

RETARDED SOLID STATE REACTIONS III [1]

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Abstract

Solid state reactions and reconstructive phase transitions exhibit more or less a large hysteresis between reaction temperatures taken from DTA-heating and -cooling curves. For ternary lanthanide chlorides the equilibrium temperatures could be obtained by *e.m.f.*-measurements in galvanic chlorine cells for solid electrolytes using A^+ -ion (A =alkaline metal) conducting diaphragms. By quenching, high-temperature phases can often be transformed to metastable room-temperature phases. In this case the equilibrium state must be established by annealing at sufficiently high temperature, or it must be tried to synthesize the compound in its stability range from suitable precursor systems.

Keywords: metastable states, reconstructive phase transitions, ternary lanthanide chlorides, thermal hysteresis

Introduction

In the last twenty years we mainly have investigated ternary lanthanide chlorides formed according to the equation



Four experimental methods were used:

- i: With differential thermal analysis (DTA) the phase diagrams of the pseudobinary systems AX/MX_n were elucidated \rightarrow ternary compounds with their composition.
- ii: X-ray diffraction \rightarrow crystal structures of the compounds.
- iii: Solution calorimetry \rightarrow enthalpies of formation from the binary compounds ($\Delta_f H$) and enthalpies of syn-reaction ($\Delta_{\text{syn}} H$): formation from the compounds adjacent in the phase diagram.
- iv: Measurements of *e.m.f.* as $f(T)$ \rightarrow free enthalpies ($\Delta_r G$) and entropies ($\Delta_r S$) of reactions.

If solid state reactions or phase transitions existed in the investigated systems the results often were falsified by kinetical hindrance. Some aspects of such 'retarded solid state reactions' are discussed in this paper.

Thermal hysteresis

DTA heating curves have shown that the compound Rb_3LaCl_6 is stable at temperatures higher than 452°C [2]. It is formed in a strong endothermic formation

from RbCl and the adjacent compound Rb_2LaCl_5 . The loss in (lattice) enthalpy is compensated by a sufficiently high reaction entropy so that the Gibbs-enthalpy of reaction is zero at the formation temperature and negative at higher temperature.

ΔG vs. T -curves were obtained with a self-constructed galvanic-cell for solid electrolytes. $E.m.f.$ vs. T -measurements in the temperature range 430–500°C revealed that the $e.m.f.$ is linearly dependent on T . Thus, the regression equation $e.m.f. = a + bT$ could be transformed directly to the Gibbs-Helmholtz equation $\Delta_r G = \Delta_r H - \Delta_r S T$ by multiplication with $-nF$ (n = transported charge; F = Faraday constant). The formation/deformation temperature then is given by $\Delta_r G = 0$ (or $e.m.f. = 0$). It was found to be 444°C, instead of 452°C found by DTA-measurements.

Below 444°C the measured $e.m.f.$ should remain zero; however, in reality it changed sign: the compound was now in a metastable state with positive $\Delta_r G$ values, and not before ~430°C the equilibrium state was attained.

The résumé of these measurements is that the reaction is kinetically hindered in both directions. As Fig. 1 shows, neither the overheating nor the undercooling can be prevented by lowering the heating/cooling rate. Also the extrapolation to a rate of zero gives a hysteresis of 14°C. Thus, it is not possible to find the equilibrium by extrapolation temperature, but one finds 'reaction temperatures' for the formation and/or decomposition.

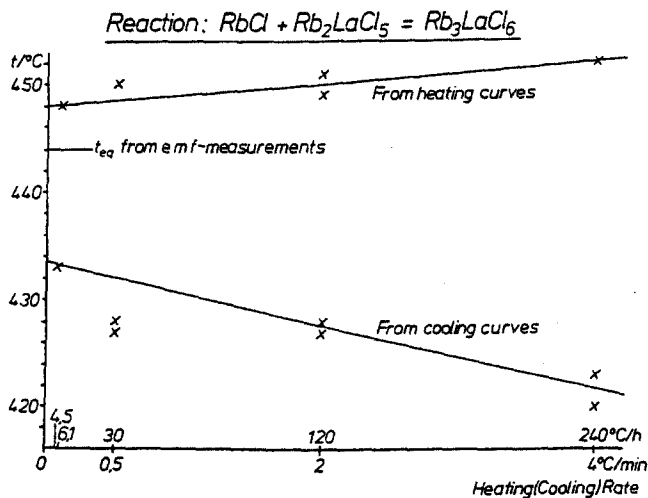


Fig. 1 $E.m.f.$ vs. T -curve for the formation of Rb_3LaCl_6

The advantage of the $e.m.f.$ -method is, that during the measurements the reaction does not have to take place; the correct temperature is obtained by the intersection of two separately measured $e.m.f.$ vs. T -lines.

All this was demonstrated very well by another example: the decomposition of RbSrCl_3 [3], continuously measured by an $e.m.f.$ vs. T -curve. With a rate of 5°C h^{-1} one needs 6 h for complete decomposition when cooling and 3 h for reformation when heating.

Such a hysteresis in reaction temperatures holds for all 'reconstructive solid state reactions' where ions have to leave their sites and must march to new positions. At lower temperatures this kinetic hindrance can become so strong, that the reaction doesn't occur at all in the time-scale of a DTA-measurement. One can often enforce such decompositions by annealing – for days, weeks, sometimes months. In a heating curve we can measure a formation temperature only once; a repetition is only possible after a second annealing procedure.

The worst situation is, if also annealing does not help any longer. An example is KMnCl_3 : At high temperature it crystallizes with the cubic perovskite structure. At 386 and 300°C displacive phase transitions occur, and at room temperature the GdFeO_3 -type is found with slightly deformed octahedra. 1982 Horowitz *et al.* [5], reported that the stable room temperature modification crystallizes with the NH_4CdCl_3 -structure. A quotation from their 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 $\text{KMnCl}_3 \cdot 2\text{H}_2\text{O}$ at 90°C. This compound reveals a thermic effect in a heating curve at 267°C with a transition enthalpy of 4.60 kJ mol^{-1} , measured by DSC [6].

It must be pointed out that there is no fundamental difference between solid state reactions, where the number of phases is changing, and reconstructive phase transition, where one phase is transformed to one other with an essentially different lattice. In both cases we must expend such a great free activation enthalpy, as well in heating and cooling, that the reaction cannot occur at its equilibrium temperature.

We have recently found situations analogous to that of KMnCl_3 with ternary lanthanide chlorides too [7]. From older DTA-measurements phase transitions of compounds A_3LnCl_6 from monoclinic modifications with space groups either $\text{C}2/c$ or $\text{P}2_1/c$ to the cubic elpasolite type $\text{Fm}3m$, occurring near 400°C, were well known. However, by evaporation of aqueous solutions at 100–120°C, another modification in the space group Pbcm can be obtained. It transforms at approx. 300°C to $\text{C}2/c$. This transition is kinetically irreversible. By solution calorimetry could be proved, that the orthorhombic form is the thermodynamically stable one at room temperature by $2\text{--}4 \text{ kJ mol}^{-1}$.

Another family of ternary chlorides with similar behaviour has the composition Cs_4LnCl_7 . This compounds can be prepared from aqueous solution with $\text{Ln} = \text{Ho–Yb}$ [8]. They decompose, again kinetically irreversible, at $\sim 250^\circ\text{C}$ to CsCl and Cs_3LnCl_6 in $\text{C}2/c$.

Metastable compounds

As discussed before, Rb_3LaCl_3 decomposes to RbCl and Rb_2LaCl_5 $\sim 20^\circ\text{C}$ below its equilibrium temperature when cooled in the time scale of DTA with 4°C min^{-1} . When quenching it from $> 444^\circ\text{C}$ to room temperature the compound is preserved as the metastable modification with the monoclinic space group $\text{C}2/c$ instead of the cubic high temperature structure.

Going to Rb_3PrCl_5 [9] a reversible transformation $\text{Fm}3m \leftrightarrow \text{C}2/c$ occurs at 376°C . According to *e.m.f.* measurements the compound becomes unstable at

284°C. However, this decomposition is suppressed when cooling with the DTA-time scale. By annealing metastable Rb_3PrCl_5 for some days at $\sim 250^\circ\text{C}$ the stable system ($\text{RbCl} + \text{Rb}_2\text{PrCl}_5$) is obtained.

Much more peculiar is the behaviour of Na_3GdCl_6 [10]. According to *e.m.f.* measurements it is stable above 265°C , crystallizing in the cryolite type. When cooling in the time-scale of DTA at $\sim 130^\circ\text{C}$ hexagonal L- Na_3GdCl_6 is formed, which is yielded by quenching too. This L-modification is metastable; after 5 days annealing at $\sim 250^\circ\text{C}$ or one week at $\sim 170^\circ\text{C}$ it decomposes to $\text{NaCl} + \text{Na}_2\text{GdCl}_5$. However, when L- Na_3GdCl_6 is heated in the time-scale of DTA this decomposition does not occur, but at $\sim 209^\circ\text{C}$ H- Na_3GdCl_6 is formed, which is metastable at this temperature: according to Ostwald's rule the first step from hexagonal Na_3GdCl_6 to ($\text{NaCl} + \text{Na}_2\text{GdCl}_5$) is the formation of monoclinic Na_3GdCl_6 – a fast reaction in contrast to the reconstructive decomposition.

During continued heating with 4°C min^{-1} or with the time scale of dynamic high temperature Guinier photos [11] ($\sim 20^\circ\text{C h}^{-1}$) the stable state is reached at 265°C without foregone decomposition.

Conclusion

1) In the case of non-reconstructive phase transitions, reaction temperatures are found with DTA near the equilibrium temperature. If the transitions are reconstructive, temperatures measured with dynamic methods can differ significantly from the equilibrium temperatures. In extreme cases the transition cannot be found with DTA at all.

2) When investigating retarded phase transitions one has to take care that the time-scale of the measuring method is of the same magnitude as the reaction time. Is the time for the measurements too quick, one can't detect the reaction. That can be true for DTA, but also for dynamic X-ray photos in the case of strongly retarded solid state reactions.

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