squares method using silicon as an internal standard.

## Experimental Results

$\text{Cr}_4\text{Ge}_7$  was synthesized at 4–5.5 GPa and 800–1000°C for 1–3 hr. The X-ray powder

TABLE II  
CRYSTALLOGRAPHIC PARAMETERS OF  $Cr_nGe_m$  WITH  
THE DEFECT DISILICIDE-TYPE STRUCTURE

	$Cr_{11}Ge_{19}$ ( $CrGe_{1.73}$ )	$Cr_4Ge_7$ ( $CrGe_{1.75}$ )
Unit cell parameters (nm)	$a = 0.580$ $c = 5.234$	$a = 0.582$ $c = 1.906$
Subcell parameters (nm)	$a = 0.580$ $c' = 0.4758$ $c'/a = 0.820$	$a = 0.582$ $c' = 0.4765$ $c'/a = 0.819$
Density ( $g/cm^3$ )	7.363	7.370

diffraction data of  $Cr_4Ge_7$  is listed in Table I. All diffraction peaks of  $Cr_4Ge_7$  were completely indexed as the defect disilicide-type ( $Mn_{11}Si_{19}$ -type) structure and were different from those of  $Cr_{11}Ge_{19}$  which was formed at atmospheric pressure (12).

The crystal structure of the defect disilicide-type compounds is of tetragonal symmetry, in which the unit cell consists of the tetragonal subcells of transition metal atoms ( $T$ -subcells) and of metalloid atoms ( $X$ -subcells) stacked along the  $c$ -axis direction (6). The number of  $Cr$ -subcells and  $Ge$ -subcells stacked along the  $c$ -axis were determined to be 4 and 7, respectively, for the present high-pressure product using the subcell reflections as standards. Therefore,

TABLE III  
X-RAY POWDER DIFFRACTION DATA OF  $VGe_2$

$h$	$k$	$l$	$I_{obs.}^a$	$d_{obs.}$ (nm)	$d_{calc.}$ (nm)
1	0	1	w	0.3526	0.3526
1	0	2	vw	0.2594	0.2594
1	1	0	m	0.2405	0.2403
1	1	1	vs	0.2260	0.2259
0	0	3	s	0.2210	0.2211
2	0	0	vw	0.2080	0.2081
1	1	2	s	0.1946	0.1946
1	1	3	w	0.1627	0.1627
3	0	0	vw	0.1388	0.1387
1	1	4	m	0.1364	0.1365
3	0	1	m	0.1358	0.1358
3	0	2	w	0.1280	0.1280
2	2	0	w	0.1202	0.1202

<sup>a</sup> v, very; w, weak; s, strong; m, medium.

the chemical composition of the present sample was determined to be  $Cr_4Ge_7$ .

The crystallographic parameters of  $Cr_4Ge_7$  are listed in Table II together with those of  $Cr_{11}Ge_{19}$  (15). The different values of  $c$  were due to the change in superstructures of chromium defect digermanides.

The high-pressure product of  $Cr_4Ge_7$  was metastable under atmospheric pressure conditions and decomposed to  $Cr_{11}Ge_{19}$  and germanium by annealing at 800°C in an evacuated silica tube.

$VGe_2$  was synthesized at 4–5.5 GPa and 800–1100°C for 1–3 hr. The X-ray powder diffraction data of  $VGe_2$  are listed in Table III. All diffraction peaks of  $VGe_2$  were completely indexed as the hexagonal C40 ( $CrSi_2$ -type) structure. Lattice constants were calculated to be  $a = 0.4806$  nm and  $c = 0.6634$  nm, respectively.

$VGe_2$  was metastable under atmospheric pressure conditions and decomposed to  $V_{17}Ge_{31}$  and Ge upon annealing at 600°C in an evacuated silica tube.

## Discussion

Transition metal disilicides and digermanides have several kinds of crystal structures such as the C1, C11b, C16, C40, C54, and defect disilicide-type structures. Among these crystal structures, the C11b, C40, and C54 structures are composed of the close-packed layers (as shown in Fig. 1) in different stacking sequences. The stacking sequences of ABAB, ABCABC, and ACBDACBD lead to the C11b (tetragonal),

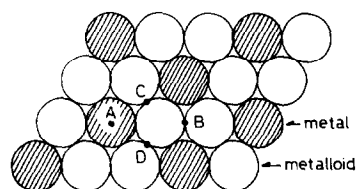


FIG. 1. Close-packed layer of C11b, C40, and C54 structures.

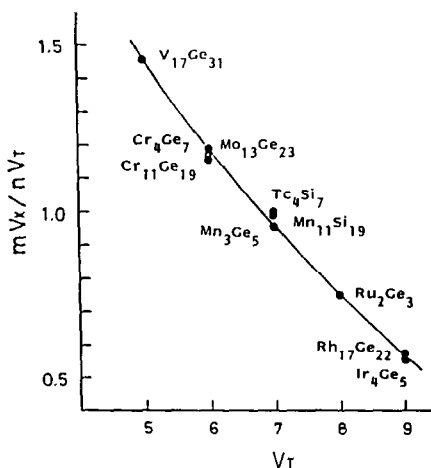


FIG. 2. Relationship between the valency of the T atom and the ratio  $mV_X/nV_T$  in the defect disilicide-type compounds ( $T_nX_m$ ).

C40 (hexagonal), and C54 (orthorhombic) crystal structures, respectively. The difference in the stacking sequences mentioned above is closely related to the valence electron concentration of the transition metal atom (1).

The defect disilicide-type structure is derived from the C54 structure. In this structure, the transition metal atoms form the  $\beta$ -Sn like subcells stacking along the  $c$ -axis by the long period (11–13). The formation of the long period superstructure is caused by ordering of metalloid atoms and metalloid vacancies (1).

The defect formation in  $TX_{2-x}$  compound is widely extended from  $x = 0.177$  ( $V_{17}Ge_{31}$ ) to  $x = 0.75$  ( $Ir_4Ge_5$ ) and is strongly dependent on the valence electron number of the transition metal atom. Therefore, the defect disilicide-type compounds are regarded as electron compounds (6). Pearson (3) reported that the ratio  $m/n$  of the defect disilicide-type compounds,  $T_nX_m$ , was approximately controlled by the relationship between the valency of the T atom ( $V_T$ ) and the ratio of  $mV_X/nV_T$  as shown in Fig. 2. The present high-pressure product of

$Cr_4Ge_7$  lays well on the curve of this relationship.

On the other hand, the number of  $\beta$ -Sn-like subcells stacked along the  $c$ -axis (the number “ $n$ ” in  $T_nX_m$ ) did not depend on the number of valence electrons, but on the synthetic temperature conditions (16). For example, manganese defect disilicides have five different superstructures ( $Mn_4Si_7$ ,  $Mn_{11}Si_{19}$ ,  $Mn_{15}Si_{26}$ ,  $Mn_{26}Si_{45}$ , and  $Mn_{27}Si_{47}$ ) (17–19) and molybdenum defect digermanides have three different superstructures ( $Mn_9Ge_{16}$ ,  $Mo_{13}Ge_{23}$ , and  $Mo_{23}Ge_{41}$ ) (15, 20).

It is expected that the applied pressure is an important factor in controlling the stacking number “ $n$ ” of the defect disilicide-type compounds,  $T_nX_m$ . The defect disilicide-type compounds synthesized at atmospheric pressure generally have large “ $n$ ” values as seen in  $Cr_{11}Ge_{19}$ ,  $V_{17}Ge_{31}$ , and  $Mn_{27}Si_{47}$ , while the compounds synthesized under high-pressure conditions have small “ $n$ ” values as seen in  $Co_2Si_3$  (14),  $Mn_3Ge_5$  (5),  $Re_4Ge_7$  (14), and  $Cr_4Ge_7$ . These results indicate that the long period superstructures tend to become more primitive short-period structures under high-pressure conditions.

According to the knowledge of high-pressure chemistry, it is believed that the defect formation hardly occurs under high-pressure conditions. It is expected that the atomic ratio of metalloid/metal in the defect disilicide-type compounds increases to be near 2 under high-pressure conditions, although the maximum of the atomic ratio was limited by the relationship shown in Fig. 2.

In the present study, chromium defect digermanide of  $Cr_{11}Ge_{19}$  ( $CrGe_{1.73}$ ) formed at atmospheric pressure was converted to  $Cr_4Ge_7$  ( $CrGe_{1.75}$ ) under high-pressure conditions. In the case of vanadium digermanide,  $V_{17}Ge_{31}$  ( $VGe_{1.82}$ ) was synthesized at atmospheric pressure and  $VGe_2$  with the C40 structure was prepared under high-

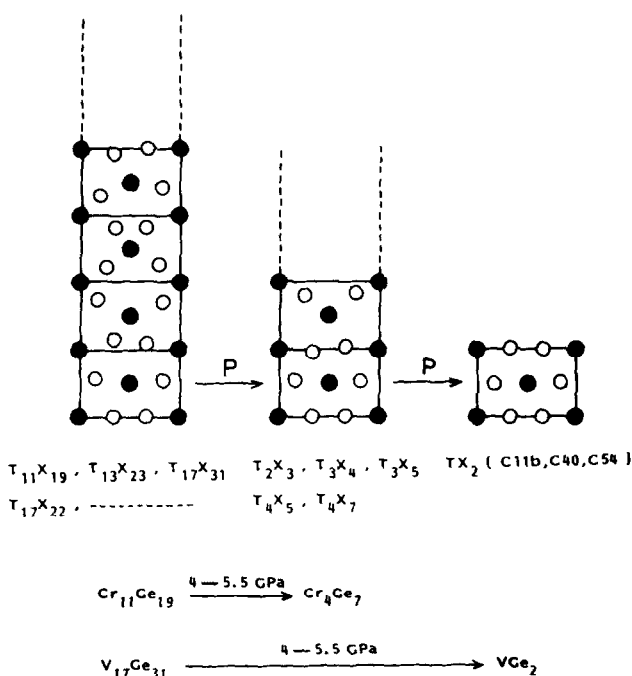


FIG. 3. Effect of pressure on the stacking sequence in the defect disilicide-type compounds (figure shows the generating plane: ●, T atom; ○, X atom).

pressure. Since the chemical compositions of disilicides and digermanides synthesized under high pressure (5, 14) ranged from  $TX_{1.25}$  to  $TX_2$ , the chemical formulas of high-pressure products are considered to be  $TX_2$ ,  $T_2X_3$ ,  $T_3X_4$ ,  $T_3X_5$ ,  $T_4X_5$ , and  $T_4X_7$ . The possible change in the stacking sequence of tetragonal sublattice is schematically summarized in Fig. 3.

### Summary

$Cr_4Ge_7$  with the defect disilicide-type structure and  $VGe_2$  with the C40 structure were synthesized under high-pressure temperature conditions. The unit cell of  $Cr_4Ge_7$  was shorter in its  $c$ -axis than that of  $Cr_{11}Ge_{19}$ , which was stable phase at atmospheric pressure. The superstructures of the defect disilicide-type compounds synthesized under high pressure became more primitive with a short period sequence

along the  $c$ -axis. The high-pressure product contained much more metalloid atoms and the transition metal digermanides with C11b, C40, or C54 structures without metalloid defect were formed under further high-pressure conditions.

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