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# Indicates presence of a phase diagram.

Gd-Si evaluation contributed by **A.B. Gokhale** and **G.J. Abbaschian,** Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611. This work was supported by ASM INTERNATIONAL under grant No. FG 101-1. The evaluators wish to thank Dr. K.A. Gschneidner, Jr., Director, Rare-earth Information Center, Iowa State University, for his help in providing some of the literature sources. Literature searched through 1985. Professor Abbaschian is the ASM/NBS Data Program Category Editor for binary silicon alloys.

The Ge-Sm (Germanium-Samarium) System

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Equilibrium Diagram

The assessed Sm-Ge equilibrium diagram is given in Fig. 1, and the monovariant and invariant equilibria are summarized in Table 1. Figure 1 is based solely on the work of [77Ere], who investigated the system over the entire composition range by microscopy, differential thermal analysis, and X-ray phase analysis. The purities of their starting materials were reported to be 99.99 at.% for Ge and 99.67 at.% for Sm. In an earlier work [74Ere], these authors reported the intermediate phases present in the system, their melting characteristics, and crystal types.

According to these investigators, the system is characterized by:

- Hexagonal Sm_5Ge_3, the richest in Sm in the system, melts congruently at 1700 °C.
- Orthorhombic Sm_5Ge_4 forms peritectically at 1500 °C.
- Orthorhombic SmGe forms peritectically at 1400 °C.
- Sm_2Ge_3 forms peritectically at 1355 °C and undergoes allotropic transformations at 1085 and 745 °C. The room-temperature modification is hexagonal, and the higher-temperature modifications remain undetermined.
- Tetragonal $SmGe_{1.63}$ forms peritectically at 760 °C.
- Two eutectic reactions occur—between (Sm) and Sm_5Ge_3 at 890 °C and 11 at.% Ge, and between (Ge) and $SmGe_{1.63}$ at 820 °C and 85 at.% Ge.

[77Ere] indicated all the intermediate phases to be nearly stoichiometric which is supported by the crystallographic data from other investigations. They indicated the presence of $Sm_{1.04}Ge_{1.56}$, which corresponds exactly with the stoichiometry of Sm_2Ge_3, the designation preferred in this evaluation.

The terminal solid solubilities of Sm in (Ge) and Ge in (Sm) have not been determined, but may be estimated as being less than 1 at.%, based on the assumed similarity with other RE-Ge systems.

The liquidus was determined with reasonable accuracy by [77Ere]. As discussed below, the process of mixing in the liquid is exothermic.

The studies of [69Rud] indicated that Sm_5Ge_3, SmGe, and "$SmGe_2$" ($SmGe_{1.63}$) are semiconducting type, based on the measurement of electrical resistivity as a function of temperature in the range 600 to 1250 K. [69Rud] claimed that in earlier works, [68Rud] and [68Sam] detected an inversion in the resistivity of these phases from metallic to semiconducting type. However, the present evaluators could not confirm this claim on the basis of data given in these references.

Crystal Structures and Lattice Parameters

Sm-Ge crystal structure and lattice parameter data are summarized in Tables 2 and 3. The data are taken from references listed under "primary reference," chosen on the basis of thoroughness of investigation, listing of diffraction data, and reported error limits. Other pertinent references are listed under "supplementary references."

The reported crystal structure and lattice parameter data show remarkable agreement. No crystal structure and lattice parameter data were available for the two high-temperature modifications of Sm_2Ge_3. How-

ever, on the basis of data from other RE-Ge systems, it may be speculated that the first modification could be orthorhombic, $\alpha GdSi_2$ type.

Thermodynamics

The present evaluators are unaware of any thermodynamic data for either the intermediate phases or the liquid solution. The characteristics of the liquid solution were assessed in this evaluation using the experimental solubility data of [77Ere] (transcribed graphically from their reported phase diagram) and the Gibbs energies of fusion for the pure components. The results indicate that the mixing process in the liquid is exothermic, with a negative deviation from Raoultian behavior. The enthalpy of mixing could be represented by:

$$\Delta_{mix}H = X_{Ge}(1 - X_{Ge})\,(-29.35 - 37.92X_{Ge})\ \text{kJ/mol}$$

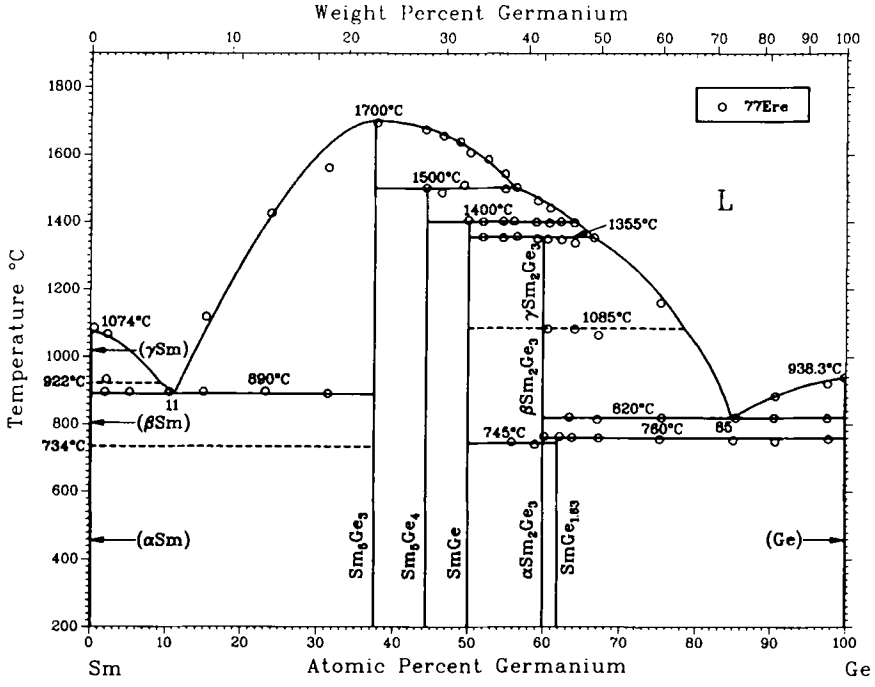
where X_{Ge} is the atomic fraction of Ge. The function indicates a maximum heat evolution of 12.51 kJ/mol at $X_{Ge} = 0.58$. These results should be used with cau-

Table 1 Special Points of the Assessed Ge-Sm Phase Diagram

Reaction	Compositions of the respective phases, at.% Ge			Temperature, °C	Reaction type	Reference
L ↔ γSm		0		1074	Melting point	[86Gsc]
γSm ↔ βSm		0		922	Allotropic	[86Gsc]
αSm ↔ βSm		0		734 (a)	Allotropic	[86Gsc]
L ↔ (αSm) + Sm_5Ge_3	11	~ 0	37.5	890	Eutectic	[77Ere]
L ↔ Sm_5Ge_3		37.5		1700	Congruent	[77Ere]
L + Sm_5Ge_3 ↔ Sm_5Ge_4	56.85	37.5	44.5	1500	Peritectic	[77Ere]
L + Sm_5Ge_4 ↔ SmGe	64.6	44.5	50	1400	Peritectic	[77Ere]
L + SmGe ↔ γSm_2Ge_3	67.26	50	60	1355	Peritectic	[77Ere]
βSm_2Ge_3 ↔ γSm_2Ge_3		60		1085	Allotropic	[77Ere]
αSm_2Ge_3 ↔ βSm_2Ge_3		60		745	Allotropic	[77Ere]
(Ge) + βSm_2Ge_3 ↔ $SmGe_{1.63}$	~ 100	60	62	760	Peritectoid	[77Ere]
L ↔ βSm_2Ge_3 + (Ge)	85	60	~ 100	820	Eutectic	[77Ere]
L ↔ Ge		100		938.3	Melting point	[Melt]

(a) Occurs at 727 °C on cooling.

Fig. 1 Assessed Sm-Ge Phase Diagram



Based on the data of [77Ere].

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tion, because they are based solely on the experimental solubility data.

The Gibbs energies of fusion were calculated by the present evaluators in the following form:

$$\Delta_{fus}G(Ge) = 32\,938.8 + 23.43\,T + 3.677 \times 10^{-3}\,T^2 - 7.761\,T \ln T \text{ J/mol}$$

and

$$\Delta_{fus}G(Sm) = 4220.84 + 20.42\,T - 3.27\,T \ln T \text{ J/mol}$$

where T is in K. The heats of fusion and heat capacities for the pure components are taken from [77Bar].

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Table 2 Sm-Ge Crystal Structure Data

Phase	Composition, at.% Ge	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
γSm (a)	0	*cI2*	$Im\bar{3}m$	*A2*	W	[86Gsc]
βSm (b)	0	*hP2*	$P6_3/mmc$	*A3*	Mg	[86Gsc]
αSm (c)	0	*hR3*	$R\bar{3}m$	*C19*	αSm	[86Gsc]
Sm_5Ge_3	37.5	*hP16*	$P6_3/mcm$	$D8_8$	Mn_5Si_3	[77Ere]
Sm_5Ge_4	44.5	(d)	*Pnma*	...	Sm_5Ge_4	[77Ere]
SmGe	50	*oC8*	*Cmcm*	B_f	CrB	[77Ere]
αSm_2Ge_3	60	*hP3*	*P6/mmm*	*C32*	AlB_2	[77Ere]
βSm_2Ge_3	60	...	...	...	...	...
γSm_2Ge_3	60	...	...	...	...	...
$SmGe_{1.63}$	62	*tI12*	$I4_1/amd$	C_c	$\alpha ThSi_2$	[77Ere]
Ge	100	*cF8*	$Fd\bar{3}m$	*A4*	C(diamond)	[King1]

(a) From 1074 to 922 °C. **(b)** From >922 to >734 °C (727 °C on cooling). **(c)** From 734 °C. **(d)** Orthorhombic.

Table 3 Sm-Ge Lattice Parameter Data

Phase	Composition, at.% Ge	Lattice parameters, nm *a*	*b*	*c*	Comment	References Primary	Supplementary
γSm	0	...	...	...	...	[86Gsc]	...
βSm	0	0.36630	...	0.58448	(a)	[86Gsc]	...
αSm	0	0.36290	...	2.6207	(b)	[86Gsc]	...
Sm_5Ge_3	37.5	0.866(1)	...	0.649(1)	...	[77Ere]	[64Gla1, 67Bus, 69May]
Sm_5Ge_4	44.5	0.774(1)	1.495(2)	0.784(2)	...	[77Ere]	[67Smi]
SmGe	50	0.4374(3)	1.0885(4)	0.3996(7)	...	[77Ere]	[65Gla, 66Tha, 66Bus, 66Hoh]
αSm_2Ge_3	60	0.4005(2)	...	0.4250(4)	...	[77Ere]	...
βSm_2Ge_3	60	...	...	...	...	...	...
γSm_2Ge_3	60	...	...	...	...	...	...
$SmGe_{1.63}$	62	0.412(1)	...	1.396(2)	...	[77Ere]	[64Gla2(c), 64Gla3(c), 67May, 68May]
Ge	100	0.56574	...	...	...	[King1]	...

(a) At 450 °C, by stabilizing with addition of impurities. **(b)** Primitive cell is rhombohedral; values given are for nonprimitive hexagonal cell. **(c)** Reported phase as $SmGe_2$.

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* Indicates key paper.

\# Indicates presence of a phase diagram.

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