

## Structure and Stability of the Low-Temperature Modification of Compounds $\text{Cs}_3\text{LnCl}_6$ ( $\text{Ln} = \text{La}–\text{Gd}$ )

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The crystal structure of the low-temperature modification of  $\text{Cs}_3\text{LaCl}_6$  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  $\text{Cs}_3\text{BiCl}_6$ -type (space group  $C2/c$ ). All other compounds  $\text{Cs}_3\text{LnCl}_6$  ( $\text{Ln} = \text{Ce}–\text{Gd}$ ) 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  $\text{Cs}_2\text{LnCl}_5$ : they crystallize with the  $\text{K}_2\text{PrCl}_5$ -structure (CN = 7 for  $\text{Ln}^{3+}$ ) for the compounds with  $\text{Ln} = \text{La}–\text{Nd}$ , while the other compounds belong to the  $\text{Cs}_2\text{DyCl}_5$ -type with octahedral surroundings for the  $\text{Ln}^{3+}$  ions. © 1993 Academic Press, Inc.

### 1. Introduction

In the course of investigations on the existence of ternary chlorides in the systems  $\text{ACl/LnCl}_3$  ( $A = \text{Na}–\text{Cs}$ ,  $\text{Ln} = \text{La}–\text{Gd}$ ) (1) we have found compounds  $\text{A}_3\text{LnCl}_6$  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  $400^\circ\text{C}$ . It could be proved by measurements of the emf's for the reactions  $\text{ACl} + \text{A}_2\text{LnCl}_5 = \text{A}_3\text{LnCl}_6$  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  $\text{Cs}^+$ -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  $\text{K}_3\text{MoCl}_6$  structure, using the site parameters of the atomic positions in  $\text{K}_3\text{MoCl}_6$  (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  $\text{K}_3\text{MoCl}_6$ -type could not be found at all. An investigation of  $\text{Cs}_3\text{LaCl}_6$  by the X-ray Riet-

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veld procedure then revealed that the true structure is that of the  $\text{Cs}_3\text{BiCl}_6$ -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  $\text{K}_3\text{MoCl}_6$ ). An accurate inspection of the X-ray patterns of all other Cs and Rb compounds showed that they must be described with the  $\text{Cs}_3\text{BiCl}_6$  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  $\text{Cs}^+$ -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  $\text{Cs}_3\text{LnCl}_6$  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 C,  $\text{Cl}_2$ ,  $\text{CsCl}|\text{Cs}^+$ -conducting diaphragm| $\text{Cs}_3\text{LnCl}_6$ ,  $\text{Cs}_2\text{LnCl}_5$ ,  $\text{Cl}_2$ , 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  $\text{Cs}^+$ -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  $\text{Cs}_3\text{LaCl}_6$

$2\theta$ 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)
$\beta$ (deg)	99.64(1)
$D_{\text{calc}}$ ( $\text{g} \cdot \text{cm}^{-3}$ )	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

<sup>a</sup> The  $I$  values are approximately integrated intensities derived from the powder profiles.

to a linear regression analysis (temperature range of linearity  $\geq 580$  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 ( $a = 4.7592$  Å,  $c = 12.9900$  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 <sub>1</sub>	0.25000	0.25000	0.50000	0.012
La <sub>2</sub>	0.00000	0.789(7)	0.25000	
Cs <sub>1</sub>	0.050(1)	0.726(6)	0.930(3)	0.025
Cs <sub>2</sub>	0.162(1)	0.815(6)	0.305(3)	
Cs <sub>3</sub>	0.346(1)	0.187(5)	0.851(3)	
Cl <sub>1</sub>	0.247(5)	0.389(1)	0.693(10)	0.026
Cl <sub>2</sub>	0.322(5)	0.491(16)	0.482(9)	
Cl <sub>3</sub>	0.324(6)	0.068(16)	0.579(11)	
Cl <sub>4</sub>	0.045(5)	0.544(17)	0.173(10)	
Cl <sub>5</sub>	-0.060(4)	0.798(16)	0.060(10)	
Cl <sub>6</sub>	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) ( $r(La^{3+}) = 1.06 \text{ \AA}$ ;  $r(Cl^-) = 1.81 \text{ \AA}$ ;  $r(Cs^+; \text{CN } 8) = 1.74 \text{ \AA}$ ;  $r(Cs^+; \text{CN } 11) = 1.85 \text{ \AA}$ ) gave good results: for Cs<sub>2</sub> and Cs<sub>3</sub> 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 <sub>1</sub> -Cl <sub>4</sub>	3.56	Cs <sub>2</sub> -Cl <sub>2</sub>	3.22
-Cl <sub>4</sub>	3.59	-Cl <sub>1</sub>	3.40
-Cl <sub>3</sub>	3.68	-Cl <sub>1</sub>	3.46
-Cl <sub>6</sub>	3.68	-Cl <sub>6</sub>	3.46
-Cl <sub>6</sub>	3.77	-Cl <sub>3</sub>	3.52
-Cl <sub>5</sub>	3.79	-Cl <sub>5</sub>	3.56
-Cl <sub>5</sub>	3.95	-Cl <sub>4</sub>	4.05
-Cl <sub>4</sub>	4.08	-Cl <sub>2</sub>	4.17
-Cl <sub>2</sub>	4.10		
-Cl <sub>5</sub>	4.36		
-Cl <sub>6</sub>	4.42		
Aver. ((CN 11)	3.91	Aver. (CN 8)	3.60
Cs <sub>3</sub> -Cl <sub>2</sub>	3.31	La <sub>1</sub> -Cl <sub>3</sub>	2.60 (2 $\times$ )
-Cl <sub>6</sub>	3.43	-Cl <sub>1</sub>	2.82 (2 $\times$ )
-Cl <sub>1</sub>	3.54	-Cl <sub>2</sub>	2.84 (2 $\times$ )
-Cl <sub>1</sub>	3.54	Aver. (CN 6)	2.75
-Cl <sub>5</sub>	3.56		
-Cl <sub>4</sub>	3.57	La <sub>2</sub> -Cl <sub>4</sub>	2.68 (2 $\times$ )
-Cl <sub>3</sub>	3.69	-Cl <sub>5</sub>	2.78 (2 $\times$ )
-Cl <sub>3</sub>	3.84	-Cl <sub>6</sub>	2.93 (2 $\times$ )
Aver. (CN8)	3.56	Aver. (CN 6)	2.80

Angles: Cl-La<sub>1</sub>-Cl, 84.9–95.1°;  
Cl-La<sub>2</sub>-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  $CsCl + Cs_2LnCl_5 = Cs_3LnCl_6$ . 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  
 $\text{Cs}_3\text{LnCl}_6$  AND  $\text{Rb}_3\text{LnCl}_6$  WITH  $\text{Ln}=\text{La}-\text{Gd}$

Composition	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\beta$ (°)	$V$ (cm <sup>3</sup> mol <sup>-1</sup> )
$\text{Cs}_3\text{LaCl}_6$	27.286(5)	8.291(2)	13.305(2)	99.64(2)	223.4
$\text{Cs}_3\text{CeCl}_6$	27.346(7)	8.277(2)	13.329(3)	99.71(2)	223.9
$\text{Cs}_3\text{PrCl}_6$	27.209(7)	8.240(2)	13.316(3)	99.87(2)	221.4
$\text{Cs}_3\text{NdCl}_6$	27.193(7)	8.248(2)	13.279(2)	99.96(2)	220.8
$\text{Cs}_3\text{SmCl}_6$	27.084(8)	8.195(2)	13.202(3)	99.94(2)	217.3
$\text{Cs}_3\text{EuCl}_6$	27.065(8)	8.192(2)	13.203(4)	99.93(2)	217.1
$\text{Cs}_3\text{GdCl}_6$	27.020(7)	8.189(2)	13.181(3)	100.01(2)	216.2
$\text{Rb}_3\text{LaCl}_6$	26.171(9)	8.219(3)	12.832(4)	96.49(3)	206.4
$\text{Rb}_3\text{CeCl}_6$	26.324(6)	8.073(2)	12.869(3)	98.62(2)	203.6
$\text{Rb}_3\text{PrCl}_6$	26.227(7)	8.011(3)	12.885(4)	98.76(2)	201.4
$\text{Rb}_3\text{NdCl}_6$	26.139(5)	7.743(2)	13.402(4)	100.65(2)	200.7
$\text{Rb}_3\text{SmCl}_6$	26.076(7)	7.703(3)	13.339(4)	100.54(2)	198.3
$\text{Rb}_3\text{EuCl}_6$	25.983(8)	7.920(2)	12.928(2)	99.50(2)	197.5
$\text{Rb}_3\text{GdCl}_6$	25.917(11)	7.900(2)	12.938(5)	99.52(3)	196.4

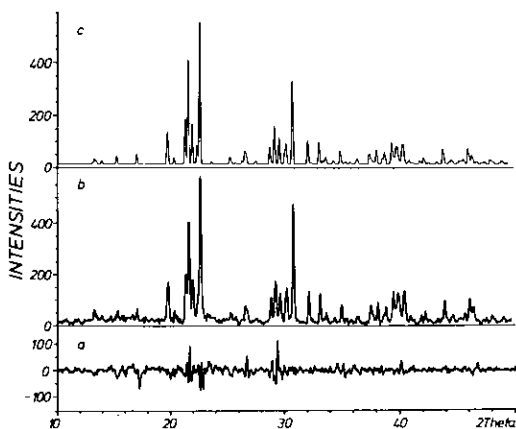


FIG. 1. Observed (b), calculated (c), and difference (a) diffraction patterns for  $\text{Cs}_3\text{LaCl}_6$ .

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  $360^\circ\text{C}$  (Eu compound) and  $430^\circ\text{C}$  the diaphragms began to react with the electrolytes. Thus, for  $\text{Cs}_3\text{EuCl}_6$  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  $\text{Cs}_3\text{SmCl}_6$  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  $\pm 0.4 \text{ kJ mol}$  for  $\Delta H^0$  and  $\pm 0.6 \text{ JK}^{-1} \text{ mol}$  for  $\Delta S^0$ . 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 $\text{CsCl} + \text{Cs}_2\text{LnCl}_5 = \text{Cs}_3\text{LnCl}_6$

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

$\text{Cs}_3\text{CeCl}_6$  H-modif.:  $\Delta G^0/\text{kJ mol}^{-1} = 21.6 - 0.0582 T/\text{K}$   
 ( $T = 586\text{--}711 \text{ K}$ ) L-modif.:  $\Delta G^0/\text{kJ mol}^{-1} = 12.6 - 0.0446 T/\text{K}$

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

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

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

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

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

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 twelfold environment. This cubic structure is realized in the high temperature modifications of the compounds  $A_3LnCl_6$  which must be written  $A_2A'LnCl_6$ . (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  $M = Fe, Cr, V$  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  $\text{Cs}_3\text{LnCl}_6$  AND  $\text{Rb}_3\text{LnCl}_6$

Compound	$\Delta_{\text{syn}}H^0/\text{kJ mol}^{-1}$	$\Delta_{\text{syn}}S^0/\text{J K}^{-1} \text{mol}^{-1}$	$T_D/\text{K}$
$\text{Cs}_3\text{LaCl}_6$	24.8	53.7	462
$\text{Cs}_3\text{CeCl}_6$	12.6	44.6	283
$\text{Cs}_3\text{PrCl}_6$	5.6	39.3	143
$\text{Cs}_3\text{NdCl}_6$	[1.6] <sup>c</sup>	—	—
$\text{Cs}_3\text{SmCl}_6$	-19.7	4.4	0
$\text{Cs}_3\text{EuCl}_6$	-16.2	11.7	0
$\text{Cs}_3\text{GdCl}_6$	-17.1	9.1	0
$\text{Rb}_3\text{LaCl}_6$ [12]	51.9 <sup>b</sup>	72.4	717
$\text{Rb}_3\text{CeCl}_6$ [13]	38.2 <sup>b</sup>	60.1	636
$\text{Rb}_3\text{PrCl}_6$ [14]	26.5	47.6	557
$\text{Rb}_3\text{NdCl}_6$ [15]	24.1	49.1	490
$\text{Rb}_3\text{SmCl}_6$ [16]	14.5	45.9	316
$\text{Rb}_3\text{EuCl}_6$ [17]	9.7	43.3	224
$\text{Rb}_3\text{GdCl}_6$ [1]	6.8	42.1	162

<sup>a</sup> From solution calorimetry [15].

<sup>b</sup> Cubic H- $\text{Rb}_3\text{LnCl}_6$ ; D- $\text{Rb}_3\text{LnCl}_6$  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  $\text{Cs}_2\text{LnCl}_5$ . Those with  $\text{Ln} = \text{La-Nd}$  crystallize with the  $\text{K}_2\text{PrCl}_5$  structure (18); monocapped trigonal prisms (CN = 7) are connected to chains via common edges ( $[\text{LnCl}_3\text{Cl}_{4/2}]^{2-}$ ). From Sm onward the compounds have the  $\text{Cs}_2\text{DyCl}_5$  structure (19); the CN is now six with cis-corner-connected octahedra  $[\text{LnCl}_4\text{Cl}_{2/2}]^{2-}$ .

The formation of the compounds  $\text{Cs}_3\text{LnCl}_6$  with  $[\text{LnCl}_6]^{3-}$  octahedra from  $\text{CsCl}$  and  $\text{Cs}_2\text{LnCl}_5$  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  $\text{Cs}_2\text{DyCl}_5$  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  $\text{kJ mol}^{-1}$ . 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  $\text{Cs}_3\text{LnCl}_6$  is influenced by the stability of the  $\text{Cs}_2\text{LnCl}_5$  compounds. For the Rb compounds the situation is more uniform: all compounds  $\text{Rb}_2\text{LnCl}_5$  crystallize with the  $\text{K}_2\text{PrCl}_5$  structure, so that all hexachloro-compounds are formed with a loss in lattice enthalpy.

The transition from the  $\text{K}_2\text{PrCl}_5$  to the  $\text{Cs}_2\text{DyCl}_5$  type can be explained by the decreasing ionic radii (9):  $\text{Ln} = 1.061 \text{Å}$ ;  $\text{Nd} = 0.995 \text{Å}$ ;  $\text{Sm} = 0.964 \text{Å}$ . 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  $\text{Cs}_2\text{LnCl}_5$  has decreased from 517°C for  $\text{Cs}_2\text{LaCl}_5$  over 443°C ( $\text{Cs}_2\text{CeCl}_5$ ) and 391°C ( $\text{Cs}_2\text{PrCl}_5$ ) to 333°C for  $\text{Cs}_2\text{NdCl}_5$ . The consequence is that for  $\text{Cs}_2\text{PrCl}_5$  and  $\text{Cs}_2\text{NdCl}_5$  these de-

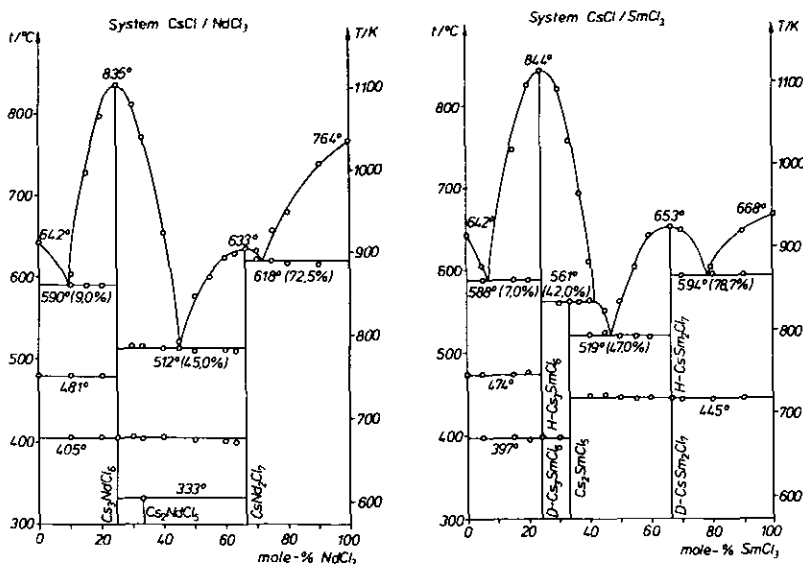


FIG. 2. Phase diagrams of the systems  $CsCl/NdCl_3$  (15) and  $CsCl/SmCl_3$  (16).

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  $400^\circ C$  with only small hystereses of a max.  $4^\circ$  between the values from heating and cooling curves. The values from the emf measurements are in most cases considerably lower; e.g.,  $378^\circ C$  for  $Cs_3SmCl_6$  (Fig. 3). A more

accurate inspection of the emf vs  $T$  values in the range up to  $400^\circ C$  reveals that there no longer exists an exactly linear dependence between  $\Delta G$  and  $T$ . This might be due to the presence of a  $\lambda$ -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).

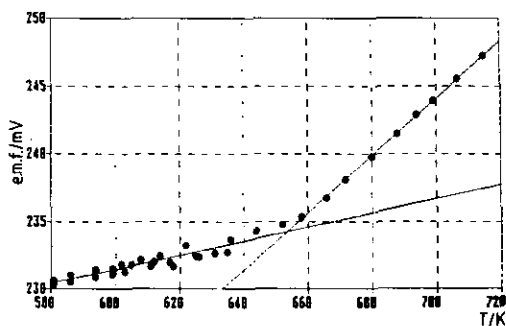


FIG. 3. Computer plot emf vs  $T$  for the reaction  $CsCl + Cs_2SmCl_5 = Cs_3SmCl_6$ .

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).