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High-Pressure Synthesis and Electrical Properties of Mn_3Ge_5 with $Mn_{11}Si_{19}$-Type Structure

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The new germanium-rich manganese germanide, Mn_3Ge_5, was synthesized at 600–1000°C and 4 GPa using a Belt-type apparatus. The crystal structure of Mn_3Ge_5 was identified as possessing the $Mn_{11}Si_{19}$ type with a tetragonal cell (Schoenflies symbol D_{2d}). The electrical resistivity of Mn_3Ge_5 increased with increasing temperature and saturated above 200 K. The thermoelectric power was 50–70 $\mu V/K$ and its sign was positive. These data indicated that Mn_3Ge_5 was a *p*-type semiconductor or a semimetal.

Introduction

A number of investigations have focused on the physical properties of transition metal silicides (*1–8*) and germanides (*9–13*) because they show various kinds of electrical and magnetic properties, such as metal, semimetal, semiconductor, ferromagnetism, ferrimagnetism, and antiferromagnetism.

Most metal-rich silicides are metallic, while some silicon-rich transition metal silicides such as $MnSi_{2-x}$ ($0.250 \leqq x \leqq 0.273$), β-$FeSi_2$, and $CrSi_2$ are semiconductors. Many of the germanides have crystal structures and physical properties similar to those of silicides.

The crystal structure of the *M*Ge (M = Cr, Fe, Ru) compounds is a cubic *B*20 structure type, similar to FeSi, while that of the MGe_2 phases (M = V, Cr, Mo, Ru, Rh) possesses the tetragonal defect disilicide structure type as $Mn_{11}Si_{19}$.

In the Mn–Ge system, there exists five intermetallic compounds, $Mn_{3.25}Ge$, Mn_5Ge_2, Mn_2Ge, Mn_5Ge_3, and $Mn_{11}Ge_8$, under equilibrium conditions (*9, 13*). The crystal structures of these compounds are different from those of the silicides, except for Mn_5Ge_3 which has the Mn_5Si_3 structure type (*13*). However, germanium-rich germanides containing more than 50 at.% germanium have not been synthesized.

In the present study, the synthesis of manganese germanide containing more than 50 at.% germanium, which is expected to be a semiconductor, was carried out under high temperature and pressure conditions, and its electrical properties were examined.

Experimental

Manganese powder and germanium powder with purities above 99 and 99.99%, respectively, were used as starting materials. These powders were mixed with Ge/Mn

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atomic ratios varying from 1.5 to 2.0 and uniaxially pressed to form pellets, 5 mm in diameter and 3 mm in thickness; these were placed into a cylindrical BN capsule, which was placed in a carbon heater. This assembly was placed into a cell filled with NaCl and was subjected to high temperature and pressure conditions using a Belt-type apparatus. The high-pressure cell assembly of the apparatus is shown in Fig. 1. The magnitude of pressure inside the cell was calibrated to the electrical transition of Bi (2.55 GPa) and Ba (5.5 GPa), and the temperature of the sample was measured by use of a Pt–Pt/13% Rh thermocouple placed in the center of the cell. The reactions were carried out at 600–1000°C and 4 GPa for 1–8 hr. The sample was quenched to room temperature prior to the release of the applied pressure. Vacuum synthesis was also performed by heating the sample at 900°C for 20 hr in an evacuated silica tube. The pellets obtained were pulverized and the residual germanium was removed by leaching with a concentrated HNO_3 solution at room temperature. The amounts of manganese and germanium ions in the products after leaching were determined by means of atomic absorption spectroscopy and colorimetry (*14*) after dissolving the samples in a concentrated HNO_3–H_2SO_4 solution at 80°C. The products were identified by X-ray diffraction with Ni-filtered Cu*Kα* radiation.

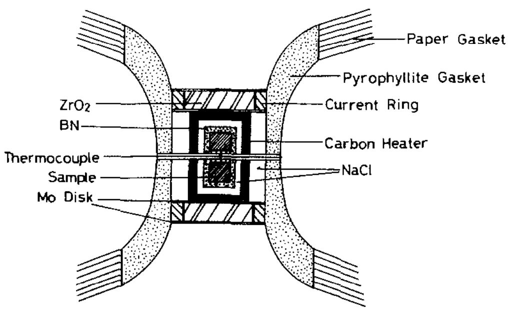

FIG. 1. Cell arrangement for Belt-type apparatus.

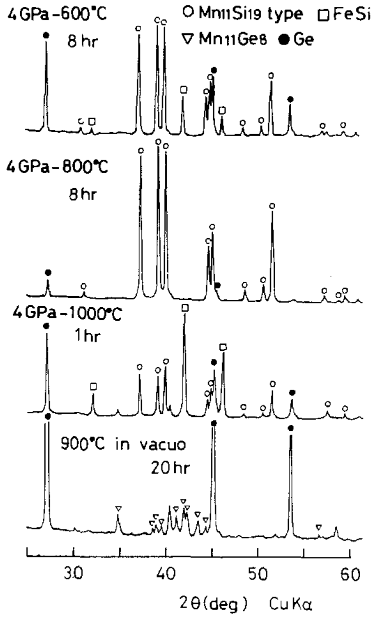

FIG. 2. X-ray diffraction patterns of products synthesized under various conditions (Ge/Mn = 1.70).

Results and Discussion

The starting powder with the Ge/Mn atomic ratio of 1.7 was reacted under various temperature and pressure conditions. X-ray diffraction patterns of the products are shown in Fig. 2.

$Mn_{11}Ge_8$ was formed at 900°C under vacuum conditions, while two new phases were synthesized at 600–1000°C and 4 GPa. These two phases were identified as possessing the tetragonal $Mn_{11}Si_{19}$ structure type and the cubic FeSi structure type, respectively. The samples synthesized at 4 GPa and 600°C for 8 hr and 1000°C for 1 hr were composed of mixed phases of $Mn_{11}Si_{19}$ and FeSi structure types as seen in Fig. 2. Similar results were obtained at 4 GPa and 800°C for 1–4 hr. The X-ray diffraction peaks corresponding to the FeSi structure type decreased with increasing reaction time. The product synthesized at 800°C and 4 GPa for 8 hr consisted of the $Mn_{11}Si_{19}$ structure type. These results indicated that the FeSi structure type was formed by the reaction between manganese and germanium at first, and then was converted to the $Mn_{11}Si_{19}$ structure type by reaction with the residual germanium. The reason the FeSi structure type was formed at 4 GPa and 1000°C might be due to the incongruent decomposition of the $Mn_{11}Si_{19}$ structure type. The product with the $Mn_{11}Si_{19}$ structure type was synthesized with a small amount of residual germanium in the range of $Ge/Mn > 1.68$. In the range of $Ge/Mn \leqq 1.68$, the products were composed of phases possessing both the $Mn_{11}Si_{19}$ and the FeSi structure types.

A single phase possessing the $Mn_{11}Si_{19}$ structure type was obtained by leaching out the residual germanium by use of a HNO_3 solution from the high-pressure products. X-ray powder diffraction data and the chemical composition of a sample with the $Mn_{11}Si_{19}$ structure type obtained in this way are listed in Tables I and II.

TABLE I

X-RAY POWDER DIFFRACTION DATA OF Mn_3Ge_5

h	*k*	*l*	I_{obs}	d_{obs} (nm)	d_{calc} (nm)
2	0	0	vw	0.2872	0.2872
2	1	2	s	0.2407	0.2409
1	1	5	vs	0.2290	0.2293
2	1	3	vs	0.2247	0.2246
2	2	0	m	0.2301	0.2031
1	1	6	m	0.2013	0.2011
1	0	7	w	0.1870	0.1875
2	0	6	w	0.1803	0.1802
3	0	3	s	0.1770	0.1770
3	1	4	w	0.1609	0.1610
2	1	7	vw	0.1568	0.1570
3	2	2	vw	0.1553	0.1553
3	1	5	vw	0.1520	0.1520
3	2	3	vw	0.1493	0.1506
1	0	9			0.1490
2	1	8	w	0.1438	0.1438
4	1	1	vw	0.1387	0.1386
3	0	7	vw	0.1376	0.1377
4	1	2	w	0.1367	0.1366
4	1	3	vw	0.1336	0.1334
2	1	9	vw	0.1326	0.1323
4	2	0	w	0.1285	0.1285
3	3	4	w	0.1261	0.1261
2	0	10	w	0.1249	0.1250
3	2	7	w	0.1242	0.1242
3	0	9	vw	0.1203	0.1202
3	2	8	vw	0.1174	0.1174
3	3	6	w	0.1170	0.1169
4	3	1	vw	0.1145	0.1145

Note. v, very; w, weak; s, strong; m, medium.

TABLE II

CHEMICAL COMPOSITIONS OF Mn_3Ge_5

	Found (at.%)	Calculated (at.%)
Mn	31.2 ± 0.1	31.2
Ge	68.8 ± 0.1	68.8

The crystal structure of defect-type disilicide compounds such as $Mn_{11}Si_{19}$ possesses tetragonal symmetry (Schoenflies symbol D_{2d}) in which the unit cell consists of many tetragonal pseudocells stacked along the *c*-axis direction. From the results of X-ray powder diffraction analysis, the number of subcells stacked along the *c*-axis was estimated to be three for the high-pressure product of Mn_3Ge_5. The analytical results of chemical composition of the sample were in good agreement with the calculated values for the chemical formula of Mn_3Ge_5 (see Table II).

The crystallographic parameters of Mn_3Ge_5 are listed in Table III along with those of other defect disilicide type compounds (*10*). Although the values of *c* vary in relation to the number of subcells, those of c'/a are in the range of 0.79–0.83 for all of these compounds. From the results of thermal analysis, Mn_3Ge_5 was stable up to 300°C and decomposed to MnGe, $Mn_{11}Ge_8$, and Ge at 300–350°C under atmospheric pressure.

The temperature dependence of the electrical resistivity and thermoelectric power of Mn_3Ge_5 is shown in Figs. 3 and 4. Electrical resistivity increased with increasing temperature in the range of 80–200 K, and was almost constant above 200 K. Thermo-

TABLE III

CRYSTALLOGRAPHIC PARAMETERS OF DEFECT DISILICIDE-TYPE COMPOUNDS

Compound	Lattice parameters (nm) *a*	*c*	*c′*	*c′/a*
$Mn_{11}Si_{19}$	0.5518	4.814	0.4376	0.793
$Mn_{26}Si_{45}$	0.5515	11.336	0.4360	0.791
$Mn_{15}Si_{26}$	0.5525	6.555	0.4370	0.791
$Mn_{27}Si_{47}$	0.5530	11.794	0.4368	0.790
Mn_4Si_7	0.5525	1.746	0.4365	0.790
Tc_4Si_7	0.5737	1.810	0.4525	0.789
$Rh_{10}Ga_{17}$	0.5813	4.746	0.4746	0.816
Ir_3Ga_5	0.5823	1.420	0.4732	0.813
$V_{17}Ge_{31}$	0.591	8.365	0.4921	0.833
$Cr_{11}Ge_{19}$	0.580	5.234	0.4758	0.820
$Mo_{13}Ge_{23}$	0.5987	6.354	0.4888	0.816
Ru_2Ge_3	0.5718	0.924	0.4620	0.808
Ir_4Ge_5	0.564	1.824	0.4560	0.809
Mn_3Ge_5[a]	0.5745	1.389	0.4630	0.806

[a] Present work.

electric power was relatively large, 50–70 μV/K, and its sign was positive. These results indicated that Mn_3Ge_5 was a *p*-type degenerate semiconductor or a semimetal.

It was reported that $MnSi_{2-x}$ ($0.250 \leqq x \leqq 0.273$) was a *p*-type degenerate semiconductor and its energy gap was 0.4–0.8 eV (7). Mn_3Ge_5 was also expected to be a semiconductor, having a narrow energy gap, or a semimetal.

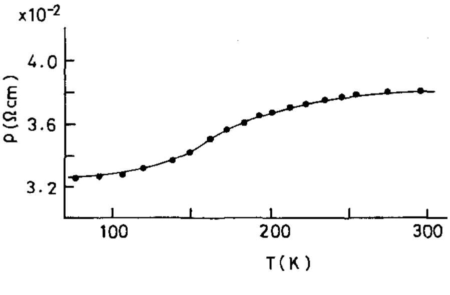

FIG. 3. Temperature dependence of electrical resistivity of Mn_3Ge_5.

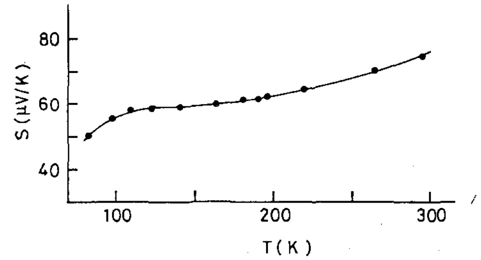

FIG. 4. Temperature dependence of thermoelectric power of Mn_3Ge_5.

Summary

High-pressure synthesis of germanium-rich manganese germanide with more than 50 at.% Ge was carried out using a Belt-type apparatus. A new phase possessing the $Mn_{11}Si_{19}$-type structure was synthesized at 800°C and 4 GPa.

The chemical formula of the present phase was determined to be Mn_3Ge_5 from the results of chemical analysis. The crystallographic parameters of Mn_3Ge_5 are $a = 0.5745$ and $c = 1.389$ (nm), which indicates that its unit cell consists of three subcells along the *c*-axis.

Thermal analysis data indicated that Mn_3Ge_5 was stable up to 300°C and decomposed to MnGe, $Mn_{11}Ge_8$, and Ge at 300–350°C under atmospheric pressure. From the results of electrical property measurements on Mn_3Ge_5, it was found to be a *p*-type conductor and it may possibly be a degenerate semiconductor or a semimetal. Its thermoelectric power was 50–70 μV/K over the temperature range 80–300 K.

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