Standard Gibbs Energy of Formation of Zn$_8$La Determined by Solution Calorimetry and Measurement of Heat Capacity from Near Absolute Zero Kelvin

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The thermodynamic properties of Zn$_8$La were investigated by calorimetry. The standard entropy of formation at 298 K, $\Delta S_{298}^f$, was determined from measuring the heat capacities, $C_p$, from near absolute zero (2 K) to 300 K by the relaxation method. The standard enthalpy of formation at 298 K, $\Delta H_{298}^f$, was determined by solution calorimetry in hydrochloric acid solution. The standard Gibbs energy of formation at 298 K, $\Delta G_{298}^f$, was determined from these data. The results obtained were as follows: $\Delta H_{298}^f$(Zn$_8$La)/kJ·mol$^{-1}$ = 297.18 $\pm$ 18, $\Delta S_{298}^f$(Zn$_8$La)/J·mol$^{-1}·K^{-1}$ = 25.02 $\pm$ 3.60; $\Delta G_{298}^f$(Zn$_8$La)/kJ·mol$^{-1}$ = -289.71 $\pm$ 18. The coefficient, $\gamma$, of the electronic term contributing to the heat capacity of Zn$_8$La was small, indicating that decrease of the density of states for 4f component of the lanthanum atom in the vicinity of $E_F$. [doi:10.2320/matertrans.47.1555]

(Received March 10, 2006; Accepted April 28, 2006; Published June 15, 2006)

Keywords: Zn$_8$La, calorimetry, heat capacity, enthalpy of formation, Gibbs energy of formation

1. Introduction

Mg alloys are light and have excellent mechanical properties. Also, they are easy to recycle. Therefore, they are expected to be used as construction materials for airplanes, motorcars and other applications. Since Zn and La are effective alloying elements to improve mechanical-properties and corrosion-resistance of magnesium, the phase diagram of the Mg–Zn–La ternary system is inevitably necessary. Although Dovatokina$^1$ investigated the magnesium rich corner of the Mg–Zn–La ternary system, it’s almost composition range has not yet been experimentally constructed due to difficulties associated with the high vapor pressure of the components. For such a system, the phase diagram has been constructed by thermodynamic calculation. In order to calculate the phase diagram of the Mg–Zn–La ternary system, the Gibbs energies of formation, $\Delta G_f^r$, of the intermediate binary compounds in the Mg–Zn, Zn–La and Mg–La binary system and the intermediate ternary compounds in the Mg–Zn–La ternary system are needed.

Previously Biltz$^{2,3}$ and King and Kleppa$^3$ investigated the standard enthalpy of formation at 298 K, $\Delta H_{298}^r$, of MgZn$_2$$^3$ (−53.4 kJ·mol$^{-1}$) and Mg$_{48}$Zn$_{52}$ (−837 kJ·mol$^{-1}$) by solution calorimetry in an acid solution$^2$ and in a tin melt$^3$, respectively. Schneider et al.$^4$ measured $\Delta H_{298}^r$ values of Mg$_{48}$Zn$_{52}$ (−1046 kJ·mol$^{-1}$), Mg$_2$Zn$_2$ (−45.3 kJ·mol$^{-1}$) and Mg$_2$Zn$_{11}$ (−130.0 kJ·mol$^{-1}$) by a direct reaction method. There are discrepancies among these data$^2,4$ considering their experimental errors. Terpilowski,$^5$ Chiotti and Stevens,$^6$ and Kouzuka$^7$ measured the activities of the melt of the Mg–Zn binary system by the electromotive method$^5,6$ and vapor pressure.$^5$ Terpilowski$^5$ reported positive excess relative partial molar entropy ($\Delta S_{ME}^r$) values, while Chiotti and Stevens$^6$ derived negative values. Agarwal et al.$^8$ found that a virtual contradiction between the phase diagram and the temperature dependence of the enthalpy of mixing, $\Delta_{mix}H$, of the liquid phase assessed from the data of references$^5,7$ was detected during optimizing the thermodynamic functions of the Mg–Zn binary system. Liang$^9$ updated data of the heat capacities of the liquid phase ($C_{p,liq}^r$) and solved such a contradiction.$^8$

In our previous study, the $\Delta G_{298}^r$ values of Mg$_{48}$Zn$_{52}$ (−1177 $\pm$ 300 kJ·mol$^{-1}$), Mg$_2$Zn$_3$$^{11}$ (−66.55 $\pm$ 20 kJ·mol$^{-1}$), Mg$_2$Zn$_2$$^{12}$ (−37.83 $\pm$ 9 kJ·mol$^{-1}$) and Mg$_2$Zn$_{11}$$^{13}$ (−109.72 $\pm$ 39 kJ·mol$^{-1}$) were measured by calorimetry. The $\Delta H_{298}^r$ values$^{10–13}$ were determined by using a new Calvet-type calorimeter equipped with a new thermoelectric device$^{14}$ and the standard entropies of formation, $\Delta S_{298}^r$,$^{10–13}$ were determined by measuring $C_p$ from near absolute zero (2 K) to 400 K by the recently developed method of relaxation calorimetry.$^{15–18}$ Also, the $C_p$ values over 400 K of the compounds were measured by a heat-flaw stabilized DSC, and their $\Delta H_{298}^r$’s up to high temperature were determined$^{12}$ by combining the $C_p$ values$^{10–13}$ with the obtained $\Delta H_{298}^r$ values.$^{10–13}$

Regarding the thermodynamic data of Zn–La binary system, in our previous study, $\Delta G_{298}^r$ of Zn$_{12}$La was measured$^{19}$ by calorimetry as in the same way of the studies for the Mg–Zn binary system.$^{10–13}$ that is $\Delta G_{298}^r$ was determined by the solution calorimetry and $\Delta S_{298}^r$ was determined by measuring $C_p$ from near absolute zero Kelvin. However, besides our study,$^{19}$ thermodynamic properties of the Zn–La binary system have not yet been investigated.

In the present study, $\Delta G_{298}^r$ of Zn$_8$La was determined by the solution calorimetry$^{10–13,19}$ and measuring $C_p$ from near absolute zero (2 K) to 300 K by the relaxation calorimetry.$^{10–13,19}$ Also, to clarify the density of states in the vicinity of the Fermi level, $E_F$, the coefficient, $\gamma$, of the electronic term contributing to the heat capacity was determined from $C_p$ values near absolute zero Kelvin.

2. Experimental

2.1 Preparation of the specimens

Commercial Zn (99.9 mass%, Nilaco., Japan) and La (99.9 mass%, HPCI., Japan) were used as starting materials. In order to construct thermodynamic cycles for measurements and compare thermodynamic properties of com-
pounds, a formulation for one mole atoms is convenient. Zn₄La is rewritten as Zn₀.₈₈₉La₀.₁₁₁. Since an oxidation loss of La occurred during melting and heat treatment, the addition of an excess of 3 mol% La was necessary. The amount of the addition of excess La was determined from a prior experiment.

Zn₀.₈₈₉La₀.₁₁₁ was prepared by melting in a high-frequency induction furnace. The starting materials were inserted into magnesia crucibles and covered by flux (40.3KCl, 8.2MgCl₂, 51.5LiCl). Before melting, the chamber was evacuated and filled with Ar, and then melting was carried out. After melting, the sample was vacuum-sealed in silica tube and then subjected to a homogenizing treatment at 593 K for 14 days.

Since there is no X-ray diffraction data for Zn₄La as reference data such as JCPDS, the composition of the material was analyzed by a JEOL JXA-8900 electron microprobe (EPMA). It was homogeneous and single phase. Averages of atomic ratios of Zn and La of five analyses were 0.895 and 0.105, corresponding to the stoichiometric composition. Therefore, the material was submitted to calorimetry.

2.2 Calorimetric methods

2.2.1 Cₚ at 2–300 K

The entropy of a material at 298 K, \( S_{298} \), is given by

\[
S_{298} = \int_{T_0}^{298 K} \frac{C_p}{T} dT
\]

where \( T \) is the absolute temperature. The heat capacities for Zn₀.₈₈₉La₀.₁₁₁ were measured in the temperature range 2 to 300 K by using a relaxation method¹⁵–¹⁸ instrument (Quantum Design, San Diego, USA), in the same way as in our previous study.¹⁰–¹³,¹⁹ The masses of samples were 20–30 mg (\( \approx 2.5 \times 2.5 \times 1.5' \)). Six series of measurements were carried out and their average was adopted as the result.

The determined \( C_p \) values were fitted to a polynomial expression:

\[
C_p = \sum_{n=1}^{n} a_n T^n
\]

The polynomials were integrated to determine the \( S_{298} \) of Zn₀.₈₈₉La₀.₁₁₁.

The \( \Delta_{\text{mix}} S_{298} \) of Zn₀.₈₈₉La₀.₁₁₁ is given by

\[
\Delta_{\text{mix}} S_{298}(Zn₀.₈₈₉La₀.₁₁₁) = S_{298}(Zn₀.₈₈₉La₀.₁₁₁) - S_{298}(Zn) \times 0.₈₈₉ - S_{298}(La) \times 0.₁₁₁
\]

(3)

The \( \Delta_{\text{f}} S_{298} \) of the Zn-La is given by

\[
\Delta_{\text{f}} S_{298}(Zn-La) = \Delta_{\text{mix}} S_{298}(Zn₀.₈₈₉La₀.₁₁₁) \times 9
\]

(4)

2.2.2 \( \Delta H_{298} \)

The enthalpy of solution, \( \Delta_{\text{sol}} H \), was measured by using a new Calvet-type calorimeter (Tokyo Rikou) equipped with a thermo-module composed of p-type thermoelectric semiconductors of Bi₂(Se,Te)₃, PbTe and Gd₂Se.¹⁴ Therefore, this calorimeter is able to measure precise enthalpy changes with a very high sensitivity.¹⁰–¹³,¹⁹

The samples were vacuum-sealed in glass ampoules at 373 K. As in the same way, empty glass ampoules were vacuum-sealed. The glass ampoule, in which a sample was sealed, was set into one of the calorimetric cell poured with solvent and the empty glass ampoule was set into the other calorimetric cell poured with the solvent, and then they were kept in an adiabatic chamber. The calorimetric cell was made of fluorine resin. After thermo-equilibrium was obtained at 298 K, both of the glass ampoules were broken by using a manipulator. The temperature difference, \( \Delta T \), between the sample cell and the empty glass ampoule cell was detected by the thermo-module, counter-balancing the both heats of crises of the glass ampoules, and \( \Delta T \text{sol} \)–time curve was obtained. After returning baseline, Joule’s heat, \( Q_{\text{Joule}} \), was supplied by an electric heater to the sample cell and \( \Delta T \text{Joule} \)–time curve was obtained. The areas, \( S_{\text{sol}} \) and \( S_{\text{Joule}} \), of \( \Delta T \text{sol} \)–time and \( \Delta T \text{Joule} \)–time curves were calculated. \( \Delta_{\text{sol}} H_{298} \) is given by

\[
\Delta_{\text{sol}} H_{298} = \frac{S_{\text{sol}}}{S_{\text{Joule}}} \times Q_{\text{Joule}}
\]

Commercial 5N hydrochloric acid solution (25 mL) was used as a solvent to dissolve Zn₀.₈₈₉La₀.₁₁₁. The amount of dissolved material was 1.10⁻³ mol, corresponding to 73.6 mg of Zn₀.₈₈₉La₀.₁₁₁. When configuration of \( \Delta T \text{sol} \)–time curve is similar to \( \Delta T \text{Joule} \)–time curve, enough accuracy is obtained. \( Q_{\text{Joule}} \) was determined as 429.43 J based on a prior experiment.

The chemical reaction during dissolving of Zn₀.₈₈₉La₀.₁₁₁ is defined by eq. (6), namely

\[
Zn₀.₈₈₉La₀.₁₁₁ = 0.₈₈₉ Zn_{aq} + 0.₁₁₁ La_{aq}
\]

(6)

where \( Zn_{aq} \) and \( La_{aq} \) are zinc ion and lanthanum ion in the solvent, respectively.

In the same way for the intermediate phase, the chemical reaction of the mechanical mixtures of the requisite amounts of pure zinc and pure lanthanum, \( \Delta_{\text{sol}} H_{298}(0.₈₈₉ Zn + 0.₁₁₁ La) \) is defined by eq. (7) namely

\[
0.₈₈₉ Zn + 0.₁₁₁ La = 0.₈₈₉ Zn_{aq} + 0.₁₁₁ La_{aq}
\]

(7)

The \( \Delta_{\text{mix}} H \) of Zn₀.₈₈₉La₀.₁₁₁ is defined by subtracting \( \Delta_{\text{sol}} H_{298}(Zn₀.₈₈₉La₀.₁₁₁) \) from \( \Delta_{\text{sol}} H_{298}(0.₈₈₉ Zn + 0.₁₁₁ La) \).

\[
\Delta_{\text{mix}} H(Zn₀.₈₈₉La₀.₁₁₁) = \Delta_{\text{sol}} H_{298}(0.₈₈₉ Zn + 0.₁₁₁ La) - \Delta_{\text{sol}} H_{298}(Zn₀.₈₈₉La₀.₁₁₁)
\]

(8)

The \( \Delta_{\text{f}} H_{298} \) of the Zn-La is given by

\[
\Delta_{\text{f}} H_{298}(Zn-La) = \Delta_{\text{mix}} H(Zn₀.₈₈₉La₀.₁₁₁) \times 9
\]

(9)

The \( \Delta_{\text{sol}} H_{298} \) values of the intermediate phase and the mechanical mixture were determined as the average of 5 measurements, respectively, and the \( \Delta_{\text{f}} H_{298} \) was determined from each average \( \Delta_{\text{sol}} H_{298} \). In the present study, error was treated by general error propagation theory.²²
3. Experimental Results and Discussion

3.1 \( C_p \) and \( S^\circ \) at 2 to 300 K

Figure 1 shows the measured \( C_p \) values of Zn\(_{0.889}\)La\(_{0.111}\) in the temperature range 2–300 K. Table 1 shows the coefficients of the polynomials to fit the measured \( C_p \) values of Zn\(_{0.889}\)La\(_{0.111}\). In order to obtain enough fitting accuracy, the \( C_p \) values of three temperature ranges were fitted separately. That is, three polynomials were used to evaluate \( C_p \) below and above 50 K. The results of calculations using the polynomials are shown as solid lines in Fig. 1.

The \( S_{298} \) of Zn\(_{0.889}\)La\(_{0.111}\) was obtained from the integral of the polynomials and the result was

\[
S_{298}(\text{Zn}_{0.889}\text{La}_{0.111})/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 40.62 \pm 0.40 \quad (10)
\]

Previously, \( C_p \) of pure copper (99.9999 mass%, Nilaco, Tokyo) was measured, and the measured \( C_p \) data and the calculated \( S_{298} \) data deviate by less than 1%.\(^{10}\) Thus, the present \( C_p \) and \( S_{298} \) of Zn\(_{0.889}\)La\(_{0.111}\) was treated as having an uncertainty of 1% as given in Eq. (10). Values of \( C_p \), \( S_T \) and \( H_T - H_{298} \) data calculated for different temperatures from the polynomials (Table 1) are summarized in Table 2.

3.2 Electronic contribution to heat capacity

At low temperature, almost all lattice vibrations cease to contribute, leaving dominant the thermal excitations of the electrons. The electronic term contributing to the constant volume heat capacity, \( C_V \), is proportional to temperature, \( T \), and the vibrational term is proportional to \( T^3 \). Consequently, \( C_V \), is:

\[
C_V = \gamma T + AT^3 \quad (11)
\]

where \( \gamma \) and \( A \) are defined as the coefficients of the electronic and the vibrational terms, respectively. Since \( C_V \) and \( C_p \) are very similar at low temperatures,\(^{23}\) \( C_p \) can be approximately used instead of \( C_V \). The quantity \( \gamma \) reflects thermal excitation probability of electrons in the vicinity of the Fermi level, \( E_F \) with respect to the density of states and their effective mass.\(^{23}\)

Figure 2 shows the relationship between \( (C_p/T) \) and \( (\gamma + AT^2) \) for Zn\(_{0.889}\)La\(_{0.111}\). For \( T^2 < 23.91 \text{ K}^2 \) (\( T < 4.89 \text{ K} \)), a linear relationship is generally observed. The intercept at \( T = 0 \) and the slope yield \( \gamma \) and \( A \), respectively.

The obtained values of \( \gamma \) and \( A \) for Zn\(_{0.889}\)La\(_{0.111}\) are compared in Table 3 with those of Zn\(_{0.928}\)La\(_{0.071}\).\(^{19}\) pure zinc\(^{24}\) and lanthanum.\(^{24}\) Previously, the \( \gamma \) and \( A \) of pure

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**Table 1** Coefficients for the polynomial \( C_p/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = a + b T + c T^2 + d T^3 + e T^4 + f T^5 + g T^6 \) for Zn\(_{0.889}\)La\(_{0.111}\).

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( a )</th>
<th>( b \times 10^3 )</th>
<th>( c \times 10^5 )</th>
<th>( d \times 10^7 )</th>
<th>( e \times 10^7 )</th>
<th>( f \times 10^8 )</th>
<th>( g \times 10^{12} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2–50</td>
<td>0.018</td>
<td>0.105</td>
<td>-0.499</td>
<td>5.58</td>
<td>-113</td>
<td>8.12</td>
<td>-141</td>
</tr>
<tr>
<td>50–150</td>
<td>-7.85</td>
<td>3.83</td>
<td>0.059</td>
<td>-0.265</td>
<td>0.481</td>
<td>0.0756</td>
<td>-2.81</td>
</tr>
<tr>
<td>150–300</td>
<td>7.08</td>
<td>1.51</td>
<td>-0.0246</td>
<td>0.00269</td>
<td>-0.104</td>
<td>0.00506</td>
<td>-0.0679</td>
</tr>
</tbody>
</table>

**Table 2** Thermodynamic functions for Zn\(_{0.889}\)La\(_{0.111}\).

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( C_p ) (J/K\cdot\text{mol}^{-1})</th>
<th>( S_T ) (J/K\cdot\text{mol}^{-1})</th>
<th>( H_T - H_{298} ) (kJ/mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.72</td>
<td>0.27</td>
<td>-51.57</td>
</tr>
<tr>
<td>50</td>
<td>90.18</td>
<td>40.95</td>
<td>-50.13</td>
</tr>
<tr>
<td>100</td>
<td>174.24</td>
<td>133.74</td>
<td>-43.20</td>
</tr>
<tr>
<td>150</td>
<td>206.91</td>
<td>211.32</td>
<td>-33.57</td>
</tr>
<tr>
<td>200</td>
<td>223.11</td>
<td>273.24</td>
<td>-22.77</td>
</tr>
<tr>
<td>250</td>
<td>232.38</td>
<td>324.09</td>
<td>-11.34</td>
</tr>
<tr>
<td>298</td>
<td>239.13</td>
<td>365.58</td>
<td>0</td>
</tr>
<tr>
<td>300</td>
<td>239.31</td>
<td>367.11</td>
<td>0.45</td>
</tr>
</tbody>
</table>

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Fig. 1 Temperature dependence of heat capacity, \( C_p \), for Zn\(_{0.889}\)La\(_{0.111}\).

Fig. 2 \( C_p/T \) with \( T^2 \) for Zn\(_{0.889}\)La\(_{0.111}\).
copper were measured in order to evaluate the accuracy achieved with the applied measurement setup.\textsuperscript{(10)} The $\gamma$ of pure copper deviates by 5.61% from the reference datum.\textsuperscript{(10)} Thus, such an extrapolation to determine $\gamma$ includes the quantity cited as deviation: we evaluated the error range of $\gamma$ in the same size.\textsuperscript{(10)} Since $A$ values of many substances have not yet been clarified, the errors are unknown. Similarly, we approximately adopted 5.61% deviation as the error range of $A$.\textsuperscript{(10)}

The $\gamma$ of pure lanthanum are extremely large (Table 3). It is possible that the DOS for 4f component trap the conduction electrons and their effective mass increase, resulted in such a large value of $\gamma$. Previously the $\gamma$ of Zn$_{0.925}$La$_{0.075}$\textsuperscript{(19)} was found to be as simple composition average of the $\gamma$ values of pure zinc and lanthanum. Thus it is concluded that the DOS for 4f component of the lanthanum atoms are localized above $E_F$ and they trap the DOS for 4s and 4p components for the zinc atoms around the lanthanum atoms.

In the present study, the $\gamma$ of Zn$_{0.889}$La$_{0.111}$ was smaller than simple composition average value: 0.64 $\times$ 0.889 + 10 $\times$ 0.111 = 1.679 mJ K$^{-2}$ mol$^{-1}$, indicating that decrease of the DOS for 4f component above $E_F$. Electronegativity of zinc is larger than lanthanum. Therefore, charge transfer appears to be caused from the DOS for 4f component of the lanthanum atoms to the DOS for 4s and 4p components for the zinc atoms, resulted in decrease of the DOS for 4f component above $E_F$. The reason for such a charge transfer in Zn$_{0.889}$La$_{0.111}$ caused is unknown, compared with Zn$_{0.925}$La$_{0.075}$ keeping strong localization of the DOS for 4f component above $E_F$. This problem should be further investigated by studying their atomic configurations and electronic structures.

### 3.3 $\Delta_t H^\circ$ at 298 K

Table 4 shows the measured $\Delta_{av}H_{298}$ values and their average values of the intermediate phase and the mechanical mixture (0.889Zn + 0.111La), respectively. Standard deviations, $\sigma$, of $\Delta_{av}H$(Zn$_{0.889}$La$_{0.111}$) values and $\Delta_{av}H_{298}$(Zn$_{0.889}$Zn + 0.111La) values were 2.14 and 0.57 kJ mol$^{-1}$, respectively. Statistical error (pct) is generally given by the ratio of $\sigma$ to an average value. Therefore, the errors of the present measurements were 1.26 pct and 0.28 pct, respectively, convincing enough accuracy. Thus we evaluated that error ranges of the intermediate phase and the mechanical mixture were approximately $\pm$ 2 kJ mol$^{-1}$ and $\pm$ 1 kJ mol$^{-1}$, neglecting the values below decimal point of the $\sigma$ values.

The $\Delta_{av}H_{298}$ values of Zn$_{0.889}$La$_{0.111}$ and the mechanical mixture (0.889Zn + 0.111La) were measured as

$$\Delta_{av}H_{298}$(Zn$_{0.889}$La$_{0.111}$)/kJ mol$^{-1}$
$$\Delta_{av}H_{298}$(0.889Zn + 0.111La)/kJ mol$^{-1}$

(12) (13)

The given error ranges are based on the standard deviation of 5 measurements for each sample.

The $\Delta_{mix}H_{298}$ of Zn$_{0.889}$La$_{0.111}$ was obtained as

$$\Delta_{mix}H_{298}$(Zn$_{0.889}$La$_{0.111}$)/kJ mol$^{-1}$ = $-$33.02 $\pm$ 2

(14)

Error was evaluated as $(2^2 + 12^2)^{1/2} \approx \pm 2$ kJ mol$^{-1}$ on the basis of the error propagation theory.$^{(22)}$ Consequently, $\Delta_t H_{298}$ of Zn$_4$La was obtained as

$$\Delta_t H_{298}$(Zn$_4$La)/kJ mol$^{-1}$ = $-$297.18 $\pm$ 18

(15)

In our previous study, $\Delta_{mix}H_{298}$(Zn$_{0.925}$La$_{0.075}$)\textsuperscript{(19)} was obtained as $-24.02 \pm 2$ kJ mol$^{-1}$. The present $\Delta_{mix}H_{298}$(Zn$_{0.889}$La$_{0.111}$) obtained was smaller than $\Delta_{mix}H_{298}$(Zn$_{0.925}$La$_{0.075}$).\textsuperscript{(10)} The atomic bond between the zinc and lanthanum atoms in Zn$_{0.889}$La$_{0.111}$ was found to be strong, consistent with that its melting point is the highest of zinc–lanthanum binary intermediate phases.$^{(25)}$

### 3.4 $\Delta_t S^\circ$ and $\Delta_t G^\circ$ at 298 K

The $\Delta_{mix}S_{298}$ of Zn$_{0.889}$La$_{0.111}$ was obtained from eq. (4).

$$\Delta_{mix}S_{298}$(Zn$_{0.889}$La$_{0.111}$)/J mol$^{-1}$ K$^{-1}$
$$\Delta_{mix}S_{298}$(Zn$_{0.889}$La$_{0.111}$)/J mol$^{-1}$ K$^{-1}$

(16) (17)

$\Delta_t S_{298}$ was found to be negative. This is due to the entropy of vibration, $\Delta_t S_{vib}$, which generally decreases in a compound due to an increase of lattice vibration frequencies.$^{(26)}$

Consequently, $\Delta_t G_{298}$ of Zn$_{0.889}$La$_{0.111}$ was calculated from $\Delta_t S_{298}$ and $\Delta_t H_{298}$:

$$\Delta_{mix}G_{298}$(Zn$_{0.889}$La$_{0.111}$)/kJ mol$^{-1}$ = $-$32.19 $\pm$ 2

(18)

$$\Delta_{mix}G_{298}$(Zn$_4$La)/kJ mol$^{-1}$ = $-$289.71 $\pm$ 18

(19)

The errors of $\Delta_t G_{298}$ were negligibly small, compared with those of $\Delta_t H_{298}$. Therefore, the errors of $\Delta_t G_{298}$ are given by the errors of $\Delta_t H_{298}$. In our previous study,$^{(12)}$ $\Delta_t G_{298}$’s of Mg$_{84}$Zn$_{52}$, Mg$_{2}$Zn$_{3}$, Mg$_{2}$Zn$_{2}$ and Mg$_{2}$Zn$_{1}$ in the temperature range from near absolute zero kelvin to high temperature

<table>
<thead>
<tr>
<th>Zn$<em>{0.889}$La$</em>{0.111}$</th>
<th>Measured $\Delta_{av}H$ [kJ mol$^{-1}$]</th>
<th>$\Delta_{av}H_{AV}$ [kJ mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.889Zn + 0.111La</td>
<td>-170.34</td>
<td>-169.23 $\pm$ 2</td>
</tr>
<tr>
<td>Zn$<em>{0.889}$La$</em>{0.111}$</td>
<td>-167.27</td>
<td>-166.81</td>
</tr>
<tr>
<td></td>
<td>-169.87</td>
<td>-171.87</td>
</tr>
<tr>
<td></td>
<td>-166.81</td>
<td>-171.87</td>
</tr>
<tr>
<td></td>
<td>-169.23 $\pm$ 2</td>
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<td>-202.22</td>
</tr>
<tr>
<td></td>
<td>-202.22</td>
<td>-202.25 $\pm$ 1</td>
</tr>
</tbody>
</table>

Table 4 The measured enthalpies of solution, $\Delta_{av}H$ and their average values, $\Delta_{av}H_{AV}$ of Zn$_{0.889}$La$_{0.111}$ and the Mechanical Mixture (0.889Zn + 0.111La).
were determined by combining $\Delta_fH_{298}^{\circ}$'s10–13 with low $\Delta_fG_{298}^{\circ}$'s. Therefore, such a determination12) of $\Delta_fG_{298}^{\circ}$ will be further applied to other compounds in the Zn–La and Mg–La binary systems and the Mg–Zn–La ternary system in order to calculate the phase diagram of the Mg–Zn–La ternary system.

4. Conclusion

The value of $\Delta_fG_{298}^{\circ}$ of Zn$^8$La was determined by combining the acid solution calorimetry at 298 K with the measurement of the heat capacity in the temperature range from 2 K to 300 K. The coefficient, $\gamma$, of the electronic term contributing to the heat capacity was investigated. The $\gamma$ of Zn$^8$La was small, indicating that decrease of the density of states for 4f component of the lanthanum atom in the vicinity of $E_F$. Such a determination of $\Delta_fG_{298}^{\circ}$, followed by measuring $C_p$ in the temperature range from 298 K to high temperatures, is attractive since it gives a complete thermodynamic description of the Zn$^8$La phase from 298 K to high temperature, which is indispensable for phase diagram calculations.

REFERENCES

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