

INTERACTION OF THULIUM, YTTERBIUM(III) AND LUTETIUM CHLORIDES WITH SODIUM CHLORIDE

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Abstract

The pseudobinary systems NaCl–LnCl₃ (Ln=Tm, Yb, Lu) were investigated by DTA and X-ray diffraction. Two types of ternary chlorides exist: congruently melting compounds Na₃LnCl₆ with the cryolite-structure, incongruently melting compounds NaLnCl₄ with the NaErCl₄–Ln (Ln=Tm) or the NaLnCl₄-structure (Ln=Yb, Lu). All these structure types contain [LnCl₆]-octahedra.

By solution calorimetry and *e.m.f.* measurements in galvanic cells for solid electrolytes could be proved that all compounds are formed from NaCl and LnCl₃ by gain in lattice enthalpy.

Keywords: crystal structures, phase diagrams, ternary lanthanide chlorides, thermodynamic properties

Introduction

In a preceding publication [1] we have shown that in the systems NaCl–HoCl₃ and NaCl–ErCl₃ the tendency of forming compounds with octahedrally coordinated Ln³⁺-ions with decreasing radii of these cations is continued. The series of investigations about ternary sodium lanthanide chlorides is finished and completed with this paper which contains our results on the corresponding systems with TmCl₃, YbCl₃ and LuCl₃.

DTA measurements on the systems NaCl–YbCl₃ and NaCl–LuCl₃ were performed in 1968 by Korshunov *et al.* [2]. They found in both systems incongruently melting compounds Na₃LnCl₆. Meyer and coworkers determined the crystal structure of all 3:1-compounds [3] and also of compounds NaLnCl₄ with Ln=Tm, Yb [4] and Ln=Lu [5].

Experimental

Chemicals

Starting compounds were the hexahydrates LnCl₃·6H₂O, prepared from solutions of Ln₂O₃ (99.9%, Heraeus/Hanau) in hot hydrochloric acid. The hexahydrates loose water at ~80°C, forming trihydrates. Further dehydration to LnCl₃·H₂O at 100–120°C

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and to anhydrous LnCl_3 at 180–220°C must be performed in a HCl-stream to avoid hydrolysis. For a sample of 10 g, the last step needs three days slow temperature elevation.

NaCl (p.a., Merck, Darmstadt) was dried in a HCl-stream at 500°C.

DTA

The DTA measurements were performed in a home-built device for samples (~0.5 g) in vacuum-sealed silica glass ampoules. Samples with less than 50 mol% LnCl_3 were homogenized by melting in a gas flame, shaking and annealing. Because melts of the trichlorides react with silica, LnCl_3 -rich mixtures were melted in the DTA furnace approximately 20 K above the alleged liquidus temperatures.

X-ray investigations

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 kept under He-atmosphere. Corundum powder was used as internal standard; at 20°: $a_{\text{hex}}=475.92$ pm, $c_{\text{hex}}=1299.00$ pm.

Solution calorimetry

The heats of solution were measured using an isoperibolic underwater calorimeter firstly described in 1978 [6]. In a silver vessel of 1.3 l volume samples of 2–4 g in thin-walled glass ampoules are cracked under water at the beginning of the measurement. The change of temperature ΔT vs. the surroundings, a thermostat with a temperature constancy of $2 \cdot 10^{-4}$ K, generated by the solution enthalpy is measured with a thermopile. The calibration is done by Joule's heat.

At least two samples of each substance were measured. From the enthalpies of solution, $\Delta_{\text{sol}}H_{298}^\circ$, the enthalpies of formation of the ternary chlorides from ($n\text{NaCl}+\text{LnCl}_3$), $\Delta_f H_{298}^\circ$, were calculated according to:

$$\Delta_f H^\circ = [\Delta_{\text{sol}}H^\circ(\text{LnCl}_3) + n\Delta_{\text{sol}}H^\circ(\text{NaCl})] - \Delta_{\text{sol}}H^\circ(\text{A}_n\text{LnCl}_{3+n})$$

E.m.f. measurements

A detailed description of the galvanic cell was given earlier [7]. It was not possible to obtain stable potentials for samples with more than 50 mol% LnCl_3 . Thus, only potentials generated by the solid state reactions $2\text{NaCl}+\text{NaLnCl}_4=\text{Na}_3\text{LnCl}_6$, could be measured in the temperature range of 300–400°C. The solid electrolytes (compressed discs) were separated by Na^+ -conducting diaphragms of sintered glass powder.

Phase diagrams and crystal structures

The phase diagrams of the three investigated systems together with the previously elucidated diagram for the system $\text{NaCl}-\text{ErCl}_3$ [1] are given in Fig. 1. The

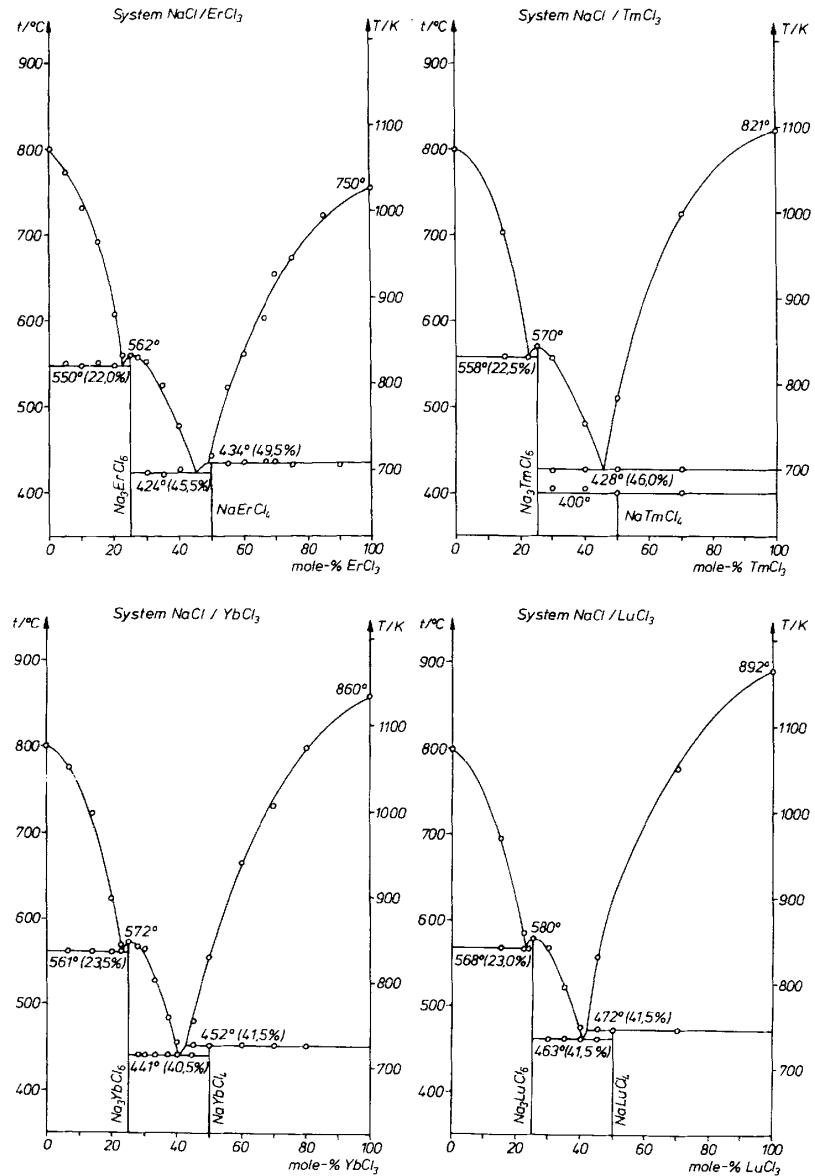


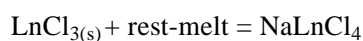
Fig. 1 Phase diagrams of the systems NaCl-LnCl₃ (Ln=Er, Tm, Yb, Lu)

data were in general taken from heating curves, however, for the liquidus curves near the eutectics also temperatures from cooling curves were used.

Compared with the findings of Korshunov [2] – eutectic systems, even with one incongruently melting compound Na₃LnCl₆ – two differences exist:

1. The compounds Na_3LnCl_6 are congruently melting with distectica near the eutectic at the NaCl-rich side and less than ten degrees above the eutectic temperatures. The congruently melting was proved accurately for the system NaCl–YbCl₃ by measurements of five compositions in the range 20–30 mol% YbCl₃.

2. Additionally, incongruently melting compounds NaLnCl_4 with peritectica ~10 degrees above the eutectics at ~40 mol% LnCl₃. Because of the relatively far distance in composition and temperature of the next neighbour compound in the phase diagram, namely the pure trichloride LnCl₃, in the range 50–80 mol% LnCl₃ peaks for the eutectic temperature are still found, originated by incomplete peritectic reactions



Equilibrium conditions could be obtained by annealing samples, quenched from the melt, for approximately two weeks at temperatures ~10 degrees below the peritectic temperatures. Heating curves with these annealed samples exhibited only one peak at the peritectic temperature.

X-ray diffraction on crystal powders approved with one exception the results of Meyer and coworkers. Thus, all compounds Na_3LnCl_6 have the cryolite structure [3]; also the structures of NaErCl₄ [4] NaLuCl₄ [5] could be confirmed. However, for NaYbCl₄ we found the NaLuCl₄-type structure and not that of the NaErCl₄-type. In the NaErCl₄-type strong reflections must exist, e.g. at $\theta=7.06$ (1 0 0), $\theta=11.19$ (1 1–1), $\theta=11.51$ (1 1 1) [4], they were not observed.

NaYbCl₄ in S.G. Pbcn, Z=4 (NaLuCl₄-type)

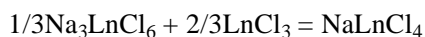
$$a = 626.01(2), b = 1612.0(7), c = 655.93(2), V_{\text{mol}} = 99.6 \text{ cm}^3 \text{ mol}^{-1}$$

Thermodynamic properties

For solution calorimetry the 3:1-compounds could be prepared directly by melting mixtures of appropriate composition in sealed quartz glass ampoules, while the compounds NaLnCl_4 must be annealed after quenching for at least one week at temperatures ~10 degrees beneath the peritectic temperatures. The success of the annealing process was controlled by XRD. The solution enthalpies $\Delta_{\text{sol}}H_{298}^0$ (in kJ mol⁻¹) of the binary compounds are [8]:

$$\text{NaCl} = 4.5; \text{TmCl}_3 = -212.2; \text{YbCl}_3 = -212.9; \text{LuCl}_3 = -211.6$$

The solution enthalpies of the ternary chlorides and their enthalpies of formation from the binary compounds, $\Delta_f H_{298}^0$, are compiled in Table 1, in the fourth column syn-reaction enthalpies, $\Delta_{\text{syn}} H_{298}^0$, are given. These are the enthalpies of formation from the two adjacent compounds in the phase diagrams according to the following equations:



$$\Delta_{\text{syn}}H_{298}^{\circ}(\text{NaLnCl}_4) = \Delta_{\text{f}}H_{298}^{\circ}(\text{NaLnCl}_4) - 1/3\Delta_{\text{f}}H_{298}^{\circ}(\text{Na}_3\text{LnCl}_6)$$

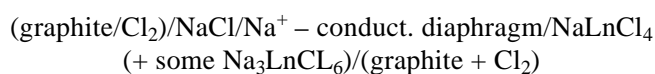


$$\Delta_{\text{syn}}H_{298}^{\circ}(\text{Na}_3\text{LnCl}_6) = \Delta_{\text{f}}H_{298}^{\circ}(\text{Na}_3\text{LnCl}_6) - \Delta_{\text{f}}H_{298}^{\circ}(\text{NaLnCl}_4)$$

Table 1 Solution enthalpies and derived enthalpy values (in kJ mol⁻¹)

Compound	$\Delta_{\text{sol}}H_{298}^{\circ}$	$\Delta_{\text{f}}H^{\circ}$	$\Delta_{\text{syn}}H^{\circ}/\text{calor.}$	$\Delta_{\text{syn}}H^{\circ}/e.m.f.$
NaTmCl ₄	-200.6(4)	-7.1	-3.5	-
NaYbCl ₄	-189.4(3)	-19.0	-10.6	-
NaLuCl ₄	-206.2(2)	-1.1	+1.9	-
Na ₃ TmCl ₆	-187.9(6)	-10.8	-3.7	-3.4
Na ₃ YbCl ₆	-173.6(7)	-25.1	-6.1	-5.8
Na ₃ LuCl ₆	-189.1(12)	-9.0	-7.9	-8.2

The thermodynamic functions of the syn-reactions for Na₃LnCl₆ could be obtained directly from *e.m.f.*-measurements in cells with the set-up:



In the temperature range 300–400°C the *e.m.f.*-values are linearly dependent on *T*. Thus, the regression equations $e.m.f./\text{mV} = a + bT/\text{K}$ could be transformed to the Gibbs-Helmholtz-equations, $\Delta G^{\circ}/\text{kJ mol}^{-1} = \Delta H^{\circ} - \Delta ST/\text{K}$ by multiplication with $-2F$, using the relation $\Delta G^{\circ} = -nF e.m.f.$ Values $\Delta_{\text{syn}}H^{\circ}/e.m.f.$ are given in the last column of Table 1. They are not very different from the $\Delta_{\text{syn}}H^{\circ}/\text{calor.}$ -values.

Results (mean of two measurements)

Na₃TmCl₆:

$$\begin{aligned} \overline{e.m.f.}/\text{mV} &= 17.7 + 0.1107T/\text{K} \\ \Delta_{\text{f}}G^{\circ}/\text{kJ mol}^{-1} &= -3.4 - 0.0214T/\text{K} \end{aligned}$$

Na₃YbCl₆:

$$\begin{aligned} \overline{e.m.f.}/\text{mV} &= 30.0 + 0.1032T/\text{K} \\ \Delta_{\text{f}}G^{\circ}/\text{kJ mol}^{-1} &= -5.8 - 0.0199T/\text{K} \end{aligned}$$

Na₃LuCl₆:

$$\begin{aligned} \overline{e.m.f.}/\text{mV} &= 42.7 + 0.0792T/\text{K} \\ \Delta_{\text{f}}G^{\circ}/\text{kJ mol}^{-1} &= -8.2 - 0.0153T/\text{K} \end{aligned}$$

Discussion

In our last paper on the systems NaCl–HoCl₃ and NaCl–ErCl₃ [1] we have discussed the variation of compounds, their structures and stabilities in the series Eu³⁺ to Er³⁺. We had found that with holmium the last compounds with seven-coordinated Ln³⁺ – NaHo₂Cl₇ and T-NaHoCl₄ – exist. Beginning with erbium only two compounds with octahedrally coordinated Ln³⁺ – Na₃LnCl₆ and NaLnCl₄ – exist. We predicted, that this should hold also for the three last lanthanides, Tm, Yb and Lu. This prognosis was confirmed by this paper.

However, also the IIIA group elements can be included. While yttrium has the same features as holmium [9] with nearly identical ionic radius [10], scandium ($r=0.75 \text{ \AA}$) is smaller than lutetium ($r=0.86 \text{ \AA}$). Meyer and coworkers have shown, that the two existing chloro-scandates, Na₃ScCl₆ [11] and NaScCl₄ [12] have the same crystal structures as the Lu-compounds.

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