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# Ternary chlorides in the systems ACl/$YbCl_3$ (A=Cs,Rb,K)

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## Abstract

The phase diagrams of the ACl/$YbCl_3$ (A=Cs,Rb,K) systems were investigated by DTA and XRD. Compounds $A_3YbCl_6$, $A_2YbCl_5$ and $AYb_2Cl_7$ exist in all systems, enneachlorides $A_3Yb_2Cl_9$ in the systems with A=Cs,K. In the group $AYb_2Cl_7$, the Yb ions have coordination number 7, in all other compounds the coordination is octahedral. Thermodynamic functions determined by solution calorimetry and emf vs $T$ measurements in galvanic cells for solid electrolytes reveal that the ternary chlorides $A_nYbCl_{3+n}$ are stable compared with mixtures ($n$ACl+$YbCl_3$); the compounds $Cs_2YbCl_5$ and $Rb_2YbCl_5$ are stable only at temperatures >0 K. © 1998 Elsevier Science B.V.

*Keywords:* Phase diagrams; Ternary ytterbium chlorides; Thermodynamic properties

## 1. Introduction

In connection with our research work on ternary lanthanide chlorides, we have investigated the pseudobinary systems of ytterbium(III) chloride with the alkali metal chlorides CsCl, RbCl and KCl. Hitherto, DTA measurements on the KCl/$YbCl_3$ [1] and CsCl/$YbCl_3$ systems [2] were performed and the unit cells of those compounds, which could be prepared directly from melts, were determined by Meyer [3] with X-ray powder patterns.

Our special interests were directed to the question of whether systematic rules found recently from investigations of the analogous systems with $HoCl_3$ [4], $ErCl_3$ [5] and $TmCl_3$ [6] are also valid for ytterbium compounds. In addition to DTA and XRD, we have measured solution enthalpies and (free) Gibbs'enthalpies with galvanic cells for solid electrolytes – methods which have proved very successful for yielding predictions about the mutual stabilities of all ternary chlorides in the respective systems.

## 2. Experimental

### 2.1. Chemicals

The starting compound was $YbCl_3{\cdot}6H_2O$, prepared from a solution of $Yb_2O_3$ (99.9%, Heraeus/Hanau) in hot hydrochloric acid. Alkali metal chlorides were dried at 500°C.

### 2.2. Differential thermal analysis (DTA)

The DTA measurements were performed in a home-built device for samples (~0.5 g) in vacuum-sealed silica ampoules. Samples with <50 mol% $YbCl_3$ were homogenized by melting in a gas flame, shaking and

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annealing. Because $YbCl_3$ melts react with silica, $YbCl_3$-rich mixtures were melted in the DTA furnace $\approx$20 K above the alleged liquidus temperatures. In general, heating curves were recorded (heating rate$=$2 K $min^{-1}$).

### 2.2.1. *X-ray powder patterns*

Powder patterns at ambient temperature were taken with a Philips PW 1050/25 goniometer equipped with a proportional counter and a vacuum attachment. During exposure ($CuK_\alpha$ radiation) the samples were kept under He atmosphere. For high-temperature photographs, a Simon–Guinier camera (Enraf-Nonius) was applied. Corundum powder was used as the internal standard; at 20°C: $a$=475.92 pm and $c$= 1299.00 pm; at 500°C, $a$=479.32 and $c$=1308.92 pm.

### 2.2.2. *Solution calorimetry*

The heats of solution were measured using an isoperibolic underwater calorimeter first described in 1978 [7]. In a silver vessel of 1.3 l volume, samples of 2 to 4 g in thin-walled glass ampoules are cracked under water at the beginning of the measurement. The change of temperature, $T$, against the surroundings, in a thermostat with a temperature constancy of $2–10^{-4}$ K, generated by the solution enthalpy is measured with a thermopile. The calibration is done by Joule heating.

At least two samples of each substance were measured. From the enthalpies of solution, $\Delta_{sol}H^0{}_{298}$, the enthalpies of formation of the ternary chlorides from ($n$ACl+$YbCl_3$), $\Delta_f H^o{}_{298}$ were calculated according to the following:

$$\Delta_f H^0 = \{\Delta_{sol}H^0(YbCl_3) + n\Delta_{sol}H^0(ACl)\} - \Delta_{sol}H^0(A_nYbCl_{3+n})$$

### 2.2.3. *Measurement of emf*

A detailed description of the galvanic cell has been given earlier [8]. The measured potentials were generated by the solid state reactions:

$$nACl + A_xYbCl_{3+x} = A_{(n+x)}YbCl_{(3+n+x)}$$

in the 300–400°C range. The solid electrolytes (compressed discs) were separated by $A^+$-conducting diaphragms of sintered glass powder. It was not possible to prepare Cs-glasses, stable against $YbCl_3$; furthermore, $YbCl_3$ itself gave no stable potentials with each kind of glass. Therefore, measurements could be performed only for Rb- and K-compounds, $AYb_2Cl_7$ excluded.

## 3. Results

### 3.1. *Ytterbium(III) chloride*

The starting compound $YbCl_3{\cdot}6H_2O$ with a correct content of crystal water was prepared by precipitation from a saturated solution at 0°C with HCl-gas. After filtration and washing with ether it was dried at 40°C. Surprisingly, its crystal structure was still unknown [9]. As for the other hexahydrates, it is isotypic to $PrCl_3{\cdot}6H_2O$ [10], space group $P2/n$, $Z$=2:

$$a = 777.3(4)\,\text{pm};\quad b = 643.0(5)\,\text{pm};$$
$$c = 947.4(9)\,\text{pm}$$

In this structure type, the lanthanide ion is surrounded by two chloride ions and six water molecules, $[YbCl_2(H_2O)_6]^+$. These cationic groups are held together by the third $Cl^-$-ions.

When heated in a drying oven at 100°C, a trihydrate, $YbCl_3{\cdot}3H_2O$, is formed. According to X-ray powder patterns, it is isotypic to $ErCl_3{\cdot}3H_2O$ and $TmCl_3{\cdot}3H_2O$; the structure is still unknown.

Further dehydration must occur in a stream of HCl to avoid hydrolysis. At 120°C, a monohydrate $YbCl_3{\cdot}H_2O$ with unknown structure is formed. Above 180°C, the last water is removed. For the preparation of ca. 10 g $YbCl_3$, the temperature must be raised slowly up to 350°C. (If the product looks grey because of impurities of carbon, it can be purified by heating for 1 h in a stream of $Cl_2$ at ca. 500°C.)

Laptev [11] has prepared $YbCl_3$ from the oxide and $CCl_4-$ gas at 700°C. His product crystallizes with the layer structure of $AlCl_3$ (space group $C2/m$, $Z$=2). If the compound is prepared at a lower temperature, e.g. by dehydration of the hydrate, the structure is more or less disturbed. We have already described this phenomenon previously for $DyCl_3$ [12].

### 3.2. *Ternary ytterbium(III) chlorides from solutions*

Some ternary chlorides could be prepared conveniently from aqueous solutions or from acetic acid, as far as they are congruently soluble in these solvents. In the case of aqueous solutions, ACl and $Yb_2O_3$ were dissolved with the correct molar ratio in hydrochloric acid. These solutions were evaporated to dryness at temperatures of 100–120°C. The following compounds could be prepared.

$Cs_4YbCl_7$ – The crystal structure could be solved by single-crystal measurements, as previously described [13];
$Cs_3YbCl_6$ – In the orthorhombic modification, space group *Pbcm* [14];
$Cs_2YbCl_5{\cdot}H_2O$ – Erythro-siderite structure (space group *Pnma*, $Z$=4).

The othorhombic cell parameters are: $a$=1455.3(9) pm; $b$=1046.6(9) pm; $c$=751.9(2) pm – $Cs_2YbCl_5{\cdot}H_2O$ can be dehydrated by heating in a stream of HCl at temperatures rising slowly from 200 to 300°C.

From acetic acid the compounds $Cs_3YbCl_6$ and $Rb_3YbCl_6$, both with the $Cs_3BiCl_6$ structure (space group *C*2/*c*) could be precipitated with HCl gas, $K_3YbCl_6$ (space group $P2_1/c$) was formed with KCl. The solutions were prepared from $YbCl_3{\cdot}6H_2O$ and alkali metal carbonate in the correct molar ratio.

### 3.3. Phase diagrams and crystal structures

Fig. 1 illustrates the results of the DTA measurements on the systems ACl/$YbCl_3$ (A=Cs,Rb,K). As already found for $ErCl_3$, $YbCl_3$ also melts and reacts slowly with quartz. Therefore, the melting point was measured in a corundum crucible; the value is 1133 K (860°C). (In the literature: 864°C [11] and 854–880°C)

In the CsCl/$YbCl_3$ system, four compounds were found: one congruently melting ($Cs_3YbCl_6$) and the others, incongruently melting $Cs_2YbCl_5$, $Cs_3Yb_2Cl_9$ and $CsYb_2Cl_7$. This result is in good agreement with the findings of Blachnik and Selle [2].

In the RbCl/$YbCl_3$ system, one congruently melting compound, $Rb_3YbCl_6$, and the incongruently melting compounds $Rb_2YbCl_5$ and $RbYb_2Cl_7$ exist.

In the KCl/$YbCl_3$ system, according to Novikov [1], one congruently melting compound, $K_3YbCl_6$, exists with a phase transition at 385°C. We found this transition at 392°C and a second, which is not shown in Fig. 1, at 47°C. Another compound – $KYb_2Cl_7$ – for which the structure was determined by Meyer [17], melts incongruently at 453°C. Still unknown were two other incongruently melting ternary chlorides: $K_2YbCl_5$ and $K_3Yb_2Cl_9$, which are stable only in the temperature range from 394° to 425°C.

A typical difficulty for the investigations of phase diagrams with incongruently melting compounds arose. Because of the large temperature difference of the melting point of $K_3YbCl_6$ (820°C) and the eutectic (409°C at 49.3 mol% $YbCl_3$) a large amount of $K_3YbCl_6$ crystallizes from the melt above the peritectic for $K_2YbCl_5$ at 455°C. The crystals separate from the melt and, therefore, the peritectic reaction at 455°C is not complete. As a consequence, all other effects at lower temperatures, namely the peritectic for $K_3Yb_2Cl_9$ at 425°C and the eutectic, will appear also in the range from $K_3YbCl_6$ to $K_2YbCl_5$. Thus, the quenched samples have to be annealed to get equilibrium conditions. The proof for the existence of the two compounds was eventually found by a combination of DTA measurements for these annealed samples and X-ray patterns:

$K_2YbCl_5$: A sample with 33.3 mol% $YbCl_3$, annealed at ca. 430°C, only gave one effect at 455°C (peritectic temperature). The X-ray photo was different from that of a mixture between $K_3YbCl_6$ and $KYb_2Cl_7$.
$K_3Yb_2Cl_9$: A 40% sample, annealed at ca. 380°C, gave two thermal effects in a heating curve at 394° and 425°C in addition to the peritectic effect of $K_2YbCl_5$ at 455°C. The X-ray pattern was a superposition of the peaks of $K_2YbCl_5$ and $KYb_2Cl_7$. In a dynamic high temperature photo new lines appeared at ca. 400°C.

#### 3.3.1. Thermodynamic measurements

*Solution enthalpies* could be measured for all compounds, $K_3Yb_2Cl_9$ excepted, since is not stable at ambient temperature. The results are given in Table 1, together with two values determined by Blachnik and Selle [15]. For the calculation of the $\Delta_fH^0$ values, the solution enthalpies of the alkali metal chlorides were taken from published papers: CsCl=18.1; RbCl=17.6; KCl=17.9 kJ mol$^{-1}$. The solution enthalpy of $YbCl_3$ was found to be $-212.8(7)$ kJ mol$^{-1}$ (Ref. [16]: 212.9–216.1 kJ mol$^{-1}$). In the last column of Table 1 'syn-reaction enthalpies' are listed. These are enthalpies of formation from the two direct neighbours of a compound in the phase diagram at ambient temperature.

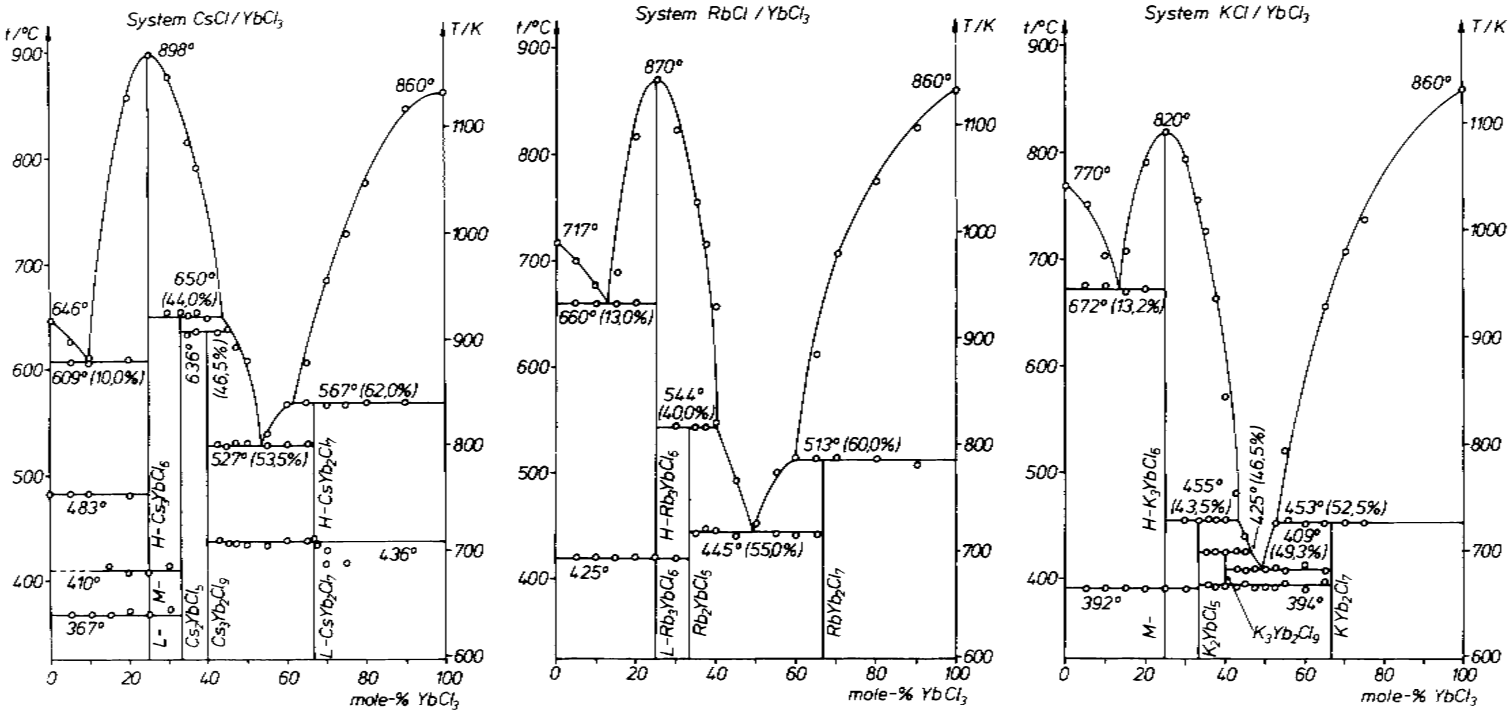

Fig. 1. Phase diagrams of ACl/YbCl$_3$ (A=Cs, Rb, K) systems.

Table 1
Solution enthalpies ($\Delta_{sol}H^0$), enthalpies of formation from the binary compounds ($\Delta_f H^0$) and synreaction enthalpies ($\Delta_{syn}H^0{}_{289}$) (all in kJ mol$^{-1}$) (Range of error for the last digit within parentheses)

| Compound | $\Delta_{sol}H^0{}_{289}$ | Ref. [15] | $\Delta_f H^0{}_{298}$ | $\Delta_{syn}H^0{}_{289}$ |
|---|---|---|---|---|
| $Cs_4YbCl_7$ | −54.(2) | | −86.1 | +8.8 |
| $Cs_3YbCl_6$ (*Pbcm*) | −63.6(3) | | −94.9 | −14.3 |
| $Cs_3YbCl_6$ (*C2/c*) | −64.6(1) | −65.3 | −93.9 | — |
| $Cs_2YbCl_5$ | −101.4(1) | | −75.2 | +6.3 |
| 1/2 $Cs_3Yb_2Cl_9$ | −110.8(6) | | −74.8 | −14.8 |
| 1/2 $CsYb_2Cl_7$ | −174.2(3) | | −29.5 | −4.6 |
| | | | | |
| $Rb_3YbCl_6$ | −74.6(1) | | −85.4 | −22.3 |
| $Rb_2YbCl_5$ | −114.5(1) | | −63.1 | +2.3 |
| 1/2 $RbYb_2Cl_7$ | −166.7(1) | | −35.4 | −21.5 |
| | | | | |
| $K_3YbCl_6$ | −105.5(1) | −105.0 | −53.8 | −10.5 |
| $K_2YbCl_5$ | −133.7(1) | | −43.3 | −5.0 |
| 1/2 $KYb_2Cl_7$ | −188.8(4) | | −15.1 | −4.3 |

These reactions are:

$$\text{Cs compounds}: \begin{array}{lcl} Cs_{0.5}YbCl_{3.5} & = & 1/3Cs_{1.5}YbCl_{4.5} + 2/3YbCl_3 \\ Cs_{1.5}YbCl_{4.5} & = & 1/3Cs_{0.5}YbCl_{3.5} + 2/3Cs_2YbCl_5 \\ Cs_2YbCl_5 & = & 2/3Cs_{1.5}YbCl_{4.5} + 1/3L - Cs_3YbCl_6 \\ L - Cs_3YbCl_6 & = & 1/2Cs_4YbCl_7 + 1/2Cs_2YbCl_5 \\ Cs_4YbCl_7 & = & CsCl + L - Cs_3YbCl_6 \end{array}$$

$$\text{Rb, K compounds}: \begin{array}{lcl} A_{0.5}YbCl_{3.5} & = & 1/4A_2YbCl_5 + 3/4YbCl_3 \\ A_2YbCl_5 & = & 0.4A_{0.5}YbCl_{3.5} + 0.6L - A_3YbCl_6 \\ A_3YbCl_6 & = & ACl + A_2YbCl_5 \end{array}$$

Measurements on emf could be performed only for the compounds $A_2YbCl_5$ and $A_3YbCl_6$ (A=Rb,K) as pointed out in Section 2.2.3. The dependence of emf ($\varepsilon$) on $T$ was linear. Thus, the measured regression lines $\varepsilon=a+b-T$ would be transformed to Gibbs–Helmholtz equation, $\Delta_r G^0=\Delta_r H^0-\Delta_r S^0 T$, by means of the relation $G=-nF\varepsilon$.

### 3.3.2. Rubidium compounds

Reaction: 1.5 $RbCl+Rb_{0.5}YbCl_{3.5}=Rb_2YbCl_5$ ($T$=620–690 K)

emf/ mV=211.3+0.1346 $T$/K

$\Delta_r G^0$/kJ mol$^{-1}$=−30.6-0.0195 T/K

Reaction: $RbCl+Rb_2YbCl_5=Rb_3YbCl_6$ ($T$=620–690 K)

emf/mV=259.8

$\Delta_r G^0$/kJ mol$^{-1}$=−25.1

### 3.3.3. Potassium compounds

Reaction: 1.5 $KCl+K_{0.5}YbCl_{3.5}=K_2YbCl_5$

(Samples of 50 and 37.5 mol% $YbCl_3$ in the range of 580–635 K)

emf/mV=179.4+0.1152 $T$/K

$\Delta_r G^0$/kJ mol$^{-1}$=−26.0−0.0167 $T$/K

Measurements above the formation temperature of $K_3Yb_2Cl_9$ yield two reactions:

50 mol%: $KCl+K_{0.5}YbCl_{3.5}=K_{1.5}YbCl_{4.5}$ ($T$=630–670 K)

emf/mV=252.3+0.0014 $T$/K

$\Delta_r G^0$/kJ mol$^{-1}$=−24.3

with emf($K_2YbCl_5$)=emf($K_{1.5}YbCl_{4.5}$), the formation temperature $T_f$ for $K_3YbCl_6$ is 641 K (368°C)

37.5 mol%: $0.5KCl+K_{1.5}YbCl_{4.5}=K_2YbCl_5$ ($T$=630–670 K)

emf/mV=121.3+0.2045 $T$/K

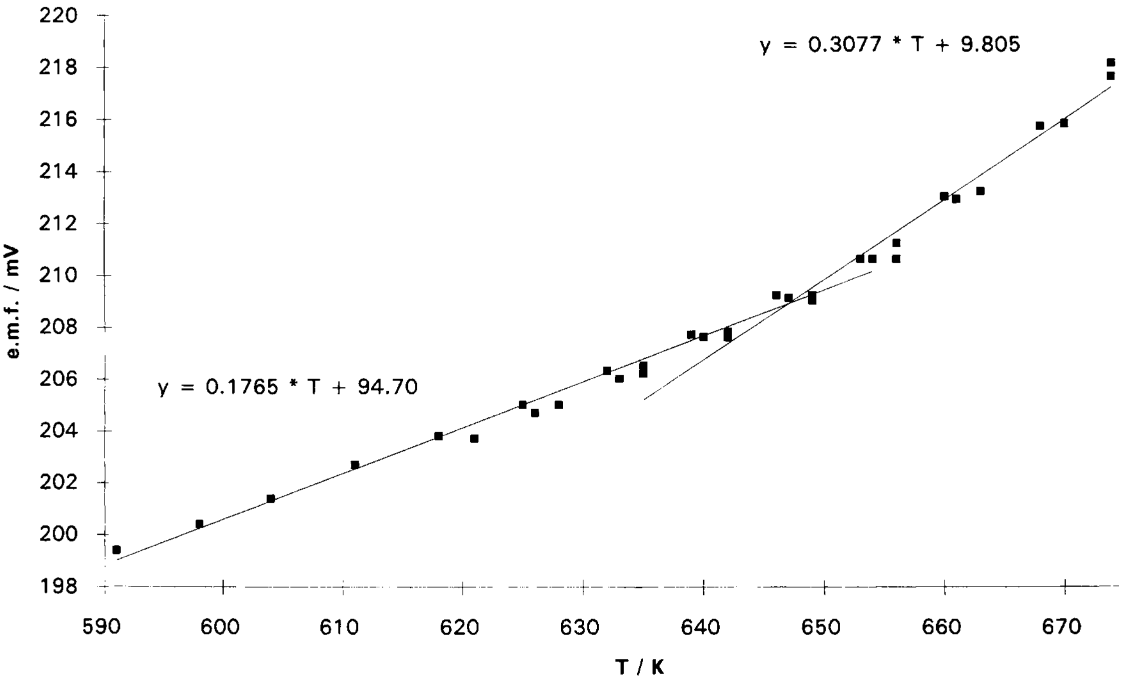

Fig. 2. Plot of emf vs. $T$ for $K_3YbCl_6$.

$\Delta_rG^0$/kJ mol$^{-1}$=$-5.8-0.0099$ $T$/K.

From emf(HT)=emf(LT), it follows that $T_f$=650 K (377°C)

Reaction: $KCl+K_2YbCl_5$=H$-K_3YbCl_6$ ($T$=650–680 K)

emf/mV=9.4+0.3065 $T$/K

$\Delta_rG^0$/kJ mol$^{-1}$=$-0.9-0.0296$ $T$/K

Reaction: KCl + $K_2YbCl_5$ = M$-$ $K_3YbCl_6$ (T= 590 to 650 K)

emf/mV=90.4+0.1818 T/K

$\Delta_rG^0$/kJ mol$^{-1}$=$-8.7-0.0175T$/K

The results of the measurements are depicted in Fig. 2.

From emf(H$-K_3YbCl_6$)=emf(M$-K_3YbCl_6$), it follows that $T$=650 K (377°C). The transformation enthalpy is $\Delta_rH^0$=7.8 kJ mol$^{-1}$, the entropy $\Delta_rS^0$=12.1 J K$^{-1}$ mol$^{-1}$. It should be pointed out that $T_t$ from the emf measurements is lower than the value from DTA heating curves (392°C) because of kinetic effects. In DTA cooling curves, the transformation could not be detected at all.

The $\Delta_rG^0$ values for the reactions $ACl+A_2YbCl_5$= $A_3YbCl_6$ are identical with $\Delta_{syn}G^0$. For $T$=0, both (A=Rb, K) are negative, and the compounds are stable at all temperatures.

The synreactions of the 2 : 1 compounds are $0.4A_{0.5}YbCl_{3.5}+0.6\ A_3YbCl_6=A_2YbCl_5$, the free enthalpies $\Delta_{syn}G^0=\Delta_fG^0(A_2YbCl_5)-\{0.4\Delta_fG^0(A_{0.5}YbCl_{3.5})+0.6\Delta_fG^0(A_3YbCl_6)\}$. With $A_{0.5}YbCl_{3.5}$ as standard compound, one can formulate) $\Delta_fG^0$ values:

$\Delta_fG^0(A_{0.5}YbCl_{3.5})=0$

$\Delta_fG^0(A_2YbCl_5)=\Delta_rG^0$

$\Delta_fG^0(A_3YbCl_6)=\Delta_rG^0(A_2YbCl_5)+\Delta_rG^0(A_3YbCl_6)$.

Then: $\Delta_{syn}G^0(A_2YbCl_5)=0.4\Delta_rG^0(A_2YbCl_5)-0.6\ \Delta_rG^0(A_3YbCl_6)$.

For $Rb_2YbCl_5$: $\Delta_{syn}G^0$/kJ mol$^{-1}$=+2.8$-0.0078T$/K

$\Delta_{syn}G^0$=0 at 359 K (86°C)

For $K_2YbCl_5$: $\Delta_{syn}G^0$/kJ mol$^{-1}$=$-5.2+0.0038T$/K

### 3.3.4. Crystal structures

For several compounds, the unit cells have already been determined by Meyer et al. from powder patterns.

| | |
|---|---|
| [17] $CsYb_2Cl_7$ and $RbYb_2Cl_7$: | $RbDy_2Cl_7$ type; space group *Pnma* |
| [17] $KYb_2Cl_7$: | $KDy_2Cl_7$ type; space group $P2_1/c$ |
| [18] $Rb_3YbCl_6$: | $Cs_3BiCl_6$ type; space group $C2/c$ |

[19] $Cs_2YbCl_5$: $Cs_2DyCl_5$ type; space group *Pbnm* (id. *Pnma*)
[20] $Cs_3Yb_2Cl_9$: $Cs_3Tl_2Cl_9$ type; space group $R\bar{3}_c$

Our own results about hitherto unknown crystal structures are compiled in Table 3:

> $Cs_4YbCl_7$: The structure for this compound was solved recently by single-crystal work [13].
>
> $Cs_3YbCl_6$: The structure of the modification in *Pbcm* is discussed elsewhere [14], the structure of the modification in *C*2/*c* was determined by single-crystal work.

We succeeded in growing suitable crystals from supercritical acetic acid, as recently described for $Cs_3CrCl_6$ [21]. The results of the single-crystal work are shown in Tables 2 and 3.

*H-$Cs_3YbCl_6$ and H-modifications of $A_3YbCl_6$ (A=Rb,K)*: Guinier patterns at 500°C could be indexed in the cubic space group $Fm\bar{3}m$.

$Rb_2YbCl_5$: isotypic to $Cs_2YbCl_5$, space group *Pnma*.

L-and M-$K_3YbCl_6$: recently we found, by structure determination with single crystals of the analogous erbium compound, again obtained from supercritical acetic acid, that L-$K_3ErCl_6$ has the monoclinic $K_3MoCl_6$-structure [22] in space group $P2_1/c$. L-$K_3YbCl_6$ proved to be isotypic. From an X-ray photo at 100°C, we found that the monoclinic *a*- and *c*-axes had become equal, the angle $\beta$ was 109.4°, which is

Table 2
Single crystal data for $Cs_3YbCl_6$ and structure refinement

*Crystal data*
$Cs_3YbCl_6$; $M_r$=784.47; monoclinic;
S.G. *C*2/*c*; *Z*=8

| single-crystal data | powder diffraction data |
|---|---|
| $a$=26.748(7) Å | $a$=26.837(8) Å |
| $b$=8.1010(5) Å | $b$=8.174(4) Å |
| $c$=13.028(2) Å | $c$=13.035(3) Å |
| $\beta$=100.00(2)° | $\beta$=100.2(3)° |
| $V$=2780.1(9) Å$^3$ | |
| *Data collection* | |
| Mo$K_\alpha$ radiation | $\lambda$=0.71073 Å |
| Enraf Nonius CAD-4 diffr. | $\theta$=2–24° |
| $\mu$=15.570 mm$^{-1}$ | $T$=293(2) K |
| $\omega$ scans | $h=-30\rightarrow0$; $k=-9\rightarrow0$;<br>$l=-14\rightarrow14$ |
| *Refinement* | |
| Full-matrix least sqares on $F^2$ | Goodness-of-fit on $F^2$ =1.077 |
| $R$[I>2sigma (I)] | $R_1$=0.0365, $wR_2$=0.1008 |
| $R$(all data) | $R_1$=0.0459, $wR_2$=0.1073 |
| $R_{int}$=0.0321 | |

Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$)

| | *x* | *y* | *z* | *U*(eq) |
|---|---|---|---|---|
| $Yb_1$ | 2500 | 2500 | 0 | 22(1) |
| $Yb_2$ | 0 | −2193(1) | −2500 | 21(1) |
| $Cs_3$ | 1525(1) | 3135(1) | −3545(1) | 33(1) |
| $Cs_4$ | 3367(1) | 3095(1) | −3016(1) | 35(1) |
| $Cs_5$ | −502(1) | 2530(1) | −4330(1) | 53(1) |
| $Cl_1$ | 2502(1) | 1154(3) | −1807(2) | 32(1) |
| $Cl_2$ | 561(1) | 139(4) | −3076(2) | 40(1) |
| $Cl_3$ | −568(1) | −2240(4) | −4306(2) | 45(1) |
| $Cl_4$ | −557(1) | −4444(4) | −1847(2) | 42(1) |
| $Cl_5$ | 1825(2) | 405(4) | 367(2) | 52(1) |
| $Cl_6$ | 3260(1) | 637(4) | 786(2) | 45(1) |

Table 3
Hitherto unknown cell parameters of ternary ytterbium chlorides

| Compound | Space group | *Z* | *a*/pm | *b*/pm | *c*/pm | *β*/° |
|---|---|---|---|---|---|---|
| $Cs_4YbCl_7$ | $R\bar{3}m$ | 3 | 764.6(4) | | 2628.9(10) | 120.00 |
| $Cs_3YbCl_6$(aq.sol.) | *Pbcm* | 8 | 808.9(3) | 1307.7(3) | 2636.6(7) | |
| L-$Cs_3YbCl_6$ | *C2/c* | 8 | 2683.7(8) | 817.4(4) | 1303.5(3) | 100.2(3) |
| H-$Cs_3YbCl_6$ | *Fm3m* | 4 | 1152.2(3) | | | |
| H-$Rb_3YbCl_6$ | *Fm3m* | 4 | 1114.5(2) | | | |
| $Rb_2YbCl_5$ | *Pnma* | 4 | 952.7(3) | 726.1(3) | 1494.2(4) | |
| L-$K_3YbCl_6$ | $P2_1/c$ | 4 | 1299.8(5) | 762.4(3) | 1248.5(4) | 109.85(2) |
| M-$K_3YbCl_6$ | *Cmmm* | 8 | 1504.4(3) | 2128.1(5) | 752.7(2) | |
| H-$K_3YbCl_6$ | *Fm3m* | 4 | 1086.4(2) | | | |
| $K_2YbCl_5$ | ($P2_1/c$) | 4 | 1141 | 1008 | 824 | 104.1 |

the tetrahedral angle. Thus, the cell could be transformed into an orthorhombic C-centred cell, space group *Cmmm*. We tried to find the point positions by a Rietveld analysis, by constructing a suitable surveyor's cell.

$K_2YbCl_5$: The structure of this compound neither belongs to the $K_2PrCl_5$ nor to the $Cs_2DyCl_5$ type. Because of a certain similarity to the X-ray pattern of L-$K_3YbCl_6$, we could perform a monoclinic trial indexing with the extinctions of space group $P2_1/c$.

$K_3Yb_2Cl_9$: A dynamic Guinier photo in a small temperature range above ca. 380°C displayed lines in addition to those of the mixture ($K_2YbCl_5$+$KYb_2Cl_7$). The structure is probably that of the $K_3W_2Cl_9$ type, space group $P6_3/m$.

## 4. Discussion

Comparing the systems of ytterbium chloride with the foregoing systems ACl/$TmCl_3$, only one difference exists; with ytterbium a high-temperature compound $K_3Yb_2Cl_9$ is formed. It does not have the structure of $Cs_3Yb_2Cl_9$, but probably belongs to the $K_3W_2Cl_9$ type. In the group $ALn_2Cl_7$, the lanthanide ion has coordination number 7, in other groups – $A_3LnCl_6$, $A_2LnCl_5$ and $A_3Ln_2Cl_9$ – the $Ln^{3+}$ ions are octahedrally surrounded by chloride ions. That will be true also for the still unknown structures of $K_2YbCl_5$ and $K_2TmCl_5$. It is to be expected that there the coordination number of $K^+$ will be smaller than 10/11 in the $Cs_2DyCl_5$ type in which the compounds $Cs_2YbCl_5$ and $Rb_2YbCl_5$ crystallize.

The compounds $Rb_2LnCl_5$ have an increasing stability with decreasing radius of the $Ln^{3+}$ ion. $Rb_2HoCl_5$ has only a range of existence between 687 and 785 K. $Rb_2ErCl_5$ is stable above 593 K, its synreaction enthalpy is $+6.0\ \mathrm{kJ\ mol^{-1}}$. The values for $Rb_2TmCl_5$ are 353 K and $+2.4\ \mathrm{kJ\ mol^{-1}}$, for the ytterbium compound – 359 K and $+2.8\ \mathrm{kJ\ mol^{-1}}$, respectively. The 10/11 interstices, generated by the [$LnCl_6$]-octahedra reach the optimal size for the $Rb^+$ ions.

The synreaction enthalpies for the compounds $Cs_2LnCl_5$ are: $-6.1\ \mathrm{kJ\ mol^{-1}}$ for Ln=Ho, $-1.7$ for Er, $-1.7$ for Tm and $+6.3$ for Yb. The explanation must be, that the $Cs^+$ ion increase for the 10/11 coordination.

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