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Structure and Alloy Chemistry of Metastable GeSb

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In the simple eutectic Ge–Sb system, a metastable phase GeSb with a tetragonally distorted NaCl–B1 type structure ($a_0 = 5.87_4$ Å; $c_0 = 6.20_4$ Å; $c_0/a_0 = 1.05_6$) has been prepared by rapid quenching from the melt (splat cooling). The solid solubility of Ge in Sb was enhanced from ~8 at. % Ge in equilibrium to >17 at. % Ge.

GeSb represents a new structure type; its atomic configuration can be considered as intermediate between those of Sb and Ge. The tetragonal distortion is related to the presence of 7 bonding electrons per formula unit. A metastable Ge–Sb phase diagram including GeSb is proposed.

Introduction

Even considering the general scarcity of intermediate equilibrium phases in binary combinations of B elements of the IIB(Zn) to VB(As) groups (*1*), binary compounds of IVB(Si) group elements with VB(As) group semimetals are especially rare. This is not necessarily due to large absolute structural energies of potential intermediate phases, but rather to the relatively high stability of Si or Ge which prevents occurrence of intermediate phases in equilibrium. Thus, the only IVB element that forms an equilibrium phase with Sb is Sn, whose solid modifications are the least stable of the IVB elements. This equilibrium phase, SnSb, has a NaCl–B1 type high temperature modification, with a small rhombohedral distortion occurring at low temperatures ($\alpha \approx 89°30'$) (*2*). The Pb–Sb system does not contain an equilibrium phase, but in rapidly quenched alloys a metastable phase PbSb, probably also of the NaCl–B1 type, has been found (*3, 4*). Pertinent structure types are listed in Table I.

Ge and Sb form a binary system with a simple eutectic phase diagram, shown in solid lines in Fig. 1(a). The solid solubility of Ge in Sb was reported to be 2.5 at. % Ge (*2a*) (for a redetermination, see Footnote 1) and Ge dissolves $< \approx 0.02$ at. % Sb (*2b*). The question of whether a Ge–Sb phase analogous to SnSb could be retained as a metastable phase prompted an investigation of Ge–Sb alloys rapidly quenched from the liquid by splat cooling (*1, 5, 6*). Metastable ternary Ge–Sn–Sb alloys with compositions on the GeSb–SnSb section were also studied.

Experimental Methods and Results

Ge_xSb_{1-x} alloys with $0 < x < 0.5$ and $(Ge_{1-x}Sn_x)_{0.5}Sb_{0.5}$ alloys with $0 < x < 1.0$ were prepared by the arc-melting of >99.99% pure component elements; small samples were then splat-quenched using the shock-wave atomization technique described in detail in Refs. *5–7*. Substrates were held both at room and liquid nitrogen temperatures. The resulting thin films were examined on an X-ray diffractometer with CuK_α radiation with procedures and error limits as described in Refs. (*3*) and (*7*).

Ge–Sb

Results of the quenching experiments are summarized in Table II and are indicated in Fig. 1(b); mean atomic volumes and rhombohedral angles are plotted in Fig. 2. The solid solubility of Ge in Sb is extended from the revised maximum equilibrium value of 6 ± 1.5 at. % Ge (see Footnote 1) to >17 at. % Ge, with a concomitant decrease of the rhombohedral angle α from $87°24'$ for Sb to $85°56'$ for $Ge_{0.17}Sb_{0.03}$. The setting used here is the rhombohedral setting II with 8 atoms per unit cell

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[1] The equilibrium solid solubility of Ge in Sb at 520°C was redetermined by the isoparametric method. The Sb solid solution present in two-phase samples annealed for 8 days at 520°C had lattice parameters corresponding to $Ge_{0.06\pm1}Sb_{0.94\pm1}$; the maximum solid solubility of Ge in Sb at the eutectic temperature of 590°C was therefore estimated to be 8 ± 2 at. % Ge, as indicated in Fig. 1(a).

TABLE I

GeSb AND PHASES STRUCTURALLY RELATED TO GeSb

Phase designation	Crystal system	Structure type	Atoms per unit cell	Representative Phase[a]
π	cubic	α-Po–A_h	1	π-$Au_{0.2}Sb_{0.8}$[b]
π'	rhombohedral	β-Po–A_i	1	π'-$Au_{0.4}Bi_{0.6}$[b]
π''	tetragonal	—	1	hypothetical, not observed as disordered phase
A7	rhombohedral	As–A7	8[c]	As, Sb, Bi
B1	cubic	NaCl–B1	8	SnSb(h), PbSb[b]
B1′	rhombohedral	B1(D_{Rh})	8	SnSb(l)
B1″	tetragonal	new type	8	GeSb[b]

[a] See also Ref. (*1*).

[b] Metastable phase.

[c] In rhombohedral setting II, with unit cell edges corresponding to NaCl–B1 type.

(*3*, *8*); this setting brings out the similarity of the As-A7 structure type to the simple cubic α-Po–A_h structure type (1 atom/cell, $\alpha = 90°$; π phase) and its ordered superstructure, the NaCl–B1 structure type (see Table I).

In rapidly quenched alloys with compositions between $Ge_{0.35}Sb_{0.65}$ and $Ge_{0.45}Sb_{0.55}$ a new phase appears, which was identified as metastable GeSb. Appreciable quantities of GeSb were found only in $Ge_{0.4}Sb_{0.6}$ alloys; GeSb constituted up to

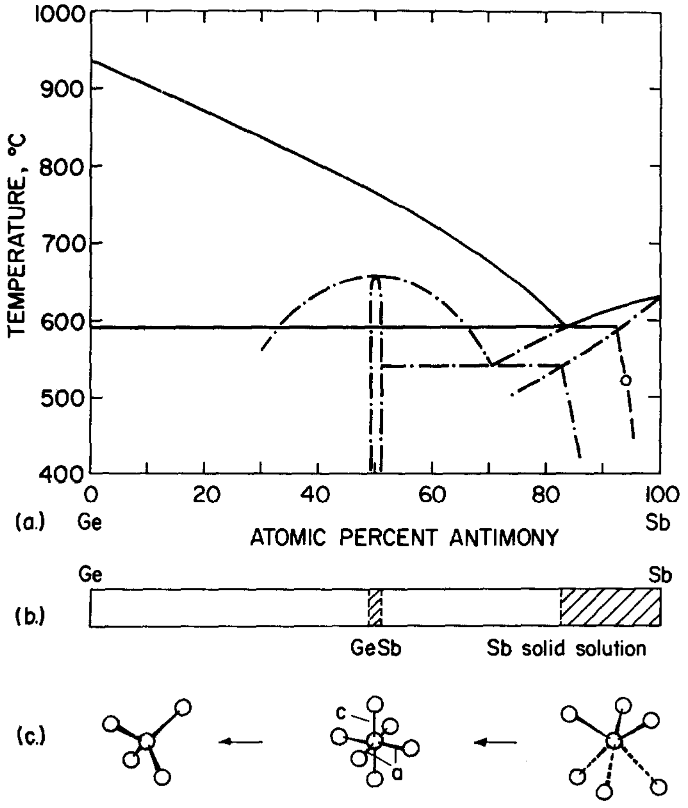

FIG. 1. (a) Equilibrium phase diagram Ge–Sb (*2*) (solid lines), with tentative metastable equilibria involving GeSb (dashed lines). (b) Schematic representation of Ge–Sb equilibrium phases (marked above the diagram) and nonequilibrium phases (marked below the diagram) obtained by splat cooling. (c) Atomic coordination in Ge, GeSb, and Sb.

TABLE II

CONSTITUTION OF SPLAT-COOLED Ge–Sb AND $(Ge_xSn_{1-x})Sb$ ALLOYS

Composition	Constitution after rapid quenching to 20°C[a]	Lattice parameters				
		Phase	a (Å)	c (Å) or α (deg)	c/a	V/atom (Å^3)
Sb	Sb	Sb	6.233	87°24′	—	30.1_9
$Ge_{0.10}Sb_{0.90}$	Sb s.s.	Sb s.s.	6.161	86°17′	—	29.0_5
$Ge_{0.17}Sb_{0.83}$	Sb s.s.	Sb s.s.	6.127	85°50′	—	28.5_2
$Ge_{0.25}Sb_{0.75}$	Sb s.s. + GeSb(trace)					
$Ge_{0.35}Sb_{0.65}$	Sb s.s. + GeSb(trace) + Ge(trace)					
$Ge_{0.40}Sb_{0.60}$	Sb s.s. + GeSb + Ge(trace)	GeSb	5.87_4	6.20_4	1.05_6	26.7_5
$Ge_{0.45}Sb_{0.55}$	Sb s.s. + GeSb(trace) + Ge					
$Ge_{0.50}Sb_{0.50}$	Sb s.s. + GeSb(trace) + Ge					
$Ge_{0.125}Sn_{0.375}Sb_{0.5}$	B1	B1	6.10_8	—	—	28.5_0
$Ge_{0.25}Sn_{0.25}Sb_{0.5}$	B1 + Ge(trace)	B1	6.06_6	—	—	27.9_0
$Ge_{0.32}Sn_{0.18}Sb_{0.5}$	B1 + B1″ + Sb s.s. + Ge(trace)	B1	6.03_4	—	—	27.4_6
		B1″	5.92_6	6.31_6	1.06_6	27.7_2
$Ge_{0.375}Sn_{0.125}Sb_{0.5}$	B1 + B1″ + Sb s.s. + Ge(trace)	B1″	5.92_6	6.28_4	1.06_0	27.5_8
$Ge_{0.44}Sn_{0.06}Sb_{0.5}$	Sb s.s. + B1″ + Ge(trace)	B1″	5.89_6	6.23_2	1.05_7	27.0_8

[a] Sb s.s. = solid solution of Ge (or Ge and Sn) in Sb
B1 = cubic (Sn, Ge)Sb solid solution based on SnSb(h) (NaCl–B1 type)
B1″ = tetragonal (Ge, Sn)Sb solid solution based or GeSb.

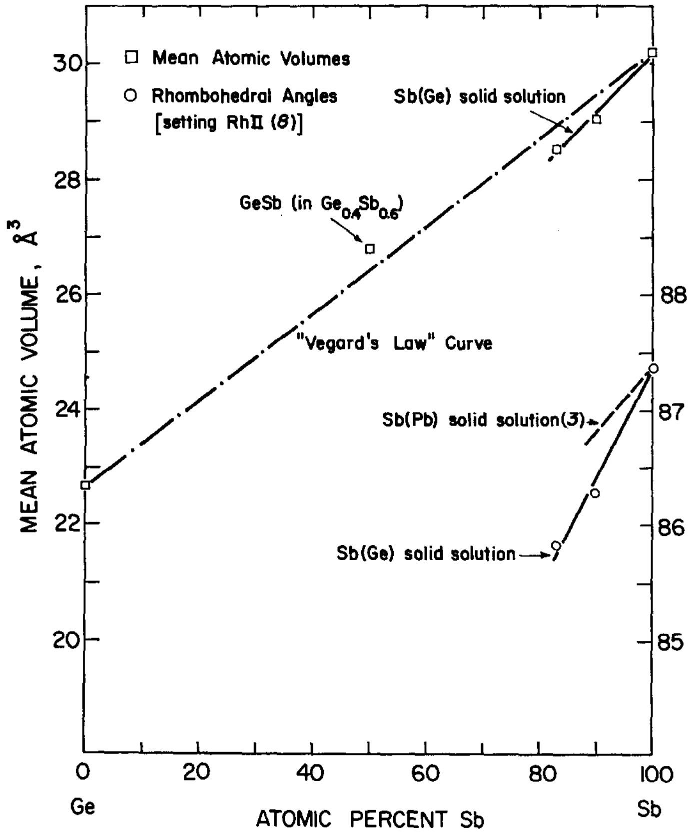

FIG. 2. Mean atomic volumes and rhombohedral angles (setting II, see text) of Ge, Sb, and splat-cooled Ge–Sb alloys.

~50% in the fastest quenched foils, the remainder being Sb solid solution and Ge. At the stoichiometric composition $Ge_{0.5}Sb_{0.5}$, GeSb failed to form.

Structure of GeSb

The diffraction pattern of this new intermediate phase is given in Table III. It was indexed with a body-centered tetragonal unit cell, space group *Immm*, with $a_0' = 4.15_4$ Å, $c_0' = 6.20_4$ Å and 4 atoms in the following positions: 2 Ge in (a): 0, 0, 0; 1/2, 1/2, 1/2 and 2 Sb in (b): 1/2, 1/2, 0; 0, 0, 1/2.

GeSb belongs to a new structure type. The identity of its structure with a tetragonally distorted NaCl–B1 type structure is brought out more clearly by the choice of a face-centered tetragonal unit cell with $a_0 = 5.87_4$ Å $(= a_0' \times \sqrt{2})$ and $c_0 = 6.20_4$ Å, $(c_0/a_0 = 1.05_6)$ with 4 Ge in 0, 0, 0; 1/2, 1/2, 0; $\circlearrowright$; and 4 Sb in 1/2, 1/2, 1/2; 1/2, 0, 0; $\circlearrowright$. The indexing of the diffraction pattern in Table II is based on the doubled unit cell. Considering that some texture is common in splat-cooled alloys (*3*, *9*), the agreement of the observed and calculated intensities is satisfactory.

The presence of NaCl type ordering in GeSb must be deduced from the observation of the odd-index reflections 111, 113, 311, 313, and 331. Of these, only 111 has a substantial calculated intensity; 111 is, however, consistently found to be too weak. GeSb may thus be partly disordered; completely disordered GeSb would be of the hypothetical π'' type (Table I) which is simple tetragonal, with an axis ratio $c''/a'' = 1.05_6$ and 1 atom in 0, 0, 0. The π'' phase type is formed by a tetragonal distortion of the simple cubic π phase (Table I) which is found in metastable alloys of Sb with additions of Au, Ni, and Pd (*10*).

TABLE III

X-RAY DIFFRACTION PATTERN OF GeSb (FROM SPLAT-COOLED $Ge_{0.40}Sb_{0.60}$ ALLOY)[a]

	$10^5 \times \sin^2 \theta$		Intensity	
hkl	Obsd	Calcd	Obsd	Calcd
111	498	499	6.8	17.9
002	~614[b]	618	~60[b]	58.0
200	687	689	100.0	100.0
202	1304	1307	55.1	78.7
220	~1385[b]	1378	~35[b]	36.2
113	1740[b]	1734	~8[b]	3.3
311	1881	1877	4.5	5.8
222	~2005[b]	1996	—[b]	40.1
004	~2463	2470	4.1	7.0
400	2757	2756	19.8	11.7
313	—[c]	3112	—[c]	2.6
204	~3167[c]	3159	—[c]	18.5
331	—	3255	—	1.2
402	~3372[b]	3373	—[b]	16.6
420	~3446[b]	3445	~20[b]	16.0
224	3849	3848	9.2	13.4
422	4083	4062	25.4	24.6

[a] Face-centered-tetragonal (see text); $a_0 = 5.87_4$ Å; $c_0 = 6.20_4$ Å; Cu K_α Radiation.

[b] Overlap with reflections of Sb solid solution.

[c] Overlap with reflections of Pt substrate.

GeSb–SnSb

As shown, the structure of GeSb is related to the NaCl–B1 type structure of the high temperature modification SnSb(h) (Table I) by a small tetragonal distortion. Therefore, the possibility of a continuous transition between these two phases existed and the constitution of metastable $(Ge_{1-x}Sn_x)_{0.5}Sb_{0.5}$ alloys was investigated. The results are given in Table II and Fig. 3. Solid solutions of both GeSb and SnSb extend far into the ternary system; the solid solution based on SnSb(h) (designated B1) can dissolve >64% GeSb, and the solid solution based on GeSb (designated B1″) can dissolve >36% SnSb.

While the atomic volumes of B1 and B1″ vary linearly with composition (with the atomic volumes of the distorted phase B1″ lying slightly higher), there is *no* gradual transition of the axial ratio *c*/*a* from 1.000 for SnSb(B1) to 1.05_6 for GeSb(B1″); in fact, rather than decreasing, *c*/*a* of GeSb increases further if SnSb is added. This shows GeSb to be a distinct, new phase.

Discussion

Crystal Chemistry of GeSb

Geometrically, the atomic arrangement in GeSb can be interpreted as intermediate between the arrangements in Sb and Ge, as seen in Fig. 1(c) and Table IV. The atomic coordination number changes in the sequence:

$$\text{Sb: } 3(+3) \rightarrow \text{GeSb: } 4(+2) \rightarrow \text{Ge: } 4(+12).$$

In GeSb, the approximately octahedral atomic coordination found in the Sb structure is retained while the number of first nearest neighbors is increased from three in the Sb structure to four, which is the coordination number in the tetrahedral A4 type structure of Ge (*11*). Continuing in the sequence indicated, the local atomic environment in the Ge structure can be related to that in GeSb by

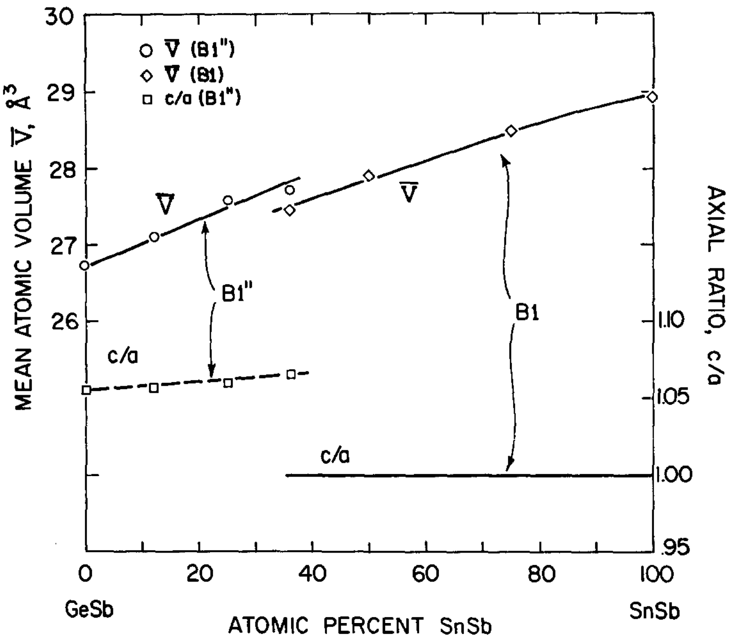

FIG. 3. Mean atomic volumes and tetragonal axial ratios *c*/*a* for SnSb and metastable phases present in splat-cooled GeSb–SnSb alloys. B1: Phases based on SnSb; B1″: Phases based on GeSb.

a further increase in the distance of the two second nearest neighbors in GeSb (with their ultimate replacement by twelve second nearest neighbors) and a buckling of the plane formed by the four first nearest neighbors in GeSb to form the coordination tetrahedra in Ge.

The first nearest neighbor distances in GeSb are slightly larger than those in Sb, despite the introduction of the smaller Ge atoms. However, as Fig. 2 shows, the mean atomic volume of GeSb lies only slightly above the "Vegard's Law" value; the distance increase is therefore due to the change from the 3(+3) coordination in Sb to the 4(+2) coordination in GeSb.

Simple symmetric structure types, such as the face-centered cubic A1 type, are often unstable with respect to small tetragonal distortions (such as the In-A6 type with $c/a > 1$ or the α_1 type with $c/a < 1$) (*1*, *12*) or rhombohedral distortions (Hg-A10 type) (*13*). By the use of the pseudopotential method these features have been explained at least qualitatively as due to an improved distribution of the structural weights on the energy characteristic (*12*). Instability of the simple cubic π type and its B1 superstructure with respect to rhombohedral distortions are well known (Table I); as the existence of GeSb shows, a tetragonal distortion of the π type is also possible. A complete calculation might show why the tetragonal distortion is energetically favored in GeSb over the undistorted B1 type or the rhombohedral distortion found in SnSb(I). One may try to interpret the structure of GeSb qualitatively on the basis of a Jahn–Teller type distortion.

It was shown by detailed band structure calculations (*14*, *15*) of group V elements and IV–VI compounds that here the conventional chemical bond picture can be applied to the band structure in first approximation (*16*): in A7-type semimetals the *s* bonding and antibonding bands are occupied without net bonding effect; the occupied *p* bonding bands lead to bonding in a distorted octahedral coordination. Sublattice displacement and spin–orbit coupling contributions cause the semimetallic character. In IV–VI compounds, large potential differences of the components may remove the rhombohedral distortion and internal atomic displacement, producing a cubic semiconductor. A rhombohedral–cubic transition is observed in

TABLE IV

ATOMIC DISTANCES (Å) AND NUMBER OF NEIGHBORS IN Ge–Sb PHASES

Sb	GeSb	Ge
2.903 (3*x*)	2.93_7 (4*x*)	2.450 (4*x*)
3.361 (3*x*)	3.10_2 (2*x*)	4.001 (12*x*)

GeTe–SnTe alloys which is believed to be due to the stronger Sn pseudo potential.

In GeSb, the primitive unit cell with 1 GeSb/cell is triclinic. There are 9 electrons/formula unit which probably occupy bands similar to those in A7 but leave the *s* antibonding band half filled. The tetragonal distortion in GeSb is accompanied by a reduction of the cubic symmetry of the *s*-like band to a tetragonal one. A preferential occupation of the *s* antibonding band by the extra electron in the *z* direction, with smaller antibonding contributions in the *x*, *y* directions seems to lead to a reduction of the energy of GeSb.

In any case, the cohesive energy of GeSb is due to 3.5 bonding electrons/atom and should be at least comparable to that of Sb. The question then arises why GeSb is not an equilibrium phase. The answer lies in the higher relative stability of Ge which makes a Ge–Sb equilibrium more favorable than the Ge–GeSb and GeSb–Sb equilibria. This argument would apply even more strongly to a hypothetical phase SiSb.

The Metastable Ge–Sb Phase Diagram

Calorimetric measurements on splat-cooled metastable phases (*17*) have shown that generally a supercooling of 100–200°K is induced by the rapid quenching process. Phase diagrams including metastable phases can then be drawn (*6*). With this supercooling temperature interval as a guide, a tentative metastable Ge–Sb phase diagram incorporating GeSb has been drawn and is shown by dashed lines in Fig. 1(a). This diagram also illustrates the large metastable solid solubility of Ge in Sb and gives a qualitative explanation for the experimental observation mentioned above that GeSb can only be retained in alloys with nonstoichiometric compositions, especially $Ge_{0.4}Sb_{0.6}$. This effect is common in liquid-quenched materials (*17*, *18*); it is due to the composition-dependence of the supercooling ΔT_s required to retain a given metastable phase. ΔT_s is the difference of the liquidus temperatures of the stable and metastable phases [see Fig. 1(a)]; due to the zero slope of the liquidus of any compound at the composition x_M of its stable or metastable melting point maximum, there will always be some range of composition not including x_M where ΔT_s is smaller than at x_M.

Acknowledgments

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