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# The 673 K isothermal section of the La–Ni–Sn ternary system

Yinghong Zhuang*, Haixia Deng, Jingqi Liu, Qingrong Yao

*Institute of Materials Science, Guangxi University Nanning, 530004, PR China*

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**Abstract**

The phase relationships in the La–Ni–Sn ternary system at 673 K have been investigated by means of X-ray powder diffraction (XRD), differential thermal analysis (DTA), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). Most of this ternary system was studied at 673 K. At this temperature, a new ternary compound whose atomic ratio is close to La/Ni/Sn = 1:1:3 has been found. The existences of 15 binary compounds $La_7Ni_3$, LaNi, $La_2Ni_3$, $La_7Ni_{16}$, $LaNi_3$, $La_2Ni_7$, $LaNi_5$, $Ni_3Sn$, $Ni_3Sn_2$, $Ni_3Sn_4$, $La_5Sn_3$, $La_5Sn_4$, LaSn, $La_3Sn_5$, $LaSn_3$ and seven other ternary compounds $LaNi_5Sn$, $LaNi_4Sn_2$, $LaNi_2Sn_2$, $La_3Ni_2Sn_6$, $La_3Ni_2Sn_7$, $La_3Ni_8Sn_{16}$, LaNiSn have been confirmed too. There are 31 three-phase regions in the 673 K isothermal section. Due to the lower melting point of Sn (about 504 K), a small part of the ternary system that lies in the Sn-rich part was studied at 483 K.


*Keywords:* Rare earth compounds; Transition metal compounds; Phase diagram; Crystal structure; X-Ray diffraction

## 1. Introduction

Rare earth $AB_5$ Haucke phase [1] alloys are being used extensively in negative electrodes of rechargeable nickel–metal hydride (Ni–MH) batteries. Among all these alloys, $LaNi_5$-based alloys are promising negative electrodes because they have high capacity, high charge discharge ability when they store hydrogen and can be activated easily. There are some studies reporting that the substitution of a small amount of Sn for Ni in $LaNi_5$ alloys can improve the property and hydrogen storage ability of $LaNi_5$ alloys [12–14]. Moreover, as reported, some ternary compounds in the La–Ni–Sn system have interesting magnetic properties and magnetic resistances, such as LaNiSn, $LaNi_4Sn_2$ and $LaNi_2Sn_2$ [18–20]. Although a great deal of investigation has been done, there is some inconsistency about the existence of some binary compounds in the La–Sn and La–Ni system [9–11]. In Refs. [2–4,15], the La–Ni phase diagrams with eight compounds were reported. A phase-diagram of the La–Sn system with seven compounds was reported in Ref. [6] and a Ni–Sn binary phase diagram with three compounds was reported in Ref. [7]. Structural data for the intermetallic compounds in the three binary systems are given in Table 1. Seven ternary compounds in the La–Ni–Sn system were found in Ref. [8] and their structural data are given in Table 2 (the structural data for the newly found ternary compounds are being studied and we will report them in a later article).

All these results have shown that the phase relationships in the La–Ni–Sn ternary system are well worth studying completely in order to provide valuable information for improving material properties and developing new materials. Up to now, the phase diagram of the La–Ni–Sn ternary system has not been reported. In this paper, we studied the isothermal section of the La–Ni–Sn ternary system mainly at 673 K.

## 2. Experimental

Each sample was prepared with a total weight of 3 g by weighing appropriate amounts of the pure components (La: 99.9%, Ni: 99.99%, Sn: 99.99%). Three-hundred and fifty-seven alloy buttons have been produced. These buttons were prepared by arc melting on a water-cooled copper cast with a non-consumable tungsten electrode under pure argon atmosphere. Each as-arc-cast button had been melted three times and turned around after melting for better homogeneity. For most alloys, the weight loss is less than 1% after melting. Therefore, no chemical analyses were carried out.

* Corresponding author.
*E-mail address:* zhuang@gxu.edu.cn (Y. Zhuang).

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Table 1
La–Ni–Sn binary crystal structure data

| Compound | Space group | Lattice parameters (nm) | | | Reference |
|---|---|---|---|---|---|
| | | *a* | *b* | *c* | |
| $La_7Ni_3$ | $P6_3mc$ | 1.0130(9) | – | 0.6462(6) | [8] |
| LaNi | *Cmcm* | 0.3907 | 1.0810(1) | 0.4396 | [8] |
| $La_2Ni_3$ | *Cmca* | 0.51183 | 0.97316 | 0.79075 | [8] |
| $La_7Ni_{16}$ | $I\bar{4}2m$ | 0.7355 | – | 1.451(1) | [8] |
| $LaNi_3$ | $R\bar{3}m$ | 0.5086(5) | – | 2.501(1) | [8] |
| $La_2Ni_7$ | $P6_3/mmc$ | 0.5085 | – | 2.471 | [8] |
| $LaNi_5$ | $P6/mmm$ | 0.5016 | – | 0.3983 | [8] |
| $Ni_3Sn$ | $Pm\bar{3}m$ | 0.3738(1) | – | – | [17] |
| $Ni_3Sn_2$ | $P6_3/mmc$ | 0.4146 | – | 0.5253 | [17] |
| $Ni_3Sn_4$ | $C2/m$ | 1.2214(6) | 0.4060(2) | 0.5219(3) | [17] |
| $La_5Sn_3$ | $I4/mcm$ | 1.2748 | – | 0.6344 | [15] |
| $La_5Sn_4$ | *Pnma* | 0.8448 | 1.626 | 0.8604 | [15] |
| LaSn | *Cmcm* | 0.4782(3) | 1.194(1) | 0.4422(3) | [15] |
| $La_3Sn_5$ | *Cmcm* | 1.035 | 0.829 | 1.063 | [15] |
| $LaSn_3$ | $Pm\bar{3}m$ | 0.47694(2) | – | – | [15] |

Table 2
La–Ni–Sn ternary crystal structure data

| Phase | Space group | Lattice parameters (nm) | | | Reference |
|---|---|---|---|---|---|
| | | *a* | *b* | *c* | |
| $LaNi_5Sn$ | $P6_3/mmc$ | 0.4971(5) | – | 1.999(3) | [16] |
| $LaNi_4Sn_2$ | $I\bar{4}c2$ | 0.7766(3) | – | 0.7581(3) | [16] |
| $LaNi_2Sn_2$ | $I4/mmm$ | 0.4459 | – | 1.030 | [16] |
| $La_3Ni_2Sn_6$ | *Cmcm* | 0.4526(1) | 1.7790(4) | 0.4510(1) | [16] |
| $La_3Ni_2Sn_7$ | *Cmmm* | 0.4584(2) | 2.751(1) | 0.4587(2) | [16] |
| $La_3Ni_8Sn_{16}$ | $Im\bar{3}$ | 1.1965(1) | – | – | [16] |
| LaNiSn | *Pnma* | 0.7671 | 0.4652 | 0.7592 | [16] |
| $La_5Ni_{24}Sn$ | $P6/mmm$ | 0.50723 | – | 0.40389 | [16] |

After casting, the samples were sealed in an evacuated quartz tube or glass tube for homogenization treatment and then they were annealed at different temperatures in order to attain good homogenization. The heat treatment temperature of the alloys was determined by differential thermal analysis (DTA) results of some typical ternary alloys or based on previous work of the three binary phase diagrams and the La–Ni–Sn ternary system [2,6–8]. The buttons in the Sn-rich part, containing more than 75% Sn in the La–Sn binary system or 57.1% Sn in the Ni–Sn binary system or near them in the ternary system, were kept at 483 K for 960 h. The alloys in the La-rich part, which contained more than 50% La were annealed at 773 K for 720 h at first and then cooled down to 673 K at a rate of 0.15 K/min, then kept at 673 K for 240 h. The alloys in the La–Sn binary system were homogenized at 903 K for 720 h at first and then they were cooled down to 673 K at a rate of 0.15 K/min, and finally kept at 673 K for 240 h. Finally, all these annealed buttons were quenched in liquid nitrogen.

Most homogenized alloy powders or buttons were investigated by X-ray diffraction, which was carried out on a Rigaku D/Max 2500PC X-ray diffractometer (Cu Kα monochromator) using JADE5 software [5] with analyzed angle ranging from $2\theta = 20–60^\circ$ at a voltage of 50 kV, and a current of 250 mA. Some typical alloys were analyzed by an S-570 scanning electron microscope (SEM), electron probe microanalysis (EPMA) or differential thermal analysis (DTA). By all these means, the phases and the crystal structures of the alloys in the La–Ni–Sn ternary system were determined.

## 3. Results and discussion

### 3.1. Binary system

#### 3.1.1. La–Ni system

Eight kinds of La–Ni compound, $La_3Ni$, $La_7Ni_3$, LaNi, $La_2Ni_3$, $La_7Ni_{16}$, $LaNi_3$, $La_2Ni_7$, $LaNi_5$, have been reported in the La–Ni binary system [2] (Table 1). But according to Ref. [3], $LaNi_2$ exists instead of $La_7Ni_{16}$. Our investigation has shown that the phase is $La_7Ni_{16}$, not $LaNi_2$, which was found by XRD, SEM and EPMA. Secondly, the existence of $La_3Ni$ was confirmed in Ref. [2,3]. Under our present experimental conditions, we did not find the $La_3Ni$ phase. The alloys containing 75% La and 25% Ni or close to this ratio contain the La phase and the $La_7Ni_3$ phase in terms of the results of XRD.

### 3.1.2. *Ni–Sn system*

In the Ni–Sn system, three compounds were reported in the literature [7] (Table 1). They are $Ni_3Sn$, $Ni_3Sn_2$, and $Ni_3Sn_4$, which is in agreement with our experiment results.

### 3.1.3. *La–Sn system*

According to Ref. [6], there are seven kinds of compounds in the La–Sn binary system, which are $La_5Sn_3$, $La_5Sn_4$, $La_{11}Sn_{10}$, LaSn, $La_2Sn_3$, $La_3Sn_5$, and $LaSn_3$ (Table 1). But in Ref. [6], we also find that the $La_{11}Sn_{10}$ and $La_2Sn_3$ compounds might exist. That is to say, their existence has not been confirmed. In our investigation, the phases of $La_{11}Sn_{10}$ and $La_2Sn_3$ were not observed either. Their X-ray diagrams consist of $La_5Sn_4$ and LaSn, $La_3Sn_5$ and LaSn.

## 3.2. *Ternary phases*

Eight ternary compounds, $LaNi_5Sn$, $LaNi_4Sn_2$, $LaNi_2Sn_2$, $La_3Ni_2Sn_6$, $La_3Ni_2Sn_7$, $La_3Ni_8Sn_{16}$, LaNiSn and $La_5Ni_{24}Sn$, were reported in the literature [8]. All these compounds except $La_5Ni_{24}Sn$ ($LaNi_{4.8}Sn_{0.2}$) (Table 2) were confirmed in our ternary alloys. After strict analysis by XRD and DTA, we have determined that $La_5Ni_{24}Sn$ is just a solid solution which was obtained through Sn substituting for part of Ni in $LaNi_5$ alloys. $LaNi_5$ and $La_5Ni_{24}Sn$ have the same structure type, approximately the same crystal data and diffraction patterns.

A new ternary compound in the La–Ni–Sn ternary system, $LaNiSn_3$, was observed in our experiment. Therefore, there are in total eight kinds of ternary compounds in our isothermal section.

## 3.3. *The existence of $LaNiSn_3$*

By comparing and analyzing the X-ray diffraction patterns of the samples which contained almost 20% La, 20% Ni, 60% Sn, and by identifying the phases in each of these samples, evidence was found to confirm the existence of a new ternary compound, whose atomic ratio is close to La/Ni/Sn = 1:1:3. Its crystal structural data will be published in another article.

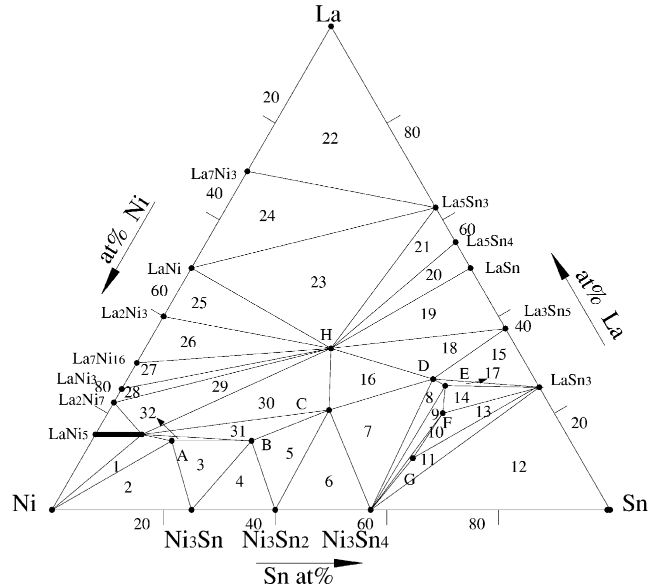


Fig. 1. The isothermal section of the La–Ni–Sn ternary system at 673 and 483 K. (A) $LaNi_5Sn$; (B) $LaNi_4Sn_2$; (C) $LaNi_2Sn_2$; (D) $La_3Ni_2Sn_6$; (E) $La_3Ni_2Sn_7$; (F) $LaNiSn_3$; (G) $La_3Ni_8Sn_{16}$; (H) LaNiSn.

## 3.4. *Isothermal section*

The isothermal sections of the ternary La–Ni–Sn system at 673 and 483 K were determined by XRD, EPMA, SEM and DTA. The isothermal sections, shown in Fig. 1, consist of 26 single-phase regions, 56 two-phase regions and 32 three-phase regions. Details of the three-phase regions are given in Table 3. The maximum solubility of Sn in $LaNi_5$ is about 8 at.%.

Table 3
Details of three-phase regions in La–Ni–Sn system

| Phase region | Phase composition | Phase region | Phase composition |
|---|---|---|---|
| 1 | $Ni + LaNi_5 + LaNi_5Sn$ | 17 | $La_3Ni_2Sn_7 + LaSn_3 + La_3Ni_2Sn_6$ |
| 2 | $Ni + Ni_3Sn + LaNi_5Sn$ | 18 | $LaNiSn + La_3Sn_5 + La_3Ni_2Sn_6$ |
| 3 | $LaNi_4Sn_2 + Ni_3Sn + LaNi_5Sn$ | 19 | $LaNiSn + La_3Sn_5 + LaSn$ |
| 4 | $LaNi_4Sn_2 + Ni_3Sn + Ni_3Sn_2$ | 20 | $LaNiSn + La_5Sn_4 + LaSn$ |
| 5 | $LaNi_4Sn_2 + LaNi_2Sn_2 + Ni_3Sn_2$ | 21 | $LaNiSn + La_5Sn_3 + LaSn$ |
| 6 | $LaNi_2Sn_2 + Ni_3Sn_4 + Ni_3Sn_2$ | 22 | $La + La_5Sn_3 + La_7Ni_3$ |
| 7 | $LaNi_2Sn_2 + Ni_3Sn_4 + La_3Ni_2Sn_6$ | 23 | $LaNiSn + La_5Sn_3 + LaNi$ |
| 8 | $La_3Ni_2Sn_7 + Ni_3Sn_4 + La_3Ni_2Sn_6$ | 24 | $La_7Ni_3 + La_5Sn_3 + LaNi$ |
| 9 | $LaNiSn_3 + Ni_3Sn_4 + La_3Ni_2Sn_7$ | 25 | $LaNiSn + La_2Ni_3 + LaNi$ |
| 10 | $LaNiSn_7 + Ni_3Sn_4 + La_3Ni_8Sn_{16}$ | 26 | $LaNiSn + La_2Ni_3 + La_7Ni_{16}$ |
| 11 | $LaSn_3 + Ni_3Sn_4 + La_3Ni_8Sn_{16}$ | 27 | $LaNiSn + LaNi_3 + La_7Ni_{16}$ |
| 12 | $LaSn_3 + Ni_3Sn_4 + Sn$ | 28 | $LaNiSn + La_2Ni_7 + La_7Ni_{16}$ |
| 13 | $LaSn_3 + LaNiSn_3 + La_3Ni_8Sn_{16}$ | 29 | $LaNiSn + LaNi_5 + La_2Ni_7$ |
| 14 | $LaSn_3 + LaNiSn_3 + La_3Ni_2Sn_7$ | 30 | $LaNi_2Sn_2 + LaNiSn + LaNi_5$ |
| 15 | $LaSn_3 + La_3Sn_5 + La_3Ni_2Sn_6$ | 31 | $LaNi_2Sn_2 + LaNi_4Sn_2 + LaNi_5$ |
| 16 | $LaNi_2Sn_2 + LaNiSn + La_3Ni_2Sn_6$ | 32 | $LaNi_5Sn + LaNi_4Sn_2 + LaNi_5$ |

## 4. Conclusion

The purpose of the present study was to determine the phase relationships in the system La–Ni–Sn at 673 and 483 K and determine the crystal structure of the observed ternary phases. A new ternary compound, $LaNiSn_3$, was found. The atomic ratio of this new phase is close to La/Ni/Sn = 1:1:3 and its crystal structural data will be published in another article. The two isothermal sections consist of 26 single-phase regions, 56 two-phase regions and 32 three-phase regions.

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