Activity of Gallium in Ga-Sb-Te Alloys Determined by EMF Method with Zirconia as Solid Electrolyte

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In order to determine the activity of gallium in liquid Ga-Sb-Te alloys the emf method with zirconia solid electrolyte was used at 1000–1150 K for nine compositions of the alloys. Combining the binary data of Ga-Sb and Ga-Te alloys with the results in this study, isoactivity curves at 1123 K were obtained in the whole composition range. There seem no published data to be compared with.

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I. Introduction

Many studies have been carried out on alloy systems containing semiconducting compounds from both scientific and technological points of view. An accurate knowledge of the thermodynamic properties and phase diagrams of them is essential, and analytical or model calculations have been tried⁽¹⁾ with the accumulation of the fundamental data. Some of the binary systems have been extensively studied but the experimental data for ternary systems are not adequate.

The present measurements were made in the course of our current program of experimental thermodynamic studies of III-V and II-VI compounds-related materials at high temperatures by use of the emf method.

The phase diagram of the Ga-Sb system is characterized by the existence of the only one-line compound GaSb. And Te forms some intermediate compounds with both of Ga and Sb.

Activity of gallium in the Ga-Sb alloys⁽²⁾ shows a moderately negative deviation from the Raoult's law and the temperature dependence of the activity is very small in the temperature range 1000–1150 K.

Activity data on liquid Ga-Te alloys were shown in our previous paper⁽²⁾. The activity of gallium shows large negative deviations from ideality and increases sharply from the middle concentration range to the gallium-rich region where the miscibility gap exists.

In this study Te is chosen as the third element which affects the activity of gallium in the liquid Ga-Sb alloys. Emf measurement of the electrochemical cell with a zirconia solid electrolyte was performed to obtain the gallium

activity of Ga-Sb-Te liquid alloys for 9 compositions with a constant mole ratio of gallium to antimony at 1000–1150 K. The reference electrode used was Ga + Ga₂O₃. There seem no thermodynamic data on the ternary Ga-Sb-Te alloys.

II. Experimental

1. Materials

The ternary alloys used in this study were prepared from high purity materials (Ga, Sb, Te: 99.999 mass% purity). Alloy elements were weighed to give mixtures with desired compositions, and were put into the zirconia solid electrolyte crucible with a small amount of Ga₂O₃ powder (99.99% purity; in a mass ratio about 7:93). Zirconia solid electrolyte crucibles (0.92ZrO₂+0.08Y₂O₃, OD 8 mm, ID 5 mm and length 90 mm) were obtained from Nikkato Co., Ltd. Japan.

2. Experimental apparatus and procedures

Experimental details are quite similar to the previous papers for liquid binary⁽²⁾ and ternary⁽³⁾⁽⁴⁾ gallium alloys. The main part of the cell assembly was shown in Fig. 1. Re wires spot-welded to W lead wires were used as the electrical contact material for both the alloy- and reference-electrodes. Both of the electrodes can be stirred with the lead wires during the experimental run. The space above the alloy electrode in the zirconia electrolyte was filled with a tight-fitting alumina tube, in which a lead wire was fixed with high temperature zirconia cement, in order to minimize the possible composition changes resulting from volatilization of the alloy component. The reference electrode was put in an alumina crucible.

After the cell was assembled in a one-end closed silica reaction tube, the reaction tube was repeatedly evacuated

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Fig. 1 Schematic diagram of the cell assembly.

and backfilled with purified argon, and the temperature was raised in a vertical type nichrom wire resistance furnace. The cell temperature was controlled to ± 1 K at a desired temperature with a thermocontroller and a Pt/13RhPt thermocouple. The emf of the cell and the cell temperature were measured with a digital voltmeter with a printer. Equilibrium was considered to have been attained, when the emf varied only by ± 0.1 mV over 1800 s.

III. Results and Discussion

The emfs of cell I were measured for the determination of Ga activity in the Ga-Sb-Te liquid alloys.

When the cell containing high concentration of Te in the alloy electrode was held at high temperatures for a long time, emf of the cell continuously decreased, and there was evidence of volatilization of Te in the cooler part of the cell assembly⁽²⁾. The higher the Te concentration in the alloys, the less stable the emf of the cell. By use of the spacer, which decreases the dead space above the alloy electrode, stable emf was obtained. In this study the temperature range of emf measurement and the life time of the cell were limited for the alloy electrodes containing higher concentrations of Te and Sb. In Table 1 the experimental results are listed. Emf (E /mV) vs temperature (T /K) plot shows a good linear relation for each alloy. They are treated by least squares regression analy-

Table 1 Experimental EMF data on cell:
(-)Ga, $Ga_2O_3 | ZrO_2(+Y_2O_3) | Ga\text{-}Sb\text{-}Te, Ga_2O_3(+)$ and activity of gallium in Ga-Sb-Te alloys at 1123 K.

Alloy	$T/K: E/mV$	a_{Ga}
$(Ga_{0.2}Sb_{0.8})_{0.8}Te_{0.2}$	1121:92.36, 1085:89.11, 1065:87.01, 1042:82.08 $E/mV = 0.1254T/K - 47.54 \pm 1.21$	0.0554 ± 0.0021
$(Ga_{0.4}Sb_{0.6})_{0.8}Te_{0.2}$	1084:56.78, 1119:59.68, 1155:60.94 $E/mV = 0.0585T/K - 6.32 \pm 0.70$	0.159 ± 0.004
$(Ga_{0.6}Sb_{0.4})_{0.8}Te_{0.2}$	1082:35.01, 1160:37.68, 1123:36.64, 1081:35.16, 1040:33.15 $E/mV = 0.0375T/K - 5.57 \pm 0.25$	0.322 ± 0.003
$(Ga_{0.8}Sb_{0.2})_{0.8}Te_{0.2}$	1083:10.44, 1159:14.63, 1118:13.26, 1081:10.92, $E/mV = 0.0526T/K - 46.05 \pm 0.54$	0.668 ± 0.011
$(Ga_{0.2}Sb_{0.8})_{0.6}Te_{0.4}$	1086:124.32, 1062:123.78, 1042:122.98 $E/mV = 0.0302T/K + 91.59 \pm 0.16$	0.0204 ± 0.0001
$(Ga_{0.4}Sb_{0.6})_{0.6}Te_{0.4}$	1119:101.26, 1158:102.23, 1110:100.66, 1070:100.00 $E/mV = 0.0257T/K + 72.35 \pm 0.22$	0.0433 ± 0.0003
$(Ga_{0.6}Sb_{0.4})_{0.6}Te_{0.4}$	1088:70.25, 1159:72.60, 1121:71.12, 1081:70.41 $E/mV = 0.0294T/K + 38.40 \pm 0.27$	0.109 ± 0.002
$(Ga_{0.8}Sb_{0.2})_{0.6}Te_{0.4}$	1161:48.95, 1144:48.38, 1118:46.11, 1104:45.16, 1081:43.91, 1057:40.97, 1026:37.91, 1026:38.31 $E/mV = 0.0829T/K - 46.63 \pm 0.53$	0.237 ± 0.004
$(Ga_{0.8}Sb_{0.2})_{0.4}Te_{0.6}$	1085:114.29, 1065:111.25, 1036:110.70, 1009:103.77, 1039:110.25 $E/mV = 0.1215T/K - 17.10 \pm 1.75$	0.0247 ± 0.0014

Table 2 Activities of Ga in Ga-Sb and Ga-Te alloys at 1123 K.

X_{Ga}	Ga-Sb	Ga-Te
0	0	0
0.1	0.048	5.19×10^{-4}
0.2	0.109	1.27×10^{-3}
0.3	0.192	3.42×10^{-3}
0.4	0.276	2.20×10^{-2}
0.5	0.377	0.230
0.6	0.485	0.536
0.7	0.628	0.805
0.8	0.765	0.940
0.9	0.882	0.940
1.0	1	1

sis, and the results are shown in Table 1.

Activities of Ga(a_{Ga}) in the alloys at 1123 K were calculated from eq. (1) and the results are also shown in Table 1.

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

where F : the Faraday constant, R : the gas constant and $\Delta \bar{G}_{Ga}/J \text{ mol}^{-1}$: partial molar free energy of mixing of Ga. Uncertainty limits in the activity values were derived from those in the emf values.

The data for liquid Ga-Sb and Ga-Te alloys⁽²⁾ shown

Table 3 Activities of Ga in Ga-Sb-Te alloys at 1123 K.

X_{Ga}	Ga-Sb _{0.9} Te _{0.1}	Ga-Sb _{0.8} Te _{0.2}	Ga-Sb _{0.7} Te _{0.3}	Ga-Sb _{0.6} Te _{0.4}	Ga-Sb _{0.5} Te _{0.5}
0	0	0	0	0	0
0.1	0.04	0.028	0.023	0.015	0.01
0.2	0.10	0.082	0.065	0.047	0.035
0.3	0.177	0.157	0.134	0.110	0.082
0.4	0.269	0.250	0.231	0.209	0.190
0.5	0.375	0.367	0.367	0.353	0.355
0.6	0.508	0.516	0.535	0.556	0.580
0.7	0.654	0.675	0.688	0.712	0.739
0.8	0.783	0.800	0.818	0.825	0.839
0.9	0.895	0.906	0.921	0.900	0.920
1.0	1	1	1	1	1

X_{Ga}	Ga-Sb _{0.4} Te _{0.6}	Ga-Sb _{0.3} Te _{0.7}	Ga-Sb _{0.2} Te _{0.8}	Ga-Sb _{0.1} Te _{0.9}
0	0	0	0	0
0.1	0.005	0.0005	0.005	0.001
0.2	0.022	0.010	0.008	0.004
0.3	0.066	0.045	0.028	0.016
0.4	0.159	0.137	0.100	0.085
0.5	0.335	0.333	0.301	0.280
0.6	0.602	0.610	0.600	0.590
0.7	0.761	0.790	0.810	0.811
0.8	0.869	0.905	0.900	0.930
0.9	0.933	0.983	0.957	0.966
1.0	1	1	1	1

Fig. 2 Isoactivity curves of gallium in liquid Ga-Sb-Te alloys at 1123 K.

in Table 2 were used as the starting and ending points of the isoactivity curves for the Ga-Sb-Te ternary liquid alloys.

From the activity plots on the lines of pseudobinary systems of 1) $\text{Ga}_x\text{Sb}_{1-x}\text{-Te}$ and 2) $\text{Ga}_{1-x}\text{Te}_x\text{-Sb}_{1-x}\text{Te}_x$, where X is the mole fraction in the alloys, the isoactivity curves have been determined. The result at 1123 K is shown in Fig. 2. The characteristic of this figure is that the isoactivity curves gather from the whole composition range of Ga-Sb binary alloys to the intermediate composition range of Ga-Te system and that each curve is not so wavy. But the latter is not the case for the lower activity curve. Isoactivity curves in the Ga-Sb-Bi alloys at

1073 K are in simple forms and show only small deviation from the straight lines which connect the starting (Ga-Sb system) and ending (the Ga-Bi system) points⁽⁴⁾. Those in the Ga-Sb-In alloys at 1073 K show the wavy forms in the intermediate composition range in the pseudobinary system of $\text{Ga}_x\text{Sb}_{1-x}\text{-Ga}_y\text{In}_{1-y}$, where x and y correspond to the starting and ending composition of the isoactivity curves⁽³⁾.

From Fig. 2 one can draw the activity curves in any directions in the ternary system at that temperature. In Table 3 the values of activity of gallium in the pseudobinary $\text{Sb}_y\text{Te}_{1-y}\text{-Ga}$ system obtained by the interpolation method based on this measurement are listed. There are no thermodynamic data on this ternary system to be compared with.

IV. Conclusion

The activity of Ga in liquid Ga-Sb-Te alloys was measured by the emf method with zirconia solid electrolytes at 1000–1150 K for nine compositions. Combining the binary data of Ga-Sb and Ga-Te systems with the ternary data, isoactivity curves at 1123 K were obtained in the ternary system.

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