Monatshefte für Chemie 136, 1963–1970 (2005)
DOI 10.1007/s00706-005-0380-1

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Thermodynamics of Structural Changes in Liquid Ge–Te Alloys Around the Eutectic Composition: Specific Heat Measurements and Thermodynamic Stability

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Received September 12, 2004; accepted November 26, 2004

Summary. We have obtained the specific heat, C_p, of liquid Ge–Te alloys around the eutectic composition (15 at.% Ge) and alloys up to 50 at.% Ge by combining the data obtained by modulation and adiabatic calorimetries. The results cover a wide temperature range from deeply undercooled state to 800°C. A very pronounced peak of C_p was observed for Te and alloys up to 20 at.% Ge. The peak position of C_p takes a maximum around the eutectic composition where the peak width becomes narrowest. Using a new thermodynamic relation, we clarify a correlation between the thermodynamic stability and structural changes in the liquid Ge–Te system.

Keywords. Alloys; Calorimetry; Phase transition; Thermodynamics; Ge–Te system.

Introduction

Molten Te in the undercooled state shows the water-like density anomaly in a narrow temperature range below the melting point, 450°C. This structural change is characterized by a strongly peaked extremum in the specific heat, isothermal compressibility, and thermal expansion coefficient as a function of temperature [1]. By adding S or Se to Te, the peak position of the specific heat (referred to as the transition temperature and denoted by T^* in the following) shifts to higher temperatures. The peak width, meanwhile, becomes broadened in agreement with an intuitive understanding that alloying would obscure structural transitions [2]. Of very interest, moreover, is that segregation tendency in an atomic scale develops with increasing temperature in these systems. It becomes large enough to cause

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divergent concentration fluctuations or the two-melt phase separation with a looped boundary in the S–Te system. *Tsuchiya et al.* have elucidated the origin of this unique two-melt phase separation in the S–Te system by utilizing the new thermodynamic relations. They have demonstrated that the structural changes inevitably induce concentration fluctuations in the binary system [3, 4].

On the contrary, the alloying behavior of the structural changes in the Te-rich Ge–Te system is quite different. The addition of small amount of Ge causes sharpening of the structural change and the eutectic Ge–Te alloy (~15 at.% Ge) undergoes the sharpest structural change of this kind so far reported [5]. The thermodynamic indication of a rapid structural change in $Ge_{15}Te_{85}$ was preceded by X-ray and neutron diffraction experiments which showed that a small but well defined prepeak in the interference function, $S(Q)$, very quickly weakens at temperatures above T^* [6, 7].

Two contrasting schemes have been presented for the origin of a structural change in liquid $Ge_{15}Te_{85}$. *Neumann et al.* emphasized the eutectic reaction in which the dependence on temperature of the fraction of co-existing α-GeTe-like- and pure Te regions in the liquid plays a crucial role [6]. Based on detailed thermodynamic measurements, *Tsuchiya* has suggested the development of molecular association of which the local structure around Ge atoms changes rapidly around T^* [8]. Recent *ab initio* computer simulations and detailed structural analysis have also indicated that the local environment of Ge atoms mainly changes through the transition [9, 10]. In spite of a large number of experimental data, however, a recent thermodynamic assessment of the Ge–Te system concluded that the liquid phase around the eutectic point is unable to be described by the usual thermodynamic models [11].

The aim of this paper is to present the specific heat data of liquid Ge–Te alloys around the Te-rich eutectic composition (15 at.% Ge) and alloys up to 50 at.% Ge, which have been obtained by combining the specific heats measured by modulation-calorimetry [5] and adiabatic calorimeter direct measurements. The results cover a wide temperature range from deeply undercooled state to 800°C where the relevant structural transition in the melt has completed. Using a newly derived thermodynamic relation [3], the *Darken* stability associated with the structural changes has been evaluated as a function of temperature and composition. The nature of the structural transition in molten $Ge_{15}Te_{85}$ is discussed thereby.

Results and Discussions

The results of specific heat, C_p, of liquid Te and Ge_xTe_{100-x} ($x = 0$, 5, 10, 15, 17.5, 20, 25, 30, 40, and 50 at.% Ge) are shown in Fig. 1. For $x \leq 20$, a specimen could be undercooled substantially enough to observe the whole profile of a pronounced peak around 400°C. The peak develops with the increase of Ge fraction up to $x = 15$ and then appears to descend slightly with further increase of Ge fraction. At 800°C, where the structural changes have completed, the specific heat increases smoothly as the fraction of Ge increases. The peak position, T^*, takes a maximum of about 407 ± 3°C at $x = 15$. The sample, $Ge_{15}Te_{85}$, could be cooled continuously down to the glassy state. The glass transition point

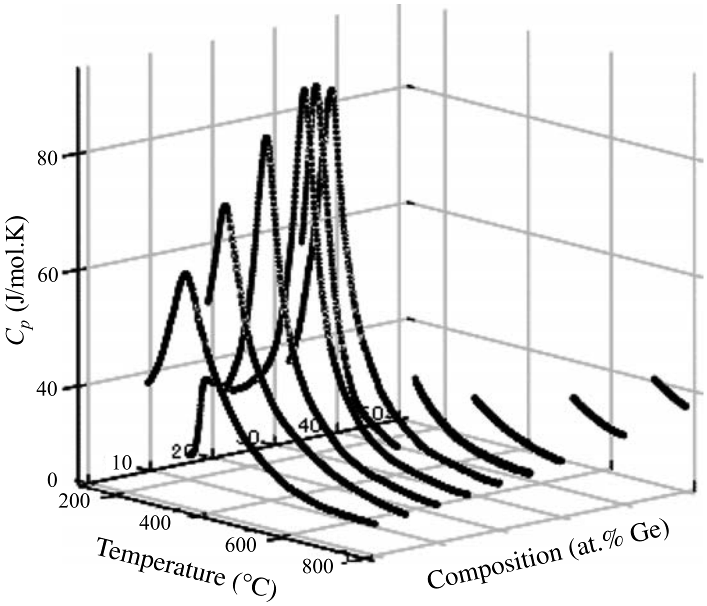

Fig. 1. Dependence on temperature and composition of the constant pressure specific heat for the liquid Ge_x–Te_{100-x} alloys ($x = 0$, 5, 10, 15, 17.5, 20, 25, 30, 40, and 50 at.% Ge)

is 151°C where the specific heat dropped by $12.5\,\mathrm{J/mol \cdot K}$ in the temperature interval of 25 K.

Structural Changes and Thermodynamic Stability

The stability of a binary mixture may be related to the stability function, D, originally introduced by *Darken* [12], which is the second derivative of the *Gibbs* free energy with respect to the composition. There has long been known that structural changes introduce an instability in the binary system [13]. *Tsuchiya* derived new thermodynamic relations that make it possible to partition off the contribution, δD, associated with the structural change and to evaluate it using experimentally available thermodynamic response functions [2, 3]. The relevant relation, which connects the *Darken* stability, D, to the constant specific heat, C_p, is given by Eq. (1) where it is assumed that the structural change can be described by the extent of structural change, $C(T, p, x)$, in which T is temperature, p pressure, and x the fraction of a constituent.

$$\delta D = -T^{-1}(\partial T/\partial x)_{p,C}{}^{2}(\delta C_p) \tag{1}$$

As the structural change proceeds, C continuously changes from $C = 0$ to 1. The symbol, δ, denotes the thermodynamic quantity associated with the structural change and $(\partial T/\partial x)_{p,C}$ is the constant C slope in the $x - T$ plane. It may be seen that the sign of δD is negative and its magnitude increases in proportion to the magnitude of δC_p. Two cases, $(\partial T/\partial x)_{p,C} \neq 0$ and $(\partial T/\partial x)_{p,C} = 0$, will apply. A peak position, T^*, of C_p indicates a temperature around which the structural change has completed about half its way and then $C = 1/2$. From the composition dependence of T^*, therefore, we readily observe whether or not structural changes induce the concentration fluctuations in a mixture. In the case of both Se–Te and S–Te systems, T^* increases with increasing Se or S, then $(\partial T/\partial x)_{p,C=1/2} \neq 0$ and structural changes induce the concentration fluctuations. Segregation tendency in a microscopic scale actually observed in the temperature region of structural change in the Se–Te system [14, 15] and the concentration fluctuations diverge to result in the unique two-melt phase separation with a looped boundary in the S–Te system [16, 4]. On the other hand if $(\partial T/\partial x)_{p,C} = 0$, then $\delta D = 0$. This implies that the structural changes in a binary mixture proceed without inducing the concentration fluctuations. As plotted in Fig. 2, the peak position, T^*, takes a maximum and $(\partial T/\partial x)_{p,C=1/2} = 0$ around $x = 15$ at.% Ge. It follows from Eq. (1) that $\delta D = 0$ for the present Ge–Te system around the eutectic point.

To go into details, use is made of the inhomogeneous structure model (referred to as IHSM) to partition C_p into two parts, one for background, $C_p{}^0$, and the other for the contribution from structural changes, δC_p [17]. The *Gibbs* free energy of

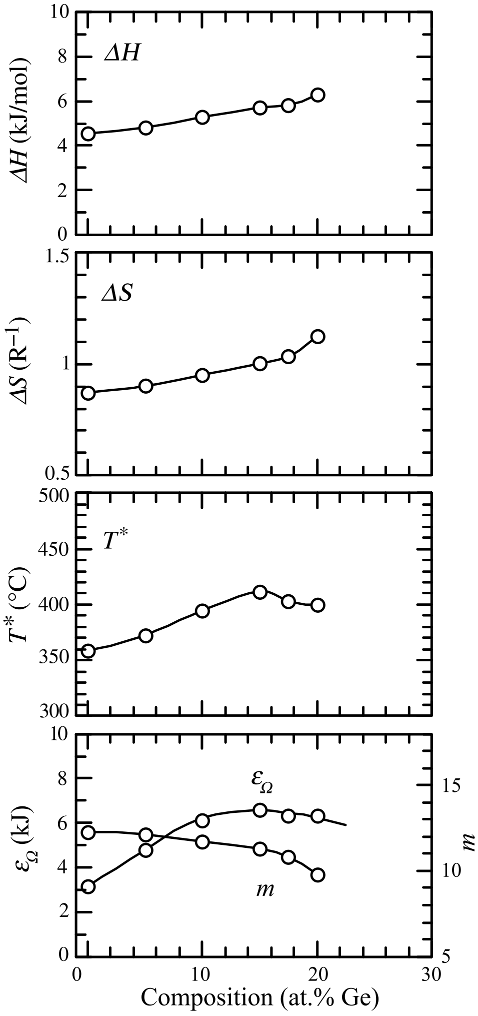

Fig. 2. Transition enthalpy, ΔH $(=\int \delta C_p \mathrm{d}T)$, transition entropy, ΔS $(=\int \delta C_p/T\mathrm{d}T)$, transition temperature T^* $(=\Delta H/\Delta S)$, ε_Ω, and m as a function of Ge composition

IHSM, is as given by Eq. (2) where subscripts H and L refer, respectively, to a high and low temperature form of a liquid.

$$\begin{aligned} G &= CG_H + (1 - C)G_L + (RT/m)[C \ln C + (1 - C)\ln(1 - C)] \\ &\quad + (\varepsilon_\Omega/m)C(1 - C) \end{aligned} \tag{2}$$

It assumes that a group of m atoms change their local structure co-operatively. R is the gas constant and ε_Ω the interaction parameter between different forms of atom groups. The fraction of H-form atoms or the extent of structural change, C, is obtained by using the stability condition, $(\partial G/\partial C)_{T,p,x} = 0$, as shown by Eq. (3) where Δ refers to a difference in the corresponding thermodynamic quantities for H- and L-form liquid.

$$\ln C/(1 - C) = -[m\Delta G + (1 - 2C)\varepsilon_\Omega]/RT \tag{3}$$

The constant pressure specific heat is given by Eq. (4).

$$\begin{aligned} C_p &= -T(\partial^2 G/\partial T^2) \\ &= \{CC_p{}^H + (1 - C)C_p{}^L\} + \Delta HC(1 - C) \\ &\quad \times [m\Delta H + (1 - 2C)\varepsilon_\Omega]/\{RT^2[1 - 2\varepsilon_\Omega C(1 - C)/RT]\} \end{aligned} \tag{4}$$

The second term represents the effect of structural change and is equal to δC_p. Fitting the data to Eq. (4) together with Eq. (3) and assuming linear temperature

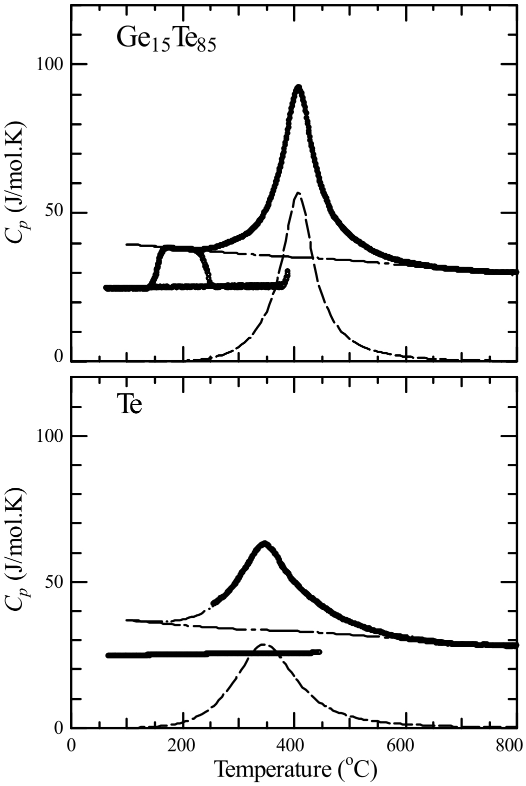

Fig. 3. Partition of C_p: background $C_p{}^0$ (dotted chin lines) and the contribution from structural changes, δC_p (broken lines) are compared with C_p for Te and $Ge_{15}Te_{85}$

dependence of $C_p{}^H$ and $C_p{}^L$, $\Delta H(=\int \delta C_p \mathrm{d}T)$, $\Delta S(=\int \delta C_p/T\mathrm{d}T)$, ε_Ω, and m have been obtained. The partitioned specific heats of Te and $Ge_{15}Te_{85}$ are shown in Fig. 3 and the parameters are plotted in Fig. 2.

δD of Eq. (1) may be rewritten as Eq. (5) and has been numerically evaluated with the parameters plotted in Fig. 3.

$$\delta D = -T^{-1}(\partial C/\partial x)_{T,p}{}^2 \Delta H^2/\delta C_p \tag{5}$$

The results are shown in Fig. 4a. δD as a function of temperature takes a peaked minimum around T^* for all alloys including Te, while it is zero for $Ge_{15}Te_{85}$ within the uncertainty of numerical calculations. The overall profile of δD in the $T - x$ plane is more clearly seen in the contour map of Fig. 4b obtained by interpolation of the data in Fig. 4a. δD is almost zero along the line $x = 15$ at.% Ge even in the

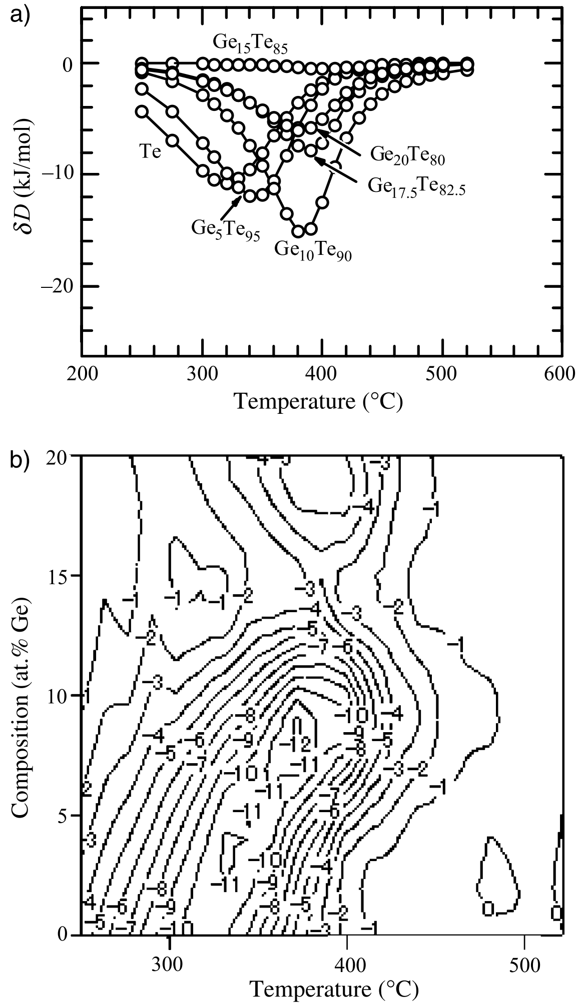

Fig. 4. a: δD for Ge–Te alloys around the eutectic composition as a function of temperature (top); b: contour map of δD; note that the eutectic temperature is ~375°C and almost all the data are for the deeply undercooled state (bottom)

domain of structural changes while as coming off to either side of this composition δD takes a pronounce minimum around T^*. It implies that structural change in liquid $Ge_{15}Te_{85}$ proceeds without inducing concentration fluctuations. On the contrary, the structural change in an alloy with composition away from 15 at.% Ge stimulates segregation tendency to a mixture of $Ge_{15}Te_{85}$ (plausibly Ge_1Te_6 clusters corresponding to 14.3 at.% Ge) and remaining Te or Ge. Actual phase separation, however, would not be expected because the magnitude of δD is much smaller even at its minimum as compared with the entropy term, $RT/x(1-x) \sim$ 40–50 kJ/mol. This type of stability map is similar to the one for the order-disorder transition in the Au–Cu solid solution, for example [18].

Recent *ab initio* computer simulations emphasize the '*Peierls*-like' distortion of the local Ge coordination as an origin of the structural change in liquid $Ge_{15}Te_{85}$ [9]. The results of computer simulations suggest that the transition could be viewed as formation of Ge_1Te_6 octahedral local order and a transition between two *pseudo*-equilibrium positions for Ge atom with respect to the center of the octahedron. At low temperatures the off center position of Ge atom is energetically favored because of the '*Peierls*-like' distortion while the symmetrical center position is entropically favored at high temperatures. If this were the case, the structural change could proceed without inducing the concentration fluctuations in liquid $Ge_{15}Te_{85}$.

From the results obtained in this work one may rule out the eutectic reaction as an origin for the structural change because it would bring about unavoidable concentration fluctuations as the precursor of phase separation into pure Te and the compound-like GeTe regions.

Experimental

The alloy sample was made from Te (6 nine grade) and Ge (6 nine grade) by alloying them in an evacuated fused silica tube.

The heat capacity above the liquidus point was measured using an adiabatic scanning calorimeter, which consists of ULVAC SH3000 calorimeter, Keithley 2182 nano-voltmeter and Ohkura EC5700 digital temperature controller. The size of the fused silica cell for measurements was about 1.7 cm in diameter and 2.3 cm in height in which approximately 0.1 mol of powdered alloy was sealed. In this calorimetry, a sample was continuously heated with a constant power supply under adiabatic condition and the resultant temperature increase was measured at every 30 s. The heating rate of 0.4 or 0.5 W was employed. It was found that the results were not dependent on these heating rates.

The specific heat below 600°C was measured by modulation calorimetry [8]. We used a very small amount of sample, totally ~2 mg, consisting of a specimen and a capillary cell of typically 0.05 cm in diameter and 1 cm in length. Therefore we could measure the heat capacity of a liquid in the deeply undercooled state. The frequency used was 1 Hz to ensure that the results were not affected by the thermal diffusivity of the specimen. After subtracting the contribution from the empty capillary, the net signal was scaled using the results obtained by the adiabatic method. The overall uncertainty of the specific heat, which was estimated to be the reproducibility of the results obtained by different samples, was 5%.

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