# Phase Diagram of the System $LaCl_3$-$CaCl_2$-NaCl

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The phase diagram of ternary system $LaCl_3-CaCl_2-NaCl$ has been constructed from the phase diagrams of the three binary systems and of thirteen quasi-binary systems determined by DTA. For the binaries $LaCl_3-CaCl_2$ and $CaCl_2-NaCl$ eutectic points were observed at 651 °C, 35.1 mol% $LaCl_3$ and at 508 °C, 49.9 mol% NaCl, respectively. For $LaCl_3-NaCl$, a peritectic point besides the eutectic point at 545 °C, 36.1 mol% $LaCl_3$ was found at 690 °C, 57.5 mol%, which is attributable to the formation of the peritectic compound $3\,LaCl_3 \cdot NaCl$. The phase diagram of the ternary system has a ternary eutetic point and a ternary peritectic point due to $3\,LaCl_3 \cdot NaCl$, the former at 462 °C and 12.1 – 39.7 – 48.2 mol% ($LaCl_3-CaCl_2-NaCl$) and the latter at 612 °C and 26.9 – 55.1 – 18.0 mol%.

## Introduction

The phase diagram of the system $LaCl_3-CaCl_2-NaCl$ is reported to be of the simple eutectic type without binary and ternary compounds [1]. The melting point of $LaCl_3$ used in [1] (850 °C) is by 27 °C lower than that found in [2]. This suggests that the temperature of the liquidus surface was underestimated in [1] due to impurities of the $LaCl_3$. From the phase diagram of ternary $PrCl_3-CaCl_2-NaCl$ it was concluded that a binary peritectic compound $3\,PrCl_3 \cdot NaCl$ is formed in the solid phase of that system [3]. Solid $LaCl_3$ has the same crystal structure [4] as $PrCl_3$. The present work was undertaken to determine the accurate liquidus surface of the system $LaCl_3-CaCl_2-NaCl$ and to examine whether the compound $3\,LaCl_3 \cdot NaCl$ is formed.

## Experimental

### *Chemicals*

$LaCl_3$ was prepared and purified in the same way as reported in [5]. The impurities were almost the same as in [6]. The chemicals NaCl and $CaCl_2$ were of analytical reagent grade and dried in the usual way [6]. All the chemicals were treated in a glove box filled with dry argon.

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### *DTA measurements*

The DTA measurements were carried out on cooling in an atmosphere of purified argon using a chromel-alumel thermocouple and $\alpha$-$Al_2O_3$ powder as reference material. The cooling rates were 11 °C/min. at 800 °C, 7 °C/min. at 600 °C, and 4 °C/min. at 400 °C. If necessary, the measurements were repeated with slower cooling rates (2 or 3 °C/min.) and newly prepared samples.

The obtained melting points of NaCl and $CaCl_2$ were 802 °C and 772 °C, respectively, in excellent agreement with the accepted data. As in [2] the melting point of $LaCl_3$ was found to be 877 °C, which is the highest value reported in literature.

## Results and Discussion

### *$CaCl_2$–NaCl*

The phase diagram (Fig. 1) shows an eutectic point at 508 °C and 49.9 mol% NaCl. Of the several phase diagrams published [1, 3, 7 – 12], the present one is in good agreement with those by Seltveit and Flood [7] and Hattori et al. [3]. As can be seen in Fig. 1, for concentrations 80 mol% NaCl no the eutectic temperature was observed. In general this indicates that a solid solution and an incongruently melting compound are formed at that composition. Seltveit and Flood [7] investigated in detail the phase diagram with both thermal analysis and tracer experiments using a small amount of radioactive compound as a third component. They concluded that the incongruently melting compound is

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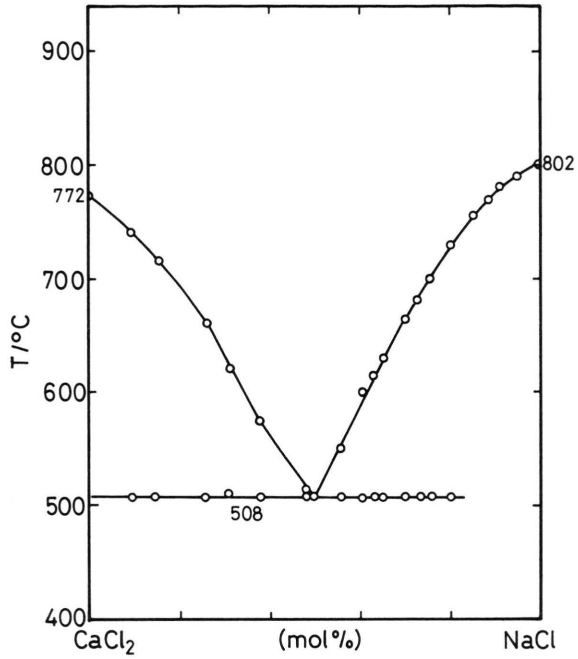


Fig. 1. Phase diagram of $CaCl_2$–NaCl.

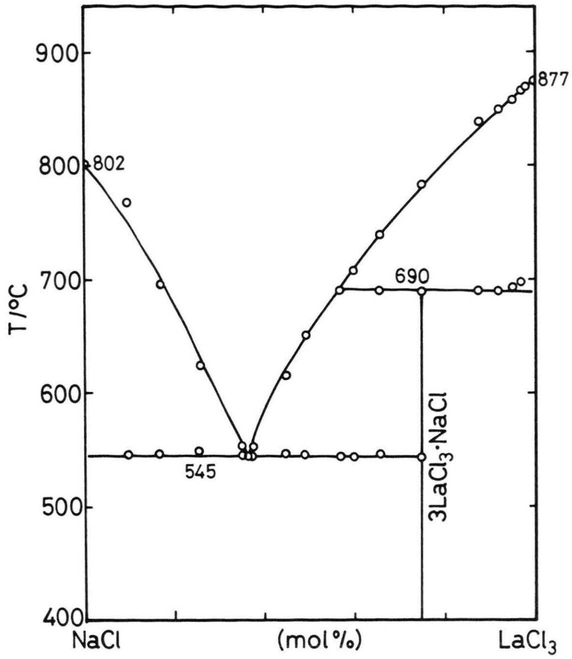


Fig. 2. Phase diagram of $LaCl_3$–NaCl.

$Na_4CaCl_6$. The disappearance of the eutectic temperature seems to support their result, although the thermal change to be expected, i.e., a solidus curve and a peritectic temperature were not detected.

*$LaCl_3$–NaCl*

The phase diagram (Fig. 2) indicates the formation of an incongruently melting compound. The peritectic point is at 690 °C and 57.5 mol% $LaCl_3$, and the eutectic point is at 545 °C and 36.1 mol% $LaCl_3$. The phase diagrams of Morozov et al. [1] and Kuroda [13] show no peritectic compound. In [1] the eutectic point is at 525 °C and 27 mol% $LaCl_3$, and in [13] it is at 537 °C and 33 mol% $LaCl_3$.

Hattori et al. [3] found anew the peritectic compound 3 $PrCl_3$ · NaCl in the phase diagram of $PrCl_3$–NaCl by DTA measurements, the composition of which was already known from DSC measurements. We tried to determine in the same way the composition of the compound in the $LaCl_3$–NaCl system but failed because of the high incongruent melting temperature. However, from the fact that the eutectic temperature disappears at 75.0 mol% $LaCl_3$, the composition of the compound can be concluded to be 3 $LaCl_3$ · NaCl.

*$LaCl_3$–$CaCl_2$*

The phase diagram (Fig. 3) shows an eutectic point at 651 °C and 35.1 mol% $LaCl_3$. Morozov et al. [1] found the eutectic point at 630 °C and 27 mol% $LaCl_3$, and Kuroda [13] at 645 °C and 33 mol% $LaCl_3$.

*$LaCl_3$–$CaCl_2$–NaCl*

In order to construct the ternary phase diagram, 8 quasi-binary phase diagrams, corresponding to the lines a–h in Fig. 4 were first measured by DTA. As in the $CaCl_2$–NaCl diagram (Fig. 1) no solid solutions were seen in these diagrams. From the changes of the liquidus curves and the lines which show a minimum temperature (462 °C) in their diagram, the ternary eutectic point and three eutectic boundary curves falling to it from the eutectic points of the three binary systems were determined approximately. In the diagram of line h no minimum temperature was observed. This suggests that

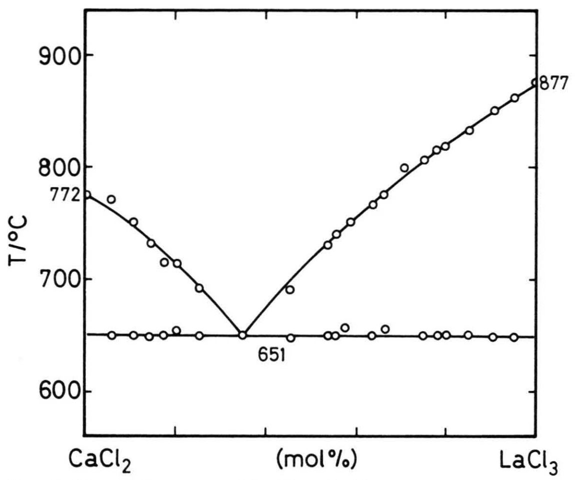


Fig. 3. Phase diagram of $LaCl_3-CaCl_2$.

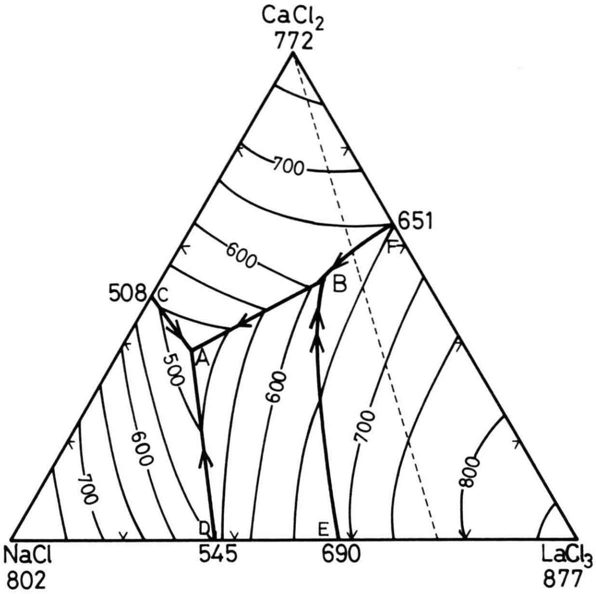


Fig. 5. Phase diagram of $LaCl_3-CaCl_2-NaCl$ (unit: °C).

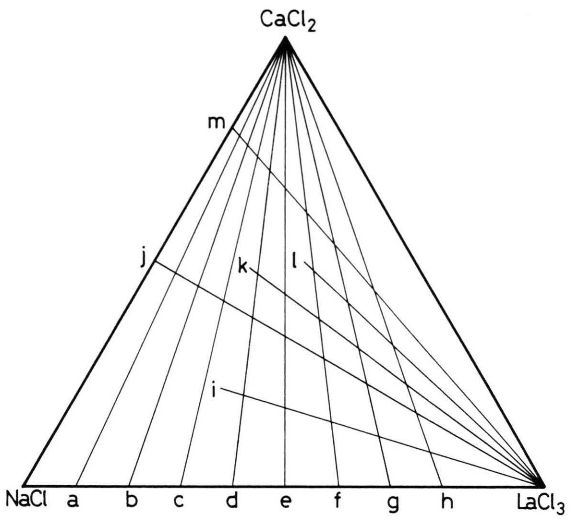


Fig. 4. Quasi-binary lines. a: 10 mol% $LaCl_3$, b: 20, c: 30, d: 40, e: 50, f: 60, g: 70, h: 80, i: 30 mol% $CaCl_2$, j: 50, k: 60, l: 80, m: 80.

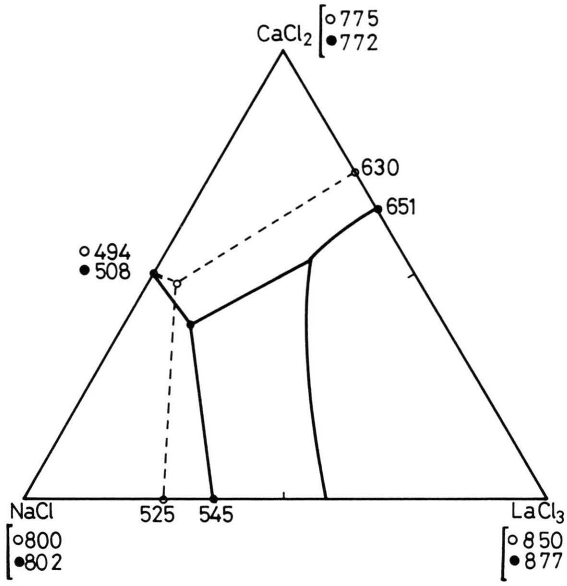


Fig. 6. Comparison with the diagram reported by Morozove et al. [1] (unit: °C). Open circles and dotted lines: [1]. Full circles and solid lines: this work.

there exists a ternary peritectic point instead of the eutectic point. If a peritectic point as in the $PrCl_3-CaCl_2-NaCl$ system [3] exists, and if the point is based on the formation of a binary peritectic compound, a peritectic boundary curve falling to it from the peritectic point in the system $LaCl_3-NaCl$ must be present. However, the curve falls parallel to the line f and is therefore difficult to determine this way. In order to elucidate its existence, the 5 quasi-binary phase diagrams along the lines i – m in Fig. 4 were measured. Apparently these diagrams showed the peritectic boundary curve, and from the curve the temperature and composition of the peritectic point was determined. Finally, the ternary phase diagram was constructed (Fig. 5) according to the phase rule, using all the phase diagrams measured. Point A is the ternary eutectic point, point B the ternary peritectic point, the dotted line presents the Alkemade line, and the double arrows mean the peritectic boundary curve. The composition and temperature at the points marked in Fig. 5 are shown in Table 1.

This ternary phase diagram had been reported by Morozov et al. [1] as of the simple eutectic type. Our result is compared with that of [1] in Figure 6.

Table 1. Composition and temperature at the points marked in Figure 5.

| Point | Temp./°C | Composition/mol% | | |
|---|---|---|---|---|
| | | $LaCl_3$ | $CaCl_2$ | NaCl |
| A | 462 | 12.1 | 39.7 | 48.2 |
| B | 612 | 26.9 | 55.1 | 18.0 |
| C | 508 | 0 | 50.1 | 49.9 |
| D | 545 | 36.1 | 0 | 63.9 |
| E | 690 | 57.5 | 0 | 42.5 |
| F | 651 | 35.1 | 64.9 | 0 |

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