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Experimental study on gallium activity in the liquid Ga–In–Tl alloys by EMF method with zirconia solid electrolyte

Iwao Katayama [a,*], Keiko Shimazawa [b], Dragana Zivkovic [c], Dragan Manasijevic [c], Zivan Zivkovic [c], Hiromi Yamashita [a]

[a] *Department of Materials Science and Processing, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita Osaka 565-0871, Japan*
[b] *Sumitomo Electric Hardmetal Corp. Ltd., Manufacturing Department, 1-1-1 Koya-kita, Itami 664-0016, Japan*
[c] *Technical Faculty, University of Belgrade, VJ12, 19210 Bor, Serbia and Montenegro*

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Abstract

EMF of galvanic cells with zirconia solid electrolytes was measured to determine the activity of gallium in liquid Ga–In–Tl alloys in the temperature range of 950–1300 K along three pseudo-binary lines of (In_yTl_{1-y})–Ga where $y = 0.25$, 0.50 and 0.75. A mixture of Ga and Ga_2O_3 was used as a reference electrode. The activity curves of Ga show positive deviations from ideality in the whole composition range. Isoactivity curves at 1073 K in the ternary Ga–In–Tl alloys were derived by combining the activity data of Ga–In and Ga–Tl alloys. Excess free energy of mixing $\Delta G^{Ex}(=\Delta G - \Delta G^{ideal})$ at 1073 K was derived by Darken's equation using the binary data of In–Tl and ternary data in this study. The values in this study are smaller than those calculated from the general model calculation proposed by Chou.
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Keywords: Gallium–indium–thallium alloy; Activity; Liquid alloy; Electromotive force method; Thermodynamics

1. Introduction

Many studies have been carried out on alloy systems related to semi-conducting and soldering materials which are of interest from both the scientific and technological points of view. An accurate information of the thermodynamic properties and phase diagrams of these systems is essential. Some of the binary systems have been studied extensively, but the experimental data for ternary and/or multi-component systems are not always adequate. The method for predicting of thermodynamic properties for ternary alloys has been developed by model calculations based on the data of constituent three binary systems.

The present study is performed in the course of our program of experimental thermodynamic studies of liquid gallium–antimony and gallium–indium based ternary alloys at high temperatures by use of an EMF method to determine the activity of gallium in the liquid Ga–In–Tl alloys.

Activities of gallium in the liquid Ga–In and Ga–Tl alloys show moderately and largely positive deviations from Raoult's law, respectively. They are shown in our previous papers [1,2], but there seem no thermodynamic data for Ga–In–Tl alloys hitherto.

2. Experimental

2.1. Materials

The alloys used in this study were prepared from high-purity materials (Ga: 99.9999 mass% purity from Sumitomo Chemicals Co. Ltd.; In and Tl: 99.999% from Mitsubishi Materials Co. Ltd.). Ga_2O_3 powder added to the alloy electrode and reference electrode in a mass ratio about 1:9 was of 99.99% purity from Mitsubishi Materials Co. Ltd.

* Corresponding author. Tel.: +81 668 797 460; fax: +81 668 797 522.
E-mail address: katayama@mat.eng.osaka-u.ac.jp (I. Katayama).

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Zirconia solid electrolyte crucibles (0.92 ZrO_2 + 0.08 Y_2O_3, OD 8 mm, ID 5 mm and length 50 mm) were produced by co-precipitation method in Nikkato Co. Ltd.

2.2. Experimental apparatus and procedures

The experimental equipment and procedure used in this study are quite similar to the previous one for Ga–Tl alloys [2] and Ga–In–Bi alloys [3]. As Tl metal is easily oxidized in air atmosphere, the shots of Tl were shielded in an evacuated silica ampoule, and melted partly from the bottom to the top in the ampoule several times to get clean Tl. The ampoule was broken in an argon glove box. All of the handling for cell construction described below was performed in the glove box.

The alloy elements, weighed to desired compositions, and Ga_2O_3 powder were put in a zirconia crucible with a tungsten lead wire (φ0.5 mm), and the crucible was settled in the reference electrode (Ga, Ga_2O_3) put in an alumina crucible in which another tungsten wire was settled as a lead wire for the reference electrode. The cell was settled in a reaction tube.

After the reaction tube filled with purified argon gas was moved into a vertical type electric resistance furnace to hold the cell in the homogeneous temperature region, the reaction tube was evacuated and then filled with purified argon gas at room temperature. This operation was two or three times repeated. Further, the temperature was raised to a desired value. Immediately after the cell temperature became constant, the alloy electrode was stirred with the tungsten lead wire in order to shorten the equilibrium time required (3–5 h), and the EMF measurement started. The cell temperature was raised

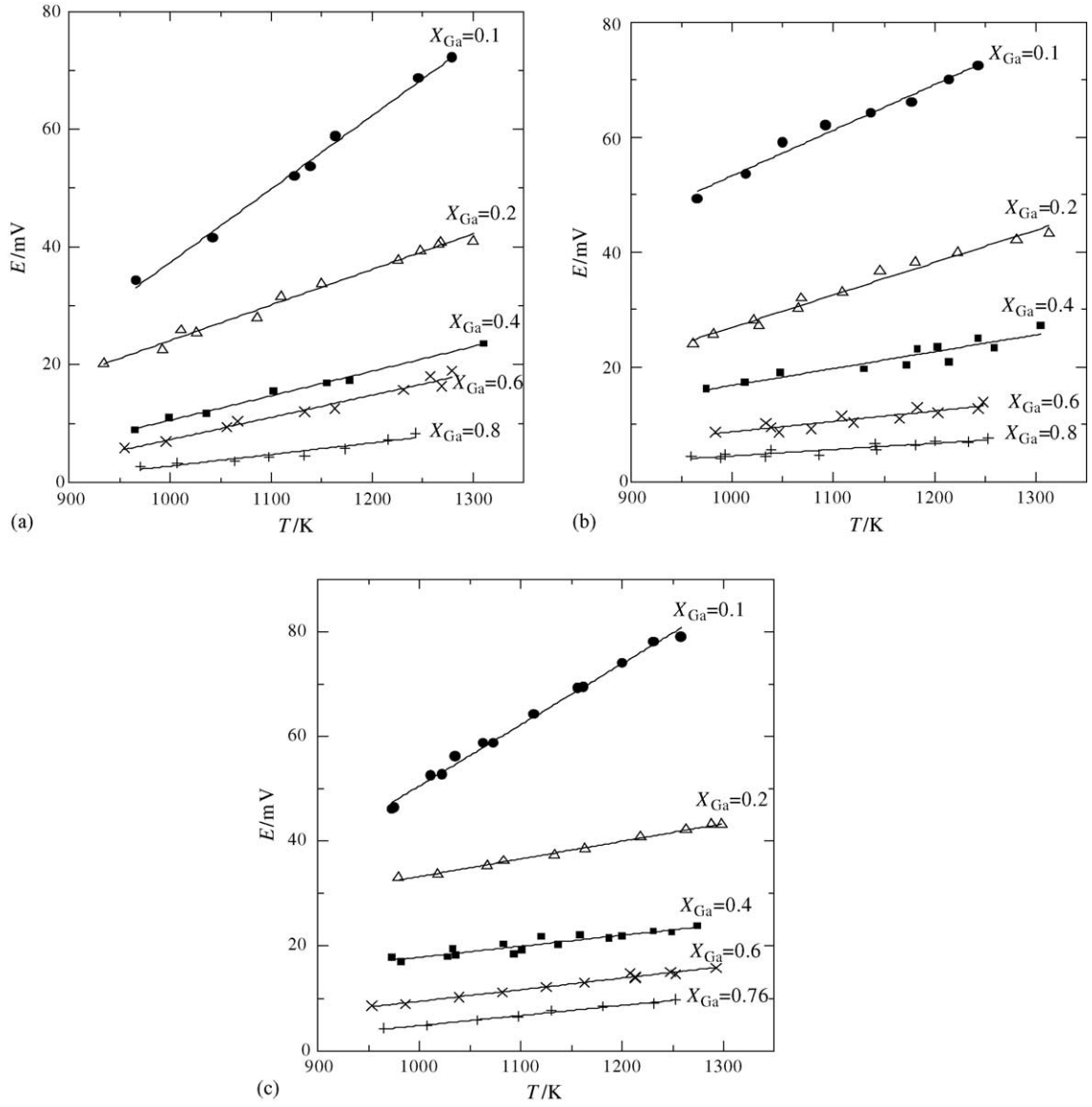

Fig. 1. (a) Temperature dependence EMF of cell: Ga,Ga_2O_3|ZrO_2(+Y_2O_3)|$Ga_x(In_{0.25}Tl_{0.75})_{1-x}$,$Ga_2O_3$; (b) Ga,$Ga_2O_3$|$ZrO_2$(+$Y_2O_3$)|$Ga_x(In_{0.50}Tl_{0.50})_{1-x}$, Ga_2O_3; and (c) Ga,Ga_2O_3|ZrO_2(+Y_2O_3)|$Ga_x(In_{0.75}Tl_{0.25})_{1-x}$,$Ga_2O_3$.

and lowered, as alternatively as possible, and controlled to ±1 K at each temperature with a thermo-controller (Thermolet, Eiko Electric Co. Ltd., TPC-A202C2) and a Pt-13RhPt thermocouple. The EMF of the cell and the cell temperature were measured with a digital voltmeter (Multi-Logging Meter AD-5311, A&D Co. Ltd.).

3. Results

The EMF of the cell for the ternary alloys were measured:

$$(-)\mathrm{W, Ga, Ga_2O_3|ZrO_2(+Y_2O_3)|Ga–In–Tl}\,(\ell)$$

$$\mathrm{Ga_2O_3, W}(+)$$

The compositions of the ternary alloys are chosen for pseudo-binary systems of $(\mathrm{In}_y\,\mathrm{Tl}_{1-y})_{1-x}$—$\mathrm{Ga}_x$, where $y = 0.25, 0.50$ and 0.75; $x = 0.1$, 0.2, 0.4, 0.6 and 0.8 (or 0.76).

Experimental EMF data for Ga–In–Tl ternary alloys are shown in Fig. 1a–c for 15 different compositions. As all the data points distribute around a linear line for each composition, the relations between EMF (E, mV) and temperature (T, K) are obtained by least squares regression analysis, and are listed in Table 1.

Using the results shown in Table 1, activities of Ga (a_{Ga}) in the alloys are calculated from Eq. (1).

$$-3EF = RT\ln a_{\mathrm{Ga}} = \Delta\bar{G}_{\mathrm{Ga}} \quad (1)$$

where F is the Faraday constant, R the gas constant and $\Delta\bar{G}_{\mathrm{Ga}}(\mathrm{J\,mol^{-1}})$: partial molar free energy of mixing of Ga. Uncertainty limits in the activity values can be easily derived from those in the EMF values. The activity values and some thermodynamic properties which can be derived by Eq. (1) are shown in Table 2 at each temperature for three pseudo-binary systems, some of which are derived by extrapolation of E versus T relations to lower or higher temperature range. Fig. 2 shows the concentration dependence of the gallium

Table 1
Temperature dependence of EMF of cell: (−)Ga,$\mathrm{Ga_2O_3}$|$\mathrm{ZrO_2(+Y_2O_3)|Ga}_x(\mathrm{In}_y\mathrm{Tl}_{1-y})_{1-x}$,$\mathrm{Ga_2O_3}$ (+)

$y/(1-y)$	x_{Ga}	E/mV
0.75/0.25	0.1	0.1168T-66.26 ± 0.90
0.75/0.25	0.2	0.0337T-0.46 ± 0.25
0.75/0.25	0.4	0.0209T-3.06 ± 0.73
0.75/0.25	0.6	0.0221T-12.68 ± 0.29
0.75/0.25	0.76	0.0193T-14.52 ± 0.20
0.50/0.50	0.1	0.0792T-25.94 ± 1.08
0.50/0.50	0.2	0.0564T-29.55 ± 0.86
0.50/0.50	0.4	0.0294T-12.67 ± 1.19
0.50/0.50	0.6	0.0182T-9.55 ± 0.67
0.50/0.50	0.8	0.0109T-6.42 ± 0.44
0.25/0.75	0.1	0.1246T-87.23 ± 0.86
0.25/0.75	0.2	0.0604T-36.29 ± 0.81
0.25/0.75	0.4	0.0413T-30.64 ± 0.43
0.25/0.75	0.6	0.0378T-30.53 ± 0.72
0.25/0.75	0.8	0.0197T-16.92 ± 0.55

Table 2
Experimental date of Ga-In-Tl alloys

T/K	1073	1173	1273
$\mathrm{Ga}_x(\mathrm{In}_{0.25}\mathrm{Ti}_{0.75})_{1-x}$			
X_{Ga}	$\ln a_{\mathrm{Ga}}$	$\ln a_{\mathrm{Ga}}$	$\ln a_{\mathrm{Ga}}$
0.1	−1.508	−1.749	−1.952
0.2	−0.925	−1.026	−1.110
0.4	−0.441	−0.527	−0.600
0.6	−0.325	−0.410	−0.481
0.8	−0.137	−0.184	−0.223
X_{Ga}	a_{Ga}	a_{Ga}	a_{Ga}
0.1	0.221	0.174	0.142
0.2	0.396	0.359	0.329
0.4	0.643	0.590	0.549
0.6	0.722	0.664	0.618
0.8	0.872	0.832	0.800
X_{Ga}	γ_{Ga}	γ_{Ga}	γ_{Ga}
0.1	2.214	1.740	1.420
0.2	1.982	1.793	1.647
0.4	1.608	1.476	1.372
0.6	1.204	1.106	1.030
0.8	1.090	1.040	1.000
X_{Ga}	$\Delta G^{\mathrm{XS}}_{\mathrm{Ga}}/\mathrm{J\,mol^{-1}}$	$\Delta G^{\mathrm{XS}}_{\mathrm{Ga}}/\mathrm{J\,mol^{-1}}$	$\Delta G^{\mathrm{XS}}_{\mathrm{Ga}}/\mathrm{J\,mol^{-1}}$
0.1	637800	444200	281100
0.2	548800	468300	400400
0.4	381200	312100	253900
0.6	148800	81070	23970
0.8	69220	31680	30
$\mathrm{Ga}_x(\mathrm{In}_{0.50}\mathrm{Ti}_{0.50})_{1-x}$			
X_{Ga}	$\ln a_{\mathrm{Ga}}$	$\ln a_{\mathrm{Ga}}$	$\ln a_{\mathrm{Ga}}$
0.1	−1.916	−1.987	−2.048
0.2	−1.005	−1.086	−1.155
0.4	−0.612	−0.647	−0.677
0.6	−0.324	−0.350	−0.372
0.8	−0.171	−0.189	−0.204
X_{Ga}	a_{Ga}	a_{Ga}	a_{Ga}
0.1	0.147	0.137	0.129
0.2	0.366	0.337	0.315
0.4	0.542	0.523	0.508
0.6	0.723	0.705	0.689
0.8	0.843	0.828	0.816
X_{Ga}	γ_{Ga}	γ_{Ga}	γ_{Ga}
0.1	1.473	1.371	1.290
0.2	1.831	1.687	1.575
0.4	1.355	1.308	1.270
0.6	1.206	1.174	1.148
0.8	1.053	1.035	1.019
X_{Ga}	$\Delta G^{\mathrm{XS}}_{\mathrm{Ga}}/\mathrm{J\,mol^{-1}}$	$\Delta G^{\mathrm{XS}}_{\mathrm{Ga}}/\mathrm{J\,mol^{-1}}$	$\Delta G^{\mathrm{XS}}_{\mathrm{Ga}}/\mathrm{J\,mol^{-1}}$
0.1	310400	252900	204400
0.2	485100	419500	364300
0.4	243800	215600	191900
0.6	150100	128900	111000
0.8	41690	27450	15440
$\mathrm{Ga}_x(\mathrm{In}_{0.75}\mathrm{Ti}_{0.25})_{1-x}$			
X_{Ga}	$\ln a_{\mathrm{Ga}}$	$\ln a_{\mathrm{Ga}}$	$\ln a_{\mathrm{Ga}}$
0.1	−1.916	−2.100	−2.254
0.2	−1.158	−1.160	−1.161
0.4	−0.628	−0.637	−0.644
0.6	−0.358	−0.393	−0.423
0.76	−0.201	−0.241	−0.275

Table 2 (*Continued*)

T/K	1073	1173	1273
X_{Ga}	a_{Ga}	a_{Ga}	a_{Ga}
0.1	0.147	0.122	0.105
0.2	0.314	0.314	0.313
0.4	0.533	0.529	0.525
0.6	0.699	0.675	0.655
0.76	0.818	0.786	0.760
X_{Ga}	γ_{Ga}	γ_{Ga}	γ_{Ga}
0.1	1.471	1.225	1.050
0.2	1.570	1.568	1.566
0.4	1.334	1.322	1.313
0.6	1.165	1.125	1.092
0.76	1.076	1.034	1.000
X_{Ga}	ΔG^{XS}_{Ga}/J mol^{-1}	ΔG^{XS}_{Ga}/J mol^{-1}	ΔG^{XS}_{Ga}/J mol^{-1}
0.1	309800	162800	38830
0.2	361900	360900	360000
0.4	231000	224200	218500
0.6	122600	94480	70770
0.76	59070	26850	−303

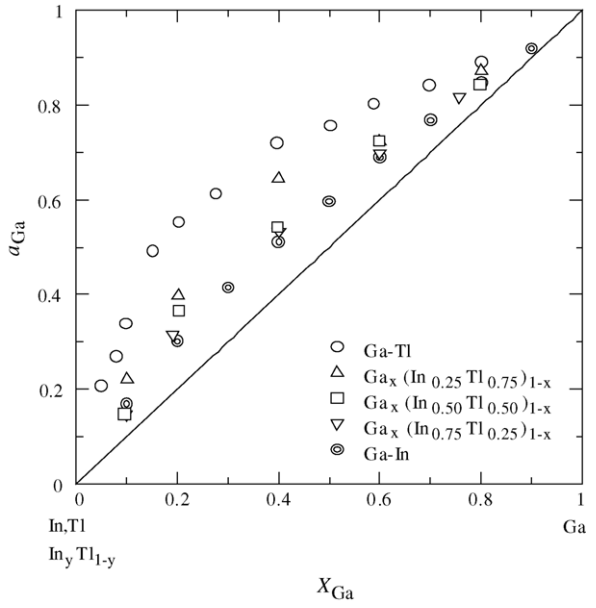

Fig. 2. Activity of Ga in Ga-In, Ga-Tl and $Ga_x(In_yTl_{1-y})_{1-x}$ alloys at 1073 K.

activity along the pseudo-binary systems (In_yBi_{1-y})–Ga ($y = 0.25$, 0.5, 0.75) with those of the binary systems of Ga–In and Ga–Tl. In the whole concentration range, activity of Ga shows largely to moderately positive deviations from ideality depending on the Tl composition.

4. Discussion

In order to obtain the iso-activity curve of Ga in the liquid Ga–In–Tl alloys, activity values for liquid Ga–Tl [2], and fitting parameter of Ga–In [1] alloys are used as the starting and ending points, and the experimental results for the ternary alloys are used. From the smoothing curves of a_{Ga} versus X_{Ga} plots in each binary and pseudo binary system, the alloy compositions corresponding to the activity values of every one tenth were read. The iso-activity curves at 1073 K are shown in Fig. 3. Each curve in the ternary alloy region is convex type from the straight line (Ga–In to Ga–Tl). Small amount of In addition to the Ga–Tl binary alloys decreases the activity sharply, that means In depresses the phase separation tendency in Ga–Tl alloys. In the Ga-rich compositions iso-activity curves become complex form, but it may be caused by the experimental uncertainty, because EMF values in such a region becomes too low to determine accurately.

From the iso-activity curves one can draw the activity curves in any directions in the ternary system at that temperatures. It enables us to calculate integral values of excess free energy of mixing in the ternary alloys. By use of the following Darken's equations, ΔG^{XS} can be derived by two methods i.e. from (i) two binary data of Ga–In and Ga–Tl and ternary data along pseudo-binary system of (In_yTl_{1-y})–Ga (Eq. (2)) and (ii) basal binary data of In–Tl and the same ternary data (Eq. (3));

$$\Delta G^{Ex} = (1 - X_{Ga})\left[\int_1^{X_{Ga}} \frac{\Delta \bar{G}^{Ex}_{Ga}}{(1 - X_{Ga})^2}\, dX_{Ga}\right]_{X_{In}/X_{Tl}} - X_{In}\left[\int_1^0 \frac{\Delta \bar{G}^{Ex}_{Ga}}{(1 - X_{Ga})^2}\, dX_{Ga}\right]_{X_{Tl}/X_{In}=0} - X_{Tl}\left[\int_1^0 \frac{\Delta \bar{G}^{Ex}_{Ga}}{(1 - X_{Ga})^2}\, dX_{Ga}\right]_{X_{In}/X_{Tl}=0} \quad (2)$$

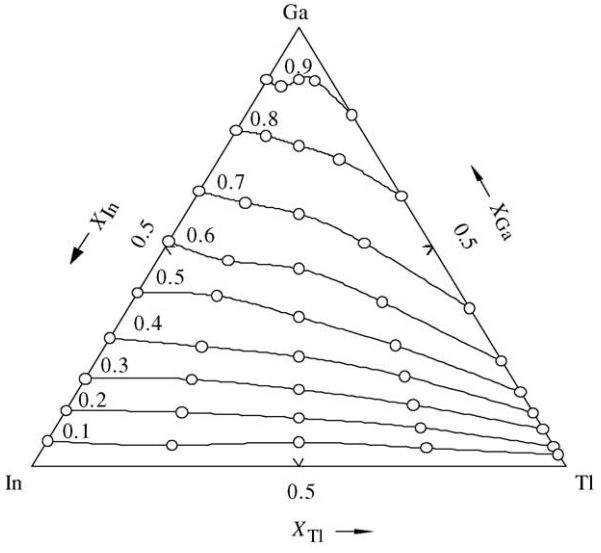

Fig. 3. Isoactivity curves of Ga in Ga-In-Tl alloys at 1073 K.

Table 3
Excess Gibbs energy of mixing in Ga-In-Tl alloys at 1073 K

x_{Ga}	Eq. 2	Eq. 3
ΔG^{ex}(J/mol)		
$Ga_x(In_{0.25}Tl_{0.75})_{1-x}$		
0.1	2930	1086
0.2	3339	1704
0.4	3771	2542
0.6	3408	2587
0.8	2295	1886
$Ga_x(In_{0.50}Tl_{0.50})_{1-x}$		
0.1	4554	718
0.2	4591	1185
0.4	4381	1828
0.6	3657	1946
0.8	2267	1430
$Ga_x(In_{0.75}Tl_{0.25})_{1-x}$		
0.1	4809	724
0.2	4732	1064
0.4	4377	1661
0.6	3552	1734
0.76	2542	1441

or

$$\Delta G^{\mathrm{Ex}} = (1 - X_{\mathrm{Ga}})[\Delta G^{\mathrm{Ex}}(X_{\mathrm{Ga}} = 0)]_{X_{\mathrm{In}}/X_{\mathrm{Tl}}=k} + (1-X_{\mathrm{Ga}})\left[\int_{X_{\mathrm{Ga}}=0}^{X_{\mathrm{Ga}}=X_{\mathrm{Ga}}} \frac{\Delta \bar{G}_{\mathrm{Ga}}^{\mathrm{Ex}}}{(1 - X_{\mathrm{Ga}})^2}\,\mathrm{d}X_{\mathrm{Ga}}\right]_{X_{\mathrm{In}}/X_{\mathrm{Tl}}=k} \quad (3)$$

ΔG^{XS} values at 1073 K obtained in this study by Eqs. (2) and (3) are shown in Table 3. The values obtained by Eq. (2) are bigger than those by Eq. (3). In the first term in Eq. (2), integration must be performed from $x_{\mathrm{Ga}} = 1$ toward $x_{\mathrm{Ga}} = 0$ in Eq. (2), and uncertainty limits in the first term accumulate more in the range of less gallium content. On the contrary calculated values based on Eq. (3) has little problem and more reliable in this system. Binary data of In–Tl system by Kameda and Yamaguchi [4], and ternary data by this study are used to calculate the ternary values by Eq. (3), because Eq. (2) gives the unusual forms of the excess free energy curves and too big values as shown below.

Model calculation methods are proposed by several researchers to get ternary data from the constituent three binary data. In order to use these calculation methods, the binary data are arranged to Redlich–Kister's polynomial form shown Eq. (4) by data fitting.

$$\Delta G^{\mathrm{Ex}} = X_i X_j \sum_{v=0}^{n} (X_i - X_j)^v L_{i,j}^{(v)}(T),$$

$$L_{i,j}^{(v)}(T) = a_{i,j}^{(v)} + b_{i,j}^{(v)}(T) + c_{i,j}^{(v)} T^2 \quad (4)$$

The parameters obtained are shown in Table 4.

The calculating methods are applied to this system and the results will be presented elsewhere by Zivkovic [5]. As the results each model gives similar values but cannot reproduce the experimental values obtained in this study, although the agreement is better in the systems of Ga–Sb–Bi, Ga–Sb–Tl, Ga–In–Te, etc. Chou's model [6] gives bigger values than the experimental ones by Eq. (3). One of the examples is shown in Fig. 4 at 1073 K for the $In_{0.5}Tl_{0.5}$–Ga section. In the figure solid line is from Chou's model, circles from Eq. (3) and black triangles from Eq. (2).

Table 4
Parameter fitting for three binary alloys using Redlich–Kister polynomial equation

System	n	$a_{i,j}(n)$	$b_{i,j}(n)$	$c_{i,j}(n)$	Temperature (K)
	0	9220	4.65	0	
Ga-Tl	1	3499	−2.18	0	973–1273
	2	6931	−4.81	0	
	0	20412	−18	0	
Ga-In	1	17614	−15.1	0	973–1273
	2	4915	0.773	0	
	0	−212	0.536	0	
In-Tl	1	907	−0.561	0	973–1273
	2	2063	−0.0522	0	

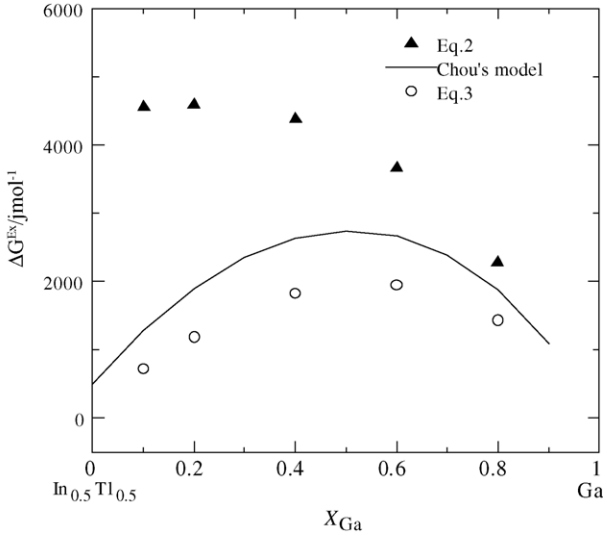

Fig. 4. Excess free energy of mixing at 1073 K for $In_{0.5}Tl_{0.5}$-Ga alloys.

5. Conclusions

EMF of the galvanic cells with the solid electrolyte (ZrO_2(+Y_2O_3)) was measured in the temperature range of 1070–1270 K to derive the activity of Ga for liquid Ga–In–Tl alloys by use of Ga,Ga_2O_3 reference electrode. The following results are obtained: The activity of Ga shows positive deviations from ideality in the whole composition range.

Combining the binary data for Ga–In and Ga–Tl alloys with the ternary data in this study, iso-activity curves in the whole composition range of the ternary system are obtained. Excess Gibbs energy of mixing is derived by Darken's equation and is compared with the model calculation by Chou's model.

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