

## Review Papers

# TERNARY CHLORIDES OF THE TRIVALENT LATE LANTHANIDES

## Phase diagrams, crystal structures and thermodynamic properties

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A comprehensive review on phase diagrams, crystal structures and thermodynamic properties of ternary chlorides formed in the systems  $ACl/LnCl_3$  ( $A=Na, K, Rb, Cs$ ) is presented. It continues an earlier review with the same contents on the lanthanides from La to Gd [1]. In both papers the author's own studies, published since 1985, together with original papers from other scientists are treated. With the three larger cations compounds of the composition  $A_3LnCl_6$ ,  $A_2LnCl_5$ ,  $ALn_2Cl_7$  and beginning with holmium  $Cs_3Ln_2Cl_9$  are formed. With sodium the compounds  $Na_3Ln_5Cl_{18}$  ( $Ln=La$  to  $Sm$ ) and  $NaLnCl_4$  ( $Ln=Eu$  to  $Lu$ ) also exist. The stability of a ternary chloride in a system  $ACl/LnCl_3$  is given by the 'free enthalpy of synreaction', the formation of a compound from its neighbour compounds in its system. This  $\Delta G_{syn}^0$  must be negative. A surprising result is that the highest – melting compounds in the systems,  $A_3LnCl_6$ , are formed from  $ACl$  and  $A_2LnCl_5$  with a loss of lattice energy,  $U$ . They exist as high-temperature compounds due to a sufficiently high gain in entropy at temperatures where the entropy term  $T\Delta S$  compensates the endothermic  $\Delta H$ .

**Keywords:** alkali-metal, crystal structures, phase diagrams, lanthanide ions, ternary chlorides, thermodynamic data

### Introduction

Recently a comprehensive review on phase diagrams, crystal structures and thermodynamics of ternary chlorides formed in systems  $ACl-LnCl_3$  ( $A=Na, K, Rb, Cs$ ;  $Ln=La-Gd$ ) was published in this journal [1]. The paper summarized the authors own studies, published since 1985, and original papers of other scientists. The present compilation completes this synopsis with the heavier lanthanide metals, including yttrium, where the ionic radius of its trivalent cation is comparable with those of holmium and erbium.

Again we have elucidated the phase diagrams with DTA using samples of ~0.5 g, encapsulated in quartz ampoules. This technique allows for the annealing of samples after quenching them from the melt or from existing high-temperature phases, so that heating curves and also X-ray powder patterns could be performed with material in the stable state. Because  $LiCl$  melts react with quartz, systems  $LiCl-LnCl_3$  were excluded. A special problem in such investigations is the identification of the kind of solid-state reactions; the DTA-peak alone only tells us that such a reaction has occurred, but does not distinguish between a polymorphic structure transformation, decomposition or formation reaction.

One suitable method to solve this problem is high-temperature X-ray analysis. Another, more profound way, is the measurement of  $\Delta G_T$  vs.  $T$  curves. The exact temperature of a solid-state transition, 'phase I  $\rightleftharpoons$  phase II' is given by  $\Delta G_I = \Delta G_{II}$ . In case of decomposition,  $I \rightarrow$  components,  $\Delta G_T$  is 0 at temperatures  $\geq T_i$ ; if a high-temperature phase II is formed from its components  $\Delta G_T$  is 0 when  $T \leq T_i$ .

We have measured such  $\Delta G$  vs.  $T$  curves with galvanic cells for solid electrolytes using the relation  $\Delta G = -nFE$ , with  $E = e.m.f.$  of the cell,  $n =$  transported charge,  $F =$  Faraday constant. The set up of the cells is: (graphite,  $Cl_2$ )/ $ACl/A^+$ -conducting diaphragm/ $LnCl_3$  (or  $A_nLnCl_{3+n}$ )/(graphite+ $Cl_2$ ). In all measurements the dependence of  $E$  on  $T$  has proven to be linear in temperature ranges between ~280 to ~500°C, where  $E = a + bT$ . By multiplication of the found regression equation with  $-nF$  the Gibbs-Helmholtz equation for the reaction  $ACl + LnCl_3 = A_nLnCl_{3+n}$  was obtained,  $\Delta G_r^0 = \Delta H_r^0 - T\Delta S_r^0$ , with enthalpy and entropy independent on the temperature. As well,  $\Delta H_r^0$  at  $T = 298$  K was measured by solution calorimetry.

In Table 1 our publications, which contain the results on ternary chlorides of the late lanthanides and yttrium are compiled.

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**Table 1** A list of the investigations on ternary lanthanide chlorides carried out in our laboratory

A: The systems $ACl/LnCl_3$ with $A=Cs, Rb, K$	
1995: Systems $ACl/TbCl_3$	[2]
1994: Systems $ACl/DyCl_3$	[3]
1997: Systems $ACl/HoCl_3$	[4]
1998: Systems $ACl/YCl_3$	[5]
1995: Systems $CsCl, RbCl/ErCl_3$	[6]
2001: System $KCl/ErCl_3$	[7]
1998: Systems $ACl/TmCl_3$	[8]
1998: Systems $ACl/YbCl_3$	[9]
B: The systems $NaCl/LnCl_3$	
1995: Systems $NaCl/TbCl, DyCl_3$	[10]
1997: Systems $NaCl/HoCl_3, ErCl_3$	[11]
1999: Systems $NaCl/TmCl_3, YbCl_3, LuCl_3$	[12]
1998: System $NaCl/YCl_3$	[5]
C: Ternary chlorides from solutions	
1995: Compounds $Cs_3LnCl_6 \cdot 3H_2O$ ( $Ln=La-Nd$ )	[13]
1996: Compounds $Cs_4LnCl_7$ ( $Ln=Ho-Yb$ )	[14]
1997: Compounds $Cs_3LnCl_6$ ( $Ln=Na-Yb$ )	[15]
in space group $Pbcm$	

## Phase diagrams of systems $ACl/LnCl_3$ ( $Ln=Tb-Lu, Y$ )

### Literature survey

The pioneer-work in elucidating phase diagrams of systems  $ACl/LnCl_3$  with the late lanthanides from terbium to lutetium was done in the years 1964 to 1969, mainly at the Lomonosov University in Moscow (I. S. Morosov, B. G. Korshunov, D. V. Drobot *et al.*). This work treated all the  $NaCl/LnCl_3$  and  $KCl/LnCl_3$  systems, excluding only the systems with thulium, and the systems of the rare earth element yttrium with  $RbCl$  [16] and  $CsCl$  [17]. A synopsis of the results was given by Drobot *et al.* [18], in a paper on systems with  $LuCl_3$ .

More extensive summaries about chloride systems up to 1977 can be found in the handbook of Gmelin [19] or in the monograph of Prosypaiko and Allseeva [20].

The above-mentioned investigations were performed with the visual-polythermal method. The temperature-time curves were recorded on a Kurnakov apparatus. It is a feature of this technique that it gives good results for the liquidus lines and thus for the existence of congruently melting compounds, however, data about the composition of incongruently melting compounds are sometimes doubtful (e.g.  $KDy_3Cl_{10}$  instead of  $KDy_2Cl_7$  [21]). Furthermore, solid-state reactions with small reaction enthalpies were often overlooked. As a consequence, all investigated systems with  $NaCl$  are incomplete.

Taxometric models about the number of existing compounds in  $LnCl_3$ -systems were already discussed in 1968 by Korshunov *et al.* [18], later by Morozow [22] and in 1974 by Schneider [23]. However, crystal structures were not considered in any of the papers.

In 1979 Blachnik and Selle [24] elucidated the systems  $CsCl/LnCl_3$  (with  $Ln=Dy, Er, Yb, Pr$ ) and the system  $KCl/DyCl_3$  by the DTA-technique as a basis for the measurement of the thermodynamic data by solution calorimetry. Likewise, the teams of Gaune-Escard in Marseille and of Rycerz in Wrocław were also engaged in thermodynamic problems concerning lanthanide halides. They measured mixing enthalpies of the systems  $ACl-DyCl_3$  [25],  $ACl-TbCl_3$  [26] and calculated formation enthalpies of the liquid ternary chlorides.

In 1992 Qiao *et al.* [27] investigated all phase diagrams of  $ACl/YCl_3$  by combining thermodynamic and taxometric reflections. To the best of our knowledge these were the last investigations on systems with the trichlorides of the heavier lanthanide metals.

### The binary chlorides $LnCl_3$

The preparation of anhydrous chlorides of the late lanthanides is more difficult than that of the early ones. Because of the shrinking ionic radii, their Pearson-acidity and by this their sensitivity to hydrolysis increases. Korshunov and Drobot [21] prepared the chlorides by chlorinating the oxides with carbon tetrachloride [28] while Morozov [29] started with the hydrated chlorides  $LnCl_3 \cdot 6H_2O$ , which were mixed with ammonium chloride in the ratio 2:1 and slowly heated in a stream of dry chlorine to the melting point of the chloride. In 1978 Mochinaga *et al.* [30] prepared anhydrous  $LnCl_3$  by reacting of the oxides with  $NH_4Cl$  at  $350^\circ C$  and purified the crude products by sublimation under reduced pressure. The same method was applied in 1969 by Schneider [31] and later by Blachnik. Meyer [32] applied both, the 'wet and the dry ammonium chloride route', for the preparation of  $YCl_3$ . He investigated the existing intermediates and in 1989 he published a detailed prescription for this method [33].

The hexahydrates of the lanthanide-trichlorides can be dehydrated in vacuo to trihydrates  $LnCl_3 \cdot 3H_2O$  at temperatures below  $100^\circ C$  without hydrolysis. Two exceptions are the compounds of Ho and Y; here at  $\sim 70^\circ C$  dihydrates are formed. Further dehydration must occur in a stream of HCl. The temperatures must be raised slowly so that the next steps of dehydration, the formation of di- and monohydrates of Tb and Er or directly monohydrates of the other lanthanides, and eventually anhydrous  $LnCl_3$ , do not start before the foregoing step is completed. We have determined the respective temperatures by thermogravimetry and preparative work together with X-ray control [34]. For  $YbCl_3 \cdot H_2O$  the final temperatures are between 280 and  $350^\circ C$ . The time for dehydrating  $\sim 10$  g monohydrates is approximately three days. A more convenient procedure is to heat anhydrous formates,  $Ln(HCOO)_3$ , in a stream of HCl for  $\sim 20$  h to  $250-320^\circ C$  [4, 5, 8]. The formates can be obtained for

all lanthanides, except Yb and Lu, as precipitates when boiling the hexahydrates in concentrated formic acid.

The anhydrous chlorides  $\text{LnCl}_3$  ( $\text{Ln}=\text{La}-\text{Gd}$ ) crystallize in the  $\text{UCl}_3$ -type [35] where the  $\text{Ln}^{3+}$  ions are coordinated by nine chloride ions; for  $\text{Ln}=\text{Ho}-\text{Lu}$  the coordination number (CN) is six in the layer structure of the  $\text{ACl}_3$ -type [36].

In the polymorphic  $\text{TbCl}_3$  [37] the L-modification crystallizes with the  $\text{UCl}_3$ -structure, the M-modification in the  $\text{PuBr}_3$ -type (CN=8). The transition  $\text{L}\rightarrow\text{M}$  at  $\sim 360^\circ\text{C}$  is irreversible for kinetic reasons. Thus, the  $\text{UCl}_3$ -type is formed only by preparation of  $\text{TbCl}_3$  below  $360^\circ\text{C}$ , either by dehydration of  $\text{TbCl}_3\cdot\text{H}_2\text{O}$  or by deposition from the gaseous phase. On cooling, M- $\text{TbCl}_3$  remains metastable at ambient temperature. In 1988 Simon and Urland [38] found an H- $\text{TbCl}_3$ , stable at  $T>517^\circ\text{C}$ . It crystallizes in S.G. $\text{P4}_2/\text{mnm}$  and is built up by double-octahedra, linked together as in the trirutile-structure  $\text{AB}_2\text{X}_6$  with empty positions of  $A$ . The transition  $\text{M}\rightarrow\text{H}$  is reversible with a large transition enthalpy of  $23.1\pm 4.6\text{ kJ mol}^{-1}$  at  $793\text{ K}$  [39].

Dysprosiumchloride is dimorphic. L- $\text{DyCl}_3$  ( $\text{PuBr}_3$ -type) transforms at  $342^\circ\text{C}$  to H- $\text{DyCl}_3$  ( $\text{AlCl}_3$ -type). In DTA cooling-curves the transition-temperature is  $270^\circ\text{C}$ . When quenching molten or H- $\text{DyCl}_3$ , a metastable hexagonal phase is formed [3]. If it is heated again in a DTA apparatus it is transformed at  $\sim 240^\circ\text{C}$  to the stable  $\text{PuBr}_3$ -phase. The transition enthalpy is exothermic; the difference between the solution enthalpies of L- $\text{DyCl}_3$  ( $-197.1\text{ kJ mol}^{-1}$ ) and metastable  $\text{DyCl}_3$  ( $-205.0\text{ kJ mol}^{-1}$ ) is  $\Delta H_{\text{tr}}^0(298)=-7.9\text{ kJ mol}^{-1}$ . Such metastable phases with strongly distorted layers of the  $\text{ACl}_3$ -type structure also are formed when dehydrating the monohydrates  $\text{LnCl}_3\cdot\text{H}_2\text{O}$  ( $\text{Ln}=\text{Ho}-\text{Lu}$ ). The reaction of Ln-formates with HCl yields products with undistorted structures.

In Table 2 temperatures of fusion  $T_{\text{m}}$ , measured in our group for the anhydrous trichlorides are compiled together with some other thermodynamic data.

A difficulty in measuring  $T_{\text{m}}$  arises from the effect that melts of trichlorides of the smaller lanthanides react with  $\text{SiO}_2$ . (With scandium, Polyachenok *et al.* [40]

found that  $\text{ScCl}_3$  melts react with  $\text{SiO}_2$  forming  $\text{Sc}_2\text{Si}_2\text{O}_7$ .) We have found for  $\text{ErCl}_3$  a  $T_{\text{m}}=751^\circ\text{C}$  when melting the compound for the first time in a quartz crucible. When repeating the melting process the DTA effect splits. The splitting becomes more pronounced with further melting cycles. In the third cycle we found two effects of the same magnitude at  $743$  and  $770^\circ\text{C}$ . This is in agreement with the findings of Gaune-Escard [41] ( $752$  and  $773^\circ\text{C}$ ). For getting accurate  $T_{\text{m}}$  values in DTA corundum or platinum crucibles are to be used for the trichlorides or  $\text{LnCl}_3$ -rich samples. As the second column in Table 2 demonstrates  $T_{\text{m}}$  values from the literature are in general too high. (Here the highest values from compilations of Goryushkin [42] and Kahwa [43] are not considered.) In the other columns lattice energies  $U$  and solution enthalpies are compiled. The lattice enthalpies are taken from the paper of Goryushkin [42]. A compilation of the most recent values of formation enthalpies was given by Cordfunke [44].

One may have the impression that the melting points are directly proportional to  $1/U$  caused by the decreasing ionic radii of the  $\text{Ln}^{3+}$  ions with increasing atomic number. However, in the group of  $\text{Ln}=\text{La}-\text{Gd}$  the temperatures of fusion decrease with decreasing radii! The reason for this contradiction is that fusion is not only determined by the solid-state but also by the properties of the liquid. However, melts of  $\text{LnCl}_3$  near the temperature of fusion do not consist of the ions  $\text{Ln}^{3+}$  and  $\text{Cl}^-$ , but contain polymeric units [45]. Up to now no effort has been made to explain this peculiarity. It may be of interest, that the volume increase on melting is 19–26% for  $\text{LaCl}_3$  to  $\text{GdCl}_3$  and nearly zero for  $\text{DyCl}_3$  and  $\text{YCl}_3$  [46]. Recently we have compiled and critically evaluated all the results from the literature, dealing with melting points of lanthanides trichlorides, showing the relationship between melting points and polymeric units appearing in the melts [47].

#### Results of the phase diagram investigations

In Table 3 the characteristic data for all known ternary chlorides with  $\text{Ln}=\text{Tb}-\text{Lu}$ , Y are compiled. They are taken from our own publications on the phase dia-

**Table 2** Thermal properties of the trichlorides,  $\text{LnCl}_3$ , with  $\text{Ln}=\text{Tb}-\text{Lu}$  and Y

Compound	Fusion temperature, $T_{\text{f}}/^\circ\text{C}$ (K)	$T_{\text{f}}$ -ranges from the literature/ $^\circ\text{C}$	Lattice enthalpies, $\Delta H_{\text{lat}}^0/\text{kJ mol}^{-1}$ [42]	Solution enthalpies, $\Delta H_{\text{sol}}^0/\text{kJ mol}^{-1}$ [34]	$\Delta H_{\text{sol}}^0/\text{kJ mol}^{-1}$ [88]
$\text{TbCl}_3$	575 (848)	578–587	$-4476\pm 12$	$-188.8$ (4)	$-186.9$ to $-191.8$
$\text{DyCl}_3$	646 (919)	636–655	$-4483\pm 32$	$-197.1$ (3)	$-197.9$ to $209.0$
$\text{HoCl}_3$	700 (973)	704–720	$-4528\pm 12$	$-209.4$ (9)	$-209.2$ to $-213.4$
$\text{YCl}_3$	692 (965)	700–714	–	$-212.8$ (1)	$-189.9$ to $-224.7$
$\text{ErCl}_3$	751 (1024)	764–773	$-4542\pm 12$	$-211.9$ (1)	$-207.3$ to $-215.0$
$\text{TmCl}_3$	821 (1094)	819	$-4581\pm 13$	$-212.2$ (7)	$-213.0$ to $-215.9$
$\text{YbCl}_3$	860 (1133)	854–865	$-4608\pm 42$	$-212.9$ (7)	$-212.9$ to $-216.1$
$\text{LuCl}_3$	892 (1165)	892	$-4569\pm 40$	$-211.6$	$-211.6$ to $-218.1$

**Table 3** Characteristic data for ternary chlorides in the systems ACI/LnCl<sub>3</sub>

Compound	I. Highest temperature of existence/K	II. Solid-state reactions/K	III. Literature
Cs <sub>3</sub> TbCl <sub>6</sub>	1153 M	673 T	Seifert, 1995 [2]
Cs <sub>2</sub> TbCl <sub>5</sub>	873 P		Seifert, 1995 [2]
CsTb <sub>2</sub> Cl <sub>7</sub>	945 M	928 T 688 T	Seifert, 1995 [2]
Rb <sub>3</sub> TbCl <sub>6</sub>	1115 M	681 T	Seifert, 1995 [2]
RbTb <sub>2</sub> Cl <sub>7</sub>	883 M	836 T	Seifert, 1995 [2]
K <sub>3</sub> TbCl <sub>6</sub>	1049 M	640 T 394 F	Korshunov, 1966 [49]
K <sub>2</sub> TbCl <sub>5</sub>	770 P		Korshunov, 1966 [49]
KTb <sub>2</sub> Cl <sub>7</sub>	842 M		Korshunov, 1966 [49]
Na <sub>3</sub> TbCl <sub>6</sub>	791 P	426 T	Korshunov, 1966 [49]
Na <sub>2</sub> TbCl <sub>5</sub>	618 D		Seifert, 1995 [10]
NaTbCl <sub>4</sub>	692 P		Seifert, 1995 [10]
NaTb <sub>2</sub> Cl <sub>7</sub>	729 P		Korshunov, 1966 [49]
Cs <sub>3</sub> DyCl <sub>6</sub>	1148 M	669 T	Blachnik, 1979 [24]
Cs <sub>2</sub> DyCl <sub>5</sub>	903 P		Blachnik, 1979 [24]
CsDy <sub>2</sub> Cl <sub>7</sub>	921 M	686 T 641 T	Blachnik, 1979 [24]
Rb <sub>3</sub> DyCl <sub>6</sub>	1121 M	688 T	Seifert, 1994 [3]
RbDy <sub>2</sub> Cl <sub>7</sub>	888 M	619 T	Seifert, 1994 [3]
K <sub>3</sub> DyCl <sub>6</sub>	1073 M	646 T	Korshunov, 1965 [21]
K <sub>2</sub> DyCl <sub>5</sub>	728 P		Seifert, 1994 [3]
KDy <sub>2</sub> Cl <sub>7</sub>	841 M		Blachnik, 1979 [24]
Na <sub>3</sub> DyCl <sub>6</sub>	808 P	393 T	Korshunov, 1965 [21]
NaDyCl <sub>4</sub>	696 P		Seifert, 1995 [10]
NaDy <sub>2</sub> Cl <sub>7</sub>	733 P		Seifert, 1995 [10]
Cs <sub>3</sub> HoCl <sub>6</sub>	1150 M	676 T	Seifert, 1997 [4]
Cs <sub>2</sub> HoCl <sub>5</sub>	915 P		Seifert, 1997 [4]
Cs <sub>3</sub> Ho <sub>2</sub> Cl <sub>9</sub>	842 P		Seifert, 1997 [4]
CsHo <sub>2</sub> Cl <sub>7</sub>	913 M	703 T 585 T	Seifert, 1997 [4] Seifert, 1997 [4]
Rb <sub>3</sub> HoCl <sub>6</sub>	1147 M	693 T	Seifert, 1997 [4]
Rb <sub>2</sub> HoCl <sub>5</sub>	785 P	687 F	Seifert, 1997 [4]
RbHo <sub>2</sub> Cl <sub>7</sub>	886 M	833 T	Seifert, 1997 [4]
K <sub>3</sub> HoCl <sub>6</sub>	1077 M	649 T	Korshunov, 1966 [50]
K <sub>2</sub> HoCl <sub>5</sub>	688 D		Seifert, 1997 [4]
KHo <sub>2</sub> Cl <sub>7</sub>	841 M		Korshunov, 1966 [50]
Na <sub>3</sub> HoCl <sub>6</sub>	823 P		Korshunov, 1965 [51]
NaHoCl <sub>4</sub>	694 P	647 T	Seifert, 1997 [11]
NaHo <sub>2</sub> Cl <sub>7</sub>	710 P		Seifert, 1997 [11]
Cs <sub>3</sub> YCl <sub>6</sub>	1166 M	671 T	Korshunov, 1965 [17]
Cs <sub>2</sub> YCl <sub>5</sub>	904 P		Seifert, 1998 [5]
Cs <sub>3</sub> Y <sub>2</sub> Cl <sub>9</sub>	808 D		Seifert, 1998 [5]
CsY <sub>2</sub> Cl <sub>7</sub>	917 M	690 T 618 T	Qiao, 1992 [27]
Rb <sub>3</sub> YCl <sub>6</sub>	1142 M	690 T	Morozov, 1969 [16]
RbY <sub>2</sub> Cl <sub>7</sub>	876 M	827 T	Qiao, 1992 [27]
K <sub>3</sub> YCl <sub>6</sub>	1083 M	650 T	Morozov, 1964 [52]
K <sub>2</sub> YCl <sub>5</sub>	685 D		Korshunov, 1964 [53]
KY <sub>2</sub> Cl <sub>7</sub>	837 M	819 T	Seifert, 1998 [5]
Na <sub>3</sub> YCl <sub>6</sub>	821 P		Morozov, 1964, [52]
NaYCl <sub>4</sub>	704 M	668 T	Korshunov, 1964 [53]
NaY <sub>2</sub> Cl <sub>7</sub>	603 D		Seifert, 1998 [5] Seifert, 1998 [5]

**Table 3** Continued

Compound	I. Highest temperature of existence/K	II. Solid-state reactions/K	III. Literature
Cs <sub>3</sub> ErCl <sub>6</sub>	1163 M	665 T	Blachnik, 1979 [24]
Cs <sub>2</sub> ErCl <sub>5</sub>	923 P		Blachnik, 1979 [24]
Cs <sub>3</sub> Er <sub>2</sub> Cl <sub>9</sub>	874 P		Blachnik, 1979 [24]
CsEr <sub>2</sub> Cl <sub>7</sub>	915 M	708 T 511 T	Blachnik, 1979 [24]
Rb <sub>3</sub> ErCl <sub>6</sub>	1140 M	696 T	Seifert, 1995 [6]
Rb <sub>2</sub> ErCl <sub>5</sub>	793 P	621 F	Seifert, 1995 [6]
RbEr <sub>2</sub> Cl <sub>7</sub>	861 M	823 T	Seifert, 1995 [6]
K <sub>3</sub> ErCl <sub>6</sub>	1083 M	648 T 321 T	Korshunov, 1966 [50]
KEr <sub>2</sub> Cl <sub>7</sub>	811 P		Seifert, 2001 [7]
Na <sub>3</sub> ErCl <sub>6</sub>	835 M		Korshunov, 1965 [51]
NaErCl <sub>4</sub>	707 P		Seifert, 1997 [11]
Cs <sub>3</sub> TmCl <sub>6</sub>	1168 M	682 T 649 T	Seifert, 1998 [8]
Cs <sub>2</sub> TmCl <sub>5</sub>	913 P		Seifert, 1998 [8]
Cs <sub>3</sub> Tm <sub>2</sub> Cl <sub>9</sub>	890 P	705 T	Seifert, 1998 [8]
CsTm <sub>2</sub> Cl <sub>7</sub>	881 M	445 T	Seifert, 1998 [8]
Rb <sub>3</sub> TmCl <sub>6</sub>	1153 M	695 T	Seifert, 1998 [8]
Rb <sub>2</sub> TmCl <sub>5</sub>	808 P		Seifert, 1998 [8]
RbTm <sub>2</sub> Cl <sub>7</sub>	835 M	808 T	Seifert, 1998 [8]
K <sub>3</sub> TmCl <sub>6</sub>	1086 M	659 T	Seifert, 1998 [8]
K <sub>2</sub> TmCl <sub>5</sub>	718 P		Seifert, 1998 [8]
KTm <sub>2</sub> Cl <sub>7</sub>	774 P		Seifert, 1998 [8]
Na <sub>3</sub> TmCl <sub>6</sub>	843 M		Seifert, 1999 [12]
NaTmCl <sub>4</sub>	673 D		Seifert, 1999 [12]
Cs <sub>3</sub> YbCl <sub>6</sub>	1171 M	683 T 640 T	Blachnik, 1979 [24]
Cs <sub>2</sub> YbCl <sub>5</sub>	923 P		Blachnik, 1979 [24]
Cs <sub>3</sub> Yb <sub>2</sub> Cl <sub>9</sub>	909 P		Blachnik, 1979 [24]
CsYb <sub>2</sub> Cl <sub>7</sub>	840 P	709 T	Blachnik, 1979 [24]
Rb <sub>3</sub> YbCl <sub>6</sub>	1143 M	698 T	Seifert, 1998 [9]
Rb <sub>2</sub> YbCl <sub>5</sub>	817 P		Seifert, 1998 [9]
RbYb <sub>2</sub> Cl <sub>7</sub>	786 P		Seifert, 1998 [9]
K <sub>3</sub> YbCl <sub>6</sub>	1093 M	665 T	Novikov, 1964 [54]
K <sub>2</sub> YbCl <sub>5</sub>	728 P		Seifert, 1998 [9]
K <sub>3</sub> Yb <sub>2</sub> Cl <sub>9</sub>	698 P	667 F	Seifert, 1998 [9]
KYb <sub>2</sub> Cl <sub>7</sub>	726 P		Seifert, 1998 [9]
Na <sub>3</sub> YbCl <sub>6</sub>	845 M		Korshunov, 1968 [18]
NaYbCl <sub>4</sub>	725 P		Seifert, 1999 [12]
CsCl/LuCl <sub>3</sub> RbCl/LuCl <sub>3</sub>		not investigated	Gmelin Handb., 1977 [19]
K <sub>3</sub> LuCl <sub>6</sub>	1089 M	647 T	Korshunov, 1968 [18]
Na <sub>3</sub> LuCl <sub>6</sub>	853 M		Korshunov, 1968 [18]
NaLuCl <sub>4</sub>	745 P		Seifert, 1999 [12]

*M* – melting-temperatures for congruently melting compounds; *P* – peritectic-temperatures for incongruently melting compounds;  
*D* – decomposition-temperatures for compounds, that are stable at low temperature and decompose in the solid-state when heated;  
*T* – phase transitions between polymorphic modifications; *F* – formation temperatures for compounds stable at temperatures  $\geq T_T$ .

grams  $ACl/LnCl_3$  with  $A=Cs, Rb, K, Na$ . Phase diagrams are given in Figs 1–4. Ternary chlorides prepared from solutions are described in ‘Ternary chlorides from aqueous solutions’.

In column I of Table 3 the highest temperatures of existence for each solid compound taken from DTA heating curves are given: melting temperatures (*M*) for congruently melting compounds (all compounds

$A_3LnCl_6$  with  $A=Cs, Rb, K$ ); peritectic temperatures ( $P$ ) for incongruently melting compounds (most compounds  $A_2LnCl_5$  and  $A_3Ln_2Cl_9$ ); decomposition temperatures ( $D$ ) for compounds, that are stable at low temperature and decompose in the solid-state when heated (examples are the compounds  $Cs_3Y_2Cl_9$  in Fig. 1,  $K_2HoCl_5$  in Fig. 3 and  $K_2YCl_5$ ). Temperatures for other solid-state reactions are given in column II: phase transitions between polymorphic modifications ( $T$ ) or formation temperatures ( $F$ ) for compounds stable at temperatures  $\geq T_T$ . (These are the Rb compounds  $Rb_2HoCl_5$ ,  $Rb_2YCl_5$ ,  $Rb_2ErCl_5$  (Fig. 2),  $K_3Yb_2Cl_9$  and several compounds  $K_3LnCl_6$ , described in [7]).

Solid-state reactions are a special kind of reconstructive phase transitions. These are transitions in which the arrangement of the ions is drastically changed. Ions have to move from one site to another passing strong potential walls of other ions. The resulting ‘kinetic hindrance’ can cause great differences be-

tween reaction temperatures, measured in DTA heating and cooling curves (thermal hysteresis). In extreme cases in cooling experiments the ‘undercooling’ can become so strong that the reaction does not occur in the time-scale of DTA and must be forced by sufficiently long annealing. We have discussed the issue of these ‘retarded reactions’ in several papers, the last in [48].

The true equilibrium temperatures can be detected by measurement of  $\Delta G$  vs.  $T$  curves in galvanic cells for solid electrolytes. Such measurements are described in ‘Gibbs free energies from *e.m.f.* measurements’, results are represented in the second column of Table 3. These temperatures are in general lower than the temperatures recorded in DTA heating curves and higher than those recorded in cooling curves.

Column III of Table 3 contains literature references from the research groups who were first to published correct data about the appropriate compound, not regarding data for polymorphic phase transitions.

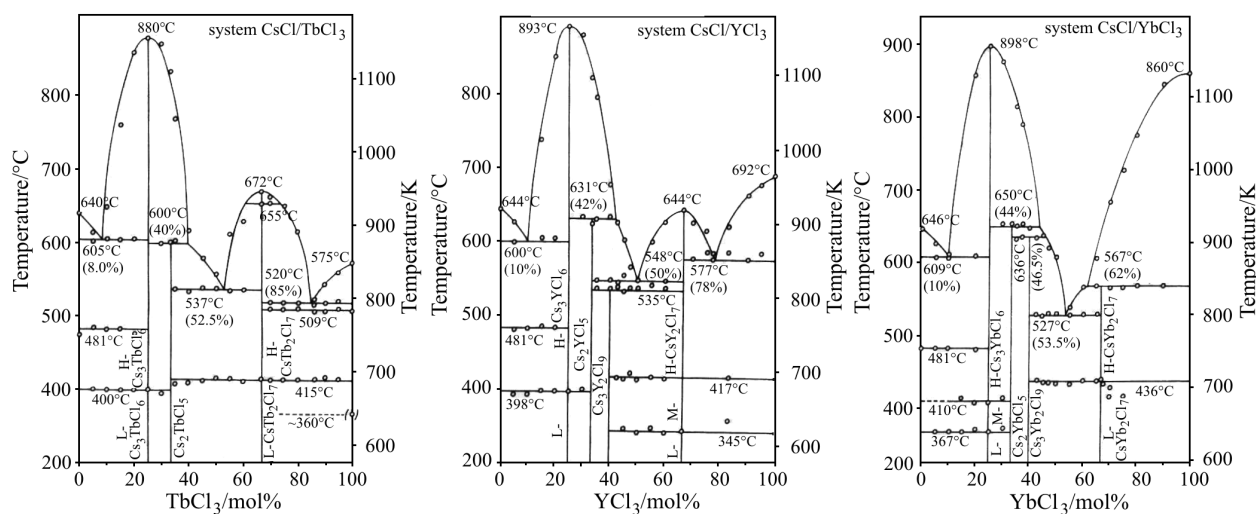


Fig. 1 Phase diagrams of CsCl with  $TbCl_3$ ,  $YCl_3$  and  $YbCl_3$

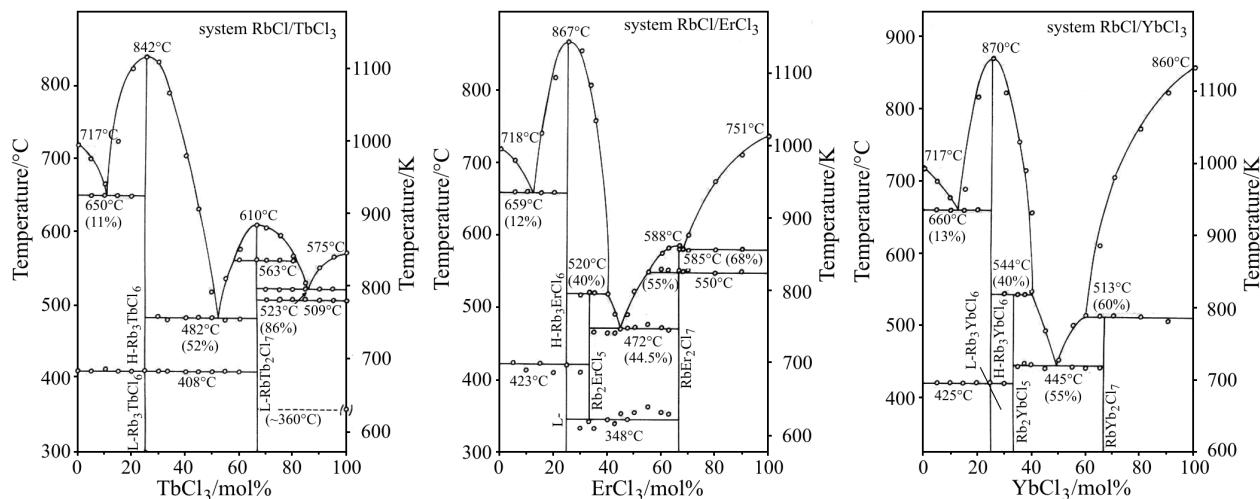


Fig. 2 Phase diagrams of RbCl with  $TbCl_3$ ,  $ErCl_3$  and  $YbCl_3$

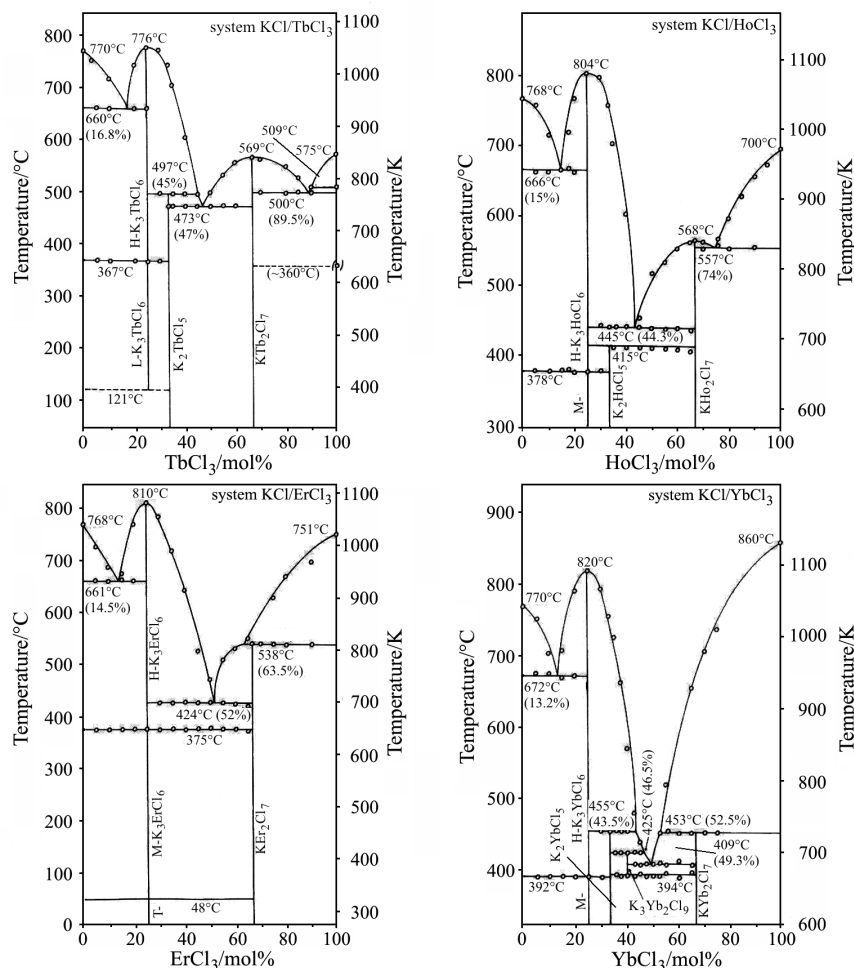


Fig. 3 Phase diagrams of KCl with TbCl<sub>3</sub>, HoCl<sub>3</sub>, ErCl<sub>3</sub> and YbCl<sub>3</sub>

### Ternary chlorides from aqueous solutions

Hydrates of ternary chlorides belonging to the erythrosiderite family (K<sub>2</sub>FeCl<sub>5</sub>·H<sub>2</sub>O-type; Pnma) are known with trivalent transition metal cations [55] and as Cs-compounds, Cs<sub>2</sub>LnCl<sub>5</sub>·H<sub>2</sub>O with Ln=Tm [8], Yb [9], Y, Er [5] and Lu [56]. In more extensive investigations Reuter and Frenzen found the following hydrates CsLaCl<sub>4</sub>·3H<sub>2</sub>O and ALnCl<sub>4</sub>·4H<sub>2</sub>O (A=NH<sub>4</sub>, K, Rb, Cs; Ln=La–Sm) [57], Rb<sub>3</sub>LnCl<sub>6</sub>·2H<sub>2</sub>O (Ln=La–Nd) [58] and Cs<sub>2</sub>LnCl<sub>5</sub>·6H<sub>2</sub>O (Ln=Sm–Ho [4]).

For all groups the crystal structures were determined with single crystals. However, the most important results were that in the systems CsCl/LnCl<sub>3</sub>/H<sub>2</sub>O two groups of anhydrous compounds were precipitated by saturating nearly concentrated solutions of CsCl and LnCl<sub>3</sub>·xH<sub>2</sub>O with HCl. With a molar ratio Cs/Ln 3:1, hexachloro compounds precipitate with a previously unknown structure (S. G. Pbcm; Ln=Nd–Lu) [15]; if the ratio is 4:1 compounds with the composition Cs<sub>4</sub>LnCl<sub>7</sub> are obtained with Ln=Ho–Lu [14]. (For Ln=La–Pr trihydrates, Cs<sub>3</sub>LnCl<sub>3</sub>·3H<sub>2</sub>O, are obtained independent of the molar ratio [13].)

The Pbcm-modification of Cs<sub>3</sub>LnCl<sub>3</sub> is stable at ambient temperature, as proved by solution calorimetry ('Solution enthalpies' and Table 5). The transformation to the 'L-modification' is kinetically so strongly hindered, that it takes place only after long annealing (10 h) at 300°C. In a DTA heating curve only the transformation to the cubic H-modification at ~400°C can be detected. The compounds Cs<sub>4</sub>LnCl<sub>7</sub> decompose to Cs<sub>3</sub>LnCl<sub>6</sub>+CsCl when heated to 250°C.

### The crystal structures

In 1980 the first structures of ternary chlorides of trivalent rare earth elements, namely those of Cs<sub>2</sub>DyCl<sub>5</sub> [59] and Cs<sub>3</sub>Sc<sub>2</sub>Cl<sub>9</sub> [60] were determined by G. Meyer with single crystal techniques. Two years later he collected all known data on halides of RE-elements including his own unpublished results and presented them in a review article [56], which was continued in 1991 [61]. Earlier, only tables with peak positions of debyeograms for some compounds were published [62]. After determining the structure of one member of

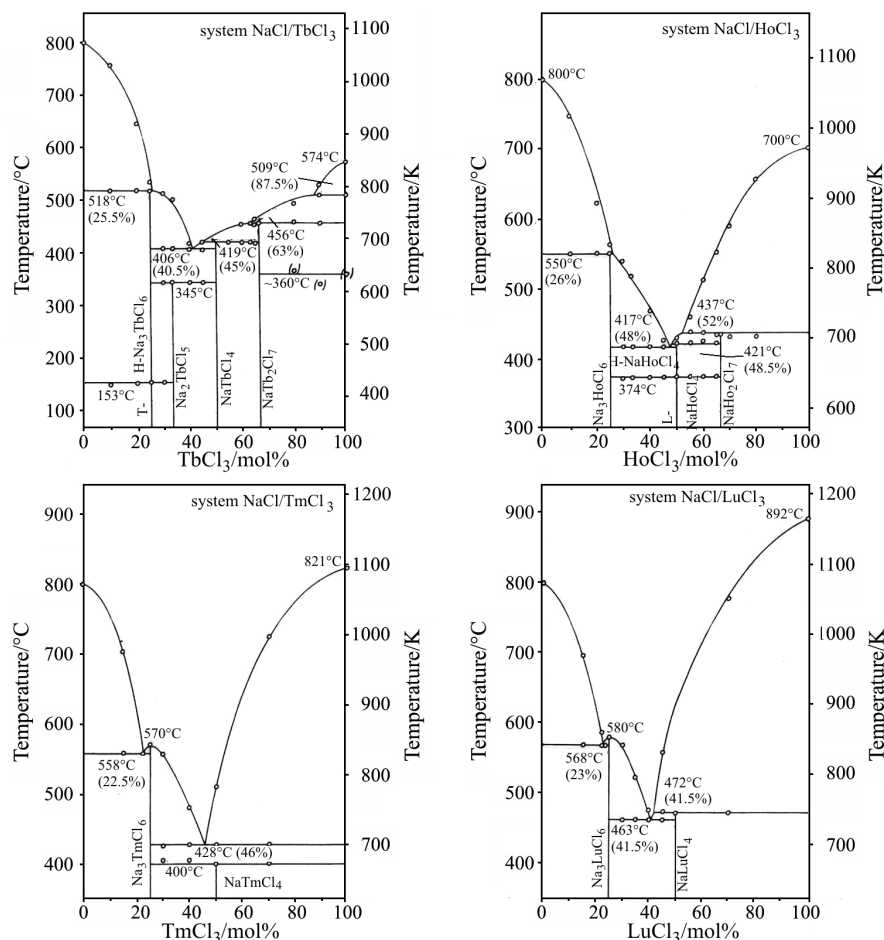


Fig. 4 Phase diagrams of NaCl with TbCl<sub>3</sub>, HoCl<sub>3</sub>, TmCl<sub>3</sub> and LuCl<sub>3</sub>

a family, e.g. Cs<sub>2</sub>DyCl<sub>5</sub>, with single crystals, he prepared other compounds with the same stoichiometry, but with different A<sup>+</sup> and Ln<sup>3+</sup> ions. We completed this project, finding such compounds systematically by elucidating phase diagrams with DTA.

In Table 4 unit cell parameters and molar volumes  $V_{m(\text{exp})}$  (in cm<sup>3</sup> mol<sup>-1</sup>) of all actually known compounds are compiled. Literature references are given to the compounds, which were first investigated by Meyer. Our results are taken from references [1–15]. In the last column of the table  $\Delta V_m$  values are given. They are the differences between  $V_{m(\text{exp})}$  and the sum of molar volume  $pV_m(\text{ACl})+qV_m(\text{LnCl}_3)$  for compounds of the type A<sub>p</sub>Ln<sub>q</sub>Cl<sub>(p+q)</sub>. A positive value stands for a volume increase by formation from the binary parent compounds. The  $V_m(\text{ACl})$  values used are:  $V_m(\text{CsCl, NaCl-type})=52.4$ ;  $V_m(\text{RbCl})=42.3$ ;  $V_m(\text{KCl})=37.3$ ;  $V_m(\text{NaCl})=27.0$  cm<sup>3</sup> mol<sup>-1</sup>. The analogous values for the lanthanide trichlorides were calculated from their most reliable lattice parameters and they are L-TbCl<sub>3</sub>=57.6; L-DyCl<sub>3</sub>=57.8; HoCl<sub>3</sub>=73.0; ErCl<sub>3</sub>=72.1; TmCl<sub>3</sub>=71.4; YbCl<sub>3</sub>=70.5; LuCl<sub>3</sub>=70.3; YCl<sub>3</sub>=74.8 cm<sup>3</sup> mol<sup>-1</sup> (HoCl<sub>3</sub> to LuCl<sub>3</sub>: YCl<sub>3</sub>-type [36]).

#### Compounds A<sub>3</sub>LnCl<sub>6</sub>

All compounds A<sub>3</sub>LnCl<sub>6</sub> are genuine solid complexes. Negatively charged [LnCl<sub>6</sub>]<sup>3-</sup> octahedra are held together by A<sup>+</sup> cations. According to our own investigations with high-temperature Guinier-patterns of crystal powders, all A<sub>3</sub>LnCl<sub>6</sub> with the larger alkali-metal cations A=K, Rb, Cs crystallize at temperatures higher than ~400°C in a cubic pseudo elpasolite-structure. The chloride ions together with 2/3 of the alkali-metal cations form a cubic-close packed structure in which all octahedral holes, formed by Cl<sup>-</sup> ions only, are occupied by 1/3 of the A<sup>+</sup> and the Ln<sup>3+</sup> ions. The general formula can be written as A<sub>2</sub>A'LnCl<sub>6</sub>. The coordination number (CN) of A is 12 and that of A' is 6. The elpasolite-type is related to the (halogeno) perovskite-structure in the following manner, in two [ABX<sub>3</sub>] units the two B<sup>2+</sup> are substituted by A<sup>+</sup> plus Ln<sup>3+</sup>.

In addition to these high-temperature modifications all hexachloro compounds with Cs and Rb form low-temperature modifications with the monoclinic Cs<sub>3</sub>BiCl<sub>6</sub>-type structure (S.G. C2/c) [63], while the analogous potassium compounds beginning with Ln=Pr, have the near related monoclinic K<sub>3</sub>MoCl<sub>6</sub>-type structure, S.G. P2<sub>1</sub>/c [64]. Furthermore, with A=Cs



**Table 4** Unit cell parameters and molar volumes  $V_{m(\text{exp.})}$  (in  $\text{cm}^3 \text{mol}^{-1}$ ) of ternary lanthanide chlorides**Table 4a** High-temperature modification of compounds  $\text{A}_3\text{LnCl}_6$  (Fm3m;  $Z=4$ )

Compound	$a/\text{\AA}$	$V_{m(\text{exp.})}$	$\Delta V_m$		$a/\text{\AA}$	$V_{m(\text{exp.})}$	$\Delta V_m$
$\text{Cs}_3\text{TbCl}_6$	11.597	234.8	+20.0	$\text{Rb}_3\text{TbCl}_6$	11.257	214.8	+30.3
$\text{Cs}_3\text{DyCl}_6$	11.553	232.1	+17.1	$\text{Rb}_3\text{DyCl}_6$	11.271	215.6	+30.9
$\text{Cs}_3\text{HoCl}_6$	11.522	230.3	+0.1	$\text{Rb}_3\text{HoCl}_6$	11.214	212.3	+12.4
$\text{Cs}_3\text{ErCl}_6$	11.535	231.1	+3.8	$\text{Rb}_3\text{ErCl}_6$	11.191	211.0	+12.0
$\text{Cs}_3\text{TmCl}_6$	11.560	232.6	+4.0	$\text{Rb}_3\text{TmCl}_6$	11.103	206.1	+7.8
$\text{Cs}_3\text{YbCl}_6$	11.522	230.3	+2.6	$\text{Rb}_3\text{YbCl}_6$	11.145	208.4	+11.0
$\text{Cs}_3\text{LuCl}_6$	11.478	227.7	+0.2	$\text{Rb}_3\text{YCl}_6$ [65]	11.133	207.8	+6.1
$\text{Cs}_3\text{YCl}_6$	11.582	233.9	+1.9				
$\text{K}_3\text{TbCl}_6$	11.018	201.4	+31.9	$\text{K}_2\text{TmCl}_6$	10.901	195.0	+11.7
$\text{K}_3\text{DyCl}_6$	10.944	197.3	+27.6	$\text{K}_3\text{YbCl}_6$	10.864	193.0	+10.6
$\text{K}_3\text{HoCl}_6$	10.952	197.8	+12.9	$\text{K}_3\text{LuCl}_6$	10.857	192.7	+10.1
$\text{K}_3\text{ErCl}_6$	10.918	195.9	+11.9	$\text{K}_3\text{YCl}_6$ [65]	10.887	194.3	+7.6

**Table 4b** Low-temperature modification of compounds  $\text{A}_3\text{LnCl}_6$  (C2/c;  $Z=8$ ;  $\text{Cs}_3\text{BiCl}_6$ -type)

Compound	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$\beta/\text{degree}$	$V_{m(\text{exp.})}$	$\Delta V_m$
$\text{Cs}_3\text{TbCl}_6$	26.990	8.180	13.171	99.97	215.8	+1.0
$\text{Cs}_3\text{DyCl}_6$	26.946	8.154	13.137	100.15	213.9	-1.1
$\text{Cs}_3\text{HoCl}_6$	26.927	8.131	13.139	100.23	213.1	-17.1
$\text{Cs}_3\text{ErCl}_6$	26.907	8.132	13.077	99.96	212.2	-17.1
$\text{Cs}_3\text{TmCl}_6$	26.851	8.115	13.089	100.14	211.3	-17.3
$\text{Cs}_3\text{YbCl}_6$	26.838	8.174	13.035	100.22	211.8	-15.9
$\text{Cs}_3\text{YCl}_6$ [62]	26.908	8.157	13.126	100.01	213.6	-18.4
Compounds $\text{Rb}_3\text{LnCl}_6$ [65]						
$\text{Rb}_3\text{TbCl}_6$	25.865	7.911	12.856	99.55	195.3	+10.8
$\text{Rb}_3\text{DyCl}_6$	25.812	7.889	12.830	99.56	193.9	+9.2
$\text{Rb}_3\text{HoCl}_6$	25.772	7.868	12.802	99.56	192.7	-7.2
$\text{Rb}_3\text{ErCl}_6$	25.753	7.868	12.792	99.65	192.4	-6.6
$\text{Rb}_3\text{TmCl}_6$	25.700	7.867	12.770	99.62	191.6	-6.7
$\text{Rb}_3\text{YbCl}_6$	25.656	7.839	12.750	99.62	190.3	-7.1
$\text{Rb}_3\text{LuCl}_6$	25.630	7.823	12.740	99.80	189.5	-7.7
$\text{Rb}_3\text{YCl}_6$	25.804	7.881	12.830	99.61	193.7	-8.0

**Table 4c** Compounds  $\text{Cs}_3\text{LnCl}_6$  from aqueous solution (Pbcm;  $Z=8$ ) [15]

Compound	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$V_{m(\text{exp.})}$	$\Delta V_m$
$\text{Cs}_3\text{NdCl}_6$	8.247	13.242	26.686	219.3	+1.6
$\text{Cs}_3\text{SmCl}_6$	8.224	13.175	26.609	217.0	+0.6
$\text{Cs}_3\text{EuCl}_6$	8.204	13.153	26.580	215.9	+0.1
$\text{Cs}_3\text{GdCl}_6$	8.185	13.142	26.557	215.0	-0.3
$\text{Cs}_3\text{TbCl}_6$	8.160	13.114	26.522	213.6	-1.2
$\text{Cs}_3\text{DyCl}_6$	8.155	13.082	26.481	212.7	-2.3
$\text{Cs}_3\text{HoCl}_6$	8.158	13.066	26.457	212.3	-17.9
$\text{Cs}_3\text{ErCl}_6$	8.146	13.074	26.442	211.9	-17.4
$\text{Cs}_3\text{TmCl}_6$	8.115	13.043	26.366	210.1	-18.5
$\text{Cs}_3\text{YbCl}_6$	8.089	13.077	26.366	209.9	-17.8
$\text{Cs}_3\text{YCl}_6$	8.144	13.084	26.479	212.4	-19.6

**Table 4** Continued**Table 4d** Low-temperature modification of compounds  $K_3LnCl_6$  ( $P2_1/c$ ;  $Z=4$ ;  $K_3MoCl_6$ -type) [7]

Compound	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$\beta/\text{degree}$	$V_{m(\text{exp.})}$	$\Delta V_m$
$K_3TbCl_6$	13.00	7.61	13.02	109.2	183.0	+13.5
$K_3DyCl_6$	12.985	7.559	12.882	108.86	180.1	+10.4
$K_3HoCl_6$	13.084	7.721	12.636	110.02	180.6	-4.3
$K_3ErCl_6$	13.098	7.671	12.526	109.94	178.1	-5.9
$K_3TmCl_6$	13.076	7.715	12.567	109.96	178.8	-4.5
$K_3YbCl_6$	12.998	7.642	12.485	109.85	175.6	-6.8
$K_3LuCl_6$	13.010	7.699	12.485	109.82	176.4	-6.2
$K_3YCl_6$	13.093	7.735	12.585	110.13	180.2	-6.5

**Table 4e** Compounds  $Na_3LnCl_6$  with the cryolite-structure ( $P2_1/n$ ;  $Z=2$ ) [73]

Compound	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$\beta/\text{degree}$	$V_{m(\text{exp.})}$	$\Delta V_m$
H- $Na_3TbCl_6$ [10]	6.891	7.276	10.193	90.2	155.9	+17.3
H- $Na_3DyCl_6$	6.883	7.285	10.182	90.8	153.7	+14.9
$Na_3HoCl_6$ [74]	6.868	7.274	10.167	90.8	152.9	-1.1
$Na_3ErCl_6$	6.844	7.257	10.125	90.8	151.4	-1.7
$Na_3TmCl_6$	6.834	7.239	10.106	90.8	150.5	-1.9
$Na_3YbCl_6$	6.822	7.229	10.088	90.7	149.8	-1.7
$Na_3LuCl_6$ [75]	6.805	7.218	10.068	90.7	148.9	-2.4
$Na_3YCl_6$ [75]	6.869	7.275	10.164	90.8	152.9	-2.9

**Table 4f** Low-temperature modification of  $Na_3LnCl_6$  ( $Ln=Tb, Dy, Y$ ) ( $R3$ ;  $Z=3$ ) [66]

Compound	$a/\text{\AA}$	$c/\text{\AA}$	$V_{m(\text{exp.})}$	$\Delta V_m$
L- $Na_3TbCl_6$ [73]	7.000	18.758	159.8	+21.2
L- $Na_3DyCl_6$ [10]	6.974	18.687	158.0	+19.2
L- $Na_3YCl_6^*$ [76]	6.973	18.684	157.9	+2.1

\* - &lt;243 K

**Table 4g** Compounds  $A_2LnCl_5$  with the  $Cs_2DyCl_5$ -structure ( $Pbnm$ ;  $Z=4$ ) [68]

Compound	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$V_{m(\text{exp.})}$	$\Delta V_m$
$Cs_2TbCl_5$ [2]	15.258	9.569	7.509	165.1	+2.7
$Cs_2DyCl_5$	15.233	9.549	7.497	164.2	+1.6
$Cs_2HoCl_5$	15.202	9.515	7.454	162.4	-15.4
$Cs_2ErCl_5$	15.191	9.499	7.442	161.7	-15.2
$Cs_2TmCl_5$	15.177	9.481	7.418	160.7	-15.2
$Cs_2YbCl_5$	15.147	9.456	7.408	159.8	-15.5
$Cs_2LuCl_5$	15.142	9.448	7.385	159.1	-16.0
$Cs_2YCl_5$	15.226	9.533	7.469	163.2	-16.4
$Rb_2HoCl_5$ [4]	14.642	9.570	7.279	153.6	-4.0
$Rb_2ErCl_5$	14.666	9.513	7.274	152.8	-3.9
$Rb_2TmCl_5$	14.621	9.465	7.271	151.5	-4.5
$Rb_2YbCl_5$ [9]	14.942	9.527	7.261	155.6	+0.5
$Rb_2LuCl_5$	14.609	9.398	7.246	149.8	-5.1
$Rb_2YCl_5$ [5]	14.638	9.587	7.341	155.0	-4.4

**Table 4** Continued**Table 4h** Compounds  $A_2LnCl_5$  with the  $K_2PrCl_5$ -structure (Pnma;  $Z=4$ )

Compound	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$V_{m(\text{exp.})}$	$\Delta V_m$
$K_2TbCl_5$ [66]	12.627	8.592	7.925	129.5	-2.7
$K_2DyCl_5$ [66]	12.608	8.565	7.910	128.6	-3.8
$K_2HoCl_5$	12.642	8.562	7.928	129.2	-18.4
$K_2YCl_5$	12.646	8.573	7.928	129.4	-20.0
$Na_2TbCl_5$	12.010	8.274	7.643	114.3	+2.7

**Table 4i** Compounds  $ALn_2Cl_7/RbDy_2Cl_7$ -structure (Pnma;  $Z=4$ ) [66]

Compound	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$V_{m(\text{exp.})}$	$\Delta V_m$
$CsTb_2Cl_7$	13.291	7.015	12.747	178.9	+11.3
$CsDy_2Cl_7$	13.322	6.984	12.685	177.7	+9.7
$CsHo_2Cl_7$	13.343	6.956	12.647	176.7	-21.7
$CsEr_2Cl_7$	13.360	6.928	12.582	175.3	-21.3
$CsTm_2Cl_7$	13.377	6.906	12.524	174.2	-21.0
$CsYb_2Cl_7$	13.402	6.887	12.479	173.4	-20.0
$CsLu_2Cl_7^*$	13.304	6.857	12.448	171.0	(-22.0)
$CsY_2Cl_7$	13.354	6.967	12.663	177.4	-24.6
$RbTb_2Cl_7$	12.885	6.940	12.692	170.9	+13.4
$RbDy_2Cl_7$	12.878	6.939	12.668	170.5	+12.6
$RbHo_2Cl_7$	12.869	6.921	12.636	169.5	-18.8
$RbEr_2Cl_7$	12.851	6.898	12.609	168.3	-18.2
$RbTm_2Cl_7$	12.831	6.872	12.570	166.9	-18.2
$RbYb_2Cl_7$	12.811	6.850	12.534	165.6	-17.7
$RbY_2Cl_7$	12.896	6.917	12.644	169.8	-22.1
M-KY $_2Cl_7$	13.003	6.929	12.714	172.5	-14.5

\*at  $-100^\circ\text{C}$ **Table 4j** Compounds  $KLn_2Cl_7/KDy_2Cl_7$ -structure ( $P2_1/a$ ;  $Z=4$ ) [66]

Compound	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$\beta/\text{degree}$	$V_{m(\text{exp.})}$	$\Delta V_m$
$KTb_2Cl_7$	12.770	6.890	12.649	89.52	167.6	+15.0
$KDy_2Cl_7$	12.726	6.878	12.616	89.34	166.3	+13.4
$KHo_2Cl_7$	12.721	6.867	12.583	89.19	165.5	-17.8
$KEr_2Cl_7$	12.692	6.851	12.538	89.05	164.1	-17.4
$KTm_2Cl_7$	12.660	6.829	12.493	88.93	162.6	-17.5
$KYb_2Cl_7$	12.661	6.807	12.435	88.87	161.3	-17.0
$KY_2Cl_7$	12.731	6.874	12.600	89.33	166.0	-20.9

**Table 4k** Compounds  $Cs_3Ln_2Cl_9$  with the  $Cs_3Tl_2Cl_9$ -structure ( $R\bar{3}c$ ;  $Z=6$ ) [60]

Compound	$a/\text{\AA}$	$c/\text{\AA}$	$V_{m(\text{exp.})}$	$\Delta V_m$
$Cs_3Ho_2Cl_9$ [4]	13.113	18.429	275.4	-27.8
$Cs_3Er_2Cl_9$	13.015	18.29	269.3	-32.1
$Cs_3Tm_2Cl_9$ [8]	12.997	18.274	268.3	-31.7
$Cs_3Yb_2Cl_9$	12.963	18.29	267.4	-30.8
$Cs_3Lu_2Cl_9$ [78]	12.945	18.264	266.0	-31.8
$Cs_3Y_2Cl_9$ [79]	13.107	18.333	272.7	-34.1

**Table 4** Continued**Table 4l** Compounds  $\text{Cs}_4\text{LnCl}_7$  ( $R\bar{3}m$ ;  $Z=3$ ) [14]

Compound	$a/\text{\AA}$	$c/\text{\AA}$	$V_{m(\text{exp.})}$	$\Delta V_m$
$\text{Cs}_4\text{ErCl}_7$	7.709	26.139	270.0	-13.0
$\text{Cs}_4\text{TmCl}_7$	7.682	26.214	268.0	-13.0
$\text{Cs}_4\text{YbCl}_7$	7.646	26.290	267.2	-12.9
$\text{Cs}_4\text{YCl}_7$	7.716	26.512	273.5	-10.9

**Table 4m** Compounds with the  $\text{NaGdCl}_4$ -structure ( $P\bar{1}$ ;  $Z=2$ ) [80]

Compound	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$\alpha/\text{degree}$	$\beta/\text{degree}$	$\gamma/\text{degree}$	$V_{m(\text{exp.})}$	$\Delta V_m$
$\text{NaEuCl}_4$	7.040	6.783	6.682	100.96	91.97	89.96	94.7	+9.1
$\text{NaGdCl}_4$	7.028	6.763	6.667	100.85	91.70	89.76	93.7	+8.6
$\text{NaTbCl}_4$	7.013	6.748	6.653	100.76	91.86	89.71	93.1	+8.5
$\text{NaDyCl}_4$	7.003	6.738	6.643	100.71	91.62	89.76	92.7	+7.9
$\text{L-NaHoCl}_4$	6.992	6.728	6.633	100.66	91.60	89.62	92.3	-7.7
$\text{NaYCl}_4$	6.992	6.727	6.633	100.66	91.60	89.61	92.3	-5.2

**Table 4n** Compounds with the  $\alpha\text{-NiWO}_4$ -structure ( $P2/c$ ;  $Z=2$ ) [81]

Compound	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$\beta/\text{degree}$	$V_{m(\text{exp.})}$	$\Delta V_m$
$\text{H-NaHoCl}_4$	not given in [81]					
$\text{NaErCl}_4$ [12]	6.322	7.598	6.742	92.3	97.5	-1.6
$\text{NaTmCl}_4$	6.293	7.571	6.722	92.2	96.4	-2.0

**Table 4o** Compounds with the  $\text{NaLuCl}_4$ -structure ( $Pbcm$ ;  $Z=4$ ) [82]

Compound	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$V_{m(\text{exp.})}$	$\Delta V_m$
$\text{NaYbCl}_4$	6.260	16.120	6.559	99.6	-0.9
$\text{NaLuCl}_4$	6.182	15.925	6.572	97.4	+0.1

hexachloro-lanthanides prepared from aqueous solutions crystallize in the orthorhombic space group  $Pbcm$  [15]. All these structures can be described as distortions of the cubic elpasolite-type by variations of the mutual orientation of the  $\text{LnCl}_6^{3-}$  octahedra. The coordination of  $A^+$  by  $\text{Cl}^-$  ions decreases from 12 to only 8 in the  $\text{Cs}_3\text{BiCl}_6$ -type, which is a less symmetric low-temperature modification. For the sodium-compounds two structure types exist. In both the coordination number is 6 for the  $\text{Ln}^{3+}$  and  $\text{Na}^+$  ions. The reason is that the radii of  $\text{Na}^+$  and  $\text{Ln}^{3+}$  are of a comparable size.  $\text{H-Na}_3\text{TbCl}_6$ ,  $\text{H-Na}_3\text{DyCl}_6$  and the compounds with  $\text{Ln}=\text{Ho-Lu}$  have a distorted cryolite-type structure, while  $\text{L-Na}_3\text{TbCl}_6$  and  $\text{L-Na}_3\text{DyCl}_6$  crystallize with hexagonal cells, in which  $\text{Na}^+$  and  $\text{Ln}^{3+}$  ions occupy slightly distorted octahedral holes in a hexagonal closed-packed chloride framework.

For the compounds  $\text{A}_3\text{LnCl}_6$  the transitions between the cubic H-type and the monoclinic structures are of the non-reconstructive type; there is no significant hysteresis between heating and cooling, and therefore the cubic high-temperature phase cannot be ob-

tained metastably at ambient temperature by quenching. As a consequence it is difficult to prepare single crystals. Meyer succeeded to obtain  $\text{Rb}_3\text{YCl}_6$  [65] by a transport reaction. Therefore, we have taken all values for compounds  $\text{Rb}_3\text{LnCl}_6$  in Table 4b from his paper. Analogously we have proceeded for the Cs and K compounds and could obtain single-crystals of  $\text{Cs}_3\text{YbCl}_6$  [9] and  $\text{K}_3\text{ErCl}_6$  [7] from supercritical acetic acid as described in detail for  $\text{Cs}_3\text{CrCl}_6$  [55].

The phase transition of  $\text{L-A}_3\text{LnCl}_6$  to  $\text{H-A}_3\text{LnCl}_6$  occurs between 392 and 403°C for  $A=\text{Cs}$  and 408–425°C for the Rb compounds. For  $\text{Cs}_3\text{TmCl}_6$  and  $\text{Cs}_3\text{YbCl}_6$  a third M-modification exists between ~370 and ~410°C; the still unknown structure is nearly related to the cubic elpasolite-type. For the K compounds the situation is more complicated as Fig. 5 shows [7]. Only the compounds  $\text{K}_3\text{LnCl}_6$  with  $\text{Ln}=\text{Er-Lu}$  are stable at 0 K. All other compounds are high-temperature compounds. While a La compound does not exist at all, the range of existence increases from  $\text{K}_3\text{CeCl}_6$  (>521°C) to  $\text{K}_3\text{HoCl}_6$  (>27°C). However, all compounds could be prepared in a metastable

**Table 5** Solution enthalpies ( $\Delta H_{\text{sol}}^0$ ), formation enthalpies ( $\Delta H_f^0$ ) and calculated transition enthalpies ( $\Delta H_{\text{tr}}^0$ ) in  $\text{kJ mol}^{-1}$  for compounds  $\text{Cs}_3\text{LnCl}_6$  [15] and  $\text{Cs}_4\text{LnCl}_7$ **Table 5a** Compounds with the composition  $\text{Cs}_3\text{LnCl}_6$ 

Compound	Pbcm modification		C2/c modification		
	$\Delta H_{\text{sol}}^0$	$\Delta H_f^0$	$\Delta H_{\text{sol}}^0$	$\Delta H_f^0$	$\Delta H_{\text{tr}}^0$
$\text{Cs}_3\text{NdCl}_6$	-50.3	-44.9	-56.3	-38.9	6.0
$\text{Cs}_3\text{SmCl}_6$	-50.5	-59.9	-54.1	-56.3	3.6
$\text{Cs}_3\text{EuCl}_6$	-52.9	-64.3	-54.3	-59.9	4.4
$\text{Cs}_3\text{GdCl}_6$	-54.9	-74.1	-59.3	-66.7	4.4
$\text{Cs}_3\text{TbCl}_6$	-56.1	-78.4	-61.0	-73.5	4.9
$\text{Cs}_3\text{DyCl}_6$	-57.6	-85.2	-60.4	-82.4	2.8
$\text{Cs}_3\text{HoCl}_6$	-60.1	-95.0	-63.1	-92.0	3.0
$\text{Cs}_3\text{ErCl}_6$	-61.0	-96.6	-63.6	-94.0	2.6
$\text{Cs}_3\text{TmCl}_6$	-62.7	-95.2	-63.8	-94.1	1.1
$\text{Cs}_3\text{YbCl}_6$	-63.6	-94.9	-64.6	-93.9	1.0

**Table 5b** Compounds with the composition  $\text{Cs}_4\text{LnCl}_7$ 

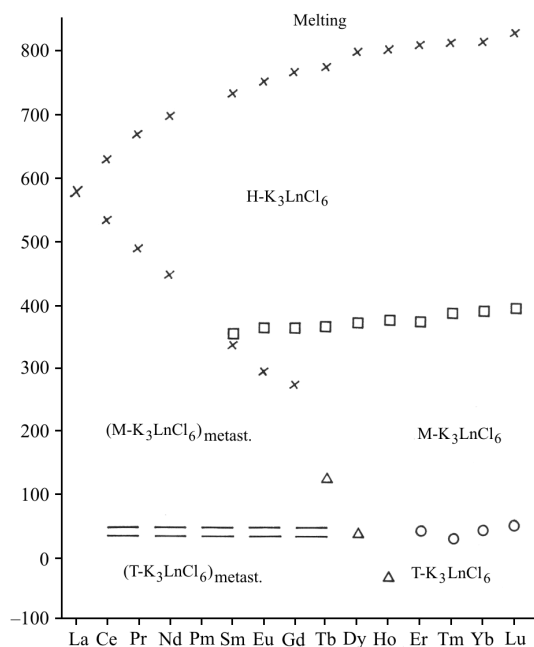
Compound	$\Delta H_{\text{sol}}^0$	$\Delta H_f^0$	$\Delta H_{\text{syn}}^0$	Compound	$\Delta H_{\text{sol}}^0$	$\Delta H_f^0$	$\Delta H_{\text{syn}}^0$
$\text{Cs}_4\text{YbCl}_7$	-54.8	-86.1	+8.8	$\text{Cs}_4\text{YCl}_7$	-53.3	-87.3	+3.3

state with the  $\text{K}_3\text{MoCl}_6$ -type structure at ambient temperature by quenching. Beginning with samarium M-modifications are stable ( $333^\circ\text{C}$ ). The transformation temperatures  $\text{M-K}_3\text{LnCl}_6 \rightarrow \text{H-K}_3\text{LnCl}_3$  increase slowly from  $342^\circ\text{C}$  for  $\text{K}_3\text{SmCl}_6$  to  $397^\circ\text{C}$  for  $\text{K}_3\text{LuCl}_6$ . Beginning with holmium a third, low-temperature modification of the  $\text{K}_3\text{MoCl}_6$ -type exists as a stable phase. The transition to the M-modification occurs at  $50\text{--}80^\circ\text{C}$ . The structure of the M-phase is still unknown, but is related to the  $\text{K}_3\text{MoCl}_3$ -type structure; the monoclinic  $a$ - and  $c$ -axis are equal and  $\beta=109.4^\circ$  (tetrahedral angle).

Sodium hexachloro compounds with Sm and earlier lanthanides do not exist;  $\text{Na}_3\text{EuCl}_6$  and  $\text{Na}_3\text{GdCl}_6$  even melt congruently, the compounds with Tb, Dy, Ho and Y incongruently. The melting point of the other compounds increases slightly from  $562^\circ\text{C}$  for  $\text{Na}_3\text{ErCl}_6$  to  $580^\circ\text{C}$  for  $\text{Na}_3\text{LuCl}_6$  [12]. Low temperature phases with the 'stuffed  $\text{LiSbF}_6$ '-type structure are known for compounds with  $\text{Ln}=\text{Eu, Gd, Tb, Dy}$ .

### Compounds $\text{A}_2\text{LnCl}_5$

The panorama of the compounds  $\text{A}_2\text{LnCl}_5$  is much less complicated than that of the hexachloro lanthanides. Only three structure families exist: in the  $\text{Cs}_2\text{DyCl}_5$ -type [59] the coordination of the  $\text{Ln}^{3+}$  ions is octahedral  $[\text{LnCl}_4\text{Cl}_2]^{2+}$ ; the  $\text{A}^+$  ions have a  $\text{CN}=(10+1)$ . The  $\text{K}_2\text{PrCl}_5$ -type [66], derived from  $\text{Y}_2\text{HfS}_5$  [67], contains chains, formed by monocapped trigonal prisms sharing two common edges. The coordination numbers are seven for  $\text{Ln}^{3+}$  and eight for  $\text{A}^+$ . The still unknown struc-



**Fig. 5** Stability ranges for the modifications of compounds  $\text{K}_3\text{LnCl}_6$ ;  $\times$  – melting and formation temperatures from DTA heating-curves;  $\Delta$  – formation temperatures from *e.m.f.* measurements;  $\circ$  – and  $\square$  – transition-temperatures of stable modifications by DTA;  $=$  – transition range of metastable modifications (from [7])

ture of the third group, realized by  $\text{K}_2\text{TmCl}_5$ ,  $\text{K}_2\text{YbCl}_5$  and probably  $\text{K}_2\text{LuCl}_5$ , is assumed to be built up by linked octahedra too, but with a smaller CN for the  $\text{A}^+$  ions than in the  $\text{Cs}_2\text{DyCl}_5$ -type.

With the larger  $\text{Ln}^{3+}$  ions La–Nd,  $\text{A}_2\text{LnCl}_5$ -compounds ( $A=\text{Cs, Rb, K}$ ) with the  $\text{K}_2\text{PrCl}_5$ -type structure exist, but no sodium compounds. Beginning with samarium the  $\text{Cs}_2\text{DyCl}_5$ -type was found in all Cs compounds. For compounds with the smaller Rb ion its CN=8 stabilizes the  $\text{K}_2\text{PrCl}_5$ -type from  $\text{Rb}_2\text{LaCl}_5$  to  $\text{Rb}_2\text{GdCl}_5$ . Tb and Dy compounds do not exist, and beginning with holmium the  $\text{LnCl}_6^{3-}$  octahedra have sufficiently shrinkage, therefore, the  $\text{Cs}_2\text{DyCl}_5$ -type with the CN=(10+1) for  $\text{Rb}^+$  can be realized. The situation for the  $\text{K}^+$  compounds is similar:  $\text{K}_2\text{PrCl}_5$ -type from La to Ho, no  $\text{K}_2\text{ErCl}_5$  and then the still unknown structure type. With Na only  $\text{Na}_2\text{LnCl}_5$ -type compounds with  $\text{Ln}=\text{Sm–Tb}$  exist with the  $\text{K}_2\text{PrCl}_5$ -type structure.

In Table 4g the unit cell parameters in the space group Pbnm (not in the equivalent Pnma) are taken from Meyer's paper [68]. The space group for the  $\text{K}_2\text{PrCl}_5$ -type compounds in Table 4h is Pnma [66].

### Compounds $\text{ALn}_2\text{Cl}_7$

Compounds  $\text{ALn}_2\text{Cl}_7$  exist in all Cs, Rb, K systems, and in the Na systems of Gd–Ho. At ambient temperature their structures belong to one of two types: the orthorhombic  $\text{RbDy}_2\text{Cl}_7$ -type or the symmetry-reduced monoclinic  $\text{KDy}_2\text{Cl}_7$ -type. Both structures were determined by Meyer [69] from single-crystal data. They contain layers of face- and edge-sharing monocapped trigonal prisms that are stacked in the [100] direction. The CN is seven for the  $\text{Ln}^{3+}$  and (10+2) for the  $\text{A}^+$  ions. Most of the compounds have one or more high-temperature modifications. Their structures are unknown as those of  $\text{NaGd}_2\text{Cl}_7$  and  $\text{NaHo}_2\text{Cl}_7$ . It should be pointed out that  $\text{ALn}_2\text{Cl}_7$ -type compounds with  $\text{Ln}=\text{La–Nd}$  exist in another structure type.

### Compounds with miscellaneous composition

The family of the 'enneachlorides'  $\text{Cs}_3\text{M}_2\text{Cl}_9$  contains pairs of face-sharing octahedra [ $\text{M}_2\text{Cl}_6\text{Cl}_{6/2}$ ] and is well known for compounds  $\text{Cs}_3\text{M}_2\text{Cl}_9$  ( $M=\text{Cr}^{3+}, \text{Mo}^{3+}, \text{W}^{3+}$ , etc.), which are examples of metal-metal bonds in the double-octahedra. In 1980 Meyer and Schönemund [60] described several compounds with  $M=\text{Ln}^{3+}$ , having the  $\text{Cs}_3\text{Tl}_2\text{Cl}_9$ -type structure [70, 71]. The structure of the enneachlorides is related to the  $\text{CsNiCl}_3$ -type structure: [ $\text{NiCl}_{6/2}$ ]-octahedra are twofold shared to infinite columns. If in [ $\text{Ni}_3\text{Cl}_9$ ] $^{3-}$  each third  $\text{Ni}^{2+}$  is removed and the two other are substituted by two  $\text{M}^{3+}$  ions, the  $\text{Cs}_3\text{Tl}_2\text{Cl}_9$  arrangement results. The structure is also related to the perovskite family: [ $\text{CsCl}_3$ ]-units form hexagonal-dense (ABAB...) stacking, while in the  $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ -type the stacking is ABCACB... The CN twelve of the  $\text{Cs}^+$  ions by the  $\text{Cl}^-$  ions fits well because of the similar ionic radii [72]:  $r_{\text{CN}12}(\text{Cs}^+)=1.88 \text{ \AA}$ ;  $r(\text{Cl}^-)=1.81 \text{ \AA}$ . The  $\text{Ln}^{3+}$  ions are better fitted to octahe-

dral holes the smaller they are. Thus, the existence of enneachlorides begins with  $\text{Ln}=\text{Ho}$ . In the phase diagram  $\text{KCl/YbCl}_3$  [9] an Yb compound, stable from  $394^\circ\text{C}$  was found, but nothing is known about its structure. In Table 4 the unit parameters from the most actual measurements are listed.

Compounds of the  $\text{Cs}_4\text{LnCl}_7$ -type exist with the smaller lanthanide ions Ho to Yb, with Y and probably with Lu, too. Their structure was determined with single crystals for  $\text{Cs}_4\text{YbCl}_7$  [14], and for some other compounds from powder patterns (Table 4i). The description of the structure is similar to that of the elpasolite-like compounds by Benachenhou *et al.* [63]. Layers with the composition  $\text{Cs}_2\text{LnCl}_6$ , containing isolated [ $\text{LnCl}_6$ ] $^{3-}$  octahedra all with the same orientation, are isolated from each other by layers of composition  $\text{Cs}_2\text{Cl}$ , containing sixfold disordered chloride ions.

### Sodium compounds

Beginning with europium compounds  $\text{NaLnCl}_4$  exist with all late lanthanides. For the larger ones, Eu to Dy, the coordination number for both cations is seven. This is the  $\text{NaGdCl}_4$ -type with monocapped trigonal prisms for  $\text{Ln}^{3+}$  and  $\text{Na}^+$ . According to Meyer [80] the triclinic structure is related to the fluorite-type. With  $\text{Ln}=\text{Er–Lu}$  all cations have octahedral coordination in two closely related types: monoclinic  $\alpha$ - $\text{NiWO}_4$ -type [81] for  $\text{Ln}=\text{Er, Tm}$  and orthorhombic  $\text{NaLuCl}_4$ -type [82] for  $\text{Ln}=\text{Yb}$  [9] and Lu.  $\text{NaHoCl}_4$  is dimorphic. L- $\text{NaHoCl}_4$  crystallizes with the  $\text{NaGdCl}_4$ -type structure, while H- $\text{NaHoCl}_4$  belongs to the  $\text{NiWO}_4$  family.

Meyer postulated [81] that all double-chlorides  $\text{NaLnCl}_4$  are dimorphic. With decreasing temperatures there is a transition from the  $\text{NaGdCl}_4$ -type to the  $\text{NaErCl}_4$ -type. This transition occurs at  $\sim 360^\circ\text{C}$  for  $\text{NaEuCl}_4$ , at  $\sim 50^\circ\text{C}$  for  $\text{NaHoCl}_4$  and  $\text{NaYCl}_4$ , at  $\sim -30^\circ\text{C}$  for  $\text{NaErCl}_4$  and at  $\sim -50^\circ\text{C}$  for  $\text{NaLuCl}_4$ . However, he did not report unit cell parameters for the respective structures. We have found with DTA and *e.m.f.* measurements dimorphism of this type only for  $\text{NaHoCl}_4$  [4] and  $\text{NaYCl}_4$  [5] with transition-temperatures of  $374$  and  $395^\circ\text{C}$ , respectively. We observed phase transitions in  $\text{NaEuCl}_4$  ( $360^\circ\text{C}$ ) and  $\text{NaGdCl}_4$  ( $283^\circ\text{C}$ ), but we only can say that one modification crystallizes in the  $\text{NaGdCl}_4$ -type structure, while the structure of the second modification is unknown.

## Thermodynamic properties

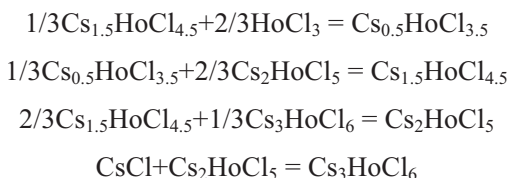
### Solution enthalpies

Solution enthalpies,  $\Delta H_{\text{sol}}^0$ , were measured of all ternary chlorides which are either stable at ambient tem-

perature or, in case of high-temperature modifications, were obtained metastably without partial decomposition by quenching. Samples of 2–5 g were dissolved in an isoperibolic under-water-calorimeter [83]. Because of the relatively high sample mass no compounds of the very expensive elements Tm and Lu were measured. An exception was made with their Na-compounds. The solvent H<sub>2</sub>O was slightly acidified with HCl (10<sup>-2</sup> mol L<sup>-1</sup>) to prevent hydrolysis. The volume of the solution was 1.3 l; thus with a dissolution rate 1:15000 virtually ideal solutions were obtained. At least two samples of each substance were measured. Together with the similarly measured solution enthalpies of the binary chlorides LnCl<sub>3</sub> and ACl, enthalpies of formation  $\Delta H_f^0$  according to  $n\text{ACl}_{(s)} + \text{LnCl}_{3(s)} = \text{A}_n\text{LnCl}_{3+n(s)}$  could be calculated:

$$\Delta H_f^0(\text{A}_3\text{LnCl}_{3+n}) = [n\Delta H_{\text{sol}}^0(\text{ACl}) + \Delta H_{\text{sol}}^0(\text{LnCl}_3)] - \Delta H_{\text{sol}}^0(\text{A}_3\text{LnCl}_{3+n})$$

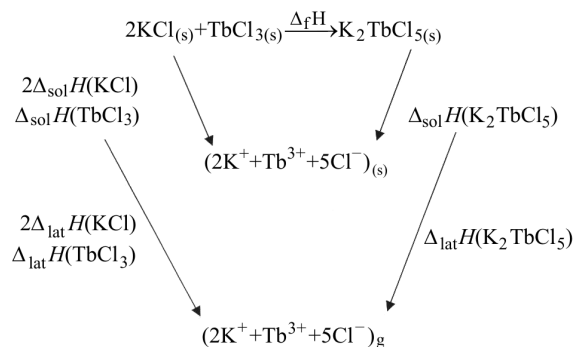
As the cycle in Fig. 6 shows the enthalpies  $\Delta H_f^0$  are identical with the change in lattice enthalpies at 298 K when forming the ternary chlorides from their binary ‘parent compounds’. However, still more important is the change in lattice enthalpies relative to the ‘neighbour compounds’ in the phase diagrams. We have called this difference ‘synreaction enthalpy’,  $\Delta H_{\text{syn}}^0$ . These enthalpies must be calculated from the original  $\Delta H_f^0$  values. The  $\Delta H_f^0$  values for the binary compounds ACl and LnCl<sub>3</sub> as a basis for the calculations were set equal zero. Taking the system CsCl/HoCl<sub>3</sub> as an example, the syn-reactions for the four existing compounds are:



All equations are normalized to one Ln<sup>3+</sup> ion per formula unit so that  $1/2\text{Cs}_2\text{Ln}_2\text{Cl}_7 = \text{Cs}_{0.5}\text{LnCl}_{3.5}$  and  $1/2\text{Cs}_3\text{Ln}_2\text{Cl}_9 = \text{Cs}_{1.5}\text{LnCl}_{4.5}$ . For the simplest reaction, that of Cs<sub>3</sub>HoCl<sub>6</sub>, the syn-reaction is  $\Delta H_{\text{syn}}^0(\text{Cs}_3\text{HoCl}_6) = \Delta H_f^0(\text{Cs}_3\text{HoCl}_6) - \Delta H_f^0(\text{Cs}_2\text{HoCl}_5)$ .

Most compounds are formed from their neighbours with exothermic lattice enthalpies,  $\Delta H_{\text{syn}}^0$  which are negative quantities. However, some compounds exhibit endothermic synreaction enthalpies. Here must be taken into account, that the true thermodynamic function for stability is not enthalpy but the free (Gibbs) enthalpy  $\Delta G$ . Both functions are connected by the Gibbs–Helmholtz relation  $\Delta G = \Delta H - T\Delta S$ . In Table 7 results of *e.m.f.* measurements are compiled, from which reaction entropies can be derived.

The exothermic solution enthalpies of the anhydrous lanthanide chlorides are compiled in Table 2; the



$$\begin{array}{ll} 2\Delta_{\text{sol}} H_{298}^0(\text{KCl}) = 2 \cdot 17.9 & \Delta_{\text{sol}} H_{298}^0(\text{K}_2\text{TbCl}_5) = -100.3 \\ \Delta_{\text{sol}} H_{298}^0(\text{TbCl}_3) = -188.8 & \\ \hline & -153.0 \end{array}$$

$$\Delta_f H_{298}^0(\text{K}_2\text{TbCl}_5) = -52.7 \text{ kJ mol}^{-1}$$

Fig. 6 Energy values for the formation of K<sub>2</sub>TbCl<sub>5</sub>

measured values for the alkali-metal chlorides are endothermic (in kJ mol<sup>-1</sup>): CsCl=18.1(2); RbCl=17.6(2); KCl=17.9(1); NaCl=4.5(1). It should be pointed out that we have measured the solution enthalpies of all hydrates LnCl<sub>3</sub>·xH<sub>2</sub>O, too [34].

In Table 5 solution- and formation-enthalpies from improved measurements [15] for the Pbcm and C2/c-modifications of the compounds Cs<sub>3</sub>LnCl<sub>6</sub> are compiled. From these data transition enthalpies (Pbcm)→(C2/c) are calculated. They are endothermic; consequently, the Pbcm-modification is stable at ambient temperature. Furthermore, values for Cs<sub>4</sub>YbCl<sub>7</sub> and Cs<sub>4</sub>YCl<sub>7</sub> are given. The syn-reaction enthalpies for the formation from the two neighbour-compounds CsCl+Cs<sub>3</sub>LnCl<sub>6</sub>=Cs<sub>4</sub>LnCl<sub>4</sub> are positive. Thus, these compounds are formed with a loss of lattice energy.

In Table 6 solution enthalpies,  $\Delta H_{\text{sol}}^0$ , enthalpies of formation from ACl and LnCl<sub>3</sub>,  $\Delta H_f^0$ , and syn-reaction enthalpies,  $\Delta H_{\text{syn}}^0$ , are compiled for all compounds found in phase diagrams, supplemented by values from the literature,  $\Delta H_f^0$ (lit.). Some incongruently melting compounds A<sub>2</sub>LnCl<sub>5</sub> could not be formed stoichiometrically pure by annealing. In this case we have taken  $\Delta H_f^0$  values from *e.m.f.* measurements (next chapter) for calculating  $\Delta H_{\text{syn}}^0$  values. They are given in brackets. The fourth column brings values taken from the literature (Blachnik and Selle [84]).

#### Gibbs free energies from *e.m.f.* measurements

It is a fundamental theorem in thermodynamics that not the enthalpy,  $\Delta H$ , but the Gibbs free energy,  $\Delta G$ , is the true criterion for stability. As explained in the last chapter, in a system ACl/LnCl<sub>3</sub> energies of synreaction are the crucial quantities. That is, a certain compound is stable at a certain temperature, if its  $\Delta G_{\text{syn}}^0$  is negative! From the Gibbs–Helmholtz relation it follows that

at  $T=0$  K stability is given by  $\Delta H_{\text{syn}}^0$  alone: a gain in (lattice) energy,  $U$ , (negative  $\Delta H$ ) must exist. However, at higher temperatures the entropy term becomes more and more important. A sufficiently high gain in entropy might compensate a positive change in enthalpy. The critical temperature can be calculated by the relation  $\Delta G_{\text{syn}}^0=0$  or  $\Delta H_{\text{syn}}^0=T\Delta S_{\text{syn}}^0$ .

$\Delta G$  values can be determined by *e.m.f.* measurements of the reactions  $n\text{AlCl}_3 + \text{A}_m\text{LnCl}_{m+3} = \text{A}_{(m+n)}\text{LnCl}_{(m+n+3)}$  in galvanic chlorine cells for solid electrolytes [85], using the relation  $\Delta G = -nFE$  ( $n$ =transported charge;  $F$ =Faraday constant;  $E$ =measured *e.m.f.*). For  $\text{Rb}_3\text{TbCl}_6$ , for instance, the electrolytes are  $\text{RbCl}$  and  $\text{Rb}_{0.5}\text{TbCl}_{3.5}$  separated by  $\text{Rb}^+$  conducting diaphragm.

The dependence of the *e.m.f.* on  $T$  has been proved to be linear at temperatures  $\geq 250^\circ\text{C}$ , so that a regression equation  $E=a+bT$  can be transformed directly to  $\Delta G = \Delta H - T\Delta S$  by multiplication with  $-nF$ . That means,  $\Delta H$  and  $\Delta S$  are temperature-independent in the range of measurement. The whole procedure will be explained, using the system  $\text{RbCl}/\text{TbCl}_3$  [2] as an example. According to the DTA measurements two compounds exist,  $\text{RbTb}_2\text{Cl}_7 = 2\text{Rb}_{0.5}\text{TbCl}_{3.5}$  and  $\text{Rb}_3\text{TbCl}_6$  with  $\text{L} \rightarrow \text{H}$  transformation at  $408^\circ\text{C}$ .

The cell for the *e.m.f.* measurements of the reaction  $0.5\text{RbCl} + \text{H-TbCl}_3 = \text{Rb}_{0.5}\text{TbCl}_{3.5}$  was built from discs of  $\text{RbCl}$  vs. mixtures containing 95 and 75 mol%  $\text{TbCl}_3$ , respectively. Approximately 30 pairs of *e.m.f./mV* vs.  $T/\text{K}$  values were measured for each run in the temperature range 600 to 635 K. The mean of both calculated regression lines gave *e.m.f./mV* =  $377.3 + 0.3400T/\text{K}$ . Multiplied with  $-0.5F$ :  $\Delta G_{\text{r}}^0/\text{kJ mol}^{-1} = -18.2 - 0.0164T/\text{K}$  with an accuracy of  $\Delta G_{\text{r}}^0$  is  $\pm 0.4 \text{ kJ mol}^{-1}$ .

For this reaction is  $\Delta G_{\text{r}}^0 = \Delta G_{\text{f}}^0$ ,  $\Delta H_{\text{r}}^0 = 18.2 \pm 0.3 \text{ kJ mol}^{-1}$  and  $\Delta S_{\text{r}}^0 = 16.4 \pm 0.5 \text{ J K}^{-1} \text{ mol}^{-1}$ .

$\Delta H_{\text{f}}^0$  from solution enthalpy measurements is  $-22.5 \text{ kJ mol}^{-1}$ . The agreement between both measurements of  $\Delta H$  is not excellent, but sufficient ( $\Delta$  up to max.  $4 \text{ kJ mol}^{-1}$ ). One has to take into account that the linearity, i.e.  $\Delta H$  independent of  $T$ , may not be given down to ambient temperature. Therefore,  $\Delta c_p$  measurements are necessary to explain the differences.

For the second reaction,  $2.5\text{RbCl} + \text{Rb}_{0.5}\text{TbCl}_{3.5} = \text{Rb}_3\text{TbCl}_6$  two samples with 55 and 45 mol%  $\text{TbCl}_3$  were used. For the  $\text{RbCl}/55 \text{ mol\% TbCl}_3$ -sample the computer plot *e.m.f.* vs.  $T$  is shown in Fig. 7. The curve consists of two lines with a kink at the transition-temperature  $\text{L} \rightarrow \text{H}(\text{Rb}_3\text{TbCl}_6)$ . Thus, two mean regression equations result:

For  $\text{H-Rb}_3\text{TbCl}_6$  *e.m.f./mV* =  $112.3 + 0.1948T/\text{K}$  and  $\Delta G_{\text{r}}^0/\text{kJ mol}^{-1} = -27.1 - 0.0470T/\text{K}$ , for  $\text{L-Rb}_3\text{TbCl}_6$  *e.m.f./mV* =  $156.3 + 0.1285T/\text{K}$  and  $\Delta G_{\text{r}}^0/\text{kJ mol}^{-1} = -37.7 - 0.0310T/\text{K}$ .

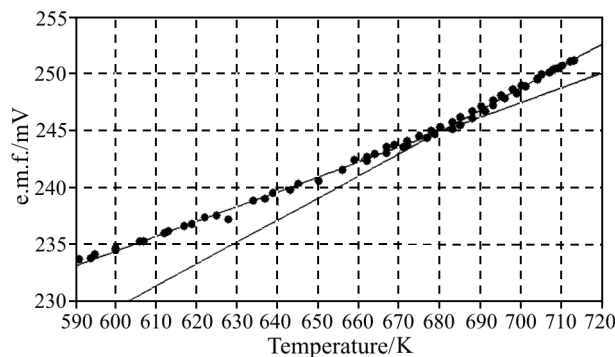


Fig. 7 Computer plot of *e.m.f.* vs.  $T$  for the reaction  $2.5\text{RbCl} + \text{Rb}_{0.5}\text{TbCl}_{3.5}$  (from [2])

The transition enthalpy is  $+10.6 \text{ kJ mol}^{-1}$  and the transition entropy  $16.0 \text{ J mol}^{-1} \text{ K}^{-1}$ . The transition-temperature is given by  $\Delta G^0(\text{H}) = \Delta G^0(\text{L})$  or  $T_{\text{tr}} = \Delta_{\text{tr}}H^0 / \Delta_{\text{tr}}S^0 = 663^\circ\text{K}$  ( $390^\circ\text{C}$ ). The temperature from DTA heating-curves is higher for kinetic reasons, being  $408^\circ\text{C}$ . Obviously, the functions for synreaction are identical with  $\Delta G_{\text{r}}^0(\text{Rb}_3\text{TbCl}_6)$ .

The Gibbs free energy of formation from  $3\text{RbCl} + \text{TbCl}_3$  is

$$\Delta G_{\text{f}}^0(\text{Rb}_3\text{TbCl}_6) = \Delta G_{\text{f}}^0(\text{Rb}_{0.5}\text{TbCl}_{3.5}) + \Delta G_{\text{r}}^0(\text{Rb}_3\text{TbCl}_6)$$

Therefore, for  $\text{H-Rb}_3\text{TbCl}_6$   $\Delta H_{\text{f}}^0 = -45.3 \text{ kJ mol}^{-1}$  and  $\Delta S_{\text{f}}^0 = 63.4 \text{ J K}^{-1} \text{ mol}^{-1}$  and for  $\text{L-Rb}_3\text{TbCl}_6$   $\Delta H_{\text{f}}^0 = -55.9 \text{ kJ mol}^{-1}$  and  $\Delta S_{\text{f}}^0 = 47.4 \text{ J K}^{-1} \text{ mol}^{-1}$ . For the 1:2-compound the synreaction is



and

$$\Delta G_{\text{syn}}^0 = \Delta G_{\text{f}}^0(\text{Rb}_{0.5}\text{TbCl}_{3.5}) - 1/6\Delta G_{\text{f}}^0(\text{Rb}_3\text{TbCl}_6) - 5/6\Delta G_{\text{f}}^0(\text{TbCl}_3)$$

with  $\Delta G_{\text{f}}^0(\text{TbCl}_3) = 0$ , because  $\text{TbCl}_3$  (and  $\text{RbCl}$ ) are chosen as basic compounds. With the foregoing relation between  $\Delta G_{\text{f}}^0$  and the  $\Delta G_{\text{r}}^0$  it is

$$\Delta G_{\text{syn}}^0(\text{Rb}_{0.5}\text{TbCl}_{3.5}) = 5/6\Delta G_{\text{r}}^0(\text{Rb}_{0.5}\text{TbCl}_{3.5}) - 1/6\Delta G_{\text{r}}^0(\text{Rb}_3\text{TbCl}_6)$$

The calculated functions related to  $\text{L-Rb}_3\text{TbCl}_6$  are  $\Delta H_{\text{syn}}^0(\text{Rb}_{0.5}\text{TbCl}_{3.5}) = -8.9 \text{ kJ mol}^{-1}$  and  $\Delta S_{\text{syn}}^0(\text{Rb}_{0.5}\text{TbCl}_{3.5}) = 8.5 \text{ J K}^{-1} \text{ mol}^{-1}$ . For both compounds  $\Delta G_{\text{syn}}^0$  cannot become zero; the compounds should be stable at all temperatures, on the premises of temperature-independence of  $\Delta H$  and  $\Delta S$ .

There is another situation in the system  $\text{KCl}/\text{TbCl}_3$ . Here for  $\text{M-K}_3\text{TbCl}_6$   $\Delta G_{\text{syn}}^0 = \Delta G_{\text{r}}^0$

$$\Delta G/\text{kJ mol}^{-1} = 14.5 - 0.0464T/\text{K}$$

with  $\Delta G_{\text{syn}}^0 = 0$  at  $312 \text{ K}$  ( $39^\circ\text{C}$ ).



**Table 6** Solution-, formation- and synreaction enthalpies of ternary chlorides of the trivalent late lanthanides [kJ mol<sup>-1</sup>]

Compound	$\Delta H_{\text{sol}}^0$	$\Delta H_f^0$	$\Delta H_{\text{syn}}^0$	$\Delta H_f^0/\text{literature [84]}$
0.5CsTb <sub>2</sub> Cl <sub>7</sub>	-151.4	-28.3	-16.0	
Cs <sub>2</sub> TbCl <sub>5</sub>	-95.1	-57.5	-2.1	
L-Cs <sub>3</sub> TbCl <sub>6</sub>	-61.0	-73.5	-13.9	
0.5CsDy <sub>2</sub> Cl <sub>7</sub>	-155.4	-32.4	-14.9	-39.0
Cs <sub>2</sub> DyCl <sub>5</sub>	-90.2	-71.8	-9.2	
L-Cs <sub>3</sub> DyCl <sub>6</sub>	-60.4	-82.4	-10.6	-85.4
0.5CsHo <sub>2</sub> Cl <sub>7</sub>	-167.6	-32.8	-11.4	
0.5Cs <sub>3</sub> Ho <sub>2</sub> Cl <sub>9</sub>	-117.9	-64.4	+1.5	
Cs <sub>2</sub> HoCl <sub>5</sub>	-	(-82.0)	-7.4	
L-Cs <sub>3</sub> HoCl <sub>6</sub>	-60.1	-95.0	-13.0	
0.5CsEr <sub>2</sub> Cl <sub>7</sub>	-166.0	-36.8	-13.2	-41.9
0.5Cs <sub>3</sub> Er <sub>2</sub> Cl <sub>9</sub>	-113.9	-70.8	-5.0	
Cs <sub>2</sub> ErCl <sub>5</sub>	-	(-80.3)	-1.8	
L-Cs <sub>3</sub> ErCl <sub>6</sub>	-63.3	-94.0	-13.7	-98.5
0.5CsYb <sub>2</sub> Cl <sub>7</sub>	-174.2	-29.5	-4.6	
0.5Cs <sub>3</sub> Yb <sub>2</sub> Cl <sub>9</sub>	-110.8	-74.8	-14.8	
Cs <sub>2</sub> YbCl <sub>5</sub>	-101.4	-75.2	+6.0	
L-Cs <sub>3</sub> YbCl <sub>6</sub>	-64.6	-93.9	-18.7	-96.7
0.5CsY <sub>2</sub> Cl <sub>7</sub>	-171.2	-32.6	-12.0	
0.5Cs <sub>3</sub> Y <sub>2</sub> Cl <sub>9</sub>	-123.8	-61.8	+0.7	
Cs <sub>2</sub> YCl <sub>5</sub>	-	(-77.4)	-5.4	
L-Cs <sub>3</sub> YCl <sub>6</sub>	-66.2	-92.3	-14.9	
<hr/>				
0.5RbTb <sub>2</sub> Cl <sub>7</sub>	-157.5	-22.5	-12.2	
L-Rb <sub>3</sub> TbCl <sub>6</sub>	-74.3	-61.7	-39.2	
0.5RbDy <sub>2</sub> Cl <sub>7</sub>	-163.6	-24.7	-13.2	
L-Rb <sub>3</sub> DyCl <sub>6</sub>	-75.9	-68.8	-44.1	
0.5RbHo <sub>2</sub> Cl <sub>7</sub>	-168.1	-32.5	-19.7	
L-Rb <sub>3</sub> HoCl <sub>6</sub>	-79.8	-76.8	-44.3	
(Rb <sub>2</sub> HoCl <sub>5</sub> stable>414°C)				
0.5RbEr <sub>2</sub> Cl <sub>7</sub>	-171.9	-31.3	-18.4	
L-Rb <sub>3</sub> ErCl <sub>6</sub>	-81.7	-77.4	-46.1	
(Rb <sub>2</sub> ErCl <sub>5</sub> stable>348°C)				
0.5RbYb <sub>2</sub> Cl <sub>7</sub>	-166.7	-37.3	-21.5	
Rb <sub>2</sub> YbCl <sub>5</sub>	-114.5	-63.1	+3.1	
L-Rb <sub>3</sub> YbCl <sub>6</sub>	-74.6	-85.4	-22.3	
0.5RbY <sub>2</sub> Cl <sub>7</sub>	-175.1	-28.9	-16.6	
L-Rb <sub>3</sub> YCl <sub>6</sub>	-86.2	-73.8	-44.9	
<hr/>				
0.5KTb <sub>2</sub> Cl <sub>7</sub>	-167.6	-12.2	+1.0	
K <sub>2</sub> TbCl <sub>5</sub>	-100.3	-52.7	-25.6	
L-K <sub>3</sub> TbCl <sub>6</sub>	-98.1	-37.0	+15.7	
0.5KDy <sub>2</sub> Cl <sub>7</sub>	-167.2	-20.9	-6.8	-23.9
K <sub>2</sub> DyCl <sub>5</sub>	-104.8	-56.5	-22.3	
L-K <sub>3</sub> DyCl <sub>6</sub>	-100.3	-43.1	+13.4	-43.9
0.5KHo <sub>2</sub> Cl <sub>7</sub>	-173.2	-27.3	-10.8	-24.8
K <sub>2</sub> HoCl <sub>5</sub>	-	(-65.7)	-22.7	
L-K <sub>3</sub> HoCl <sub>6</sub>	-102.2	-53.5	+12.2	
0.5KEr <sub>2</sub> Cl <sub>7</sub>	-177.2	-25.8	-16.8	
L-K <sub>3</sub> ErCl <sub>6</sub>	-104.5	-53.7	-28.0	-56.9
0.5KYb <sub>2</sub> Cl <sub>7</sub>	-188.8	-15.1	-4.2	
K <sub>2</sub> YbCl <sub>5</sub>	-133.7	-43.3	-5.1	
L-K <sub>3</sub> YbCl <sub>6</sub>	-105.5	-53.6	-10.3	-57.0
0.5KY <sub>2</sub> Cl <sub>7</sub>	-183.8	-20.05	-4.4	
K <sub>2</sub> YCl <sub>5</sub>	-	(-63.4)	-26.7	
L-K <sub>3</sub> YCl <sub>6</sub>	-111.4	-47.7	+15.7	

Table 6 Continued

Compound	$\Delta H_{\text{sol}}^0$	$\Delta H_{\text{f}}^0$	$\Delta H_{\text{syn}}^0$	$\Delta H_{\text{f}}^0/\text{literature [84]}$
NaTb <sub>2</sub> Cl <sub>7</sub>	-193.1	+6.6	+6.2	
NaTbCl <sub>4</sub>	-185.0	+0.7	-4.4	
Na <sub>2</sub> TbCl <sub>5</sub>	-182.0	+2.2	±0	
L-Na <sub>3</sub> TbCl <sub>6</sub>	-179.1	+3.8	+1.6	
0.5NaDy <sub>2</sub> Cl <sub>7</sub>	-198.8	+4.0	+4.9	
NaDyCl <sub>4</sub>	-190.7	-1.9	-4.7	
L-Na <sub>3</sub> DyCl <sub>6</sub>	-181.7	-1.9	±0	
0.5NaHo <sub>2</sub> Cl <sub>7</sub>	-204.7	-2.45	+1.6	
L-NaHoCl <sub>4</sub>	-196.8	-8.1	-5.1	
Na <sub>3</sub> HoCl <sub>6</sub>	-190.6	-5.3	+2.8	
NaErCl <sub>4</sub>	-201.7	-5.7	-2.1	
Na <sub>3</sub> ErCl <sub>6</sub>	-187.5	-10.9	-5.2	
NaTmCl <sub>4</sub>	-200.6	-7.1	-3.5	
Na <sub>3</sub> TmCl <sub>6</sub>	-187.9	-10.8	-3.7	
NaYbCl <sub>4</sub>	-189.4	-19.0	-10.4	
Na <sub>3</sub> YbCl <sub>6</sub>	-173.6	-25.8	-6.8	
NaLuCl <sub>4</sub>	-206.2	-0.9	+2.1	
Na <sub>3</sub> LuCl <sub>6</sub>	-189.1	-9.0	-8.1	
Na <sub>3</sub> YCl <sub>6</sub>	-190.9	-8.4		

That is, below this temperature the compound is no longer stable; the entropy term  $-\Delta ST$  cannot any longer compensate the endothermic synreaction-enthalpy.

The inverted case is realized too. In the system KCl/HoCl<sub>3</sub> the compound K<sub>2</sub>HoCl<sub>5</sub> decomposes according to DTA measurements at 445°C to H-K<sub>3</sub>HoCl<sub>6</sub> and K<sub>0.5</sub>HoCl<sub>3.5</sub>. For the formation from 1.5KCl+K<sub>0.5</sub>HoCl<sub>3.5</sub>,  $\Delta G_{\text{r}}^0/\text{kJ mol}^{-1} = -38.4 + 0.01107T/\text{K}$ . The synreaction is 0.6K<sub>3</sub>HoCl<sub>6</sub>+0.4K<sub>0.5</sub>HoCl<sub>3.5</sub>=K<sub>2</sub>HoCl<sub>5</sub> with  $\Delta G_{\text{syn}}^0/\text{kJ mol}^{-1} = -22.2 + 0.03227T/\text{K}$ . It becomes zero at 689 K (416°C), the temperature of decomposition.

The reported evaluations are restricted by two experimental deficiencies:

- The temperature range for the measurements is restricted. If solid-state reactions take place outside this range extrapolations beyond the reaction temperature are not reasonable.
- Our experiences have shown that the *e.m.f.* cells break down for *e.m.f.* values higher than ~450 mV and/or temperatures higher than 450 K. ('Break down' means that no constant potentials are yielded.) These limits are deeper in general for Cs compounds and with the smaller Ln<sup>3+</sup> ions. Thus, no  $\Delta G_{\text{f}}^0$  values for the compounds A<sub>0.5</sub>LnCl<sub>3.5</sub> could be calculated. The situation is different for the synreaction-functions. Here the  $\Delta G_{\text{r}}^0$  values for the LnCl<sub>3</sub>-rich neighbours are eliminated in terms for  $\Delta G_{\text{syn}}^0$ . For the ternary Cs compounds of Yb no *e.m.f.* values could be measured at all.

In Table 7 the expressions  $\Delta G_{\text{r}}^0 = \Delta H_{\text{r}}^0 - \Delta S_{\text{r}}^0 T$  and  $\Delta G_{\text{syn}}^0 = \Delta H_{\text{syn}}^0 - \Delta S_{\text{syn}}^0 T$  for all the compounds, for which *e.m.f.* measurements could be performed, are

compiled together with the temperature range of the measurements. They are comprehended in blocks with all compounds of a system ACl/LnCl<sub>3</sub>. If measurements with H- and L-modifications could be done synreactions with both of them are given. Then also transformation functions are calculated. Furthermore, formation temperatures for compounds with endothermic (positive)  $\Delta H_{\text{syn}}^0$  values are listed.

## The relation between thermodynamics and structure

### General connections

As has been already explained the radii of the Ln<sup>3+</sup> and A<sup>+</sup> ions determine the crystal structures of the different ternary chlorides. This relation should result from the different energetic functions, namely, the enthalpies of formation from ACl and LnCl<sub>3</sub>,  $\Delta H_{\text{f}}^0$ , and the synreaction energies,  $\Delta H_{\text{syn}}^0$  and  $\Delta G_{\text{syn}}^0$ .

- $\Delta H_{\text{f}}^0$  reflects the loss in lattice enthalpy by the formation of the ternary chlorides.

For the compound A<sub>n</sub>LnCl<sub>3+n</sub> it is

$$\begin{aligned} \Delta H_{\text{lat}}^0(\text{A}_n\text{LnCl}_{3+n}) &= \\ &= n\Delta H_{\text{lat}}^0(\text{ACl}) + \Delta H_{\text{lat}}^0(\text{LnCl}_3) + \Delta H_{\text{f}}^0(\text{A}_n\text{LnCl}_{3+n}) \end{aligned}$$

The lattice enthalpies of the alkali-metal chlorides can be taken from textbooks of solid-state chemistry. They range, for instance, from  $\Delta H_{\text{lat}}^0(\text{CsCl}) = -640.6 \text{ kJ mol}^{-1}$  to  $\Delta H_{\text{lat}}^0(\text{NaCl}) = -767.8 \text{ kJ mol}^{-1}$ . The  $\Delta H_{\text{lat}}^0(\text{LnCl}_3)$  values are given in Table 2 and range from  $\Delta H_{\text{lat}}^0(\text{TbCl}_3) = -4476$  to  $\Delta H_{\text{lat}}^0(\text{LnCl}_3) =$

**Table 7** Enthalpies  $\Delta H$  (in  $\text{kJ mol}^{-1}$ ) and entropies  $\Delta S$  (in  $\text{J K}^{-1} \text{mol}^{-1}$ ) determined by *e.m.f.* measurements (H – high-temperature modification; L – low-temperature modification)

Cs-compounds	$\Delta G_r^0 = \Delta H_r^0 - \Delta S_r^0 T$	Temperature range/K	$\Delta G_{\text{syn}}^0 = \Delta H_{\text{syn}}^0 - \Delta S_{\text{syn}}^0 T$
Cs <sub>2</sub> TbCl <sub>5</sub>	-30.1-0.0242 <i>T</i>	575-690 K	H: -6.2-0.0065 <i>T</i> L: -11.8-0.0109 <i>T</i>
H-Cs <sub>3</sub> TbCl <sub>6</sub>	-9.8-0.0200 <i>T</i>	665-725	id. $\Delta G_r^0$
L-Cs <sub>3</sub> TbCl <sub>6</sub>	-17.0-0.0091 <i>T</i>	580-660	id. $\Delta G_r^0$
Transform. L→H-Cs <sub>3</sub> TbCl <sub>6</sub> : $\Delta H_{\text{tr}}^0=7.2 \text{ kJ mol}^{-1}$ ; $\Delta S_{\text{tr}}^0=10.9 \text{ J K}^{-1} \text{mol}^{-1}$ ; $T_{\text{tr}}=661 \text{ K}$ ; (388°C; DTA=400°C)			
Cs <sub>2</sub> DyCl <sub>5</sub>	-37.1-0.0161 <i>T</i>	560-650	-6.0-0.0047 <i>T</i>
L-Cs <sub>3</sub> DyCl <sub>6</sub>	-14.8-0.0123 <i>T</i>	580-650	id. $\Delta G_r^0$
0.5Cs <sub>3</sub> Ho <sub>2</sub> Cl <sub>9</sub>	-32.3-0.0020 <i>T</i>	580-670	+1.0-0.0029 <i>T</i>
Cs <sub>2</sub> HoCl <sub>5</sub>	-17.6+0.0034 <i>T</i>	600-660	-6.1+0.0053 <i>T</i>
L-Cs <sub>3</sub> HoCl <sub>6</sub>	-16.8-0.0093 <i>T</i>	570-660	id. $\Delta G_r^0$
$\Delta G_{\text{syn}}^0(\text{Cs}_{1.5}\text{HoCl}_{4.5})=0$ at 330 K (57°C)			
0.5Cs <sub>3</sub> Er <sub>2</sub> Cl <sub>9</sub>	-30.0-0.0102 <i>T</i>	580-630	-3.7+0.0014 <i>T</i>
Cs <sub>2</sub> ErCl <sub>5</sub>	-9.5-0.0072 <i>T</i>	580-640	-0.3-0.0024 <i>T</i>
L-Cs <sub>3</sub> ErCl <sub>6</sub>	-18.2-0.0073 <i>T</i>	580-610	id. $\Delta G_r^0$
0.5Cs <sub>3</sub> Tm <sub>2</sub> Cl <sub>9</sub>	-38.8-0.0024 <i>T</i>	620-650	-5.7+0.0017 <i>T</i>
Cs <sub>2</sub> TmCl <sub>5</sub>	-10.9-0.0038 <i>T</i>	600-650	-1.7+0.0006 <i>T</i>
M-Cs <sub>3</sub> TmCl <sub>6</sub>	-12.5-0.0162 <i>T</i>	645-670	id. $\Delta G_r^0$
L-Cs <sub>3</sub> TmCl <sub>6</sub>	-16.8-0.0095 <i>T</i>	600-645	id. $\Delta G_r^0$
Transform. L→M-Cs <sub>3</sub> TmCl <sub>6</sub> : $\Delta H_{\text{tr}}^0=4.3 \text{ kJ mol}^{-1}$ ; $\Delta S_{\text{tr}}^0=6.7 \text{ J K}^{-1} \text{mol}^{-1}$ ; $T_{\text{tr}}=642 \text{ K}$ ; (369°C; DTA=376°C)			
0.5Cs <sub>3</sub> Y <sub>2</sub> Cl <sub>9</sub>	-28.7-0.0065 <i>T</i>	610-655	1.2-0.0022 <i>T</i>
Cs <sub>2</sub> YCl <sub>5</sub>	-16.1±0	600-640	-5.0+0.0033 <i>T</i>
L-Cs <sub>3</sub> YCl <sub>6</sub>	-17.1-0.0100 <i>T</i>	615-655	id. $\Delta G_r^0$
$\Delta G_{\text{syn}}^0(\text{Cs}_{1.5}\text{YCl}_{4.5})=0$ at 545 K (272°C)			
Rb-compounds	$\Delta G_r^0 = \Delta H_r^0 - \Delta S_r^0 T$	Temperature range/K	$\Delta G_{\text{syn}}^0 = \Delta H_{\text{syn}}^0 - \Delta S_{\text{syn}}^0 T$
0.5RbTb <sub>2</sub> Cl <sub>7</sub>	-18.2-0.0164 <i>T</i>	600-635	H: -10.6-0.0058 <i>T</i> L: -8.9-0.0085 <i>T</i>
H-Rb <sub>3</sub> TbCl <sub>6</sub>	-27.1-0.0470 <i>T</i>	685-715	id. $\Delta G_r^0$
L-Rb <sub>3</sub> TbCl <sub>6</sub>	-37.7-0.0310 <i>T</i>	590-680	id. $\Delta G_r^0$
Transform. L→H-Rb <sub>3</sub> TbCl <sub>6</sub> : $\Delta H_{\text{tr}}^0=10.6 \text{ kJ mol}^{-1}$ ; $\Delta S_{\text{tr}}^0=16 \text{ J K}^{-1} \text{mol}^{-1}$ ; $T_{\text{tr}}=663 \text{ K}$ ; (390°C; DTA=408°C)			
L-Rb <sub>3</sub> DyCl <sub>6</sub>	-41.1-0.0292 <i>T</i>	560-680	id. $\Delta G_r^0$
L-Rb <sub>3</sub> HoCl <sub>6</sub>	-39.4-0.0371 <i>T</i>	600-690	id. $\Delta G_r^0$
Rb <sub>2</sub> ErCl <sub>5</sub>	-21.0-0.0303 <i>T</i>	560-640	5.9-0.0111 <i>T</i>
L-Rb <sub>3</sub> ErCl <sub>6</sub>	-23.9-0.0017 <i>T</i>	560-640	id. $\Delta G_r^0$
$\Delta G_{\text{syn}}^0(\text{Rb}_2\text{ErCl}_5)=0$ at 535 K (262°C; DTA=348°C)			
Rb <sub>2</sub> TmCl <sub>5</sub>	-31.3-0.0171 <i>T</i>	610-670	2.5-0.0068 <i>T</i>
L-Rb <sub>3</sub> TmCl <sub>6</sub>	-25.1±0	610-650	id. $\Delta G_r^0$
$\Delta G_{\text{syn}}^0(\text{Rb}_2\text{TmCl}_5)=0$ at 371 K (98°C)			
Rb <sub>2</sub> YbCl <sub>5</sub>	-30.6-0.0195 <i>T</i>	620-690	2.8-0.0078 <i>T</i>
L-Rb <sub>3</sub> YbCl <sub>6</sub>	-25.1±0	620-690	id. $\Delta G_r^0$
$\Delta G_{\text{syn}}^0(\text{Rb}_2\text{YbCl}_5)=0$ at 362 K (88°C)			
L-Rb <sub>3</sub> YCl <sub>6</sub>	-41.9-0.0322 <i>T</i>	600-670	id. $\Delta G_r^0$
K-compounds	$\Delta G_r^0 = \Delta H_r^0 - \Delta S_r^0 T$	Temperature range/K	$\Delta G_{\text{syn}}^0 = \Delta H_{\text{syn}}^0 - \Delta S_{\text{syn}}^0 T$
0.5KTb <sub>2</sub> Cl <sub>7</sub>	-11.5-0.0162 <i>T</i>	520-670	1.1-0.0146 <i>T</i>
K <sub>2</sub> TbCl <sub>5</sub>	-39.1+0.0099 <i>T</i>	575-675	H: -31.5+0.0395 <i>T</i> M: -26.7+0.0319 <i>T</i>
H-K <sub>3</sub> TbCl <sub>6</sub>	26.5-0.0592 <i>T</i>	640-685	id. $\Delta G_r^0$
M-K <sub>3</sub> TbCl <sub>6</sub>	18.4-0.0466 <i>T</i>	590-640	id. $\Delta G_r^0$
Transform. M→H-K <sub>3</sub> TbCl <sub>6</sub> : $\Delta H_{\text{tr}}^0=8.1 \text{ kJ mol}^{-1}$ ; $\Delta S_{\text{tr}}^0=12.6 \text{ J K}^{-1} \text{mol}^{-1}$ ; $T_{\text{tr}}=642 \text{ K}$ ; (369°C; DTA=367°C); $\Delta G_{\text{syn}}^0(\text{L-K}_3\text{TbCl}_6)=0$ at 395 K (122°C); $\Delta G_{\text{syn}}^0(\text{K}_{0.5}\text{TbCl}_{3.5})=0$ at 79 K (-194°C)			

Table 7 Continued

K-compounds	$\Delta G_r^0 = \Delta H_r^0 - \Delta S_r^0 T$	Temperature range/K	$\Delta G_{\text{syn}}^0 = \Delta H_{\text{syn}}^0 - \Delta S_{\text{syn}}^0 T$
K <sub>2</sub> DyCl <sub>5</sub>	-38.5+0.0099T	570–720	H: -29.3+0.0399T M: -24.1+0.0318T
H-K <sub>3</sub> DyCl <sub>6</sub>	23.2-0.0599T	640–720	id. $\Delta G_r^0$
M-K <sub>3</sub> DyCl <sub>6</sub>	14.5-0.0464T	570–640	id. $\Delta G_r^0$
Transform. L→M-K <sub>3</sub> DyCl <sub>6</sub> : $\Delta H_{\text{tr}}^0=8.7$ kJ mol <sup>-1</sup> ; $\Delta S_{\text{tr}}^0=13.5$ J K <sup>-1</sup> mol <sup>-1</sup> ; $T_{\text{tr}}=644$ K; (371°C; DTA=373°C); $\Delta G_{\text{syn}}^0(\text{M-K}_3\text{DyCl}_6)=0$ at 312 K (39°C)			
K <sub>2</sub> HoCl <sub>5</sub>	-38.4+0.0110T	600–640	-22.2+0.0322T
M-K <sub>3</sub> HoCl <sub>6</sub>	11.4-0.0464T	600–640	id. $\Delta G_r^0$
$\Delta G_{\text{syn}}^0(\text{M-K}_3\text{HoCl}_6)=0$ at 246 K (-27°C)			
M-K <sub>3</sub> ErCl <sub>6</sub>	-31.8-0.0356T		id. $\Delta G_r^0$
K <sub>2</sub> TmCl <sub>5</sub>	-23.1-0.0177T	610–670	H: -8.8-0.0071T M: -4.6+0.0046T
H-K <sub>3</sub> TmCl <sub>6</sub>	-0.8-0.0294T	660–680	id. $\Delta G_r^0$
M-K <sub>3</sub> TmCl <sub>6</sub>	-7.3-0.0195T	610–660	id. $\Delta G_r^0$
Transform. M→H-K <sub>3</sub> TmCl <sub>6</sub> : $\Delta H_{\text{tr}}^0=6.5$ kJ mol <sup>-1</sup> ; $\Delta S_{\text{tr}}^0=9.9$ J K <sup>-1</sup> mol <sup>-1</sup> ; $T_{\text{tr}}=657$ K; (384°C; DTA=386°C)			
K <sub>2</sub> YbCl <sub>5</sub>	-26.0-0.0167T	580–635	H: -9.9+0.0111T L: -5.2+0.0038T
H-K <sub>3</sub> YbCl <sub>6</sub>	-0.9-0.0296T	650–680	id. $\Delta G_r^0$
M-K <sub>3</sub> YbCl <sub>6</sub>	-8.7-0.0175T	590–650	id. $\Delta G_r^0$
Transform. M→H-K <sub>3</sub> YbCl <sub>6</sub> : $\Delta H_{\text{tr}}^0=7.8$ kJ mol <sup>-1</sup> ; $\Delta S_{\text{tr}}^0=12.1$ J K <sup>-1</sup> mol <sup>-1</sup> ; $T_{\text{tr}}=650$ K; (377°C; DTA=392°C)			
K <sub>2</sub> YCl <sub>5</sub>	-43.1+0.0198T	605–645	H: -27.4+0.0411T L: -23.4+0.0349T
H-K <sub>3</sub> YCl <sub>6</sub>	16.9-0.0553T	650–680	id. $\Delta G_r^0$
M-K <sub>3</sub> YCl <sub>6</sub>	10.3-0.0449T	615–650	id. $\Delta G_r^0$
Transform. M→H-K <sub>3</sub> YCl <sub>6</sub> : $\Delta G_{\text{tr}}^0=6.6$ kJ mol <sup>-1</sup> ; $\Delta S_{\text{tr}}^0=10.4$ J K <sup>-1</sup> mol <sup>-1</sup> ; $T_{\text{tr}}=635$ K; (362°C; DTA=377°C); $\Delta G_{\text{syn}}^0(\text{M-K}_3\text{YCl}_6)=0$ at 229 K (-44°C)			
Na-compounds	$\Delta G_r^0 = \Delta H_r^0 - \Delta S_r^0 T$	Temperature range/K	$\Delta G_{\text{syn}}^0 = \Delta H_{\text{syn}}^0 - \Delta S_{\text{syn}}^0 T$
0.5NaTb <sub>2</sub> Cl <sub>7</sub>	6.1-0.0213T	570–670	5.5-0.0107T
NaTbCl <sub>4</sub>	-4.9±0	310–410	-2.7+0.0007T
Na <sub>2</sub> TbCl <sub>5</sub>	-1.6-0.0051T	290–320	-4.3+0.0091T
H-Na <sub>3</sub> TbCl <sub>6</sub>	7.1-0.0232T	290–400	id. $\Delta G_r^0$
0.5NaDy <sub>2</sub> Cl <sub>7</sub>	+6.4-0.0025T	570–670	+5.8-0.0012T
NaDyCl <sub>4</sub>	-5.2±0	570–670	-4.9+0.0051T
H-Na <sub>3</sub> DyCl <sub>6</sub>	3.6-0.0257T	580–670	id. $\Delta G_r^0$
0.5NaHo <sub>2</sub> Cl <sub>7</sub>	-3.7-0.0036T	580–650	0.9-0.0018T
L-NaHoCl <sub>4</sub>	-5.3±0	570–650	-5.0+0.0062T
Na <sub>3</sub> HoCl <sub>6</sub>	3.8-0.0312T	570–630	id. $\Delta G_r^0$
NaErCl <sub>4</sub>	-5.8-0.0074T	580–640	-2.4+0.0019T
Na <sub>3</sub> ErCl <sub>6</sub>	-4.4-0.0204T	590–670	id. $\Delta G_r^0$
Na <sub>3</sub> TmCl <sub>6</sub>	-3.4-0.0214T		id. $\Delta G_r^0$
Na <sub>3</sub> YbCl <sub>6</sub>	-5.8-0.0199T		id. $\Delta G_r^0$
Na <sub>3</sub> LuCl <sub>6</sub>	-8.2-0.0153T		id. $\Delta G_r^0$
0.5NaY <sub>2</sub> Cl <sub>7</sub>	-3.9-0.0024T	590–620	-0.6+0.0010T
NaYCl <sub>4</sub>	-2.7-0.0045T	570–620	-1.7+0.0005T
Na <sub>3</sub> YCl <sub>6</sub>	-2.3-0.0205T	560–680	id. $\Delta G_r^0$

-4569 kJ mol<sup>-1</sup>. Thus,  $\Delta H_{\text{lat}}^0(\text{Cs}_3\text{TbCl}_6) = 3(-640.6) - 4476 - 73.5 = -6471.3$ , all in kJ mol<sup>-1</sup>. That is, the measured  $\Delta H_r^0 = -73.5$  kJ mol<sup>-1</sup> contributes with only 1.1% to the total lattice enthalpy, mainly given by the binary chlorides. For a row of compounds with the same *A*, for instance Cs<sub>3</sub>LnCl<sub>6</sub>, it becomes more exothermic with decreasing radius  $r(\text{Ln}^{3+})$  and for a given *Ln* from Cs to Na compounds. Consequently,

the total values are not sensitive for small energetic effects, which are reflected better by the measured enthalpy differences.

At  $T=0$  the entropy term in the Gibbs–Helmholtz equation is zero and stability is controlled by enthalpy alone. The lattice enthalpies depend on the fitting of the cations in the voids of the Cl<sup>-</sup> packing. Thus, with decreasing size of the Ln<sup>3+</sup> ion first the lattice enthalpy

decreases because the Ln–Cl distance becomes smaller until a ‘critical radii relation’ is reached; then a transition to a structure type with a smaller CN occurs. The radii of the Ln<sup>3+</sup> ions [72] decrease from Ln<sup>3+</sup> (103 pm) to Lu<sup>3+</sup> (86 pm). This leads to a decreasing tendency of occupying interstices of the CN7 in the chloride packing in favour of an octahedral coordination.

Generally the LnCl<sub>x</sub> polyhedra get smaller with decreasing distance Ln–Cl and thus also the Cl–Cl distances are shrinking. These shrinkages affect as well the coordination of the A<sup>+</sup> ions. The CN in the main structure types are:

	Cs <sub>3</sub> LnCl <sub>6</sub>	K <sub>2</sub> PrCl <sub>5</sub>	Cs <sub>2</sub> DyCl <sub>5</sub>
CN for Ln <sup>3+</sup>	6	7	6
CN for A <sup>+</sup>	2.12+1.6	8	10/11
	KEr <sub>2</sub> F <sub>7</sub>	RbDy <sub>2</sub> Cl <sub>7</sub>	Cs <sub>3</sub> Tl <sub>2</sub> Cl <sub>9</sub>
CN for Ln <sup>3+</sup>	8	7	6
CN for A <sup>+</sup>	9/11	(10+2)	12

From Cs to Na the tendency for formation of the CN6 of the alkali ions increases. For all groups of compounds the volumes of the unit cells diminish from La to Lu due to the diminishing ionic radii. For the same reason compounds of Rb form smaller unit cells compared with the Cs compounds of the same composition.

The (Gibbs) synreaction enthalpies,  $\Delta G_{\text{syn}}^0$ , describe the stabilities of given ternary chlorides related to their neighbour compounds in their phase diagrams, and due to their temperature dependence allow the calculation of the range of stability. As can be seen from the Gibbs–Helmholtz equation,  $\Delta G = \Delta H - T\Delta S$ ,  $\Delta G$  is negative if  $\Delta H$  is negative and the entropy term becomes negligible. That is the common assumption in solid-state chemistry. However, as we have seen the  $\Delta H^0$  values are relatively small compared with the total lattice energies. Therefore, entropy can also be of importance for the

sign of  $\Delta G$ . For a  $\Delta S_{\text{syn}}^0$  of +10 J K<sup>-1</sup> mol<sup>-1</sup>, e.g., at ambient temperature the term  $-T\Delta S^0$  is about –3 kJ mol<sup>-1</sup> and can compensate a loss in lattice energy of the same magnitude. The compound then is stable only up from ambient temperature. Otherwise, a loss in entropy makes the  $-T\Delta S$  term positive, and a compound stable at 0 K will decompose to its neighbours at  $T = \Delta H_{\text{syn}}^0 / \Delta S_{\text{syn}}^0$ . One can observe these relations by starting the temperature scale of phase diagrams at 0 K (Fig. 8). The expression ‘high-temperature phase’ has now not its usual meaning.

The basis for these considerations is the linear temperature dependence of  $\Delta G$ . Then  $\Delta H$  and  $\Delta S$  are constants. It follows that  $c_p = c_p(A_n \text{LnCl}_{3+n}) - n c_p(\text{A}^+\text{Cl}) + c_p(\text{LnCl}_3) = 0$ . By measurements of  $c_p$  with ternary lanthanum chlorides [86] it is proven that this condition is fulfilled down to 200 K. It can be assumed that the further change of  $c_p$  is at least monotonous, so that our considerations about stability ranges are correct at least qualitatively.

### Compounds A<sub>3</sub>LnCl<sub>6</sub>

The compounds A<sub>3</sub>LnCl<sub>6</sub> form the most homogenous group of ternary lanthanide chlorides. They all belong to the elpasolite-structure family with isolated [LnCl<sub>6</sub>]<sup>3-</sup> octahedra, which are held together by the A<sup>+</sup> ions. Cs and Rb compounds exist with all lanthanides; for Ln=La to Gd a survey is given in [87]. The structural and energetic relations of the K compounds with Ln=Ce–Yb have been described recently [7]. The La compound does not exist. Sodium compounds Na<sub>3</sub>LnCl<sub>6</sub> exist with Ln=Eu to Lu; they will be treated later together with the other families of Na compounds.

Compounds A<sub>3</sub>LnCl<sub>6</sub> with A=Cs, Rb, K have the highest melting points among the compounds of their respective systems. Their melting points first increase

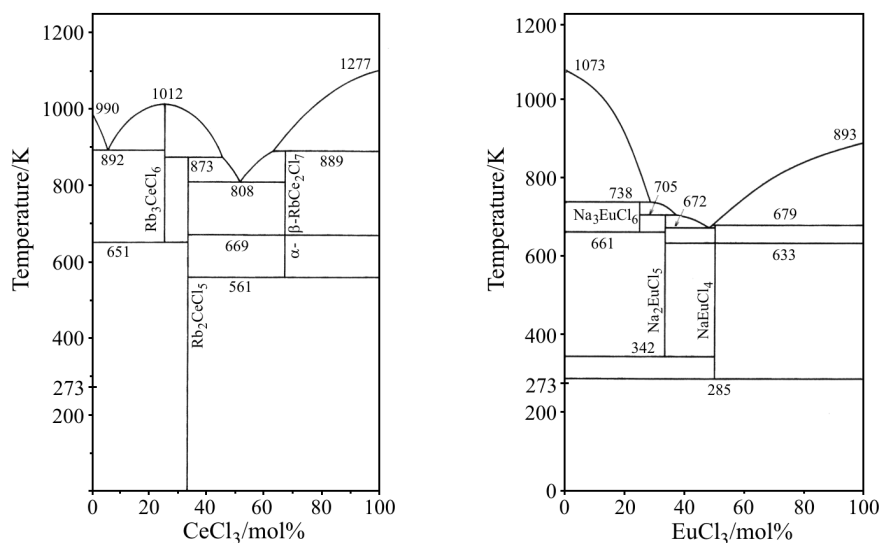
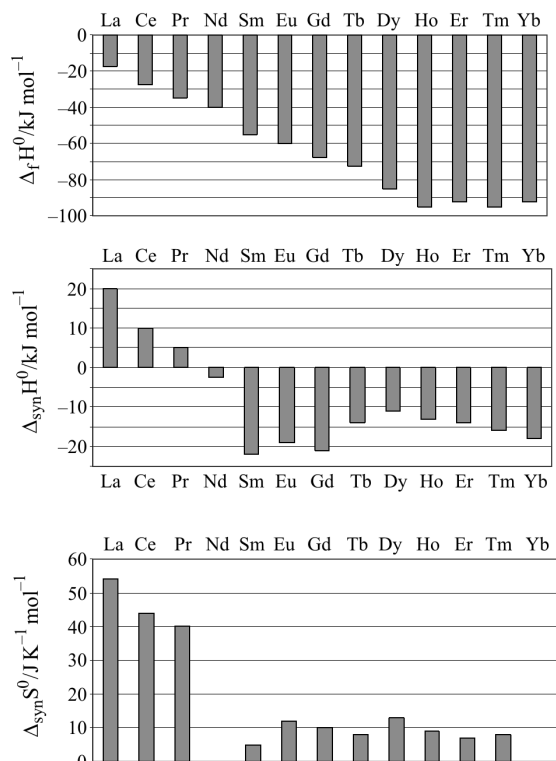


Fig. 8 Systems RbCl/CeCl<sub>3</sub> and NaCl/EuCl<sub>3</sub> up from 0 K



**Fig. 9** Thermodynamic data for compounds  $\text{Cs}_3\text{LnCl}_6$  (formation:  $3\text{CsCl} + \text{LnCl}_3$ ; synreaction:  $\text{CsCl} + \text{Cs}_2\text{LnCl}_5$ )

distinctively from 1053 K ( $\text{Cs}_3\text{LaCl}_6$ ) to 1153 K ( $\text{Cs}_3\text{TbCl}_6$ ), less in the second half of the lanthanides (*m.p.* ( $\text{Cs}_3\text{YbCl}_6$ )=1171 K). The same tendency exists for the enthalpies of formation from ( $3\text{ACl} + \text{LnCl}_3$ ), which are the differences in the lattice enthalpies (Fig. 9). According to the electrostatic binding model, for the compounds of Cs and K, Blachnik and Selle already in 1979 found an almost linear variation of their lattice energies with decreasing  $r(\text{Ln}^{3+})$ , derived from measured solution enthalpies [24]. That the  $\Delta H_f^\circ$  values for the last lanthanides are nearly constant must be attributed to the fact that here the CN6 is just fitting to their ionic radii.

Thus, the binary  $\text{LnCl}_3$  compounds from Dy to Lu crystallize in the  $\text{AlCl}_3$ -type with  $\text{LnCl}_{6/2}$  octahedra linked together while the CN of the  $\text{Ln}^{3+}$  ions in the  $\text{UCl}_3$ -type ( $\text{Ln}=\text{La}-\text{Gd}$ ) is nine. For the first members in the rows of compounds  $\text{Rb}_3\text{LnCl}_6$  ( $\text{Ln}=\text{La}, \text{Ce}$ ) and  $\text{K}_3\text{LnCl}_6$  ( $\text{Ln}=\text{La}-\text{Nd}$ ) the formation from  $\text{ACl}$  and  $\text{LnCl}_3$  is endothermic. The reason is that  $\text{Rb}^+$  and  $\text{K}^+$  are too small for their CN ( $2 \times 8$  and  $1 \times 10$ ) in the  $\text{Cs}_3\text{BiCl}_6$  or  $\text{K}_3\text{MoCl}_6$ -type structure. If the chloride packing shrinks with decreasing  $r(\text{Ln}^{3+})$  the situation gets more and more favourable for these smaller alkali-metal ions.

These relations are partially reflected by the variation in the  $\Delta V_m$  values. For the compounds from La to Dy they are positive. The increase is small for the Cs

compounds ( $4 \text{ cm}^3 \text{ mol}^{-1}$  to  $-1$ ) and increases over the Rb ( $16 \text{ cm}^3 \text{ mol}^{-1}$  to 9) to the K-compounds ( $20 \text{ cm}^3$  to 10). For  $\text{Ln}=\text{Ho}$  to Lu the binary chlorides crystallize with a layer structure, the  $\text{AlCl}_3$ -type; the volume decreases with the formation of the ternary chloride.

The measured enthalpies for the synreaction  $\text{ACl} + \text{A}_2\text{LnCl}_5 = \text{A}_3\text{LnCl}_6$  reveal that there are two groups:

- Positive  $\Delta H_{\text{syn}}^\circ$  values are found for Cs compounds from La to Nd, for Rb compounds from La to Gd and for K compounds from Ce to Ho. These compounds are formed in a synreaction from  $\text{ACl}$  and the pentachloro compounds with the  $\text{K}_2\text{PrCl}_5$ -type structure, in which monocapped trigonal prisms are fourfold linked to  $(\text{LnCl}_3\text{Cl}_{4/2})^{2-}$  chains. The transition from this rigid coordination to the isolated  $(\text{LnCl}_6)^{3-}$  octahedra produces a gain in entropy between 40 and  $55 \text{ J K}^{-1} \text{ mol}^{-1}$ . The endothermic  $\Delta H_{\text{syn}}^\circ$ , caused by the transition from CN7 to CN6 for the ions is compensated by a high  $T\Delta S$  term, the compounds being stable if  $T\Delta S_{\text{syn}} > \Delta H_{\text{syn}}^\circ$ . The temperatures in which these compounds are stable, decrease with decreasing  $r(\text{Ln}^{3+})$  and therefore increasing stability of the  $\text{A}_3\text{LnCl}_6$  compounds.
- All other hexachloro complexes have negative (exothermic)  $\Delta H_{\text{syn}}^\circ$  values. They should be stable at 0 K.

As reported in the chapter 'Crystal structures' all 3:1-compounds have cubic high-temperature-modifications. For several compounds we were able to determine transition enthalpies ( $\Delta H_{\text{tr}}^\circ$ ), and entropies ( $\Delta S_{\text{tr}}^\circ$ ), by *e.m.f.* measurements. They are in the range 6 to  $10 \text{ kJ mol}^{-1}$  and 7 and  $16 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively. The modifications of  $\text{Cs}_3\text{LnCl}_6$  compounds in Pbcm, crystallizing from aqueous solution (Table 5), exist only if they are stable at ambient temperature, that is, it begins with neodymium.  $\text{Cs}_3\text{NdCl}_6$  (Pbcm) is formed only from hot solutions ( $>60^\circ\text{C}$ ). Below this temperature a hydrate is formed as with solutions of lanthanum, cerium and praseodymium.

#### Compounds $\text{A}_2\text{LnCl}_5$

All 2:1-compounds with  $\text{A}=\text{Cs}, \text{Rb}, \text{K}$  are formed from their binary parent compounds with exothermic lattice enthalpies. They exist in three structure types, the  $\text{K}_2\text{PrCl}_5$ -type with  $\text{CN}(\text{Ln}^{3+})=7$  and  $\text{CN}(\text{A}^+)=8$ , the  $\text{Cs}_2\text{DyCl}_5$ -type with  $\text{CN}(\text{Ln}^{3+})=6$  and  $\text{CN}(\text{A}^+)=7$  and a third type with three members  $\text{K}_2\text{LnCl}_5$  ( $\text{Ln}=\text{Er}, \text{Tm}, \text{Yb}$ ) of still unknown structure.

The  $\text{K}_2\text{PrCl}_5$ -type exists from  $\text{A}_2\text{LaCl}_5$  to  $\text{Cs}_2\text{NdCl}_5$ ,  $\text{Rb}_2\text{GdCl}_5$  and  $\text{K}_2\text{HoCl}_5$ , respectively. Sodium compounds with this structure exist from  $\text{Na}_2\text{SmCl}_5$  to  $\text{Na}_2\text{TbCl}_5$ . They are formed from  $\text{NaCl}$  and  $\text{LnCl}_3$  with endothermic enthalpies ( $+14.4$  to  $\sim 0 \text{ kJ mol}^{-1}$ ). All Cs, Rb and K compounds have distinctly exothermic synreaction enthalpies. They are sta-

ble at 0 K. The Cs compounds and  $\text{Rb}_2\text{EuCl}_5$ ,  $\text{Rb}_2\text{GdCl}_5$ ,  $\text{K}_2\text{HoCl}_5$  decompose in the solid-state. That is, their synreaction must occur with such a high loss in entropy, that the now positive  $-T\Delta S$  term at  $T_D$  compensates the exothermic  $\Delta H_{\text{syn}}^0$ . The other Rb compounds and the compounds  $\text{K}_2\text{LnCl}_5$  with the  $\text{K}_2\text{PrCl}_5$ -structure melt incongruently; only the compounds with  $Ln = \text{La-Nd}$  have congruent melting points. The highest temperatures of existence decrease with decreasing radii of the  $\text{Ln}^{3+}$  ions. The reason is that the  $\text{CN}=7$  becomes increasingly too high for the lanthanide ions.

A new structure family, the  $\text{Cs}_2\text{DyCl}_5$ -type, now becomes stable, for the Cs compounds starting with  $\text{Cs}_2\text{SmCl}_5$ . With rubidium the Tb and Dy compounds, with potassium an Er compound do not exist. These borderlines of existence for the  $\text{K}_2\text{PrCl}_5$ -type compound are the same as for the positive  $\Delta H_{\text{syn}}^0$  values of the compounds  $\text{A}_3\text{LnCl}_6$ .

In the  $\text{K}_2\text{PrCl}_5$ -type the packing is very dense because of fourfold bound trigonal prisms. Thus, a gain in lattice energy is connected with the synreaction from the  $\text{A}_3\text{LnCl}_6$  neighbours with their isolated octahedra. On the other hand a high loss in entropy exists. The coordination in the  $\text{Cs}_2\text{DyCl}_5$ -structure is less rigid, the octahedra are twofold connected. Thus, the synreaction entropy is smaller ( $\sim 10 \text{ J K}^{-1} \text{ mol}^{-1}$  for the Cs compounds), the synreaction enthalpies are exothermic and a slight increase of the molar volumes compared with  $2\text{AlCl} + \text{LnCl}_3$  exists. However, the formation from the chlorides with layer structure occurs with a decrease in  $\Delta V_m$ . The formation of the  $\text{K}_2\text{PrCl}_5$ -type compounds is accompanied by a loss in  $V_m$ .

For the Cs compounds the transition from  $\text{CN}(\text{Ln}^{3+})=7$  to 6 occurs very early in the series of  $Ln$ . The increase of the CN from 8 to 11 for the large  $\text{Cs}^+$  is well tolerated. With the smaller  $\text{Rb}^+$  the  $\text{K}_2\text{PrCl}_5$ -type exists up to  $\text{Rb}_2\text{GdCl}_5$ . The  $\Delta H_f^0$  values get more exothermic from La to Eu ( $-33.3$  to  $-61.1 \text{ kJ mol}^{-1}$ ), but the  $\text{Gd}^{3+}$  ion seems already to be too small for the  $\text{CN}7$ , the enthalpy is now only  $-53.7 \text{ kJ mol}^{-1}$ . Beginning with  $\text{Ho}^{3+}$  the octahedral coordination is so favourable, that now a  $\text{CN}(\text{A}^+)=11$  is possible. However, their synreaction enthalpies are positive, they are high temperature compounds, existing above 687 K ( $\text{Rb}_2\text{HoCl}_5$ ) or 362 K ( $\text{Rb}_2\text{YbCl}_5$ ). The 2:1-compounds of the  $\text{K}_2\text{PrCl}_5$ -type have exothermic synreaction enthalpies and are stable at 0 K.

Considering the synreaction enthalpies it must be taken into account that the structure of the neighbour compounds may change, mainly for the Cs compounds. For  $\text{Cs}_2\text{LaCl}_5$  with  $\text{CN}=7$  for  $\text{Ln}^{3+}$  ion, they are  $\text{Cs}_3\text{LaCl}_6$  and  $\text{CsLa}_2\text{Cl}_7$  ( $\text{KEr}_2\text{F}_7$ -type) with coordination numbers 6 and 8 for  $\text{La}^{3+}$ , respectively. Beginning with  $\text{Cs}_2\text{SmCl}_5$ , with  $\text{CN}(\text{Sm}^{3+})=6$ , they are  $\text{Cs}_3\text{SmCl}_6$  and  $\text{CsSm}_2\text{Cl}_7$  ( $\text{RbDy}_2\text{Cl}_7$ -type) with  $\text{CN}=7$

for  $\text{Ln}^{3+}$ . From Ho to Yb the neighbours are  $\text{Cs}_3\text{LnCl}_6$  and  $\text{CsLn}_2\text{Cl}_7$  both with  $\text{CN}=6$  for  $\text{Ln}^{3+}$ .

### Compounds $\text{ALn}_2\text{Cl}_7$

The  $\text{ALn}_2\text{Cl}_7$  compounds with  $A = \text{Cs}$  and  $\text{Rb}$  of the first four lanthanides La to Nd, crystallize in the  $\text{KEr}_2\text{Cl}_7$ -type where  $\text{CN}(\text{Ln}^{3+})=8$  and the  $\text{CN}(\text{A}^+)$  is 9 and 11. The formation from  $\text{AlCl} + 2\text{LnCl}_3$  is exothermic,  $\sim -10 \text{ kJ mol}^{-1}$  for  $A = \text{Cs}$  and only between  $-2$  and  $-5 \text{ kJ mol}^{-1}$  for the Rb compounds. The larger  $\text{Cs}^+$  fits better the 9/11 coordination than the  $\text{Rb}^+$  ion. With the smaller  $\text{K}^+$  only one compound exists,  $\text{KNd}_2\text{Cl}_7$  with a small endothermic change in lattice energy.

The synreaction enthalpies of the Cs compounds are not very different from zero,  $+1.6 \text{ kJ mol}^{-1}$  for  $\text{CsLa}_2\text{Cl}_7$ , and  $-3.1 \text{ kJ mol}^{-1}$  for  $\text{CsNd}_2\text{Cl}_7$ . For the compounds of the other alkali-metals they are distinctly positive,  $+6.5 \text{ kJ mol}^{-1}$  for  $\text{RbNd}_2\text{Cl}_7$  and  $+11.5 \text{ kJ mol}^{-1}$  for  $\text{KNd}_2\text{Cl}_7$ . These compounds should exist only at temperatures higher than 0 K. Because *e.m.f.* measurements for these Ln-rich compounds could not be performed, the formation temperatures could not be calculated. With DTA, for  $\text{KNd}_2\text{Cl}_7$  a stability range at 766–783 K was determined.

From Sm to Yb all compounds with Cs, Rb, K exist, crystallizing with the structures of  $\text{RbDy}_2\text{Cl}_7$  or  $\text{KDy}_2\text{Cl}_7$ . In both very similar structures the CN are 7 for  $\text{Ln}^{3+}$  and 10+2 for the  $\text{A}^+$  ions. All compounds are formed from  $\text{AlCl} + 2\text{LnCl}_3$  exothermically. The synreaction enthalpies are exothermic for Cs and Rb compounds and K compounds with  $Ln = \text{Dy}$  to Yb. They are stable at 0 K. The other K compounds exist only at temperatures  $>0$  K. Sodium compounds  $\text{NaLn}_2\text{Cl}_7$  exist with  $Ln = \text{Gd}$  to Ho. The  $\Delta H_f^0$  values are positive for compounds with Gd, Tb and Dy, slightly negative for the Ho compound; all  $\Delta H_{\text{syn}}^0$  values are positive. It must be pointed out that in several systems high-temperature modifications exist with unknown structures.

### Enneachlorides

Enneachlorides  $\text{Cs}_3\text{Ln}_2\text{Cl}_9$  were found in the systems with  $Ln = \text{Ho}$  to Lu. The existence of a  $\text{K}_3\text{Yb}_2\text{Cl}_9$  is unsure. The  $\text{Cs}_3\text{Tl}_2\text{Cl}_9$  structure is nearly related to that of perovskite with  $\text{CN}6$  for the  $\text{Ln}^{3+}$  ions and 12 for the  $\text{A}^+$  ions. The formation enthalpies from  $3\text{CsCl} + 2\text{LnCl}_3$  are strongly negative ( $\sim -70 \text{ kJ mol}^{-1}$  for  $\text{Cs}_{1.5}\text{LnCl}_{4.5}$ ), comparable with those of the 2:1 compounds with the same Ln. The enthalpies of the synreactions from  $\text{Cs}_2\text{LnCl}_5$  and  $\text{Cs}_{0.5}\text{LnCl}_{3.5}$  are slightly negative with the exception of  $\text{Cs}_3\text{Ho}_2\text{Cl}_9$  which is stable at  $>330$  K. It can be concluded that enneachlorides exist, if the octahedral voids in the  $\text{Cl}^-$  packing suit the  $\text{Ln}^{3+}$  ions but only with the large  $\text{Cs}^+$  ion being surrounded by 12  $\text{Cl}^-$  ions.

## Sodium compounds

The systems NaCl/LnCl<sub>3</sub> with Ln=La to Sm are dominated by solid solutions between LnCl<sub>3</sub> and NaCl up to the composition Na<sub>3</sub>Ln<sub>5</sub>Cl<sub>18</sub>. As explained in [1] the  $r(\text{Na}^+)=102$  pm is of a comparable size with the radii of the first lanthanide ions, for instance  $r(\text{Ce}^{3+})=103$  pm. The phase A<sub>3</sub>Ln<sub>5</sub>Cl<sub>18</sub>, which also exists with A=K for Ln=La and Ce, can be derived from (LnCl<sub>3</sub>)<sub>6</sub>=Ln<sub>6</sub>Cl<sub>18</sub> by the substitution of one Ln<sup>3+</sup> ion by three A<sup>+</sup> ions. The miscibility ranges diminish with decreasing size of the Ln<sup>3+</sup> ions; with Eu<sup>3+</sup> this phase no longer exists. The formation enthalpies are positive ( $\sim 6$  kJ mol<sup>-1</sup>), compensated by entropies of  $\sim 15$  J K<sup>-1</sup> mol<sup>-1</sup> for Na<sub>0.6</sub>LnCl<sub>3.6</sub>.

From Sm to Tb the existing compounds are with the composition Na<sub>2</sub>LnCl<sub>5</sub> and from Gd to Ho additional existing compounds are with the composition NaLn<sub>2</sub>Cl<sub>7</sub>. They crystallize with the same structures as the potassium compounds and thus the same considerations are valid.

Another situation is found for the compounds Na<sub>3</sub>LnCl<sub>6</sub> with Ln=Eu to Lu. For them the monoclinic cryolite-type is formed, from Eu to Dy as a high-temperature modification. The low-temperature modifications crystallize according to Meyer with a trigonal stuffed LiSbF<sub>6</sub>-structure. Both structure types appear with CN6 for both cations. The cryolite-structure is stable above 666 K for Na<sub>3</sub>EuCl<sub>6</sub> and 538 K for Na<sub>3</sub>GdCl<sub>6</sub>. Their trigonal modifications can be obtained only by quenching and only as metastable phases, as found with *e.m.f.* measurements. For the Tb and Dy compounds the phase transitions are reversible, at 426 and  $\sim 390$  K (120°C), respectively. Beginning with Na<sub>3</sub>HoCl<sub>6</sub> the cryolite-type is stable at ambient temperature. The stability borders to low temperatures decrease from 388°C (Eu) to  $\sim 120^\circ\text{C}$  (Dy). Thus, it may be speculated that for Ho and the following lanthanides the trigonal phase might be formed at temperatures below ambient temperature; but no experimental evidence exists.

Beginning with Na<sub>3</sub>ErCl<sub>6</sub> the compounds have exothermic  $\Delta H_f^0$  and  $\Delta H_{\text{syn}}^0$  values. For Na<sub>3</sub>HoCl<sub>6</sub> the formation enthalpy is negative, but  $\Delta H_{\text{syn}}^0$  is positive with  $+2.8$  kJ mol<sup>-1</sup>; this compound does not exist at 0 K but is stable  $>122$  K. The formation enthalpies

of the trigonal modifications from 3NaCl + LnCl<sub>3</sub> and their synreaction enthalpies are endothermic, and Na<sub>3</sub>DyCl<sub>6</sub> is accepted. The transition enthalpy to the high-temperature modifications with the cryolite-structure is about  $+5$  kJ mol<sup>-1</sup>.

Unique for the ternary lanthanide chlorides with sodium are compounds with the composition NaLnCl<sub>4</sub>. From NaEuCl<sub>4</sub> to L-NaHoCl<sub>4</sub> they have the triclinic NaGdCl<sub>4</sub>-structure with CN7 for both cations. Beginning with H-NaHoCl<sub>4</sub> two near related structure types exist with CN6 for both cations, resulted from the shrinkage of the  $r(\text{Ln}^{3+})$ : the  $\alpha$ -NaWO<sub>4</sub>-type for H-NaHoCl<sub>4</sub> and the compounds with Ln=Er and Tm, and the NaLuCl<sub>4</sub>-type for Ln=Yb, Lu.

The energetic relations in the systems NaCl/EuCl<sub>3</sub> and NaCl/GdCl<sub>3</sub> are similar. All compounds in the systems are formed from NaCl and LnCl<sub>3</sub> with endothermic enthalpies. For the EuCl<sub>3</sub> system all necessary energies could be measured, so that we could construct the system up from 0 K (Fig. 8). As the figure demonstrates no compound is stable at 0 K. The largest stability range has NaEuCl<sub>4</sub> with a formation temperature of 285 K. Its formation reaction NaCl+EuCl<sub>3</sub>=NaEuCl<sub>4</sub> is the synreaction too. The relations in the system with GdCl<sub>3</sub> are analogous. For the next two systems (Ln=Tb and Dy) no concrete interpretations can be given, because the necessary energy values are too close to  $\pm 0$ . Again all Tb compounds have endothermic  $\Delta H_f^0$  values. For dysprosium no 2:1-compound exists, but as with Tb the compound NaLn<sub>2</sub>Cl<sub>7</sub> exists. The  $\Delta H_f^0(\text{NaDyCl}_4)$  has become slightly negative. The system NaCl/HoCl<sub>3</sub> is the last, containing compounds with CN higher than 6 in NaHo<sub>2</sub>Cl<sub>7</sub> and L-NaHoCl<sub>4</sub>. The transition to H-NaHoCl<sub>4</sub> occurs at 647 K. The formation enthalpies for all compounds are negative, but  $\Delta H_{\text{syn}}^0$  is exothermic only for NaHoCl<sub>4</sub> which is stable at 0 K.

The system NaCl/ErCl<sub>3</sub> is the first to contain only two compounds, Na<sub>3</sub>ErCl<sub>6</sub> and NaErCl<sub>4</sub>, both with octahedral surroundings for Er. The formation and reaction enthalpies are both exothermic. These findings are also valid for the last three systems with Ln=Tm, Yb, Lu; only  $\Delta H_{\text{syn}}^0$  for NaLuCl<sub>4</sub> is slightly endothermic with  $+1.9$  kJ mol<sup>-1</sup>. A summary of these relations is given in Table 8.

Table 8 Sodium compounds

Compound	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Na <sub>3</sub> LnCl <sub>6</sub>	–	●/⊖	●/⊖	●/○	●/○	●	●	●	●	●
Na <sub>2</sub> LnCl <sub>5</sub>	+	+	+	+	–	–	–	–	–	–
NaLnCl <sub>4</sub>	–	(X/?)	(?/X)	X	X	●/X	●	●	□	□
NaLn <sub>2</sub> Cl <sub>7</sub>	–	–	(+)	+	+	(+)	–	–	–	–

Na<sub>3</sub>LnCl<sub>6</sub>: ● – cryolite-type, ○ – stuffed LiSbF<sub>6</sub>-type, ⊖ – metastable; Na<sub>2</sub>LnCl<sub>5</sub>: + – K<sub>2</sub>PrCl<sub>5</sub>-type; NaLnCl<sub>4</sub>: X – NaGdCl<sub>4</sub>-type; ● –  $\alpha$ -NaWO<sub>4</sub>-type; □ – NaLuCl<sub>4</sub>-type; ? – unknown structure; NaLn<sub>2</sub>Cl<sub>7</sub>: + – KDy<sub>2</sub>Cl<sub>7</sub>-type; + – unknown structure



## Conclusions

### Synopsis of the results

As discussed in the chapter about thermodynamics and structure the existence of ternary chlorides with their special structures is determined by the relative sizes of the ions  $\text{Ln}^{3+}$  and  $\text{A}^+$ . These range for the lanthanide ions from  $r(\text{La}^{3+})=103$  pm to  $r(\text{Lu}^{3+})=86$  pm. The alkali-metal ions  $\text{K}^+$  to  $\text{Cs}^+$  are larger,  $r(\text{K}^+)=138$  pm. They occupy interstices in the chloride packing with coordination numbers eight to eleven. The sodium ion with 102 pm is of comparable size with the largest lanthanide ions and somewhat larger than the others.

The lattices of compounds for which the number of chloride ions per formula unit is smaller than the  $\text{CN}(\text{Ln}^{3+})$  have chloride skeletons of linked  $\text{LnCl}_x$  polyhedra. The polyhedra are antiprisms ( $\text{CN}=8$ ), monocapped trigonal prisms ( $\text{CN}=7$ ), and corner- or edge-linked octahedra ( $\text{Cs}_2\text{DyCl}_5$ - or  $\text{NaLnCl}_4$ -type). In the hexachloro compounds  $\text{A}_3\text{LnCl}_6$  the number of chloride ions is equal to the  $\text{CN}(\text{Ln}^{3+})$ , isolated  $(\text{LnCl}_6)^{3-}$  octahedra in elpasolite/perovskite-related structure types exist. Related to the perovskites are the enneachlorides  $\text{Cs}_3\text{Ln}_2\text{Cl}_9$  consisting of face-sharing double octahedra  $(\text{Ln}_2\text{Cl}_9)^{3-}$ , held together by the  $\text{Cs}^+$  ions.

Most ternary chlorides are formed with exothermic enthalpies  $\Delta H_f^0$  from their binary parent compounds  $\text{ACl}$  and  $\text{LnCl}_3$ . Their lattices are energetically more favourable than those of mixtures  $n\text{ACl}+\text{LnCl}_3$ . However, the existence of a ternary chloride at a given temperature depends on its stability relative to that of its neighbours in the system, namely,  $\Delta G_{\text{syn}}^0$  must be negative. On discussing such synreaction energies, when going from one lanthanide element to another, one has to consider that also the change in the energetic properties of the neighbour compounds may have an influence on the system.

At 0 K, when  $\Delta G=\Delta H$ , a compound is stable if  $\Delta H_{\text{syn}}^0$  is exothermic where its stability arises only from lattice energy effects. That is true for all the compounds shown in Table 9, the indices of which are not in brackets. One can recognize clearly that both the  $r(\text{Ln}^{3+})$  and the  $r(\text{A}^+)$  are of significant influence for the existence of a compound in a special structure.

The stability at 0 K of the elpasolite-like compounds  $\text{A}_3\text{LnCl}_6$ , begins with Sm for  $\text{A}=\text{Cs}$ , with Tb for Rb and with Er for K. Hexachloro compounds with the larger  $\text{Ln}^{3+}$  are not stable at  $T=0$  K because these ions are too large for octahedral coordination. They are formed from their neighbours  $\text{ACl}$  and  $\text{A}_2\text{LnCl}_5$  with endothermic enthalpy, which must be compensated by a sufficiently high gain in entropy at the formation temperature. For instance,  $\text{Rb}_3\text{LaCl}_6$  is formed from its two neighbours with  $\Delta H_f^0$  of nearly  $+50$   $\text{kJ mol}^{-1}$ , which is compensated at  $444^\circ\text{C}$  by a gain in entropy of  $72$   $\text{J K}^{-1} \text{mol}^{-1}$ . An explanation for this high entropy might be based on the fact that a compound with isolated octahedra with the freedom of oscillation, is formed from two compounds with rigidly linked octahedra.

There are two other groups of compounds stabilized by an entropy gain, which can be explained by a statistical model. These are  $\text{A}_3\text{Ln}_5\text{Cl}_{18}$ , where three  $\text{A}^+$  ions are statistically distributed over 1/6 of the  $\text{Ln}^{3+}$  sites, and  $\text{Cs}_4\text{LnCl}_7$ , with a seventh  $\text{Cl}^-$  ion statistically integrated in the chloride skeleton. For other groups of compounds the positive reaction enthalpy, and therefore the necessary gain in entropy, is smaller. For Na-compounds the energetic effects are often so small that their synreaction enthalpies are not significantly different from zero.

Comprehending the results one will recognize that  $\sim 70\%$  of the ternary lanthanide chlorides are stable at 0 K, so that their existence can be discussed with the

**Table 9** Ternary lanthanide chlorides  $\text{ALn}_2\text{Cl}_7$  and  $\text{A}_2\text{LnCl}_5$

Compound $\text{ALn}_2\text{Cl}_7$	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Cs	●	●	●	●	■	■	■	■	■	■	■	■	■	■
Rb				(●)	■	■	■	■	■	■	■	■	■	?
K	–	–	–	(●)					■	■	■	■	■	?
Na	–	–	–	–	–	–	(+)			(+)	–	–	–	–

● –  $\text{KEr}_2\text{F}_7$ -type ( $\text{CN}=8$ ), ■ –  $\text{RbDy}_2\text{Cl}_7/\text{KDy}_2\text{Cl}_7$ -type ( $\text{CN}=7$ )

Compound $\text{A}_2\text{LnCl}_5$	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Cs	●	●	●	●	■	■	■	■	■	■	■	■		■
Rb	●	●	●	●	●	●	●	–	–					(■)
K	●	●	●	●	●	●	●	●	●	●	–	?	?	?
Na	–	–	–	–	(●)	(●)	(●)	(●)	–	–	–	–	–	–

● –  $\text{K}_2\text{PrCl}_5$ -type ( $\text{CN}=7$ ), ■ –  $\text{Cs}_2\text{DyCl}_5$ -type ( $\text{CN}=6$ )

usual tools for lattice energies. The rest are ‘high-temperature’ compounds relative to 0 K. For them the entropy term  $-T\Delta S$  is of co-decisive importance. That is possible because formation and synreaction energies are very small compared with the total lattice energies of the ternary chlorides ( $\sim 4000 \text{ kJ mol}^{-1}$ ). That situation is similar to a discussion on the existence of hills in the tableland of Tibet!

### Open issues

The main future work for finding an explanation for the existence of ternary lanthanide chlorides should be to determine their absolute entropies by measuring heat capacities  $c_p$  down to 0 K. That is, we have to explain how energy is dissipated over the lattices of the compounds, when heated in their range of existence.

Beside this there are other tasks of more limited importance:

- to elucidate the systems  $ACl/LuCl_3$  ( $A=Cs, Rb, K$ ) with the normally applied methods
- to determine the structures of the compounds  $K_2LnCl_5$  with  $Ln=Tm, Yb, Lu$
- to determine the structure of at least one compound of the  $KEr_2F_7$  group by single crystal methods
- to determine the structures of the H-modified compounds  $ALn_2Cl_7$
- to clarify the dimorphism of the compounds  $NaGdCl_4$  and  $NaEuCl_4$
- to prove the existence of the compounds  $NaGd_2Cl_7$ ,  $NaHo_2Cl_7$ , and  $K_3Yb_2Cl_9$

Finally a somewhat speculative issue: As the example  $Cs_3NdCl_6$  has shown, reconstructive solid-state reactions, like formation and decomposition, do not occur below  $\sim 250^\circ\text{C}$ , because of the very low mobility of the ions in the crystal lattice. Thus, it might be possible that compounds, formed at temperatures  $< 0^\circ\text{C}$ , for instance by matrix isolation, are kept metastable at ambient temperature. Candidates could be compounds  $ALnCl_4$  with tetrahedral coordination of the  $Ln^{3+}$  ions. Such species were observed in the gaseous-state.

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