Phase equilibria in the AgCl–LnCl₃ (Ln = Ce, Nd, Sm, Gd) binary systems

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Abstract

Differential thermal analysis and differential scanning calorimetry were used to investigate phase equilibria in the AgCl–LnCl₃ (Ln = Ce, Sm, Gd) binary systems. It was found that systems under investigation represent typical examples of simple eutectic systems. The eutectic compositions and eutectic temperatures were found to be: $x(\text{CeCl}_3) = 0.095$, $T_{\text{eut}} = 700$ K (for AgCl–CeCl₃), $x(\text{SmCl}_3) = 0.228$, $T_{\text{eut}} = 644$ K (for AgCl–SmCl₃) and $x(\text{GdCl}_3) = 0.288$, $T_{\text{eut}} = 609$ K (for AgCl–GdCl₃). The thermodynamic functions of mixing in AgCl–LnCl₃ systems (Ln = Ce, Nd, Sm, Gd) were predicted on the basis of experimental data using the CALPHAD method by association model (AM) and Redlich–Kister model (RKM). The possibility of existence of the associates in the liquid phase was discussed.

Keywords Phase diagram · DSC · DTA · Silver chloride · Lanthanide chlorides · Thermodynamic functions · CALPHAD method

Introduction

The luminescence of AgCl, AgBr and AgCl_xBr_{1–x} crystals and fibers doped with lanthanide ions Ln³⁺ was investigated because of the potential use as solid-state lasers that operate in the middle-infrared spectral range [1–7]. These materials are highly transparent in the near- and mid-IR ranges and have desirable mechanical and optical properties. Rare earth ions are characterized by complex energy level schemes, with some optical transitions of these ions being in the mid-IR range. Similar transitions or transitions between higher excited states may exist in silver halides. Incorporating rare earth in silver halide crystals and fibers may induce amplification and lasing in mid-IR. All experiments and calculations indicate that these doped crystals and fibers would be good candidates for the fabrication of mid-IR solid-state lasers or fiber lasers [1–7].

Therefore, the knowledge of basic thermodynamic properties for the silver halide–lanthanide halide systems is

required. Unfortunately, the only data reported in the literature are four phase diagrams: AgCl–NdCl₃ [8], AgBr–PrBr₃ [9], AgBr–NdBr₃ [9, 10] and AgBr–TbBr₃ [11], and electrical conductivity of molten mixtures in whole composition range for the AgCl–NdCl₃ and AgBr–NdBr₃ binary systems [8, 10].

The present paper reports the phase diagrams of three pseudo-binary systems: AgCl–CeCl₃, AgCl–SmCl₃ and AgCl–GdCl₃, determined experimentally for the first time. Moreover, the thermochemical calculations on these systems and additional one (AgCl–NdCl₃) have been done using CALPHAD method. The functions of mixing in the liquid phase for all liquid mixtures have been calculated.

Experimental

Chemicals and sample preparation

Cerium(III) chloride and gadolinium(III) chloride were synthesized from Ce₂(CO₃)₃ and Gd₂O₃ (both 99.9% purity, Aldrich), respectively. The syntheses were carried out by dissolution of Ce₂(CO₃)₃ and Gd₂O₃ in hot concentrated HCl acid (35–38%, pure, POCH S.A.) and further evaporation and crystallization of LnCl₃·xH₂O (Ln = Ce, Gd).

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Ammonium chloride was then added, and these wet mixtures of hydrated LnCl_3 and NH_4Cl were slowly heated first up to 450 K and then up to 570 K to remove the water. The resulting mixtures were subsequently heated to 650 K for sublimation of unreacted NH_4Cl . Finally, the salts were melted at 1223 K (CeCl_3) and 1023 K (GdCl_3) under argon atmosphere. Crude CeCl_3 and GdCl_3 were purified by distillation under reduced pressure (~ 0.1 Pa) in a quartz ampoule at 1253 K.

Samarium(III) chloride was prepared by chlorinating the samarium(III) oxide (99.9%, Aldrich) with a current of high-purity argon (water and oxygen content less than 2 and 0.5 ppm, respectively) saturated with carbon tetrachloride CCl_4 (pure p.a., chemPUR) vapor in a quartz reactor, at 973 K for 3 h.

Purity of lanthanide chlorides was verified by complexometric and mercurimetric titration for lanthanide and chloride, respectively. The results presented in Table 1 confirm the high purity of obtained products.

Silver chloride was POCH S.A. reagent (pure for analysis). Before use, it was dried at 450 K.

The mixtures of AgCl and LnCl_3 ($\text{Ln} = \text{Ce}, \text{Sm}, \text{Gd}$) were prepared in a glove box filled with argon (purity $> 99.9999\%$, Messer). Moreover, due to silver chloride UV–Vis light sensitivity, all laboratory steps were carried out in the red light. The weighted mixtures of chlorides were melted in the vacuum-sealed quartz ampoules in an electric furnace, homogenized by shaking and solidified. Then samples were ground in an agate mortar in the glove box and placed into smaller quartz ampoules, especially for DTA/DSC measurements, and sealed under vacuum using propane–butane–oxygen burner. Ampoules for DTA measurements were about 11 mm diameter and 30 mm length, for DSC—about 6 mm and 15 mm, respectively. Mass of individual samples was 1.300–2.000 g for DTA and 0.200–0.400 g for DSC. Compositions of starting mixtures are given in Table 2.

Table 1 Chemical composition of synthesized lanthanide chlorides determined by titration methods

LnCl_3	Mass%			
	$\text{Ln}^{\text{experimental}}$	$\text{Ln}^{\text{theoretical}}$	$\text{Cl}^{\text{experimental}}$	$\text{Cl}^{\text{theoretical}}$
CeCl_3	56.89 ± 0.16	56.85	43.51 ± 0.15	43.15
SmCl_3	58.52 ± 0.17	58.58	40.28 ± 0.65	41.42
GdCl_3	59.69 ± 0.24	59.65	41.58 ± 1.16	40.35

Measurements

Phase diagrams of the AgCl – CeCl_3 and AgCl – GdCl_3 systems were studied using differential thermal analysis (DTA) on modified Paulik–Paulik–Erdey MOM Q-1500 D derivatograph controlled by a programmer Eurotherm 2604 coupled to the PC computer equipped with i-Tools data acquisition interface. The temperature was measured with a Pt/Pt–Rh(10) thermocouple placed in the recess in the bottom of the ampoule, calibrated with high-purity metals, whose melting points were in the temperature range of our measurements. Cooling and heating were carried out at a rate of 5 K min^{-1} .

Phase equilibria measurements of the AgCl – SmCl_3 system were carried out using the 121 SETARAM differential scanning calorimeter, conducted at heating and cooling rates ranging between 1 and 5 K min^{-1} . The details of the DSC calibration and measurements procedure were described previously [12].

Results

Determination of phase diagram by DTA and DSC methods

The phase diagrams of the AgCl – LnCl_3 ($\text{Ln} = \text{Ce}, \text{Sm}, \text{Gd}$) binary systems were determined for the first time in this work. DTA and DSC investigations were performed on samples with different compositions in the $x(\text{LnCl}_3)$ range from 0.0 to 1.0. Due to supercooling effect observed in the samples (Fig. 1), all temperature and enthalpy values reported in this work were determined from heating curves. Solidus and liquidus temperatures were determined as T_{onset} and T_{peak} of appropriate effects, respectively. Figure 2 shows the example curves obtained for investigated systems. All experimental data are given in Table 2.

Almost all heating curves, for all investigated systems, showed only two peaks, which were ascribed to the eutectic and the liquidus effects, respectively. A few exceptions (one peak observed for the samples with composition close to eutectic point) resulted from overlapping of both thermal effects. It means that AgCl – LnCl_3 ($\text{Ln} = \text{Ce}, \text{Sm}, \text{Gd}$) phase diagrams were found to be of the simple eutectic type (points, Figs. 3, 5, 6) with no intermediate solid compounds, similarly to AgCl – NdCl_3 system (Fig. 4).

The eutectic contributions to the enthalpy of fusion are determined and plotted against composition in Figs. 3–6. These so-called Tamman constructions make it possible to evaluate accurately the eutectic compositions from the intercept of the two linear parts in Figs. 3–6. In these Tamman constructions, it was assumed that there is no

Table 2 Eutectic and liquidus temperatures in the AgCl–LnCl₃ (Ln = Ce, Nd, Sm, Gd) systems derived from heating DTA or DSC curves, x is the mole fraction of respective lanthanide chloride

AgCl–CeCl ₃ , DTA				AgCl–NdCl ₃ , DSC [8]				AgCl–SmCl ₃ , DSC				AgCl–GdCl ₃ , DTA			
x (CeCl ₃)	T_{eut}/K	$\Delta H/\text{kJ mol}^{-1}$	T_{liq}/K	x (NdCl ₃)	T_{eut}/K	$\Delta H/\text{kJ mol}^{-1}$	T_{liq}/K	x (SmCl ₃)	T_{eut}/K	$\Delta H/\text{kJ mol}^{-1}$	T_{liq}/K	x (GdCl ₃)	T_{eut}/K	$\Delta H/\text{kJ mol}^{-1}$	T_{liq}/K
0.000	–	–	747	0.000	–	0	736	0.000	–	–	724	0.000	–	–	730
0.011	701	1.952	738	0.055	667	3.574	722	0.050	640	2.660	711	0.075	613	4.25	712
0.018	699	9.379	728	0.104	668	7.638	698	0.099	642	7.845	693	0.100	612	6.35	694
0.018	699	8.526	729	0.104	666	7.331	698	0.149	645	9.744	676	0.154	612	11.87	671
0.031	702	9.833	723	0.126	667	10.42	699	0.196	643	14.88	651	0.252	614	18.82	–
0.051	700	–	–	0.149	668	18.48	–	0.250	646	15.28	674	0.301	610	20.62	634
0.102	702	20.98	–	0.176	669	15.48	–	0.296	643	13.92	708	0.396	614	19.42	661
0.199	703	17.84	793	0.196	669	15.75	–	0.349	647	13.06	729	0.435	611	16.16	687
0.299	702	15.39	856	0.252	669	14.67	725	0.396	643	11.99	761	0.501	609	14.59	741
0.401	701	13.61	914	0.318	670	13.17	769	0.498	642	9.421	798	0.531	608	14.24	758
0.500	701	10.77	965	0.377	669	12.26	806	0.596	644	7.379	849	0.560	609	11.01	776
0.604	701	8.529	1000	0.377	671	12.13	809	0.671	645	6.886	872	0.560	608	12.30	774
0.701	701	7.081	1031	0.407	669	11.50	823	0.793	643	3.611	913	0.601	607	9.40	791
0.800	700	4.338	1065	0.502	669	9.993	876	0.889	643	2.545	934	0.694	607	7.60	819
0.900	697	2.061	1089	0.606	669	8.071	922	1.000	–	–	948	0.820	593	2.58	836
1.000	–	–	1097	0.719	668	5.609	968	–	–	–	–	0.902	605	5.26	852
				0.797	668	4.137	988					1.000	–	–	871
				0.901	667	1.735	1018								
				1.000	–	–	1029

Fig. 1 DTA heating (solid lines) and cooling (dashed lines) curves for: AgCl–CeCl₃ mixtures with $x(\text{CeCl}_3) = 0.011$ (a); AgCl–GdCl₃ mixtures with $x(\text{GdCl}_3) = 0.560$ (c); and DSC heating curves for AgCl–SmCl₃ mixtures with $x(\text{SmCl}_3) = 0.099$ (b); heating rate: 5 K min^{-1}

Fig. 2 DTA heating curves for: AgCl–CeCl₃ mixtures with $x(\text{CeCl}_3) = 0.011$ (a) and $x(\text{CeCl}_3) = 0.701$ (b); AgCl–GdCl₃ mixtures with $x(\text{GdCl}_3) = 0.075$ (e) and $x(\text{GdCl}_3) = 0.560$ (f); and DSC heating

curves for AgCl–SmCl₃ mixtures with $x(\text{SmCl}_3) = 0.099$ (c) and $x(\text{SmCl}_3) = 0.793$ (d); heating rate: 5 K min^{-1}

solubility in the solid state. Thus, straight lines intercept the composition axis at $x(\text{LnCl}_3) = 0.00$ and $x(\text{LnCl}_3) = 1.00$. The eutectic temperatures, compositions and enthalpies of fusion for the systems under investigation are given in Table 3.

Phase diagram calculations by CALPHAD method

The phase diagrams of the AgCl–LnCl₃ (Ln = Ce, Sm, Gd) systems measured in this work and the phase diagram of the AgCl–NdCl₃ system investigated by Szymanska-Kolodziej et al. [8] were calculated by the CALPHAD

method using the BINGSS and BINFKT program [13]. The data, used in calculations, for solid and liquid AgCl and LnCl₃ (Ln = Ce, Nd, Gd, Sm) are presented in Table 4. SGTE description was used for these compounds:

$$G^\circ(T) - H^{\text{SER}} = A + BT + CT \ln T + DT^2 + E/T \quad (1)$$

The coefficients of this equation for all of pure system components are presented in Table 5.

Interpretation by the CALPHAD method was made with using two models describing liquid phase. The first one was an association model (AM) [16], which assumes the

Fig. 3 Phase diagram of the AgCl–CeCl₃ binary system (top) and respective Tamman plot (bottom). Open circles—experimental data, black circles—eutectic composition determined from Tamman plot, solid lines (top)—phase equilibria calculated by CALPHAD method using association model (AM), dashed lines (top)—phase equilibria calculated by CALPHAD method using Redlich–Kister model (RKM), solid lines (bottom)—calculated Tamman plot

Fig. 4 Phase diagram of the AgCl–NdCl₃ binary system (top) and respective Tamman plot (bottom). Open circles—experimental data, black circles—eutectic composition determined from Tamman plot, solid lines (top)—phase equilibria calculated by CALPHAD method using association model (AM), dashed lines (top)—phase equilibria calculated by CALPHAD method using Redlich–Kister model (RKM), solid lines (bottom)—calculated Tamman plot

existence of associates in the liquid phase. They are formed according to equation:

where p and q are stoichiometry coefficients. From the mass balance in liquid phase, it has been obtained:

$$n = n_{\text{AgCl}} + n_{\text{LnCl}_3} + n_a \quad (3)$$

where n is the total number of moles, n_{AgCl} , n_{LnCl_3} and n_a are number of mole of AgCl, LnCl₃ and associate, respectively. The mole fractions of AgCl (y_{AgCl}) and LnCl₃ (y_{LnCl_3}) in this pseudoternary system have been represented by the following formulas:

$$y_{\text{AgCl}} = x_{\text{AgCl}} \cdot [1 + (p + q - 1) \cdot y_a] - p \cdot y_a \quad (4)$$

$$y_{\text{LnCl}_3} = x_{\text{LnCl}_3} \cdot [1 + (p + q - 1) \cdot y_a] - q \cdot y_a \quad (5)$$

where y_a is a mole fraction of associate.

The Gibbs energy of mixing of the liquid phase in this model has been described as:

$$\begin{aligned} G^{\text{MIX}} = R \cdot T \cdot [& (y_{\text{AgCl}} \cdot \ln(y_{\text{AgCl}}) + y_{\text{LnCl}_3} \cdot \ln(y_{\text{LnCl}_3}) \\ & + y_a \cdot \ln(y_a)) \cdot n + C_1 \cdot y_a \cdot n \\ & + (C_2 \cdot y_{\text{AgCl}} \cdot y_{\text{LnCl}_3}) \cdot n \end{aligned} \quad (6)$$

where C_i is the calculated coefficients. In this work, we assume the stoichiometry (p/q ratio) of associate as an additional adjustable coefficient found by iterative method. The criterion of fitting was the standard deviation of the liquidus temperature. The dependences of coefficients C_i on temperature have been not observed. The values of mixing entropies are slightly higher than ideal ones. It means that the amount of associates in liquid phase is very small and ambiguous.

The second model used for the description of the liquid phase was the Redlich–Kister model (RKM) [17], in which Gibbs energy of mixing of the liquid phase has been described as:

Fig. 5 Phase diagram of the AgCl–SmCl₃ binary system (top) and respective Tamman plot (bottom). Open circles—experimental data, black circles—eutectic composition determined from Tamman plot, solid lines (top)—phase equilibria calculated by CALPHAD method using association model (AM), dashed lines (top)—phase equilibria calculated by CALPHAD method using Redlich–Kister model (RKM), solid lines (bottom)—calculated Tamman plot

Fig. 6 Phase diagram of the AgCl–GdCl₃ binary system (top) and respective Tamman plot (bottom). Open circles—experimental data, black circles—eutectic composition determined from Tamman plot, solid lines (top)—phase equilibria calculated by CALPHAD method using association model (AM), dashed lines (top)—phase equilibria calculated by CALPHAD method using Redlich–Kister model (RKM), solid lines (bottom)—calculated Tamman plot

$$G^{\text{MIX}} = R \cdot T \cdot [(x_{\text{AgCl}} \cdot \ln(x_{\text{AgCl}}) + x_{\text{LnCl}_3} \cdot \ln(x_{\text{LnCl}_3}) + x_{\text{AgCl}} \cdot x_{\text{LnCl}_3} \cdot [L_1 + L_2 \cdot (x_{\text{AgCl}} - x_{\text{LnCl}_3})]] \quad (7)$$

where L_i is the calculated coefficients.

The results of calculations using both models are shown in Table 6.

Taking into account that we have only liquidus data for these systems, we compared standard deviations of liquidus fitting for both models. It turned out that fitting was very similar in both cases. The consequence of this has very similar dependences of G^{MIX} on composition and temperature which is shown in Fig. 7.

Differences between Gibbs energies of mixing in liquid phase calculated by both models were insignificant. The main difference was the presence of small amount of configurational mixing entropy which appeared in AM interpretation. The values of p/q and correlated values of mixing entropies are shown in Table 6. All of the mixing entropies at obtained mole fraction of associate were very similar and higher about 20% than ideal mixing entropy. The RKM assumed the ideal entropy of mixing. This small difference between mixing entropies resulted in the distinctive difference in calculated values of mixing enthalpies of liquid phases, as shown in Fig. 8.

The presence of the configuration entropy (AM) causes a decrease in the absolute value of the calculated enthalpy

Table 3 The eutectic temperatures, compositions and enthalpies of fusion obtained experimentally (by Tamman plots) and by CALPHAD calculations using association model (AM) and Redlich–Kister model (RKM)

System	T_{eut}/K			$x_{\text{eut}} (\text{LnCl}_3)$			$H_{\text{eut}}/\text{kJ mol}^{-1}$
	Exp.	Calc. (AM)	Calc. (RKM)	Exp.	Calc. (AM)	Calc. (RKM)	
AgCl–CeCl ₃	700 ± 2	699	700	0.095 ± 0.014	0.102	0.098	20.1 ± 1.6
AgCl–NdCl ₃	668 ± 1	669	668	0.154 ± 0.015	0.172	0.170	16.4 ± 1.4
AgCl–SmCl ₃	644 ± 2	645	643	0.228 ± 0.023	0.220	0.213	15.2 ± 1.0
AgCl–GdCl ₃	609 ± 5	611	610	0.288 ± 0.037	0.291	0.273	20.7 ± 1.4

Table 4 The thermodynamic data for pure chlorides used in CALPHAD calculations

Compound	$S_{298}/\text{J mol}^{-1} \text{ K}^{-1}$	T_{fus}/K	$\Delta H_{\text{fus}}/\text{J mol}^{-1}$	References
AgCl	96.2	736	13,160	[14]
CeCl ₃	151.42	1090	53,600	[15]
NdCl ₃	154.15	1032	49,200	[15]
SmCl ₃	150.26	950	47,600	[15]
GdCl ₃	151.42	875	40,600	[15]

of mixing by about 1000 J mol^{−1}. The result is that in the case of the AgCl–CeCl₃ system, the enthalpy of mixing achieves small positive values for the AM model.

We had expected the tendency to associate formation in AgCl–LnCl₃ (Ln = Ce, Nd, Sm, Gd) binary systems due to their similarity to the TiCl–SmCl₃ systems [18]. Unfortunately, the amount of associates with silver chloride turned out to be very small and may be negligible. In summary,

we found that CALPHAD calculations using both (AM and RKM) models are equally good and may be usable in future interpretation.

Taking into account the shape of DTA or DSC curves, we assumed that these systems were simple eutectic ones. But the existence of incongruently melting solid compound at temperature close to eutectic point might be possible. Therefore, the CALPHAD calculations were used for the explanation of the possibility of its appearance in the above systems. We have simulated the existence of Ag₃GdCl₆ and Ag₂GdCl₅ solid compounds in AgCl–GdCl₃ binary system. It was selected because of the lowest value of Gibbs energy of mixing (Fig. 7). Both considered hypothetical compounds had Gibbs energy of formation close to zero or positive at eutectic temperature. This excludes the possibility of their existence and confirms that the systems under investigation are simple eutectics.

Table 5 The coefficients of Eq. (1) describing $\{G^\circ(T) - H^{SER}\}/\text{J mol}^{-1}$ of pure system components

Compound	A	B	C	D	E
AgCl _{solid}	− 17,591.3529	292.713776	− 57.67	− 0.0044665	−
AgCl _{liquid}	− 92,440.8139	244.591861	− 42.097	0.583115	−
CeCl _{3solid}	− 29,627.3072	470.113312	− 90.9772	− 0.01790615	135,765
CeCl _{3liquid}	− 31,373.7523	945.543858	− 161.5	−	−
NdCl _{3solid}	− 27,603.6793	441.717110	− 87.2834	0.01929275	− 20,105.0
NdCl _{3liquid}	− 22,102.9319	848.194720	− 149.5	−	−
SmCl _{3solid}	− 28,039.7042	495.335903	− 95.3748	− 0.0167221	− 280,675
SmCl _{3liquid}	− 12,512.8437	798.934267	− 144.4	−	−
GdCl _{3solid}	− 27,988.6365	452.869645	− 88.7959	− 0.01572205	17,375.0
GdCl _{3liquid}	− 19,852.8152	774.673234	− 139.7	−	−

The presentation of coefficients is consistent with Molten Salt Database notation (SGTE 1996)

Table 6 The coefficients of Eqs. (6) and (7) describing mixing enthalpies of liquid phases at 1100 K calculated from AgCl–LnCl₃ (Ln = Ce, Nd, Sm, Gd) phase diagrams, standard deviation calculated from the unbiased estimator of the population variance of liquidus (ΔT) and the entropy of mixing at mole fraction of adjusted associate stoichiometry

System	$C_1/\text{J mol}^{-1}$	$C_2/\text{J mol}^{-1}$	$\Delta T/\text{K}$	x_{assoc}	$S^{\text{MIX a}}/\text{J mol}^{-1} \text{ K}^{-1}$	SD
<i>Association model (AM)</i>						
AgCl–CeCl ₃	– 100	200	7.42	0.417	6.9	0.62
AgCl–NdCl ₃	– 5600	0	6.30	0.465	7.0	0.48
AgCl–SmCl ₃	– 7500	1000	7.20	0.472	6.9	0.65
AgCl–GdCl ₃	– 6500	500	13.97	0.488	7.1	1.07
System	$L_1/\text{J mol}^{-1}$	$L_2/\text{J mol}^{-1}$	$\Delta T/\text{K}$	SD		
<i>Redlich–Kister model (RKM)</i>						
AgCl–CeCl ₃	– 2800	– 900	9.97	0.83		
AgCl–NdCl ₃	– 8000	0	7.45	0.57		
AgCl–SmCl ₃	– 9500	0	5.08	0.42		
AgCl–GdCl ₃	– 8600	– 700	12.33	1.03		

Note that $x_{\text{assoc}} = q/(p + q)$ for Eq. (6)

^aValue of ideal mixing entropy at x_{assoc} is close to $5.8 \text{ J mol}^{-1} \text{K}^{-1}$

Fig. 7 Gibbs energy of mixing of the AgCl–LnCl₃ (Ln = Ce, Nd, Sm, Gd) binary systems calculated by CALPHAD method using association model (a) and Redlich–Kister model (b) at 1100 K

Fig. 8 Mixing enthalpies of the AgCl–LnCl₃ (Ln = Ce, Nd, Sm, Gd) binary systems calculated by CALPHAD method using association model (a) and Redlich–Kister model (b) at 1100 K

Conclusions

1. The phase diagrams of the AgCl–LnCl₃ (Ln = Ce, Sm, Gd) binary systems have been determined for the first time in this work.
2. All the investigated systems are simple eutectics.
3. The composition of eutectics was determined with the help of constructed Tamman diagrams.
4. Thermodynamic properties of AgCl–LnCl₃ (Ln = Ce, Nd, Sm, Gd) binary systems were calculated by CALPHAD method using association model and Redlich–Kister model. Both models gave comparable results.
5. An increase in the negative value of C_1 coefficient describing associate formation with the decrease in ionic radius of lanthanide (from cerium to gadolinium) and slightly positive excess entropy of mixing lead to the conclusion that existence of small amount of associate cannot be excluded [16, 19].

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