

# High-temperature heat contents, thermal diffusivities, densities, and thermal conductivities of *n*-type SiGe(GaP), *p*-type SiGe(GaP), and *p*-type SiGe alloys

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The high-temperature heat contents of *n*-type SiGe(GaP), *p*-type SiGe(GaP), and *p*-type SiGe alloys were measured from 400 to 1400 K by using a copper block drop calorimeter. The heat capacity and related thermodynamic functions were calculated. Smoothed values of  $H_f^0 - H_{298.15}^0$ ,  $C_p$ ,  $S_f^0 - S_{298.15}^0$ , and  $-(F_f^0 - H_{298.15}^0)T^{-1}$  were tabulated at 100-K intervals. Thermal diffusivities were measured by using a laser technique. Thermal conductivities were calculated from the heat capacity, thermal diffusivity, and density.

## I. INTRODUCTION

Silicon-germanium alloys have been used as practical thermoelectric materials for radioisotope thermoelectric generators.<sup>1</sup> The conversion efficiency of a thermoelectric generator depends on the electrical and thermal properties of its thermocouple materials. The heat capacity of most semiconductors rises above the Dulong-Petit value at high temperatures as a result of anharmonicity.<sup>2</sup> The heat capacities of silicon, germanium, and silicon-germanium alloys have been studied in the temperature range 300–1000 K by a temperature modulation technique.<sup>3</sup> Recently, in order to reduce the thermal conductivity of silicon-germanium alloys, the addition of small amounts of gallium phosphide has been investigated and was shown to be beneficial.<sup>4</sup>

In the present study heat content measurements of *n*-type SiGe(GaP), *p*-type SiGe(GaP), and *p*-type SiGe alloys were made from 400 to 1400 K using a copper block drop calorimeter. The various thermodynamic functions (heat capacity, entropy, and free energy function) were calculated from these data. Thermal diffusivity measurements were made using a laser flash technique. Thermal expansion coefficients were measured from 300 to 1320 K and room-temperature densities were measured on *n*-type SiGe(GaP), *p*-type SiGe(GaP), and *p*-type SiGe alloys prepared by sintering mixtures of heavily doped SiGe and GaP powders. Thermal conductivities were then calculated for various temperatures from the measured heat capacities, thermal diffusivities, and densities of these alloys.

## II. EXPERIMENT

Samples of *n*- and *p*-type SiGe(GaP) and *p*-type SiGe were prepared by hot pressing at the Valley Forge Space Center of the General Electric Company. The *p*-type SiGe was prepared by induction melting silicon, germanium, and boron in a fused silica crucible under high vacuum. The melt

was cast into a water-cooled copper mold resulting in a 440-g ingot which was mechanically pulverized to  $\sim 80$  mesh. Comminution to the final particle size was achieved by wet grinding in a planetary ball mill using agate balls and an agate container. Sintering was performed in a double-action vacuum hot press under 138 MPa (20 kpsi) of pressure, applied after achieving a soak temperature of 1633 K, using TZM (a trade name for an Amax Corp. high-temperature alloy containing titanium-zirconium-molybdenum) molds with a light graphite coating to reduce friction during compact ejection. The heating rate to the soak temperature was about 25 K/min. After soaking at temperature, pressure was released and the compact ejected. Furnace power was then turned off and the furnace allowed to cool.

A *p*-type SiGe(GaP) was prepared by mechanically mixing, using alumina balls in an alumina container, *p*-type SiGe powder, obtained by pulverizing a compact of *p*-type SiGe prepared as described above with powders of gallium phosphide and boron. The mixture was hot pressed at 1513 K and 207 MPa (30 kpsi). An *n*-type SiGe(GaP) was prepared by sintering a mixture of heavily doped *n*-type SiGe and GaP at 1513 K and 207 MPa. The resulting hot pressed cylinders were 7.6 cm in diameter and 2.2 cm high. The samples were fine grained with a nearly uniform grain size [ $\sim 6 \mu\text{m}$  for the two SiGe(GaP) samples and  $\sim 15 \mu\text{m}$  for the *p*-type SiGe sample] and had  $>98\%$  of theoretical density. Nominal compositions of the final alloys are listed in Table I. The heat contents of *n*-type SiGe(GaP), *p*-type SiGe(GaP), and *p*-type SiGe alloys were determined in an adiabatic block drop calorimeter which has been previously described in detail.<sup>5,6</sup>

Samples weighing about 2 g were each sealed in a tantalum crucible under 0.9-atm helium. The crucibles containing the samples were heated under approximately 0.2-atm argon and held at a constant temperature for at least 30 min before dropping them into the copper block. The net temperature rise of the block was measured and related to the heat content of the sample. The correction for tantalum cru-

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TABLE I. The chemical composition of *n*-type SiGe(GaP), *p*-type SiGe(GaP), and *p*-type SiGe alloys.

Alloy	Composition (at. %)				
	Si	Ge	Ga	P	B
<i>n</i> -type SiGe(GaP)	76.41	19.10	1.96	2.53	...
<i>p</i> -type SiGe(GaP)	71.70	17.93	0.99	0.99	8.39
<i>p</i> -type SiGe	79.79	19.96	...	...	0.25

cibles was determined by measuring the heat content of the empty crucible in a series of drops. This correction included any heat loss by the crucible during the drop. The calibration giving the relationship between the temperature rise of the block and the heat content of the sample was determined electrically and was checked by measuring the heat content of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.<sup>7,8</sup> Our heat content data of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> agreed with the published data within a maximum deviation of 1%.

Thermal diffusivities were measured using a laser flash technique. The laser diffusivity apparatus is comprised of four discrete modules, a cold wall vacuum furnace, a laser and pulsing circuit, infrared lenses and detector, and a data analysis module. The cold wall vacuum furnace can be operated from ambient temperature to well in excess of 2300 K and maintain a vacuum in the 10<sup>-6</sup> Torr range. A graphite sample holder holds the sample with only point contact between the sample and the graphite holder. Other holders of tungsten, alumina, and platinum are available for other applications. The laser is a Korad neodymium glass rod, which emits a triangular pulse of 1.6 ms width. Energy can be preselected up to 20 J per pulse. The irradiated area is in the form of a circular spot of 1.25 cm<sup>2</sup>. Normally a 1-cm-diam specimen is chosen so that the entire face is irradiated. The heat pulse from the backside of the specimen is focused by an IRTRAN™ lens onto an infrared associated indium antimonide photovoltaic infrared detector. A sapphire window with a coating of germanium protects the detector from any laser energy which might be reflected within the chamber or which might pass directly to the detector should the sample crack or become displaced. Output from the detector passes to a Nicolet 2049 digital storage oscilloscope. Once stored, the output waveform can be transferred to the PDP 11-34 host computer or a PC by a RS232 interface. As a minimum, the 25%, 50%, and 75% rise times are utilized to compute the thermal diffusivities. Generally, reproducibility is better than 4% at temperatures above 600 K.

Densities were determined on the compacts by immersion in water at room temperature. Thermal expansion measurements were performed from 300 to 1320 K in a helium atmosphere using a Theta Industries "Dilatronic-II" differential dilatometer employing single-crystal sapphire (National Bureau of Standards reference material 732) as a standard. High-temperature densities were calculated using the room-temperature values corrected by the thermal expansion data.

### III. RESULTS AND DISCUSSIONS

Measured heat contents of *n*-type SiGe(GaP), *p*-type SiGe(GaP), and *p*-type SiGe alloys are listed in Table II and

TABLE II. Measured heat content values for *n*-type SiGe(GaP), *p*-type SiGe(GaP), and *p*-type SiGe alloys.

<i>n</i> -type SiGe(GaP)		<i>p</i> -type SiGe(GaP)		<i>p</i> -type SiGe	
<i>T</i> (K)	$H_T^0 - H_{298.15}^0$ (J mol <sup>-1</sup> )	<i>T</i> (K)	$H_T^0 - H_{298.16}^0$ (J mol <sup>-1</sup> )	<i>T</i> (K)	$H_T^0 - H_{298.15}^0$ (J mol <sup>-1</sup> )
374	1845	373	1711	375	1916
474	4138	473	3971	471	4192
572	6548	571	6381	574	6607
673	9125	675	8920	674	8983
781	11807	772	11276	774	11527
869	14117	882	14180	874	14230
966	16631	968	16451	972	16661
1069	19430	1068	19108	1076	19472
1181	22623	1184	22184	1176	22200
1271	25020	1275	24748	1275	24886
1376	28108	1376	27723	1375	27853
1424	30631	1426	30058	1475	30518
1472	35346	1472	31635	1525	32058

shown in Fig. 1. Heat contents of the alloys were found to be nearly linear up to ~1375 K. Figure 1 indicates that above 1375 K some melting occurs in the *n*- and *p*-type SiGe(GaP) alloys, and that up to 1475 K no melting occurs in the *p*-type SiGe alloy. Heat contents of these alloys increase in the order of *p*-type SiGe(GaP) alloy < *p*-type SiGe alloy < *n*-type SiGe(GaP) alloy for all temperatures between 300 and 1375 K.

Heat contents of the *n*-type SiGe(GaP), *p*-type SiGe(GaP), and *p*-type SiGe alloys as compared with those of pure silicon and germanium are shown in Fig. 2.<sup>9</sup> As expected, the heat contents of these alloys were found to lie between the heat contents of silicon and germanium.

The following equations relating heat contents and temperature were tested as fits to the experimental enthalpy data:

$$H_T^0 - H_{298.15}^0 = A + BT + CT^2, \quad (1)$$

$$H_T^0 - H_{298.15}^0 = A + BT + CT^2 + DT^3, \quad (2)$$

$$H_T^0 - H_{298.15}^0 = A + BT + CT^2 + DT^{-1}. \quad (3)$$

It was found that the experimental data were best represented by Eq. (3) for all three SiGe alloys as measured by the

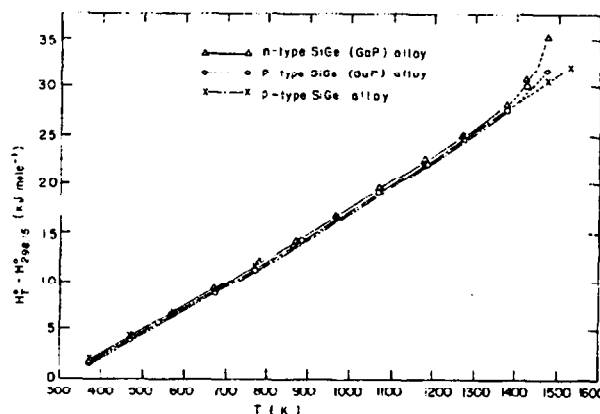


FIG. 1. High-temperature heat contents of *n*-type SiGe(GaP), *p*-type SiGe(GaP), and *p*-type SiGe alloys.

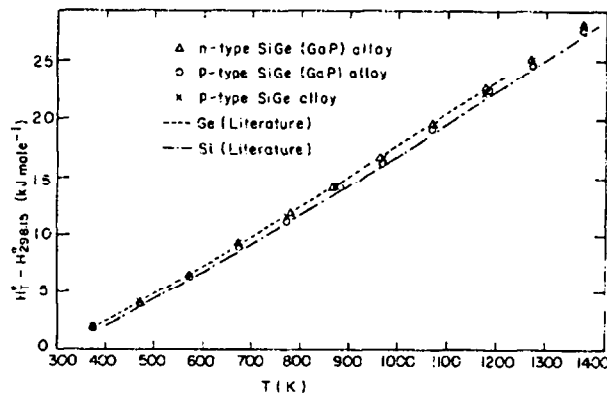


FIG. 2. High-temperature heat contents of germanium, silicon, *n*-type SiGe(GaP), *p*-type SiGe(GaP), and *p*-type SiGe alloys.

root mean square of the relative fitting error. This is consistent with the recommendation made over 50 years ago that Eq. (3) is the best one to use to represent the high-temperature enthalpy data.<sup>10</sup> For the low-temperature range, a value of zero was used as a fixed data point for  $H_T^0 - H_{298.15}^0$ . The constants  $A$ ,  $B$ ,  $C$ , and  $D$  together with the root mean square of relative fitting error are shown in Table III.

The heat capacity of a material at constant pressure,  $C_p$ , is defined as

$$C_p = \left( \frac{\delta H}{\delta T} \right)_p \quad (4)$$

Therefore, by differentiating Eq. (3) the heat capacity of the alloy as a function of temperature is

$$C_p = B + 2CT - DT^{-2}. \quad (5)$$

This expression is used to calculate the change in entropy,  $S_T^0 - S_{298.15}^0$ , from the relationship

$$S_T^0 - S_{298.15}^0 = \int_{298.15}^{T_{\max}} \left( \frac{C_p}{T} \right) dT, \quad (6)$$

provided there are no transitions and melting does not occur below  $T_{\max}$ . Combining Eqs. (5) and (6), the entropy change is calculated directly from the experimental data.

The free energy function,  $-(F_T^0 - H_{298.15}^0)/T$ , is defined as

$$-(F_T^0 - H_{298.15}^0)/T = S_T^0 - S_0^0 - (H_T^0 - H_{298.15}^0)/T, \quad (7)$$

where  $S_T^0$  is the entropy at temperature  $T$ , and  $S_0^0$  is the entropy at 0 K. In order to calculate the free energy function,

the quantity  $S_T^0 - S_0^0$  must be evaluated. Since data obtained from copper block drop calorimetry measurements give only  $S_T^0 - S_{298.15}^0$ ,  $S_{298.15}^0 - S_0^0$  must be estimated or obtained from low-temperature calorimetry data.

The entropy at 298.15 K was estimated to be equal to the sum of the products of fractional amounts of the various elements ( $f_i$ ) in the alloys times the respective elemental entropies at 298.15 K,  $S_i$ , i.e.,  $\sum f_i S_i$ . For phosphorous the entropy of the red "IV" polymorphic form was used in these calculations. This gives values of 21.71, 20.21, and 21.25 J/mol deg, respectively, for the *n*-type SiGe(GaP), *p*-type SiGe(GaP), and *p*-type SiGe alloys.

High-temperature heat contents, heat capacities, entropy increments, and free energy functions may be calculated from the fit parameters listed in Table III. The heat contents and heat capacity are given by Eqs. (3) and (5), respectively. By substitution of Eq. (5) into Eq. (6) we obtain the following expression for the entropy increment in terms of the fit parameters:

$$S_T^0 - S_{298.15}^0 = B \ln(T/298.15) + 2C(T - 298.15) + 0.5D(1/T^2 - 1/298.15^2). \quad (8)$$

The free energy function in terms of the fit parameters is obtained by combining Eqs. (3) and (8) and the estimated value for  $S_{298.15}^0$  given above:

$$-(F_T^0 - H_{298.15}^0)/T = S_{298.15}^0 - A/T - B[1 - \ln(T/298.15)] + C(T - 596.30) - 0.5D(1/T^2 - 1/298.15^2). \quad (9)$$

Gerlich, Abeles, and Miller<sup>3</sup> have studied the specific heats of silicon, germanium, and silicon-germanium alloys in the temperature range 300–1000 K by a temperature-modulation technique. They showed that the heat capacity at constant pressure  $C_p$  appreciably exceeds the Dulong-Petit values  $C_{DP}$  at high temperature (above the Debye temperature,  $\theta_D$ ). The divergence can be represented by

$$C_p/C_{DP} = 0.95 + \alpha T/\theta_D, \quad (10)$$

where  $T$  is the absolute temperature and  $\alpha = 0.081$  is independent of the alloy composition. Equation (10) fitted experimental data of silicon, germanium, and silicon-germanium alloys when  $T/\theta_D$  exceeded 1.2. The Debye temperatures of  $\text{Si}_{0.7}\text{Ge}_{0.3}$  and  $\text{Si}_{0.85}\text{Ge}_{0.15}$  alloys are 520 and 578 K, respectively.<sup>11</sup> The heat capacities of the  $\text{Si}_{0.7}\text{Ge}_{0.3}$  and  $\text{Si}_{0.85}\text{Ge}_{0.15}$  alloys, as derived from the above equation by Gerlich, Abeles, and Miller<sup>3</sup> are larger than

TABLE III. Least-squares fit parameters of the heat content of *n*-type SiGe(GaP), *p*-type SiGe(GaP), and *p*-type SiGe alloys.  $H_T^0 - H_{298.15}^0 = A + BT + CT^2 + DT^{-1}$  (J mol<sup>-1</sup>).

Alloy	A	B	$C \times 10^4$	$D \times 10^{-4}$	rms*	Temperature range (K)
<i>n</i> -type SiGe(GaP)	-6295	21.05	28.95	-7.042	0.895	298.15–1376
<i>p</i> -type SiGe(GaP)	-6649	21.07	28.03	+3.553	0.510	298.15–1376
<i>p</i> -type SiGe	-5203	19.48	34.04	-26.967	0.947	298.15–1375

\* Root mean square of relative fitting errors (%).

TABLE IV. High-temperature specific heats, thermal diffusivities, densities, and thermal conductivities of *n*-type SiGe(GaP), *p*-type SiGe(GaP), and *p*-type SiGe alloys.

Temperature (K)	Specific heat (J g <sup>-1</sup> deg <sup>-1</sup> )	Thermal diffusivity (cm <sup>2</sup> s <sup>-1</sup> )	Density (g cm <sup>-3</sup> )	Thermal conductivity (W cm <sup>-1</sup> deg <sup>-1</sup> )
<i>n</i> -type SiGe(GaP) alloy				
400	0.6350	0.0176	3.016	0.0337
500	0.6462	0.0176	3.013	0.0343
600	0.6596	0.0172	3.009	0.0341
700	0.6737	0.0167	3.005	0.0338
800	0.6881	0.0165	3.001	0.0341
900	0.7030	0.0164	2.997	0.0345
1000	0.7180	0.0162	2.993	0.0348
1100	0.7332	0.0162	2.989	0.0355
1200	0.7484	0.0165	2.985	0.0369
1300	0.7636	0.0168	2.981	0.0382
1400	0.7788	0.0172	2.978	0.0399
<i>p</i> -type SiGe(GaP) alloy				
400	0.6586	0.0191	3.000	0.0377
500	0.6768	0.0189	2.996	0.0383
600	0.6940	0.0185	2.992	0.0384
700	0.7108	0.0181	2.989	0.0384
800	0.7273	0.0176	2.985	0.0382
900	0.7436	0.0173	2.980	0.0383
1000	0.7598	0.0173	2.976	0.0391
1100	0.7758	0.0179	2.972	0.0413
1200	0.7921	0.0186	2.967	0.0437
1300	0.8080	0.0193	2.963	0.0462
1400	0.8243	0.0197	2.959	0.0481
<i>p</i> -type SiGe alloy				
400	0.6469	...	2.997	...
500	0.6488	...	2.993	...
600	0.6585	0.0224	2.990	0.0441
700	0.6715	0.0219	2.986	0.0439
800	0.6864	0.0211	2.982	0.0432
900	0.7024	0.0202	2.977	0.0422
1000	0.7192	0.0198	2.973	0.0423
1100	0.7363	0.0202	2.969	0.0442
1200	0.7539	0.0209	2.964	0.0467
1300	0.7715	0.0224	2.960	0.0512
1400	0.7893	...	2.956	...

those we have measured on the *n*-type SiGe(GaP), *p*-type SiGe(GaP), and *p*-type SiGe alloys by about 7% at 1000 K and 3% at 1400 K. However, when one compares their results for pure silicon and germanium with the accepted values,<sup>9</sup> one finds a systematic error of +5% and +3%, respectively. Thus, it is not surprising that our data do not fit Eq. (10). If one were to refit the constants in Eq. (10) to the accepted values for silicon and germanium, our results would probably be in better agreement with Eq. (10).

The measured thermal diffusivities and densities and the specific heat which was calculated from the heat capacity Eq. (5) are given in Table IV, along with the thermal conductivities as calculated from these properties for the *n*-type SiGe(GaP), *p*-type SiGe(GaP), and *p*-type SiGe alloys. The thermal conductivity of silicon-germanium alloys as a function of temperature, composition, and doping concentration have been reported by Dismukes *et al.*<sup>12</sup> and Erofeev, Jordanishvili, and Petrov.<sup>13</sup> These alloys were prepared by a zone leveling technique and by the Czochralski technique, respectively. They reported that thermal conductivities of a *p*-type Si-30 at. % Ge alloy (Ref. 12) with boron and of an *n*-type Si-20 at. % Ge alloy (Ref. 12) with phosphorus at 900

K were 0.040 and 0.041 W cm<sup>-1</sup> deg<sup>-1</sup> and those of Si-15 at. % Ge (Ref. 13) and Si-30 at. % Ge alloys (Ref. 13) at 900 K were 0.058 and 0.047 W cm<sup>-1</sup> deg<sup>-1</sup>. These results showed that the reduction in the thermal conductivity of the crystal lattice as a result of doping is explained by the scattering of phonons by impurity ions.

Thermal conductivities of *n*-type SiGe(GaP), *p*-type SiGe(GaP), and *p*-type SiGe alloys at 900 K obtained in the present study were 0.0345, 0.0383, and 0.0422 W cm<sup>-1</sup> deg<sup>-1</sup>, respectively. Thus, the thermal conductivities of *n*-type Si-19.1% Ge(GaP) and *p*-type Si-17.9% Ge(GaP) alloys doped with GaP are significantly less than those of the other silicon-germanium alloys,<sup>12,13</sup> and that of *p*-type Si-20.0% Ge alloy examined in this study, which is about the same as those reported in the literature by Dismukes *et al.*<sup>12</sup> Based on these observations, one could easily come to the conclusion, as did Pisharody and Garvey,<sup>4</sup> that the reduced thermal conductivity was due to the presence of GaP. However, when the particle size of the three samples is taken into account [i.e., *n*- and *p*-type SiGe(GaP) alloys had an average particle size of 6 μm and 4–8 μm, respectively, while the SiGe *p*-type had a particle size of 14–16 μm] the

difference in thermal conductivities could also be explained by this property. Further proof that the grain size is more important than doping with GaP comes from the data of Pisharody and Garvey, which show that about a 40% reduction in room-temperature thermal conductivity can be achieved by reducing the particle size from 180 to 44  $\mu\text{m}$ , and about a 20% reduction at 870 K, regardless of whether or not the SiGe alloys are doped with GaP. If GaP additions cause a difference it is probably a small effect. But in order to show or prove this, one needs to make measurements on undoped and doped samples with exactly the same grain size (within  $\pm 1 \mu\text{m}$ ).

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