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Na_3GdCl_6- A COMPOUND WITH UNCOMMON PHASE TRANSITIONS

H.J. SEIFERT and G. THIEL

Inorganic Chemistry, University Gh Kassel/FRG

SUMMARY

For Na_3GdCl_6 two modifications exist: at ambient temperature trigonal D-Na_3GdCl_6, below 497°C a monoclinic H-Na_3GdCl_6 . There is no direct transition from D–> H; but at 209°C D-Na_3GdCl_6 decomposes to NaCl + Na_2GdCl_5. At 265°C H-Na_3GdCl_6 is formed by the reverse reaction. This way of acting is proved by e.m.f. vs. T.-measurements with a galvanic cell for solid electrolytes, and by dynamic high-temperature X-ray diffraction patterns. For the hitherto unknown compound Na_2GdCl_5 the unit cell parameters are determined.

INTRODUCTION

The pseudobinary systems $NaCl/LnCl_3$ of the early lanthanoids Ln=La-Nd are eutectic with a range of mixed crystal formation near the composition $Na_3Ln_5Cl_{18}$: in the units $(LnCl_3)_6$ one Ln^{3+} is substituted by three Na^+-ions [1, 2, 3, 4]. In the system NaCl/ $SmCl_3$ [5] additionally a compound Na_2SmCl_5 exists, the most stable type of ternary chlorides in all systems with A=K, Rb, Cs. 1965 Korshunov et al. [6] had found two incongruently-melting compounds in the system $NaCl/EuCl_3$ (Na_3EuCl_6 and Na_2EuCl_5) and an incongruently -melting Na_3GdCl_6 in the system $NaCl/GdCl_3$. For the Gd-compound a phase transition occurs at 205°C. Meyer [7] solved by single-crystal work the structure of D-Na_3GdCl_6, a trigonal unit cell in the stuffed $LiSbF_6$-type. The high-temperature modification has a monoclinic cryolite structure, isotypic with Na_3ErCl_6 [8]. A surprising finding of Meyer, that the density of H-Na_3GdCl_6 is greater than that of the D-modification, was the reason for ourselves to re-investigate these features by e.m.f.-measurements in a galvanic cell for solid electrolytes, we had developed in 1982 [9].

EXPERIMENTAL

Preparation of compounds: $GdCl_3$: dehydration of the hydrate $GdCl_3 \cdot 6H_2O$ (Fa. Ventron, 99.99%) in an HCl-stream. - NaCl: p.a.-quality, Fa. Merck; dried at 500°C in HCl. Ternary chlorides: prepared by fusion in vacuum sealed quartz ampoules; if necessary annealed. All manipulations in a glove-box (10 ppm H_2O).

DTA-measurements: heating curves (2 deg·min^{-1}). Preparation of the samples like the ternary chlorides.

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Solution calorimetry: Home-built isoperibolic calorimeter. From the enthalpies of solution, ΔH^l, the reaction enthalpies, ΔH^f, were calculated:

$$\Delta H^f_{298} = [\Delta H^l_{298}(GdCl_3) + n\cdot \Delta H^l_{298}(ACl)] - \Delta H^l_{298}(A_nGdCl_{n+3})$$

X-ray-powder patterns: Philips PW 1050/25 goniometer. High-temperature photos: Simon-Guinier method; standard: Al_2O_3 with a=475.9 pm; c=1299.0 pm; CuK_α radiation. E.m.f.-measurements: A description of the galvanic cell is given elsewhere [9]. For the formation of Na_3GdCl_6 the set-up of the cell was $(C+Cl_2)/NaCl/Na^+$-conducting diaphragm$/Na_2GdCl_5/(C+Cl_2)$.

The solid electrolytes (compressed disks) were separated by a sintered disk of a Na^+-conducting glass powder. The collected e.m.f./T values were subjected to a linear regression analysis. Temperature range: 260-380°C.

RESULTS

By our own DTA-measurements (fig.1) the existence of Na_3GdCl_6, incongruently-melting at 497°C with a phase transition at 209°C, could be confirmed. Additionally, an incongruently-melting compound Na_2GdCl_5 was found with the peritectic at 430°C and 38.0 ± 0.5 mol-% $GdCl_3$. The correct structure of the phase diagram beyond the eutectic at 416°C and 45.0 ± 0.5 mol-% $GdCl_3$ is still unclear.

Na_2GdCl_5 crystallizes in the K_2PrCl_5 structure (space group: Pnma) [10] with the orthorhombic unit cell: a=1203.1(3); b=829.5(2); c=760.5(2) pm; Z=4.

The thermodynamic stability of Na_3GdCl_6 is given by the free (Gibbs) enthalpy of synproportionation according to the equation.

$$NaCl + Na_2GdCl_5 = Na_3GdCl_6.$$

This was measured in a galvanic cell with the electrolytes NaCl vs. Na_2GdCl_5 (+ some Na_3GdCl_6 to maintain reversibility). 30 e.m.f.-values E were measured in the temperature range 530-650 K.

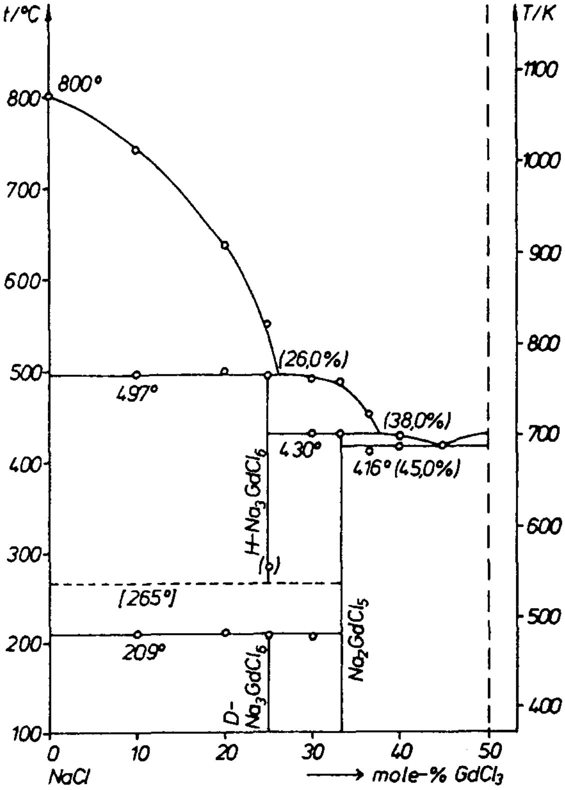


Fig. 1 System $NaCl/GdCl_3$ (0 to 50 mol-%)

A linear regression analysis (fig. 2) yielded the equation

$$E/\mathrm{mV} = -116.65\ (\pm 1.2) - 0.2169\ (\pm 0.002) \cdot T/\mathrm{K}$$

Using $\Delta G = -n \cdot F \cdot E$, the Gibbs-Helmholtz relation is formed:

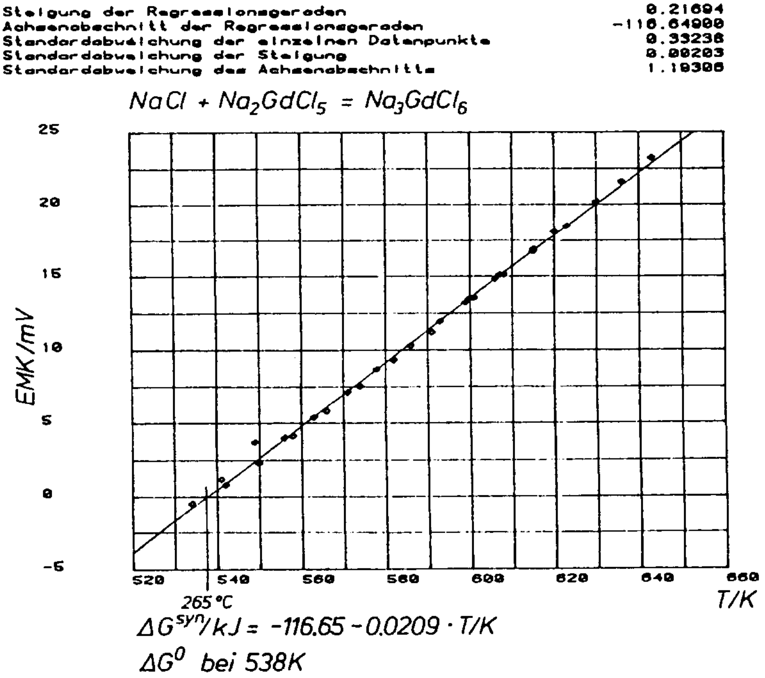
$$\Delta G^{syn}/\mathrm{kJ} = 11.26 - 0.0209 \cdot T/\mathrm{K}$$

with $\Delta H^{syn} = 11.3 \pm 0.1\ \mathrm{kJ \cdot mol^{-1}}$ and $\Delta S^{syn} = 20.9 \pm 0.2\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$.

At 539 K (265°C) ΔG^{syn} is zero; below this temperature the compound becomes instable, it must decompose to a mixture ($NaCl + Na_2GdCl_5$).

It is not possible to conduct these measurements at temperatures below ~250°C because of the growing electrical resistivity of the electrolytes. However, the distinct endothermic DTA-effect at 209°C in heating curves indicates a solid-state reaction, which is not a transition from D—>H, but a decomposition D-Na_3GdCl_6 —> $NaCl + Na_2GdCl_5$. This is confirmed by a dynamic high temperatur Guinier photo: in fig. 3, which is drawn directly from this photo, one can see the peaks of D-Na_3GdCl_6 and H-Na_3GdCl_6 separated by the reflections of the mixture ($NaCl + Na_2GdCl_5$).

The X-ray patterns of both Na_3GdCl_6-modifications could be indexed using the unit cell parameters of Meyer: the D-form with a trigonal cell, the H-form with a monoclinic cell.



Steigung der Regressionsgeraden	0.21694
Achsenabschnitt der Regressionsgeraden	-116.64900
Standardabweichung der einzelnen Datenpunkte	0.33238
Standardabweichung der Steigung	0.00203
Standardabweichung des Achsenabschnitts	1.18306

643	23.2
636	21.6
630	20.2
623	18.5
615	16.9
608	15.1
601	13.5
593	11.9
586	10.3
578	8.7
571	7.1
563	5.4
556	4.0
549	3.7
541	1.2
534	-0.5
542	0.8
550	2.3
558	4.1
566	5.8
574	7.5
582	9.3
591	11.2
599	13.2
606	14.8
615	16.7
620	18.1
615	16.7
607	15.1
600	13.5

Fig. 2 EMF vs. T values for the reaction $NaCl + Na_2GdCl_5 = Na_3GdCl_6$

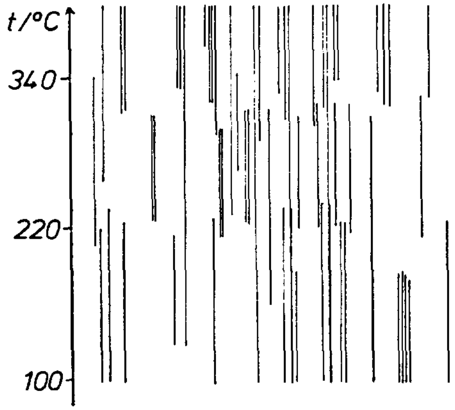


Fig. 3 Dynamic high-temperature Guinier pattern of Na_3GdCl_6

It is not possible to retain H-Na_3GdCl_6 metastable at ambient temperature by quenching; thus, no determination of ΔH by solution-calorimetry could be done. For D-Na_3GdCl_6 the following solution enthalpies were yielded:

$\Delta H^{l}_{298}(GdCl_3)$ = +4.5 kJ·mol^{-1}

$\Delta H^{l}_{298}(NaCl)$ = -180.3 kJ·mol^{-1}

$\Delta H^{l}_{298}(D\text{-}Na_3GdCl_6)$=-187.9 kJ·mol^{-1}.

With these values according to the equation $3NaCl + GdCl_3 = D\text{-}Na_3GdCl_6$ the enthalpy $\Delta H^{f}_{298}(D\text{-}Na_3GdCl_6)$ =+11.2 kJ·mol^{-1} is obtained. (It must be stated that the enthalpy, obtained by e.m.f.-measurements, is related to the formation of H-Na_3GdCl_6 from NaCl and Na_2GdCl_5).

CONCLUSIONS

H-Na_3GdCl_6 is a compound stable above 538 K. At this temperature the loss of lattice enthalpy compared with a mixture of $NaCl+Na_2GdCl_5$ (positive ΔH^{syn}) is just equal to the $T\cdot\Delta S$-term, produced by a gain in entropy. Neither by quenching nor by normal cooling it can be retained metastable at ambient temperature, but with strong undercooling it is transformed directly to D-Na_3GdCl_6 at ~400 K. The ($NaCl+Na_2GdCl_5$)-mixture stable at intermediate temperature is not formed in cooling experiments because of a too great kinetic hindrance; it can be yielded only by annealing at temperatures between 480 and 530 K for 5 or more days.

The situation with D-Na_3GdCl_6 is still much more precarious by such kinetic effects. When heating the compound either decomposition to $NaCl+Na_2GdCl_5$ occurs at ~480 K, as demanded by thermodynamics, or this reaction is kinetically suppressed and at ~570 K H-Na_3GdCl_6 is formed directly. In this case the formation of the H-modification is very slow, at temperatures slightly above 538 K in DTA - or DSC - experiments only a more or less small endothermic peak can be observed. This behaviour does not admit a direct measurement of the related **enthalpy** by DSC.

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