Standard Gibbs Energy of Formation of Mg_3La Determined by Solution Calorimetry and Heat Capacity Measurement from Near Absolute Zero Kelvin

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The standard Gibbs energy of formation, $\Delta_f G^\circ_T$, of Mg_3La in the temperature range from near absolute zero Kelvin to 525 K were determined by calorimetry. The heat capacities, C_p , from 2 K to 525 K were measured by the relaxation method and DSC. The $\Delta_f G^\circ_T(\text{Mg}_3\text{La})$ values were determined by combining the C_p data with the standard enthalpy of formation at 298 K which was measured by the Calvet-type calorimeter using hydrochloric acid solution. From 2 to 350 K, the $\Delta_f G^\circ_T$ increases gradually, and it can be evaluated as a linear function of temperature above 350 K as follows:

$$\begin{aligned}\Delta_f G^\circ_T(\text{Mg}_3\text{La})/\text{kJ mol}^{-1} \\ &= -76.204 - 2.5304 \times 10^{-2} T + 1.2160 \times 10^{-2} T \log T \\ &\quad + 1.1814 \times 10^{-5} T^2 - 0.80332 T^{-1} \pm 17.0 \text{ (2–350 K)} \\ \Delta_f G^\circ_T(\text{Mg}_3\text{La})/\text{kJ mol}^{-1} &= -79.652 + 1.9567 \times 10^{-2} T \pm 17.0 \text{ (350–525 K)}.\end{aligned}$$

This result is expected to be useful as basic thermodynamic data of Mg-based alloys. [doi:10.2320/matertrans.MRA2007603]

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1. Introduction

In the Mg-Zn-RE(RE: Rare earth elements) ternary system, there are complex metallic alloys such as amorphous alloys,^{1,2)} icosahedral phases,³⁾ and exceptional phases⁴⁾ with giant-unit-cells.⁵⁾ Also, the Mg-Zn-RE ternary system is one of the important systems for the magnesium based structural materials. Recently the applications of the magnesium alloys has been expanded for automobiles, airplanes, computers, portable telephones, and many other applications due to their lightweight, good mechanical properties, and good recyclability.

In order to design such complex magnesium based alloys, the phase diagrams of the Mg-Zn-RE ternary systems are inevitable. However, the experimental investigation of the whole region of the Mg-Zn-RE system at high temperature is difficult due to the high vapor pressure of the components. In such cases, it is desirable to construct the phase diagram by thermodynamic calculation. In order to calculate the phase diagram of the Mg-Zn-RE system, the standard Gibbs energies of formation, $\Delta_f G^\circ$, of the intermediate phases of each binary system and the Mg-Zn-RE ternary system are inevitable.

In our previous studies, the standard Gibbs energies of formation, $\Delta_f G^\circ$, of the intermediate phases of the Mg-Zn system,^{6–9)} Zn-La system,^{10,11)} and Zn-Y system¹²⁾ have been determined. The standard enthalpies of formation, $\Delta_f H^\circ$, were determined by using a new Calvet-type calorimeter equipped with a new thermoelectric device¹³⁾ and the standard entropies of formation, $\Delta_f S^\circ$, were determined by measuring C_p from near absolute zero (2 K) to 400 K by the recently developed method of relaxation calorimetry^{14–17)}

and C_p over 400 K by the differential scanning calorimeter (DSC).^{9,17)}

In this paper, we focused attention on the Mg-La system, which was a part of the Mg-Zn-RE (RE = La) system. As the composition goes from magnesium-side to lanthanum-side, there are stoichiometric compounds of Mg_{12}La , $\text{Mg}_{17}\text{La}_2$, Mg_3La , MgLa_2 , Mg_2La , and MgLa .¹⁸⁾ $\Delta_f H^\circ_{298}$ values of MgLa and Mg_3La were determined by an acid solution calorimetry.¹⁹⁾ However, such an old data is expected be updated.²⁰⁾ Thus, in the present study, $\Delta_f G^\circ$ of Mg_3La was determined by the same way of our previous study.^{6–12)}

2. Experimental

2.1 Preparation of specimen

Commercial Mg (99.99%, High Purity Chemical Institute Co., Japan (HPCI)) and La (99.9%, HPCI) were used as starting materials. Composition of Mg_3La is Mg-La (75–25 mol%). Since the formulation for one mole of atoms is convenient, it is usual to compare the molar thermodynamic properties of compounds, and Mg_3La is rewritten as $\text{Mg}_{0.75}\text{La}_{0.25}$. $\text{Mg}_{0.75}\text{La}_{0.25}$ was prepared by arc-melting the compressed compacts of the mixture of Mg and La powders in the composition of Mg-La (77–23 mol%) with a tungsten electrode in an argon atmosphere. After melting, the sample was vacuum-sealed in silica tube and then subjected to a homogenizing treatment at 623 K for 14 days. The excess addition of 2 mol% Mg, which was determined from prior experiments, was necessary in order to prepare $\text{Mg}_{0.75}\text{La}_{0.25}$, since the evaporation loss of Mg and the oxidation loss of La were counter-balanced during arc-melting and heat treatment. The structure and the composition of the sample were measured by an X-ray diffractometer (XRD, Rigaku, RINT-2200) and an electron microprobe microanalyzer (EPMA,

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JEOL, JXA-8900R), respectively. The detected XRD peaks of the sample corresponded to Mg_3La and it was homogeneous and single phase. Average of atomic ratio of Mg and La of five analyses were 0.751 and 0.249, respectively, corresponding to the stoichiometric composition within error. Thus, the sample was submitted to calorimetry.

2.2 Calorimetric methods

2.2.1 C_p measurements and entropy of mixing of $\text{Mg}_{0.75}\text{La}_{0.25}$

The entropy of a material as a function of temperature based on the third law of thermodynamics, S_T , is given by

$$S_T = \int_0^T \frac{C_p}{T} dT. \quad (1)$$

In order to determine this S_T , the temperature function of C_p is necessary. The C_p values of $\text{Mg}_{0.75}\text{La}_{0.25}$ were measured in the temperature range of 2–400 K by using a relaxation method^{14–17} instrument (PPMS, Quantum Design, San Diego, USA). The $C_p(\text{Mg}_{0.75}\text{La}_{0.25})$ values above 400 K were measured by DSC (Model DSC-404, Netzsch, Bayern, Germany). The mass of the Mg_3La samples for the relaxation method and for DSC measurement were about 16 mg and 148 mg, respectively. Details of these methods were described in our previous studies.^{6–9,11} The measured C_p values below and above 300 K were fitted to the following polynomial given by eq. (2) and the Haas-Fisher polynomial given by eq. (3), respectively.

$$C_p = \sum_{n=1}^n a_n T^n. \quad (2)$$

$$C_p = a + bT + cT^2 + dT^{-0.5} + eT^{-2} \quad (3)$$

The polynomial was integrated as shown in eq. (1) to determine the $S_T(\text{Mg}_{0.75}\text{La}_{0.25})$. The entropy of mixing of $\text{Mg}_{0.75}\text{La}_{0.25}$, $\Delta_{\text{mix}}S_T(\text{Mg}_{0.75}\text{La}_{0.25})$, is defined as

$$\begin{aligned} \Delta_{\text{mix}}S_T(\text{Mg}_{0.75}\text{La}_{0.25}) \\ = S_T(\text{Mg}_{0.75}\text{La}_{0.25}) - 0.75 \times S_T(\text{Mg}) \\ - 0.25 \times S_T(\text{La}) \end{aligned} \quad (4)$$

where $S_T(\text{Mg})$ and $S_T(\text{La})$ are the third law entropies of pure magnesium and lanthanum. These $S_T(\text{Mg})$ and $S_T(\text{La})$ were calculated by eq. (1) using the C_p data of pure Mg and La. These C_p data of Mg (about 15 mg) and La (about 31 mg) below 300 K were measured by the relaxation method in this study and fitted to eq. (2) and those of the literature data^{21,22} above 300 K were used and fitted to the Haas-Fisher polynomials shown in eq. (3).

2.2.2 Enthalpy of mixing of $\text{Mg}_{0.75}\text{La}_{0.25}$

The enthalpy of solution, $\Delta_{\text{sol}}H_{298}$, was measured by using a new Calvet-type calorimeter (Model MMC-5111, Tokyo Rikou, Tokyo, Japan) equipped with a thermo-module composed of p-type thermoelectric semi-conductors of BiSbTe, PbSnTe, SiGe and SnTe, and n-type $\text{Bi}_2(\text{Se},\text{Te})_3$, PbTe and Gd_2Se .¹³

The samples were vacuum-sealed in glass ampoules at 373 K. The empty glass ampoules were also vacuum-sealed in the same way. The glass ampoule containing a sample 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. After thermo-equilibrium was obtained at 298 K, both of the glass ampoules were broken by using a manipulator. The temperature difference, ΔT_{sol} , between the sample cell and the empty glass ampoule cell was detected by the thermo-module, counter-balancing the both heats of crashes of the glass ampoules, and ΔT_{sol} -time curve was obtained. After returning to the baseline, Joule's heat, Q_{Joule} , was supplied by an electric heater to the sample cell and ΔT_{Joule} -time curve was obtained. The areas between the baseline and the ΔT -time curves were calculated as A_{sol} and A_{Joule} . $\Delta_{\text{sol}}H_{298}$ was given by

$$\Delta H_{\text{sol}} = (A_{\text{sol}}/A_{\text{Joule}}) \times Q_{\text{Joule}}. \quad (5)$$

The mass of $\text{Mg}_{0.75}\text{La}_{0.25}$ was about 53 mg (about 1 mmol). Commercial 5 N (5 mol·dm^{−3}) hydrochloric acid solution (25 ml) was used as a solvent to dissolve $\text{Mg}_{0.75}\text{La}_{0.25}$.

$\Delta_{\text{sol}}H_{298}(\text{Mg}_{0.75}\text{La}_{0.25})$ is defined as the enthalpy of solution for the following chemical reaction during dissolving of $\text{Mg}_{0.75}\text{La}_{0.25}$,

where Mg_{aq} and La_{aq} are magnesium ion and lanthanum ion in the solvent, respectively. In the same way, $\Delta_{\text{sol}}H_{298}(0.75 \text{ Mg} + 0.25 \text{ La})$ is defined as the enthalpy of solution for the chemical reaction during dissolving of the mechanical mixtures of pure magnesium and pure lanthanum as follows:

The enthalpy of mixing of $\text{Mg}_{0.75}\text{La}_{0.25}$, $\Delta_{\text{mix}}H_{298}(\text{Mg}_{0.75}\text{La}_{0.25})$, is defined by subtracting $\Delta_{\text{sol}}H_{298}(\text{Mg}_{0.75}\text{La}_{0.25})$ from $\Delta_{\text{sol}}H_{298}(0.75 \text{ Mg} + 0.25 \text{ La})$ as follows:

$$\begin{aligned} \Delta_{\text{mix}}H_{298}(\text{Mg}_{0.75}\text{La}_{0.25}) &= \Delta_{\text{sol}}H_{298}(0.75 \text{ Mg} + 0.25 \text{ La}) \\ &- \Delta_{\text{sol}}H_{298}(\text{Mg}_{0.75}\text{La}_{0.25}). \end{aligned} \quad (8)$$

The $\Delta_{\text{sol}}H_{298}$ values of the intermediate phase and the mechanical mixture were determined as the average of five measurements, and the $\Delta_{\text{mix}}H_{298}$ was determined from each average $\Delta_{\text{sol}}H_{298}$.

The enthalpy of mixing as a function of temperature of $\text{Mg}_{0.75}\text{La}_{0.25}$, $\Delta_{\text{mix}}H_T(\text{Mg}_{0.75}\text{La}_{0.25})$, is defined as eq. (9).

$$\begin{aligned} \Delta_{\text{mix}}H_T(\text{Mg}_{0.75}\text{La}_{0.25}) \\ = \Delta_{\text{mix}}H_{298}(\text{Mg}_{0.75}\text{La}_{0.25}) + \int_{298}^T C_p(\text{Mg}_{0.75}\text{La}_{0.25}) dT \\ - 0.75 \times \int_{298}^T C_p(\text{Mg}) dT - 0.25 \times \int_{298}^T C_p(\text{La}) dT \end{aligned} \quad (9)$$

$\Delta_{\text{mix}}H_T(\text{Mg}_{0.75}\text{La}_{0.25})$ was obtained by substituting the $\Delta_{\text{mix}}H_{298}(\text{Mg}_{0.75}\text{La}_{0.25})$ value determined by eq. (8), and the C_p polynomials of $\text{Mg}_{0.75}\text{La}_{0.25}$, pure Mg, and pure La to eq. (9).

2.2.3 Standard Gibbs energy of formation of Mg_3La

The Gibbs energy of mixing as a function of temperature of $\text{Mg}_{0.75}\text{La}_{0.25}$, $\Delta_{\text{mix}}G_T(\text{Mg}_{0.75}\text{La}_{0.25})$, is determined from $\Delta_{\text{mix}}S_T$ and $\Delta_{\text{mix}}H_T$ as follows:

$$\begin{aligned} \Delta_{\text{mix}}G_T(\text{Mg}_{0.75}\text{La}_{0.25}) &= \Delta_{\text{mix}}H_T(\text{Mg}_{0.75}\text{La}_{0.25}) \\ &- T \Delta_{\text{mix}}S_T(\text{Mg}_{0.75}\text{La}_{0.25}). \end{aligned} \quad (10)$$

Table 1 Measured heat capacity, C_p , values of Mg_{0.75}La_{0.25}.

T/K	$C_p, \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	T/K	$C_p, \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	T/K	$C_p, \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	T/K	$C_p, \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
2.102	0.0047697	121.5	18.032	241.8	22.615	369.9	24.295
5.185	0.020219	125.8	18.311	246.0	22.697	375.1	24.414
9.576	0.12641	130.1	18.641	250.3	22.745	380.4	24.433
13.94	0.51149	134.4	18.899	254.6	22.815	385.7	24.521
18.29	1.1797	138.7	19.167	258.9	22.889	391.0	24.622
22.60	2.0152	143.0	19.441	263.2	22.923	396.3	24.648
26.91	2.9005	147.3	19.643	267.5	22.981	401.6	24.724
31.24	3.8696	151.6	19.840	271.8	23.085	428.0	24.727
35.54	4.6970	155.9	20.005	276.1	23.162	433.0	24.729
39.86	5.5736	160.2	20.272	280.4	23.209	438.0	24.747
44.16	6.4754	164.5	20.438	284.7	23.245	443.0	24.760
48.47	7.3690	168.8	20.620	289.0	23.325	448.0	24.764
52.77	8.2531	173.1	20.776	293.3	23.347	453.0	24.769
57.07	9.1312	177.3	20.957	297.6	23.450	458.0	24.769
61.29	9.9882	181.6	21.126	301.9	23.468	463.0	24.774
65.58	10.816	185.9	21.258	302.4	23.494	468.0	24.779
69.89	11.621	190.2	21.423	307.6	23.517	473.0	24.779
74.19	12.361	194.5	21.541	312.9	23.530	478.0	24.780
78.49	13.051	198.8	21.631	318.2	23.588	483.0	24.793
82.80	13.701	203.1	21.786	323.5	23.681	488.0	24.807
87.10	14.358	207.4	21.882	328.8	23.739	493.0	24.820
91.40	14.895	211.7	22.006	334.1	23.797	498.0	24.835
95.70	15.428	216.0	22.096	339.4	23.881	503.0	24.848
99.99	15.907	220.3	22.200	344.4	23.942	508.0	24.867
104.3	16.424	224.6	22.278	349.1	23.986	513.0	24.875
108.6	16.835	228.9	22.363	354.0	24.070	518.0	24.888
112.9	17.224	233.2	22.427	359.3	24.106	523.0	24.900
117.2	17.638	237.5	22.495	364.6	24.272	528.0	24.907

Consequently, $\Delta_f G^\circ_T(\text{Mg}_3\text{La})$ is given by the following equation.

$$\Delta_f G^\circ_T(\text{Mg}_3\text{La}) = \Delta_{\text{mix}} G_T(\text{Mg}_{0.75}\text{La}_{0.25}) \times 4 \quad (11)$$

3. Results and Discussion

3.1 C_p and S_T of Mg_{0.75}La_{0.25}

Table 1 shows the measured C_p values of Mg_{0.75}La_{0.25}. These $C_p(\text{Mg}_{0.75}\text{La}_{0.25})$ values are shown as open circle symbols in Fig. 1. At around temperatures of 400 K, there was no significant discrepancy between the C_p values measured by the relaxation method and those measured by the DSC. Table 2 shows the coefficients of the polynomials to fit the measured $C_p(\text{Mg}_{0.75}\text{La}_{0.25})$ values. In order to obtain enough fitting accuracy, the measured C_p values of four temperature ranges were fitted separately. The results of calculations of C_p are shown as solid lines in Fig. 1. These fitting functions reproduced the measured C_p values well and then the thermodynamic properties were calculated. Since the C_p value at 2 K was almost zero, the integration of eq. (1) was performed from 2 K. The results of the calculations including S_T and $H_T - H_{298}$ values of Mg_{0.75}La_{0.25} are shown in Table 3. Previously, C_p of pure copper (99.9999%, Nilaco, Tokyo) was measured, and the deviation of the measured C_p data and the calculated S_{298} data was less than 1%.^{6,8,11)} Thus, the C_p and the thermodynamic properties of Mg_{0.75}La_{0.25} were treated as having an uncertainty of 1%.

Fig. 1 Temperature dependence of heat capacity, C_p , of Mg_{0.75}La_{0.25} in the temperature range of 2–525 K.

3.2 $\Delta_{\text{mix}} H_{298}(\text{Mg}_{0.75}\text{La}_{0.25})$

Table 4 shows the measured $\Delta_{\text{sol}} H_{298}$ values and their average values of the intermediate phase (Mg_{0.75}La_{0.25}) and the mechanical mixture (0.75 Mg + 0.25 La). Standard deviations, σ , of $\Delta_{\text{sol}} H_{298}(\text{Mg}_{0.75}\text{La}_{0.25})$ values and

Table 2 Coefficients of the polynomials to fit the measured heat capacity, C_p , values of $\text{Mg}_{0.75}\text{La}_{0.25}$. Below 300 K: $C_p/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = a + bT + cT^2 + dT^3 + eT^4 + fT^5 + gT^6$, above 300 K: $C_p/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = a + bT + cT^2 + dT^{-0.5} + eT^{-2}$.

T/K	a	b	c	d	e	f	g
2–50	-3.4317×10^{-2}	6.7956×10^{-2}	-1.9151×10^{-2}	2.0356×10^{-3}	-7.3614×10^{-5}	1.1781×10^{-6}	-7.0587×10^{-9}
50–300	–7.8105	0.40198	-2.0501×10^{-3}	3.7653×10^{-6}	4.9129×10^{-9}	-2.6606×10^{-11}	2.5179×10^{-14}
300–400	-3.84923×10^3	5.07618	-3.33609×10^{-3}	5.05915×10^4	-2.43754×10^7	—	—
400–525	-8.85111×10^2	0.849017	3.96824×10^{-4}	1.40774×10^4	1.12282×10^7	—	—

Table 3 Thermodynamic properties of $\text{Mg}_{0.75}\text{La}_{0.25}$.

T/K	$C_p/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$S_T/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$H_T - H_{298}/\text{kJ}\cdot\text{mol}^{-1}$
50	7.7125	4.2898	–4.7820
100	15.902	12.453	–4.1693
150	19.821	19.745	–3.2635
200	21.662	25.729	–2.2213
250	22.742	30.686	–1.1094
298	23.417	34.744	0
300	23.435	34.901	0.046852
350	24.009	38.554	1.2321
400	24.696	41.808	2.4512
450	24.757	44.721	3.6879
500	24.839	47.334	4.9275
525	24.899	48.547	5.5492

$\Delta_{\text{sol}}H_{298}(\text{0.75 Mg} + \text{0.25 La})$ values were $2.70 \text{ kJ}\cdot\text{mol}^{-1}$ and $3.30 \text{ kJ}\cdot\text{mol}^{-1}$, respectively. Statistical error is generally given by the ratio of σ to an average value. Therefore, the errors of the present measurements for $\text{Mg}_{0.75}\text{La}_{0.25}$ and $(\text{0.75 Mg} + \text{0.25 La})$ were 0.53 pct and 0.63 pct, respectively, convincing enough accuracy. Thus, $\Delta_{\text{sol}}H_{298}(\text{Mg}_{0.75}\text{La}_{0.25})$ and $\Delta_{\text{sol}}H_{298}(\text{0.75 Mg} + \text{0.25 La})$ were determined as follows:

$$\Delta_{\text{sol}}H_{298}(\text{Mg}_{0.75}\text{La}_{0.25})/\text{kJ}\cdot\text{mol}^{-1} = -507.34 \pm 2.70 \quad (12)$$

$$\Delta_{\text{sol}}H_{298}(\text{0.75 Mg} + \text{0.25 La})/\text{kJ}\cdot\text{mol}^{-1} = -527.02 \pm 3.30. \quad (13)$$

Consequently, $\Delta_{\text{mix}}H_{298}$ of $\text{Mg}_{0.75}\text{La}_{0.25}$ was obtained by eq. (8) as follows:

$$\Delta_{\text{mix}}H_{298}(\text{Mg}_{0.75}\text{La}_{0.25})/\text{kJ}\cdot\text{mol}^{-1} = -19.68 \pm 4.26. \quad (14)$$

The error for $\Delta_{\text{mix}}H_{298}(\text{Mg}_{0.75}\text{La}_{0.25})$ was calculated using the general error propagation theory.²³⁾ G. Canneri and A. Rossi have already measured $\Delta_{\text{mix}}H_{298}$ of $\text{Mg}_{0.5}\text{La}_{0.5}$ by an acid solution calorimetry ($-3.37 \text{ kJ}\cdot\text{mol}^{-1}$).¹⁹⁾ However, Hultgen assessed that their data are not considered reliable.²⁰⁾

3.3 $\Delta_{\text{mix}}S_T$, $\Delta_{\text{mix}}H_T$, and $\Delta_{\text{mix}}G_T$

Table 5 shows the polynomials for the heat capacities of pure magnesium and lanthanum in the temperature range of 2–525 K, which are required for calculation of the thermodynamic functions. The third law entropy of pure Mg and La at 298 K calculated by eq. (1) using the polynomials shown in Table 5 were $32.957 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $56.929 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, respectively. They corresponded with the literature values of $32.671 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ²¹⁾ and $56.902 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ²²⁾ within the error of 1%. $\Delta_{\text{mix}}S_T$, $\Delta_{\text{mix}}H_T$, and $\Delta_{\text{mix}}G_T$ values

Table 4 The measured enthalpy of solution ($\Delta_{\text{sol}}H$) and their average values ($\Delta_{\text{sol}}H_{\text{AV}}$) of the intermediate phase ($\text{Mg}_{0.75}\text{La}_{0.25}$) and the mechanical mixture ($\text{0.75 Mg} + \text{0.25 La}$).

Sample	Measured $\Delta_{\text{sol}}H/\text{kJ}\cdot\text{mol}^{-1}$					$\Delta_{\text{sol}}H_{\text{AV}}/\text{kJ}\cdot\text{mol}^{-1}$
$\text{Mg}_{0.75}\text{La}_{0.25}$	–509.67	–508.40	–507.45	–508.46	–502.71	–507.34
$\text{0.75 Mg} + \text{0.25 La}$	–525.35	–530.74	–524.85	–523.74	–530.4	–527.02

Table 5 Coefficients of the polynomials to fit the measured heat capacity, C_p , values of pure Mg and La. Below 300 K: $C_p/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = a + bT + cT^2 + dT^3 + eT^4 + fT^5 + gT^6 + hT^7$, above 300 K: $C_p/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = a + bT + cT^2 + dT^{-0.5} + eT^{-2}$.

T/K	a	b	c	d	e	f	g	h
Mg								
2–50	-2.8498×10^{-2}	1.6971×10^{-2}	-1.9833×10^{-3}	8.6924×10^{-5}	2.3314×10^{-6}	-7.4134×10^{-8}	4.9405×10^{-10}	—
50–300	–15.981	0.60450	-4.0581×10^{-3}	1.4192×10^{-5}	-2.2474×10^{-8}	4.7175×10^{-12}	1.6926×10^{-14}	—
300–525	36.5142	-9.4887×10^{-3}	1.17343×10^{-5}	-1.66886×10^2	-1.72667×10^4	—	—	—
La								
2–4	1.46740	–2.31430	1.35927	–0.341211	2.21826×10^{-2}	4.86950×10^{-3}	-6.513×10^{-4}	—
4–6	1.45140	–0.547289	4.92615×10^{-2}	3.82090×10^{-3}	-1.44368×10^{-3}	3.63090×10^{-4}	-3.15771×10^{-5}	—
6–10	2.99902×10^{-2}	-2.23850×10^{-3}	-4.32425×10^{-3}	1.98155×10^{-3}	-2.35704×10^{-5}	-2.01909×10^{-6}	4.19643×10^{-8}	—
10–50	–0.180248	–0.267267	5.05063×10^{-2}	-1.15946×10^{-3}	5.33733×10^{-6}	1.02915×10^{-7}	-9.41870×10^{-10}	—
50–110	2.13470	0.391351	-4.60813×10^{-4}	-1.33332×10^{-6}	-4.9046×10^{-7}	3.75680×10^{-9}	1.04753×10^{-11}	-1.08517×10^{-13}
110–300	17.4350	8.82910×10^{-2}	-3.09010×10^{-4}	5.67842×10^{-7}	-2.67879×10^{-9}	1.14042×10^{-11}	-1.41860×10^{-14}	—
300–525	9.89198	1.95676×10^{-2}	-8.94597×10^{-6}	2.41491×10^2	-1.58275×10^5	—	—	—

Table 6 Thermodynamic functions for Mg_{0.75}La_{0.25}.

T /K	$\Delta_{\text{mix}}S_T$ /J·K ⁻¹ ·mol ⁻¹	$\Delta_{\text{mix}}H_T$ /kJ·mol ⁻¹	$\Delta_{\text{mix}}G_T$ /kJ·mol ⁻¹
10	-0.042320	-19.112	-19.112
25	-0.36909	-19.118	-19.109
50	-0.93803	-19.140	-19.093
75	-1.6095	-19.185	-19.065
100	-2.1612	-19.264	-19.048
150	-2.9022	-19.394	-18.958
200	-3.4176	-19.483	-18.800
250	-3.8449	-19.579	-18.618
298	-4.2057	-19.678	-18.425
300	-4.2201	-19.682	-18.416
350	-4.5329	-19.784	-18.197
400	-4.7794	-19.876	-17.964
450	-5.0064	-19.972	-17.720
500	-5.2468	-20.087	-17.463
525	-5.3693	-20.149	-17.331

Fig. 2 The standard Gibbs energy of mixing, $\Delta_{\text{mix}}G_T$, of Mg_{0.75}La_{0.25} in the temperature range of 2–525 K. Solid lines are fitting functions for $\Delta_{\text{mix}}G_T(\text{Mg}_{0.75}\text{La}_{0.25})$.

for Mg_{0.75}La_{0.25} calculated from eqs. (4), (9), and (10) are summarized in Table 6. The $\Delta_{\text{mix}}S_{298}$ value of Mg_{0.5}La_{0.5} is $-4.206 \text{ J·K}^{-1}\cdot\text{mol}^{-1}$. This value is considerably smaller than that of the Mg-Zn intermediate phases^{6–9)} which are complicated atomic configuration; for example, $\Delta_{\text{mix}}S_{298}(\text{Mg}_{0.48}\text{Zn}_{0.52}) = -1.23 \text{ J·K}^{-1}\cdot\text{mol}^{-1}$.⁸⁾ This is due to the small entropy of vibration attributable to the simple structure of Mg₃La (fcc (D0₃) structure isotypic with BiF₃).

Open circle symbols in Fig. 2 show the obtained $\Delta_{\text{mix}}G_T(\text{Mg}_{0.75}\text{La}_{0.25})$ values from 2 K to 525 K. The temperature dependence of $\Delta_{\text{mix}}G_T(\text{Mg}_{0.75}\text{La}_{0.25})$ was small below 100 K. $\Delta_{\text{mix}}G_T(\text{Mg}_{0.75}\text{La}_{0.25})$ increased monotonically above 100 K and increased linearly with temperature above 350 K.

The $\Delta_{\text{mix}}G_T(\text{Mg}_{0.75}\text{La}_{0.25})$ values were tried to express as polynomial. Since $\Delta_{\text{mix}}S_T$ and $\Delta_{\text{mix}}H_T$ are defined as the values resulted from the integration of C_p values which are generally expressed as polynomials, Kubashevski defines $\Delta_{\text{mix}}G_T$ as the function of integral terms of the polynomials fitted with the C_p values,²⁴⁾ namely,

Fig. 3 C_p/T with T^2 for Mg_{0.75}La_{0.25}.

$$\Delta_{\text{mix}}G_T = \Delta_{\text{mix}}H_0 + aT + bT \log T + cT^2 + dT^{-1} \quad (15)$$

where $\Delta_{\text{mix}}H_0$ is enthalpy of mixing at 0 K. The $\Delta_{\text{mix}}G_T(\text{Mg}_{0.75}\text{La}_{0.25})$ values were fitted to eq. (15) below 350 K, and to a linear function above 350 K separately. The results are shown as follows:

$$\begin{aligned} \Delta_{\text{mix}}G_T(\text{Mg}_{0.75}\text{La}_{0.25})/\text{kJ mol}^{-1} \\ = -19.051 - 6.3260 \times 10^{-3} T + 3.0399 \\ \times 10^{-3} T \log T + 2.9535 \\ \times 10^{-6} T^2 - 0.20083 T^{-1} \pm 4.26, \quad (2-350 \text{ K}) \end{aligned} \quad (16)$$

$$\begin{aligned} \Delta_{\text{mix}}G_T(\text{Mg}_{0.75}\text{La}_{0.25})/\text{kJ mol}^{-1} \\ = -19.913 + 4.8917 \times 10^{-3} T \pm 4.26, \\ (350-525 \text{ K}). \end{aligned} \quad (17)$$

$\Delta_{\text{mix}}G_T(\text{Mg}_{0.75}\text{La}_{0.25})$ calculated from these temperature functions are shown as solid lines in Fig. 2. The temperature functions fitted well with the $\Delta_{\text{mix}}G_T(\text{Mg}_{0.75}\text{La}_{0.25})$ values. As described above, the error of the C_p values measured by the relaxation method and the error of the $\Delta_{\text{mix}}S_T$ values as integral values of the C_p values were below 1 pct. Therefore, they were negligibly small, compared with the error of the $\Delta_{\text{mix}}H_{298}$ value. The error of $\Delta_{\text{mix}}G_T(\text{Mg}_{0.75}\text{La}_{0.25})$ values was evaluated as the error of the $\Delta_{\text{mix}}H_{298}(\text{Mg}_{0.75}\text{La}_{0.25})$ value, and it resulted in $\pm 4.26 \text{ kJ·mol}^{-1}$. Consequently, $\Delta_f G^0_T(\text{Mg}_3\text{La})$ is obtained by eq. (11) as follows:

$$\begin{aligned} \Delta_f G^0_T(\text{Mg}_3\text{La})/\text{kJ mol}^{-1} \\ = -76.204 - 2.5304 \times 10^{-2} T + 1.2160 \\ \times 10^{-2} T \log T + 1.1814 \\ \times 10^{-5} T^2 - 0.80332 T^{-1} \pm 17.0, \quad (2-350 \text{ K}) \end{aligned} \quad (18)$$

$$\begin{aligned} \Delta_f G^0_T(\text{Mg}_3\text{La})/\text{kJ mol}^{-1} \\ = -79.652 + 1.9567 \times 10^{-2} T \pm 17.0, \\ (350-525 \text{ K}). \end{aligned} \quad (19)$$

Table 7 Experimental coefficients of the electronic contribution, γ [$\text{mJ K}^{-2} \text{mol}^{-1}$], and coefficient of the vibrational contribution, A [$\text{mJ K}^{-4} \text{mol}^{-1}$], to the heat capacities of $\text{Mg}_{0.75}\text{La}_{0.25}$, pure Mg,²⁷ and pure La.²⁷

	$\text{Mg}_{0.75}\text{La}_{0.25}$	pure Mg	pure La
γ	1.86 ± 0.10	1.3	10
A	0.0509 ± 0.0029	—	—

3.4 Electronic contribution to heat capacity

The valence band of Mg_3La is composed of Mg electrons spread over the crystal as if they are nearly free electrons in pure magnesium and very strongly localized La-4f electrons. Therefore, it is very important to know how the de-localization or the localization of their valence electrons is caused. In order to clarify the electronic states of the compounds, the coefficient, γ , of the electronic contribution to C_p , which reflects the density of states (DOS) in the vicinity of Fermi level (E_F),²⁵⁾ was determined from C_p near absolute zero Kelvin.

At low temperature, almost all lattice vibrations cease to contribute, leaving the dominant 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 defined as follows:

$$C_v = \gamma T + AT^3 \quad (20)$$

where A is the coefficient of the vibrational terms. The relationship between (C_p/T) and T^2 for $\text{Mg}_{0.75}\text{La}_{0.25}$ is shown in Fig. 3. A linear relationship is observed in the range of $T^2 < 12 \text{ K}^2$ ($T < 3.46 \text{ K}$). Since C_p can be approximately used instead of C_v at low temperature,²⁵⁾ (C_p/T) is equal to $(\gamma + AT^2)$ from eq. (20). Thus, the intercept at $T^2 = 0$ and the slope of a solid line in Fig. 3 correspond with γ and A , respectively. The obtained values of γ and A for $\text{Mg}_{0.75}\text{La}_{0.25}$ are summarized in Table 7 with those of pure magnesium²⁶⁾ and lanthanum.²⁶⁾ We adopted 5.61% deviation as the error range of A and γ in consideration of previous results for pure copper.⁸⁾ It was found that this γ value of $\text{Mg}_{0.75}\text{La}_{0.25}$ ($1.86 \text{ mJ K}^{-2} \text{mol}^{-1}$) was smaller than the simple composition average value of $3.48 \text{ mJ K}^{-2} \text{mol}^{-1}$ and close to that of pure magnesium. A Mg-Mg-bond should be formed in $\text{Mg}_{0.75}\text{La}_{0.25}$ according to the chemical formula. In such a case, the 3s and 3p components for Mg appear to be released from the trapped states by 4f components for La, acting like free electron. As a result, γ of $\text{Mg}_{0.75}\text{La}_{0.25}$ is close to pure magnesium.

4. Conclusions

The standard Gibbs energy of formation of Mg_3La , $\Delta_f G^\circ_T$ (Mg_3La), in the temperature range of 2–525 K was determined by combining the acid solution calorimetry at 298 K with the measurement of the heat capacity by the relaxation method and DSC in the temperature range of 2–525 K.

Recently phase diagrams are constructed by thermodynamic calculation as well as experiments. Thermodynamic calculation is advantageous to determine phase equilibria which have been unsolved due to experimental difficulties such as high vapor pressure of components, and high or low temperature regions. The present results are expected to be useful as basic thermodynamic data of Mg-La based alloys.

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