Phase diagram of HgTe–ZnTe pseudobinary and density, heat capacity, and enthalpy of mixing of Hg$_{1-x}$Zn$_x$Te pseudobinary melts

Ching-Hua Su, Yi-Gao Sha, a) K. Mazuruk, a) and S. L. Lehoczky
Space Science Laboratory, NASA Marshall Space Flight Center, Huntsville, Alabama 35812

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In this article, the solidus temperatures of the Hg$_{1-x}$Zn$_x$Te pseudobinary phase diagram for several compositions in the low $x$ region were measured by differential thermal analysis and the HgTe–ZnTe pseudobinary phase diagram was constructed. The densities of two HgZnTe melts, $x=0.10$ and 0.16, were determined by an in situ pycnometric technique in a transparent furnace over, respectively, 110 and 50 °C ranges of temperature. The thermodynamic properties of the melts, such as the heat capacity and enthalpy of mixing, were calculated for temperatures between the liquidus and 1500 °C by assuming an associated solution model for the liquid phase.

I. INTRODUCTION

During the process of crystal growth of semiconductors from the melts, the thermodynamic and thermophysical properties of the melts are important parameters for growth process optimization as well as in the theoretical modeling of the process. However, in general, there exist only a limited amount of data on the thermodynamic and thermophysical properties of the Hg-based molten semiconductors due to their high vapor pressures and chemical reactivity. The Hg$_{1-x}$Zn$_x$Te (0<$x$<1) solid solutions have been studied extensively in the low $x$ ($x<0.2$) region as a potentially superior material for the IR detector applications because the chemical bonding makes the material relatively more stable compared to HgCdTe. The only available thermodynamic data for this system are the pseudobinary liquids and solidus curves for $x>0.3$, a few liquidus points near the Te corner of the phase diagram, and the partial pressures of Hg and Te$_2$ for various values of $x$.

This article describes the results for selected solidus temperatures determined by differential thermal analysis (DTA) and, together with previous data, provides a description of the HgTe–ZnTe pseudobinary phase diagram. In Sec. III, measured melt density variation with temperature is reported over 110 and 50 °C ranges of temperature.

II. PSEUDOBINARY PHASE DIAGRAM

A. Sample preparation

The ampoules used in the measurements were made from fused silica tubing supplied by Heraeus Amersil, Inc.

B. Experimental method for differential thermal analyses

The experimental apparatus for the DTA measurements is similar to that described previously, except for the following modifications: (1) type S (Pt/Pt–10% Rh) thermocouples were used instead of type K (chromel-alumel) thermocouples, (2) the Inconel tube previously used in between the samples and the furnace was removed, and (3) the data were recorded and stored by a microcomputer. As in Ref. 25, the Sb ampoule, besides being the thermal capacity reference, also served as an internal thermocouple calibration reference. A series of heating rates, 1, 1.5, 2, 4 °C/min, were initially employed for a 14x8 mm fused silica tubing. The HgZnTe ampoules were homogenized inside a rocking furnace using a specially designed heating schedule that utilizes the solid state diffusion process. The Sb ampoules were simply melted at 720 °C. Following sample casting, all the ampoules were then opened and resealed under vacuum to shorten the length to about 13 cm.
TABLE I. Compositions, excess Hg, and total weights of the DTA samples Hg$_{1-x}$Zn$_x$Te.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$x$</th>
<th>Excess Hg (g)</th>
<th>Total Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DZ10</td>
<td>0.1002</td>
<td>0.4114</td>
<td>39.7456</td>
</tr>
<tr>
<td>DZ16</td>
<td>0.1586</td>
<td>0.3260</td>
<td>42.3574</td>
</tr>
<tr>
<td>DZ20</td>
<td>0.2001</td>
<td>0.0033</td>
<td>38.2699</td>
</tr>
<tr>
<td>DZ30</td>
<td>0.2998</td>
<td>-0.007</td>
<td>38.5011</td>
</tr>
<tr>
<td>DZ40</td>
<td>0.4001</td>
<td>0.0023</td>
<td>37.1281</td>
</tr>
</tbody>
</table>

idly solidified following casting and uniformly cooled after each DTA run. To improve alloy homogeneities, the samples were annealed at temperatures just below their solidus points before most of the runs as shown in Table II. To make a clear determination on the thermal arrest onset at the solidus temperature, the furnace was usually heated from 55 to 650 °C, cooled to 630 °C, held for 20 min and then heated again to temperatures between 790 and 880 °C, depending on the alloy composition. Several cooling curves were also measured and, similar to the previous DTA study on HgCdTe, thermal hysteresis in the form of 50–80 °C supercooling, depending on the cooling rate, for the HgZnTe samples and the Sb reference was observed. Therefore, only heating curves at the optimum rate of 2 °C/min were used for the determination of the thermal arrest onset. A typical DTA heating curve, showing the differential thermocouple voltage as a function of sample temperature, is plotted in Fig. 1. The melting point of Sb, serving as an internal thermal calibration, can be determined accurately. The solidus temperature of each sample was determined from the intersection of the initial part of the melting curve and the baseline extension. This measured solidus temperature was then corrected using a melting point of 630.5 °C for the Sb standard.

FIG. 1. Typical differential thermal analysis (DTA) data.

C. Results and discussion

Similar to the previous report on the Hg$_{1-x}$Cd$_x$Te system, the onset at the liquidus temperature was not clear for samples of small $x$ ($x < 0.2$), as shown in Fig. 1. As for the high-$x$ samples, the liquidus temperatures were too high so that the ampoules fractured from the high Hg partial pressures. Table II summarizes the annealing conditions, the heating rates, the measured Sb reference melting temperatures, the measured solidus temperatures, and the corrected solidus temperatures for all the samples.

The pseudobinary phase diagram of HgTe–ZnTe pseudobinary shown in Fig. 2 includes the data given in Table II as well as the liquidus and solidus temperatures previously reported. The present data agree well with

TABLE II. Summary of the solidus temperatures for HgZnTe samples in Table I.

<table>
<thead>
<tr>
<th>Run</th>
<th>Heating rate (°C/min)</th>
<th>Measured Sb melting point in (°C)</th>
<th>Measured solidus temperature (°C)</th>
<th>Corrected solidus temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DZ10A</td>
<td>2</td>
<td>629.0</td>
<td>680.3</td>
<td>681.8</td>
</tr>
<tr>
<td>DZ10H</td>
<td>2</td>
<td>630.4</td>
<td>679.9</td>
<td>680.0</td>
</tr>
<tr>
<td>DZ10F</td>
<td>2</td>
<td>630.8</td>
<td>678.8</td>
<td>678.5</td>
</tr>
<tr>
<td>DZ16A</td>
<td>2</td>
<td>631.9</td>
<td>689.0</td>
<td>687.6</td>
</tr>
<tr>
<td>DZ16B</td>
<td>2</td>
<td>630.9</td>
<td>693.1</td>
<td>692.7</td>
</tr>
<tr>
<td>DZ16O</td>
<td>2</td>
<td>631.5</td>
<td>692.8</td>
<td>691.8</td>
</tr>
<tr>
<td>DZ20A</td>
<td>2</td>
<td>630.2</td>
<td>683.3</td>
<td>683.6</td>
</tr>
<tr>
<td>DZ30A</td>
<td>2</td>
<td>623.4</td>
<td>698.9</td>
<td>697.0</td>
</tr>
<tr>
<td>DZ30B</td>
<td>2</td>
<td>641.7</td>
<td>708.0</td>
<td>696.8</td>
</tr>
<tr>
<td>DZ40A</td>
<td>2</td>
<td>635.2</td>
<td>707.2</td>
<td>702.5</td>
</tr>
</tbody>
</table>

aAnnealed at 660 °C for 2 days.

bAnnealed at 670 °C for 3.8 days.

cAnnealed at 670 °C for 5 days.

dAnnealed at 670 °C for 10 days.

eAnnealed at 675 °C for 7 days.

J. Appl. Phys., Vol. 80, No. 1, 1 July 1996
others and establish the low $x$ region where no data were available before. The liquidus can be well fit by a straight line between the melting points of the end members, i.e., 670 °C for HgTe (Ref. 26) and 1290 °C for ZnTe (Ref. 27). The solidus curve can be fit, for practical purpose, by the polynomials

$$T_x \, (°C) = \begin{cases} 
670.5 + 156.4x - 339.6x^2 + 521.3x^3 & \text{for } 0 < x < 0.79 \\
342.1 + 2208.8x - 4285.1x^2 + 2894.2x^3 & \text{for } 0.79 < x < 0.96, \\
-80641.8 + 279213x - 319330x^2 + 122032x^3 & \text{for } 0.96 < x < 1.0. 
\end{cases}$$

The above expressions for the liquidus and solidus temperatures agree well with the calculated results from a quantitative fit\(^\ast\) to the diverse thermodynamic and phase diagram data for the Hg–Cd–Zn–Te quaternary system by assuming an associated solution model for the liquid phase.

DTA curves observed during cooling indicated considerable supercooling. For instance, a freezing temperature of 743 °C was observed during the cooling of the DZ20A cycle whereas the phase diagram indicates a liquidus temperature of 795 °C for an alloy composition of $x=0.20$.

There are several sources of error in the phase diagram data determined here. It is believed that the error in the thermocouple calibration was negligible because of the small temperature difference between the melting points of the Sb internal reference and the measured solidus temperatures. The uncertainties in the sample compositions, $x$, due to the loss of Hg are assumed to be negligible because of the small free volumes and the large masses. Although the shape of the solidus curve as a function of the stoichiometry, i.e., the metal to Te ratio, in the vicinity of $y$ near 1/2 in (Hg$_{1-y}$Zn$_y$)$_{1-x}$Te, is not known, we assumed that the errors in the solidus temperatures associated with small deviations in $y$ from 1/2 are negligible. Another uncertainty, probably the major source of error, is the subjectivity in selecting the proper phase transformation points from the DTA curves. The sharpness of the onset depends on the compositional homogeneity of the sample and in the case of HgCdTe an annealing time of 15 h (Ref. 25) was adequate to result in a sharp transformation point. However, because of the lower solid state diffusivity of the HgZnTe than that of the HgCdTe (Ref. 18) even 4 days annealing was not long enough to show any significant difference in the sharpness of the onset. In general, this uncertainty was estimated to be about ±2 °C.

III. DENSITY

A. Experiment

The densities of the HgZnTe melts were determined from the measurements of the meniscus height of the melts inside a transparent furnace by in situ visual observation. The thermometer-shaped ampoules were made from fused silica. The 15×9 mm “bulb” was 7–8 cm long and the stem that extended from the “bulb” was made from 6×3 mm fused silica tubing. The volume of the ampoule as a function of its height was measured by filling the ampoule with distilled water to various levels from a reference mark on the stem and measuring the corresponding weight of the ampoule in each case at room temperature. The value of 0.997 63 g/cm$^3$ (Ref. 29) was used for the density of water at 22 °C. The effective cross section areas determined from the measurements correspond to the values of 3.015 mm and 3.189 mm for the diameters of the stem section of two ampoules used. The samples were prepared using the method described in Sec. II A. The total weight was 43.4822 g with 0.018 g excess Hg and 43.7654 g with 0.003 g excess Hg, respectively, for the Hg$_{0.90}$Zn$_{0.10}$Te and Hg$_{0.84}$Zn$_{0.16}$Te samples. The sample length in the stem region was 3 cm and 15 cm for $x=0.10$ and $x=0.16$, respectively.

The liquid level was visible inside the gold-plated transparent furnace and the separation between the meniscus and the reference mark was measured by a cathetometer with 0.05 mm resolution. During several measurements an air gap developed in the stem section and the levels of the meniscus for the air gap were measured. By subtracting the volume of the air gap, the total volume of the melt was obtained. Three calibrated thermocouples were strategically placed along the length of the ampoule for temperature measurements and a small positive vertical thermal gradient (hotter above) was maintained along the ampoule during the measurements.

B. Results and discussion

The densities of Hg$_{0.84}$Zn$_{0.16}$Te melts were measured in the temperature range of 795–850 °C. The high liquidus temperature and the associated high Hg pressure limited the measurements to a small temperature range of 50 °C. After four heating cycles between 790 and 850 °C the sample was equilibrated at 847 °C and the measurements were performed in an order of descending temperature. The width of the air gap was 7.8 mm at the highest temperature and shrunk to 1.8 mm at the lowest temperature. Figure 3 shows the measured density for the Hg$_{0.84}$Zn$_{0.16}$Te melt which displays a slight increase of 0.6% from 797 to 847 °C and, for all practical purposes, can be treated as a constant of 7.476 g/cm$^3$.  

![FIG. 2. Pseudobinary phase diagram of HgTe–ZnTe.](image.png)

J. Appl. Phys., Vol. 80, No. 1, 1 July 1996

Su et al. 139
As for the Hg$_{0.90}$Zn$_{0.10}$Te melts, the densities were measured along a heating and cooling cycle. The measurements started from a temperature of 737 °C to a maximum of 846 °C and then back to 736 °C. The heating and cooling data showed a hysteresis behavior with the largest discrepancy of ±0.8% at 795 °C and almost no difference at 736 °C. The density results for the cooling measurements are shown in Fig. 3, and are believed to be more reliable because of the longer equilibration time at higher temperatures. An air gap developed for the three highest temperature runs. The width of the air gap was 15.4 mm, 11.3 mm, and 1.3 mm for the Hg$_{0.84}$Zn$_{0.16}$Te sample contracts 4% from melt to solid at 25 °C. The measured density of the Hg$_{0.90}$Zn$_{0.10}$Te melt, despite of the hysteresis, decreases by 2.3%, from 7.85 g/cm$^3$ at 736 °C to 7.67 g/cm$^3$ at 846 °C in a temperature range of 110 °C.

The measured density of the HgTe melt reported in Ref. 6 is also shown in Fig. 3. Similar to the HgCdTe system, the increasing ZnTe (or CdTe) content in the alloys results in a decrease in the density of the ternary melts. However, a maximum in the melt density away from the liquidus reported for the Hg$_{0.95}$Cd$_{0.05}$Te and Hg$_{0.90}$Cd$_{0.10}$Te melts was not observed here. The Hg$_{0.90}$Zn$_{0.10}$Te melt displays the behavior of normal thermal expansion and the data for the Hg$_{0.84}$Zn$_{0.16}$Te melt are essentially constant in the measured temperature range. The density of the solid solution at room temperature, derived from the lattice constant data, is 7.8835 and 7.7584 g/cm$^3$, respectively, for Hg$_{0.90}$Zn$_{0.10}$Te and Hg$_{0.84}$Zn$_{0.16}$Te. Comparing these density values with those of the melts, the volume of a Hg$_{0.90}$Zn$_{0.10}$Te sample contracts 4% from melt to solid at 25 °C.

As for the hysteresis seen in the measured densities of the Hg$_{0.90}$Zn$_{0.10}$Te sample, similar behavior was also reproducibly observed during viscosity measurements in the Hg-ZnTe melt. Possible mechanisms for this observed phenomenon might be attributed to the macroscopic or microscopic inhomogeneities. The macroscopic inhomogeneity can be present, for instance, due to (1) insufficient mixing during material preparation, (2) small size bubbles forming in the melt, or (3) evaporation/condensation of Hg into/from a free volume in the ampoule, which creates a thin boundary layer around the sample, thus modifying the wetting condition of the melt and changing the surface tension at the melt/free surface interface. The nature of the effect can also be microscopic. The subcritical clusters of the second phase or the formation of associated molecular species in the melt can be present in such a case. Any changes in the temperature will induce the redistribution in the cluster size and composition. This process is diffusion controlled and can be very slow.

The major error in the measured density of the melts is believed to come from the error in determining the liquid meniscus height. The shape of the meniscus was, most of the time, concave (toward the liquid) and an average, or effective, level was measured. For the ampoules used here (with an approximated melt volume of 5.9 cm$^3$) an error of 1 mm in the measured meniscus height results in an error of 0.12% in the measured volume and the corresponding error in density. The same error in the melt height would cause an error of about 0.25% in the measured density of HgCdTe for the ampoules used in Ref. 6, because of the larger i.d. of the stem section. The contribution from thermal expansion of the fused silica crucibles to the measured melt volumes was found to be negligible.

IV. HEAT CAPACITY AND ENTHALPY OF MIXING

A. Associated solution model

Thermodynamic properties, such as heat capacity and enthalpy of mixing, of HgZnTe pseudobinary melts cannot be easily determined experimentally, because of the limitations imposed by the high Hg partial vapor pressures. However, a fit of the diverse thermodynamic and phase diagram data for the Hg–Cd–Zn–Te quaternary system by an associated solution model for the liquid phase was used to obtain good estimates. We also use this approach to establish thermodynamic properties for the melts of the Hg–Zn–Te ternary system. The detailed description of the model was described in Ref. 26. A brief summary of the model and the calculated results for the heat capacity and enthalpy of mixing in the pseudobinary melts are described below.

We assume that the liquid phase of HgZnTe consists of species Hg, Zn, Te, HgTe, and ZnTe, numbering consecutively as species 1–5, with mole fractions $x_i$, $i=1,...,5$. The thermodynamic components Hg, Zn, and Te are numbered consecutively 1–3 with atom fraction $x_j$, $i=1,2,3$. Mass balance leads to the following relations:

$$y_i = x_i(1 + y_4 + y_5) + [\delta(i,2) - 1]y_4 + [\delta(i,1) - 1]y_5,$$

$$i = 1,2,3,$$

(1)

where

$$\delta(i,j) = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases}.$$
TABLE III. Interaction coefficients for Hg-Zn-Te system [Hg(1), Zn(2), Te(3), HgTe(4), ZnTe(5)] in calories per mole. (Note: 1 cal = 4.184 J and T in K.) $\Delta G_4^0 = 10,093.3 - 6,423.78T$; $\Delta G_5^0 = 21,151.7 - 3,253.23T$.

<table>
<thead>
<tr>
<th></th>
<th>$\alpha_i$</th>
<th>$\beta_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg-Zn</td>
<td>$\alpha_{12} = 176 + 0.436T$</td>
<td>$\beta_{12} = 0$</td>
</tr>
<tr>
<td>Hg-Te</td>
<td>$\alpha_{13} = -339.99 - 0.594 874T$</td>
<td>$\beta_{13} = 942.498$</td>
</tr>
<tr>
<td>Hg-HgTe</td>
<td>$\alpha_{14} = 1916.31 - 0.317 398T$</td>
<td>$\beta_{14} = 0$</td>
</tr>
<tr>
<td>Hg-ZnTe</td>
<td>$\alpha_{15} = 455.423 + 0.791 065T$</td>
<td>$\beta_{15} = 0$</td>
</tr>
<tr>
<td>Zn-Te</td>
<td>$\alpha_{23} = 22 744.4 + 15.965 T$</td>
<td>$\beta_{23} = -3,245.99 + 0.408 075T$</td>
</tr>
<tr>
<td>Zn-HgTe</td>
<td>$\alpha_{24} = 2350.9 - 8.519 38T$</td>
<td>$\beta_{24} = 0$</td>
</tr>
<tr>
<td>Zn-ZnTe</td>
<td>$\alpha_{25} = 16 850.3 - 9.094 15T$</td>
<td>$\beta_{25} = -311.69 - 0.266 161T$</td>
</tr>
<tr>
<td>Te-HgTe</td>
<td>$\alpha_{34} = 1752.27 - 0.852 56T$</td>
<td>$\beta_{34} = 0$</td>
</tr>
<tr>
<td>Te-ZnTe</td>
<td>$\alpha_{35} = 656.931 - 2.908 17T$</td>
<td>$\beta_{35} = 0$</td>
</tr>
</tbody>
</table>

Independent of the specific form assumed for the excess Gibbs energy of mixing, one can obtain the following relations between the relative chemical potentials of species from solution thermodynamics:

$$\bar{\mu}_{4} = \bar{\mu}_1 + \bar{\mu}_3,$$  \hspace{1cm} (2)

and

$$\bar{\mu}_{5} = \bar{\mu}_2 + \bar{\mu}_3.$$  \hspace{1cm} (3)

The thermodynamic description of the liquid phase is completed by assuming a functional form for the excess Gibbs energy of mixing from the liquid elements:

$$\Delta G_m^{ij} = \sum_{i=1}^{5} \sum_{j=1}^{5} (\alpha_{ij} + \beta_{ij}Y_{ij})Y_{ij} - y_4\Delta G_4^0 - y_5\Delta G_5^0,$$  \hspace{1cm} (4)

where $\alpha_{ij} = \alpha_{ji}$, $\beta_{ij} = 0$, and $\beta_{ij} = -\beta_{ji}$. The $\alpha_i$ and $\beta_i$ are composition-independent interaction coefficients that are the adjustable parameters of the model along with the Gibbs energy of dissociation of the molecular species, $\Delta G_4^0$ and $\Delta G_5^0$. The relative excess chemical potential of species $p$ can be derived from Eq. (4) and is given by

$$\bar{\mu}_p = 2 \sum_{i=1}^{5} \left[ \alpha_{ip} + \left( \frac{y_i}{2} - y_p \right) \beta_{pi} \right] y_i - \sum_{i=1}^{5} \sum_{j=1}^{5} (\alpha_{ij} + 2\beta_{ij}y_j)y_iy_j - \delta(p,4)\Delta G_4^0 - \delta(p,5)\Delta G_5^0,$$  \hspace{1cm} (5)

Once the thermodynamic model has been defined the thermodynamic properties of the melts can be derived using basic thermodynamic equations. The relative partial molar enthalpies and entropies of the species are related to the corresponding relative chemical potentials by the thermodynamic equations

$$\bar{h}_k = \left( \frac{\partial}{\partial(1/T)} \left( \frac{\bar{\mu}_i}{T} \right) \right)_{y_k}$$  \hspace{1cm} (6)

and

$$\bar{s}_i = -\left( \frac{\partial \bar{\mu}_i}{\partial T} \right)_{y_k}, \hspace{1cm} i = 1, \ldots, 5.$$  \hspace{1cm} (7)
The enthalpy and entropy of mixing per mole of species are given by

$$Z_m = \sum_{i=1}^{5} y_i z_i,$$

where $Z$ denotes either enthalpy or entropy. These properties can be further converted to the corresponding quantities per gram-atomic weight of components to provide a comparison with the experimental results by the relation

$$\Delta Z_m^{\text{atom}} = \frac{\Delta Z_m}{(1 + y_4 + y_5)}.$$

The constant pressure relative heat capacity is defined as

$$\Delta C_p^{\text{atom}} = \frac{(\partial \Delta H_m^{\text{atom}})/(\partial T))_{x_1, x_2, p}}{x_1 C_{p1} + x_2 C_{p2} + x_3 C_{p3}},$$

where $C_{p1}$, $C_{p2}$, and $C_{p3}$ are the heat capacities of the pure liquid elements, Hg, Zn, and Te, respectively, and the values used are 6.61, 7.5, and 7.874 cal/g atom K, respectively.

B. Results and discussion

As given in Ref. 28, the interaction parameters were determined by a simultaneous fit to the diverse and extended phase diagram and thermodynamic data for the Hg–Cd–Zn–Te system. The set of parameters pertaining to the Hg–Zn–Te system is tabulated in Table III. The values of the heat capacity for various pseudobinary melts at temperatures between the corresponding liquidus temperatures and 1500 °C are summarized in Figs. 4 and 5. The dotted lines connect the data points along the liquidus temperatures. The magnitude and the trend of the calculated values are similar to that of the HgCdTe melts reported in Ref. 32 for temperatures between 670 and 1100 °C. When the temperature gets above 1100 °C, the calculated heat capacity values for the HgZnTe melts increase monotonically with increasing temperature and reach above 19 cal/g atom K at 1500 °C for Hg0.1Zn0.9Te. The calculated enthalpies of mixing are given in Figs. 6 and 7.

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