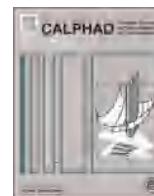




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# CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry

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## Calculation and optimization of LaBr<sub>3</sub>–MBr (Li–Cs) phase diagrams by CALPHAD method

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### ABSTRACT

Phase diagram of LaBr<sub>3</sub>–MBr (M=Li–Cs) pseudo-binary systems were reassessed by CALPHAD method with Associate Model and Redlich–Kister Model. In addition the LaBr<sub>3</sub>–LiBr system was optimized through the application of the Quasichemical Model, and LaBr<sub>3</sub>–RbBr system was optimized by Partially Ionic Two-sublattice Model. Optimized thermodynamic properties were compared with the data previously calculated by Quasichemical Model and Partially Ionic Two-sublattice Model as well as with experimental data. The influence of the used models for calculated thermodynamic properties has been discussed.

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### 1. Introduction

Thermodynamic modeling is the critical assessment of all available data from literature of thermochemical properties in the system. This includes all available experimental data and descriptions of previously published phase diagrams and assessments. The aim of the CALPHAD method is to find a consistent description of the phase diagram and the thermodynamic properties of investigated system. This paper presents the results of optimization and calculation of the phase diagrams of lanthanide halide – alkali metal halide systems by the CALPHAD method, using various models for description of liquid phase [1–3]. Each diagram describes the liquid phase of the system with one model only. Therefore one of the aims of this work was to assess the influence of used model on thermodynamic properties of the lanthanide halide-alkali metal halide pseudo-binary systems. For this purpose LaBr<sub>3</sub>–MBr (M=Li–Cs) were reassessed by the CALPHAD method with: Redlich–Kister Model [4], which is a typically used mathematical model (regular solution), Associate Model [5], Partially Ionic Two-sublattice Model [6] and Quasichemical Model Modified by Pelton and Blander [7], which focus on physical properties. Physical models take into account the nature of the liquid phase, although they are more complicated than

mathematical models. The usability and modifications of models describing various interactions between molecules and ions in liquid phase were also discussed by Krull et al. [8], Besmann and Spear [9] and Saulov et al. [10,11]. The consideration of the Associate Model also concerns the so called “entropy paradox”. The paradox lies in the fact that the configurational entropy, which is a measure of disorder, appears to be higher in a solution with ordering than in a completely disordered solution. This is true for relatively small amount of associate. Some aspects of this problem are discussed in next part of this work. The model used to describe the liquid phase determines the results obtained for the solid phases in the investigated system. The small differences between results of various models may significantly impact the further interpretation. It is preferred to minimize the number of coefficients because it facilitates the process of optimization. The Redlich–Kister Model was treated as a reference model for comparisons.

The experimental data, which were used for construction of the phase diagrams (liquidus points and enthalpy of mixing) are usually obtained at high temperatures. Extrapolation of this data down to ambient temperatures may lead to relatively high errors. Therefore, the next aim of this paper was to verify the compatibility of the data at standard conditions and in high temperatures by the CALPHAD method. For this purpose, the values of formation enthalpies measured by Seifert and Yuan [12] at standard conditions of ternary compounds were used to verify the thermodynamic interpretation of the data at wide temperature range.

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## 2. Thermodynamic models

### 2.1. Redlich–Kister Model (RKM)

The Redlich–Kister Model [4] is the most common standard model for solution modeling. This model is based upon the sub-regular solution however it is extension of modeling of all kinds asymmetric shapes. The Redlich–Kister Model assumes development of sub-regular solution model, because in this case interaction energies change with composition in a non-linear manner. This model is useful for substitutional phases in simple metallic systems. The complexity of the polynomial equation is selected relatively to obtained experimental data. The Redlich–Kister Model is typical mathematical representation of thermodynamic properties of phases. The Gibbs excess energy of mixing is given by formula:

$$G^{\text{ex}} = x_{\text{MBr}} x_{\text{LaBr}_3} \sum_{i=0}^n K_i (x_{\text{MBr}} - x_{\text{LaBr}_3})^i \quad (1)$$

The Gibbs energy is given by equation:

$$G^\circ(T) - H^{\text{SER}} = [{}^0G_{\text{MBr}}^\circ(T) - {}^0H_{\text{MBr}}^{\text{SER}}(298.15 \text{ K})] x_{\text{MBr}} + [{}^0G_{\text{LaBr}_3}^\circ(T) - {}^0H_{\text{LaBr}_3}^{\text{SER}}(298.15 \text{ K})] x_{\text{LaBr}_3} + RT \left[ x_{\text{MBr}} \ln(x_{\text{MBr}}) + x_{\text{LaBr}_3} \ln(x_{\text{LaBr}_3}) \right] + x_{\text{MBr}} x_{\text{LaBr}_3} \sum_{i=0}^n K_{3+i} (x_{\text{MBr}} - x_{\text{LaBr}_3})^i \quad (2)$$

Redlich et al. [4] gave a detailed description of the Redlich–Kister. Physical meaning of the variables in the Eqs. (1) and (2) are explained in paragraph 2.5.

### 2.2. Associate Solution Model (ASM)

The Associate Model [5] is one of ionic liquid models. This model can be used when describing the properties of alloy that melts with compound formation tendency indicating chemical short-range order. It assumes the following formation of associates:  $pA + qB = A_pB_q$ . The liquid phase is therefore treated as though it is composed of a molecular species  $A_pB_q$  in equilibrium with species A and B ( $n_{\text{Al}}$  and  $n_{\text{Bl}}$ ). The mole fractions of A, B and  $A_pB_q$  in a system containing 1 mole of A and B atoms, are given by equations [13]:

$$x_{\text{A}} = n_{\text{Al}} + pn_{\text{A}_p\text{B}_q}; \quad x_{\text{B}} = n_{\text{Bl}} + qn_{\text{A}_p\text{B}_q}; \quad x_{\text{A}_p\text{B}_q} = n_{\text{A}_p\text{B}_q} \quad (3)$$

The excess Gibbs energy of mixing is given by the general formula [13]:

$$G^{\text{ex}} = G^{\text{ass}} + G^{\text{reg}} \quad (4)$$

$G^{\text{ass}}$  and  $G^{\text{reg}}$  are defined as:

$$G^{\text{ass}} = n_{\text{A}_p\text{B}_q} G_{\text{A}_p\text{B}_q}^\circ \quad (5)$$

$$G^{\text{reg}} = G_{\text{A,B}}^{\text{reg}} n_{\text{Al}} n_{\text{Bl}} / n + G_{\text{A,A}_p\text{B}_q}^{\text{reg}} n_{\text{Al}} n_{\text{A}_p\text{B}_q} / n + G_{\text{B,A}_p\text{B}_q}^{\text{reg}} n_{\text{Bl}} n_{\text{A}_p\text{B}_q} / n \quad (6)$$

Existence of an associate in a system often results in large deviation from regular behavior. The Associate Model calculations are based on fitting of experimental data for enthalpies of mixing. This approach allows selection of the most appropriate associate in the substantial number of cases. The enthalpies of mixing curves are often characterized by minimum near composition where the associate exist [13]. This is also marked by non-ideal mixing entropy. This phenomenon is observed in the case of  $\text{LnX}_3\text{--MX}$  systems (where  $\text{Ln}=\text{La}\dots\text{Lu}$ ,  $\text{M}=\text{Li}\dots\text{Cs}$  metal and  $\text{X}=\text{Cl}\dots\text{I}$ ) [14]. However, observed minima are not as sharp as in pure model.

Therefore the stoichiometry of associate (p/q), is described by iterating quantity. The model assumes that there is only one associate in the system ( $A_pB_q$ ). If the system finds the more than one type of associate, it is not always obvious which types of associates actually exist.

The Gibbs energy of liquid phase is given by equation:

$$G^\circ(T) - H^{\text{SER}} = K_1(1-x) + K_2x + RT [n_{\text{MBr}} \ln(n_{\text{MBr}}) + n_{\text{LaBr}_3} \ln(n_{\text{LaBr}_3}) + n_{\text{A}_p\text{B}_q} \ln(n_{\text{A}_p\text{B}_q}) - n \ln(n)] + K_3 n_{\text{A}_p\text{B}_q} + (K_4 n_{\text{MBr}} n_{\text{LaBr}_3} + K_5 n_{\text{MBr}} n_{\text{A}_p\text{B}_q} + K_6 n_{\text{LaBr}_3} n_{\text{A}_p\text{B}_q}) / n \quad (7)$$

$K_1$  and  $K_2$  have identical meaning to the other models.  $K_3$  describes the functions of formation of the associate, while  $K_4$  to  $K_6$  are polynomial interaction terms. A detailed description of the Associate Model was given by Sommer et al. [5]. Physical meaning of the variables in the Eq. (3)–(7) are explained in paragraph 2.5.

### 2.3. Partially Ionic Two-sublattice Liquid Model (PIM)

The Partially Ionic Two-sublattice Model is an extension of the sublattice model. Application of the sublattice model is limited to the systems where no neutral ions exist. The model proposed by Hillert et al. [6] overcomes this problem. This model uses several forms of artificial remediation to optimize the thermodynamics of different kind of systems, salts and alloys. In terms of mathematical properties this model and Associate Model are strongly related. The Partially Ionic Liquid Model can be used to describe the liquid phase in a pseudo-binary  $\text{LaBr}_3\text{--MBr}$  system. The Special Binary Case of Hillert's Model of Partially Ionic Liquids has the following form:  $(A^{+i})_p(B^{-j}, B, Va^{-i})_q$ . The more electropositive component forms cation sublattice (in case of  $\text{LaBr}_3\text{--RbBr}$  system it is  $(\text{Rb}^+)_p$ ), and gives it the natural valency  $(\text{Br}^-)_q$ . The  $\text{LaBr}_3$  component forms anion sublattice as  $(\text{LaBr}_6^{-3})_q$  and as neutral molecule  $(\text{LaBr}_3)_q$ .

The Gibbs excess energy of mixing is given by the following formula:

$$G^{\text{ex}} = K_3 y_{\text{LaBr}_3} + K_4 y_{\text{Br}^-} + K_5 y_{\text{LaBr}_6^{-3}} + K_6 y_{\text{LaBr}_3} y_{\text{Br}^-} + K_7 y_{\text{LaBr}_3} y_{\text{LaBr}_6^{-3}} + K_8 y_{\text{Br}^-} y_{\text{LaBr}_6^{-3}} + K_9 y_{\text{LaBr}_3} y_{\text{Br}^-} (y_{\text{LaBr}_3} y_{\text{Br}^-}) \quad (8)$$

The Gibbs energy is given by equation:

$$G^\circ(T) - H^{\text{SER}} = \left[ ({}^0G_{\text{MBr}}^{\text{ref}}(T) - {}^0H_{\text{MBr}}^{\text{SER}}) x_{\text{MBr}} + ({}^0G_{\text{LaBr}_3}^{\text{ref}}(T) - {}^0H_{\text{LaBr}_3}^{\text{SER}}) x_{\text{LaBr}_3} \right] N + RTp2 \left[ y_{\text{LaBr}_3} \ln(y_{\text{LaBr}_3}) + y_{\text{Br}^-} \ln(y_{\text{Br}^-}) + y_{\text{LaBr}_6^{-3}} \ln(y_{\text{LaBr}_6^{-3}}) \right] + G^{\text{ex}} \quad (9)$$

Hillert et al. [6] gave a detailed description of the Partially Ionic Two-sublattice Model. Physical meaning of the variables in the Eqs. (8) and (9) is explained in paragraph 2.5.

### 2.4. Quasichemical Model Modified by Pelton and Blander (QM)

The Quasichemical Model Modified by Pelton and Blander belongs to the family of ionic liquid models. The model can be widely applied, especially to molten oxide or molten salts. A detailed description of the Modified Quasichemical Model was given by Pelton and Blander [7]. It assumes a strong tendency to order in liquid phase around specific composition. This specific composition is determined by specific physical or chemical phenomena [13]. The quasichemical theory assumes that in a binary system

with components “A” and “B” particles mix substitutionally on a quasi-lattice with a constant coordination number  $z$ . It also assumes existence of three types of nearest-neighbor pairs (A–A, B–B, A–B). When components are mixed, A–B pairs are formed at the expense of A–A and B–B pairs by the following reaction:



(If the molar Gibbs energy of reaction (Eq. (7)) is zero the solution is ideal. For non-ideal solutions, the composition of the maximum ordering is fixed by ratio  $r$  [7].

In the model, the Gibbs excess energy of mixing is given by the following formula:

$$G^{ex} = (Rz)/2T \left[ X_{11} \ln(X_{11}/X_{MBr}^2) + X_{22} \ln(X_{22}/X_{LaBr_3}^2) + X_{12} \ln(X_{12}/2X_{MBr}X_{LaBr_3}) \right] + Y_{MBr}Y_{LaBr_3} S_{i=0}^n K_{3+i} (x_{MBr} - x_{LaBr_3})^i \tag{11}$$

We use polynomial excess terms by Redlich–Kister Model implemented in BINGSS program. We assumed that the influence of kind of polynomial in this model is negligible for the purpose of this paper.

The Gibbs energy is expressed by the following equation:

$$G^\circ(T) - H^{SER} = \left[ \left( {}^0G_{MBr}^{ref}(T) - {}^0H_{MBr}^{SER} \right) x_{MBr} + \left( {}^0G_{LaBr_3}^{ref}(T) - {}^0H_{LaBr_3}^{SER} \right) x_{LaBr_3} \right] + RT \left[ x_{LaBr_3} \ln(x_{LaBr_3}) + x_{LaBr_3} \ln(x_{LaBr_3}) \right] + G^{ex} \tag{12}$$

### 2.5. Physical meaning of the variables

The temperature dependence of the Gibbs energy of a pure element or any composition of the LaBr<sub>3</sub>–MBr systems is given by the following formula (SGTE description):

$$G^\circ(T) - H_i^{SER}(298.15 \text{ K}) = A + BT + CT \ln(T) + DT^2 + ET^{-1} + FT^3 \tag{13}$$

The explanation of all the variables in the equations (Eq. (1)–(13)) that describe each of the models is described below:

- $G^\circ$  Gibbs energy of phase  $\phi$ ,
- $G^{ass}$  Gibbs energy of formation of the associate
- $G_{A_p B_q}^\circ$  Gibbs energy of formation of one mole of associate
- $G_{FeG}$  Gibbs energy of interactions between the species A and B themselves and with associate  $A_p B_q$
- $H^{SER}$  enthalpy of pure elements at 298.15 K in their stable states (enthalpy of “stable element reference”),

- $K_i$  each  $K_i$  is given as function of temperature after Eq. (5) by the  $i$ th line of coefficients (if the coefficient  $K_i$  contains A and B values only, the coefficient  $A_i$  describes enthalpy of mixing, and the coefficient  $B_i$  describes entropy of mixing),
  - $K_1$  contribution to  ${}^{ref}G^\circ$  from component LaBr<sub>3</sub>,  ${}^0G_{LaBr_3}^\circ(T) - {}^0G_{LaBr_3}^{ref}(T)$
  - $K_2$  contribution to  ${}^{ref}G^\circ$  from component MBr, T–T.
- For stable phases, equation: T–T, is set equal to zero.
- $x$  concentration of sample,
  - $y_i$  site fraction of component  $i$ ,
  - $n_i$  moles of component  $i$  in 1 mole of atoms,
  - $n_{ApBq}$  moles of associate in 1 mole of atoms,
  - $n$  the total number of moles,
  - $N$  the total number of atoms in the formula (vacancies are not counted),
  - $p2$  the number of lattice sites of this sublattice in one mole of formula units.
  - $X_{ij}$  the fraction of nearest-neighbor pairs which are  $i$ – $j$  pairs. It is defined as:  $X_{ij} = n_{ij} / (n_{11} + n_{22} + n_{12})$ , where  $n_{ij}$  is the number of moles of each type of pair in solution.

### 3. Calculation and optimization procedure

The calculation by the CALPHAD method was made using data of pure system components presented by Kubashewski et al. [15] for alkali metal bromides and presented by Rycerz and Gaune-Escard [16] for LaBr<sub>3</sub> compound. The coefficients of Eq. (13) for pure system components are presented in Table 1. The LaBr<sub>3</sub>–LiBr phase diagram has been measured by Rycerz et al. [17], while the LaBr<sub>3</sub>–NaBr, LaBr<sub>3</sub>–KBr, LaBr<sub>3</sub>–RbBr and LaBr<sub>3</sub>–CsBr phase diagrams have been measured by Seifert et al. [12]. The experiments prove that the LaBr<sub>3</sub>–LiBr and LaBr<sub>3</sub>–NaBr systems are simple eutectic systems. In LaBr<sub>3</sub>–KBr system exists only congruently melting  $K_2LaBr_5$  compound. In case of LaBr<sub>3</sub>–RbBr and LaBr<sub>3</sub>–CsBr systems there are congruently melting  $M_3LaBr_6$  compounds and incongruently melting  $M_2LaBr_5$  compounds. In addition LaBr<sub>3</sub>–CsBr system displays existence of  $CsLa_2Br_7$  compound that melts incongruently.

The experimental data were obtained by digitization of phase diagrams [12,17]. The mixing enthalpies of LaBr<sub>3</sub> mole fraction were given by Gaune-Escard et al. [18]. The negligible difference between heat capacity measured by Rycerz and Gaune-Escard [16] and obtained by Neumann–Kopp rule had been observed for whole temperature range for all compounds formed in

**Table 1**  
The coefficients used in Eq. (13) which describes properties of pure alkali halides, used in this work.

Compound	T range/K	A	B	C	D × 10 <sup>3</sup>	E × 10 <sup>−5</sup>	F × 10 <sup>6</sup>	Ref.
LiBr (s)	298–823	−8443.35	136.79	−30.25	−20.69	−3.60	0	[15]
LiBr (l)	Above 823	−6425.72	351.87	−65.27	0	0	0	[15]
NaBr (s)	298–1020	−14875.95	237.95	−47.91	−6.66	0	0	[15]
NaBr (l)	Above 1020	3429.31	313.18	−62.34	0	0	0	[15]
KBr (s)	298–1007	−21169.55	359.37	−69.16	22.78	3.24	−7.50	[15]
KBr (l)	Above 1007	−3516.05	362.40	−69.87	0	0	0	[15]
RbBr (s)	298–965	−15193.91	223.84	−49.37	−5.33	0	0	[15]
RbBr (l)	Above 965	−3880.88	327.71	−66.94	0	0	0	[15]
CsBr (s)	298–911	−15400.37	226.97	−50.38	−4.27	0	0	[15]
CsBr (l)	Above 911	−12871.83	404.43	−77.40	0	0	0	[15]
LaBr <sub>3</sub> (s)	298–1058	−29659.47	470.18	−96.48	−10.06	0	0	[16]
LaBr <sub>3</sub> (l)	Above 1058	−25011.70	835.67	−151.12	0	0	0	[16]

**Table 2**The comparison of calculated values of coefficients of Eqs. (2), (7), (9), (12) for the  $\text{LaBr}_3\text{-MBr}$  ( $\text{M}=\text{Li-Cs}$ ) system. All data are in  $\text{J mol}^{-1}$  for one mole of solution.

Model	Calculated coefficients							Main associate / $x(\text{LaBr}_3)$
	$K_3$	$K_4$	$K_5$	$K_6$	$K_7$	$K_8$	$K_9$	
<b>LaBr<sub>3</sub>-LiBr</b>								
Associate Model	-2400+9.0T	-1000-6.0T	-8200	-3200+4.0T				0.50
Redlich-Kister Model	-3300-6.5T	-1800	1700					-
Quasichemical Model	-8700-17.5T	2000	4500					0.50
<b>LaBr<sub>3</sub>-NaBr</b>								
Associate Model	-1500-6.9T	-8700	-26,700	-14,800				0.50
Redlich-Kister Model	-19,000-10.4T	-7600						-
<b>LaBr<sub>3</sub>-KBr</b>								
Associate Model	-25,250+15.0T	-40,000+3.0T	-40,500-15.0T	-40,000-26.0T				0.33
Redlich-Kister Model	-48,800-3.1T	-15,500+4.4T	-8000					-
<b>LaBr<sub>3</sub>-RbBr</b>								
Associate Model	-80,200+39.0T	-46,400-8.0T	-20,000+5.0T	-47,000-43.0T				0.25
Redlich-Kister Model	-66,680	3000+20.0T	3900	10,000				-
Partially Ionic Two-sublattice Model	-19,500	-6500	45,000	-16,000	22,000-10.1T	-20,000	31,000	0.25
<b>LaBr<sub>3</sub>-CsBr</b>								
Associate Model	-71,000+27.0T	-63,000+4.0T	-34,000+3.0T	-57,000-30.0T				0.25
Redlich-Kister Model	-75,000+2.9T	-28,000+5.0T	-8000	3000				-

**Table 3**The comparison of thermodynamics properties of intermediate compounds. All data are in  $\text{J mol}^{-1}$  for one mole of solution.  $\Delta_f G^\circ = \Delta_f H^\circ - T\Delta_f S^\circ$ .

Parameter	Calculated coefficient				Experimental values
	ASM	RKM	PIM	QM	
<b>K<sub>2</sub>LaBr<sub>5</sub></b>					
$\Delta_f H^\circ$	-8919.0	-12000.0	-20777.7 <sup>[2]</sup>	-6833.3 <sup>[1]</sup>	-6833.3 <sup>[12]</sup>
$\Delta_f S^\circ$	4.0	0.3	-4.0 <sup>[2]</sup>	-1.7 <sup>[1]</sup>	5.0 <sup>[12]</sup>
$\Delta_f G^\circ(298\text{ K})$	-10111.0	-12089.4	-19585.7 <sup>[2]</sup>	-6326.7 <sup>[1]</sup>	-8323.3 <sup>[12]</sup>
<b>Rb<sub>3</sub>LaBr<sub>6</sub></b>					
$\Delta_f H^\circ$	5862.6	3725.5	4055.3	6198.4 <sup>[1]</sup>	3775.0 <sup>[12]</sup>
$\Delta_f S^\circ$	22.9	21.0	23.4	-24.3 <sup>[1]</sup>	15.8 <sup>[12]</sup>
$\Delta_f G^\circ(701\text{ K})$	-10252.6	-10995.5	-12620.4	23222.4 <sup>[1]</sup>	-8201.4 <sup>[12]</sup>
<b>Rb<sub>2</sub>LaBr<sub>5</sub></b>					
$\Delta_f H^\circ$	-13850.8	-12813.2	-11894.0	-9291.9 <sup>[1]</sup>	-9300.0 <sup>[12]</sup>
$\Delta_f S^\circ$	2.4	-9.0	6.9	-7.4 <sup>[1]</sup>	0.5 <sup>[12]</sup>
$\Delta_f G^\circ(298\text{ K})$	-13923.0	-21657.2	-14992.6	-7072.0 <sup>[1]</sup>	-9704.3 <sup>[12]</sup>
<b>H-Cs<sub>3</sub>LaBr<sub>6</sub></b>					
$\Delta_f H^\circ$	-3273.1	-14123.5	1182.3 <sup>a</sup>	-1600.3 <sup>[1]</sup>	750.0 <sup>[12]</sup>
$\Delta_f S^\circ$	17.4	8.0	18.9 <sup>a</sup>	-16.0 <sup>[1]</sup>	18.0 <sup>[12]</sup>
$\Delta_f G^\circ(721\text{ K})$	-15818.0	-19894.5	-11775.5 <sup>a</sup>	9935.7 <sup>[1]</sup>	-12228.0 <sup>[12]</sup>
<b>L-Cs<sub>3</sub>LaBr<sub>6</sub></b>					
$\Delta_f H^\circ$	5756.9	-12034.1	-1668.7 <sup>a</sup>	-1600.3 <sup>[1]</sup>	-1600.0 <sup>[12]</sup>
$\Delta_f S^\circ$	29.9	10.9	14.6 <sup>a</sup>	-16.0 <sup>[1]</sup>	14.6 <sup>[12]</sup>
$\Delta_f G^\circ(298\text{ K})$	-3153.3	-15282.3	-6039.0 <sup>a</sup>	3167.7 <sup>[1]</sup>	-5950.8 <sup>[12]</sup>
<b>Cs<sub>2</sub>LaBr<sub>5</sub></b>					
$\Delta_f H^\circ$	-8126.0	-14900.0	569585 <sup>a</sup>	-8205.0 <sup>[1]</sup>	-8200.0 <sup>[12]</sup>
$\Delta_f S^\circ$	10.0	4.5	-126.4 <sup>a</sup>	-6.6 <sup>[1]</sup>	4.7 <sup>[12]</sup>
$\Delta_f G^\circ(298\text{ K})$	-11106.0	-16241.0	607500 <sup>a</sup>	-6238.2 <sup>[1]</sup>	-9600.6 <sup>[12]</sup>
<b>CsLa<sub>2</sub>Br<sub>7</sub></b>					
$\Delta_f H^\circ$	-9542.5	9543.2	160,840 <sup>a</sup>	-2127.5 <sup>[1]</sup>	-1066.7 <sup>[12]</sup>
$\Delta_f S^\circ$	1.3	25.6	12.9 <sup>a</sup>	-9.0 <sup>[1]</sup>	2.5 <sup>[12]</sup>
$\Delta_f G^\circ(298\text{ K})$	-9929.9	1914.7	164,726 <sup>a</sup>	554.5 <sup>[1]</sup>	-1811.7 <sup>[12]</sup>

<sup>a</sup> The reference [22] contains not enough data to comparison. The values were calculated using data from references cited there.

investigation systems. This means that enthalpy of formation and entropy of formation is not dependent on temperature.

All calculations were made by BINGSS and BINFKT programs of Lukas et al. [19] and the special management program PHDMAN [20] was used for fast optimization. The PHDMAN was expanded for fast data change in trial-and-error approach and Bayes regression. The process of optimization of the phase diagram is discussed below:

1. Preparation of appropriate data in supported format, used by the programs.

2. Fitting curves, which represent the dependence of interaction parameter ( $\lambda$ ) and mixing enthalpy ( $\Delta H^{\text{MIX}}$ ) on mole fraction of  $\text{LaBr}_3$ . The Gibbs energies of mixing were modeled by the formula Eqs. (2), (7), (9), (12) depends on chosen model. In this step we change only the  $A_i$  coefficient for liquid phase to fit the curves. Optimized results should be in a good agreement with experimental data.
3. Finding a good fit of liquidus and eutectic points with iteration method by changing the parameters, which describe solid and liquid phases. Eq. (13) describes the thermodynamic properties (Gibbs energy of formation) of solid phases in these systems, obtained by the CALPHAD method. In this step we change all of

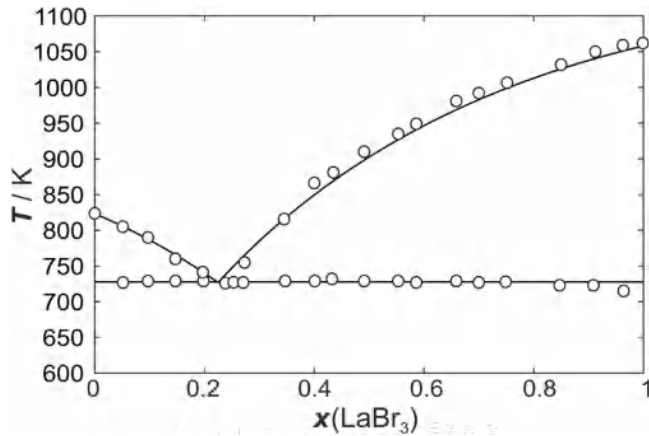


Fig. 1. The measured and calculated phase diagram of the  $\text{LaBr}_3$ -LiBr system. All models give the same results. Open circles – experimental data [17].

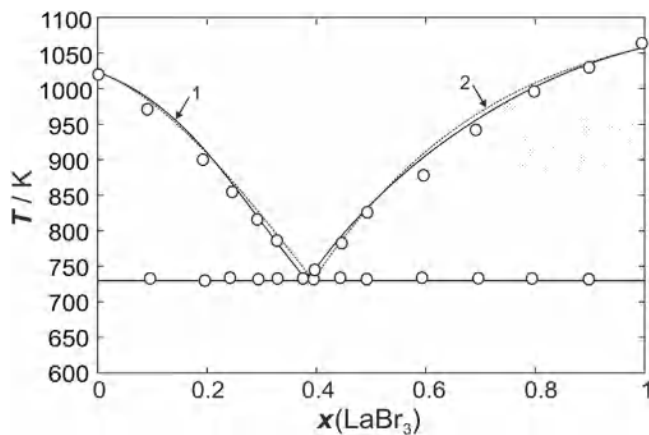


Fig. 2. The comparison of the phase diagram of the  $\text{LaBr}_3$ -NaBr system, using: 1 – Associate Solution Model, 2 – Redlich-Kister Model. Open circles – experimental data [12].

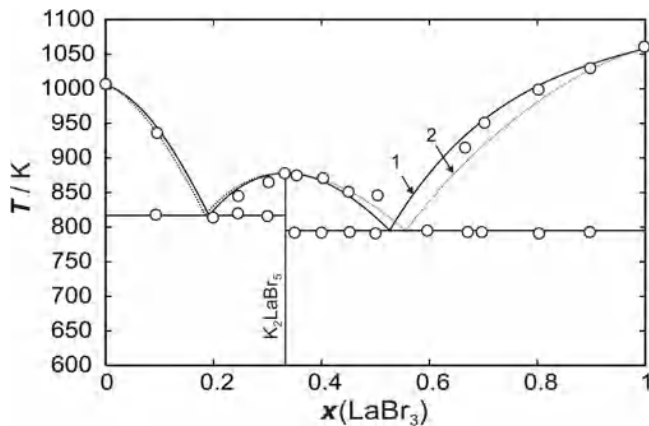


Fig. 3. The comparison of the phase diagram of the  $\text{LaBr}_3$ -KBr system, using: 1 – Associate Solution Model, 2 – Redlich-Kister Model. Open circles – experimental data [12].

coefficient for solid and liquid phases, but the  $A_i$  (enthalpy of mixing) coefficient for liquid phase is only slightly corrected. The calculated values of all coefficients of the investigated system are shown in Tables 2 and 3.

- The quality of the fit has been controlled by the least squares method applied to enthalpy of mixing and liquidus points, simultaneously.

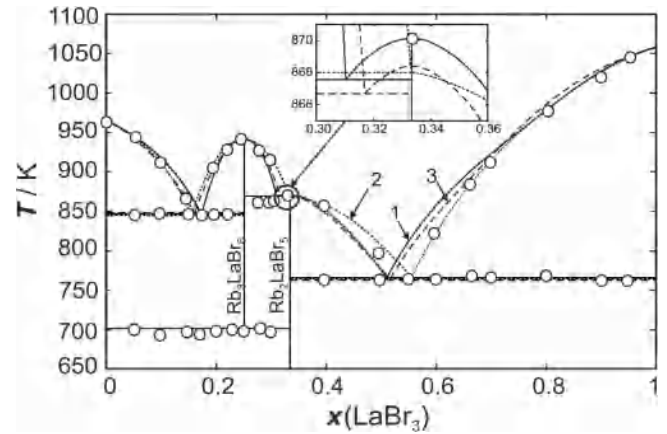


Fig. 4. The comparison of the phase diagram of the  $\text{LaBr}_3$ -RbBr system, using: 1 – Associate Solution Model, 2 – Redlich-Kister Model, 3 – Partially Ionic Two-sublattice Model. Open circles – experimental data [12].

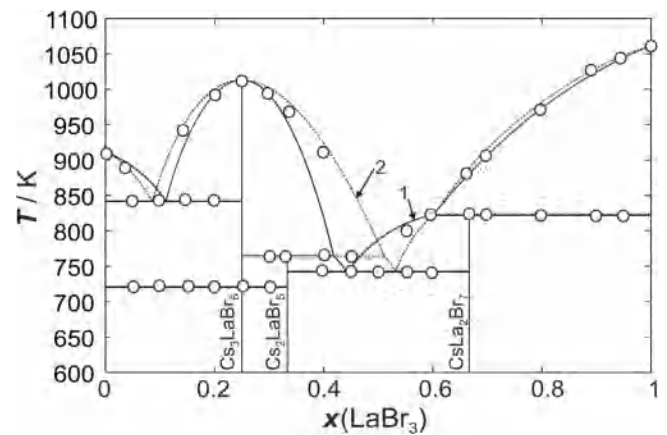


Fig. 5. The comparison of the phase diagram of the  $\text{LaBr}_3$ -CsBr system, using: 1 – Associate Solution Model, 2 – Redlich-Kister Model. Open circles – experimental data [12].

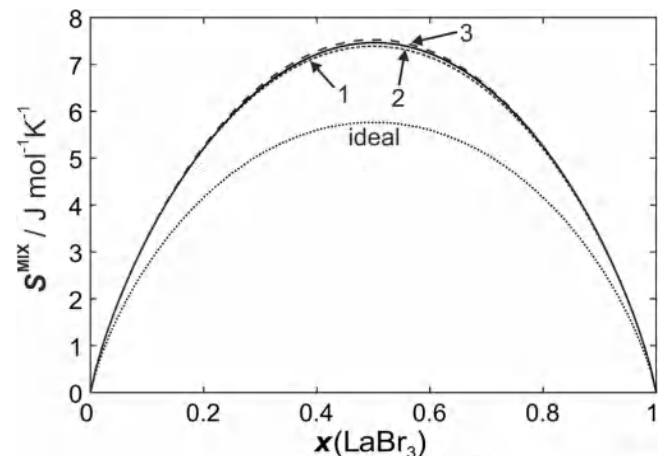


Fig. 6. The comparison of the mixing entropies of  $\text{LaBr}_3$ -LiBr system, calculated using: 1 – Associate Solution Model, 2 – Redlich-Kister Model, 3 – Quasichemical Model Modified by Pelton and Blander.

A detailed description of the optimization procedure by BINGSS and BINFKT programs was given by Lukas and Fries [21].

In this paper, the phase diagrams of the  $\text{LaBr}_3$ -MBr ( $M = \text{Li} \dots \text{Cs}$ ) systems were optimized using Redlich-Kister Model [4] and Associate Model [5]. The  $\text{LaBr}_3$ -RbBr system was in additionally

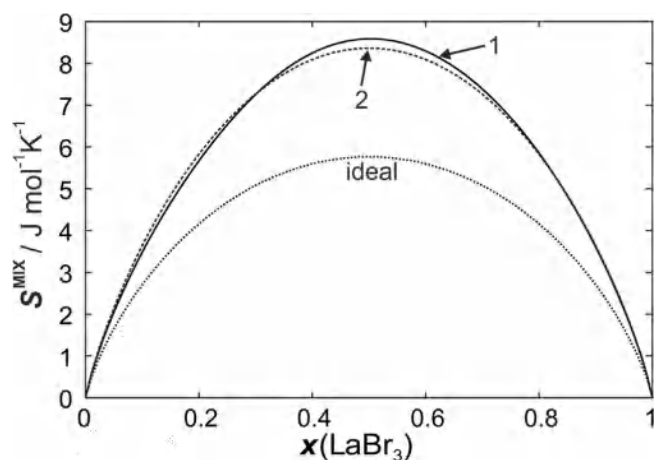


Fig. 7. The comparison of the mixing entropies of LaBr<sub>3</sub>-NaBr system, calculated using: 1 - Associate Solution Model, 2 - Redlich-Kister Model.

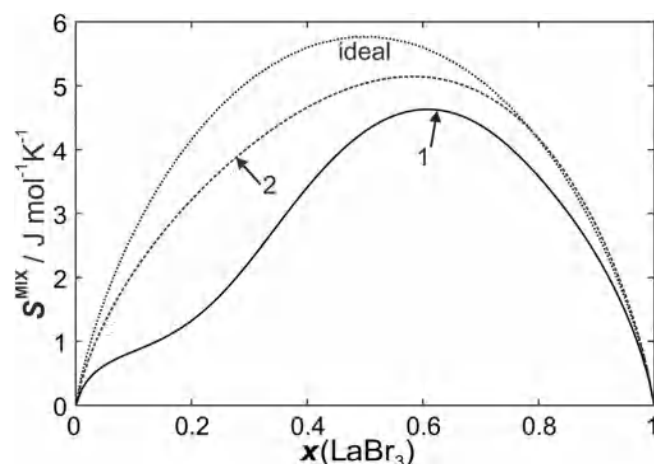


Fig. 10. The comparison of the mixing entropies of LaBr<sub>3</sub>-CsBr system, calculated using: 1 - Associate Solution Model, 2 - Redlich-Kister Model.

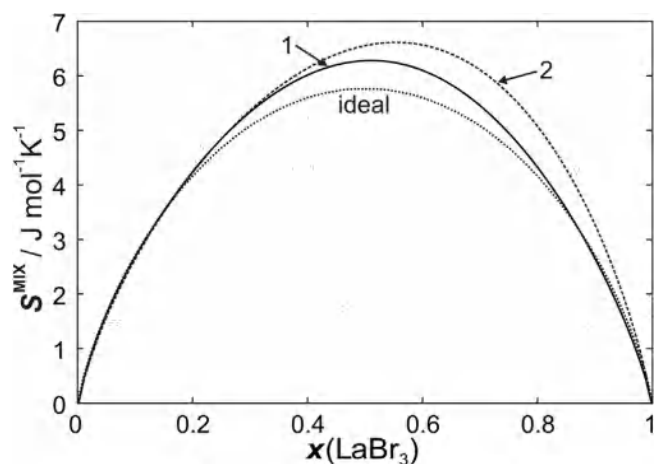


Fig. 8. The comparison of the mixing entropies of LaBr<sub>3</sub>-KBr system, calculated using: 1 - Associate Solution Model, 2 - Redlich-Kister Model.

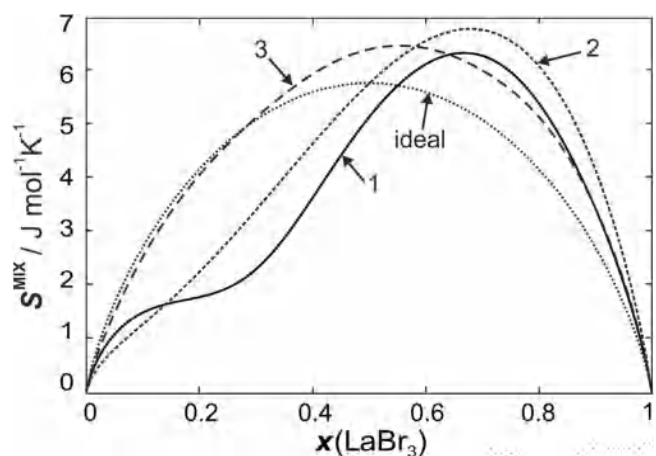


Fig. 9. The comparison of the mixing entropies of LaBr<sub>3</sub>-RbBr system, calculated using: 1 - Associate Solution Model, 2 - Redlich-Kister Model, 3 - Partially Ionic Two-sublattice Model.

Table 4

The standard deviations of fit of liquidus ( $\Delta L/K$ ) and dependence of mixing enthalpy on mole fractions ( $\Delta H^{\text{MIX}} / \text{J mol}^{-1}$ ) obtained for all of calculated systems and models.

System	Model	$\Delta L$	$\Delta H^{\text{MIX}}$
LaBr <sub>3</sub> -LiBr	ASM	9.2	85.5
	RKM	7.5	68.4
	QM	6.2	70.6
LaBr <sub>3</sub> -NaBr	ASM	11.0	129.8
	RKM	14.4	127.6
LaBr <sub>3</sub> -KBr	ASM	24.1	597.8
LaBr <sub>3</sub> -RbBr	RKM	17.2	646.9
	ASM	22.4	770.5
	RKM	19.3	802.7
LaBr <sub>3</sub> -CsBr	PIM	20.2	880.0
	ASM	26.8	719.7
	RKM	28.7	681.3

#### 4. Discussion

All of the lanthanide(III) halide – alkali halide systems show similar topology of phase diagrams, which are similar to the ones presented in Figs. 1 and 5. The standard deviations of the fit of all calculations made for the purpose of this paper are presented in Table 4. These results show that differences between fit of the models are not statistically important. This led us to the conjecture that all models lead to the mathematically correct solution. Therefore, it can be assumed that differences between obtained outcomes result only from the intrinsic nature of a particular model used to calculation. We assume the same for calculations made by other authors [1,2,22].

Calculated results for various systems and models of liquid phase are shown in Table 2. Table 3 contains the results for solid phases and Table 5 contains invariant points found for various models compared with experimental values.

In the case of LaBr<sub>3</sub>-LiBr, LaBr<sub>3</sub>-NaBr all of the calculated phase diagrams correspond well with experimental data (Figs. 1 and 2). In the calculation of these systems using Associate Model, it was assumed that a constant value of  $p(\text{MBr})/q(\text{LnBr}_3)$  equal to 1, where  $p$  and  $q$  are stoichiometric coefficients. In the case of Quasichemical Model Modified by Pelton and Blander we assumed the maximum ordering of the mixture at the AB composition ( $r=1/2$ ) and coordination number  $z=6$ . The optimization of LaBr<sub>3</sub>-LiBr, LaBr<sub>3</sub>-NaBr systems is possible for each stoichiometry of associate. We stated that kind of associate does not have real influence on the results, so we assume the most basic one. For simple

calculated with Partially Ionic Two-sublattice Model [6]. The LaBr<sub>3</sub>-LiBr system was calculated with Quasichemical Model Modified by Pelton and Blander [7]. All calculated phase diagrams and mixing entropies are shown in Figs. 1–10.

**Table 5**Comparison of the calculated and the experimental invariant points in the LaBr<sub>3</sub>–MBr (Li–Cs) systems.

Reaction	Properties:		T/K ( $x_{\text{LaBr}_3}$ )			
	Model:	ASM	RKM	PIM	QM	Experimental value
L = LiBr + LaBr <sub>3</sub>		727 (0.225)	728 (0.231)	727 (0.233) <sup>[2]</sup>	727 (0.232)	727 (0.241) <sup>[17]</sup>
L = NaBr + LaBr <sub>3</sub>		730 (0.383)	731 (0.394)	730 (0.382) <sup>[2]</sup>	730 (0.380) <sup>[1]</sup>	730 (0.38) <sup>[12]</sup>
L = KBr + K <sub>2</sub> LaBr <sub>5</sub>		818 (0.189)	818 (0.184)	819 (0.180) <sup>[2]</sup>	825 (0.199) <sup>[1]</sup>	818 (0.20) <sup>[12]</sup>
L = K <sub>2</sub> LaBr <sub>5</sub>		878 (0.333)	878 (0.333)	878 (0.333) <sup>[2]</sup>	880 (0.333) <sup>[1]</sup>	878 (0.33) <sup>[12]</sup>
L = K <sub>2</sub> LaBr <sub>5</sub> + LaBr <sub>3</sub>		795 (0.547)	795 (0.556)	795 (0.54) <sup>[2]</sup>	787 (0.584) <sup>[1]</sup>	794 (0.60) <sup>[12]</sup>
L = RbBr + Rb <sub>3</sub> LaBr <sub>6</sub>		846 (0.173)	846 (0.156)	846 (0.161)	848 (0.165) <sup>[1]</sup>	846 (0.17) <sup>[12]</sup>
L = Rb <sub>3</sub> LaBr <sub>6</sub>		942 (0.250)	942 (0.250)	942 (0.250)	943 (0.250) <sup>[1]</sup>	942 (0.25) <sup>[12]</sup>
L = Rb <sub>3</sub> LaBr <sub>6</sub> + Rb <sub>2</sub> LaBr <sub>5</sub>		868 (0.310)	868 (0.334)	868 (0.317)	864 (0.304) <sup>[1]</sup>	860 (0.31) <sup>[12]</sup>
L = Rb <sub>2</sub> LaBr <sub>5</sub>		870 (0.333)	868 (0.333)	868 (0.333)	868 (0.333) <sup>[1]</sup>	868 (0.33) <sup>[12]</sup>
L = Rb <sub>2</sub> LaBr <sub>5</sub> + LaBr <sub>3</sub>		764 (0.511)	765 (0.555)	764 (0.515)	765 (0.543) <sup>[1]</sup>	764 (0.55) <sup>[12]</sup>
Rb <sub>3</sub> LaBr <sub>6</sub> = Rb <sub>2</sub> LaBr <sub>5</sub> + RbBr		701 (–)	701 (–)	701 (–)	705 (–) <sup>[1]</sup>	701 (–) <sup>[12]</sup>
L = CsBr + H–Cs <sub>3</sub> LaBr <sub>6</sub>		842 (0.111)	842 (0.086)	842 (0.110) <sup>[22]</sup>	842 (0.106) <sup>[1]</sup>	842 (0.10) <sup>[12]</sup>
L = Cs <sub>3</sub> LaBr <sub>6</sub>		1013 (0.250)	1013 (0.250)	1014 (0.250) <sup>[22]</sup>	1013 (0.250) <sup>[1]</sup>	1013 (0.25) <sup>[12]</sup>
L + Cs <sub>3</sub> LaBr <sub>6</sub> = Cs <sub>2</sub> LaBr <sub>5</sub>		765 (0.418)	765 (0.511)	764 (0.440) <sup>[22]</sup>	771 (0.448) <sup>[1]</sup>	765 (0.45) <sup>[12]</sup>
L = CsLa <sub>2</sub> Br <sub>7</sub> + Cs <sub>2</sub> LaBr <sub>5</sub>		742 (0.443)	744 (0.531)	742 (0.470) <sup>[22]</sup>	742 (0.478) <sup>[1]</sup>	743 (0.48) <sup>[12]</sup>
L + LaBr <sub>3</sub> = CsLa <sub>2</sub> Br <sub>7</sub>		822 (0.589)	823 (0.603)	820 (0.682) <sup>[22]</sup>	820 (0.597) <sup>[1]</sup>	824 (0.60) <sup>[12]</sup>
H–Cs <sub>3</sub> LaBr <sub>6</sub> = L–Cs <sub>3</sub> LaBr <sub>6</sub>		721 (0.250)	726 (0.250)	722 (0.250) <sup>[22]</sup>	–	732 (0.25) <sup>[12]</sup>

eutectic systems in the liquid phase an increase of mixing entropy is observed, and the excess entropy is positive (Figs. 6 and 7). This is probably caused by the increased number of objects in liquid phase. It also means that amount of associate in the liquid phase is very small and it has got no apparent effect on dependence of mixing entropy on mole fraction. Note, that dependence of Gibbs energy on temperature between melting point and eutectic point in liquid NaBr has been corrected by  $\Delta A = -5200.0 \text{ J mol}^{-1}$ ,  $\Delta B = 5.0 \text{ J mol}^{-1} \text{ K}^{-1}$  (Eq. (4)). Similar effect for NaBr has been observed in previous works [3,23].

In LnBr<sub>3</sub>–MBr (Ln = La...Lu, M = Li...Cs) systems compound with stoichiometry 3:1 (M<sub>3</sub>LnX<sub>6</sub>) usually exists and melts congruently. This is the premise of assumption that associates in liquid phase in LaBr<sub>3</sub>–RbBr and LaBr<sub>3</sub>–CsBr systems show the same stoichiometry {3M<sup>+</sup> + LaBr<sub>6</sub><sup>3-</sup>}, but the LaBr<sub>3</sub>–KBr system contains only congruently melting compound with stoichiometry 2:1. In case of this system the assumption of 3:1 stoichiometry has no solution, thus our calculation used associate {2K<sup>+</sup> + LaBr<sub>5</sub><sup>2-</sup>}. The maximum of mixing entropy is observed for values of  $x(\text{LaBr}_3)$  higher than 0.5 for both RKM, ASM models (Fig. 8). The value of mixing entropy at maximum is significantly lower than in LaBr<sub>3</sub>–LiBr and LaBr<sub>3</sub>–NaBr systems (Figs. 6 and 7). Moreover, the dependence of mixing entropy on mole fractions is explicitly asymmetric. This dependence between system with the lighter and heavier alkali metals is intermediate. The asymmetry comes from the interactions of proposed associate, which decreases the number of objects in solution and consequently decreases mixing entropy in compositions lower than 0.5.

The systems LaBr<sub>3</sub>–RbBr and LaBr<sub>3</sub>–CsBr are considerably similar. In both systems congruently melting compounds of stoichiometry 3:1 and incongruently melting compounds of stoichiometry 2:1 exist. In addition, in LaBr<sub>3</sub>–CsBr system contains incongruently melting compound of stoichiometry 1:2. Therefore the calculation of these systems has been done by using Associate Model and a constant value of  $p(\text{MBr})/q(\text{LnBr}_3)$  equal to 3. Differences in calculated phase diagrams, depending on used model, are shown in Figs. 4 and 5 and in Table 5. In both systems for all used models there are observed smaller values of mixing entropies than ideal entropy for mole fraction lower than 0.5. This is shown in Figs. 9 and 10. This is especially visible in Associate Model, which is significantly more flexible. The dependences of mixing entropy on mole fraction for this model contain characteristic inflection range. This fact suggests the existence of relatively large amount of associate {3M<sup>+</sup> + LaBr<sub>6</sub><sup>3-</sup>}. Estimated amount of this

associate is probably more than 80% of maximal possible value (which is 0.25 mole associate per mole of solution at  $x(\text{LaBr}_3)$  equal to 0.25). The amount of associates {3M<sup>+</sup> + LaBr<sub>6</sub><sup>3-</sup>} for the LaBr<sub>3</sub>–RbBr and LaBr<sub>3</sub>–CsBr systems and {2M<sup>+</sup> + LaBr<sub>6</sub><sup>3-</sup>} for LaBr<sub>3</sub>–KBr system is outside the range (higher) of “entropy paradox”. The kind of used model has no visible influence on obtained values of mixing entropies in the liquid phases in the LaBr<sub>3</sub>–LiBr and LaBr<sub>3</sub>–NaBr systems. It means that “entropy paradox” is naturally omitted. We assume the same for other lanthanide halide–alkali halide systems.

The calculated and measured thermodynamic functions of formation of compounds from constituent system components are shown in Table 3. The calculated values of formation enthalpies of K<sub>2</sub>LaBr<sub>5</sub> compound at standard conditions, obtained by calculation throughout various models differs significantly, depending on model used. The acceptable agreement with measured data [12] for ASM and QM [1] has been observed. Note that identical values of enthalpy of formation in QM suggest that the experimental value were fixed during calculations but in our calculations [1] by ASM this value was not fixed. The values of calculated thermodynamic functions of formation obtained for Rb<sub>3</sub>LaBr<sub>6</sub> and Rb<sub>2</sub>LaBr<sub>5</sub> also shows significant differences between models. The QM model gives nonrealistic value of Gibbs energy of formation of Rb<sub>3</sub>LaBr<sub>6</sub> at 701 K. This value should be negative. Additionally, negative values of entropy of formation for both compounds shows that QM model is not respective for this system. The negative values of entropy of formation of Rb<sub>3</sub>LaBr<sub>6</sub> disqualify the RKM for this system. The LaBr<sub>3</sub>–CsBr system contains three solid compounds Cs<sub>3</sub>LaBr<sub>6</sub>, Cs<sub>2</sub>LaBr<sub>5</sub>, and CsLa<sub>2</sub>Br<sub>7</sub>. The positive values of Gibbs free energy of formation shows that usability of RKM, PIM, and QM models may be questionable.

Taking into account the Gibbs energy of formation of compounds the most stable compounds at the standard conditions are K<sub>2</sub>LaBr<sub>5</sub>, Rb<sub>2</sub>LaBr<sub>5</sub>, and Cs<sub>2</sub>LaBr<sub>5</sub> (Table 3). The existence of L–Cs<sub>3</sub>LaBr<sub>6</sub> and CsLa<sub>2</sub>Br<sub>7</sub> compounds at standard conditions may be disputable due to inconsistencies of functions of formation.

## 5. Conclusion

Taking into account all models used for optimization of above phase diagrams we conclude the following:

- The fitting of phase diagrams' points is possible for all used models, excluding LaBr<sub>3</sub>-KBr system with stoichiometry ratio p/q equal to 3.
- The differences between fitting of liquidus points by various models are statistically not important. The same conclusion concerns fitting of mixing enthalpies at liquid phase.
- The amount of associate increases in sequence from LaBr<sub>3</sub>-LiBr to LaBr<sub>3</sub>-CsBr.
- The Quasichemical Model, Partially Ionic Two-sublattice Model and Redlich-Kister Model may lead to unacceptable values of Gibbs energy of formation, which do not agree with fact of existence of solid compounds,  $\Delta_f G^\circ > 0$  (Table 3).
- In the calculations by Associated Model, negative values of formation entropy of compound have not been observed (Table 3).

The considerations above lead to the conclusion that the effectiveness of the used model cannot be assessed exclusively on the basis of simultaneous fit to the experimental points of liquidus and the mixing enthalpy. The same data used with various models lead to significantly different results. We think that these differences are caused by the nature of the model used. This means that selection of the specific model may be crucial for interpretation. Furthermore, the correspondence between physical models used and the reality (model's accuracy) shows different limits and may be the main cause of the inconsistency between obtained results. The Associate Model has been selected as the best one for the description of liquid phases of lanthanide(III) halide-alkali metal halide systems. This conclusion is justified to systems with relatively big amount of associates. For systems with small amount of associates, where the calculation gives an ambiguous solution, any model can be used, because the result is not dependent on the used model.

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### Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.calphad.2014.10.005>.

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