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Ternary chlorides in the systems CsCl/$ErCl_3$ and RbCl/$ErCl_3$[1]

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Abstract

The phase diagram of the system RbCl/$ErCl_3$ was investigated by means of DTA and the system CsCl/$ErCl_3$ was re-investigated. The existence of the caesium compounds Cs_3ErCl_6 (dimorphic), Cs_2ErCl_5, $Cs_3Er_2Cl_7$ and $CsEr_2Cl_7$ was confirmed. In the system RbCl/$ErCl_3$, there are two dimorphic, congruently melting compounds, Rb_3ErCl_6 and $RbEr_2Cl_7$. The incongruently melting compound Rb_2ErCl_5 (Cs_2DyCl_5 structure) is stable at temperatures higher than 348°C. The thermodynamic stabilities of the compounds were determined by solution calorimetry and e.m.f. measurements in a galvanic chlorine cell for solid electrolytes.

Keywords: Alkali metal chloride/erbium chloride systems; Phase diagrams; Ternary erbium chlorides; Thermodynamics

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1. Introduction

Our systematic investigations on the stability of ternary lanthanide chlorides have revealed that in the systems RbCl/$LnCl_3$, with Ln being La–Gd[1], compounds Rb_2LnCl_5 exist, crystallizing with K_2PrCl_5 structure [2] (Y_2HfS_5-type [3]), in which the coordination number (CN) of the Ln^{3+} against the chloride ions is 7; in the systems RbCl/$TbCl_3$ [4] and RbCl/$DyCl_3$ [5], analogous compounds do not exist. Compounds Cs_2LnCl_5 with this structure were found in the systems from Ln = La–Nd,

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[1] Dedicated to Takeo Ozawa on the Occasion of his 65th Birthday.

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while, beginning with Cs_2SmCl_5 [6], the 2:1 compounds have the Cs_2DyCl_5 structure with an octahedral coordination for samarium. It was now of great interest to determine with lanthanides smaller than Dy, whether compounds Rb_2LnCl_5 exist crystallizing with the Cs_2DyCl_5 structure. Therefore, we have investigated the hitherto unknown system $RbCl/ErCl_3$ and have also reinvestigated the $CsCl/ErCl_3$ system. In the $KCl/ErCl_3$ system, unsolved difficulties still exist concerning the polymorphy of K_3ErCl_6; we will publish this system and the $KCl/HoCl_3$ system later on.

2. Experimental

The starting compounds were $ErCl_3 \cdot 6H_2O$, prepared by dissolving Er_2O_3 (99.9%, Fa. Heraeus, Hanau) in hydrochloric acid, and the alkali metal chlorides CsCl and RbCl (Fa. E. Merck, Darmstadt; quality p.A.). They were dried at 500°C.

The equipment for the thermochemical and structural investigations has been described earlier.

(i) DTA [7]. A homemade device was used with samples either in vacuum-sealed quartz ampoules, or in open corundum crucibles, when rich in $ErCl_3$.

(ii) XRD. A Philips X-ray goniometer PW 1050/25 was used for crystal powders in He atmosphere; dynamic high-temperature photos by the Simon–Guinier method.

(iii) Solution calorimetry [8]. A homemade isoperibolic calorimeter for samples of 2–4 g, dissolved in 1.1 liter 0.01 M hydrochloric acid.

(iv) E.m.f. measurements [9]. For the formation of the most $ErCl_3$-rich compounds, the set-up of the cell was: (graphite + Cl_2)/ACl/A^+-conduct diaphragm/$ErCl_3$ (+ AEr_2Cl_7)/(graphite + Cl_2). The collected e.m.f. vs. T values were subjected to a linear regression analysis.

3. Results

3.1. Preparation of anhydrous compounds

For the preparation of anhydrous $ErCl_3$ the hexahydrate was first dehydrated to $ErCl_3 \cdot H_2O$ by heating in a vacuum furnace from 80 to 100°C. Then the last water was removed by heating the monohydrate slowly from 120 to 250°C in an HCl stream. The product was soluble in water or methanol. Its structure was composed of strongly distorted layers; the $AlCl_3$-type structure was formed after melting.

The anhydrous compounds Cs_3ErCl_6 and Rb_3ErCl_6, both with the Cs_3BiCl_6 structure, can be prepared from a solution of $ErCl_3 \cdot 6H_2O$ and Cs_2CO_3 in concentrated acetic acid by precipitation with HCl gas. We have recently described this method for ternary chlorides of trivalent iron, chromium and vanadium [10].

For Rb_3ErCl_6, 3.8 g of $ErCl_3 \cdot 6H_2O$ were dissolved at 80°C in 30 ml acetic acid. A solution of 3.4 g Rb_2CO_3 in 20 ml $H_3C \cdot COOH$ was added. When saturating the solution with HCl gas, a pink precipitate was formed. This was filtered and washed with ether under exclusion of moisture: yield, 5.6 g Rb_3ErCl_6 (85%).

3.2. Phase diagrams and crystal structures

Fig. 1 illustrates the results of the DTA measurements on the systems $RbCl/ErCl_3$ and $CsCl/ErCl_3$.

The melting temperature of $ErCl_3$ found by measurements in a corundum crucible was 751°C; this differs distinctly from the data given in the literature, namely 764°C by Korshunov et al. [11], 791°C by Goryuskin et al. [12], and 776°C by Dworkin and Bredig [13]. In 1994 Gaune-Escard et al. [14] found by measurements of 300 mg samples in quartz cells, that $ErCl_3$ should have a melting point of 773°C and a phase transition at 752°C. In our own experiments, this double effect originated in a reaction of the $ErCl_3$ melt with SiO_2. As Fig. 2 demonstrates, we found for the first melting only one peak at 751°C. When repeating the melting process, the effect splits; the splitting becomes more pronounced the more melting cycles are run. (The reaction of $ScCl_3$ and SiO_2 with the formation of $Sc_2Si_2O_7$ is described by Polyachenok et al. [15].)

In the system $RbCl/ErCl_3$, two dimorphic compounds exist: Rb_3ErCl_6 and $RbEr_2Cl_7$. A third, incongruently melting compound, Rb_2ErCl_5, is stable from 348 to 520°C. However, the formation temperature of 348°C could be observed only in heating curves with samples of quenched melts. When cooling, the

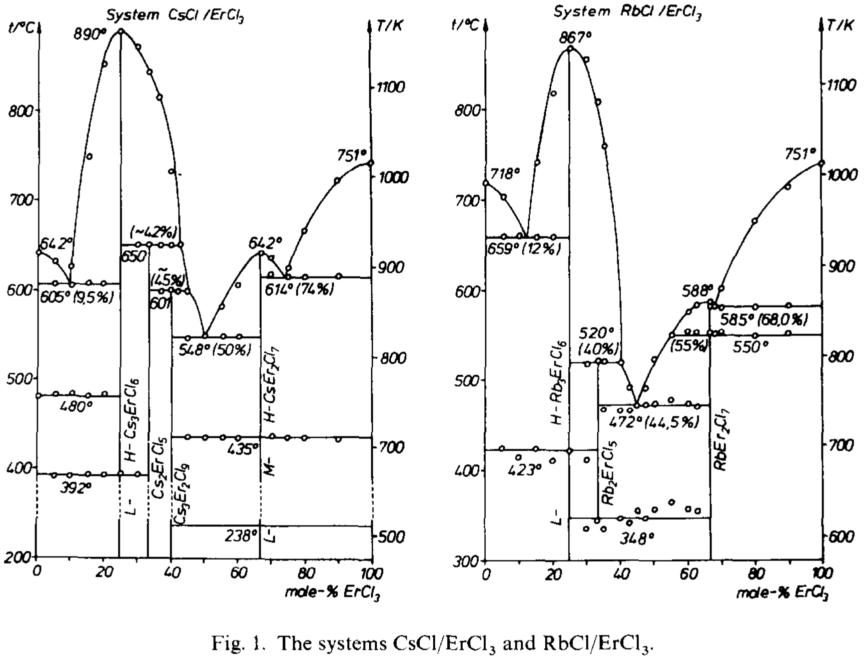

Fig. 1. The systems $CsCl/ErCl_3$ and $RbCl/ErCl_3$.

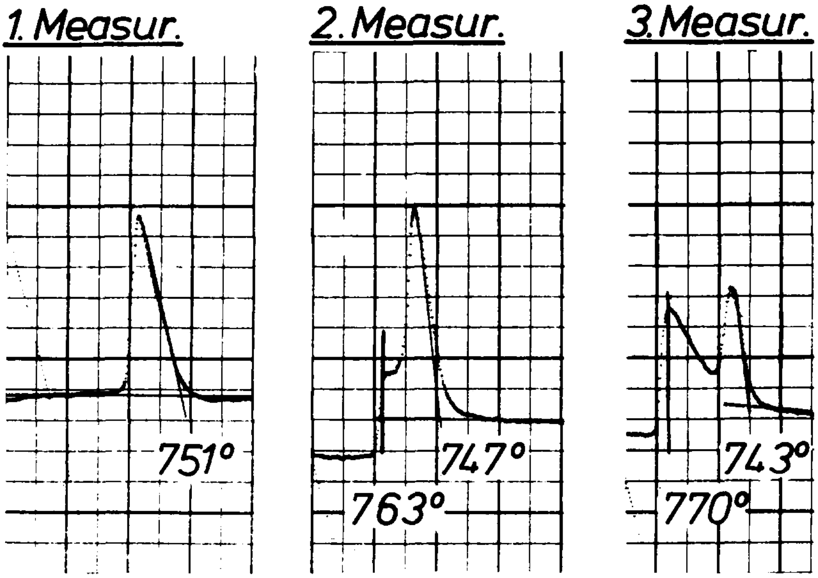

Fig. 2. Melting cycles for $ErCl_3$ in quartz ampoules.

decomposition does not occur in the time scale of DTA. X-ray measurements of samples cooled to ambient temperature reveal only a partial decomposition after some days.

The results of Blachnik and Selle [16] concerning the system $CsCl/ErCl_3$ were confirmed. In particular, we corroborate that two incongruently melting compounds exist: Cs_2ErCl_5 (peritectic temp., 650°C) and $Cs_3Er_2Cl_9$ (peritectic temp., 602°C).

The unit cells of all low-temperature compounds were determined by Meyer and coworkers from powder patterns: L-Cs_3ErCl_6 and L-Rb_3ErCl_6 [17], Cs_3BiCl_6-type (S.G. C 2/c); Cs_2ErCl_5 and Rb_2ErCl_5 [18], Cs_2DyCl_5-type (S.G. Pbnm); $Cs_3Er_2Cl_9$ [19], $Cs_3Tl_2Cl_7$-type (S.G.R$\bar{3}$c); L-$CsEr_2Cl_7$ and L-$RbEr_2Cl_7$ [20], (S.G. Pnma).

The high-temperature modifications of the 3:1 compounds crystallize with the cubic elpasolite structure (S.G. Fm3m); lattice parameters at 500°C are: H-Cs_3ErCl_6, $a = 11.535(2)$ Å; H-Rb_3ErCl_6, $a = 11.191$ (4) Å.

3.3. Solution calorimetry

All solution enthalpies were determined as the mean of three measurements. For $ErCl_3$, a value of $-211.9(1)$ kJ mol^{-1} was found (Ref. [21]: -210 to -216 kJ mol^{-1}). The values for the alkali metal chlorides were taken from previous measurements: CsCl, 18.1 (2) kJ mol^{-1}; RbCl, 17.6 (2) kJ mol^{-1}. With the solution enthalpies, $\Delta_{sol}H^\circ_{298}$, the enthalpies of formation from nACl + $ErCl_3$ were calculated

$$\Delta_f H^\circ_{298} = [\Delta_{sol}H^\circ_{298}(ErCl_3) + n\Delta_{sol}H^\circ_{298}(ACl)] - \Delta_{sol}H^\circ_{298}(A_nErCl_{n+3})$$

Table 1
Solution enthalpies/kJ mol^{-1}

	$\Delta_{sol}H^\circ_{298}$	$\Delta_f H^\circ_{298}$	$\Delta_f H^\circ_{298}$ [16]
0.5 $CsEr_2Cl_7$	−166.0(1)	−36.8	−41.9
0.5 $Cs_3Er_2Cl_9$	−113.9(6)	−70.8	
Cs_3ErCl_6	−63.6(3)	−94.4	−98.5
0.5 $RbEr_2Cl_7$	−171.9(12)	−31.3	
Rb_3ErCl_6	−81.7(9)	−77.4	

The measured values for all compounds which could be prepared as pure phases are compiled in Table 1 together with some values from the paper of Blachnik and Selle [16].

3.4. E.m.f. measurements

A comprehensive description of the method was given recently [22]. The e.m.f. values were measured for the formation of each compound from ACl and the adjacent $ErCl_3$-rich compound in a temperature range from ~ 300 to 500°C. In this range, the dependence of e.m.f. on T was linear. Thus, equations for the regression lines could be transformed by multiplication by $-nF$ to the Gibbs–Helmholtz equation $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$. By means of thermodynamic cycles, other functions could be calculated, for instance, if the free enthalpies of syn-reaction, $\Delta_s G^\circ$, from the two neighbouring compounds. For high-temperature modifications the temperatures of formation (decomposition) were calculated by the condition $\Delta_s G^\circ = 0$.

E.m.f. measurements could not be performed for the most $ErCl_3$-rich compounds, $CsEr_2Cl_7$ and $RbEr_2Cl_7$. According to our present experiments, the e.m.f. cells break down for e.m.f. values higher than ~ 500 mV.

The Gibbs–Helmholtz equations for the reaction in the cell are listed below, together with the temperature ranges of the measurements. The range of error was smaller than 1 kJ mol^{-1} for the energy values and 0.8 J K^{-1} mol^{-1} for the entropies.

Cs compounds

Reaction $CsCl + \text{M-}Cs_{0.5}ErCl_{3.5} = Cs_{1.5}ErCl_{4.5}$ $(T = 580\text{–}630\,K)$

$\Delta_r G^\circ/\text{kJ mol}^{-1} = -30.0 - 0.0102\ T/K$

Reaction $0.5CsCl + Cs_{1.5}ErCl_{4.5} = Cs_2ErCl_5$ $(T = 580\text{–}640\,K)$

$\Delta_r G^\circ/\text{kJ mol}^{-1} = -9.5 - 0.0072\ T/K$

Reaction $CsCl + Cs_2ErCl_5 = \text{L-}Cs_3ErCl_6$ $(T = 580\text{–}610\,K)$

$\Delta_r G^\circ/\text{kJ mol}^{-1} = -18.2 - 0.0073\ T/K$

Rb compounds

Reaction $1.5\text{RbCl} + \text{L-Rb}_{0.5}\text{ErCl}_{3.5} = \text{Rb}_2\text{ErCl}_5 \quad (T = 560\text{–}640\,\text{K})$

$$\Delta_r G^\circ/\text{kJ mol}^{-1} = -21.0 - 0.0303\ T/\text{K}$$

Reaction $\text{RbCl} + \text{Rb}_2\text{ErCl}_5 = \text{L-Rb}_3\text{ErCl}_6 \quad (T = 560\text{–}640\,\text{K})$

$$\Delta_r G^\circ/\text{kJ mol}^{-1} = -23.9 - 0.0017\ T/\text{K}$$

From both reactions, the Gibbs–Helmholtz relation for the formation of Rb_2ErCl_5 from its two neighbouring compounds ('syn-reaction') can be calculated:

Reaction ${}^2/_5\text{Rb}_{0.5}\text{ErCl}_{3.5} + {}^3/_5\text{Rb}_3\text{ErCl}_6 = \text{Rb}_2\text{ErCl}_5$

$$\Delta_S G^\circ = 6.0 - 0.0111\ T/\text{K};\quad \Delta_S H^\circ = 6.0\,\text{kJ mol}^{-1};\quad \Delta_S S^\circ = 11.1\,\text{J K}^{-1}\,\text{mol}^{-1}$$

The enthalpy for this reaction is positive (endothermic reaction). At 539 K (266°C), $\Delta_S G^\circ = 0$. Below this temperature, Rb_2ErCl_5 is no longer stable.

In Fig. 3 the enthalpies from e.m.f. measurements are compared with those from solution calorimetry.

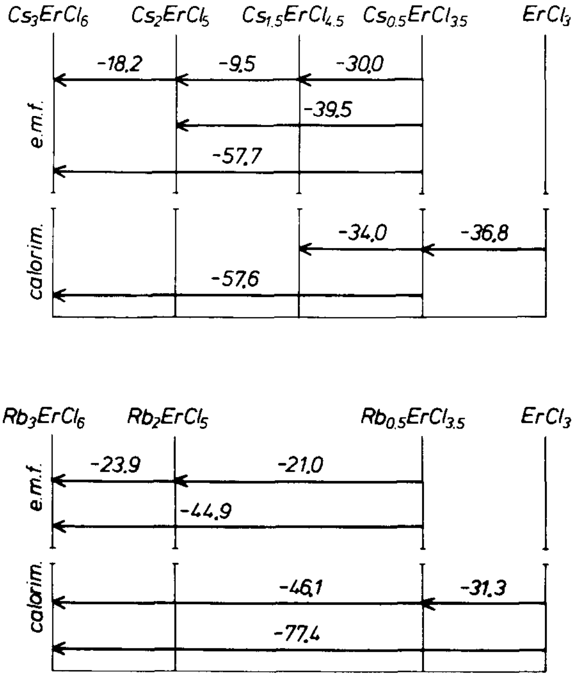

Fig. 3. Enthalpies in kJ mol^{-1} from e.m.f. measurements and solution calorimetry for reactions $n\text{ACl} + \text{A}_x\text{ErCl}_{3+x} = \text{A}_{(n+x)}\text{ErCl}_{(3+x+n)}$.

4. Discussion

As pointed out in the introduction the main purpose of these investigations was to find out which differences appear on going from the $DyCl_3$ systems [5] to the analogous $ErCl_3$ systems.

(1) In the system $CsCl/ErCl_3$, there is an additional incongruently melting compound, $Cs_3Er_2Cl_9$. In this ennea-chloride, isolated pairs of face-sharing $ErCl_6$ octahedra exist. Such double octahedra $[Er_2Cl_9]^{3-}$ are less deformable than isolated octahedra. Therefore, they are only formed if the radius ratio $r^{3+}_{\mathrm{Ln}}/r^{-}_{\mathrm{Cl}}$ is near to the ideal value for six ligands, i.e. 0.41. With $r^{3+}_{\mathrm{Er}} = 0.881$ Å [23] and $r^{-}_{\mathrm{Cl}} = 1.81$ Å, the ratio is 0.49. An analogous Rb compound does not exist because the Rb^+ ion is too small to surrounded by the necessary twelve Cl^- ions. With the bigger Br^- ion, there is an ennea-bromide with Sm^{3+} ($r = 0.964$ Å) [24].

(2) In the Rb system a compound Rb_2ErCl_5 exists having the Cs_2DyCl_5 structure with corner-connected $[ErCl_4Cl_{2/2}]$ octahedra. The analogous compounds with Dy and Tb do not exist, while Rb_2GdCl_5 crystallizes in the K_2PrCl_5 type with CN7 for Ln^{3+}.

As can be seen from the e.m.f. measurements, the Gibbs function for the syn-reaction $0.2RbEr_2Cl_7 + 0.6Rb_3ErCl_6 = Rb_2ErCl_5$ is zero at 266°C. Above this temperature, the endothermic enthalpy $\Delta_s H^\circ = 6.0$ kJ mol^{-1} is compensated by a sufficiently high $(-T\Delta S)$ term so that $\Delta_S G$ becomes < 0. This is the equilibrium temperature of formation for the high-temperature phase Rb_2ErCl_5. This solid state reaction is strongly kinetically hindered so that in the time scale of DTA (heating rate 2 K min^{-1}) the reaction temperature is found at 348°C. In the cooling period, the decomposition does not occur at all: the cooling product is metastable Rb_2ErCl_5. We have found the same feature for many other systems with such 'reconstructive phase reactions' [25].

The $\Delta_S H^\circ$ values of all other syn-reactions are negative therefore, these compounds should be stable down to $T = 0$ K if no anomalies in heat capacities occur at low temperature.

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