Ge – Te (Germanium – Tellurium)

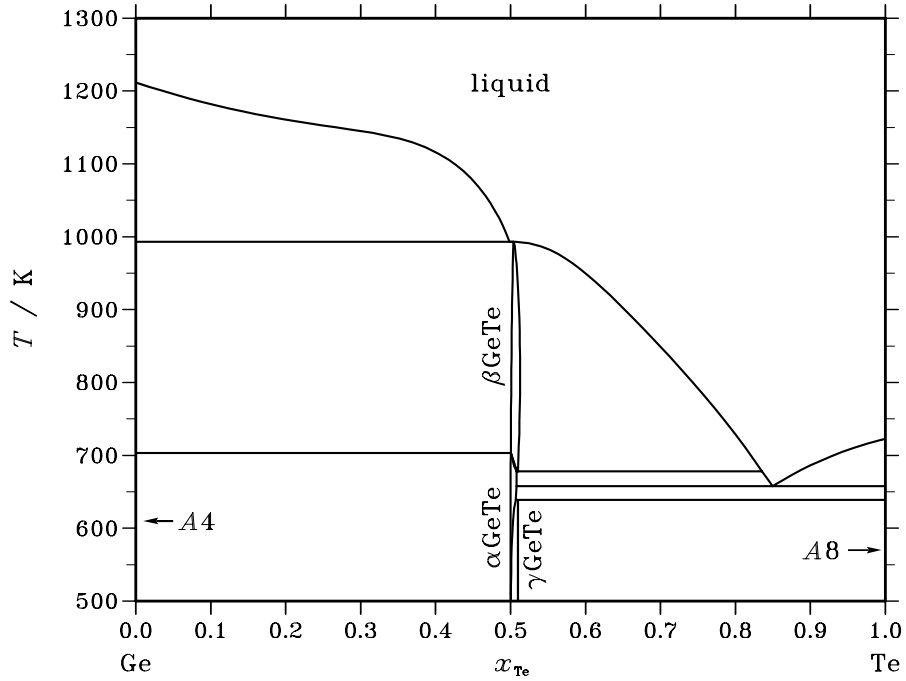

Fig. 1. Calculated phase diagram for the system Ge-Te.

Germanium-tellurium alloys are interesting materials for semiconductor and optical applications. Ge-Sb-Te alloys are used in fast phase-change optical data storage disks. The literature about the Ge-Te system has been reviewed and a thermodynamic assessment has been provided by [99Sch]. The optimisation takes into account many investigations on the phase diagram which cover the whole composition range and the temperature range up to the liquidus. The liquid has been optimised using mainly the mixing enthalpy data of [96Sch] which cover the temperature range between 973 and 1213 K. Furthermore, literature data for enthalpy increments and heat capacities in the liquid for αGeTe as well as for βGeTe have been considered. The liquid has been described with an associate model using the species Ge, Te, and GeTe. Although the optimisation provides generally a good description of the system, certain deviations from the experimental data remain especially in the melt at low temperatures. Here, the behaviour of the melt is considerably influenced by short-range order which is not treated adequately by the model.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Ge,GeTe,Te)_1$
$A4$	$A4$	C(diamond)	$cF8$	$Fd\overline{3}m$	DIAMOND_A4	Ge_1
αGeTe	$\cdots$	$\cdots$	$hR*$	$R3m$	GETE_LOW	$(Ge,\Box)_1Te_1$
βGeTe	$B1$	NaCl	$cF8$	$Fm\overline{3}m$	GETE_HIGH	$(Ge,\Box)_1Te_1$
γGeTe	$\cdots$	$\cdots$	$o**$	$\cdots$	GETE_GAMMA	$Ge_{49}Te_{51}$
$A8$	$A8$	γSe	$hP3$	$P3_121$	TRIGONAL_A8	Te_1

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Te}			$\Delta_{\mathrm{r}}H$ / (J/mol)
liquid $\rightleftharpoons$ βGeTe	congruent	993.1	0.504	0.504		−19214
liquid $\rightleftharpoons$ $A4$ + βGeTe	eutectic	993.0	0.499	0.000	0.504	−19325
$A4$ + βGeTe $\rightleftharpoons$ αGeTe	peritectoid	703.1	0.000	0.500	0.500	−549
βGeTe $\rightleftharpoons$ αGeTe + liquid	metatectic	678.2	0.510	0.508	0.836	−890
liquid $\rightleftharpoons$ αGeTe + $A8$	eutectic	658.0	0.849	0.508	1.000	−15041
αGeTe + $A8$ $\rightleftharpoons$ γGeTe	peritectoid	638.8	0.507	1.000	0.510	−889

Table IIIa. Integral quantities for the liquid phase at 1213 K.

x_{Te}	ΔG_{m} [J/mol]	ΔH_{m} [J/mol]	ΔS_{m} [J/(mol·K)]	$G_{\mathrm{m}}^{\mathrm{E}}$ [J/mol]	$S_{\mathrm{m}}^{\mathrm{E}}$ [J/(mol·K)]	ΔC_P [J/(mol·K)]
0.000	0	0	0.000	0	0.000	0.000
0.100	−4033	−1570	2.030	−754	−0.673	1.873
0.200	−6841	−3505	2.750	−1794	−1.410	3.790
0.300	−9303	−5868	2.832	−3142	−2.247	6.003
0.400	−11515	−8577	2.422	−4727	−3.174	8.863
0.500	−13204	−10853	1.938	−6213	−3.825	10.811
0.600	−13732	−11128	2.147	−6944	−3.449	7.446
0.700	−12641	−9411	2.662	−6480	−2.417	3.303
0.800	−10010	−6857	2.599	−4963	−1.561	1.601
0.900	−6001	−3735	1.868	−2723	−0.835	0.751
1.000	0	0	0.000	0	0.000	0.000

Reference states: Ge(liquid), Te(liquid)

Table IIIb. Partial quantities for Ge in the liquid phase at 1213 K.

x_{Ge}	ΔG_{Ge} [J/mol]	ΔH_{Ge} [J/mol]	ΔS_{Ge} [J/(mol·K)]	$G_{\mathrm{Ge}}^{\mathrm{E}}$ [J/mol]	$S_{\mathrm{Ge}}^{\mathrm{E}}$ [J/(mol·K)]	a_{Ge}	γ_{Ge}
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−926	171	0.904	137	0.028	0.912	1.014
0.800	−1657	778	2.007	594	0.152	0.849	1.061
0.700	−2259	1872	3.406	1338	0.441	0.799	1.142
0.600	−3379	2318	4.697	1773	0.450	0.715	1.192
0.500	−7075	−3336	3.082	−85	−2.681	0.496	0.992
0.400	−15262	−16765	−1.239	−6021	−8.857	0.220	0.550
0.300	−25951	−25181	0.635	−13809	−9.375	0.076	0.254
0.200	−36619	−29519	5.854	−20387	−7.528	0.026	0.132
0.100	−48559	−34531	11.565	−25337	−7.580	0.008	0.081
0.000	$-\infty$	−40496	∞	−29089	−9.404	0.000	0.056

Reference state: Ge(liquid)

Table IIIc. Partial quantities for Te in the liquid phase at 1213 K.

x_{Te}	ΔG_{Te} [J/mol]	ΔH_{Te} [J/mol]	ΔS_{Te} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{Te}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{Te}}$ [J/(mol·K)]	a_{Te}	γ_{Te}
0.000	$-\infty$	−14090	∞	−6241	−6.471	0.000	0.539
0.100	−31994	−17237	12.165	−8771	−6.980	0.042	0.419
0.200	−27576	−20635	5.723	−11344	−7.659	0.065	0.325
0.300	−25736	−23928	1.491	−13594	−8.520	0.078	0.260
0.400	−23719	−24920	−0.990	−14477	−8.609	0.095	0.238
0.500	−19332	−18370	0.793	−12341	−4.970	0.147	0.294
0.600	−12711	−7369	4.404	−7559	0.157	0.284	0.473
0.700	−6936	−2653	3.531	−3339	0.566	0.503	0.718
0.800	−3357	−1191	1.786	−1107	−0.070	0.717	0.896
0.900	−1273	−313	0.791	−210	−0.085	0.881	0.979
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Te(liquid)

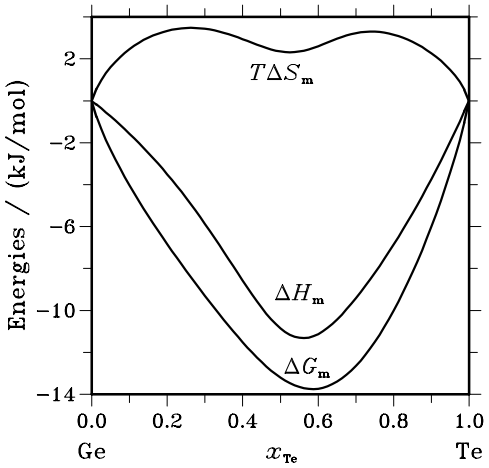

Fig. 2. Integral quantities of the liquid phase at T=1213 K.

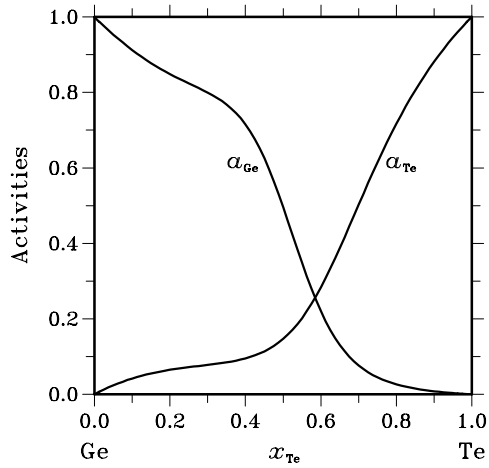

Fig. 3. Activities in the liquid phase at T=1213 K.

Table IV. Standard reaction quantities at 298.15 K for the compounds per mole of atoms.

Compound	x_{Te}	$\Delta_{\mathrm{f}}G^{\circ}$ / (J/mol)	$\Delta_{\mathrm{f}}H^{\circ}$ / (J/mol)	$\Delta_{\mathrm{f}}S^{\circ}$ / (J/(mol·K))	$\Delta_{\mathrm{f}}C^{\circ}_{P}$ / (J/(mol·K))
αGeTe	0.500	−8394	−6866	5.123	1.727
βGeTe	0.500	−7604	−5024	8.653	−1.504
γGeTe	0.510	−8288	−6511	5.961	0.000

References

[96Sch] A. Schlieper, R. Blachnik: J. Alloys Com. **235** (1996) 237–243.
[99Sch] A. Schlieper, Y. Feutelais, S.G. Fries, B. Legendre, R. Blachnik: Calphad **23** (1999) 1–18.