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# TRIANGULATION OF THE La-Mg-Zn SYSTEM

# TRIANGULACJA UKŁADU La-Mg-Zn

This work is a contribution to the study of the La-Mg-Zn phase diagram. Several alloys were prepared from pure constitutive elements by classical synthesis in tantalum crucibles. These alloys were characterized by X-ray diffraction and Electron Probe MicroAnalysis. The results of these characterization measurements allowed the authors to suggest a full triangulation of the La-Mg-Zn system : six ternary solid solutions and one ternary compound were evidenced.

*Keywords*: Lanthanum, magnesium, zinc, phase diagram, triangulation

Celem tej pracy jest zebranie nowych danych niezbędnych do opracowania diagramu fazowego układu La-Mg-Zn. Dostępne dane literaturowe są nieliczne i częściowo sprzeczne. Przygotowano 26 stopów o różnym składzie poprzez stopienie czystych składników w tyglach tantalowych w atmosferze ochronnej argonu. Otrzymane stopy zbadane zostały za pomocą dwóch technik: dyfraktografii i mikrosondy elektronowej. Otrzymane rezultaty pozwoliły zaproponować pełną triangukację układu La-Mg-Zn: stwierdzono istnienie sześciu potrójnych roztworów stałych i jednego potrójnego związku międzymetalicznego.

## 1. Introduction

Mg-based alloys are very attractive for the transport industry because of their light weight. However since they have a weak strength, they cannot be used without additives.

Among the common alloying elements, the addition of zinc can strengthen these alloys by precipitation [1] and this effect is more effective if rare-earth elements are moreover added [2-4].

The optimisation of these alloys requires knowledge on their stability and as a consequence on their phase diagrams. Up to now, in the Mg-Zn-RE (RE = Rare Earth) systems, phase diagrams are scarcely and incompletely studied. Thus, the aim of this work was to start to fill this gap by re-investigating the La-Mg-Zn phase diagram at low temperatures.

## 2. Literature data

Only a few data are available in literature on the ternary phase diagram La-Mg-Zn.

Dobatkina et al. [5,6] gave a first description of this system. The suggested isothermal section at 573K is presented in Figure 1. These authors reported three ternary

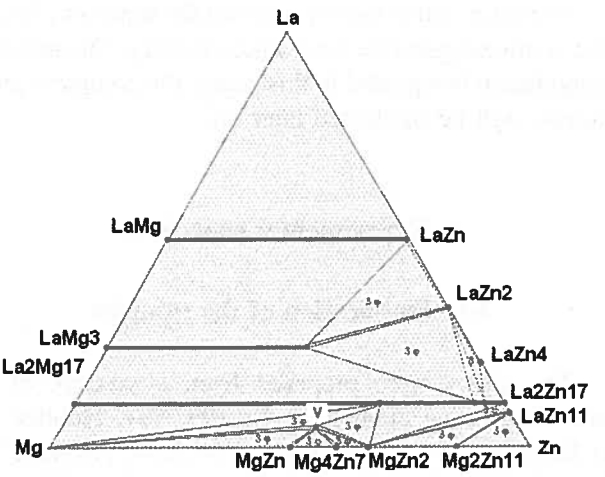


Fig. 1. Isothermal section of the La-Mg-Zn system at 573K, suggested by Dobatkina et al. [5]

solid solutions: a first one which is a total one between LaMg and LaZn; a second one based on $LaMg_3$ with a solubility limit of 42 at.%Zn and a third one which goes

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from $La_2Mg_{17}$ to $La_2Zn_{17}$. They also reported the presence of a ternary compound called V with a composition of 5 at.%La, 42 at.%Mg and 53 at.%Zn. The existence of this compound was confirmed later on by Tsai et al. [7], even though the composition they found (8 at.% La, 42 at.% Mg, 50 at.% Zn) is slightly different from that determined by Dobatkina et al.

The Mg-rich corner was recently re-investigated by Li et al. [8]. These authors gave a description of this region at 623K. They also evidenced a ternary compound, though with a composition (8.3 at.% La, 47.1 at.% Mg, 44.6 at.% Zn) different from that of V, and a ternary solution which they called Linear Compound (LC). According to these authors, this Linear Compound is close to $La_2Mg_{17}$ but it is not based on it. They found for this solid solution a crystalline structure similar to that of the T-phase encountered in the ternary system based on Mg, Zn and Mishmetal [9].

In addition to the low amount of data on the La-Mg-Zn system, the available data are neither consistent with one another nor with the constitutive binary phase diagrams. Some binary compounds are missing: one is missing in the La-Mg system ($LaMg_{12}$) and three are missing in the La-Zn system ($LaZn_5$, $La_3Zn_{22}$, $LaZn_{13}$). A total description of the constitutive binary phase diagrams based on a critical review of literature data and an additional experimental work is given by the present authors in [10-11]. Furthermore, the crystal structure of $La_2Mg_{17}$ ($Ni_{17}Th_2$-type, [12]) differs from that of $La_2Zn_{17}$ ($Th_2Zn_{17}$-type, [12]), thus the existence of a total solid solution between these two compounds seems to be doubtful.

Therefore, after having checked the binaries [10], we have re-investigated the La-Mg-Zn ternary. The obtained triangulation is reported in this paper, the complete phase diagram will be published later on.

## 3. Experimental procedure

### 3.1. Elaboration of the samples

The alloys were prepared from a mixture of the pure constitutive elements : La (99.9%+, Huhhot Jinrui Rare Earth Co. LTD) Mg ( 99.98%, Aldrich) and Zn (99.999%, Alpha Aeser). Because of a high reactivity of La and Mg with oxygen and because of high vapour pressures in the case of Mg and Zn, these samples were prepared in sealed tantalum crucibles. These crucibles (18mm in diameter and 11mm of height) were cold-stamped from a tantalum sheet, with a thickness of 0.25mm, supplied by Technicome. They were filled in and sealed by a TIG (Tungsten Inert Gas) welding, under argon atmosphere in a glove box (<1 ppm $O_2$ and <20 ppm $H_2O$).

The mixtures were heated up to 1220K for about 30 minutes. This temperature is higher than the highest melting temperature of the constitutive elements (1193K for La). It was chosen in order to rapidly get a homogeneous alloy.

This heat treatment was followed by an annealing at 595K for about 40 days. This temperature, lower than the lowest binary eutectic temperature (598.2K in Mg-Zn) was chosen in order to reach the equilibrium state of the samples at low temperatures.

### 3.2. Characterization of the samples

The elaborated samples were characterized by X-Ray powder Diffraction measurements and Electron Probe MicroAnalyses (EPMA).

Diffraction patterns were recorded on a Phillips Expert diffractometer (with a copper $K_{\alpha 1}$ anticathode) in the [10°-100°] $2\theta$ range, with a step size of 0.01671° and a step time of 130 s. The lattice parameters were determined from these X-ray diffraction patterns using PowderCell program [13]. From the crystal structure of a phase, PowderCell calculates its theoretical pattern and by using a refinement algorithm, this program determines the lattice parameter(s) corresponding to the experimental diffraction pattern.

The Electron Probe MicroAnalyses were performed with a CAMECA SX100 Analyser equipped with five Wave Dispersion Spectrometers (WDS).

## 4. Results and discussion

Twenty six alloys were synthesized in this study. Their compositions and the characterization techniques to which these samples were subjected are given in Table 1.

TABLE 1

List of the samples synthesised in this work with their composition. The characterization techniques to which these samples were subjected are given as well (XRD=X-ray Diffraction, EPMA=Electron Probe MicroAnalysis)

| Number | Composition (at.%La/Mg/Zn) | Characterization Techniques |
|---|---|---|
| 1 | 50/48/2 | DRX + EPMA |
| 2 | 25/75/0 | DRX |
| 3 | 10.5/89.5/0 | DRX |
| 4 | 10.5/0/89.5 | DRX |
| 5 | 20/0/80 | DRX |
| 6 | 50/12.5/37.5 | DRX + EPMA |
| 7 | 25/51/24 | DRX |
| 8 | 25/33/42 | DRX |
| 9 | 25/10/65 | DRX + EPMA |
| 10 | 10.5/80/9.5 | DRX |
| 11 | 10.5/60/29.5 | DRX |
| 12 | 10.5/38.5/51 | DRX |
| 13 | 10.5/30/59.5 | DRX + EPMA |
| 14 | 10.5/20.5/69 | DRX |
| 15 | 10.5/10/79.5 | DRX |
| 16 | 44.4/33.3/22.2 | DRX + EPMA |
| 17 | 33.3/56.7/10 | DRX |
| 18 | 33.3/46.7/20 | DRX + EPMA |
| 19 | 33.3/33.3/33.3 | DRX |
| 20 | 33.3/21.5/45.2 | DRX |
| 21 | 33.3/10/56.7 | DRX + EPMA |
| 22 | 18/56/26 | DRX |
| 23 | 4/34/62 | DRX |
| 24 | 4/21/75 | DRX |
| 25 | 4/13/83 | DRX |
| 26 | 4/4/92 | DRX |

### 4.1. Solid solution based on $LaMg_3$

One binary ($LaMg_3$, n°2) and three ternary samples (n°7,8,9) containing 25 at.% La were synthesized. Their positions in the phase diagram are given in Figure 2.

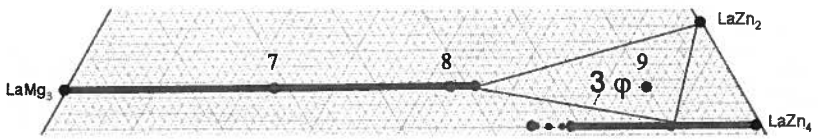


Fig. 2. Positions of the synthesized samples with 25 at.% La (n°7, 8 and 9)

Results of their characterization are given in Table 2. Since the space group of $LaZn_4$ is not known with precision [11], its cell parameters cannot be calculated with PowderCell.

TABLE 2

Characterization results of the ternary alloys with 25 at.%La complemented by those of the binary compound $LaMg_3$

| Number | Composition (at.%La/Mg/Zn) | XRD | | EPMA | |
|---|---|---|---|---|---|
| | | Phases | Lattice parameters (Å) | Phases | Composition (at.%La/Mg/Zn) |
| 2 | 25/75/0 | $LaMg_3$ | a = 7.48(9) | | |
| 7 | 25/51/24 | ($LaMg_3$) | a = 7.29(6) | | |
| 8 | 25/33/42 | ($LaMg_3$) | a = 7.13(0) | | |
| 9 | 25/10/65 | ($LaMg_3$) | a = 7.10 (0) | ($LaMg_3$) | 25/30/45 |
| | | $LaZn_2$ | a = 4.68, b = 7.62, c = 7.57 | $LaZn_2$ | 33/0/67 |
| | | ($LaZn_4$) | 7($LaZn_4$) | 21.5/9/69.5 | |

The existence of a ternary solid solution based on $LaMg_3$ was confirmed in this work. By using the cell parameters calculated from the X-ray diffraction patterns presented in Figure 3, we were able to determine the limit of solubility of this phase ; its value is 45 at.% Zn. The lattice parameter varies linearly in the solid solution and it is constant in the three phase region (see Figure 4). The limit of solubility is then given by the intersection of these two corresponding lines.

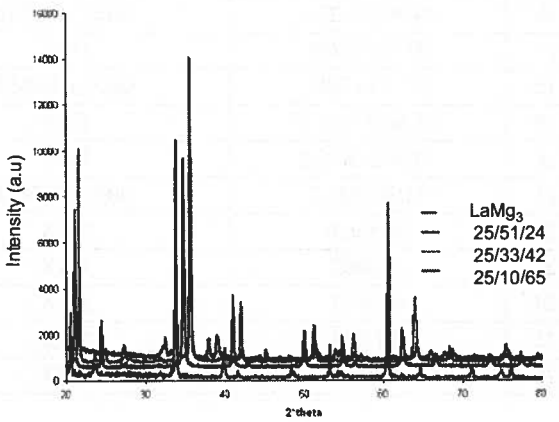


Fig. 3. X-ray diffraction patterns for samples with 25 at.% La

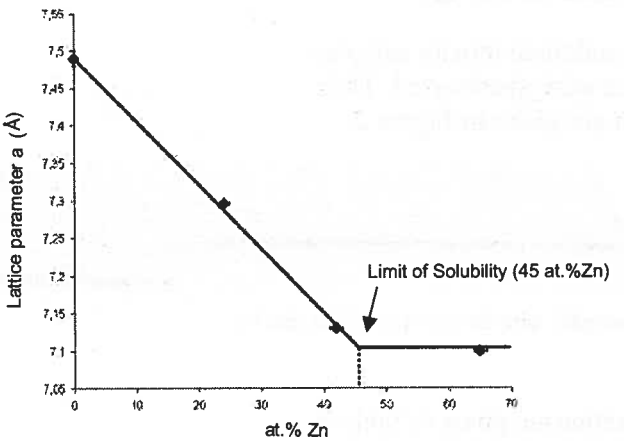


Fig. 4. Lattice parameter versus zinc content for samples with 25 at.% Zn

Microprobe analysis of sample 9 which contains three phases ($LaMg_3$), $LaZn_2$, and ($LaZn_4$), gave 45 at.% Zn for the composition of the ($LaMg_3$) phase (see Table 1). Therefore results obtained by XRD are in concordance with those obtained by EPMA and both agree with literature data which gave 42 at. % Zn for this limit of solubility [5].

### 4.2. Solid solution based on LaMg

Two ternary samples (n°1,6) containing 50 at.% La were synthesized.

Results of their characterization are reported in Table 3 with those of the samples n°16, 18 and 19. The positions of all these samples in the phase diagram are given in Figure 5.

TABLE 3

Characterization results of the samples with 50 at.%La (n°1 and 6) complemented with those of samples n° 16,18 and 19

| Number | Composition (at.%La/Mg/Zn) | XRD | | EPMA | |
|---|---|---|---|---|---|
| | | Phases | Lattice parameters (Å) | Phases | Composition (at.%La/Mg/Zn) |
| 1 | 50/48/2 | (LaMg) | a = 3.96(1) | (LaMg) | 50/49/1 |
| | | ($LaMg_3$) | | | |
| | | (La) | | | |
| 6 | 50/12.5/37.5 | (La) | a = 5.65(1) | (La) | 98.1./0.1/1.8 |
| | | (LaZn) | a = 3.78(2) | (LaZn) | 49/8/43 |
| | | ($LaMg_3$) | a = 7.18(1) | ($LaMg_3$) | 25.3/37.1/37.6 |
| 16 | 44.4/33.3/22.2 | (La) | a = 5.65(1) | (La) | 96-99/0/1-4 |
| | | ($LaMg_3$) | a = 7.22(5) | ($LaMg_3$) | 24.8/43.3/31.9 |
| 18 | 33.3/46.7/20 | (La) | a = 5.65(1) | | |
| | | ($LaMg_3$) | a = 7.30(7) | ($LaMg_3$) | 25.2/52.6/22.2 |
| 19 | 33.3/33.3/33.3 | (La) | a = 5.65(1) | | |
| | | ($LaMg_3$) | a = 7.17(0) | | |

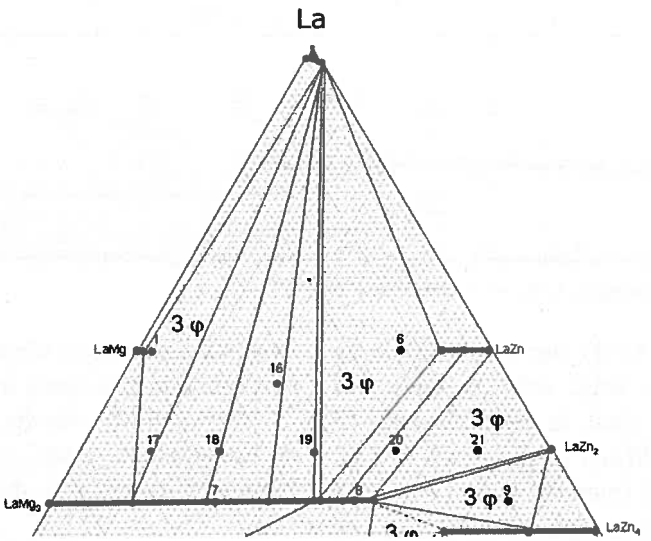


Fig. 5. Positions of the synthesized samples with 50 at.% La (n°1 and 6) and samples n°16, 18 and 19

In contrast with literature data, only a partial solid solution was found between LaMg and LaZn. Three phases were identified from XRD and EPMA measurements both in sample 1 and in sample 6 : Sample 1 is made of (LaMg), ($LaMg_3$) and (La) and sample 6 is made of (La), (LaZn) and ($LaMg_3$). Moreover, samples 16, 18 and 19 are made of (La) and ($LaMg_3$). Results from analyses of sample 1 and 6 led us to suggest the following limits of solubility : 1 at. %Zn for the solid solution based on LaMg and 43 at. %Zn for the solid solution based on LaZn.

### 4.3. Solid solution based on $La_2Mg_{17}$

Two binary (n°3-4) and six ternary samples (n°10-15) containing 10.5 at.% La were synthesized.

Results of their characterization are reported in Table 4. The positions of these samples in the phase diagram are given in Figure 6.

TABLE 4

Characterization results of the samples with 10.5 at.% La

| Number | Composition (at.%La/Mg/Zn) | XRD | | EPMA | |
|---|---|---|---|---|---|
| | | Phases | Lattice parameters (Å) | Phases | Composition (at.%La/Mg/Zn) |
| 3 | 10.5/89.5/0 | $La_2Mg_{17}$ | a = 10.3(7)<br>c = 10.2(2) | | |
| 4 | 10.5/0/89.5 | $La_2Zn_{17}$ | a = 9.12(9)<br>a = 13.335 | | |
| 10 | 10.5/80/9.5 | ($La_2Mg_{17}$) | a = 10.2(2)<br>c = 10.1(3) | | |
| 11 | 10.5/60/29.5 | ($La_2Mg_{17}$) | a = 9.8(6)<br>c = 9.7(8) | | |
| 12 | 10.5/38.5/51 | ($La_2Mg_{17}$) | a = 9.5(8)<br>a = 9.4(5) | | |
| 13 | 10.5/30/59.5 | ($La_2Zn_{17}$) | a = 9.5(4)<br>a = 13.6(9) | ($La_2Zn_{17}$) | 10.7/23/66.3 |
| | | ($La_2Mg_{17}$) | a = 9.5(5)<br>a = 9.4(4) | | |
| | | | | ($LaZn_4$) | 20.5/22/57.5 |
| 14 | 10.5/20.5/69 | ($La_2Zn_{17}$) | a = 9.3(6)<br>a = 13.6(9) | | |
| 15 | 10.5/10/79.5 | ($La_2Zn_{17}$) | a = 9.1(9)<br>a = 13.4(2) | | |

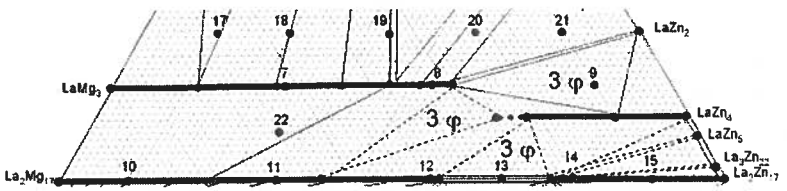


Fig. 6. Positions of the synthesized samples with 10.5 at.% La (n°10-15)

As in the previous case (§V.2), our results disagree with the literature data. The solid solution based on $La_2Mg_{17}$ was not found to be total. In effect, sample 13 is made of three phases : $La_2Mg_{17}$, $La_2Zn_{17}$ and $LaZn_4$. The presence of a third phase (namely, $LaZn_4$), in very small amount, might indicate a slight deviation of the alloy composition from the expected one. By using the evolution of the cell parameters versus zinc content, the limits of solubility were found to be 52 at.%Zn and 66 at.%Zn for $La_2(Mg,Zn)_{17}$ and $La_2(Zn,Mg)_{17}$ respectively. The composition of ($La_2Zn_{17}$) in sample n°13; determined by EPMA, is in agreement with these results.

### 4.4. Solid solution based on $LaZn_4$

A solid solution based on LaZn4 was evidenced in samples 9 and 13 (see Tables 1 and 3). This solid solution has never been mentioned in literature so far. It is evidenced in this work for the first time.

From EPMA results, we can suggest for this phase an homogeneity range up to at least 22 at.% Mg. This homogeneity range is shown in Figure 6.

### 4.5. Multi-phased domains

Eleven samples (n°16-26) with composition in lanthanum different from that of the ternary solid solutions were synthesized. Results of their characterization are reported in Table 5. The positions of these samples in the phase diagram are given in Figures 5 and 7.

TABLE 5

Characterization results of the samples with composition in La different from that of the ternary solid solutions

| Number | Composition (at.%La/Mg/Zn) | XRD | | EPMA | |
|---|---|---|---|---|---|
| | | Phases | Lattice parameters (Å) | Phases | Composition (at.%La/Mg/Zn) |
| 16 | 44.4/33.3/22.2 | (La) | a = 5.65(1) | (La) | 96-99/0/1-4 |
| | | ($LaMg_3$) | a = 7.22(5) | ($LaMg_3$) | 24.8/43.3/31.9 |
| 17 | 33.3/56.7/10 | (La) | a = 5.65(1) | | |
| | | (LaMg) | a = 3.95(6) | | |
| | | ($LaMg_3$) | a = 7.42(4) | | |
| 18 | 33.3/46.7/20 | (La) | a = 5.65(1) | | |
| | | ($LaMg_3$) | a = 7.30(7) | ($LaMg_3$) | 25.2/52.6/22.2 |
| 19 | 33.3/33.3/33.3 | (La) | a = 5.65(1) | | |
| | | ($LaMg_3$) | a = 7.17(0) | | |
| 20 | 33.3/21.5/45.2 | (LaMg) | a = 3.76(8) | | |
| | | ($LaMg_3$) | a = 7.14(2) | | |
| 21 | 33.3/10/56.7 | ($LaMg_3$) | a = 7.09(5) | ($LaMg_3$) | 25/30/45 |
| | | (LaZn) | a = 3.75(5) | | |
| | | $LaZn_2$ | a = 4.68, b = 7.62, c = 7.57 | | |
| 22 | 18/56/26 | ($La_2Mg_{17}$) | a = 10.0(7), c = 9.9(4) | | |
| | | ($LaMg_3$) | a = 7.16(9) | | |
| 23 | 4/34/62 | $MgZn_2$ | a = 5.2(2), c = 8.5(6) | | |
| | | ($LaZn_{11}$) | a = 10.68, c = 6.88 | | |
| | | V? | | | |
| 24 | 4/21/75 | $MgZn_2$ | a = 5.2(2), c = 8.5(6) | | |
| | | ($LaZn_{11}$) | a = 10.68, c = 6.88 | | |
| 25 | 4/13/83 | $MgZn_2$ | a = 5.2(2), c = 8.5(6) | | |
| | | ($LaZn_{11}$) | a = 10.68, c = 6.88 | | |
| | | $Mg_2Zn_{11}$ | a = 8.55(2) | | |
| 26 | 4/4/92 | ($LaZn_{11}$) | a = 10.68, c = 6.88 | | |
| | | $Mg_2Zn_{11}$ | a = 8.55(2) | | |
| | | (Zn) | a = 2.66, c = 4.95 | | |

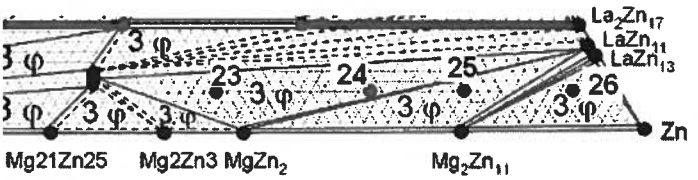


Fig. 7. Positions of the samples (n°23-26) with composition in La different from that of ternary solid solutions

These results allowed us to plot some tie-lines in the bi-phased domains. For the samples 18 and 19, these tie-lines are in perfect concordance with the nominal composition of the samples. For samples 16, 20 and 22, even if the composition of the sample does not belong to its corresponding tie line, it is close to it.

A ternary compound which could correspond to the V compound (5 at.%La, 42 at.%Mg, 53 at.%Zn), previously reported in literature [5], was evidenced in the low lanthanum content region of the La-Mg-Zn phase diagram.

### 4.6. Triangulation of the La-Mg-Zn system

The triangulation suggested from our results is presented in Figure 8. The Mg-rich corner of this phase

diagram has not been re-investigated in this work; The pertaining description corresponds to that given by Li et al. [8].

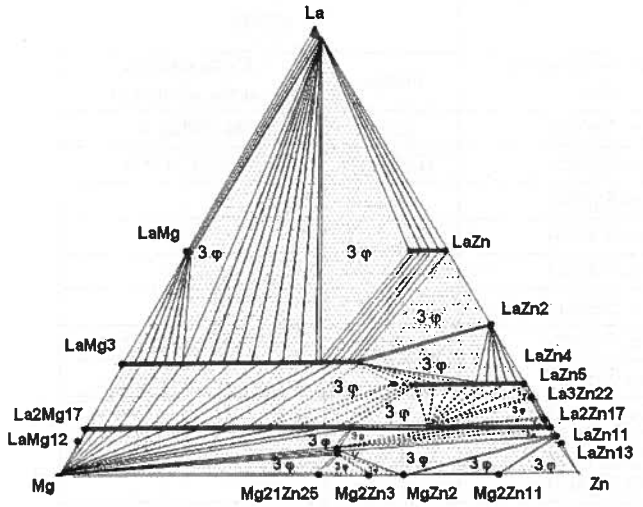


Fig. 8. Triangulation of the La-Mg-Zn system suggested from the present results

## 5. Conclusion

In this work, we performed a re-investigation of the La-Mg-Zn phase diagram. Up to now, only a few data are available in literature on this phase diagram. In addition these data were neither consistent with one another nor with the constitutive binary phase diagrams (some binary compound were missing).

The contribution of this work is to suggest a full triangulation of the La-Mg-Zn phase diagram which is in concordance with its constitutive binaries. Six ternary solid solutions, La(Mg,Zn), La(Zn,Mg), $La(Mg,Zn)_3$, $La(Zn,Mg)_4$, $La_2(Mg,Zn)_{17}$ and $La_2(Zn,Mg)_{17}$, and one ternary compound which could correspond to the V one, previously reported in literature, were evidenced.

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