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THERMOCHEMICAL AND STRUCTURAL INVESTIGATIONS
Systems alkalimetal bromides/samarium(III)-bromid

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Abstract

The phase diagrams of the systems ABr/$SmBr_3$ were reinvestigated. The findings of Blachnik for the systems with A=Cs, Rb, K were confirmed; however, the dimorphic compound K_3SmBr_6 is stable only above 572 K. The equilibrium temperature, found by *e.m.f.*-measurements in a solid state galvanic cell for the reaction $KBr+K_2SmBr_5$=L-K_3SmBr_6, is smaller (522 K). The formation temperature for Rb_3SmBr_6 is 279 K (DTA) and 256 K (e.m.f.) resp. By solution calorimetry was proved that the compounds Cs_2SmBr_5 and KSm_2Br_7 don't exist at 0 K. In the system NaBr/$SmBr_3$ only one hitherto unknown dimorphic compound Na_3SmBr_3 exists above 473 K. L-Na_3SmBr crystallizes in the hexagonal space group $R\bar{3}$, above 519 K H-Na_3SmBr_6 has the monoclinic cryolite-structure. Powder patterns of other compounds not yet investigated – H-/L-A_3SmBr_6, ASm_2Br_7 (A=Cs, Rb, K) and Cs_2SmBr_5 – were indexed analogously to known structure families. The structure parameters of $SmBr_3{\cdot}6H_2O$ were determined by single-crystal measurements.

Keywords: DTA, galvanic bromine cells for solid electrolytes, pseudobinary systems ABr/$SmBr_3$, solution calorimetry, XRD

Introduction

In the course of investigations on the existence of ternary lanthanide chlorides A_nLnCl_{n+3} (A=Na–Cs; Ln=La–Gd) we had found [1] that there is a change in coordination numbers from seven to six for the compounds Cs_2LnCl_5 when passing from Nd to Sm. 1991 Yuan [2] could show, that the compounds in the bromide systems ABr/$LnBr_3$ has very similar structural and energetical features like the analogous chlorides in spite of the bigger radius and the better polarizability of the bromide ion. Thus, it was of interest to find out, if with decreasing $r(Ln^{3+})$ also in the bromide group a change in the properties begins with samarium. Therefore, we have reinvestigated the systems ABr/$SmBr_3$ by means of differential thermoanalysis (DTA), X-ray diffraction (XRD) and calorimetry.

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Older, but very reliable investigations of the pseudobinary systems with A=Cs, Rb, K exist from Blachnik [3]. He found evidence for the existence of an ennea-bromide $Cs_3Sm_2Br_9$, the structure of which was determined by Meyer [4]. Only vague items exist for the system $NaBr/SmBr_3$ [5].

Experimental

Preparative methods

$SmBr_3$

Starting compound for the preparation of anhydrous $SmBr_3$ was the hexahydrate $SmBr_3{\cdot}6H_2O$, yielded by dissolution of Sm_2O_3 (Fa. Johnson Matthey, 99.99%) in hydrobromic acid. According to TG-measurements two lower hydrates exist: $SmBr_3{\cdot}3H_2O$ in the range 95–160°C; $SmBr_3{\cdot}H_2O$ in the range 160–180°C. The trihydrate is isotypic to $LaBr_3{\cdot}3H_2O$, the monohydrate to $LaBr_3{\cdot}H_2O$ and to the group $LnCl_3{\cdot}H_2O$ (Ln=La–Tb). However, the structures of both families are unknown.

For the preparation of $SmBr_3$ the hexahydrate was primarily heated in a vacuum dry-box to 100°C (p~50 bar). Then, the formed $SmBr_3{\cdot}3H_2O$ was dehydrated in an HBr-stream first at 180°C ($SmBr_3{\cdot}H_2O$) and finally with slowly increasing temperature at 230°C.

Ternary bromides

From a solution of 2 CsBr and 1 $SmBr_3{\cdot}6H_2O$ in conc. hydrobromic acid a crystalline solid could be obtained by evaporation at ~80°C. After drying at 120°C the compound $Cs_2SmBr_5{\cdot}H_2O$ was formed: It is isotypic with $K_2FeCl_5{\cdot}H_2O$ (erythrosiderite-type; S. G. Pnma, $Z=4$). The lattice parameters are: $a=1525.1(4)$ pm; $b=1117.3(9)$ pm; $c=790.8(4)$ pm. Experiments, to prepare anhydrous ternary bromides with a recently developed procedure [6] using the solvo-system $H_3C{\cdot}COOH/H_3C{\cdot}COX$ (X=Cl, Br) succeeded only for Cs_3SmBr_6.

A solution of 5 g $SmBr_3{\cdot}6H_2O$ in 20 ml acetic acid was refluxed with 10 ml acetyl bromide for one hour. After adding a solution of 5.7 g Cs-acetate in 10 ml acetic acid white crystals of Cs_3SmBr_6 precipitated. They were washed with ether and dried at 150°C (yield: 90%).

Differential thermal analysis (DTA)

The DTA measurements were performed in a homebuilt device for samples (0.5 g) in vacuum-sealed quartz ampoules. If necessary the material could be annealed after melting with a gas flame and homogenizing by shaking and quenching. In general, heating curves were measured (heating rate (2 K min^{-1}).

For quantitative measurements of transition enthalpies the DSC 7, Perkin-Elmer was used.

X-ray powder patterns

Powder patterns were taken at ambient temperature with a Philips PW 1050/25 goniometer equipped with a proportional counter and a vacuum attachment. During exposure (CuK_α radiation) the samples were kept under a helium atmosphere. For dynamic high-temperature photographs, the Simon-Guinier method was applied. Corundum (a=475.92 pm; c=1299.00 pm) was used as an internal standard. Instructions for an single-crystal measurement are given in Table 2.

Solution calorimetry

The device for solution calorimetry was a homebuilt calorimeter. Samples of 2–4 g were dissolved in 1.11 liter H_2O, which is a good approximation of an infinitely diluted system. From the enthalpies of solution, $\Delta_{sol}H^o_{298}$, the enthalpies for the formation from $ABr+SmBr_3$, Δ_fH^o, were calculated:

$$\Delta_fH^o_{298} = [\Delta_{sol}H^o_{298}(SmBr_3) + n\Delta_{sol}H^o_{298}(ABr)] - \Delta_{sol}H^o_{298}(A_nSmBr_{n+3})$$

E.m.f. measurement

A detailed description of the galvanic cell was given previously [7]. As example, for the reaction $KBr+K_2SmBr_5=K_3SmBr_6$ the set-up of the cell was: (Br_2+graphite)/KBr/K-conduct. diaphragm/K_2SmBr_5(+K_3SmBr_6)/ (Br_2+graphite).

The diaphragm was a disk of an A^+-conducting sintered glass powder, containing only one alkali metal. The collected *e.m.f. vs. T*-values could be subjected to a linear regression analyse.

Differently from former measurements the regulation of the heating steps and the data-recording was done with an on-line computer. A description of the software is given in the dissertation M. Alsmann, Kassel 1995.

Results

Phase diagrams

The phase diagrams, elucidated by DTA and confirmed by XRD measurements on crystal powders, are shown in Fig. 1.

The systems $CsBr/SmBr_3$ and $RbBr/SmBr_3$ agree well with the findings of Blachnik [3]. His assumption about the existence of the compound $Cs_3Sm_2Br_9$

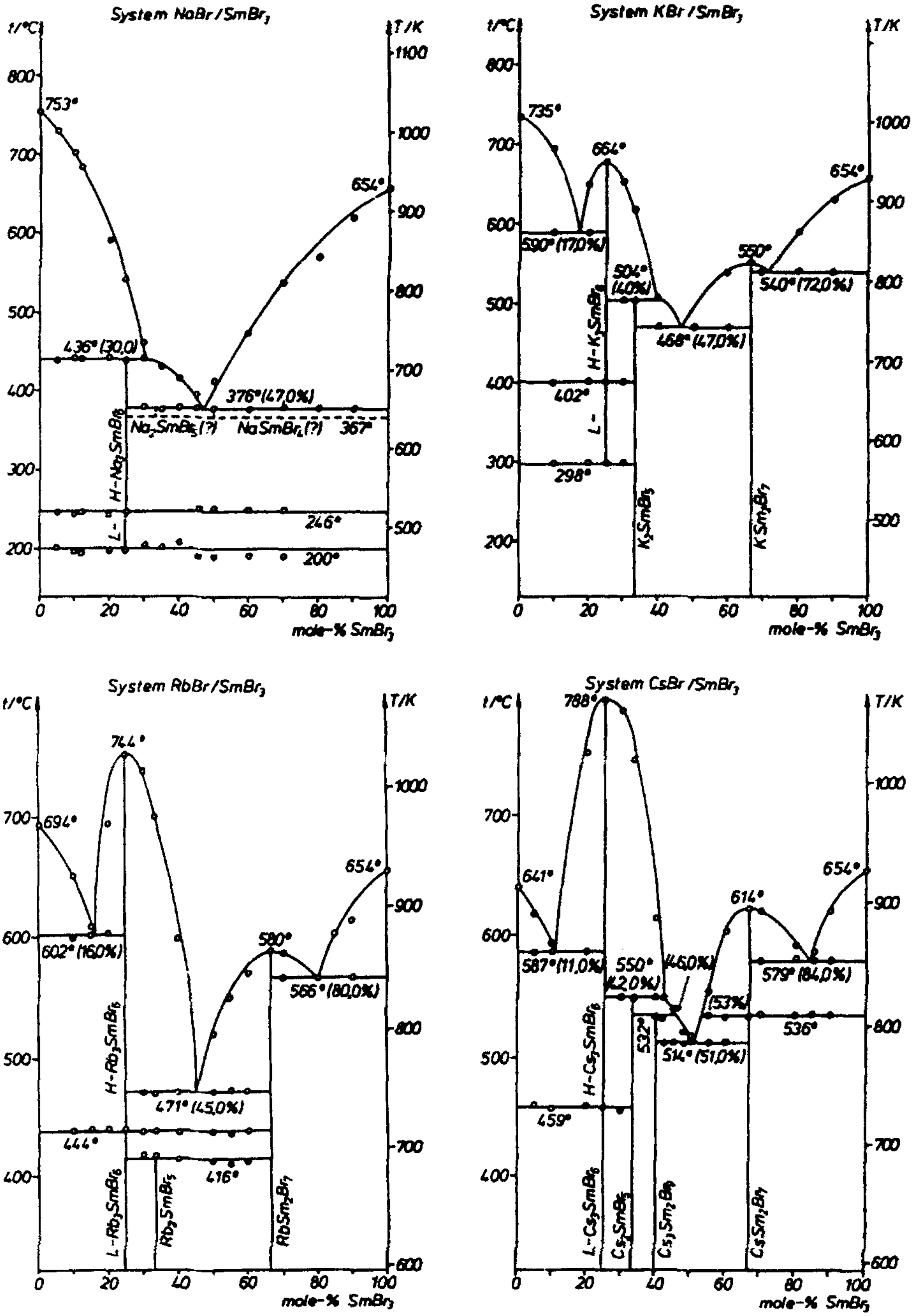

Fig. 1 Phase diagrams of the systems ABr/SmBr3 (A=Cs, Rb, K, Na)

could be confirmed. For the system $KBr/SmBr_3$ one correction must be done; K_3SmBr_6 is stable only at elevated temperature (>298°C). The systems $NaBr/SmBr_3$ is different to the description of Vogel [5]: a compound Na_3SmCl_6 is stable above 200°C, it has a reversible phase transition at 246°C.

A shoulder at ~367°C on the peak for the eutectic (376°C) indicates the existence of a second compound (dashed line in the phase diagram) which must have an incongruently melting point a little higher than the eutectic. Its composition is uncertain.

Crystal structures

Unit cell parameters of all ternary samarium bromides together with molar volumes of the compounds are compiled in Table 1. Already known values are marked by references to literature. For KSm_2Cl_7 only the strongest reflections could be observed because of distinct texture effects; the cell parameters are not corrected.

The complete crystal structure of the hydrate $SmBr_3{\cdot}6H_2O$ was determined with single crystal methods. A yellow crystal (0.18×0.2×0.3 mm) was obtained by evaporation of a concentrated solution at ambient temperature. The monoclinic cell (space group P2/n) for two formula units is:

$$a=817(1)\ \text{pm};\ b=656.7(1)\ \text{pm};\ c=1003.0(2)\ \text{pm};\ \beta=93.53(1)^\circ.$$

The characteristic data for the structure determination and the yielded site parameters and isotropic temperature factors Ueq are given in Table 2; a sketch of the unit cell together with bond-lengths is to be seen in Fig. 2.

$SmBr_6{\cdot}6H_2O$ is isotypic with the hexahydrates $LnCl_3{\cdot}6H_2O$, the structure of which is with most details described for $PrCl_3{\cdot}6H_2O$ [9]. It contains $[SmBr_2(H_2O)_6]^+$-units and isolated Br^--anions. The polyhedron with the coordination number 8 for samarium can be described as a square antiprism.

Thermodynamic measurements

The solution enthalpy for $SmBr_3$ was found to be −194.6±1.2 kJ mol^{-1}. The solution enthalpies for the alkali metal bromides are: CsBr=20.3(1) (Lit.: 20.29 [10]; RbBr=22.2(1) (Lit.: 22.18 [11, 12]); KBr=26.2(1) (Lit.: 26.22 [10]).

The solution enthalpies for the ternary bromides, stable at ambient temperature (all compounds except K_3SmBr_6 and Na_3SmBr_6) together with the calculated reaction enthalpies for the formation from $nABr+SmBr_3$ ($\Delta_f H^\circ$) and from the adjacent compounds in the systems ($\Delta_{syn}H^\circ$) are compiled in Table 3.

E.m.f. measurements on ternary samarium bromides were restricted by two limits: 1) the temperature must be lower than ~700 K; 2) $SmBr_3$-rich com-

Table 1 Unit cell parameters of ternary samarium bromides

Compound	S. g.	*a*/pm	*b*/pm	*c*/pm	β/ °	V_m/cm^3 mol^{-1}	ΔV_m^*/cm^3 mol^{-1}
H-Cs_3SmBr_6**	*Fm3m*	1241.9(9)				288.42(7)	+40.4
H-Rb_3SmBr_6**	*Fm3m*	1180.2(4)				247.50(9)	+31.3
H-K_3SmBr_6**	*Fm3m*	1161.5(4)				235.93(1)	+35.3
L-Cs_3SmBr_6	*C2/c*	2832.8(8)	856.3(9)	1380.0(2)	99.66(3)	248.43(9)	+0.4
L-Rb_3SmBr_6	*C2/c*	2727.3(8)	832.4(4)	1360.4(6)	99.12(1)	229.56(6)	+13.4
L-K_3SmBr_6	$P2_1/c$	1395.4(6)	819.2(1)	1340.6(4)	110.56(9)	216.01(9)	+15.4
H-Na_3SmBr_6**	$P2_1/n$	726.4(1)	759.2(6)	1056.5(3)	93.01(3)	175.21(1)	+8.2
L-Na_3SmBr_6	$R\bar{3}$	740.4(7)		1997.0(6)		190.35(5)	+23.3
Cs_2SmBr_5	*Pbnm*	1009.9(1)	795.1(5)	1600.8(6)		193.53(7)	+4.6
Rb_2SmBr_5[8]	*Pnma*	1365.3(6)	927.6(3)	859.3(5)		163.87(1)	–3.8
K_2SmBr_5[8]	*Pnma*	1328.3(1)	911.4(9)	840.6(7)		153.23(6)	–4.1
$Cs_3Sm_2Br_9$[4]	$R\bar{3}c$	1380.7(5)		1942.9(0)		322.24(8)	+3.5
$CsSm_2Br_7$	*Pnma*	1382.3(8)	745.0(8)	1357.6(1)		210.51(7)	+10.0
$RbSm_2Br_7$	*Pnma*	1362.7(2)	743.1(7)	1351.9(7)		206.13(1)	+16.2
KSm_2Br_7	$P2_1/c$	737.8	1332.2	1351.8	91.46	200.12	+26.6

*$\Delta V_m = V_m(\text{exp.}) - \sum V_m$; $\sum V_m = nV_m\,(\text{ABr}) + V_m(\text{SmBr}_3)$ mit V_m von $SmBr_3$ = 70.7 cm^3 mol^{-1}; CsBr = 59.1 cm^3 mol^{-1}; RbBr = 48.5 m^3 mol^{-1}; KBr = 43.3 cm^3 mol^{-1}; NaBr = 32.1 cm^3 mol^{-1}

** exposition temperature: 500°C; for H–Na_3SmBr_6: 400°C

Table 2 Experimental data and structure refinement parameters for $SmBr_3{\cdot}6H_2O$

Crystal data	
Formula	$SmBr_3{\cdot}6H_2O$
Color	yellow
Crystal system	monoclinic
Space Group, Number of F. U.	P2/n, Z = 2
Lattice parameters [pm, °]	a =817.10(10), b=656.70(10), c =1003.0(2), β = 93.530(10)
Volume [10^6 pm^3]	537.2(2)
Calculated density [g cm^{-3}]	3.005
Temperature	293(2) K
Reflections	25
Absorption coefficient μ [mm^{-1}]	16.603 numeric absorption corrections
Data collection	
Instrument	four-circle diffractometer, Enraf-Nonius CAD4
Radiation	$Mo_{K\alpha}$ (graphite/monochromator)
Scan-width (ω-scan)	1.0° + 0.70(tan Θ)°
Scan speed	variable, max. 30 sec./reflection
Range	2Θ: 6.24–57.10° $-10 \leq h \leq 10$, $-8 \leq k \leq 0$, $-13 \leq l \leq 13$
Reflections measured (gesamt /independent)	2643/1328
Agreement factors of equivalent reflections	R_{int} = 0.1474
Stucture refinement	
Absorption correction	full-matrix, least-squares
Number of refined parameters	106
Daten/Parameter	1280/48
Goodness of Fit	1.239
Reliability factors	R = 0.0395, wR2 = 0.0873

Atomic positions and equivalent thermal parameters/pm^2

	x	y	z	U_{eq}
Sm	0.2500	0.6637(1)	0.7500	12(1)
Br(1)	0.2597(1)	0.3401(1)	0.5529(1)	24(1)
Br(2)	0.2500	−0.1318(1)	0.2500	26(1)
O(1)	0.1093(6)	0.8088(5)	0.9337(6)	26(1)
O(2)	−0.0369(5)	0.5609(5)	0.7233(6)	24(1)
O(3)	0.0902(6)	0.9286(5)	0.6480(6)	30(1)

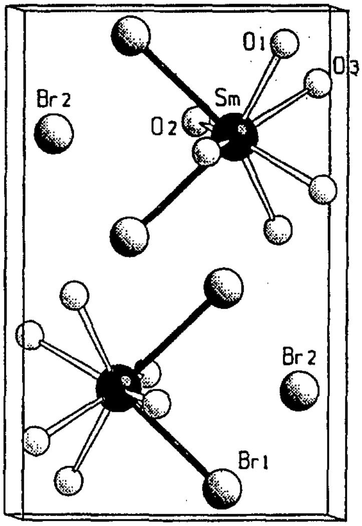

Fig. 2 Crystal structure of $SmBr_3 \cdot 6H_2O$
Bond distances [pm]: Sm–Br (1) 290.66(7) Sm-0(1) 242.6(4) Sm-0(2) 243.8(4) Sm-0(3) 236.9(4)

pounds reacted with the silicate of the diaphragms – an effect, we had already observed with chlorides of the smaller lanthanides. As consequence, only measurement on Rb_3SmBr_6 and K_3SmBr_6 could be performed.

Reaction: $RbBr+Rb_2SmBr_5=L\text{-}Rb_3SmBr_6$ Temp. range: 655–700 K
Sample: 30 mol% $SmBr_3$. Measured points: 10 Δ_rG° id. $\Delta_{syn}G^\circ$
e.m.f./mV= –107.9(8)+0.417(12) *T*/K; Δ_rG°/kJ mol^{-1}= 10.4–0.0402 *T*/K
$\Delta_{syn}H^\circ$= 10.4±0.8 kJ mol^{-1}. From sol. calorim.: 10.1 kJ mol^{-1}.
$\Delta_{syn}S^\circ$=40.2±0.1 J K^{-1} min^{-1} $\Delta_{syn}G^\circ$=0 at 259 K (–14°C)

Reaction: $KBr+K_2SmBr_5=L\text{-}K_3SmBr_6$ Temp. range: 575–690 K
Sample: 30 mol% $SmBr_3$. Measured points: 58 Δ_rG° id. $\Delta_{syn}G^\circ$
e.m.f./mV= –287(3.3)+0.521(5) *T*/K; Δ_rG°/kJ mol^{-1}=27.7–0.0503 *T*/K
$\Delta_{syn}H^\circ$=27.7±0.3 kJ mol^{-1}. From sol. calorim.:–
$\Delta_{syn}S^\circ$=50.3±0.5 J k^{-1} mol^{-1}
$\Delta_{syn}G^\circ$=0 at 552 K (279°C). From DTA heating curves: 298°C.

It must be pointed out that the overheating of 19 K is not uncommon for reconstructive phase transitions, and formation or decomposition reactions in the solid state can be treated as a special kind of reconstructive transitions. Otherwise, the undercooling is so great that the decomposition could not be observed at all in the time-scale of DTA.

Table 3 Solution enthalpies and derived values in kJ mol^{-1}

Compound	$\Delta_L H^\circ_{298}$	$\Delta_f H^\circ_{298}$	$\Delta_{Syn} H^\circ_{298}$	Synproportionation from:
Cs_3SmBr_6	−65.7	−50.3	−18.5	$CsBr+CS_2SmBr_5$
Cs_2SmBr_5	−110.4	−31.8	+6.4	$1/3Cs_3SmBr_6+2/3Cs_{1.5}SmBr_{4.5}$
$Cs_{1.5}SmBr_{4.5}$	−123.1	−32.3	−4.4	$2/3Cs_2SmBr_5+1/3Cs_{0.5}SmBr_{3.5}$
$Cs_{0.5}SmBr_{3.5}$	−161.7	−19.8	−9.1	$1/3Cs_{1.5}SmBr_{4.5}+2/3SmBr_3$
Rb_3SmBr_6	−93.6	−34.4	+10.1	$RbBr+Rb_2SmBr_5$
Rb_2SmBr_5	−105.7	−44.5	−20.9	$0.6Rb_3SmBr_6+0.4Rb_{0.5}SmBr_{3.5}$
$Rb_{0.5}SmBr_{3.5}$	−176.0	−7.5	+3.6	$0.25Rb_2SmBr_5+0.75SmBr_3$
K_2SmBr_5	−123.8	−30.2	−31.1	$1.5KBr+K_{0.5}SmBr_{3.5}$
$K_{0.5}SmBr_{3.5}$	−184.4	+0.9	+8.4	$0.25K_2SmBr_5+07.5SmBr_3$

$\Delta_L H^\circ_{298}$ = solution enthalpy; $\Delta_f H^\circ_{298}$ = formation from ABr and $SmBr_3$; $\Delta_{Syn} H^\circ_{298}$ = Synproportionation enthalpy

Enthalpies of the (reversible) transitions L-A_3SmBr_6→H-A_3SmBr_6 which occur for A=Cs, Rb, K between 400 and 460°C were determined by DSC measurements on at least three samples for each compound. For calibration the following substances were used according to the recommendation of GEFTA [13]. In =227.8 J g^{-1} at 156.6°C; Sn=60.4 J g^{-1} at 231.9°C; Li_2SO_4= 227.8 J g^{-1} at 578.3°C; Al=398.1 J g^{-1} at 660.3°C.

Results for $\Delta_{trans}H^\circ$: Cs_3SmBr_6: 6.93±0.1 kJ mol^{-1}; Rb_3SmBr_6: 7.0± 0.3 kJ mol^{-1}; K_3SmBr_6: 6.79±0.1 kJ mol^{-1}.

Discussion

In Table 4 the entirety of compounds in the systems of $SmBr_3$ is compared with those in the systems of $LaBr_3$ and $SmCl_3$. Two effects must be considered: a) the increased ionic radius of Br^- (196 pm) compared with Cl^{-1} (181 pm); b) the different radii of La^{3+} (106.1 pm) and Sm^{3+} (96.4 pm). (The cation radii are effective ionic radii for the CN 6, based or $r(^{VI}O^{2-})=1.40$ Å [14]).

a) The effect of the halide ions is minor, the NaX-systems excepted: The main difference is the existence of the ennea-bromide $Cs_3Sm_2Br_9$ with isolated pairs of face-sharing octahedra. For chloro compounds the first ennea-chloride is $Cs_3Er_2Cl_9$. In both cases the ratio $r(Ln^{3+})/r(X^-)$ is 0.49 ($r(Er^{3+})=88.1$ pm).

The Sm–Br distance of 290.7 pm in $SmBr_3{\cdot}6H_2O$ is the first one experimentally determined. With $r(^{VIII}Sm^{3+})=109$ pm for the CN 8 a theoretical distance of 305 pm results. The shortening of 14 pm is to be explained with the polarization of the terminal bromide ion by the threefold charged samarium ion.

b) Changing over from lanthanum to samarium leads to an increase in the number of 3:1- and 1:2-compounds (A_3SmBr_6 with A=K, Na; ASm_2Br_7 with A=Rb, K). This can be related to the fact that the 'bromide cages', accomodat-

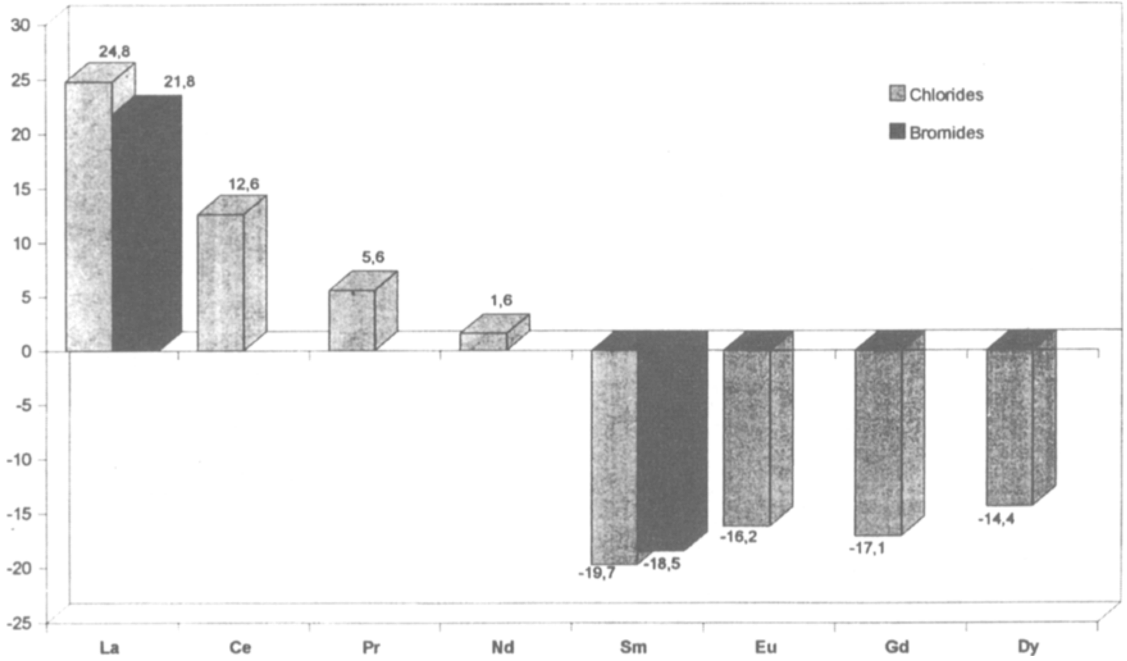

Fig. 3 $\Delta_{syn}H^{\circ}$ values for $CsX+Cs_2LnX_5=Cs_3\ Ln_6$ in kJ mol^{-1}

Table 4 Compounds in the systems of $LaBr_3$, $SmBr_3$ and $SmCl_3$

	$LaBr_3$			$SmBr_3$				$SmCl_3$		
	3:1	2:1	1:2	3:1	2:1	3:2	1:2	3:1	2:1	1:2
Cs	+	+	+	+	+	+	+	+	+	+
Rb	+	+	–	+	+	–	+	+	+	+
K	–	+	–	+	+	–	+	+	+	+
Na	–	–	–	+	–	–	–	–	+	–

ing the alkali ions, have become smaller. The number of 2:1-compound has remained unchanged, however, Cs_2SmBr_5 has the Cs_2DyCl_5 structure with connected octahedra – the same behaviour as found with Cs_2SmCl_5 [15]. This can be seen very clearly in Fig. 3. As shown earlier for the chloro compounds alone [1], the enthalpies for the synproportionation reactions $CsX+Cs_2LnX_5 = Cs_3LnX_6$ become negative from samarium, because the compounds Cs_2LnCl_2 are now formed from 2:1-compounds, with coordination octahedra and not as before from seven-coordinated lanthanide compounds.

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