Activity Measurement of Zn in ZnTe–CdTe Solid Solutions by EMF Method

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E.M.F. of galvanic cells with the solid electrolyte ($\text{ZrO}_2(+\text{Y}_2\text{O}_3)$) was measured to determine the activity of zinc in the whole composition range for ZnTe–CdTe solid solutions coexisting with tellurium-rich and poor-ternary liquid phases in the temperature ranges 831–952 K and 802–896 K, respectively. The cells used were as follows:

(–) Kanthal | Re | $(\text{ZnTe})_x(\text{CdTe})_{1-x}$, Te or Zn, $\text{ZnO} | \text{O}^{2-} |$ air, Pt (+). Activity of zinc in the Te-rich region increases monotonously from 0 to the order of 10^{-6} at 923 K with the increasing of ZnTe. On the contrary the activity of zinc at 873 K in the Te-poor region hardly increases with the ZnTe composition up to 0.7 mole fraction of ZnTe, but increases keenly in the higher range of ZnTe.

The phase relation at 873 K in the Zn–Te–Cd ternary system was determined for the quenched specimen.

The activity of ZnTe was also derived from the emf measurements in this study for the Te-rich solid solutions.

(Received October 31, 1990)

Keywords: zinc cadmium telluride, zinc telluride, cadmium telluride, activity, electromotive force method, solid electrolyte, zirconia electrolyte, thermodynamics, semiconductor, ternary solid solution

I. Introduction

Numerous methods of crystal growth have been applied to the semiconducting compounds⁽¹⁾ due to their potentially promising electrical and optical properties. In the producing processes of these materials from the melts a precise knowledge of the thermodynamic properties and of the phase diagrams is very important.

For binary II–VI compounds of Zn–Te⁽²⁾, Cd–Te⁽³⁾, and Zn–Cd⁽⁴⁾ thermodynamic values have been reported and/or analysed. As for the ternary system of Zn–Te–Cd thermodynamic study is scarce.

The pseudobinary system ZnTe–CdTe forms a complete series of solid solution⁽⁵⁾ with cubic zincblende structure and the lattice parameter⁽⁶⁾ follows Vegard's rule. Zabdyr⁽⁷⁾ has determined the thermodynamic properties of solid ZnTe and CdTe as well as ZnTe–CdTe solid solutions by means of the EMF technique with fused salt electrolyte.

The activity of zinc in the ternary system is considered to change largely across the narrow composition range of ZnTe–CdTe from Te-rich side to Te-poor side.

The purpose of this study is to measure the activity of zinc in the pseudobinary system ZnTe–CdTe on both Te-rich and Te-poor sides by use of a quite similar method with emf measurements of zirconia solid electrolyte cell for the GaAs–InAs system⁽⁸⁾. And the phase relation between the compound solid solution and liquid alloy at 873 K is examined by quenching method.

II. Experimental

1. Materials

The ternary alloys used in this study were prepared from high purity materials (ZnTe and CdTe: 99.9999 mass% purity, polycrystal, Furukawa Co. Ltd.). The polycrystals were ground to fine powder, weighed to give mixtures with desired compositions (about 2 g), mixed, pressed into a pellet and heat-treated in a sealed evacuated quartz ampoule at 913 K over 1.7×10^6 s. After the heat-treatment the formation of the solid solution was confirmed with an X-ray diffractometer, and lattice parameter was measured. For the alloy electrode, ZnO powder (99.0+ purity, Wako Pure Chemicals Ind.) was mixed with the solid solution (about 0.3 g) in a volume ratio about 1:5. And a very small amount of tellurium (99.999% purity, Osaka Asahi Metal Mfg. Co., Ltd., about 10 mg) was added to the mixture in order to keep the composition of the solid solution constant on the tellurium rich side.

For the electrode on the tellurium poor side, instead of tellurium zinc (99.9999% purity, Mitsuwa Chemical Ind.) or cadmium (99.999% purity, Wako Pure Chemicals Ind.) was added to the mixture, and pressed into a pellet and heat-treated at 843 K for 1.2×10^6 s in an evacuated sealed quartz ampoule before emf measurement. The composition of the solid solution was determined from its lattice parameter.

The electrolyte tube, closed at one end, ($0.92\text{ZrO}_2+0.08\text{Y}_2\text{O}_3$, OD 8 mm, ID 5 mm, and length 300 mm) was obtained from Nippon Kagaku Togyo Co., Ltd.

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2. Experimental apparatus and procedures

Experimental details for emf measurement have been outlined previously⁽⁸⁾. In this study air, Pt was used as a reference electrode⁽⁹⁾. Alloy electrodes were prepared by the method described above.

Re wires (0.254 mm ϕ , 5 mm) were spot-welded to kanthal wires for alloy electrode. The electrode was charged in the bottom of the zirconia tube with the lead wire. At the start of each experimental run the inside of the zirconia was evacuated and flushed with purified argon gas repeatedly, and the cell was heated in a kanthal-resistant furnace. The emf of the cell was measured with a digital voltmeter with a printer.

In order to determine the tie lines between the solid solutions of ZnTe–CdTe and the liquid alloys in the tellurium rich and poor regions, the binary compound or solid solution was sealed in a small evacuated quartz ampoule (ID=5 mm ϕ) with an appropriate amount of pure metal (tellurium, zinc or cadmium). The ampoule was held at 873 K for more than 1.6×10^6 s for equilibration, and quenched into ice-water. The specimen showed two phases (compound solid solution + alloy). The composition of the solid solution was determined from the lattice parameter by X-ray diffractometry and that of the alloy by EPMA analysis. The composition of the starting materials is shown later with the experimental results.

III. Results and Discussion

1. Lattice parameter measurement

In Fig. 1 lattice parameters of the pseudobinary solid solutions ZnTe–CdTe measured with an X-ray diffractometer are plotted against the ZnTe composition. The lattice parameters obey Vagard's law and are excellent agreement with the values⁽⁶⁾ by Woolley and Ray and Tai. This result was used to check the composition change of

Fig. 1 Lattice parameters of ZnTe–CdTe solid solutions.

the solid solutions before and after emf measurements and to determine the composition of the solid solutions in the quenched specimen for the study of the phase relation.

2. Phase relation between the liquid alloy and the ZnTe–CdTe compound solid solution

The composition of the specimens is shown as solid circle symbols in Fig. 2, and the pair of the starting materials (pure metals and compounds or compound solid solutions) are connected with the dotted lines through the composition points. After equilibration the composition of the alloy phase was determined only for tellurium by an EPMA, and that of the solid solutions from the lattice parameters. Assuming that the bulk composition of the starting material in the ternary system of Zn–Te–Cd is unchanged during equilibration, the tie lines are obtained by connecting the compositions of the solid solution and that of starting materials. The results at 873 K are shown as solid lines in Fig. 2. Open circles are the corresponding terminal compositions in the two phase region. The following conclusions are derived; (1) In the tellurium rich region, the solid solution coexists with nearly pure tellurium in the whole composition range, (2) on the contrary, the ZnTe rich solid solution coexists with the liquid Zn–Cd alloys which contain very small amount of tellurium in the tellurium poor region. These relation can be used to explain the activity curve obtained in this study as shown later.

3. Emf measurements of the pseudobinary system of ZnTe–CdTe

From the emf value of the following cell (I), activity of zinc in the ZnTe–CdTe solid solution can be calculated by the eq. (1).

Fig. 2 Tie-lines between the solid solutions of ZnTe–CdTe and Te-rich and Te-poor liquid alloys at 873 K.

where O^{2-} is a stabilized zirconia solid electrolyte, E : the emf of cell (I), F : Faraday's constant, R : the gas constant, T : the cell temperature, and a_{Zn} : the activity of zinc referring to pure liquid zinc coexisting with ZnO. M in cell (I) is Te or Zn or Cd dissolved in the alloy phase which coexists with the solid solution of ZnTe–CdTe, and very important because of holding the composition of the solid solution on the tellurium-rich or -poor side in the two phase region.

In this study the following cell was used:

In order to obtain the emf of cell (I), the emf value of cell (III) and thermo-emf between kanthal and platinum as well as the emf of cell (II) are necessary.

We measured the emf of cell (III) in the previous study⁽¹⁰⁾ in the temperature range of 767–1007 K to be:

$$E_{(m)}/\text{mV} \pm 0.9 = 1832.3 - 0.5874 T/\text{K}.$$

The temperature dependence of the thermo-emf((-) Pt/kanthal(+)) between 800 and 1000 K was measured. As the temperature range was not so wide that the result was represented by a linear line, i.e.

$$E_{th}/\text{mV} \pm 0.08 = -6.34 + 0.0137 T/\text{K}^{(11)}$$

The emfs of cell (II) for tellurium rich solid solutions were measured in the temperature range 831–952 K for $X_{\text{ZnTe}} = 0.05$ –0.8 where X_{ZnTe} represented the mole fraction of ZnTe in the solid solutions of the ZnTe–CdTe system. It required about 3.6 ks to obtain stable emf after the cell temperature reached the desired one. The stable emf value lasted 36 ks but after that the emf value increased remarkably, one probable reason of which was the vaporization of small amount of the liquid tellurium phase. The experimental results are shown in Fig. 3. The result for $X_{\text{ZnTe}} = 1$ corresponds to the binary Zn–Te

Fig. 3 Experimental emf data on the cell: (-) Kanthal | Re | (ZnTe)_x(CdTe)_{1-x}, Te, ZnO | ZrO₂(+ Y₂O₃) | air, Pt (+).

system⁽¹¹⁾. The results for $X_{\text{ZnTe}} = 0.8$ and 0.6 show the reproducibility from the two experimental runs.

In the case of the tellurium-poor solid solutions, we must consider the change in the composition of the solid solution, when cadmium or zinc is added in order to make two phase region as is shown in Fig. 2. In this case the solid solution with ZnO and a small amount of zinc or cadmium was equilibrated at 843 K for about 1.2×10^6 s and its composition was determined from the lattice parameter. Then the specimen was used as the alloy electrode for emf measurement. After emf measurement no change in the lattice parameter was confirmed for all the electrode by the X-ray diffractometer. Because of high vapour pressure of the elements added, the emf measurement was made at lower temperatures by about 50 K than that for tellurium rich solid solutions.

The relation between emf(E/mV) and temperature (T/K) of cell (II) is shown in Fig. 4. Each linear line was obtained by least squares regression analysis. These data are listed in Table 1.

Combining the result with the data by cell (III) and thermo-emf between Pt and kanthal wire, emfs of cell (I) were calculated, which are shown in Table 2 as a function of temperature for both tellurium rich and poor solid solutions. Activities of zinc in the solid solutions can be calculated from the emf values according to eq. (1). The activities at 873 and 923 K for the tellurium-rich solid solutions and at 823 and 873 K for the tellurium poor one

Fig. 4 Experimental emf data on the cell: (-) Kanthal | Re | (ZnTe)_x(CdTe)_{1-x}, Zn, ZnO | ZrO₂(+ Y₂O₃) | air, Pt (+).

Table 1 Temperature dependence of emf of the cell: (–) Kanthal |Re|(ZnTe)_x(CdTe)_{1-x}, $\underline{M}$, ZnO|ZrO₂(+Y₂O₃)|air, Pt (+).

X_{ZnTe}	M=Te (Te-rich) E/mV	X_{ZnTe}	M=Zn (Te-poor) E/mV
1	1099.3–0.3624 $T/\text{K} \pm 0.8$	0.912	1779.5–0.5354 $T/\text{K} \pm 0.3$
0.8	1097.6–0.3681 $T/\text{K} \pm 1.2$	0.779	1677.7–0.4669 $T/\text{K} \pm 0.9$
0.6	1051.3–0.3251 $T/\text{K} \pm 0.2$	0.574	1711.3–0.5417 $T/\text{K} \pm 0.9$
0.4	1044.4–0.3328 $T/\text{K} \pm 1.4$	0.189	1682.8–0.5668 $T/\text{K} \pm 1.8$
0.2	1024.7–0.3248 $T/\text{K} \pm 0.9$		
0.1	1065.2–0.3955 $T/\text{K} \pm 1.3$		
0.05	1050.6–0.4107 $T/\text{K} \pm 1.3$		

Table 2 Temperature dependence of emf of the cell: (–) Zn, ZnO|ZrO₂(+Y₂O₃)|(ZnTe)_x(CdTe)_{1-x}, $\underline{M}$, ZnO (+).

X_{ZnTe}	M=Te (Te-rich) E/mV	X_{ZnTe}	M=Zn (Te-poor) E/mV
1	739.3–0.2387 $T/\text{K} \star 1$		–0.933 + 1.215 $\times 10^3 T/\text{K} \pm 0.017$
0.8	741.0–0.2330 T/K	0.912	59.1–0.0657 T/K
0.6	787.3–0.2760 T/K	0.779	160.9–0.1342 T/K
0.4	794.2–0.2683 T/K	0.574	127.3–0.0594 T/K
0.2	813.9–0.2763 T/K	0.189	155.8–0.0343 T/K
0.1	773.4–0.2056 T/K		
0.05	788.0–0.1904 T/K		

Table 3 Activities of zinc in ZnTe–CdTe solid solutions coexisting with Te-rich or Te-poor liquid alloys.

Te-rich solid solutions		
X_{ZnTe}	$a/10^{-7}$ at 873 K	$a/10^{-7}$ at 923 K
1	7.38 ± 0.36	21.4 ± 1.0
0.8	6.17 ± 0.38	18.0 ± 1.0
0.6	4.88 ± 0.23	15.2 ± 0.9
0.4	3.40 ± 0.23	10.7 ± 0.6
0.2	2.43 ± 0.12	7.84 ± 0.38
0.1	1.38 ± 0.09	4.21 ± 0.25
0.05	0.658 ± 0.041	2.05 ± 0.12
Te-poor solid solutions		
X_{ZnTe}	a at 823 K	a at 873 K
1	0.998 ± 0.001	0.997 ± 0.025
0.912	0.868 ± 0.032	0.955 ± 0.033
0.779	0.241 ± 0.013	0.313 ± 0.016
0.574	0.110 ± 0.006	0.135 ± 0.007
0.189	0.0273 ± 0.0023	0.0351 ± 0.0027

are listed in Table 3.

In order to observe the temperature- and composition-dependence of the activity, the values are shown in Fig. 5(a) and (b) for tellurium-rich and poor solid solutions, respectively. Square symbols at $X_{\text{ZnTe}}=1$ correspond to the values for the binary system of Zn–Te.

From the figure we can conclude that (1) the activity of zinc in the tellurium-rich solid solutions is very small and increases moderately with ZnTe composition and (2) the temperature dependence of the activity is large. On the contrary, the increasing rate in activity of zinc in the tellurium-poor solid solutions becomes larger with increasing composition of ZnTe, especially in the com-

Fig. 5 (a) Activities of zinc in the ZnTe–CdTe solid solutions coexisting with Te-rich liquid alloys at 923 and 873 K. (b) Activities of zinc in the ZnTe–CdTe solid solutions coexisting with Te-poor liquid alloys at 873 and 823 K.

position larger than $X_{\text{ZnTe}}=0.7$, and the temperature dependence of the activity is not so large. The shape of the activity curve can be explained from the tie lines obtained in this study and the activity curve of the liquid Cd–Zn alloy⁽⁴⁾. The activity of zinc in the Cd–Zn binary system shows a moderate deviation from Raoult's law in the whole concentration range at 900 K⁽¹²⁾, and the temperature dependence of the activity is small. From Fig. 2 we can find that the liquid alloys coexisting with the solid solution contain only a few percent of tellurium in the whole composition range, and that the cadmium rich ternary alloys coexist with the solid solutions over a wide composition range. For these reasons the activity of zinc in the solid solutions hardly increases up to $X_{\text{ZnTe}}=0.7$, but increases keenly in the higher concentration range of ZnTe. This tendency can be observed in the InAs–GaAs

Fig. 6 Activities of ZnTe in the ZnTe–CdTe solid solutions coexisting with Te-poor liquid alloys at 900 K.

solid solutions⁽⁸⁾ in which the phase relation is a quite similar.

Using the activity data in this study and the vapour pressure of pure zinc, we can easily calculate the equilibrium vapour pressure above the solid solutions and the result gives the upper and lower limits of the pressure in the solid solutions.

4. Activity of ZnTe in the Te-rich solid solutions of the ZnTe–CdTe system

We can calculate the activity of ZnTe in the ZnTe–CdTe solid solutions from the emf of cell V as follows:

If tellurium and ZnO in both electrode are assumed to be under the same condition, respectively, we obtain the total cell reaction as; $\text{ZnTe} = \text{ZnTe}$, and $\Delta G = -2EF = \Delta \bar{G}_{\text{ZnTe}} = RT \ln a_{\text{ZnTe}}$. Emfs of cell V can be derived from the result shown in Table 1. The activity curve at 900 K was shown in Fig. 6 with the result by Zabdyr⁽⁷⁾ employing the fused salt emf method. According to our result, the activity of ZnTe shows a moderately positive deviation from Raoult's law, but Zabdyr's value obeys nearly Raoult's law. We cannot find the reasons for the discrepancy as yet. Though the principal difference in the experimental is that our electrodes are saturated with zinc-oxide in order to fix the oxygen potential of the electrodes, we do not count this point as the cause of the discrepancy.

IV. Conclusion

The activity of zinc in the solid solutions ZnTe–CdTe coexisting with tellurium and with the Te-poor ternary liquid phase was derived as functions of the composition and temperature from emf measurements of galvanic cells with the zirconia-base solid electrolyte at 831–952 K and 802–896 K, respectively. The reference was air, Pt electrode. The activity of zinc in the Te-rich solid solutions increases monotonously from 0 to the order of 10^{-6} at 923 K with increasing composition of ZnTe, and the temperature dependence is large. On the contrary the activity of zinc in the Te-poor solid solutions hardly increases with the ZnTe composition up to 0.7 mole fraction of ZnTe, but increases keenly in the higher range of ZnTe. Temperature dependence of the activity of zinc is very small. The shape of the activity curve can be explained from the tie-line between the solid solutions and the Te-poor ternary liquid phase determined in this study.

The activity of ZnTe was derived from the emf measurements in this study in the Te-rich solid solution range.

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