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In celebration of the 60^{th} birthday of Dr. Andrew K. Galwey

THE TERNARY SYSTEM $CsCl–NaCl–LaCl_3$

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Abstract

The ternary system $CsCl–NaCl–LaCl_3$ was investigated by means of differential thermal analysis and X-ray powder diffraction analysis. There exists one congruently melting compound, $Cs_2NaLaCl_6$, crystallizing with the cubic elpasolite structure. No quasi-binary section exists for the whole system, however three binaries range from the ternary compound $Cs_2NaLaCl_6$ to NaCl, $CsLa_2Cl_7$ and Cs_3LaCl_6 resp., dividing the system in three areas of composition: one triangle, $Cs_3LaCl_6–Cs_2NaLaCl_6–CsLa_2Cl_7$, containing additionally a compound Cs_2LaCl_5 below 510°C, and the two areas $CsCl–NaCl–Cs_2NaLaCl_6–Cs_3LaCl_6$ and $Cs_2NaLaCl_6–NaCl–LaCl_3–CsLa_2Cl_7$, containing a mixed crystal range between $LaCl_3$ and $Na_3La_5Cl_{18}$. These areas could be further divided in five triangles, so that the whole system contains six Alkemade triangles.

Keywords: DTA, ternary system $CsCl–NaCl–LaCl_3$, XRD

Introduction

Recently [1] we have reported on thermochemical investigations of chloro elpasolites of lanthanum. Four compounds A_2BLaCl_6 exist: $Cs_2RbLaCl_6$, Cs_2KLaCl_6, $Cs_2NaLaCl_6$ and Rb_2KLaCl_6. Only the Cs-compounds are stable at ambient temperature. $Cs_3RbLaCl_6$ and Cs_2KLaCl_6 are polymorphous; $Cs_2NaLaCl_6$ crystallizes from ambient temperature up to the (congruent) melting point at 930 K with the cubic aristotype structure in space group Fm3m [2].

In this paper we give the results of an investigation of the ternary system $CsCl–NaCl–LaCl_3$, using differential thermal analysis (DTA) and X-ray diffraction measurements (XRD) on crystal powders. We have done this work as a basis for e.m.f.-measurements for determining the Gibbs-enthalpy, $\Delta G°$, for the formation of $Cs_2NaLaCl_6$ from either the compounds CsCl, NaCl and $LaCl_3$, or from NaCl and the binary compound, Cs_2LaCl_5. First we have ascertained the triangles of existence (compatibility triangles) at ambient temperature with X-ray patterns of quenched and, if necessary, annealed samples of appropriate

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composition. In a second step, suitable sections through the systems were measured with DTA. From the results of both methods the final diagram was constructed.

Experimental

Preparation of the compounds

For the preparation of anhydrous $LaCl_3$, the hydrate $LaCl_3 \cdot 7H_2O$, obtained from a solution of La_2O_3 (p.A., Fa. Merck) in hydrochloric acid, was treated in a vacuum oven at 60°C and then dehydrated by heating in a HCl-stream for one day, raising the temperature slowly from 100 to 700°C. After subsequent cooling, all further manipulations were done in a glove-box. The alkaline metal chlorides (p.A., Fa. Merck) were dried in a HCl-stream at 500°C.

The binary and ternary chloride compounds were obtained by melting adequate mixtures in vacuum-sealed ampoules using a gas flame. The melt was homogenized by shaking and solidified by rapid cooling.

Differential thermal analysis

The home-built DTA device has already been described [3]. The samples (1.5 g) were prepared in the same way as described for the binary chlorides. The solids thus obtained were sufficiently homogeneous for the measurement of heating curves and for annealing experiments. Thermal effects could be detected down to 0.2 J for the generally used heating rate of 2 $deg \cdot min^{-1}$.

All ternary samples on the investigated sections were mixed from the compounds at the corners and not from the compounds CsCl, NaCl and $LaCl_3$. Therefore we established the following expression for determining the molar composition, σ, of each sample:

$$\sigma = \frac{t_1 - X_1 t}{X_1(s - t) + t_1 - s_1}$$

E.g., a sample on the section Cs_3LaCl_6-NaCl which contains 60 mol% CsCl.

Left corner (Cs_3LaCl_6): $s_1 = 3$, $s_2 = 0$, $s_3 = 1$ and $s = s_1 + s_2 + s_3 = 4$

right corner (NaCl): $t_1 = 0$, $t_2 = 1$, $t_3 = 0$ and $t = t_1 + t_2 + t_3 = 1$,

desired concentration of CsCl: $X_1 = 0.6$;

this leads to $\sigma = 0.5$, which means that the sample contains 50 mol% Cs_3LaCl_6

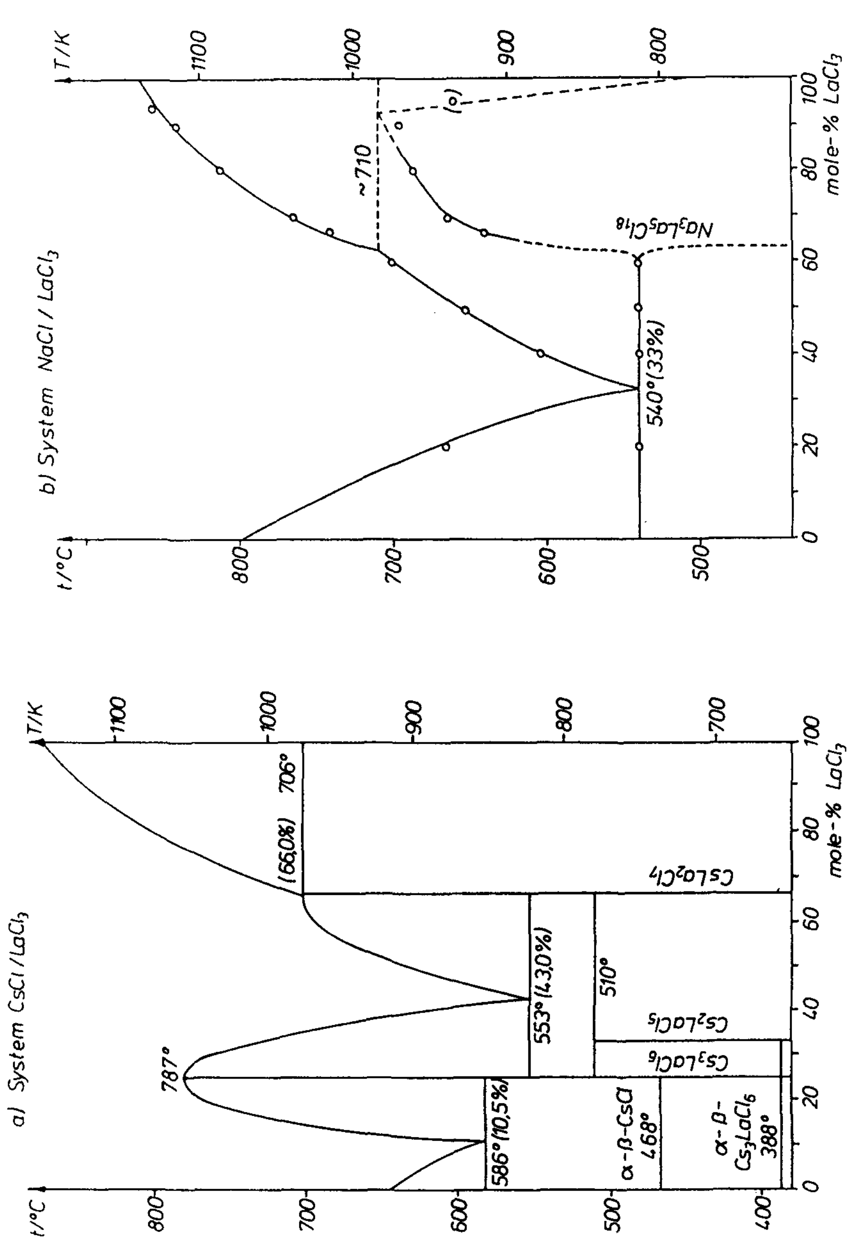

Fig. 1 The binary systems CsCl–LaCl3 and NaCl–LaCl3

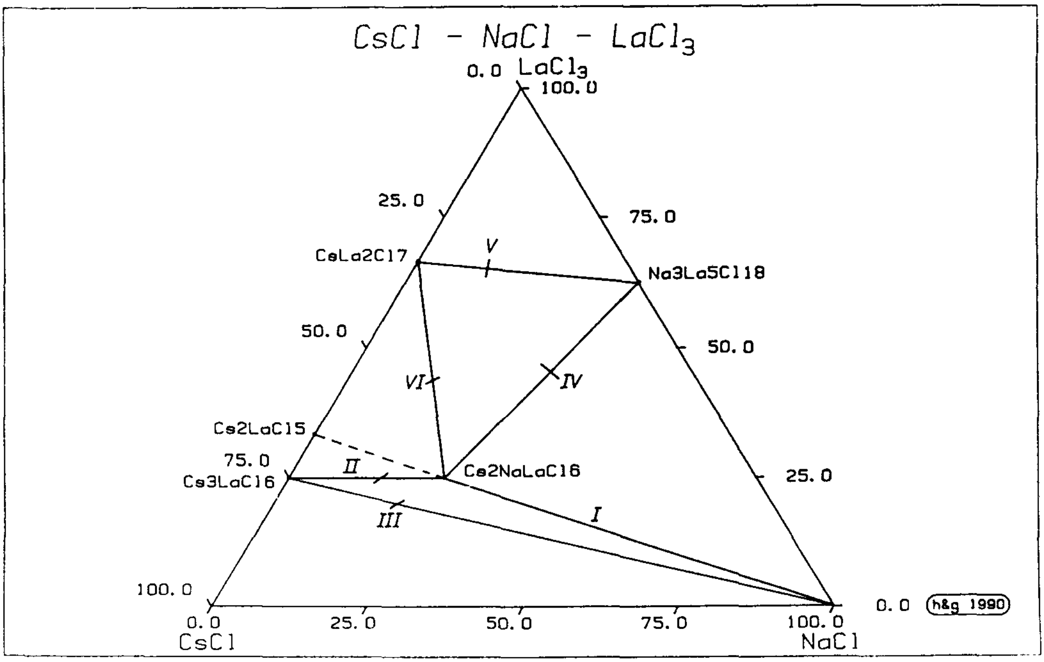

Fig. 2 The compatibility triangles

It must be pointed out that the temperatures in the binary systems CsCl–$LaCl_3$ and NaCl–$LaCl_3$, previously measured [4], are 'onset-temperatures' from heating-curves and therefore 'kinetic-temperatures' which are in general too high, as we have discussed elsewhere [5]. For instance, for the phase-transition α-β-Cs_3LaCl_6 the temperature from heating-curves was found at 401°C; in the ternary system 388°C was observed, probably under the catalytic effect of additional Na-containing compounds; recent e.m.f.-measurements gave a 'thermodynamic temperature' of 386°C [6]. Otherwise, the temperatures for the boundary curves are 'peak-temperatures' and, therefore, somewhat higher than the temperatures for the invariant points taken from onset-effects. This issue is known from binary systems too [5].

X-ray diffraction

Powder patterns at ambient temperature were taken with a Philips PW 1050/25 goniometer equipped with a proportional counter and a vacuum attachment. During exposure (CuK_α-radiation) the samples were under He atmosphere.

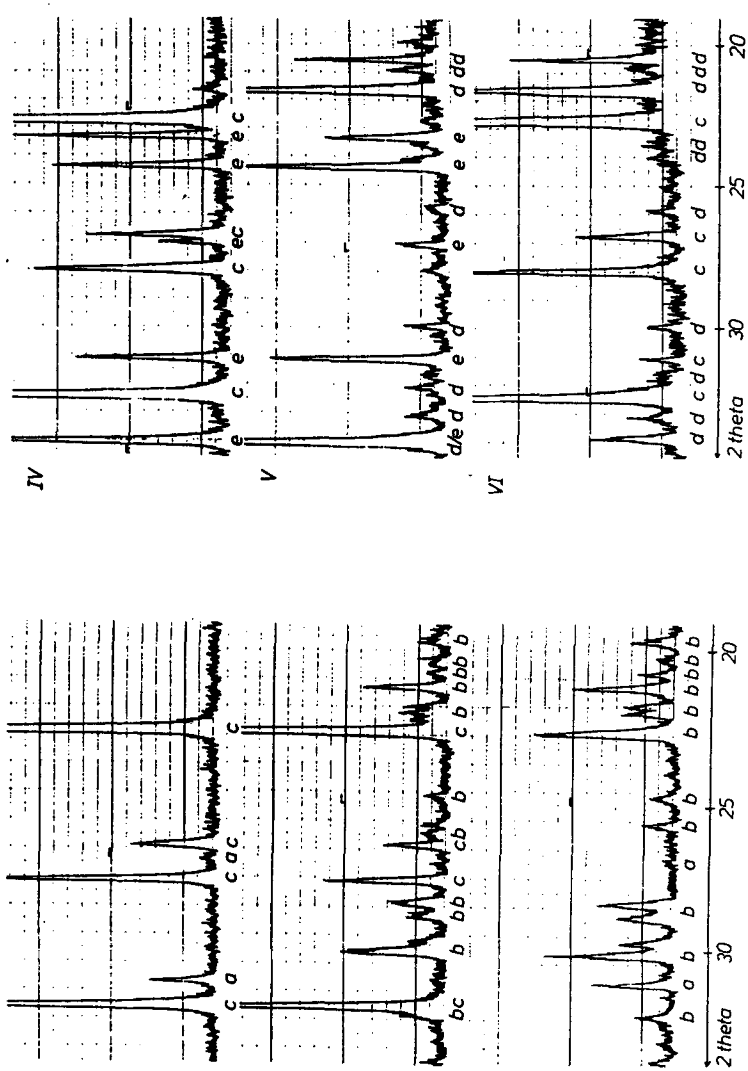

Fig. 3 X-ray patterns (CuK_α radiation) (a = NaCl, b = Cs_3LaCl_6, c = $Cs_2NaLaCl_6$, d = $CsLa_2Cl_7$, e = $Na_3La_5Cl_{18}$)

Results

The constituent binary systems

The system CsCl–NaCl is purely eutectic [7]. The eutectic temperature is 486°C (65 mol% CsCl). The phase diagrams of the (pseudo-) binary systems $CsCl$–$LaCl_3$ and $NaCl$–$LaCl_3$ were elucidated earlier by ourselves [4]. In the system $CsCl$–$LaCl_3$ (Fig. 1a) three compounds exist: Cs_3LaCl_6 (congruently melting; solid state transition at 388°C), Cs_2LaCl_5 (stable in the solid state up to 510°C), $CsLa_2Cl_7$ (congruently melting at 706°C). The system is shown in Fig. 1a in a revised form, taking into account the considerations given above. The system $NaCl$–$LaCl_3$ (Fig. 1b) is eutectic, containing a range of solid solutions from $Na_3La_5Cl_{18}$ to $LaCl_3$, up to ~710°C.

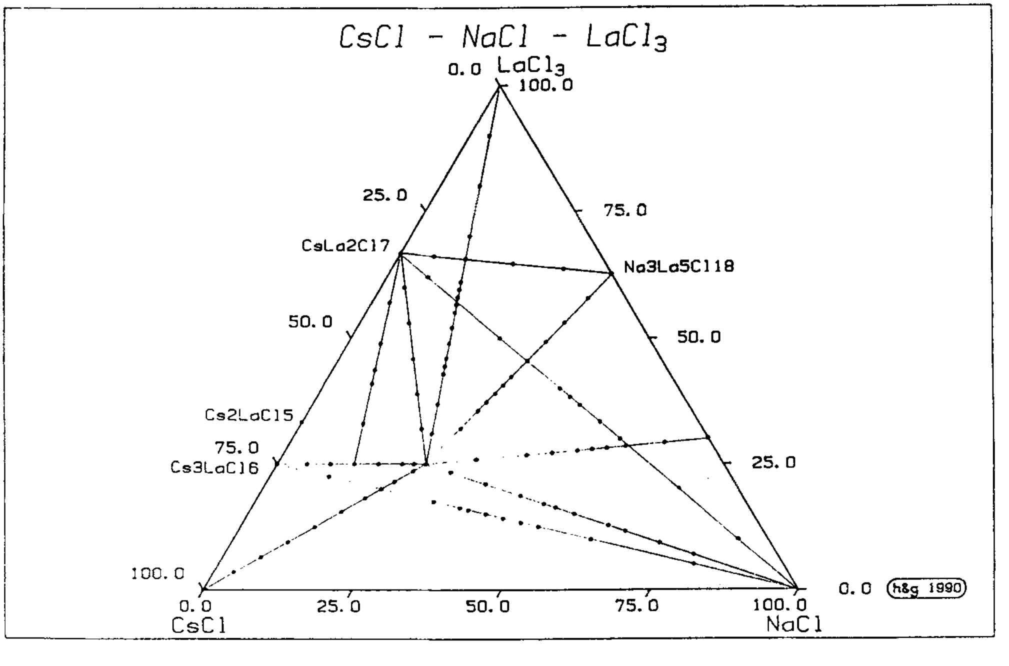

Fig. 4 Composition of samples for DTA measurements with their related sections

The compatibility triangles (Fig. 2)

The system $CsCl$–$NaCl$–$LaCl_3$ with four binary compounds and the ternary elpasolite (abbr. *Q*) can be subdivided in seven triangles, which describe (at ambient temperature) equilibrium areas of in each case three compounds, the sides are the two-phase-lines of the compounds at the corners they connect. Eleven possibilities for such a triangulation exist. For instance, in the area CsCl–NaCl-$Cs_2NaLaCl_6$–Cs_3LaCl_6 two diagonal equilibrium lines are possible: the line Cs_3LaCl_6–NaCl or CsCl–$Cs_2NaLaCl_6$. Which is real can be decided by an X-ray pattern of a sample with the composition of the intersection of the two lines (point III in Fig. 2): in the first case it must consist of Cs_3LaCl_6 and NaCl, in the second case of CsCl and $Cs_2NaLaCl_6$. To ensure equilibrium composition, the sample was quenched from the melt and then annealed at ~380°C.

Six X-ray measurements (Fig. 3) were necessary, but also sufficient. Only point I Fig. 2 was not an intersection of possible triangle sides. The line Cs_3LaCl_5–$Cs_2NaLaCl_6$ is drawn interrupted, because the compound Cs_2LaCl_5 has a solid state decomposition at 510°C. Therefore no primary solidification area exists for this compound.

DTA investigations

All DTA measurements and the related sections are collected in Fig. 4. With two exceptions, all sections extend between two compounds. The remaining two sections were selected in order to cover the system evenly with sections and to enable the determination of all ternary eutectic points. DTA investigations revealed that three of the seven equilibrium lines, all starting from the quaternary compound Q, are quasi-binary sections. The three phase diagrams for them (Q–Cs_3LaCl_6, Q–NaCl and Q–$CsLa_2Cl_7$) are shown in Fig. 5. Thus we have to deal with three areas which are independent, since they do not contain any compound from outside. These are: a) the triangle Cs_3LaCl_6–Q–$CsLa_2Cl_7$, b) the quadrangle CsCl–NaCl–Q–Cs_3LaCl_6 and c) the quadrangle Q–NaCl-$LaCl_3$–$CsLa_2Cl_7$.

The area Cs_3LaCl_6–$Cs_2NaLaCl_6$--$CsLa_2Cl_7$

In addition to the phase diagrams CsCl–$LaCl_3$ (Fig. 1a), Cs_3LaCl_6–Q and Q–$CsLa_2Cl_7$ (Fig. 5), we have used the diagram, given in Fig. 6a, to construct the liquid-solid diagram for the triangle. The result is depicted in Fig. 7: Starting from the binary eutectic e_3 and the saddle-points of Fig. 5a and 5c, the three boundary curves converge in the invariant point E_3, a ternary eutectic. It must be pointed out that below 510°C a further compound, Cs_2LaCl_5, is formed, stable only in the solid state.

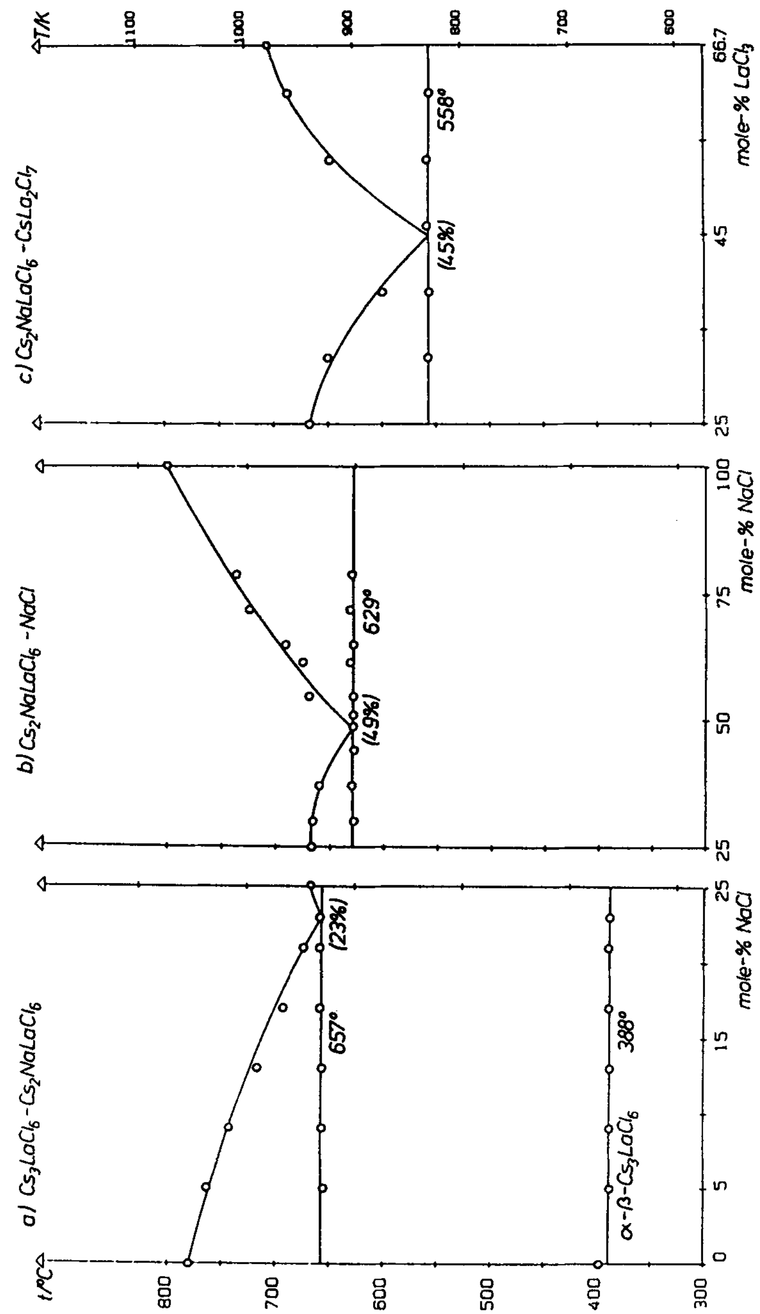

Fig. 5 Phase diagrams for the quasi-binary secting from $Cs_2NaLaCl_6$ (Q): a) Cs_3LaCl_6–$Cs_2NaLaCl_6$, b) $Cs_2NaLaCl_6$–NaCl, c) $Cs_2NaLaCl_6$–$CsLa_2Cl_7$

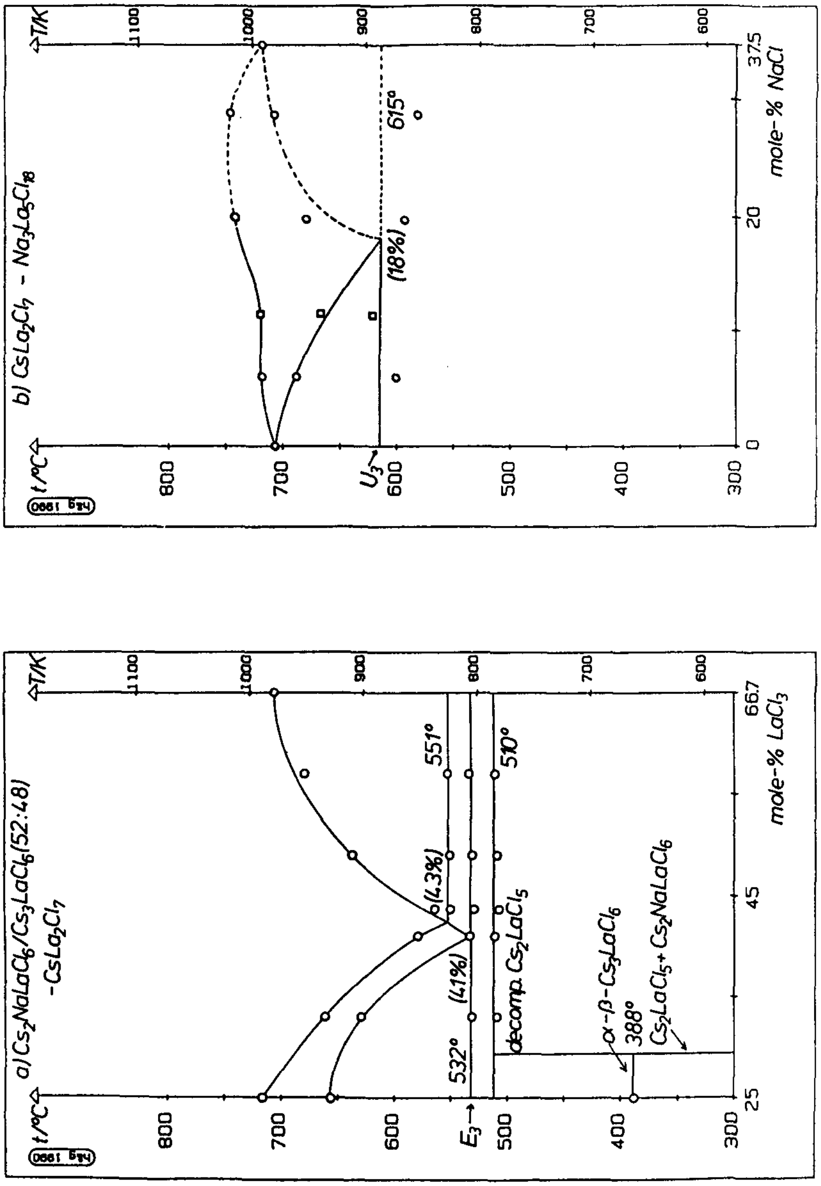

Fig. 6 Phase diagrams: a) $Cs_2NaLaCl_6/Cs_3LaCl_6(52:48)$–$CsLaCl_7$, b) $CsLa_2Cl_7$–$Na_3La_5Cl_{18}$

The area $CsCl$–$NaCl$–$Cs_2NaLaCl_6$–Cs_3LaCl_6

In addition to the edge diagrams $CsCl$–$NaCl$, $CsCl$–$LaCl_3$ (Fig. 1a), Cs_3LaCl_6–*Q* (Fig. 5a) and *Q*-$NaCl$ (Fig. 5b), two further diagrams were used: $CsCl$–*Q* and Cs_3LaCl_6–$NaCl$ (Fig. 8). Two valleys (boundary curves), starting from the saddle-points of Fig. 5a and 5b, converge in the ascending fork-point (semi-eutectic point) U_1. From there and from the eutectic e_1 and e_4 three boundary curves run together in the ternary eutectic E_1.

The area Cs_3LaCl_5–$NaCl$–$LaCl_3$–$CsLa_2Cl_7$

In this area, a complication exists in the solid state, concerning the mixed crystal range between $LaCl_3$ and $Na_3La_5Cl_{18}$. We have neglected this and have treated the system $NaCl$–$LaCl_3$ (Fig. 1b) as if only the peritectic would exist at ~710°C. The DTA measurements used for the construction of the liquid-solid surface can be taken from Fig. 4. The phase diagrams of the sections, not yet described, are given in Figs 6b and 9. An ascending fork-point U_3 is formed by two valleys, coming down from the binary peritectic u1 and u_2. From there and from the saddle-point of the section *Q*–$CsLa_2Cl_7$ (Fig. 5c) a further ascending fork-point, U_2, is reached. The lowest invariant point of the whole quadrangle, the ternary eutectic E_2, is the meeting point of valleys from U_2, the saddle-point of the section *Q*–$NaCl$ and the eutectic e_2 from the edge system $NaCl$–$LaCl_3$.

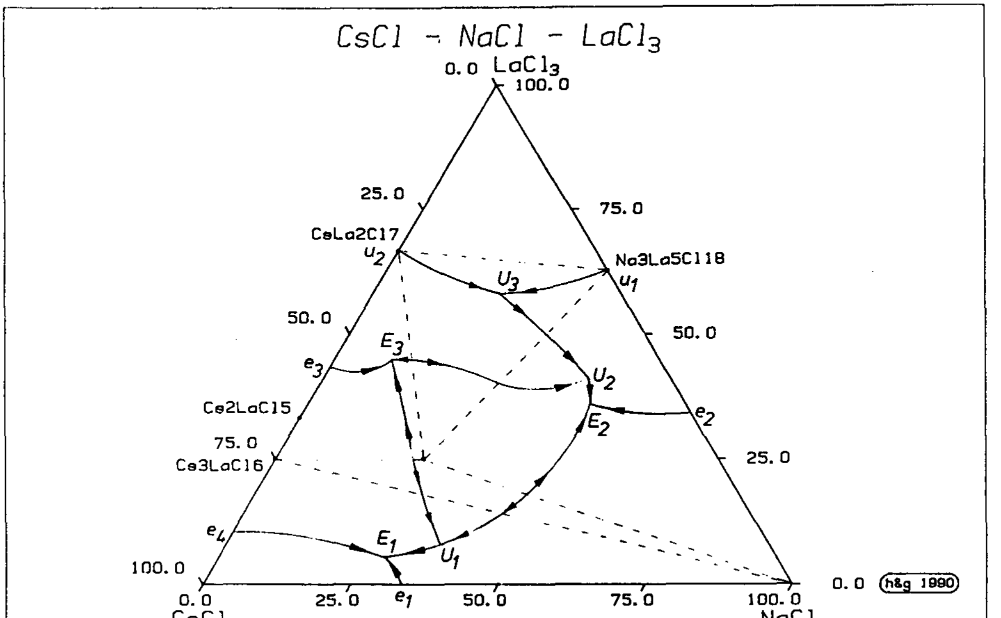

Fig. 7 Boundary curves in the ternary system $CsCl$–$NaCl$–$LaCl_3$

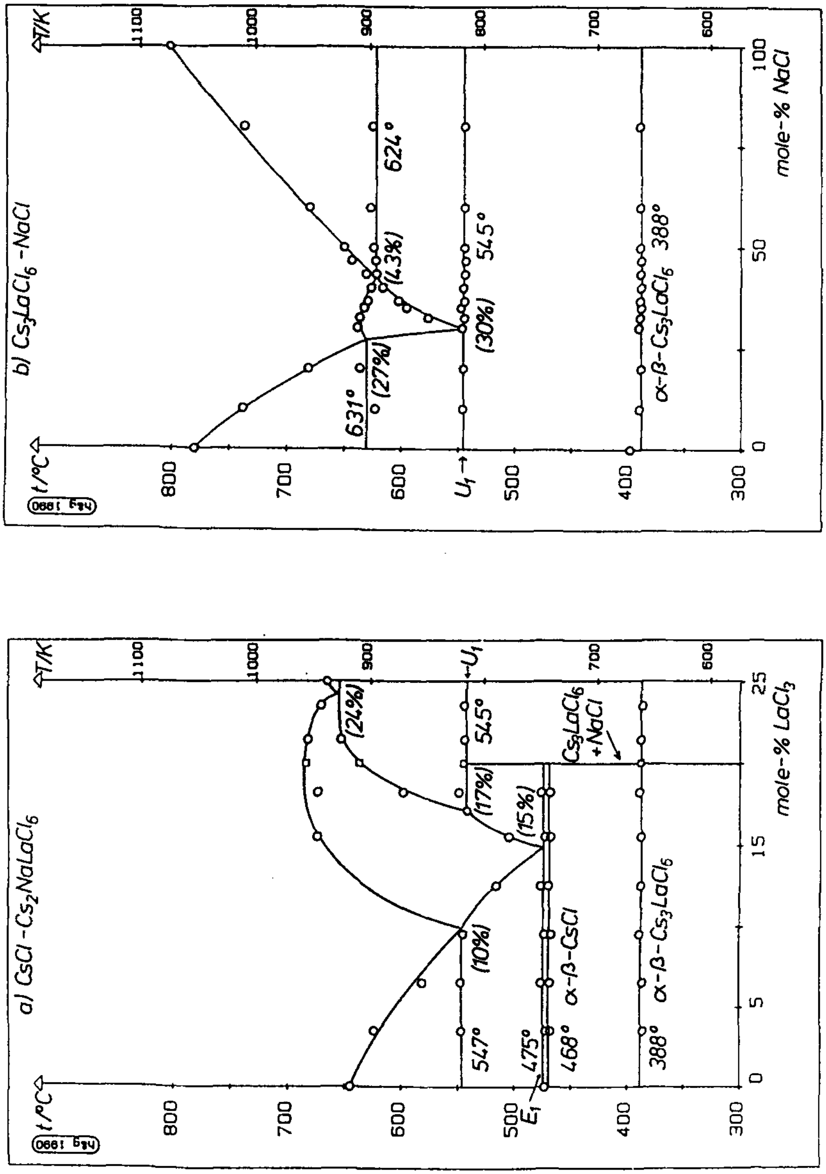

Fig. 8 Phase diagrams: a) CsCl–$Cs_2NaLaCl_6$, b) Cs_3LaCl_6–NaCl

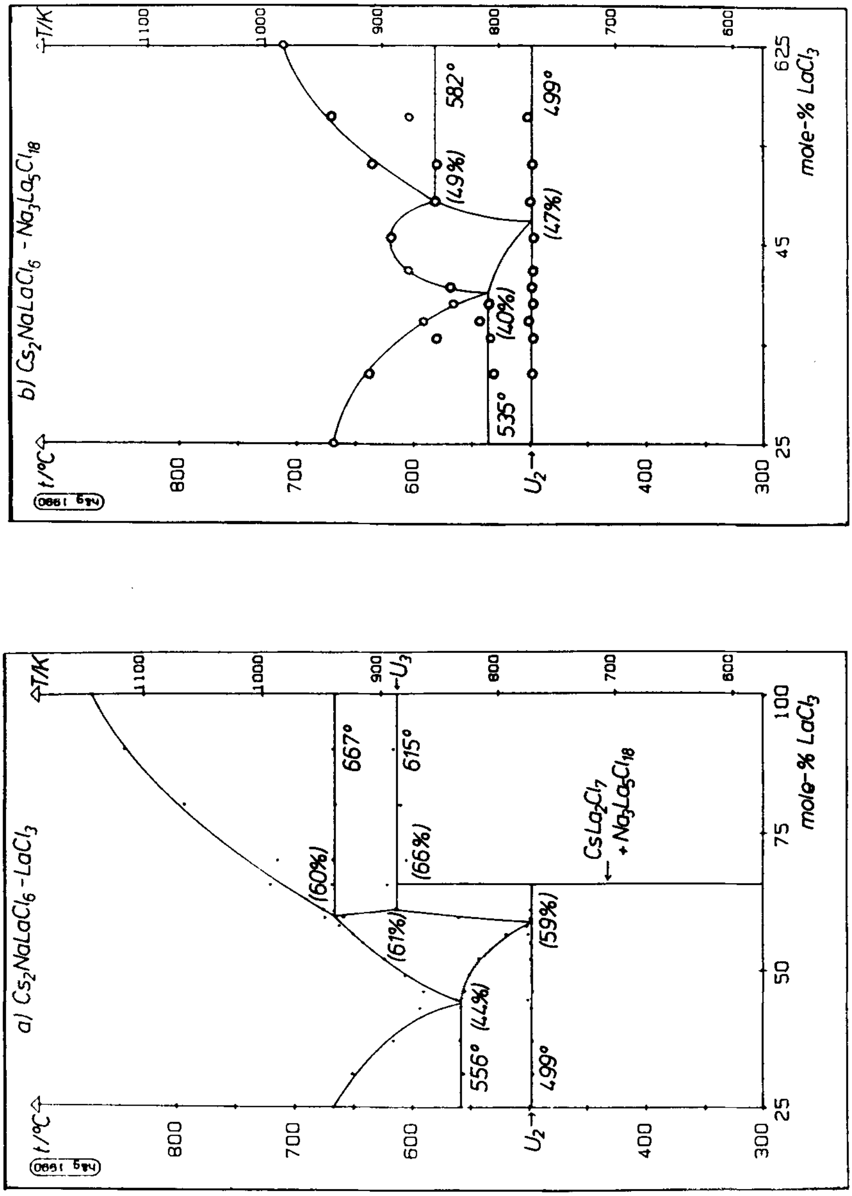

Fig. 9 Phase diagrams of sections from $Cs_2NaLaCl_6$ to a) $LaCl_3$, b), $Na_3La_5Cl_{18}$

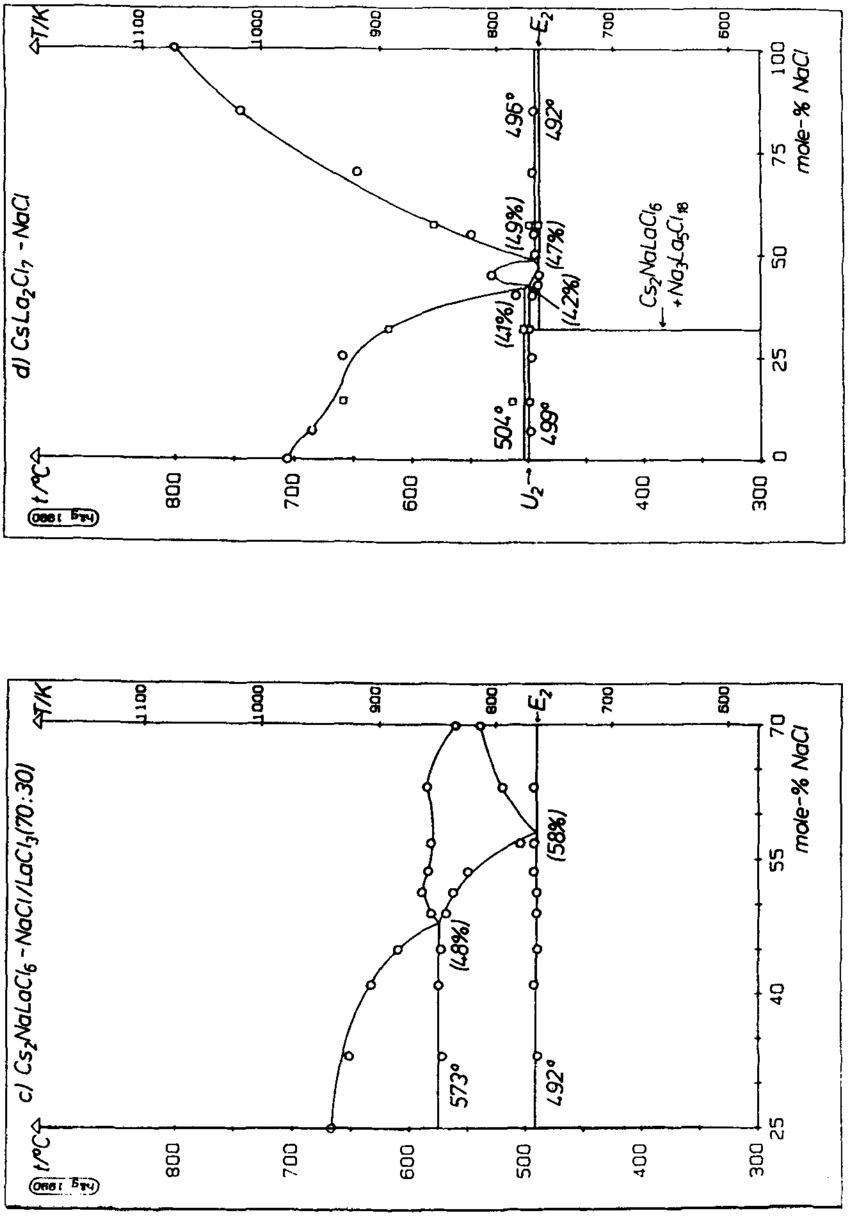

Fig. 9 Phase diagrams of sections from $Cs_2NaLaCl_6$ to c) NaCl/$LaCl_3$(70:30) and d) $CsLa_2Cl_7$–NaCl

Conclusion

The ternary phase diagram CsCl–NaCl–$LaCl_3$ with some main isotherms shown in Fig. 10. In Table 1 the compositions and the temperatures of the invariant points are complied.

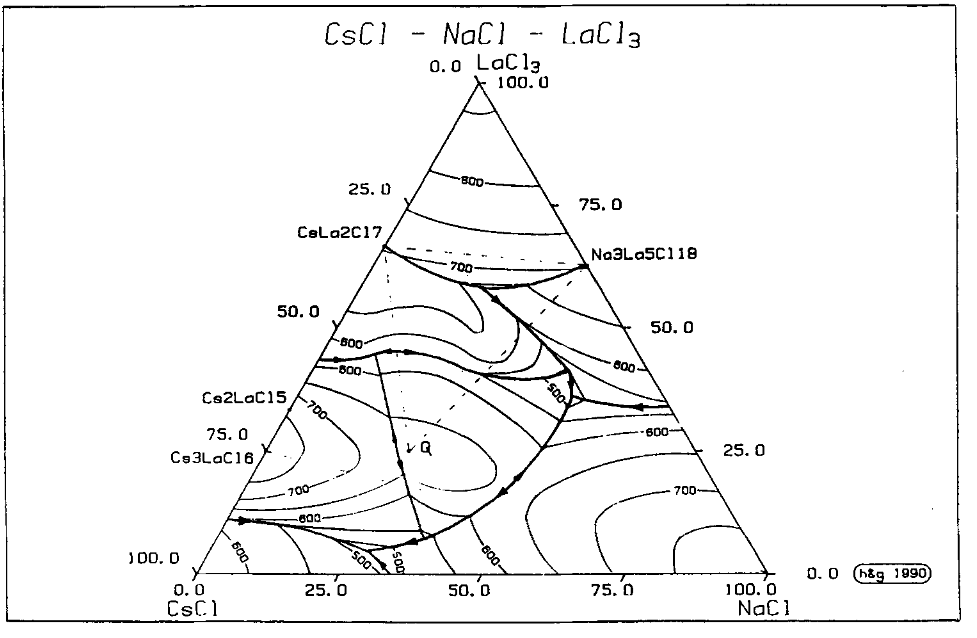

Fig.10 The system CsCl–NaCl–$LaCl_3$

Table 1 Compositions and temperatures of the ternary invariant points (For the binary systems see Fig. 1)

	mol%			
	$LaCl_3$	NaCl	t/°C	Reaction
U_1	8	37	545	L + $Cs_2NaLaCl_6$ → Cs_3LaCl_6 + NaCl
U_2	41	45	499	L + $CsLa_2Cl_7$ → $Cs_2NaLaCl_6$ + $Na_3La_5Cl_{18}$
U_3	57	22	615	L + $LaCl_3$ → $CsLa_2Cl_7$ + $Na_3La_5Cl_{18}$
E_1	5	29	475	L → CsCl + NaCl + Cs_3LaCl_6
E_2	36	48	492	L → $Cs_2NaLaCl_6$ + NaCl + $Na_3La_5Cl_{18}$
E_3	45	10	532	L → Cs_3LaCl_6 + $Cs_2NaLaCl_6$ + $CsLa_2Cl_7$

Concerning the liquid-solid surfaces, there are three binaries: NaCl–$Cs_2NaLaCl_6$, Cs_3LaCl_6–$Cs_2NaLaCl_6$ and $CsLa_2Cl_7$–$Cs_2NaLaCl_6$. The other composition joints are ternary sections in the system. However, below 510°C, the temperature for the formation of Cs_2LaCl_5, the section Cs_2LaCl_5–NaCl is built up of two solid phase regions: Cs_2LaCl_5–$Cs_2NaLaCl_6$ and $Cs_2NaLaCl_6$–NaCl. Thus, it must be possible to construct a galvanic cell for solids in which the reaction $NaCl+Cs_2LaCl_5 = Cs_2NaLaCl_6$ is performed. However, it is absolutely necessary to use a compound Cs_2LaCl_5 with exact stoichiometric composition; otherwise one would come into three-phase regions with an additional compound of the binary system CsCl–$LaCl_3$.

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Zusammenfassung — Das ternäre System CsCl–NaCl–$LaCl_3$ wurde mittels Differenzthermoanalyse und Röntgenbeugungsmessungen an Kristallpulvern untersucht. Es existiert eine kongruent schmelzende Verbindung $Cs_2NaLaCl_6$, die im kubischen Elpasolith-Typ kristallisiert. Es liegt kein quasibinärer Schnitt für das gesamte System vor, jedoch drei solcher Teilschnitte, die von der ternären Verbindung $Cs_2NaLaCl_6$ zu NaCl, $CsLa_2Cl_7$ bzw. Cs_3LaCl_6 verlaufen. Sie unterteilen das System in ein Dreieck Cs_3LaCl_6–$Cs_2NaLaCl_6$–$CsLa_2Cl_7$, das zusätzlich eine nur unterhalb von 510°C stabile Verbindung Cs_2LaCl_5 enthält, sowie die zwei Gebiete CsCl–NaCl–$Cs_2NaLaCl_6$–Cs_3LaCl_6 und $Cs_2NaLaCl_6$–NaCl–$LaCl_3$–$CsLa_2Cl_7$ mit einem Mischkristallgebiet zwischen $LaCl_3$ und $Na_3La_5Cl_{18}$. Die beiden genannten Gebiete lassen sich in fünf Dreiecke zerlegen, so dass das ternäre System insgesamt sechs Kompatibilitätsdreiecke enthält.