Thermodynamic properties of the molten Tl-As$_2$Te$_3$ and Bi-As$_2$Te$_3$ systems

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Abstract. The thermodynamic properties of the molten M–As$_2$Te$_3$ (M:Tl,Bi) systems have been measured by means of the electromotive force (EMF) method. The partial molar entropy and enthalpy of Tl in the molten Tl–As$_2$Te$_3$ system show a very drastic change at a composition of 54.54 at.% Tl, where the system shows a p–n transition. On the other hand, the activities of Bi show no such drastic change in the molten Bi–As$_2$Te$_3$ system, where the p–n transition and subsequent metallization occur at a much lower Bi concentration. However, the EMF data for the Bi-containing system were not accurate enough to separate the entropy and enthalpy contributions from the total free energy change. The present results indicate that strong interactions between Tl and Te in the Tl–As$_2$Te$_3$ system are responsible for the preservation of p-type semiconduction in the molten state.

1. Introduction

In a previous paper [1], we reported totally different behaviours for the molten Tl–As$_2$Te$_3$ and Bi–As$_2$Te$_3$ systems in their electrical conductivity and thermoelectric power. The positive sign for the thermoelectric power of molten As$_2$Te$_3$ is retained until a relatively large amount of Tl addition, i.e. about 55 at.% Tl, where the conductivity shows a sharp minimum. Further addition of Tl causes a conversion of the sign of thermoelectric power and a subsequent metallization of the system. On the other hand, a relatively small amount of Bi causes a p–n transition and the electrical conductivity increases gradually toward high values inherent in metallic conduction. Quite similar behaviours have been found in the molten Tl–GeTe$_4$ and Bi–GeTe$_4$ systems [2].

In this study, we have measured the thermodynamic activities of the dopant elements Tl and Bi in the molten As$_2$Te$_3$ as a function of composition and temperature, using the electromotive force (EMF) method. The correlation of the thermodynamic information and the electrical properties of these systems [1] will be discussed in some detail.

2. Experimental

Samples were prepared from the respective constituents of high purity, As$_2$Te$_3$ (6N), Tl (4N) and Bi (6N), melting and mixing them in a glass ampoule for one day at 600 °C. The constitution of the cell for EMF measurements was as follows:

$$\text{Tl(l)|TlCl in LiCl–KCl(l)|Tl–As}_2\text{Te}_3\text{(l)}$$

$$\text{Bi(l)|BiCl}_3\text{ in LiCl–KCl(l)|Bi–As}_2\text{Te}_3\text{(l).}$$

We used the eutectic mixture of LiCl and KCl (58 mol% LiCl), as a salt bridge, to which about 5 wt% TlCl or $BiCl_3$ was added. Mixtures of the electrolytes were dried under vacuum at about 200 °C. Four-legged H-type cells were made of Pyrex glass. The pure metal (Tl or Bi) was contained normally in a compartment of one leg and three alloys of different composition in the other three compartments. Tungsten-wire electrodes of 0.6 mm in diameter were sealed through the wall of each compartment. The cell was charged with pure metal, alloys and electrolyte mixture, evacuated and then sealed with argon gas.

Temperatures were measured with a chromel–alumel thermocouple. The stability of the EMFs of the cell was checked occasionally by measuring the EMF between two pure metals, and it did not exceed a value of ±0.3 mV. Stable EMF values for alloys were obtained after an equilibrium time of 24 h for $Tl–As_2Te_3$ alloys at 600 °C. EMF measurements were made on heating and cooling the samples at every 10 K, with an equilibrium time of 20 min at each temperature. The reproducibility of the EMF values was better than ±0.5 mV. For $Bi–As_2Te_3$ alloys, however, no stable EMF values were obtained within 24 h, and an equilibration time of 60 h was needed to obtain an EMF value stable within ±1.0 mV. Measurements were made over the temperature range from the freezing temperature of each sample to about 600 °C. The phase diagram for the $Tl–As_2Te_3$ system has already been reported by Dmitriev et al [3]. As the phase diagram for the $Bi–As_2Te_3$ system is not yet known, we have determined the freezing temperature T_f of each sample from the change of slopes of the observed EMF–temperature curves. The results are given in table 1.

Table 1. EMF data at 873 K for the molten $Bi–As_2Te_3$ system.

X_{Bi}	E (mV)	T_f (K)
0.0099	143.28	668
0.0196	136.01	681
0.0476	111.48	712
0.0789	100.61	753
0.1176	90.06	777
0.2308	63.03	817
0.3182	46.05	814
0.4444	29.07	789
0.6997	11.09	785
0.8643	3.49	728

Table 2. EMF data for the molten $Tl–As_2Te_3$ system.

|	723 K		773 K		873 K	
X_{Tl}	E (mV)	dE/dT (mV K^{-1})	E (mV)	dE/dT (mV K^{-1})	E (mV)	dE/dT (mV K^{-1})
0.1667	519.23	−0.0229	519.09	0.0223	524.92	0.0568
0.2308	473.33	−0.0592	469.89	−0.0678	469.92	0.0648
0.3750	360.83	−0.0806	356.82	−0.0795	348.97	−0.0774
0.5000	277.04	−0.1451	269.57	−0.1538	253.31	−0.1712
0.5454	181.12	−0.2286	171.08	−0.1570	173.84	0.2768
0.5652	74.04	0.4287	97.24	0.4992	154.22	0.6403
0.5833	62.55	0.4445	85.69	0.4810	137.44	0.5540
0.6667	24.74	0.0964	29.70	0.1017	40.41	0.1125
0.8471	6.99	0.0261	8.30	0.0262	10.92	0.0263
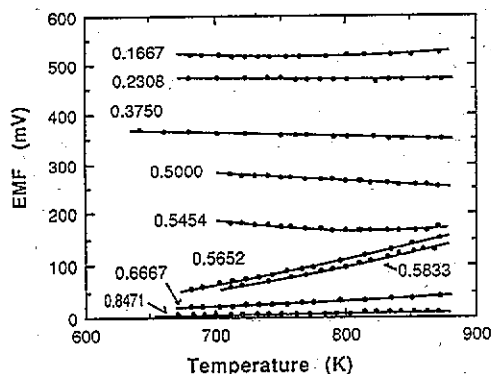
Figure 1. The temperature dependence of EMFs in the molten Tl–As$_2$Te$_3$ system. Numbers in the figure denote the atomic fraction of Tl.
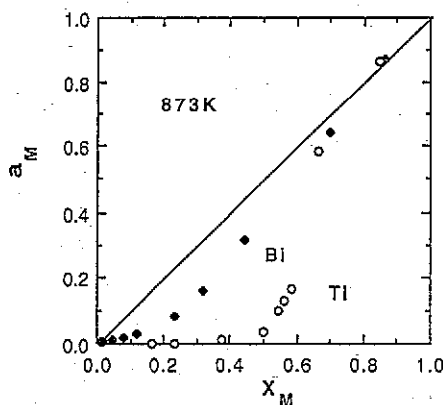
Figure 2. Activities of Tl and Bi in the molten Tl–As$_2$Te$_3$ and Bi–As$_2$Te$_3$ systems at 873 K.

3. Results

The temperature dependence of the EMF for Tl–As$_2$Te$_3$ alloys is shown in figure 1. The observed EMFs were fitted to polynominal equations of temperature, from second to fifth order, from which values for the EMF (E) and its temperature derivative (dE/dT) were derived for a given temperature. The values at 723, 773 and 873 K for the molten Tl–As$_2$Te$_3$ system are given in table 2. As mentioned above, the relatively unstable EMF values in the molten Bi–As$_2$Te$_3$ system are probably due to a slight temperature variation of the valence state of the Bi salt used in the cell for EMF measurements. Even a slight change in the valence state due to a possible reaction between Bi and BiCl$_3$ may cause considerable effects in the separation of entropy and enthalpy contributions. Thus we use here only the EMF data at 873 K, which are given in table 1. In this paper, the composition of the alloys is given in terms of the atomic fraction of each element. The atomic fraction of the added metal M is given by

$$X_M = n_M^0/(n_M^0 + 5n_{As_2Te_3}^0) \tag{1}$$

where n_M^0 and $n_{As_2Te_3}^0$ are the nominal moles of M and As$_2$Te$_3$ in each alloy. The thermodynamic functions can be determined from the values for E and dE/dT, using the relations

$$\Delta \overline{G}_M = RT \ln a_M = -nFE \tag{2}$$
$$\Delta \overline{S}_M = nF dE/dT \tag{3}$$

and

$$\Delta \overline{H}_M = \Delta \overline{G}_M + T \Delta \overline{S}_M = -nF(E - T\, dE/dT). \tag{4}$$

Here $\Delta \overline{G}_M$, $\Delta \overline{S}_M$, $\Delta \overline{H}_M$ and a_M denote the change on mixing of the partial molar Gibbs free energy, entropy and enthalpy, and the activity of the added metal M. F is the Faraday constant and n is the valence of the dissolved electrolyte in the salt bridge, i.e. $n = 1$ for Tl and $n = 3$ for Bi. Figure 2 shows the activities of Tl and Bi in the respective systems at

873 K. As shown in the figure, the activities of Tl are very small in the composition range where the system shows p-type conduction, while the activities of Bi show no such strong deviation from ideality. Figure 3 shows the composition dependence of the partial molar entropy and enthalpy of Tl at 873 K. Interesting features of the molten Tl–As$_2$Te$_3$ system are drastic changes in these quantities at the composition where the electronic properties also show drastic changes, as shown in figures 4 and 5 [1]. No such drastic changes in the electric properties have been found in the molten Bi–As$_2$Te$_3$ system. For the latter system some new data for the electric properties were added to those given in the previous paper [1].
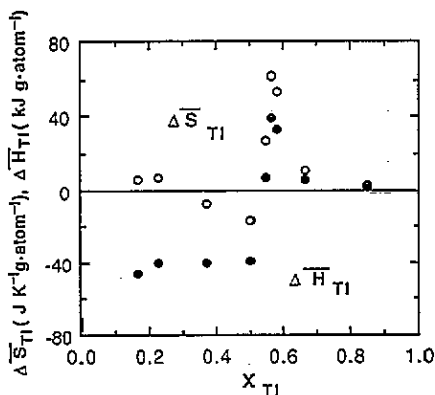

Figure 3. The partial molar entropy (O) and enthalpy (●) change of Tl in the molten Tl–As$_2$Te$_3$ system at 873 K.
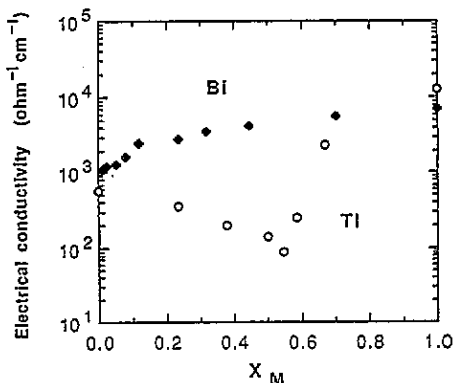

Figure 4. Electrical conductivity in the molten Tl–As$_2$Te$_3$ (O) and Bi–As$_2$Te$_3$ (◆) systems at 873 K.
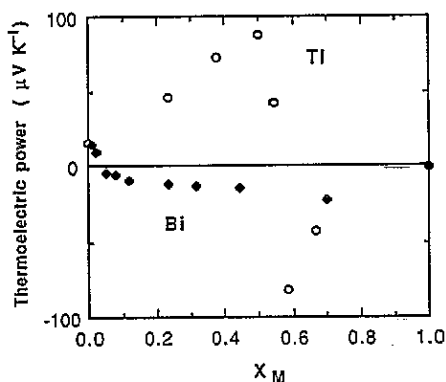

Figure 5. Thermoelectric power in the molten Tl–As$_2$Te$_3$ (O) and Bi–As$_2$Te$_3$ (◆) systems at 873 K.
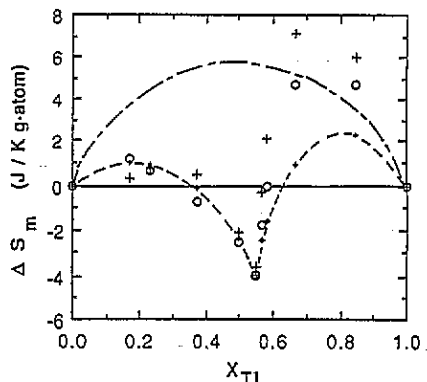

Figure 6. The integral molar entropy change of the molten Tl–As$_2$Te$_3$ system at 723 K (O) and 873 K (+). Chain curve, ideal solution; broken curve, calculated values from equations (9) and (11).

From the corresponding partial molar quantities ($\overline{A_M^e}$) for the dopant M, the excess integral molar quantities (A_m^e) can be calculated by integration of the Gibbs–Duhem

equation [4]:

$$A_m^e(X_M) = (1 - X_M) \int_0^{X_M} \frac{\overline{A}_M^e(X_M')}{(1 - X_M')^2} \, dX_M' + (1 - X_M) A_m^e(X_M = 0) \tag{5}$$

where $A_m^e(X_M = 0)$ is the excess molar quantity of the binary alloy of $As_{0.4}Te_{0.6}$. The excess quantities are defined as deviations from the ideal solution values. They are:

$$\overline{G}_M^e = \Delta \overline{G}_M - RT \ln X_M \tag{6}$$

$$\overline{S}_M^e = \Delta \overline{S}_M + R \ln X_M \tag{7}$$

and

$$\overline{H}_M^e = \overline{G}_M^e + T\overline{S}_M^e = \Delta \overline{H}_M. \tag{8}$$

In the analysis of the data, we treat the present systems as pseudo-binary systems M–As$_2$Te$_3$, and take $A_m^e(X_M = 0)$ in equation (5) to be zero, or refer to a hypothetical ideal solution of $As_{0.4}Te_{0.6}$ as the one component of the pseudo-binary system. As mentioned earlier, we use only the data for the Tl–As$_2$Te$_3$ system for the evaluation of the integral molar quantities. As shown in figures 6 and 7, the integral molar entropy and enthalpy of the Tl–As$_2$Te$_3$ system show a deep minimum at the composition Tl$_6$As$_2$Te$_3$, i.e. $X_{Tl} = 0.5454$. This behaviour indicates that very stable partially ordered alloys are formed around this composition. Such behaviour is quite similar to that found previously in the molten Tl–Te system, in which drastic changes in both the thermodynamic and electronic properties take place at the composition of Tl$_2$Te or $X_{Tl} = 0.667$ [5, 7].
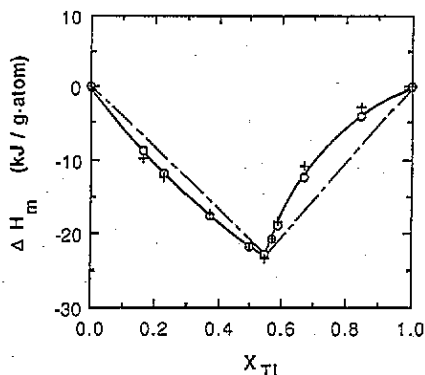

Figure 7. The integral molar enthalpy change of the molten Tl–As$_2$Te$_3$ system at 723 K (O) and 873 K (+). Chain curve, ideal solution.
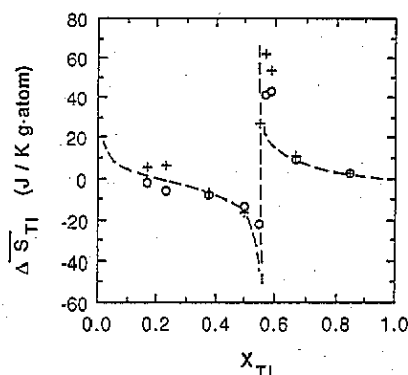
Figure 8. The partial molar entropy change of Tl in the molten Tl–As$_2$Te$_3$ system at 723 K (O) and 873 K (+). Broken curve, calculated values from equations (13) and (14).

4. Discussion

The present thermodynamic data indicate a formation of very stable alloys around the stoichiometric composition $Tl_6As_2Te_3$ in the molten Tl–As_2Te_3 system. On the other hand, in the molten Bi–As_2Te_3 system the thermodynamic behaviour is similar to that usually found in random alloys. It has thus been suggested that the added Tl atoms are strongly interacting with the Te atoms in molten As_2Te_3 to form a short-range order described as Tl_2Te. We may write this as

$$6Tl + As_2Te_3 = 3Tl_2Te + 2As \qquad (A)$$

This reaction may be completed at the stoichiometric composition $Tl_6As_2Te_3$, or $X_{Tl} = 0.5454$, where drastic changes in the thermodynamic quantities are found as shown in figures 2, 3, 6, and 7. Since we have $|\Delta G_m| = 20\,060$ J g atom$^{-1} \simeq 3.3RT$ at 723 K at this composition, we may treat the present Tl–As_2Te_3 system as consisting of the two sub-systems Te–As–Tl_2Te for $X_{Tl} \leqslant 0.5454$ (region I) and Tl–As–Tl_2Te for $X_{Tl} > 0.5454$ (region II) [7]. Then we can write the integral molar entropy of mixing, using the Flory expression [6], for region I as

$$(n_{Tl}^0 + 5n_{As_2Te_3}^0)\Delta S_m = n_{Tl_2Te}\Delta S_f - R(n_{Tl_2Te}\ln\phi_{Tl_2Te} + n_{As}\ln\phi_{As} + n_{Te}\ln\phi_{Te})$$
$$+ 5n_{As_2Te_3}^0 R(0.4\ln 0.4 + 0.6\ln 0.6) \qquad (9)$$

where ΔS_f is the entropy change for the reaction (A), ϕ_i is the volume fraction of species i, and the last term represents the entropy of demixing of the $As_{0.4}Te_{0.6}$ alloy. The numbers of moles for the assumed species Tl_2Te, As and Te are represented by the total or nominal numbers of moles of Tl and As_2Te_3, denoted by n_{Tl}^0 and $n_{As_2Te_3}^0$, respectively,

$$n_{Tl_2Te} = \tfrac{1}{2}n_{Tl}^0$$
$$n_{As} = 2n_{As_2Te_3}^0 \qquad (10)$$
$$n_{Te} = 3n_{As_2Te_3}^0 + \tfrac{1}{2}n_{Tl}^0$$

and for region II:

$$(n_{Tl}^0 + 5n_{As_2Te_3}^0)\Delta S_m = n_{Tl_2Te}\Delta S_f - R(n_{Tl_2Te}\ln\phi_{Tl_2Te} + n_{As}\ln\phi_{As} + n_{Tl}\ln\phi_{Tl})$$
$$+ 5n_{As_2Te_3}^0 R(0.4\ln 0.4 + 0.6\ln 0.6) \qquad (11)$$

where the numbers of moles for the entities Tl_2Te, As and Tl are given by the nominal numbers of moles of Tl and As_2Te_3:

$$n_{Tl_2Te} = 3n_{As_2Te_3}^0$$
$$n_{As} = 2n_{As_2Te_3}^0 \qquad (12)$$
$$n_{Tl} = n_{Tl}^0 - 6n_{As_2Te_3}^0.$$

Assuming Tl_2Te to be a trimer, and taking ΔS_f to be -16.27 J K^{-1} mol^{-1} by fitting to the present data at $X_{Tl} = 0.375$, we can calculate values for ΔS_m which are compared with the experimental data in figure 6. By differentiating the right-hand side of equations (9) and

(11) with respect to n_{Tl}^0, we can obtain expressions for the partial molar entropy change of Tl, $\Delta \bar{S}_{Tl}$, in regions I and II, respectively. The results are for region I:

$$\Delta \bar{S}_{Tl} = \tfrac{1}{2}\Delta S_f - R\{X_{Tl} - 1 + \tfrac{1}{2}\ln[15X_{Tl}/(6 - 11X_{Tl})]\} \tag{13}$$

and for region II:

$$\Delta \bar{S}_{Tl} = -R\{\tfrac{6}{5}(1 - X_{Tl}) + \ln[(11X_{Tl} - 6)/5]\}. \tag{14}$$

Calculated results with $\Delta S_f = -16.27$ J K^{-1} mol^{-1} are compared with the experimental results at two temperatures. As shown in figure 8, its general feature is also well represented by the expressions given above. It is thus found in figure 6 that the overall feature of the entropy of mixing of the molten Tl–As₂Te₃ system can be well represented by a simple Flory model for ternary mixtures of Tl₂Te–As–Te for region I. In region II for Tl₂Te–As–Tl mixtures, however, agreement with the Flory model becomes poor on the Tl-rich side. This is probably due to the dissociation of Tl₂Te trimers to form normal metallic alloys in high Tl concentrations. The entropy of mixing will be rather close to that of ideal mixing of the constituent atoms, as shown in figure 6.

The observed enthalpies of the Tl–As₂Te₃ system may also be described by analogy to binary compound-forming alloys [5, 7, 8]. From the present data for ΔH_m, the enthalpy of formation of Tl₂Te by reaction (A), ΔH_f, is obtained as -85.5 kJ per mole of Tl₂Te, with $\Delta H_f = (11/3)\Delta H_m$. This value is close to the corresponding value in the molten binary Tl–Te system, -80.0 kJ per mole of Tl₂Te [5]. As carried out in the calculation of the entropy of mixing by the Flory model, we can divide the present system into two sub-systems, Tl₂Te–As–Te (region I) and Tl₂Te–As–Tl (region II). It is seen in figure 7 that the interaction between the supposed entities is exothermic in region I, while it is endothermic in region II. This endothermic interaction may predominantly be due to Tl–Tl₂Te interaction, which is responsible for the liquid–liquid phase separation in the Tl-rich region [3]. A quantitative determination of the interaction parameters [5, 6], however, was difficult because of the uncertainty of the enthalpy data compared with the number of adjustable parameters. We therefore limit our analysis of the enthalpy data to a qualitative one.

It is known that the upper valence band of amorphous arsenic chalcogenides consists of non-bonding lone pair p orbitals of chalcogen atoms and that the conduction band is formed from σ^* anti-bonding orbitals of As and the chalcogen [9]. A similar bonding picture is expected for the molten state. When Tl atoms are added to molten As₂Te₃, a stable σ bond is formed between Tl and Te, which is reflected in the observed large negative excess enthalpy, given in figure 7. This process causes a strong chemical short-range order around the dissolved Tl atoms, which yields a large negative partial molar mixing entropy for Tl, shown in figure 6. This Tl–Te interaction also gives a strongly interacting σ^* bond, which corresponds to an increase of energy separation between the σ^* orbital and a lone-pair p orbital of the chalcogen, i.e., an increase of the energy gap. The semiconductivity of the Tl–As₂Te₃ system is thus retained until all the Te atoms are bonded to the added Tl atoms, or at the stoichiometric composition given by reaction (A), in accordance with the observed electronic properties [1]. Excess Tl atoms above the stoichiometric composition, $X_{Tl} = 0.5454$, act as a donor, and the process is endothermic giving a positive mixing entropy, as shown in figures 6 and 7. It has been reported by Sugawara *et al* [10] that the peak of the RDF due to As–Te separation in the molten Tl–As₂Te₃ system disappears around $X_{Tl} = 0.55$. This structural information is also in good agreement with the present interpretation. On the other hand, the interaction between added Bi and Te is rather weaker

than the interaction between As and Te, and thus the $Bi-As_2Te_3$ systems behaves like usual metallic alloys over the entire concentration range. The valence band due to the non-bonding chalcogen p orbitals and the conduction band formed by weak σ^* bonds merge into a partially filled conduction band, giving rise to metallic conduction [1].

In this paper we have reported the totally different behaviours of the thermodynamic properties of the molten $Tl-As_2Te_3$ and $Bi-As_2Te_3$ systems. These thermodynamic properties are fully consistent with their electronic behaviours, reported earlier [1]. In the molten $Tl-As_2Te_3$ system, a strong interaction between Tl and Te is responsible for low activities, large negative partial enthalpies and entropies of the dissolved Tl, as well as for retained p-type semiconductivity up to the stoichiometric composition of $Tl_6As_2Te_3$. Further addition of Tl to the stoichiometric compound gives rise to the formation of random metallic alloys in the n-type region. On the other hand, in the molten $Bi-As_2Te_3$ system the interaction between Bi and Te is weak and mixtures behave rather as normal random alloys, in accordance with the observed gradual metallization of the system at a relatively low Bi concentration.

Acknowledgments

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