

# Standard Gibbs energy of formation of MgLa determined by solution calorimetry and heat capacity measurement from near absolute zero kelvin

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## Abstract

The standard Gibbs energy of formation,  $\Delta_f G_T^\circ$ , of MgLa in the temperature range from near absolute 0 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. Also, a thermal anomaly at 5.9 K, which appeared to be a superconductive phase transition, was found in the obtained  $C_p$  values. The  $\Delta_f G_T^\circ$  (MgLa) 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 300 K, the  $\Delta_f G_T^\circ$  increases gradually, and it can be evaluated as a linear function of temperature above 300 K as follows:

$$\Delta_f G_T^\circ(\text{MgLa}) \text{ (kJ mol}^{-1}\text{)} = -39.236 - 6.9832 \times 10^{-3} T + 2.1016 \times 10^{-3} T \log T + 1.9114 \times 10^{-5} T^2 - 0.81004 T^{-1} \pm 7.40 \quad (2 - 300 \text{ K}),$$

$$\Delta_f G_T^\circ(\text{MgLa}) \text{ (kJ mol}^{-1}\text{)} = -41.100 + 9.9974 \times 10^{-3} T \pm 7.40 \quad (300 - 525 \text{ K}).$$

This result is expected to be useful as basic thermodynamic data of Mg-based alloys.

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**Keywords:** MgLa; Calorimetry; Heat capacity; Gibbs energy of formation

## 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 phases [4] 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 metallic alloys and 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 tempera-

ture 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 system [12] 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 device [13] 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) [9,17,18].

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,

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there are stoichiometric compounds of  $\text{Mg}_{12}\text{La}$ ,  $\text{Mg}_{17}\text{La}_2$ ,  $\text{Mg}_3\text{La}$ ,  $\text{MgLa}_2$ ,  $\text{Mg}_2\text{La}$ , and  $\text{MgLa}$  [19].  $\Delta_f H_{298}^\circ$  values of  $\text{MgLa}$  and  $\text{Mg}_3\text{La}$  were determined by an acid solution calorimetry [20]. However, such an old data is expected to be updated [21]. Thus, in the present study,  $\Delta_f G^\circ$  of  $\text{MgLa}$  was determined by the same way of our previous studies [6–12].

Since the valence band of  $\text{MgLa}$  is composed of Mg electrons spread over the crystal as if they are nearly free electrons in pure magnesium and very strongly localized-4f La electrons which are associated with super conductivity of pure lanthanum crystal,  $\text{MgLa}$  is an interesting substance from view of the electronic states. A relationship between  $C_p/T$  and  $T^2$  near absolute zero Kelvin is generally studied for distinguishing the electronic contribution from lattice vibration to heat capacity [22]. In order to understand the electronic state, the relationship between  $C_p/T$  and  $T^2$  for  $\text{MgLa}$  was also investigated in the present study.

## 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. Since the formulation for 1 mol of atoms is convenient, it is usual to compare the molar thermodynamic properties of compounds, and  $\text{MgLa}$  is rewritten as  $\text{Mg}_{0.5}\text{La}_{0.5}$ .  $\text{Mg}_{0.5}\text{La}_{0.5}$  was prepared by arc-melting the compressed compacts of the mixture of Mg and La powders in the composition of Mg–La (53–47 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 21 days. The excess addition of 3 mol% Mg, which was determined from prior experiments, was necessary in order to prepare  $\text{Mg}_{0.5}\text{La}_{0.5}$ , 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, JEOL, JXA-8900R), respectively. The detected XRD peaks of the sample corresponded to  $\text{MgLa}$  and it was homogeneous and single phase. Average of atomic ratio of Mg and La of five analyses were 0.501 and 0.499, 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 standard entropy of formation of $\text{Mg}_{0.5}\text{La}_{0.5}$

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  $\text{Mg}_{0.5}\text{La}_{0.5}$  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  $C_p(\text{Mg}_{0.5}\text{La}_{0.5})$  values above 400 K were measured by DSC (Model DSC-404, Netzsch, Bayern, Germany). Details of these methods were described in our previous studies [6–11]. 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  $S_T(\text{Mg}_{0.5}\text{La}_{0.5})$ . The standard entropy of formation of  $\text{Mg}_{0.5}\text{La}_{0.5}$ ,  $\Delta_f S_T^\circ(\text{Mg}_{0.5}\text{La}_{0.5})$ , is defined as

$$\Delta_f S_T^\circ(\text{Mg}_{0.5}\text{La}_{0.5}) = S_T^\circ(\text{Mg}_{0.5}\text{La}_{0.5}) - 0.5S_T(\text{Mg}) - 0.5S_T(\text{La}). \quad (4)$$

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  $C_p(\text{Mg})$  and  $C_p(\text{La})$  data below 300 K have already measured by several workers in several different temperature ranges [23–31]. However, we re-measured them from 2 to 300 K by ourselves in this study using the relaxation method to obtain the temperature functions of  $C_p(\text{Mg})$  and  $C_p(\text{La})$ . The measured  $C_p$  data below 300 K were fitted to Eq. (2) and those above 300 K of the literature data [32,33] were used and fitted to the Haas–Fisher polynomials shown in Eq. (3).

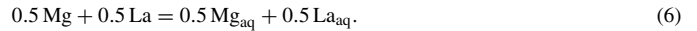
#### 2.2.2. Standard enthalpy of formation of $\text{Mg}_{0.5}\text{La}_{0.5}$

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<sub>2</sub>Se [13]. Details of the experimental procedures were described in our previous works [6–11]. The mass of  $\text{Mg}_{0.5}\text{La}_{0.5}$  was about 82 mg (about 1 mmol). Commercial 5N (5 mol dm<sup>-3</sup>) hydrochloric acid solution (25 ml) was used as a solvent to dissolve  $\text{Mg}_{0.5}\text{La}_{0.5}$ .

$\Delta_{\text{sol}}H_{298}(\text{Mg}_{0.5}\text{La}_{0.5})$  is defined as the enthalpy of solution for the following chemical reaction during dissolving of  $\text{Mg}_{0.5}\text{La}_{0.5}$ ,



where  $\text{Mg}_{\text{aq}}$  and  $\text{La}_{\text{aq}}$  are magnesium ion and lanthanum ion in the solvent, respectively. In the same way,  $\Delta_{\text{sol}}H_{298}(0.5 \text{Mg} + 0.5 \text{La})$  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 standard enthalpy of formation of  $\text{Mg}_{0.5}\text{La}_{0.5}$ ,  $\Delta_f H_{298}^\circ(\text{Mg}_{0.5}\text{La}_{0.5})$ , is defined by subtracting  $\Delta_{\text{sol}}H_{298}(\text{Mg}_{0.5}\text{La}_{0.5})$  from  $\Delta_{\text{sol}}H_{298}(0.5 \text{Mg} + 0.5 \text{La})$  as follows:

$$\Delta_f H_{298}^\circ(\text{Mg}_{0.5}\text{La}_{0.5}) = \Delta_{\text{sol}}H_{298}(0.5 \text{Mg} + 0.5 \text{La}) - \Delta_{\text{sol}}H_{298}(\text{Mg}_{0.5}\text{La}_{0.5}). \quad (7)$$

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  $\Delta_f H_{298}^\circ$  was determined from each average  $\Delta_{\text{sol}}H_{298}$ .

The standard enthalpy of formation as a function of temperature of  $\text{Mg}_{0.5}\text{La}_{0.5}$ ,  $\Delta_f H_T^\circ(\text{Mg}_{0.5}\text{La}_{0.5})$ , is defined as Eq. (8).

$$\Delta_f H_T^\circ(\text{Mg}_{0.5}\text{La}_{0.5}) = \Delta_f H_{298}^\circ(\text{Mg}_{0.5}\text{La}_{0.5}) + \int_{298}^T C_p(\text{Mg}_{0.5}\text{La}_{0.5}) dT - 0.5 \int_{298}^T C_p(\text{Mg}) dT - 0.5 \int_{298}^T C_p(\text{La}) dT. \quad (8)$$

$\Delta_f H_T^\circ(\text{Mg}_{0.5}\text{La}_{0.5})$  was obtained by substituting the  $\Delta_f H_{298}^\circ(\text{Mg}_{0.5}\text{La}_{0.5})$  value determined by Eq. (7), and the  $C_p$  polynomials of  $\text{Mg}_{0.5}\text{La}_{0.5}$ , pure Mg, and pure La to Eq. (8).

#### 2.2.3. Standard Gibbs energy of formation of $\text{MgLa}$

The standard Gibbs energy of formation as a function of temperature of  $\text{Mg}_{0.5}\text{La}_{0.5}$ ,  $\Delta_f G_T^\circ(\text{Mg}_{0.5}\text{La}_{0.5})$ , is determined from  $\Delta_f S_T^\circ$  and  $\Delta_f H_T^\circ$  as follows:

$$\Delta_f G_T^\circ(\text{Mg}_{0.5}\text{La}_{0.5}) = \Delta_f H_T^\circ(\text{Mg}_{0.5}\text{La}_{0.5}) - T \Delta_f S_T^\circ(\text{Mg}_{0.5}\text{La}_{0.5}). \quad (9)$$

Consequently,  $\Delta_f G_T^\circ(\text{MgLa})$  is given by the following equation.

$$\Delta_f G_T^\circ(\text{MgLa}) = \Delta_f G_T^\circ(\text{Mg}_{0.5}\text{La}_{0.5}) \times 2. \quad (10)$$

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