

Structure and Stability of the Low-Temperature Modification of Compounds Cs_3LnCl_6 ($\text{Ln} = \text{La}–\text{Gd}$)

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The crystal structure of the low-temperature modification of Cs_3LaCl_6 has been determined from X-ray powder diffraction data by the Rietveld method. The monoclinic lattice with $a = 27.286(5)$ Å; $b = 8.291(1)$ Å; $c = 13.305(2)$ Å; $\beta = 99.64(1)^\circ$ belongs to the Cs_3BiCl_6 -type (space group $C2/c$). All other compounds Cs_3LnCl_6 ($\text{Ln} = \text{Ce}–\text{Gd}$) and the analogous Rb-compounds are isotypic. Emf measurements in a galvanic cell for solid electrolytes for the reactions $\text{CsCl} + \text{Cs}_2\text{LnCl}_5 = \text{Cs}_3\text{LnCl}_6$ reveal that the compounds with $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$ are formed with a loss of lattice enthalpy, compensated by a considerable gain in entropy; they therefore are stable only at temperatures higher than 0 K. The compounds with $\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}$ are formed with a gain in lattice enthalpy and are stable at $T = 0\text{K}$, too. This difference is attributed to the different crystal structures of the neighboring compounds Cs_2LnCl_5 : they crystallize with the K_2PrCl_5 -structure ($\text{CN} = 7$ for Ln^{3+}) for the compounds with $\text{Ln} = \text{La}–\text{Nd}$, while the other compounds belong to the Cs_2DyCl_5 -type with octahedral surroundings for the Ln^{3+} ions. © 1993 Academic Press, Inc.

1. Introduction

In the course of investigations on the existence of ternary chlorides in the systems ACl/LnCl_3 ($A = \text{Na}–\text{Cs}$, $\text{Ln} = \text{La}–\text{Gd}$) (1) we have found compounds A_3LnCl_6 in all systems with $A = \text{Cs}$, Rb and in some systems with $A = \text{K}$. All compounds exhibit congruent melting and reveal a phase transition near 400°C . It could be proved by measurements of the emf's for the reactions $A\text{Cl} + \text{A}_2\text{LnCl}_5 = \text{A}_3\text{LnCl}_6$ in a galvanic cell for solid electrolytes (2) that the Rb and K compounds are stable only at temperatures above $\sim 350^\circ\text{C}$; however, they can be maintained metastable at ambient temperature

by quenching. Because of the lack of Cs^+ -conducting diaphragms, measurements of Cs compounds were not possible in the past.

Simon–Guinier patterns of the high-temperature phases could be indexed cubic according to the elpasolite structure (space group $Fm\bar{3}m$). Because of the phase transitions it was not possible to yield single crystals of the low-temperature phases. Thus, we tried to index powder patterns in accordance with the K_3MoCl_6 structure, using the site parameters of the atomic positions in K_3MoCl_6 (3) for the calculation of the peak intensities. While all strong peaks could be indexed without complications there were intensity discrepancies for some peaks of middle intensity, and some peaks for the K_3MoCl_6 -type could not be found at all. An investigation of Cs_3LaCl_6 by the X-ray Riet-

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veld procedure then revealed that the true structure is that of the Cs_3BiCl_6 -type (4), in which the monoclinic unit cell is doubled (space group $C2/c$ with $Z = 8$ compared with $P2_1/c$ and $Z = 4$ for K_3MoCl_6). An accurate inspection of the X-ray patterns of all other Cs and Rb compounds showed that they must be described with the Cs_3BiCl_6 structure too, while for the K compounds an exact discrimination between the two types could not be done.

In this paper these new results are given together with emf measurements for the Cs compounds which have become possible by improved Cs^+ -conducting diaphragms.

2. Experimental

Materials. Specimens were prepared by melting CsCl and anhydrous lanthanide chlorides, encapsulated in quartz ampoules, quenching the melts, and annealing the products for several days just below the transition temperatures. The lanthanide chloride hydrates were prepared by dissolving the oxides (99.99% from Johnson Matthey GmbH, Karlsruhe) in hydrochloric acid; the dehydration was performed in an HCl stream at temperatures slowly increased up to $\sim 350^\circ\text{C}$.

Emf measurements. The stability of a compound Cs_3LnCl_6 is determined by the free enthalpy of "synproportionation," $\Delta_{\text{syn}}G^0$, the Gibbs enthalpy for the formation from the two adjacent compounds in the system. The setup of the galvanic cell was $\text{C}, \text{Cl}_2, \text{CsCl}|\text{Cs}^+\text{-conducting diaphragm}|\text{Cs}_3\text{LnCl}_6, \text{Cs}_2\text{LnCl}_5, \text{Cl}_2, \text{C}$. The two sample disks were prepared by compression under exclusion of moisture analogous to the procedure used in IR spectroscopy. They were separated by a Cs^+ -conducting diaphragm, prepared according to a recipe, recently given (5). The whole sandwich was placed between two graphite disks in a chlorine atmosphere. The complete cell is described elsewhere (2). The collected emf (T)-values were subjected

TABLE I
CRYSTALLOGRAPHIC AND RIETVELD REFINEMENT
DATA FOR Cs_3LaCl_6

2 θ range (deg)	10–50
Step width (deg)	0.014
Transmission factor I/I_0	0.65
Space group	$C 2/c$
Z	8
a (Å)	27.286(5)
b (Å)	8.291(1)
c (Å)	13.305(2)
β (deg)	99.64(1)
D_{calc} ($\text{g} \cdot \text{cm}^{-3}$)	3.359
No. of steps	2858
No. of reflections	259
No. of profile parameters	15
No. of structural parameters	32
$R(P) = \sum Y_{\text{obs.}} - Y_{\text{calc.}} / \sum Y_{\text{obs.}}$	0.046
$R(\text{wp}) = (\sum [W(Y_{\text{obs.}} - Y_{\text{calc.}})^2] / \sum [W Y_{\text{obs.}}]^2)^{1/2}$	0.058
$R(I, hkl)^a = \sum I_{\text{obs.}} - I_{\text{calc.}} / \sum I_{\text{obs.}}$	0.099

^a The I values are approximately integrated intensities derived from the powder profiles.

to a linear regression analysis (temperature range of linearity $\geq 580\text{ K}$).

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 ($\text{Cu K}\alpha$ radiation) the samples were under He atmosphere.

Corundum ($a = 4.7592\text{ Å}$, $c = 12.9900\text{ Å}$) was used as an internal standard. The calculations were performed with the program "Lazy Pulverix" (6) and the least-squares program of Warczewski (7).

Rietveld refinement. The X-ray powder data were collected in transmission mode on a STOE STADI-P diffractometer equipped with a focusing germanium primary monochromator, and a linear position-sensitive detector $\text{Cu K}\alpha_1$ radiation was used. Data collection parameters are given in Table I together with the crystallographic data.

Structure refinement was carried out with the PFSR (profile fitting structure refinement) program of the STOE software pack-

TABLE II
POSITIONAL AND ISOTROPIC THERMAL PARAMETERS
FOR Cs_3LaCl_6 IN S.G. C 2/c

Atom	x/a	y/b	z/c	U_{11}
La ₁	0.25000	0.25000	0.50000	0.012
La ₂	0.00000	0.789(7)	0.25000	
Cs ₁	0.050(1)	0.726(6)	0.930(3)	0.025
Cs ₂	0.162(1)	0.815(6)	0.305(3)	
Cs ₃	0.346(1)	0.187(5)	0.851(3)	
Cl ₁	0.247(5)	0.389(1)	0.693(10)	0.026
Cl ₂	0.322(5)	0.491(16)	0.482(9)	
Cl ₃	0.324(6)	0.068(16)	0.579(11)	
Cl ₄	0.045(5)	0.544(17)	0.173(10)	
Cl ₅	-0.060(4)	0.798(16)	0.060(10)	
Cl ₆	0.063(5)	0.050(16)	0.197(10)	

age written by Langhof. A detailed description of the refinement procedure was given recently (8).

3. Results of the Structural Investigations

The Rietveld procedure, applied to a powder pattern of Cs_3LaCl_6 , showed that the compound crystallizes with the Cs_3BiCl_6 structure. Atomic positions together with an isotropic thermal parameter for each atom are given in Table II; in Table III the main bond distances are collected. The observed, calculated, and difference patterns are presented in Fig. 1. Recently, Meyer has found from single crystal investigations that Rb_3YCl_6 has the Cs_3BiCl_6 structure too (G. Meyer, Hanover; private communication).

Comparing the average of experimental distances with those from the sum of Shannon radii (9) ($r(\text{La}^{3+}) = 1.06 \text{ \AA}$; $r(\text{Cl}^-) = 1.81 \text{ \AA}$; $r(\text{Cs}^+; \text{CN } 8) = 1.74 \text{ \AA}$; $r(\text{Cs}^+; \text{CN } 11) = 1.85 \text{ \AA}$) gave good results: for Cs₂ and Cs₃ in an eightfold surrounding, 3.56 and 3.60 $\text{\AA}$, compared with the radii sum 3.55 $\text{\AA}$. In Cs_3BiCl_6 (4) these values are 3.53 and 3.55 $\text{\AA}$. The distances for the CN 110—3.91 $\text{\AA}$ for Cs_3LaCl_6 and 3.87 $\text{\AA}$ for Cs_3BiCl_6 —are both higher than the theoretical value of 3.66 $\text{\AA}$. However, one has to take into account that some experimental distances are rather

TABLE III
BOND LENGTHS ($\text{\AA}$) AND ANGLES (DEGREES)
IN Cs_3LaCl_6

Cs ₁ -Cl ₄	3.56	Cs ₂ -Cl ₂	3.22
-Cl ₄	3.59	-Cl ₁	3.40
-Cl ₃	3.68	-Cl ₁	3.46
-Cl ₆	3.68	-Cl ₆	3.46
-Cl ₆	3.77	-Cl ₃	3.52
-Cl ₅	3.79	-Cl ₅	3.56
-Cl ₅	3.95	-Cl ₄	4.05
-Cl ₄	4.08	-Cl ₂	4.17
-Cl ₂	4.10		
-Cl ₅	4.36		
-Cl ₆	4.42		
Aver. ((CN 11)	3.91	Aver. (CN 8)	3.60
Cs ₃ -Cl ₂	3.31	La ₁ -Cl ₃	2.60 (2 $\times$)
-Cl ₆	3.43	-Cl ₁	2.82 (2 $\times$)
-Cl ₁	3.54	-Cl ₂	2.84 (2 $\times$)
-Cl ₁	3.54	Aver. (CN 6)	2.75
-Cl ₅	3.56		
-Cl ₄	3.57	La ₂ -Cl ₄	2.68 (2 $\times$)
-Cl ₃	3.69	-Cl ₅	2.78 (2 $\times$)
-Cl ₃	3.84	-Cl ₆	2.93 (2 $\times$)
Aver. (CN8)	3.56	Aver. (CN 6)	2.80

Angles: Cl-La₁-Cl, 84.9–95.1°;
Cl-La₂-Cl, 81.4–97.9°

long—greater than 4.0 $\text{\AA}$. The experimental La-Cl distances are, with average values of 2.75 and 2.80 $\text{\AA}$, smaller than the theoretical value of 2.87 $\text{\AA}$ and also smaller than the distance of 2.95 $\text{\AA}$ in LaCl_3 (10), where the coordination number of La is nine.

In Table IV the unit cell parameters of all Cs and Rb compounds from La to Gd are compiled. They all have the Cs_3BiCl_6 structure, as could be determined by the crucial reflections, as in Fig. 1.

4. Results of the EMF Measurements

Disks of CsCl and a mixture of Cs_3LnCl_6 and Cs_2LnCl_5 with a composition of $\sim(0.7 \text{ mol CsCl} + 0.3 \text{ mol LnCl}_3)$ as electrodes gave emf values, resulting from the cell reactions $\text{CsCl} + \text{Cs}_2\text{LnCl}_5 = \text{Cs}_3\text{LnCl}_6$. An exception was the system CsCl/NdCl_3 ; here the compound Cs_2NdCl_5 is stable only below 333°C; it is formed by long annealing of

TABLE IV
LATTICE PARAMETERS AND MOLAR VOLUMES FOR LOW TEMPERATURE MODIFICATIONS OF COMPOUNDS
 Cs_3LnCl_6 AND Rb_3LnCl_6 WITH $\text{Ln}=\text{La}-\text{Gd}$

Composition	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	<i>V</i> (cm ³ mol ⁻¹)
Cs ₃ LaCl ₆	27.286(5)	8.291(2)	13.305(2)	99.64(2)	223.4
Cs ₃ CeCl ₆	27.346(7)	8.277(2)	13.329(3)	99.71(2)	223.9
Cs ₃ PrCl ₆	27.209(7)	8.240(2)	13.316(3)	99.87(2)	221.4
Cs ₃ NdCl ₆	27.193(7)	8.248(2)	13.279(2)	99.96(2)	220.8
Cs ₃ SmCl ₆	27.084(8)	8.195(2)	13.202(3)	99.94(2)	217.3
Cs ₃ EuCl ₆	27.065(8)	8.192(2)	13.203(4)	99.93(2)	217.1
Cs ₃ GdCl ₆	27.020(7)	8.189(2)	13.181(3)	100.01(2)	216.2
Rb ₃ LaCl ₆	26.171(9)	8.219(3)	12.832(4)	96.49(3)	206.4
Rb ₃ CeCl ₆	26.324(6)	8.073(2)	12.869(3)	98.62(2)	203.6
Rb ₃ PrCl ₆	26.227(7)	8.011(3)	12.885(4)	98.76(2)	201.4
Rb ₃ NdCl ₆	26.139(5)	7.743(2)	13.402(4)	100.65(2)	200.7
Rb ₃ SmCl ₆	26.076(7)	7.703(3)	13.339(4)	100.54(2)	198.3
Rb ₃ EuCl ₆	25.983(8)	7.920(2)	12.928(2)	99.50(2)	197.5
Rb ₃ GdCl ₆	25.917(11)	7.900(2)	12.938(5)	99.52(3)	196.4

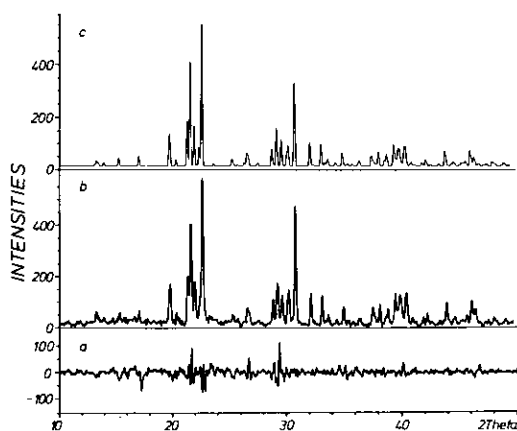


FIG. 1. Observed (b), calculated (c), and difference (a) diffraction patterns for Cs_3LaCl_6 .

quenched melts with the appropriate composition. In this case the cell reaction is $2.5 \text{ CsCl} + \text{Cs}_{0.5}\text{NdCl}_{3.5} = \text{Cs}_3\text{NdCl}_6$.

The resistivity of the solid electrolytes allowed measurement at temperatures $>300^\circ\text{C}$. At temperatures between 360°C (Eu compound) and 430°C the diaphragms began to react with the electrolytes. Thus, for Cs_3EuCl_6 the phase transition at $\sim 400^\circ\text{C}$ could not be measured.

All emf values proved to be linearly dependent on T . An example is given for Cs_3SmCl_6 in Fig. 3. The regression lines were transformed to the Gibbs–Helmholtz equation $\Delta_{\text{syn}}G^0 = \Delta_{\text{syn}}H^0 - T \cdot \Delta_{\text{syn}}S^0$ by multiplication with $-nF$. The highest range of error was $\pm 0.4 \text{ kJ mol}^{-1}$ for ΔH^0 and $\pm 0.6 \text{ JK}^{-1} \text{ mol}^{-1}$ for ΔS^0 . Transition temperatures T_T were calculated by the relation $\Delta G^0(\text{L}) = \Delta G^0(\text{H})$ (L = low-temp. modif., H = high-temp. modif.). Decomposition temperatures T_D were yielded by the condition $\Delta_{\text{syn}}G^0 = 0$.

I. Reactions $\text{CsCl} + \text{Cs}_2\text{LnCl}_5 = \text{Cs}_3\text{LnCl}_6$

Cs_3LaCl_6 H-modif.: $\Delta G^0/\text{kJ mol}^{-1} = 34.9 - 0.0691 T/\text{K}$
 ($T = 572\text{--}699 \text{ K}$) L-modif.: $\Delta G^0/\text{kJ mol}^{-1} = 24.8 - 0.0537 T/\text{K}$
 $T_T = 659 \text{ K}$ (386°C); $T_D(\text{L} - \text{Cs}_3\text{LaCl}_6) = 462 \text{ K}$ (189°C)

Cs_3CeCl_6 H-modif.: $\Delta G^0/\text{kJ mol}^{-1} = 21.6 - 0.0582 T/\text{K}$
 ($T = 586\text{--}711 \text{ K}$) L-modif.: $\Delta G^0/\text{kJ mol}^{-1} = 12.6 - 0.0446 T/\text{K}$

$$T_T = 664 \text{ K (391}^\circ\text{C)}; T_D (\text{L} - \text{Cs}_3\text{CeCl}_6) = 283 \text{ K (10}^\circ\text{C)}$$

$$\begin{aligned} \text{Cs}_3\text{PrCl}_6 \quad & \text{H-modif.: } \Delta G^0/\text{kJ mol}^{-1} = -20.2-0.0456 \text{ T/K} \\ & (T = 578-701 \text{ K}) \quad \text{L-modif.: } \Delta G^0/\text{kJ mol}^{-1} = 5.6-0.0393 \text{ T/K} \\ & T_T = 650 \text{ K (377}^\circ\text{C)}; T_D (\text{L} - \text{Cs}_3\text{PrCl}_6) = 143 \text{ K (-130}^\circ\text{C)} \end{aligned}$$

$$\begin{aligned} \text{Cs}_3\text{SmCl}_6 \quad & \text{H-modif.: } \Delta G^0/\text{kJ mol}^{-1} = -9.2-0.0205 \text{ T/K} \\ & (T = 581-715 \text{ K}) \quad \text{L-modif.: } \Delta G^0/\text{kJ mol}^{-1} = -19.7-0.0044 \text{ T/K} \\ & T_T = 651 \text{ K (378}^\circ\text{C)}; \end{aligned}$$

$$\begin{aligned} \text{Cs}_3\text{EuCl}_6 \quad & \text{L-modif.: } \Delta G^0/\text{kJ mol}^{-1} = -16.2-0.0117 \text{ T/K} \\ & (T = 582-633 \text{ K}) \end{aligned}$$

$$\begin{aligned} \text{Cs}_3\text{GdCl}_6 \quad & \text{H-modif.: } \Delta G^0/\text{kJ mol}^{-1} = -9.8-0.0199 \text{ T/K} \\ & (T = 576-745 \text{ K}) \quad \text{L-modif.: } \Delta G^0/\text{kJ mol}^{-1} = -17.1-0.0091 \text{ T/K} \\ & T_T = 675 \text{ K (402}^\circ\text{C)} \end{aligned}$$

For comparison, the results for the formation of Cs_3NdCl_6 from CsNd_2Cl_7 are also given:

$$\text{II. Reaction 2.5 CsCl} + \text{Cs}_{0.5}\text{NdCl}_{3.5} = \text{Cs}_3\text{NdCl}_6 \quad (T = 574-728 \text{ K})$$

$$\text{H-modif.: } \Delta G^0/\text{kJ mol}^{-1} = -19.1-0.0539 \text{ T/K}$$

$$\text{L-modif.: } \Delta G^0/\text{kJ mol}^{-1} = -25.2-0.0044 \text{ T/K}$$

$$T_T = 646 \text{ K (373}^\circ\text{C)}$$

5. Discussion of the Results

The Crystal Structures

Both monoclinic structures—the K_3MoCl_6 and Cs_3BiCl_6 types—can be derived from the cubic elpasolite type (space group $Fm\bar{3}m$) of compounds A_2BMX_6 , where the B and M cations are octahedrally surrounded by 6 X -ions, while the A -cations are in a twelfefold environment. This cubic structure is realized in the high temperature modifications of the compounds $A_3\text{LnCl}_6$ which must be written $A_2A'\text{LnCl}_6$. (However, a Rietveld analysis of a pattern at 680 K yielded enormously large temperature factors for all atoms except La, so that this description is to be considered only formally). At low temperature the LnCl_6 octahedra are slightly deformed and have been markedly rotated from their ideal positions. These rotations have reduced the difference in coordination between the A' and A cations: in the K_3MoCl_6 -type [3] the two K ions are coordinated by 10 to 11 Cl^- ions and K' by 8 Cl^- ; in the Cs_3BiCl_6 type [4] one Cs ion is surrounded by 11 Cl^- , the other two by 8 Cl^- . Nevertheless, the Cs_3BiCl_6 type

is found only with the big alkali metal ions Cs^+ and Rb^+ .

The K_3MoCl_6 structure is well established only for K_3MoCl_6 itself; the structures of Rb_3MoCl_6 and Cs_3MoCl_6 are still unknown. Whether the compounds K_3LnCl_6 are crystallizing with this structure cannot be decided because of the poor quality of the powder patterns of these metastable compounds.

Recently we have found that the compounds Cs_3MCl_6 with $M = \text{Fe, Cr, V}$ are crystallizing with a similar structure, which could not be solved. On the other hand, Cs_3TiCl_6 has the Cs_3BiCl_6 structure as was found in our group (11): $a = 26.201 \text{ \AA}$; $b = 7.875 \text{ \AA}$; $c = 12.765 \text{ \AA}$; $\beta = 100.50^\circ$.

Thus, an explanation for the conditions of existence for these different variations of the distorted elpasolite structure cannot yet be given. It would be very helpful if a compound could be found where a direct transition between both structures exist.

The Stabilities

The measured thermodynamic functions for the "synproportionation" reactions

TABLE V
SYNPROPORTIONATION ENTHALPIES AND ENTROPIES TOGETHER WITH DECOMPOSITION TEMPERATURES FOR THE LOW-TEMPERATURE MODIFICATIONS OF COMPOUNDS Cs_3LnCl_6 AND Rb_3LnCl_6

Compound	$\Delta_{\text{syn}}H^0/\text{kJ mol}^{-1}$	$\Delta_{\text{syn}}S^0/\text{J K}^{-1} \text{mol}^{-1}$	T_D/K
Cs_3LaCl_6	24.8	53.7	462
Cs_3CeCl_6	12.6	44.6	283
Cs_3PrCl_6	5.6	39.3	143
Cs_3NdCl_6	[1.6] ^a	—	—
Cs_3SmCl_6	-19.7	4.4	0
Cs_3EuCl_6	-16.2	11.7	0
Cs_3GdCl_6	-17.1	9.1	0
Rb_3LaCl_6 [12]	51.9 ^b	72.4	717
Rb_3CeCl_6 [13]	38.2 ^b	60.1	636
Rb_3PrCl_6 [14]	26.5	47.6	557
Rb_3NdCl_6 [15]	24.1	49.1	490
Rb_3SmCl_6 [16]	14.5	45.9	316
Rb_3EuCl_6 [17]	9.7	43.3	224
Rb_3GdCl_6 [1]	6.8	42.1	162

^a From solution calorimetry [15].

^b Cubic H- Rb_3LnCl_6 ; D- Rb_3LnCl_6 exists only metastably after quenching.

$\text{CsCl} + \text{Cs}_2\text{LnCl}_5 = \text{Cs}_3\text{LnCl}_6$ reveal that there are two groups (Table V): the one "La to Nd" has positive enthalpies $\Delta_{\text{syn}}H^0$ and positive entropies $\Delta_{\text{syn}}S^0$ with values of 40–50 $\text{JK}^{-1}\text{mol}^{-1}$; the second, "Sm to Gd," has negative $\Delta_{\text{syn}}H^0$ and positive entropies of 5–12 $\text{JK}^{-1}\text{mol}^{-1}$. This difference is originated by the change in the crystal structure of the compounds Cs_2LnCl_5 . Those with $\text{Ln} = \text{La-Nd}$ crystallize with the K_2PrCl_5 structure (18); monocapped trigonal prisms ($\text{CN} = 7$) are connected to chains via common edges ($[\text{LnCl}_3\text{Cl}_{4/2}]^{2-}$). From Sm onward the compounds have the Cs_2DyCl_5 structure (19); the CN is now six with corner-connected octahedra $[\text{LnCl}_4\text{Cl}_{2/2}]^{2-}$.

The formation of the compounds Cs_3LnCl_6 with $[\text{LnCl}_6]^{3-}$ octahedra from CsCl and Cs_2LnCl_5 of the first group occurs with a loss of lattice enthalpy which is compensated by a considerable gain in entropy, obviously originated by the transition of the fourfold associated prism to isolated octahedra. On the other hand, the formation from the twofold connected octahedra of the Cs_2DyCl_5 structure brings a smaller gain in entropy (only $\sim 10 \text{ JK}^{-1} \text{mol}^{-1}$ instead of

$\sim 50 \text{ JK}^{-1} \text{mol}^{-1}$), but an additional gain in lattice enthalpy of approx. 17 kJ mol^{-1} . Thus, in the first group the compounds are stable only at more or less high temperatures compared with $T = 0 \text{ K}$; the condition is that $|T \cdot \Delta S| \geq |\Delta H|$. In the second group, the 3 : 1 compounds are stable upward from $T = 0 \text{ K}$. Thus, the existence area of the compounds Cs_3LnCl_6 is influenced by the stability of the Cs_2LnCl_5 compounds. For the Rb compounds the situation is more uniform: all compounds Rb_2LnCl_5 crystallize with the K_2PrCl_5 structure, so that all hexachloro-compounds are formed with a loss in lattice enthalpy.

The transition from the K_2PrCl_5 to the Cs_2DyCl_5 type can be explained by the decreasing ionic radii (9): $\text{Ln} = 1.061 \text{ \AA}$; $\text{Nd} = 0.995 \text{ \AA}$; $\text{Sm} = 0.964 \text{ \AA}$. Obviously the required space for the coordination number 7 becomes too small by the transition from Nd to Sm. Beforehand the decomposition point of the compounds Cs_2LnCl_5 has decreased from 517°C for Cs_2LaCl_5 over 443°C (Cs_2CeCl_5) and 391°C (Cs_2PrCl_5) to 333°C for Cs_2NdCl_5 . The consequence is that for Cs_2PrCl_5 and Cs_2NdCl_5 these de-

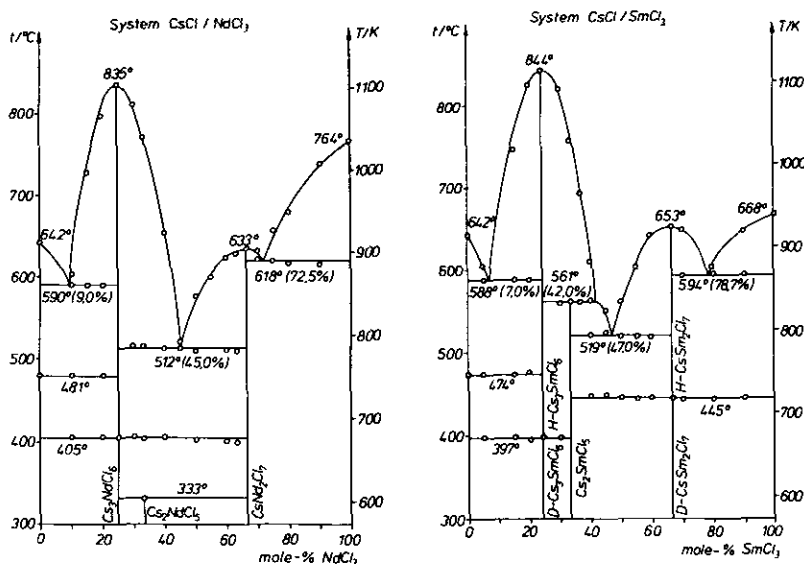


FIG. 2. Phase diagrams of the systems $\text{CsCl}/\text{NdCl}_3$ (15) and $\text{CsCl}/\text{SmCl}_3$ (16).

composition temperatures lie below the transition temperature of the Cs_3BiCl_6 modification to the cubic modification of Cs_3LnCl_6 . This situation is demonstrated in Fig. 2.

It is peculiar that these transition temperatures were all found by DTA near 400°C with only small hystereses of a max. 4° between the values from heating and cooling curves. The values from the emf measurements are in most cases considerably lower; e.g., 378°C for Cs_3SmCl_6 (Fig. 3). A more

accurate inspection of the emf vs T values in the range up to 400°C reveals that there no longer exists an exactly linear dependence between ΔG and T . This might be due to the presence of a λ -transition; in this case the condition for linearity, $\Delta c_p = 0$, is no longer valid. However, that must be proved by careful c_p measurements in this range, which are much more sensitive than the emf vs T measurement. These are intended for future research.

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References

1. H. J. SEIFERT, J. SANDROCK, AND G. THIEL, *Z. Anorg. Allg. Chem.* **599/600**, 307 (1991).
2. H. J. SEIFERT AND G. THIEL, *J. Chem. Thermodyn.* **14**, 1159 (1982).
3. Z. AMILIUS, B. VAN LAAR, AND H. M. RIETVELD, *Acta Crystallogr. Sect. B* **25**, 400 (1969).
4. F. BENACHENHOU, G. MAIRESSE, G. NOWOGROCK AND D. THOMAS, *J. Solid State Chem.* **65**, 13 (1986).

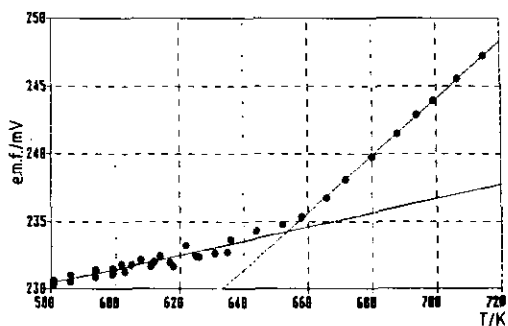


FIG. 3. Computer plot emf vs T for the reaction $\text{CsCl} + \text{Cs}_2\text{SmCl}_5 = \text{Cs}_3\text{SmCl}_6$.

5. H. J. SEIFERT AND Y. YUAN, *J. Less-Common Met.* **170**, 135 (1990).
6. K. YVON, W. JEITSCHKO, AND E. PARTHE, *J. Appl. Crystallogr.* **10**, 73 (1977).
7. J. WARCZEWSKI AND P. M. DE WOLF, *J. Appl. Crystallogr.* **7**, 585 (1974).
8. B. BAUMGARTNER AND G. MÜLLER, *Eur. J. Miner.* **2**, 155 (1990).
9. R. D. SHANNON, *Acta Cryst. Sect. A* **32**, 751 (1976).
10. B. MOROSIN, *J. Chem. Phys.* **49**, 3007 (1968).
11. H. FINK, unpublished result.
12. H. J. SEIFERT, H. FINK, AND G. THIEL, *J. Less-Common Met.* **110**, 139 (1985).
13. H. J. SEIFERT, J. SANDROCK, AND G. THIEL, *J. Therm. Anal.* **31**, 1309 (1986).
14. H. J. SEIFERT, J. SANDROCK, AND J. UEBACH, *Z. Anorg. Allg. Chem.* **555**, 143 (1987).
15. H. J. SEIFERT, H. FINK, AND J. UEBACH, *J. Therm. Anal.* **33**, 625 (1988).
16. G. THIEL AND H. J. SEIFERT, *Thermochim. Acta* **133**, 275 (1988).
17. H. J. SEIFERT AND J. SANDROCK, *Z. Anorg. Allg. Chem.* **587**, 110 (1990).
18. G. MEYER AND E. HÜTTL, *Z. Anorg. Allg. Chem.* **497**, 191 (1983).
19. G. MEYER, *Z. Anorg. Allg. Chem.* **469**, 149 (1980).