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Note

ENTHALPIES OF TRANSFORMATION OF ALKALI HALIDE—LANTHANIDE(III) HALIDE COMPOUNDS OF THE TYPE M_3LnX_6

ROGER BLACHNIK and ANJA JÄGER-KASPER

Laboratorium für Anorganische Chemie der Gesamthochschule/Universität Siegen, Adolf-Reichwein-Strasse, D 5900 Siegen 21 (W. Germany)

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The enthalpies of transformation for the compounds M_3LnX_6 (M = K, Rb, Cs; Ln = Pr, Nd, Sm, Gd, Dy, Er, Yb; X = Cl, Br) have been determined by differential scanning calorimetry. The concentration dependence of the enthalpies of transformation and the temperatures at which they take place indicate that the transformation is a polymorphic transition of reconstructive type in the Pr and Nd compounds, whereas in the systems with smaller rare earth ions it becomes the limiting case of a peritectoid and a eutectoid reaction for M_3LnX_6 and $M_{3-x}LnX_{6-x}$, respectively.

In the course of DTA investigations on alkali halide—rare earth halide phase diagrams [1,2], the congruently melting compound M_3LnX_6 was found in all systems involving potassium halide, rubidium halide or cesium halide. The structures of these compounds are not known. Thermal effects were observed in the temperature range 670—730 K for all of these compounds, and have been explained in the literature on the basis of a polymorphic transition.

The corresponding enthalpy effects were determined in a DuPont Thermal Analyser 990 with an error of ±5%. The reliability of the apparatus was checked by measuring the enthalpy of transition of CsCl. The value of 3.03 ± 0.14 kJ mole^{-1} is in good agreement with 2.89 ± 0.12 and 2.96 ± 0.08 kJ mole^{-1} reported by Pöyhönen [3] and Arell et al. [4], respectively.

Table 1 reveals that in most cases the enthalpy is of the order of 5—8 kJ mole^{-1}; however, in the compounds K_3PrBr_6, K_3NdBr_6 and K_3NdCl_6 surprisingly high values were observed. All phase changes were reversible and not quenchable.

It was observed during the determination of phase diagrams that the transition temperatures were not independent of the bulk concentration. In most of the systems the transition for compositions covering the range 66.8—74.9 mole% MCl occurred at temperatures which were 1—20 K lower than the transition temperature for the composition range 75—99.9 mole% MCl (Fig. 1). This implies that either the nucleation mechanism of the transitions is catalyzed by the presence of M_2LnX_5 (the compound observed at 66.7 mole% in these systems) or that interpretation as a polymorphic transition is incorrect.

TABLE 1

T_U, ΔH_U and ΔS_U of the M_3LnX_6 compounds (X = Cl, Br)

	T_U (K)	ΔH_U (kJ mole^{-1})	ΔS_U (J mole^{-1} K^{-1})
K_3PrBr_6	725	43.74	60.3
K_3NdBr_6	682	41.61	61.0
Rb_3NdBr_6	708	7.60	10.7
K_3SmBr_6	676	7.10	10.5
Rb_3SmBr_6	712	8.15	11.5
K_3GdBr_6	681	6.88	10.1
Rb_3GdBr_6	722	8.03	11.1
K_3DyBr_6	695	7.34	10.6
Rb_3DyBr_6	730	7.91	10.8
K_3ErBr_6	697	7.30	10.5
Rb_3ErBr_6	730	8.12	11.1
K_3YbBr_6	707	7.94	11.2
Rb_3YbBr_6	733	7.85	10.7
K_3NdCl_6	718	43.70	60.9
Rb_3NdCl_6	665	6.86	10.3
Cs_3NdCl_6	675	7.47	11.1
Rb_3SmCl_6	678	7.36	10.9
Cs_3SmCl_6	680	7.49	11.0
K_3GdCl_6	627	5.39	8.6
Cs_3GdCl_6	677	6.76	10.0
$CsSm_2Cl_7$	717	13.51	18.9
CsCl	743	3.03	4.07

In order to obtain more information about this peculiarity, the enthalpy of phase change was measured as a function of composition in the RbBr—$GdBr_3$ system. The data are plotted in Fig. 2. The fact that the two lines representing the transformation effect do not intersect 75 mole% composition at the same point enables us to gain a better understanding of the nature of this transition.

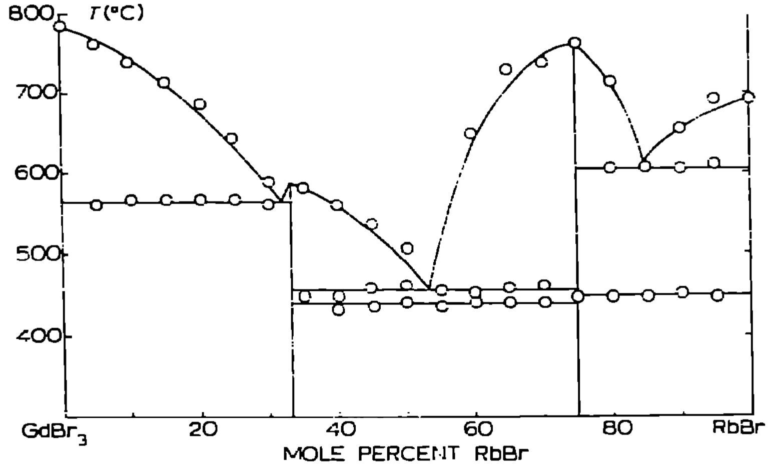

Fig. 1. Phase diagram of the RbBr—$GdBr_3$ system.

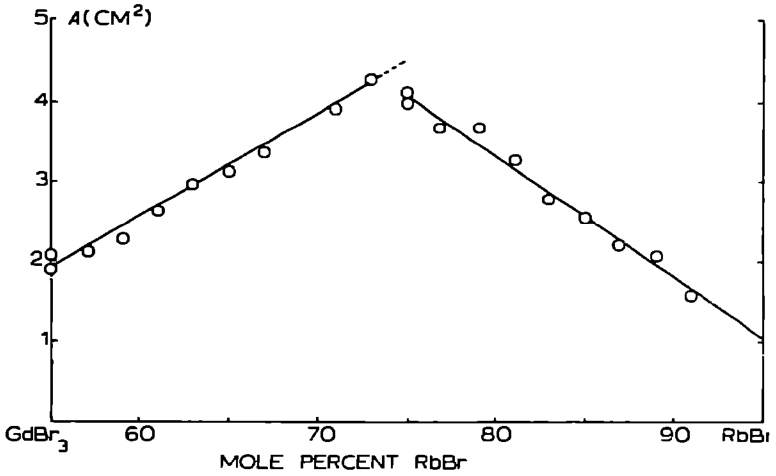

Fig. 2. Enthalpies of transformations of "Rb_3GdBr_6" in arbitrary units vs. concentration.

Obviously the jump in the transformation temperatures and the different enthalpy values of the transformation in the presence of MX and M_2LnX_5 can be resolved if the transformations are considered as limiting cases of eutectoid and peritectoid reactions, respectively, as shown in Fig. 3. The effect observed between 74.9 and 99.9 mole% MX corresponds to the peritectoid reaction

$M_3LnX_6 \rightarrow M_{3-x}LnX_{6-x} + xMX$

and that observed between 66.8 and 74.9 mole% to the eutectoid reaction

$M_2LnX_5 + M_3LnX_6 \rightarrow M_{3-x}LnX_{6-x}$

Using this interpretation, the jump in the transformation temperature can be explained by the phase rule.

The compounds at 75 mole% MX, interpreted to date as "M_3LnX_6" with a

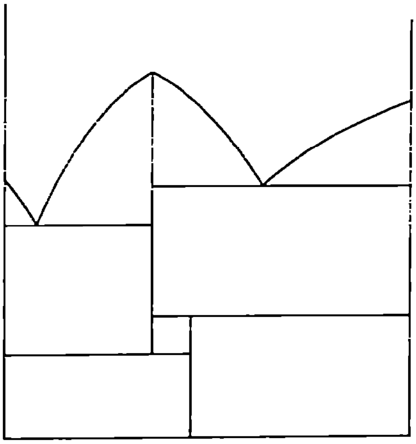

Fig. 3. Schematic construction of the phase relations in the MX—LnX_3 systems with jumping transformation temperatures (section of the phase diagram LnX_3—MX around 75 mole% not to scale).

phase transition, are therefore two compounds with slightly different stoichiometry. The unusually high enthalpies of transition observed in the cases where no transformation temperature jumps occurred may be readily understood on the basis of this interpretation.

In these cases only are we dealing with a solid phase transition which connects two phases with different structures but the same composition in a reversible process. The high enthalpy of transition classifies it as a reconstructive transition [5]. This transition is probably limited by the size ratios of the constituent ions; with decreasing size of the rare earth ion some MX is rejected by the structure and appears as a second phase, the reconstructive transition changing to a peritectoid reaction with a smaller heat effect. This is related to the difference in enthalpy of formation of the compounds participating. A determination of the structures of the compounds will be necessary for a complete understanding of the phenomenon reported in this Note.

ACKNOWLEDGEMENTS

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