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New results about ternary lanthanide chlorides

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Abstract

All systems ACl-LnCl$_3$ with A=Cs,Rb,K,Na and Ln=La-Gd were reinvestigated by difference thermal analysis. Compounds A$_3$LnCl$_6$, A$_2$LnCl$_5$ and ALn$_2$Cl$_7$ were found in most systems. Na$_3$LnCl$_4$,Na$_3$Ln$_5$Cl$_{18}$ and NaLnCl$_4$ in some systems The structures of all compounds, if unknown. were determined by X-ray-diffraction, their thermodynamic functions by solution calorimetry and e m f vs T-measurements in galvanic cells for solid electrolytes The basic function is the free (Gibbs) enthalpy $\Delta_{syn}G^{O}$ for the formation of each ternary chloride from the compounds adjacent in the phase diagram Some groups of compounds, especially hexachlorocompounds A$_3$LnCl$_6$ have positive $\Delta_{syn}H^{O}$-values. they are formed with a loss in lattice-enthalpy, compensated by a sufficiently high gain in entropy

1. WHAT IS OLD ABOUT TERNARY LANTHANIDE CHLORIDES?

In this paper old and new results about ternary chlorides existing in the systems ACl/LnCl$_3$ with A=Cs,Rb.K,Na and Ln=La-Gd shall be discussed Fig. 1 gives a survey of older measurements of the phase diagrams with thermoanalytical methods All systems marked with X or C were investigated in the past, however, all indicated by an C had to be corrected because of faults depending on not so advanced methods only cooling curves were measured and in general no X-ray measurements were done

	La	Ce	Pr	Nd	Sm	Eu	Gd
Cs	C	C	C	C	C		
Rb		C	C	X	X		
K	C	C	C	C	C	C	X
Na	C	X	C	C	C	C	C

Fig 1 Phase diagrams hitherto investigated by DTA

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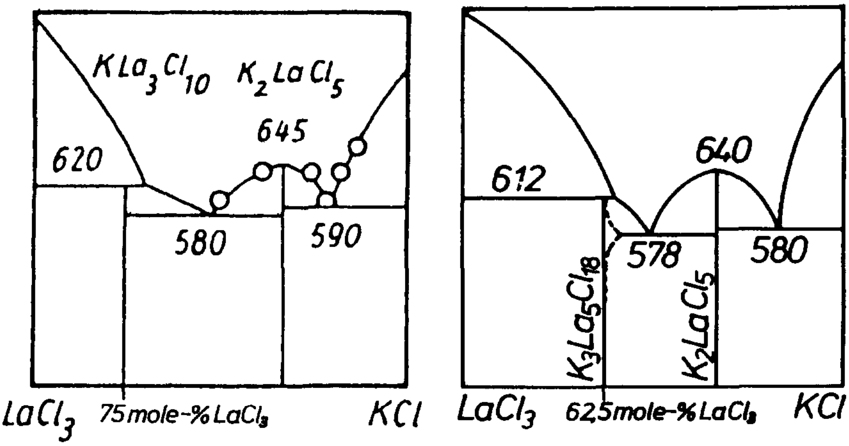

Fig 2 System KCl/$LaCl_3$ (left from [1], right, own finding [2]).

So we mainly find three types of faults
1) wrong compositions of incongruently melting compounds, as KLa_3Cl_{10} with 75 mol-% $LaCl_3$ instead of $K_3La_5Cl_{18}$ with 62,5 mol-% $LaCl_3$ (fig 2) When cooling a $LaCl_3$-rich melt, sedimentation can occur. Thus, the rest-melt becomes richer in KCl and one will find the eutectic at 580°C also in the range between 62,5% and ~ 75% $LaCl_3$ which leads to the wrong composition of the compound - We could avoid this mistake by two precautions a) we encapsulated our samples in sealed quartz ampoules and could in this way quench them from the melt So we yielded quasi-homogeneous solids which we could anneal at temperatures ~ 600°C Subsequent heating curves produced the correct effects, b) we measured X-ray powder patterns of the annealed samples and solved their structures by analogue-indexing via an intensity calculation
2.) misinterpretation of solid state reactions Rb_3NdCl_6, [3] e g , is stable only at temperatures >274°C, the thermal effect at this temperature is not a transformation from α-to β-Rb_3NdCl_6 That could be proved by an X-ray pattern of a sample annealed ~250°C
3) solid state reactions can be so slow that they can't be detected by normal DTA-runs An example is the compound Cs_2NdCl_5 [3] which is stable up to 333°C They could be prepared by two-months annealing of a sample with the correct composition, quenched from melt after having added a catalytic amount of water Afterwards we could detect the endothermic peak of the decomposition reaction in a heating experiment - We have discussed this issue in detail elsewhere [4]

Crystal structures of compounds A_2LnCl_5, $NaLnCl_4$ and ALn_2Cl_7 are known from the work of Meyer [5] We ourselves have determined the structures of the hitherto unknown compounds of these groups by analogue-indexing of powder patterns. The structures of the compounds A_3LnCl_6 and $A_3Ln_5Cl_{18}$ were solved, starting with Cs_3LaCl_6 and $K_3Ln_5Cl_{18}$, for the first compound a Rietveld analysis was performed [6], for the second a single-crystal determination [2].

Solution calorimetry was used for calculating formation enthalpies of the compounds from its direct neighbours in the phase diagrams (synproportionation enthalpies $\Delta_{syn}H^{O}$) For that the solution enthalpies of the binary compound ACl and $LnCl_3$ and of all ternary chlorides had to be measured

The most useful tool, however, for getting informations about the stabilities of the compounds was the determination of free (Gibbs) enthalpies of reactions $nACl + LnCl_3 = A_nLnCl_{3+n}$ in galvanic cells for solid electrolytes. This method is described in detail elsewhere [7]. The e m f values proved to be linear dependent from T, so that with $\Delta G = -n\ F \cdot EMF$ by a linear regression analysis the Gibbs-Helmholtz equation $\Delta G = \Delta H - T\ \Delta S$ was received

Again values $\Delta_{syn}G^{O}$ were calculated which are the fundamental functions for stability· if they become ≥ 0 at a certain temperature, the involved compound will decompose into its neighbour-compounds This behaviour can be used for the exact determination of stability ranges. For instance, Rb_3LaCl_6 [2] is formed from RbCl + Rb_2LaCl_5 at 444°C In a chlorine-cell. containig disks of RbCl and Rb_2LaCl_5 separated by a Rb^+-conducting diaphram, at temperatures up to 444°C the measured e m f. is zero About 444°C the formation of Rb_3LaCl_3 takes place, we now find a positive e.m f., which gives a negative ΔG

2. WHAT IS THE ACTUAL STATE IN THE FIELD OF TERNARY CHLORIDES OF THE EARLY LANTHANIDES?

For all systems $ACl/LnCl_3$ (A=Na-Cs, Ln=La-Gd) the phases diagrams are measured and proved by additional methods, namely X-ray crystallographie and e m f. vs T measurements The unit cells and space groups of all at ambient temperature existing compounds were determined. and by that coordina ion numbers especially of the Ln^{3+}-ions against the Cl^--ions are known.

In all systems the key-compounds are those with the composition A_2LnCl_5 According to Meyer there exist two groups. the K_2PrCl_5-type contains monocapped trigonal prisms, connected to chains via common edges ($([PrCl_3Cl_{4/2}]^{2-})$, the CN is 7 In the Cs_2DyCl_5-type the surrounding of the Ln^{3+} is octahedral (cis-corner-connected octahedra $[DyCl_4Cl_{2/2}]^{2-}$) Both structures are formed from 2 ACl and $LnCl_3$ by a loss in mole-volume and a gain in lattice enthalpy All $\Delta_{syn}G^{O}$ values are negative That is. the compounds are stable also at T=0K

In fig 3 a synopsis from a publication of Meyer [5] is given, completed by or own findings It must be pointed out that the transition from CN 7 to CN6 for Cs_2LnCl_5 with Ln=Sm-Dy is caused by the decreasing ionic radii

Hexachlorolanthanides are existing in all systems with Cs,Rb,K, the only exception is the system $KCl/LaCl_3$ Isolated $LnCl_6^{3-}$ - octahedra are hold together by the alkali-ions. The stability is increasing with the size of these alkali-ions. Thus. K_3CeCl_6 is stable at temperatures higher than 530°C, the Gd-compound already at 280°C All Cs-compounds are stable at ambient temperature The ideal radius ratio for an octahedral environment is 0,414. For lanthanide chlorides we find a decrease from 0.59 for La^{3+} ($r(La^{3+})$=1,061 Å. $r(Cl^-)$=1,81 Å $r(Gd^{3+})$=0.938 Å) to 0.51 for Gd^{3+} As fig 4 shows, this is accopanied by an increase of the melting points and an increase in $(-\Delta_f H^O)$-values, which are calculated for the reactions $CsCl + LnCl_3 = Cs_3LnCl_6$ from the solution enthalpies of all three compounds.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy
Cs	○	○	○	○	□	□	□	□	■
Rb	●	●	●	●	●	●	○	-	?
K	●	●	●	●	●	●	●	●	●
Na	-	-	-	-	○	○	○	?	?

Fig 3 Structure field map for A_2MCl_5-type chlorides Circles K_2PrCl_5-type Squares Cs_2DyCl_5-type Open circles and squares own investigations

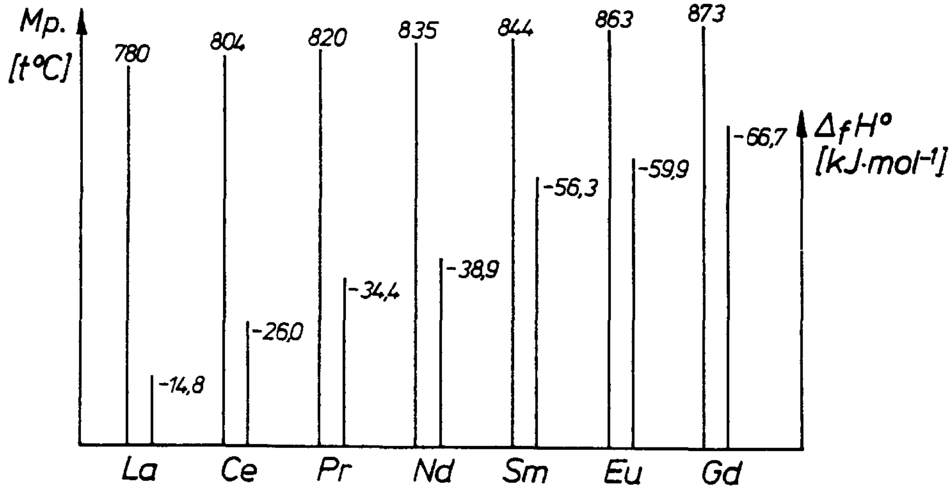

Fig 4 Melting points of Cs_3LnCl_6 and enthalpies $\Delta_f H^O$ for the reaction $3\,CsCl + LnCl_3 = Cs_3LnCl_6$

Above 400°C the structures of the compounds are cubic, like in the elpasolite type the chloride ions together with 2/3 of the alkali ions form a cubic close-packed structure, in which all octahedral holes, formed by Cl^--ions only, are occupied by 1/3 of the alkali ions and the lanthanide ions Below 400°C the $LnCl_6^{3-}$-octahedra are twisted against each other, a monoclinic structure results, either of the Cs_3BiCl_6- or of the K_3MoCl_6-type.

These structures with free octahedra are formed in their systems from compounds ACl and A_2LnCl_5 both with connected polyhedra From La to Nd A_2LnCl_5-compounds contain fourfold connected polyhedra. As fig 5 reveals the formation of the hexachloro-lanthanides is accompanied by a loss in lattice enthalpy, compensated by a considerable gain in entropy The compounds are not stable at T=0K, but at temperatures given by the relation: $\Delta_sH^o = T\ \Delta_sS^o$ From Sm-Gd the compounds Cs_2LnCl_5 contain twofold connected octahedra Now the gain

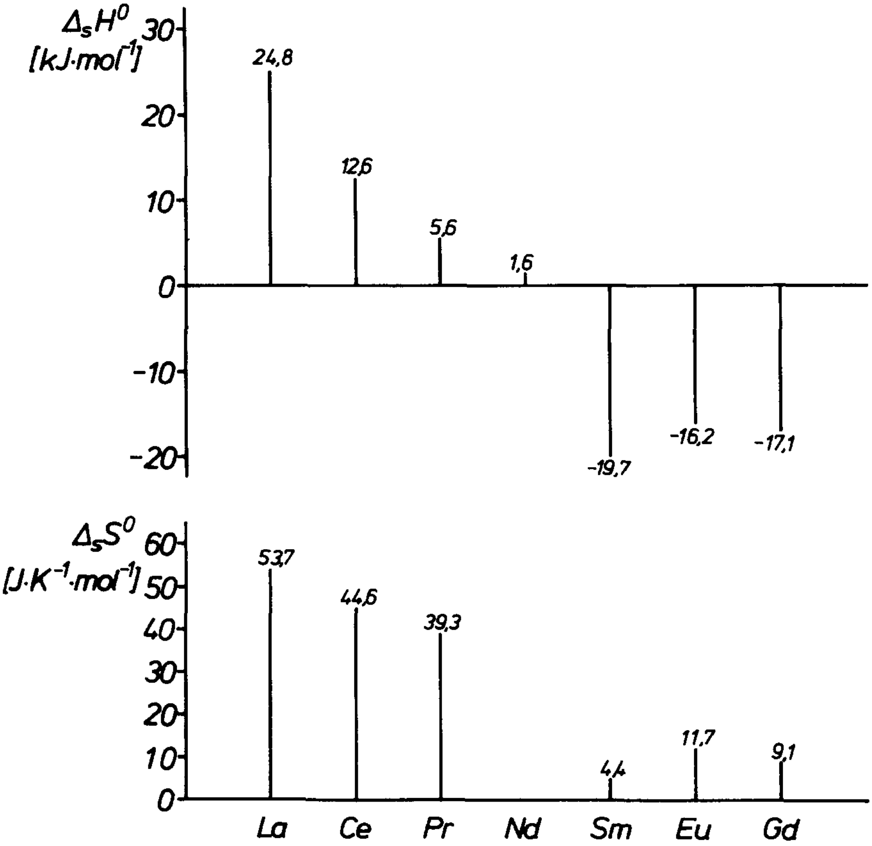

Fig. 5 Enthalpies and entropies for the reaction $CsCl + Cs_2LnCl_5 = Cs_3LnCl_6$

in entropy is only small and the compounds Cs_3LnCl_6 are formed by a gain in lattice enthalpy. They are stable down to 0K. Thus, the existence area of the Cs-hexachlorolanthanides is steered by the stability of the Cs_2LnCl_5-compounds' For the Rb- and K-compounds the situation is much more uniform; here all A_2LnCl_5-compounds are crystallizing with the K_2PrCl_5-structure: all the compounds are stable only at temperatures > 0K

For the compounds ALn_2Cl_7 we again have two groups in the $K_2Er_2F_7$-structure we find a CN 8, in the $RbDy_2Cl_7$ and the slightly distorted KDy_2Cl_7-structure [5] the CN is 7 The borderline is between Nd and Sm

The hexagonal unit cell of the compounds $A_3Ln_5Cl_{18}$ is related to the $LaCl_3$-structure [8]; in La_6Cl_{18} one La^{3+} is substituted by an A^+-ion, two other A^{3+} occupy statistically octahedral holes in planes perpendicular to the C-axis The condition is that the $r(A^+) \approx r(Ln^{3+})$. That is the case for the Ln-compounds from La-Sm and for the K-compounds with La, Ce

The special feature of the compounds Na_3LnCl_6 and $NaLnCl_4$ with Ln=Eu,Gd is discussed elsewhere [9,10]

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