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THERMOCHEMICAL STUDIES ON THE SYSTEMS $ACl/CeCl_3$ (A = Na-Cs)*

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The pseudobinary systems $ACl/CeCl_3$ (A = Na-Cs) were reinvestigated by means of DTA. The following compounds were found and identified through their X-ray patterns (primarily detected compounds in italics): $\mathit{NaCe_{1.67}Cl_6}$; K_3CeCl_6, K_2CeCl_5, $\mathit{KCe_{1.67}Cl_6}$; $\mathit{Rb_3CeCl_6}$, Rb_2CeCl_5, $\mathit{RbCe_2Cl_7}$; Cs_3CeCl_6, Cs_2CeCl_5, $\mathit{CsCe_2Cl_7}$. The compounds A_2CeCl_5 crystallize with the K_2PrCl_5 structure. The high-temperature modifications of the compounds A_3CeCl_6 have the cubic elpasolite structure. The hexagonal unit cell of $KCe_{1.67}Cl_6$ is related to the $CeCl_3$ structure: 0.33 Ce^{3+} are substituted by one K^+. The structure of $CsCe_2Cl_7$ can be described with a hexagonal subcell $Z = 4$, $a = 9.72$ and $c = 14.94$ Å; however, small superstructure reflexions reduce the symmetry.

The thermodynamic functions for the reactions

$$n\text{ACl} + \text{CeCl}_3 = \text{A}_n\text{CeCl}_{n+3}\ (\text{A} = \text{K, Rb})$$

were determined by means of e.m.f. measurements.

Measurements of the e.m.f. E *vs.* T yielded the Gibbs enthalpies ΔG^r. The temperature-dependence was found to be linear.

The most important result is the formation of the elpasolites (A_3CeCl_6) and ACe_2Cl_7.

Our method of obtaining thermodynamic functions for the formation of ternary chlorides in a galvanic cell with solid electrolytes [1] can be applied for tervalent metals, too. The first investigation in this field dealt with the systems $ACl/LaCl_3$ [2]. We then found that it was necessary to reinvestigate the phase diagrams, too, using differential thermal analysis (DTA). The main results were: the most stable compounds in the systems with K, Rb, Cs are the 2 : 1 compounds A_2LaCl_5; with Rb and Cs the compounds A_3LaCl_6 and ALa_2Cl_7 exist, which are stable at higher temperatures; with Na and K the compounds $ALa_{1.67}Cl_6$ exist, the structures of which are related to the $LaCl_3$ lattice.

This paper reports investigations on ternary chlorides in the systems $ACl/CeCl_3$ (A = Na-Cs). (A short communication on the system $KCl/CeCl_3$ has already been

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given elsewhere [3].) In addition to the elucidation of the phase diagrams, the crystal structures of the compounds were determined. By means of solution calorimetry and e.m.f. measurements, the thermodynamic functions of the ternary chlorides were measured, too; the results are compared with those for the $LaCl_3$ systems.

Experimental

Material preparation

Anhydrous $CeCl_3$ was prepared from $CeCl_3 \cdot xH_2O$, treated in a vacuum oven at 60° by heating in an HCl stream for one day, the temperature being slowly raised from 100° to melting, with subsequent cooling in an Ar stream. The hydrate was obtained from a solution of Ce_2O_3 (p.a., Merck Co.) in hydrochloric acid. The alkali metal chlorides (Merck, p.a.) were dried in an HCl stream at 500°. The double chlorides were obtained by melting appropriate mixtures in vacuum-sealed quartz ampoules using a gas flame. The melt was homogenized by shaking, and solidified by rapid cooling.

Differential thermal analysis (DTA)

The home-built DTA device was described previously [4]. The samples ($\sim$0.5 g) were prepared in the same way as described for the double chlorides. The solids thus obtained were sufficiently homogeneous for the measurement of heating curves or for annealing experiments. Thermal effects could be detected down to 0.2 J for the generally used heating rate of 2 $\text{deg} \cdot \text{min}^{-1}$.

Solution calorimetry

The apparatus used was a home-built isoperibolic calorimeter [5] with a volume of 1.3 l. Samples of 3–6 g yielded virtually ideal solutions (dissolution ratio 1 : 3500 mol). From the enthalpies of solution, ΔH^l, the reaction enthalpies, ΔH^r, were calculated from:

$$\Delta H^r_{298} = \{\Delta H^l_{298}(CeCl_3) + n\,\Delta H^l_{298}(ACl)\} - \Delta H^l_{298}(A_nCeCl_{n+3})$$

Each ΔH^l was measured at least three times; the alkali metal chlorides were dissolved in a solution of $CeCl_3$ of appropriate concentration.

X-ray techniques

Powder patterns at room temperature were taken with a Philips PW 1050/25 goniometer equipped with a proportional counter and a vacuum attachment.

During exposure (Cu-K_α radiation), the samples were under a He atmosphere. An Enraf–Nonius–553 Simon–Guinier camera was used for photographs at continuously varying temperatures. The samples were encapsulated in quartz tubes 0.3 mm in diameter. For the determination of cell dimensions, some Al_2O_3 was added to the samples as an internal standard; the calculations were performed with the least-squares computer program of Warczewski [6] for the various temperatures.

E.m.f. measurements

A detailed description of the galvanic cell is given elsewhere [1]. For the formation of the Ce-richest compound the set-up of the cell was:

$$(C+Cl_2)/ACl/A^+\text{-conducting diaphragm}/CeCl_3(+A_nCeCl_{n+3})/(C+Cl_2).$$

The solid electrolytes (compressed disks) were separated by a sintered disk of an A^+-conducting glass powder prepared according to a formula developed by Østvold [7]; for Cs^+ no suitable material could be found until recently. Two samples were measured for each compound, the temperature being varied stepwise in at least two temperature cycles. The collected e.m.f./T values were subjected to linear regression analysis, because the temperature-dependence of the e.m.f. proved to be linear down to ~300°. The upper limit was given by the temperature of the lowest adjacent eutectic. No measurements were performed for the mixed crystal region in the system $NaCl/CeCl_3$; for the dependence of the e.m.f.'s on the composition, coulometric titration is a more convenient method.

The phase diagrams

Figure 1 illustrates the results of the DTA investigations on the systems $ACl/CeCl_3$ with A = Cs, Rb, K, Na, including all the characteristic data taken from the heating curves. The melting point for $CeCl_3$ was found at 831°. All DTA findings were confirmed by X-ray patterns, if necessary the dynamic high-temperature technique being used.

Previous investigations by Morosov [8] demonstrated two compounds (K_3CeCl_6 and K_2CeCl_5) in the system $KCl/CeCl_3$, and one congruently melting double chloride, Cs_3CeCl_6, with a transition point in the solid state in the system $CsCl/CeCl_3$. Novikov and Baer [9] reported two additional compounds, KCe_3Cl_{10} and $K_3Ce_2Cl_9$, in the potassium system. Thus, our results require the following corrections: (1) K_3CeCl_3 and a new compound, $KCe_{1.67}Cl_6$, exist at higher temperature; a 3:1 compound does not exist. (2) In the system $CsCl/CeCl_3$ two additional compounds, Cs_2CeCl_5 and $CsCe_2Cl_7$, were found.

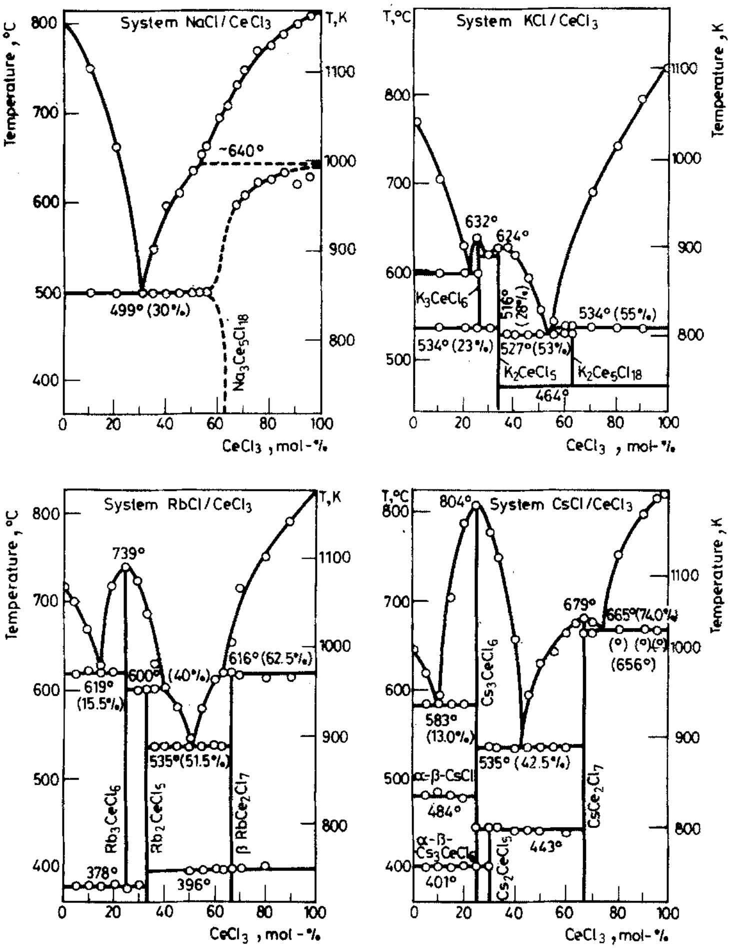


Fig. 1 Phase diagrams of the ACl/$CeCl_3$ systems

Crystal structures

The results of X-ray measurements on crystal powders, together with the results of Meyer [10] for some compounds A_2CeCl_5, are summarized in Table 1.

The compounds A_3CeCl_6 have high-temperature modifications, crystallizing in the cubic elpasolite type. The only compound of this composition stable at room temperature is Cs_3CeCl_6. Its powder pattern could be indexed with a monoclinic cell in relation to the structure of K_3MoCl_6. The transformation temperature is 401°.

The compounds $KCe_{1.67}Cl_6$ and $NaCe_{1.67}Cl_6$ have hexagonal unit cells which

Table 1 Unit cell parameters for cerium double chlorides in Å

Compound	Space group	a	b	c	β
H-Cs_3CeCl_6	Fm3m	11.834(4)	—	—	—
D-Cs_3CeCl_6	$P2_1/c$	14.129(3)	8.292(2)	13.340(3)	108.00(2)
Rb_3CeCl_6	Fm3m	11.448(2)	—	—	—
K_3CeCl_6 (830 K)	Fm3m	11.241(2)	—	—	—
Cs_2CeCl_5	Pnma	13.762(3)	9.208(2)	8.548(2)	—
Rb_2CeCl_5 [10]	Pnma	13.122(3)	8.985(2)	8.195(2)	—
K_2CeCl_5 [10]	Pnma	12.717(3)	8.815(2)	8.022(2)	—
$CsCe_2Cl_7$	hexagon. pseudocells ($Z = 4$)	9.72	—	14.94	—
$RbCe_2Cl_7$		9.58	—	14.65	—
$KCe_{1.67}Cl_6$	$P6_3/m$	7.839(2)	—	4.256(1)	—
$NaCe_{1.67}Cl_6$	$P6_3/m$	7.559(2)	—	4.319(1)	—

are related to the $CeCl_3$ structure: one-third of the Ce^{3+} sites are occupied by K^+ ions, two-thirds of the K^+ ions occupy the positions 2b: 0, 0, 0; 0, 0, 1/2 of the space group 176–$P6_3/m$. (For the analogous compound $KLa_{1.67}Cl_6$, a single-crystal investigation gave a reliability value $R = 0.085$ with a statistical occupation model [2].)

The compounds ACe_2Cl_7 have a complicated monoclinic lattice with $Z = 12$ formula units per cell; the strongest reflections, however, can be described by a hexagonal unit cell with $Z = 4$.

Solution calorimetry

The solution enthalpy for $CeCl_3$ was found to be $-138.9(8)$ kJ · mol^{-1}. This is in good agreement with values from the literature, which range from -136.8 to

Table 2 Solution enthalpies ΔH^l and related enthalpy values [kJ · mol^{-1}]

Compound	ΔH^l_{298}	ΔH^r_{298}	ΔH^s_{298}
Cs_3CeCl_6	$-$ 58.4(7)	-26.0	+ 9.9
(Cs_3CeCl_6 [12])	$-$ 54.4(14)	-32.8	—
Cs_2CeCl_5	$-$ 66.8(6)	-35.9	-16.9
1/2 $CsCe_2Cl_7$	$-121.5(8)$	$-$ 8.4	+ 0.6
Rb_2CeCl_5	$-$ 65.1(8)	-37.9	-36.0
1/2 $RbCe_2Cl_7$	$-128.2(6)$	$-$ 1.9	+ 7.6
K_2CeCl_5	$-$ 75.8(10)	-27.3	-22.3
$K_{0.6}CeCl_{3.6}$	$-123.2(8)$	$-$ 5.0	+ 3.2

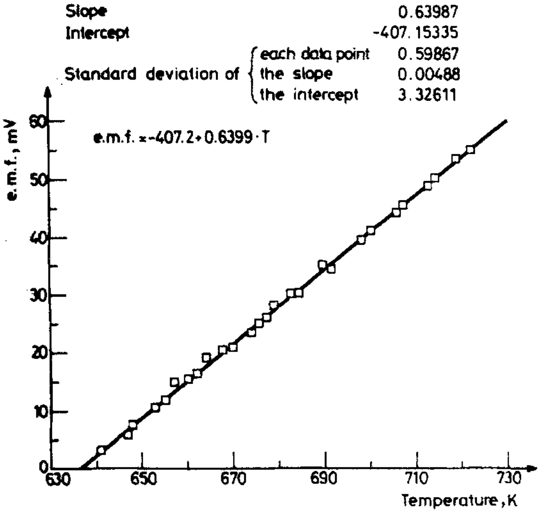
ΔH^r = reaction enthalpies from $ACl + CeCl_3$; ΔH^s = synproportionation enthalpies from the neighbour compounds.

-144.0 kJ$\cdot$mol^{-1}. (A good compilation is given in [11].) The enthalpies for dissolution of the alkali metal chlorides in $CeCl_3$ solutions are (in kJ$\cdot$mol^{-1}): for CsCl = 18.1(2); RbCl = 17.6(2); KCl = 17.9(1). The measured values for the compounds existing at room temperature are compiled in Table 2.

ΔH^l values for 'K_3CeCl_6' are also given in the literature: -59.3 kJ$\cdot$mol^{-1} [12] and -60.7 kJ$\cdot$mol^{-1} [9]. However, this compound does not exist at room temperature, but is a mixture of ($KCl+K_2CeCl_5$). Our values for it yield a 'ΔH^{l}' = $(-75.8+17.9) = -57.9$ kJ$\cdot$mol^{-1}.

E.m.f. measurements

The e.m.f. values were measured for the formation of the compounds from ACl (with A = K, Rb) and the neighbouring $CeCl_3$-richer compound. Regression analysis gave plots like that in Fig. 2 for the reaction $RbCl+Rb_2CeCl_5 = Rb_3CeCl_6$. From the mean of the regression coefficients from two samples, the thermodynamic functions ΔG^f, ΔH^f and ΔS^f were calculated. By means of thermodynamic cycles, these functions were transformed to those for the reactions $n\,ACl+CeCl_3 = A_nCeCl_{n+3}$, denoted as ΔG^r, ΔH^r and ΔS^r. In Table 3 the energy values ΔG^r_{298}, ΔH^r_{298} and $-(T\cdot S^r)_{298}$ are compiled in the first three columns.



K	mV
647	5.8
653	10.5
660	15.5
668	20.6
676	25.0
683	30.0
690	34.7
698	39.5
706	44.4
713	49.0
719	53.5
722	54.8
714	49.8
707	45.2
700	40.8
698	39.3
691	34.5
684	30.0
677	25.5
670	20.8
662	16.4
655	11.7
648	7.4
641	3.1
679	28.0
674	23.3
664	19.1
657	14.9

Fig. 2 Computer plot e.m.f. vs. T for Rb_3CeCl_6

$K_{0.6}CeCl_{3.6}$: Reaction 0.6 KCl + $CeCl_3$ = $K_{0.6}CeCl_{3.6}$ Samples: 80 and 90 mol % $CeCl_3$ e.m.f., mV = 84.71 + 0.1573 · T, deg ΔG^f, kJ · mol^{-1} = −4.9–0.0091 · T, deg (Deviations: $\Delta G^f = \pm 0.4$ kJ · mol^{-1}) · $\Delta H^f = \pm 0.1$ kJ · mol^{-1} $\Delta S^f = \pm 0.2$ J · deg^{-1} · mol^{-1})

K_2CeCl_5: Reaction 1.4 KCl + $K_{0.6}CeCl_{3.6}$ = K_2CeCl_5 Samples: 50 and 60 mol % $CeCl_3$ e.m.f., mV = 178.87 + 0.0214 · T, deg ΔG^f, kJ · mol^{-1} = −24.2–0.0029 · T, deg (Deviations: $\Delta G^f = \pm 0.3$ kJ · mol^{-1}; $\Delta H^f = \pm 0.1$ kJ · mol^{-1}; $\Delta S^f = 0.2$ J · deg^{-1} · mol^{-1})

Table 3 Energies of the formation from ACl and $CeCl_3$ at 298 K and free enthalpies of synproportionation ΔG^s_{298} [kJ · mol^{-1}]

Compound	ΔG^r	ΔH^r	$-(T \cdot \Delta S^r)$	ΔH^r (calorim.)	ΔG^s	$\Delta G^s = 0$ at T [K]
$K_{0.6}CeCl_{3.6}$	− 7.6	− 4.9	− 2.7	− 5.0	+ 2.2	691
K_2CeCl_5	−32.7	−29.1	− 3.6	−27.3	−25.1	—
K_3CeCl_6	+ 1.0	+24.8	+23.8	—	+33.7	794
$Rb_{0.5}CeCl_{3.5}$	− 6.6	− 2.0	− 4.6	− 1.9	+ 3.5	561
Rb_2CeCl_5	−34.6	−37.4	+ 2.8	−37.9	−49.8	—
Rb_3CeCl_6	+19.8	+ 0.8	−20.7	—	+20.3	636

K_3CeCl_6: Reaction KCl + K_2CeCl_5 = K_3CeCl_6 Two samples with 30 mol % $CeCl_3$ e.m.f., mV = 559.3 + 0.7041 · T, deg ΔG^f, kJ · mol^{-1} = +53.9–0.0679 · T, deg (Deviation: $\Delta G^f = \pm 0.6$ kJ · mol^{-1}; $\Delta H^f = \pm 5$ kJ · mol^{-1}; $\Delta S^f = \pm 1$ J · deg^{-1} · mol^{-1})

$Rb_{0.5}CeCl_{3.5}$: Reaction 0.5 RbCl + $CeCl_3$ = $Rb_{0.5}CeCl_{3.5}$ Samples: 70 and 95 mol % $CeCl_3$ e.m.f., mV = 41.5 + 0.3213 · T, deg ΔG^f, kJ · mol^{-1} = −2.0–0.0155 · T, deg (Deviations: $\Delta G^f = \pm 0.4$ kJ · mol^{-1}; $\Delta H^f = \pm 0.3$ kJ · mol^{-1}; $\Delta S^f = \pm 0.5$ J · deg^{-1} · mol^{-1})

Rb_2CeCl_5: Reaction 1.5 RbCl + $Rb_{0.1}CeCl_{3.5}$ = Rb_2CeCl_5 Samples: 45 and 60 mol % $CeCl_3$ e.m.f., mV = 244.7–0.0412 · T, deg ΔG^f, kJ · mol^{-1} = −35.4 + 0.0060 · T, deg (Deviations: $\Delta G^f = \pm 0.8$ kJ · mol^{-1}; $\Delta H^f = \pm 0.4$ kJ · mol^{-1}; $\Delta S^f = \pm 0.5$ J · deg^{-1} · mol^{-1})

Rb_3CeCl_6: Reaction RbCl + Rb_2CeCl_5 = Rb_3CeCl_6 Samples: 2 × 30 mol % $CeCl_3$ e.m.f., mV = −395.6 + 0.6229 · T, deg ΔG^f, kJ · mol^{-1} = +38.2–0.0601 · T, deg (Deviations: $\Delta G^f = \pm 1$ kJ · mol^{-1}; $\Delta H^f = \pm 1$ kJ · mol^{-1}; $\Delta S^f = \pm 1$ J · deg^{-1} · mol^{-1})

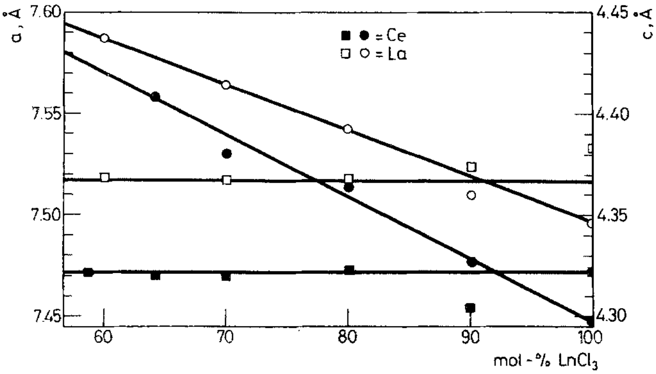


Fig. 3 Vegard's lines for $NaLn_{1.67}Cl_6$ (Ln = La, Ce). ■, ● = Ce, □, ○ = La

From the ΔG^s values in Table 3, it can be seen that only the chlorides with the formula A_2CeCl_5 are stable at room temperature. From the condition $\Delta G^s = 0$, the thermodynamically correct temperatures of formation can be calculated for these compounds; they are given in the last column. They differ considerably from the temperatures found from the DTA heating curves (HC) and cooling curves (CC). This is behaviour common for reconstructive phase transitions characterized by motion of the ions over large distances:

Temperatures of formation for:

K_3CeCl_6:	521°;	from HC: 534°;	from CC: 516°
Rb_3CeCl_6:	363°;	from HC: 378°;	from CC: —

For $KCe_{1.67}Cl_6$ the formation temperature from e.m.f. measurements is 418°. Here, an endothermic effect could be found at 464° only after annealing of the compound for 4 weeks at 402°. For $RbCe_{0.5}Cl_{3.5}$ the situation is still more extreme: the decomposition occurred only after annealing the compound at 150° together with approx. 0.1% water as catalyst for 3 months; then, in a heating curve the temperature of recombination was found to be 333°, compared with 288° calculated from the temperature-dependence of ΔG^s.

Discussion

The results of our investigations indicated that in the systems of $CeCl_3$ with KCl, RbCl and CsCl only compounds of the composition A_2CeCl_5 are stable at room temperature. For the other compounds the energies of synproportionation, ΔG^s and/or ΔH^s, are positive at 298 K. The same situation was found for the double chlorides of lanthanum (with the exception of $CsCe_2Cl_7$). This behaviour ought to be due to the structure of the 2 : 1 compounds [10]: a hexagonal arrangement of chains of edge-connected ($CeCl_7$)-polyhedra; the molar volume is somewhat smaller than the sum of the volumes ($2CsCl+CeCl_3$), e.g. 145.5 cm^3 as compared with 147.2 cm^3 for Rb_2CeCl_5.

The compound $KCe_{1.67}Cl_6 = K_3Ce_5Cl_{18}$ and the mixed crystals of NaCl with $CeCl_3$ up to $Na_3Ce_5Cl_{18}$ can be derived from the structure of $CeCl_3$ [13]: A hexagonal, closest-packed Cl^- structure is distorted in such a way that each Ce^{3+} ion is bonded to nine Cl^- ions by occupying triangular holes in a layer. In $K_3Ce_5Cl_{18}$ one Ce^{3+} is substituted by a K^+ ion; the two other K^+ ions occupy the octahedral holes of the hexagonal Cl^- packing. Because the ionic radii of Na^+ (1.02 Å) and Ce^{3+} (1.03 Å) are very similar, a range of mixed crystals exists between $CeCl_3$ and $Na_3Ce_5Cl_{18}$. As Fig. 3 demonstrates, only in the *c* direction is a widening of the lattice to be found. The features of the structures of $CsCe_2Cl_7$ and $RbCe_2Cl_7$ are still unknown. The elpasolites A_3CeCl_6 consist of isolated ($CeCl_6$)-octahedra. A considerable widening of the lattice exists for Rb_3CeCl_6 from V_m ($3RbCl+CeCl_3$) = 189.5 cm^3 to V_m (Rb_3CeCl_6) = 225.8 cm^3. The loss of lattice energy caused by this swelling is compensated by a large gain in entropy, which allows the compounds to be stable above the formation temperatures. We have found an analogous increase of entropy in other cases [14] where compounds with isolated polyhedra are formed from binary parent compounds with connected polyhedra; the gain of entropy is correlated with a gain in the number of 'degrees of freedom' in the solid arrangements.

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References

1 H. J. Seifert and G. Thiel, J. Chem. Thermodyn., 14 (1982) 1159.
2 H. J. Seifert, H. Fink and G. Thiel, J. Less-Common Metals, 110 (1985) 139.
3 G. Thiel, J. Sandrock and H. J. Seifert, Thermochim. Acta, 92 (1985) 815.
4 H. J. Seifert and G. Thiel, Thermochim. Acta, 20 (1977) 244.
5 G. Thiel and H. J. Seifert, Thermochim. Acta, 22 (1978) 363.
6 J. Warczewski and P. M. Dewolff, J. Appl. Crystallogr., 7 (1974) 585.
7 T. A. Østvold, Thesis, Univ. Trondheim/Norway, 1971.
8 Sun In' Chzhu and I. S. Morosov, Zh. Neorg. Khim., 3 (1958) 1914.
9 A. K. Baev and G. I. Novikov, Zh. Neorg. Khim., 6 (1961) 2610.
10 G. Meyer and E. Hüttl, Z. Anorg. Allg. Chem., 497 (1983) 191.
11 R. Blachnik and D. Selle, Thermochim. Acta, 33 (1979) 301.
12 R. Blachnik and D. Selle, Z. Anorg. Allg. Chem., 454 (1979) 82.
13 W. Zachariasen, J. Chem. Phys., 16 (1948) 254.
14 H. J. Seifert and G. Thiel, Thermochim. Acta, 100 (1986) 81.

Zusammenfassung — Die pseudobinären Systeme $ACl/CeCl_3$ (A = Na-Cs) wurden mittels Differenzthermoanalyse (DTA) neu untersucht. Folgende Verbindungen wurden gefunden und durch ihre Röntgenbeugungsmuster charakterisiert (erstmalig nachgewiesene Verbindungen sind kursiv):

$NaCe_{1.67}Cl_6$; $\mathrm{K_3CeCl_6}$, $\mathrm{K_2CeCl_5}$, *$KCe_{1.67}Cl_6$*; *Rb_3CeCl_6*, $\mathrm{Rb_2CeCl_5}$, *$RbCe_2Cl_7$*; $\mathrm{Cs_3CeCl_6}$, $\mathrm{Cs_2CeCl_5}$, *$CsCe_2Cl_7$*. Die Verbindungen $\mathrm{A_2CeCl_5}$ kristallisieren im $\mathrm{K_2PrCl_5}$-Typ. Die Hochtemperaturmodifikationen der Verbindungen $\mathrm{A_3CeCl_6}$ liegen in der kubischen Elpasolith-Struktur vor. Die hexagonale Elementarzelle des $\mathrm{KCe_{1.67}Cl_6}$ ist mit der $\mathrm{CeCl_3}$-Struktur verwandt: 0,33 $\mathrm{Ce^{3+}}$ sind durch ein $\mathrm{K^+}$ ersetzt. Die Struktur des $\mathrm{CsCe_2Cl_7}$ kann mit einer hexagonalen Pseudozelle beschrieben werden: a = 9,72; c = 14,94 Å; Z = 4; schwache Überstrukturreflexe reduzieren jedoch die Symmetrie. Die thermodynamischen Funktionen für die Reaktionen:

$$n\,\mathrm{ACl} + \mathrm{CeCl_3} = \mathrm{A}_n\mathrm{CeCl}_{n+3}\ (A = \mathrm{K, Rb})$$

wurden durch EMK-Messungen bestimmt. Messungen der Abhängigkeit von e. m. f. E gegen T ergaben die Gibbs-Enthalpien ΔG^r. Es wurde eine lineare Temperaturabhängigkeit gefunden. Als wichtigstes Resultat ist die Bildung von Elpasoliten ($\mathrm{A_3CeCl_6}$) und von Verbindungen ($\mathrm{ACe_2Cl_7}$) anzusehen.

Резюме — С помощью ДТА вновь исследованы псевдобинарные системы $\mathrm{ACl/CeCl_3}$, где А — рад щелочных металлов от натрия до цезия. Рентгено-структурным анализом идентифицированы следующие соединения (впервые идентифицированные соединения подчеркнуты): *$NaCe_{1,67}Cl_6$*; $\mathrm{K_3CeCl_6}$, $\mathrm{K_2CeCl_5}$, *$KCe_{1,67}Cl_6$*; *Rb_3CeCl_6*, $\mathrm{Rb_2CeCl_5}$, *$RbCe_2Cl_7$*; $\mathrm{Cs_3CeCl_6}$, $\mathrm{Cs_2CeCl_5}$ и *$CsCe_2Cl_7$*. Соединения $\mathrm{A_2CeCl_5}$ кристаллизуютсясо структурой $\mathrm{K_2PrCl_5}$. Высокотемпературные модификации соединений $\mathrm{A_3CeCl_6}$ имеют кубическую структуру элпасолита. Элементарная ячейка гексагональной решетки $\mathrm{KCe_{1,67}Cl_6}$ имеет структуру $\mathrm{CeCl_3}$, в которой 0,33 $\mathrm{Ce^{3+}}$ иона замещены одним ионом калия. Структура $\mathrm{CsCe_2Cl_7}$ может быть описана гексагональной подрешеткой с параметрами ячейки a = 9,72 Å, c = 14,94 Å и Z = 4. Однако, небольшие сверхструктурные рефлексии понижают симметрию. Термодинамические функции реакций $n\,\mathrm{ACl} + \mathrm{CeCl_3} = \mathrm{A}_n\mathrm{CeCl}_{n+3}$ (A = K, Rb) были определены с помощью измерений э. д. с. Измерения э. д. с. E показали линейную зависимость от температуры, давая значения энтальпии Гиббса ΔG^r. Важным результатом проведенного исследования является доказательство образования элпасолитов и $\mathrm{ACe_2Cl_7}$.