Journal of Thermal Analysis, Vol. 35 (1989) 1879–1890

RETARDED SOLID STATE REACTIONS

Systems of alkali metal chlorides with trichlorides of the early lanthanoides

H. J. Seifert

INORGANIC CHEMISTRY, UNIVERSITY GH KASSEL, F.R.G.

(Received June 19, 1989)

Reconstructive phase transitions and formation or decomposition reactions in the solid state exhibit in DTA-measurements a more or less great hysteresis between the temperatures from heating and cooling curves; at worst the reaction can be suppressed completely. By e.m.f. *vs.* T-measurements in appropriate galvanic cells for solid electrolytes equilibrium temperatures in the case of such kinetic hindrance can be determined and additionally the existence of metastable states can be proved.

One of the main tasks of thermal analysis is to measure temperatures at which phase transitions or chemical reactions occur. At the correct, thermodynamical temperature educt A and product B are in chemical equilibrium, given by the relation $\Delta G_A = \Delta G_B$. The most common way to determine such temperatures is to measure the reaction enthalpy by means of DTA. (This enthalpy ΔH is related to the free (Gibbs) enthalpy ΔG by the Gibbs–Helmholtz equation $\Delta G = \Delta H - T \cdot \Delta S$ (with $(\mathrm{d}\Delta G/\mathrm{d}T)_p = -\Delta S$)).

DTA (and DSC) signals are influenced by the finite transfer of heat. The magnitude of error, produced by this, depends on the heating rate, on apparative details and the mass, geometry and heat conductivity of the sample and can be corrected by theoretical calculations (see textbooks of thermal analysis [1]). Often the determination of the startpoint of solid state reactions is complicated by a too slow reaction rate which produces smeared DTA-peaks. In this case one can use other methods for detecting the "onset-temperature". We have discussed such methods elsewhere [2]; a comprehension about thermoptometric methods, which utilize the nearly infinite velocity of light, was given recently by Eysel [3].

Taking into account these corrections one should expect that the temperatures taken from heating and from cooling experiments are the same; the hysteresis $\Delta T = T_{\text{heat.}} - T_{\text{cool.}}$ should be zero. This is sufficiently realized in many cases; however, there are reactions too with a more or less great hysteresis: the reaction temperature derived from heating curves is higher than the equilibrium temperature and lower, when derived from cooling curves.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

An example for such a behaviour is the undercooling of melts, which is well understood since the work of Stranski. The compound Cs_2CdCl_4 [4], for instance, has a melting point of 473°; at 459° a solid state phase transition from β-Cs_2CdCl_4 to the high-temperature modification, α-Cs_2CdCl_4, occurs. The enthalpy of transition and the melting enthalpy are of the same magnitude. When cooling the melt a large undercooling is found and at 459° directly the β-form is crystallizing; the formation of α-Cs_2CdCl_4 from the melt is completely suppressed. Such effects are the reason why using generally heating curves for elucidating phase-diagrams.

Reconstructive phase transitions

It is an important question if one can correlate such retardations to structural variations during the phase transitions. A good example for studying this relation gives the compound $KMnCl_3$ [5]. At high temperature it is crystallizing with the cubic perovskite structure. At 386° and 360° phase transitions occur with only a small hysteresis, probably caused by methodic effects as described in the introduction. These transitions are of the non-reconstructive type; they lead at ambient temperature to the $GdFeO_3$-type with an orthorhombic unit cell, depending on a perovskite lattice, distorted by "octahedra-tilting". For such reactions the topology of the structure is maintained, the chloride ions have to shift only a little away from their ideal positions (Fig. 1).

1982 Horowitz and coworkers [6], reported that the *stable* modification at ambient temperature is crystallizing with the NH_4CdCl_3-structure. This modification is not be formed in DTA-runs. Horowitz says in his paper: "X-ray examination of these materials after storage in evacuated and sealed glass ampoules for 3–4 years revealed partial transformation of these materials to the new phase." A much better way to prepare the room temperature phase is the dehydration of the hydrate

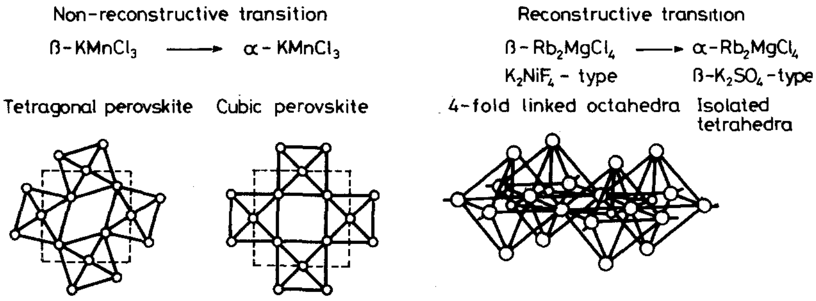

Fig. 1 Non-reconstructive and reconstructive phase transitions

$KMnCl_3 \cdot 2H_2O$ at 90°. This compound reveals a thermal effect in a heating curve at 267° with a transition enthalpy of 4.60 $kJ \cdot mol^{-1}$, measured by DSC.

In the NH_4CdCl_3-structure double-chains of face-connected octahedra are hold together by NH_4^+-ions in a surrounding of Cl^- ions, forming a tri-capped trigonal prism. The transition to the perovskite-structure and vice versa demands that the ions must leave their original sites and have to migrate to new positions, passing the potentials of other ions. This drastical rearrangement needs a great activation-energy; according to Chalmers [7], strong superheating (or undercooling) must occur. Thus, "reconstructive phase transitions" are correlated to a considerable temperature hysteresis.

For $KMnCl_3$ the transition temperature is too low, the mobility of the ions too small, so the reaction does not occur at all, even at very slow heating/cooling rates. For the double chloride Rb_2MgCl_4 the equilibrium temperature is higher, 421° as we have found by e.m.f.-measurements (see next chapter). Here DTA-measurements yield 443° from heating-curves and 415° from cooling curves. The structural change is the same as for Cs_2CdCl_4: β-Rb_2MgCl_4 has the K_2NiF_4 structure with 4-fold connected octahedra (Fig. 1); in α-Rb_2MgCl_4 (K_2SO_4-type) isolated tetrahedra exist.

Formation and decomposition reactions in the solid state can be considered as a special type of reconstructive phase transitions. An example is the compound Rb_3LaCl_6, which is existing at temperatures higher than 444°. The temperature hysteresis, measured for different heating and cooling rates is shown in Fig. 2.

Galvanic cells for solid electrolytes

All difficulties with retardations are generated by the trivial fact, that a reaction must occur, if the reaction enthalpy shall be measured. Methods, which do not require the adjusting of equilibrium, would not be disturbed by any kinetic hindrance. This condition is realized in galvanic cells: the system is far from equilibrium, and the measured e.m.f. E is related by the equation $\Delta G^r = -n \cdot F \cdot E$ (n = transported charge, F = Faraday constant) with the chemical power ΔG^r, the Gibbs enthalpy of reaction, which would be released, if the reaction would occur (measurement in the currentless state). There are two further advantages with such measurements: 1) ΔG is the real thermodynamic function for the stability of a compound, not the enthalpy ΔH, and 2) the e.m.f. is an intensive quantity, independent of the sample mass.

We have developed galvanic cells for solid state reactions of the type nACl + $MCl_x = A_nMCl_{(n+x)}$ in the late 70's. They consist of chlorine electrodes and alkali metal ion conducting diaphragms of sintered glass [10]. The set-up of a cell for the

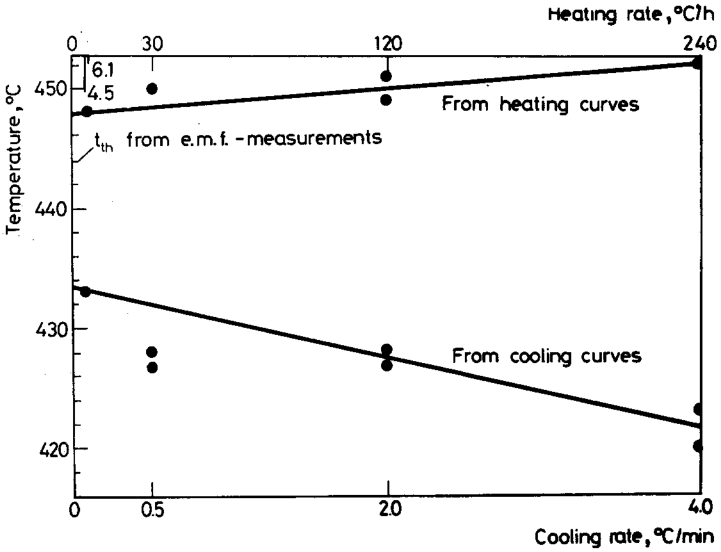

Fig. 2 Reaction temperature for Rb_3LaCl_6 (from [2])

reaction $RbCl + Rb_2LaCl_5 = Rb_3LaCl_6$ (Fig. 3a) e.g., is:

$$(C + Cl_2)/RbCl_{(s)}/Rb^+\text{-conduct. diaphragm}/Rb_2LaCl_5(+ Rb_3LaCl_6)/(C + Cl_2)$$

The anode and cathode are graphite discs in a chlorine atmosphere, the electrolytes pressed pellets of RbCl and Rb_2LaCl_5 mixed with some Rb_3LaCl_6 to give a reversible cell. The temperature dependence of the e.m.f. is measured stepwise in several temperature cycles. It proved to be linear down to ~300°. Thus, the collected e.m.f. *vs.* T-values could be subjected to a linear regression analysis, yielding an equation, which—after multiplication with $(-n \cdot F)$—is identical with the Gibbs–Helmholtz-equation $\Delta G = \Delta H - T \cdot \Delta S$.

As already pointed out, the condition for a phase transition is $\Delta G_A = \Delta G_B$. We will find this point as intersection of the e.m.f. *vs.* T-lines. This is shown for Rb_2MgCl_4 in Fig. 4b and for the formation of Rb_3LaCl_6 in Fig. 4a. Generally, the free enthalpy of formation from the two adjacent compounds in a phase diagram, the free enthalpy of synproportionation, ΔG^s, must be zero at the temperature of formation (or decomposition). With cells for the appropriate synproportionations one can measure this temperature directly or, if it is too low, by setting $E = a + b \cdot T = 0$.

As Fig. 4a demonstrates, Rb_3LaCl_6 will not decompose immediately when being cooled to temperatures <444°, but will remain in a metastable state, indicated by a

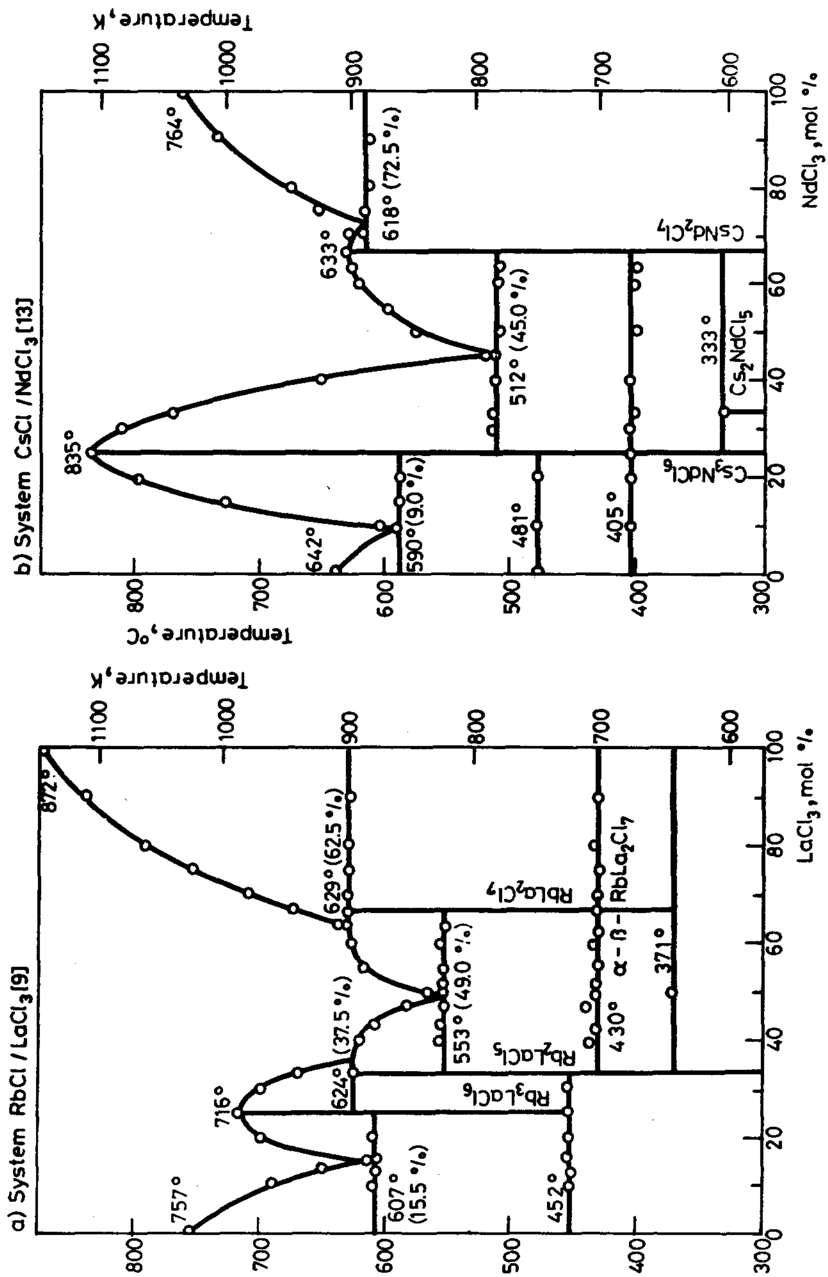

Fig. 3 Phase diagrams

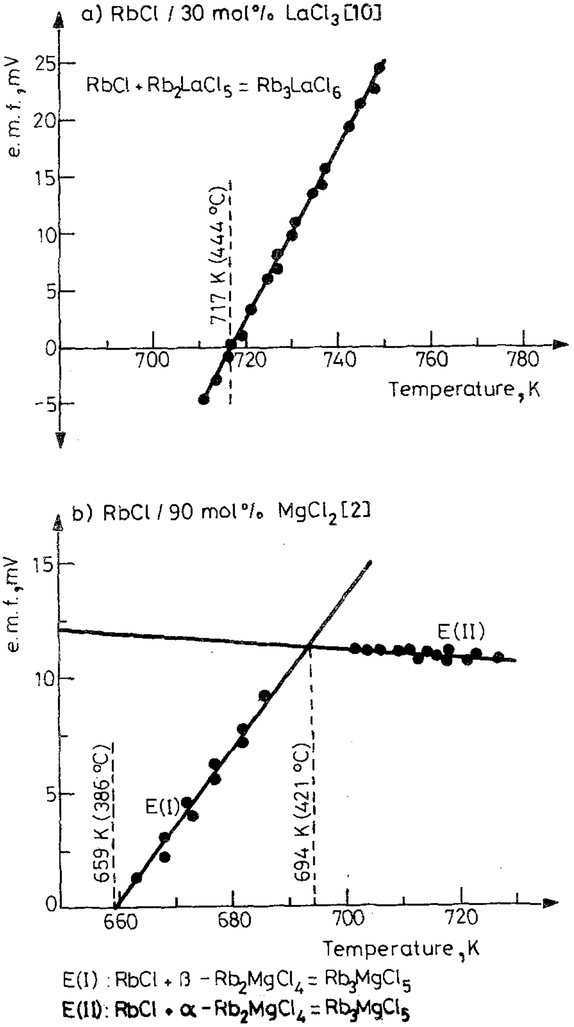

Fig. 4 Regression lines e.m.f. *vs.* T

negative e.m.f., what gives a positive ΔG^s. Thus, also metastable states can be detected by such e.m.f.-measurements.

Ternary chlorides in the systems $ACl/LnCl_3(Ln = La - Sm)$

During the last years we have investigated the systems of the early lanthanoide(III)-chlorides with the alkali metal chlorides $ACl(A = Na - Cs)$ by means of DTA, X-ray diffraction and solution calorimetry (La: [9]; Ce: [11]; Pr: [12]; Nd: [13]; Sm: [14]. For the systems with A = Rb, K, Na we could use galvanic cells for the determination of ΔG^r-values in dependence on temperature too.

There exist three groups of compounds with decomposition or formation reactions in the solid state: 1) Compounds Cs_2LnCl_5 which decompose at temperatures between 330 and 560°. No e.m.f.-measurements were possible, because no suitable diaphragms for Cs^+-ions could be found. Thus, the evidence for possible metastability must be taken from the results of the other methods. 2) In all Rb- and some K-systems compounds A_3LnCl_6 and ALn_2Cl_7 exist, which are stable at temperatures higher than ambient temperature. 3) In the systems $KCl/LaCl_3$ and $KCl/CeCl_3$ high-temperature compounds $K_3Ln_5Cl_{18}$ were detected. In the following two sub-chapters all results about the temperatures of these solid state reactions are comprehended.

High-temperature compounds in the systems with rubidium and potassium

The formation temperatures for the compounds A_3LaCl_6 in Table 1a are directly taken from our cited publications. The condition for T_{form} is, that at this temperature the Gibbs enthalpy for the reaction $ACl + A_2LnCl_5 = A_3LnCl_6$ and the correlated e.m.f. $E = a + b \cdot T$ must be zero. In the first columns regression coefficients a and b together with the T_{form}-values are compiled; in the last columns, temperatures measured with DTA are given. The hysteresis ($T_{\mathrm{heat.}} - T_{\mathrm{cool.}}$) is considerable, 20–50 K. At temperatures lower than ~400 °C the decomposition during cooling is so small, that it is no longer detectable by DTA. With further

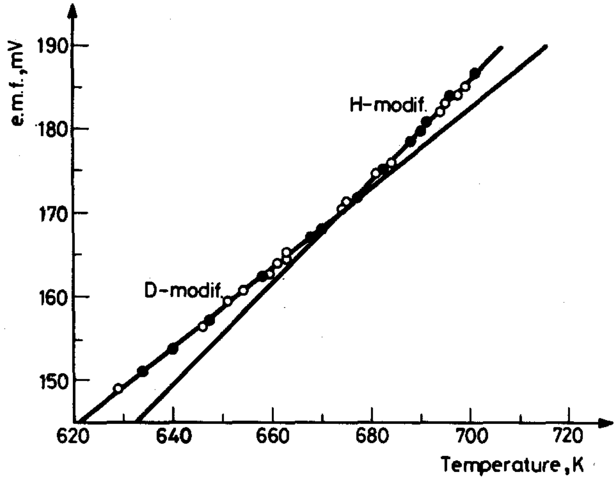

Fig. 5 E.m.f. *vs.* T for $RbCl + Rb_2SmCl_5 = Rb_3SmCl_6$ [14]

decreasing temperature the decomposition takes place only after annealing, in the case of reaction temperatures below ~300° a catalytic amount of water must be added (time: 2 days to 4 weeks).

The Rb-compounds of Pr, Nd, Sm and K_3SmCl_6 undergo a non-reconstructive phase transition $\beta \rightarrow \alpha$ (K_3MoCl_3-type →elpasolite structure), which can be detected by a kink in the e.m.f. *vs.* T-curves (Fig. 5). The condition for the equilibrium temperature is $\text{e.m.f.}(\beta) = \text{e.m.f.}(\alpha)$. The hysteresis of the DTA-temperatures is negligible (Table 1b). The same considerations as for the 3 : 1-compounds hold for the formation temperatures of compounds $K_3Ln_5Cl_{18}$ (Ln = La, Ce) and Na_2SmCl_5 (Table 1c).

A similar behaviour as the foregone compounds reveal the double chlorides ALn_2Cl_7, which are stable at temperatures higher than ~200 °C. The Rb-compounds undergo additionally non-reconstructive phase transitions between 350 and 450 °C (Table 2); however, the transition enthalpies are so small, that no kinks in the e.m.f. *vs.* T-curves could be observed.

The formation temperatures were either taken from direct measurements of the synproportionation reactions $3\,LnCl_3 + A_2LnCl_5 = 4\,A_{0.5}LnCl_{3.5}$ with electrolyte discs of 50 and 90 mole% $LnCl_3$ or they were calculated using measurements in cells $ACl/LnCl_3$ and ACl/ALn_2Cl_7 (s. original publications).

Again the problem arose to measure T_{form} for the compounds ALn_2Cl_7 with DTA. In no case decompositions occurred during normal cooling nor by normal annealing. Thus, the substances must be annealed again after adding a catalytic amount of water. After drying the products in HCl-atmosphere at ~150°, the endothermic peak for the formation reaction could be detected in DTA heating curves. Another route was the dehydration of the hydrates $RbLnCl_4 \cdot xH_2O$ to a mixture of ($1/2\,Rb_2LnCl_5 + 1/2\,LnCl_3$), and using this material for a DTA-heating experiment.

Ternary chlorides in the systems $CsCl/LnCl_3$

In the systems $CsCl/LnCl_3$ the same compounds exist as in the Rb-systems, however the double chlorides Cs_2LnCl_5 (Ln = La – Nd) are less stable than the analogous Rb-compounds and decompose at temperatures higher than 500°, for Cs_2LaCl_5 and higher than 300° for Cs_2NdCl_5. For the first two lanthanoides effects in heating and cooling curves could be observed with large hysteresis (Cs_2LaCl_5: 517/444°; Cs_2CeCl_5: 443/400°). Cs_2PrCl_5 was formed after annealing a quenched melt with the 2 : 1-composition for two weeks at 325°; in a subsequent DTA-heating run the decomposition occurred at 391°. Again this temperature lies above the equilibrium temperature, for annealing a quenched sample at 375° did not result in the formation of the compound. In the case of Cs_2NdCl_5 normal annealing (2

Table 1 Reaction temperatures for Rb- and K-compounds

Compound	Regression coeffic.		Transition temperatures			Hysteresis $T_{h.} - T_{c.}$ [grad]
	a	b	$a+b \cdot T = 0$	DTA (heat.)	DTA (cool.)	
1a) Formation temperatures of compounds A_3LnCl_6						
Rb_3LaCl_6	−537.9	0.7502	717 K (444 °C)	452 °C	420	32
Rb_3CeCl_6	−395.6	0.6229	636 K (363 °C)	378 °C	—	—
Rb_3PrCl_6	−274.8	0.4934	557 K (284 °C)	325 °C*	—	—
Rb_3NdCl_6	−249.5	0.5093	490 K (217 °C)	274 °C**	—	—
Rb_3SmCl_6	−150.6	0.4760	316 K (43 °C)	—	—	—
* After annealing at 250 °C; ** After annealing with some water at 175 °C.						
K_3CeCl_6	−559.3	0.7041	794 K (521 °C)	534 °C	516 °C	18
K_3PrCl_6	−537.6	0.7126	754 K (481 °C)	489 °C	461 °C	28
K_3NdCl_6	−502.6	0.7035	714 K (441 °C)	446 °C	385–400 °C	~50
K_3SmCl_6	−314.8	0.5204	605 K (332 °C)	338 °C*	—	—
* After annealing at 300 °C.						
1b) Transition temperatures $\beta \rightarrow \alpha$-A_3LnCl_6						
Rb_3PrCl_6	−368.1*	0.6370*	649 K (376 °C)	386 °C	384 °C	2
Rb_3NdCl_6	−332.7*	0.6346*	664 K (391 °C)	394 °C	391 °C	3
Rb_3SmCl_6	−235.4*	0.6019*	673 K (400 °C)	405 °C	404 °C	1
K_3SmCl_6	−400.4*	0.6569*	615 K (342 °C)	354 °C	346 °C	8
* Regression coefficients for the α-modification.						
1c) Formation temperatures of compounds $K_3Ln_5Cl_{18}$ and Na_2SmCl_5						
$K_3La_5C_{18}$	− 8.16	0.0776	107 K	—	—	
$K_3Ce_5Cl_{18}$	−114.1	0.1654	720 K (447 °C)	464 °C*	—	
Na_2SmCl_5	− 63.9	0.1507	423 K (150 °C)	—	—	
* After annealing at 400 °C.						
(d) Formation temperatures of compounds ALn_2Cl_7						
$RbLa_2Cl_7$	−537.9*	0.7502*	618 K (345 °C)	371 °C	—	
$RbCe_2Cl_7$	−152.4	0.2715	561 K (288 °C)	333 °C	—	
$RbPr_2Cl_7$	−340.1*	0.6083*	559 K (286 °C)	337 °C	—	
$RbNd_2Cl_7$	−242.6*	0.4880*	497 K (224 °C)	274 °C	—	
KNd_2Cl_7	−336.6*	0.4614*	730 K (457 °C)	469 °C	—	
KSm_2Cl_7	−211.0	0.3814	553 K (280 °C)	292 °C	—	

* Directly measured synprop. react.

Table 2 Transition temperatpures $\beta \rightarrow \alpha$-$RbLn_2Cl_7$ from DTA in °C

Compound	$T_{heat.}$	$T_{cool.}$	Hyster.	Compound	$T_{heat.}$	$T_{cool.}$	Hyster.
$RbLa_2Cl_7$	430	423	7	$RbPr_2Cl_7$	375	362	13
$RbCe_2Cl_7$	396	387	9	$RbNd_2Cl_7$	357	342	15

months at 250°) was successless; here again a catalytic amount of water was necessary for the formation; the decomposition was found at 333°.

All compounds Cs_3LnCl_6 feature a non-reconstructive phase transition near 400° with a negligible hysteresis (Table 3). The low-temperature modifications can be prepared by dehydration of the hydrates, e.g. $Cs_3LaCl_6 \cdot 3H_2O$ at 150° in one step according to TG-measurements [15]. It is not sure, if they are stable at ambient temperature for solution calorimetry yielded endothermic synproportionation enthalpies ΔH^s for the reactions $CsCl + Cs_2LnCl_5 = Cs_3LnCl_6$, whereas the compounds $CsLn_2Cl_7$ have exothermic ΔH^s values unlike the rubidium compounds $RbLn_2Cl_7$.

Table 3 Transition temperatures $\beta \rightarrow \alpha$-Cs_3LnCl_6 from DTA in °C

Compound	$T_{heat.}$	$T_{cool.}$	Hyster.	Compound	$T_{heat.}$	$T_{cool.}$	Hyster.
Cs_3LaCl_6	401	399	2	Cs_3NdCl_6	405	401	4
Cs_3CeCl_6	401	396	5	Cs_3SmCl_6	395	394	1
Cs_3PrCl_6	404	402	2				

Conclusions

DTA-measurements are now as ever the most common method for elucidating phase diagrams. However, for solid state reactions the so determined temperatures are no equilibrium temperatures but indicate the points at which the reactions start instead of potential kinetic hindrance. This long-known, but often neglected fact, is confirmed by the results of investigations on ternary lanthanoide chlorides, described in this paper. In general temperatures measured in heating runs are too high, those from cooling curves too low. Only some non-reconstructive phase transitions exhibit true "thermodynamic" temperatures, recognizable at a negligible hysteresis between $T_{heat.}$ and $T_{cool.}$. Examples are the compounds A_3LnCl_6, which undergo transitions from the monoclinic K_3MoCl_6-type to the cubic elpasolite structure. Otherwise, the compounds ALn_2Cl_7 reveal according to dynamic high-temperature X-ray patterns also a non-reconstructive transition of still unknown structural feature with a hysteresis of 7–15 degree. This hysteresis increases with decreasing reaction temperature. This trend is understandable by reasons of the flexibility of crystal lattices in dependence on temperature.

The situation becomes much more crucial if reconstructive phase transitions occur. Here the hysteresis can be 20 degree and greater; an example are the formation temperatures for the compounds A_3LnCl_6. If the reaction temperature is too low, it can happen that the reaction time becomes too small compared with the time constant of DTA, that it can be no longer detected in cooling runs. Possibly one has to accomplish the reaction by annealing, in extreme cases after adding a catalytic amount of water. The afterwards measured reaction temperatures in heating runs are in general strongly increased compared with equilibrium temperatures, determined by e.m.f.-measurements, as can be seen from the compounds $RbLn_2Cl_7$ in Table 1d.

From these experiences two consequences can be derived.

1) Only such substances should be used as temperature standards for DTA, which reveal a negligible hysteresis. Among the ICTA-standards only the compounds KNO_3, SiO_2, K_2SO_4 and K_2CrO_4 fulfill this requirement.

2) The temperatures of solid state reactions in phase diagrams elucidated by DTA, should be taken as "kinetic temperatures" as a precaution, if no hysteresis-values are given. That is important for the calculation of transition entropies for instance.

It is an unsolved problem what to do, if temperatures from DTA– and e.m.f.–measurements are known. Shall the phase diagrams be constructed only using DTA-temperatures or by using DTA-values for the solid-liquid reactions and e.m.f.-derived values for the solid state reactions?

However, the main issue for the future is: What can be done to detect reactions at ambient or still lower temperature, where the mobility of the ions in the lattice has become so small, that nothing happens at all? It seems that then new preparative methods must be developed, which enable us to synthesize ternary chlorides also at temperature near $T = 0$.

* * *

We have to thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industry for supporting our work from the outset.

References

1 W. F. Hemminger and H. K. Cammenga, Meth. d. Therm. Anal., Springer-Verlag 1989, p. 44.

2 H. J. Seifert, Thermochim. Acta, 114 (1987) 67.

3 S. Hess and W. Eysel, J. Thermal Anal., 35 (1989) 627.

4 H. J. Seifert, N. Preuss and J. Sandrock, Experientia, Suppl., 37 (1979) 23.

5 H. J. Seifert and J. Uebach, J. Solid State Chem., 59 (1985) 86.

6 A. Horowitz, M. Amit, J. Makovsky, L. Bendor and Z. H. Kalman, J. Solid State Chem., 34 (1982) 107.

7 B. Chalmers, Principles of Solidification, J. Wiley and Sons, New York 1964.

8 H. J. Seifert and H. Fink, Proc. 4th ICTA, Budapest 1974, Vol. I., 367.

9 H. J. Seifert, H. Fink and G. Thiel, J. Less-Common Metals, 110 (1985) 139.

10 H. J. Seifert and G. Thiel, J. Chem. Thermodyn, 14 (1982) 1159.

11 H. J. Seifert, J. Sandrock and G. Thiel, J. Thermal Anal., 31 (1986) 1309.

12 H. J. Seifert, J. Sandrock and J. Uebach, Z. anorg. allg. Chem., 555 (1987) 143.

13 H. J. Seifert, H. Fink and J. Uebach, J. Thermal Anal., 33 (1988) 625.

14 H. J. Seifert and G. Thiel, Thermochim. Acta, 133 (1988) 275.

15 H. Imgrund, Staatsexamensarbeit, Kassel 1984.

Zusammenfassung – Rekonstruktive Phasenumwandlungen sowie Bildungs- und Zersetzungsreaktionen im festen Zustand zeigen bei DTA–Messungen eine mehr oder minder große Hysteresis zwischen den aus Aufheiz- bzw. Abkühlkurven ermittelten Temperaturen; schlimmstenfalls kann die Festkörperreaktion völlig unterdrückt sein. Mißt man in geeigneten galvanischen Zellen für Festelektrolyte EMK-gegen-*T*-Kurven, so erhält man auch im Falle kinetischer Hemmungen Gleichgewichtstemperaturen und kann darüber hinaus das Vorliegen metastabiler Zustände nachweisen.

Резюме — Восстанавливаемые фазовые переходы, реакции образования или разложения в твердом состоянии проявляются при ДТА измерениях большим или меньшим гистерезисом между температурными кривыми нагрева и охлаждения: в самом худшем случае реакция может быть полностью приостановлена. С помощью температурных измерений электродвижущей силы в соответствующих гальванических ячейках могут быть определены равновесные температуры для твердых электролитов и в дополнение может быть подтверждено наличие метастабильных фаз.