Phase Diagram Measurement and Calculation of the Rare Earth Involving Halide Systems

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Several models , including power series in mole or equivalent fraction and quasi-chemical theory used for describing the Gibbs energy of rare earth involving halide liquid phase are discussed. For the $RECl_3$-ACl (RE: Y, La, Ce, Nd, Gd etc. and A: alkali metals) systems whose measured enthalpies of mixing in liquid tend to be characteristic V-shaped curves and become more negative with the variation of A from Li to Cs, the thermodynamic properties of liquid can be satisfactorily represented by power series in the equivalent fraction and a modified quasichemical model, respectively.

A series of binary rare earth involving chloride systems and rare earth involving divalent iodide systems have been optimized and their phase diagrams have been calculated, being agreed with experimental phase equilibrium data quite well.

In order to reliably predict the ternary thermodynamic properties from its sub-binary ones using geometric model, a thermodynamic criterion is proposed to reasonably identify the symmetry of ternary system. Many ternary phase diagrams of the rare earth involving chloride systems have been successfully predicted. The agreement between calculated and measured results is good enough.

For phase diagram construction of numerous rare earth involving halide systems phase diagram calculation in combination with limited accurate measurements is the best and powerful way.

1. INTRODUCTION

Molten salt electrolysis widely used for preparation of rare earth(RE) metals and their alloys. Study on phase diagrams and thermodynamic properties of the systems involving RE chloride and/or fluoride is of great significance for explaining the electrolysis mechanism and improving the metallurgical technology of RE metals and their alloys as well as for better understanding the structures and properties of RE halide systems. Also it has been reported that some RE halide involving complex compounds are excellent functional materials. For example , $NaScI_4$, $CsCeI_4$, $CsNdI_4$ and $CsLaI_4$ etc. as well as the divalent samarium compounds $NaSmI_3$ and $CsSmI_3$ show higher vapor pressures than those of the RE salts alone[1-2]. So, it is believed that the complexes of RE and alkali halides could be potentially new filling materials for discharged lamps. Therefore, it is very beneficial and significantly important to study the phase diagrams and thermodynamic properties of the mentioned systems.

For a huge number of RE involving halide systems, it is almost impossible to study their phase diagrams and thermodynamic properties one by one only using experimental methods. Thanks to the CALPHAD[3] technique, essence of which is the computer coupling of phase diagrams and thermodynamics, phase diagram and thermodynamic data can be critically assessed in a thermodynamically self-consistent manner. The phase diagram can be calculated and all thermodynamic properties, including phase diagram data can be usually represented and stored by means of a small set of coefficients. Particularly, CALPHAD technique permits us to predict thermodynamic properties and phase diagrams of ternary and then high order systems from assessed parameters of the sub-binary ones. But, there are still many RE involving halide systems having neither phase diagram nor thermodynamic information. Therefore, from our point of view, computer calculation with limited accurate experiments is the best way for phase diagram construction with money and time saving and high efficiency[4].

2. EXPERIMENTAL

As a systematic study on the measurement of the RE halide involving phase diagrams, DTA and XRD methods have been used for the determination of phase boundaries and phase analysis. The experimental details can be found out in our previous papers[1,2,5,6]. In this paper, it should only point out that the accuracy of measurements mostly depends on the sample preparation. Due to the hydration of RE chlorides and divalent iodides, they have to be carefully dehydrated before use. The purity of pure halides must be checked by X-ray and thermal analysis. All procedure for sample preparation was carried out in a dry box under a dry argon or nitrogen atmosphere, in which the oxygen concentration was less than 0.5%. Each sample was sealed in a quartz ampoule in vacuum for DTA measurement. Phase analysis was performed on the basis of X-ray powder diffraction data obtained by use of diffractometer. The two sides of sample frame were carefully sealed by transparent membranes.

3. OPTIMIZATION

3.1 Models for describing the Gibbs energy of liquid phase

3.1.1 Power series in mole or equivalent fraction

For binary molten salt systems $D_mQ_p(A)$-$E_nQ_r(B)$, in which D and E represent rare earth and alkali or alkali earth ions, respectively and Q represents halide ion. The molar and excess molar Gibbs energies in liquid phase G_m^L and ${}^EG_m^L$ can be expressed as

$$G_m^L = X_A^0 G_A^L + X_B^0 G_B^L + RT(X_A \ln X_A + X_A \ln X_B) + {}^E G_m^L \quad (1)$$

$${}^E G_m^L = \sum_\alpha \sum_\beta g_{\alpha\beta} X_A^\alpha X_B^\beta \quad (2)$$

where ${}^0G_i^L$ is the standard Gibbs energy in liquid D_mQ_p and E_nQ_r ; X_i is the mole fraction of component i; α, β are positive integers; $g_{\alpha\beta} = h_{\alpha\beta} - Ts_{\alpha\beta}$, $h_{\alpha\beta}$ and $s_{\alpha\beta}$ are temperature-independent coefficients and can be related to the mixing enthalpy and the excess entropy, respectively. By means of the least square method, the parameters $h_{\alpha\beta}$ and $s_{\alpha\beta}$ can be optimized by using available thermodynamic and phase diagram data.

If α=1, β=1 and α=1, β=2, eq. (2) was reduced to the expressions of excess Gibbs energy for regular and sub-regular solution model, respectively. According to the standard formula, the partial Gibbs energy for component i can be derived. For binary molten salt systems, if the deviation from ideal solution is small, such as in the case of $RECl_3$-LiCl and $RECl_3$-$AECl_2$ (RE: La, Ce, Pr, Nd; AE: Mg, Ca, Sr) systems, the power series in mole fraction can be reasonably used for the Gibbs energy in liquid phase.

However, for ordering molten salt systems, such as the $RECl_3$-ACl(A: alkali; metal) systems, if the excess Gibbs energy in liquid phase was expressed in terms of the equivalent fraction Z_i, rather than of the mole fraction, a better representation with fewer coefficients could be available. Z_i is defined as

$$Z_A = \frac{pX_A}{pX_A + rX_B}, \qquad Z_B = \frac{rX_B}{pX_A + rX_B} \quad (3)$$

Thus, the excess molar Gibbs energy of liquid phase is expressed as

$${}^E G_m^L = (pX_A + rX_B) \sum_\alpha \sum_\beta g_{\alpha\beta} Z_A^\alpha Z_B^\beta \quad (4)$$

Obviously, because Z_A/Z_B is the charge number ratio of D and E ions, the interaction between unit charge of D_mQ_p and E_nQ_r is considered. Therefore, using the parameters optimized from eq. (4) not only assures the good agreement between calculated and measured phase diagrams, but also makes the calculated values of molar enthalpy of mixing and molar entropy of liquid accord with the measured ones.

3.1.2 Modified quasi-chemical model[8-10].

For ordering systems, Pelton and Blander have deduced a modification of the quasi-chemical model and developed a useful optimization procedure[9] based on the robust least square technique, which has been successfully used to represent the thermodynamic properties of ordered liquidus and glasses using only a few number of parameters. Based on the model and optimization technique mentioned above, we developed QCVFIT and QCOMP programs[10] which have been used to optimize the YCl_3-ACl binary systems with much success, as discussed below.

3.1.3 Examples : YCl_3-ACl (A: alkali metals)

The calorimetric and EMF measurements of the YCl_3-ACl systems have been carried out by Papatheodorou et al[11]. From Fig.1 it is found that the measured enthalpies of mixing in liquid YCl_3-ACl mixtures tend to exhibit V-shaped curves. With the variation of A from Li to Cs, the enthalpies of mixing become more negative. While the

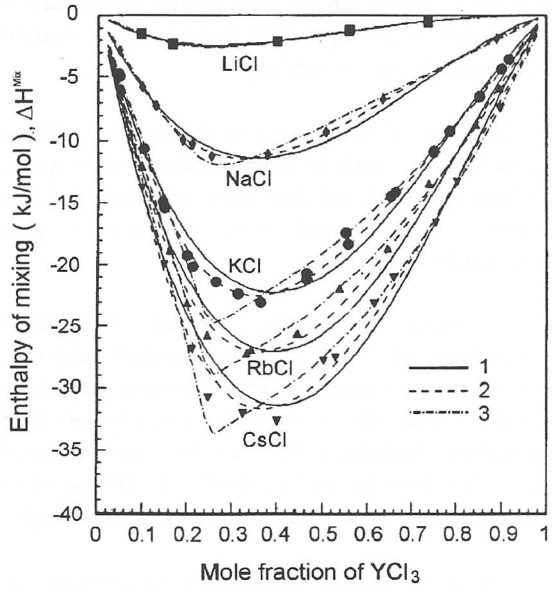

Fig.1 Enthalpy of mixing in liquid mixtures of ACl-YCl_3 (A=Li,Na, K, Rb,Cs) systems
1: Power series in mole fraction
2: Power series in equivalent fraction
3: Modified quasichemical model
(Experimental data from G. N.Papatheodorou et al., Acta Chem. Scand. A33(1979) No. 3 pp. 173-178)

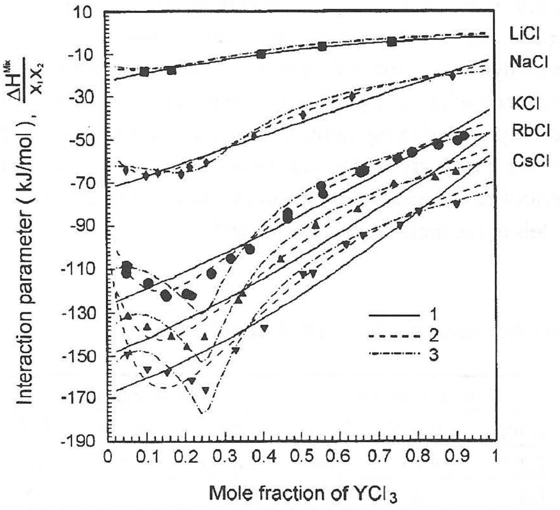

Fig.2 Enthalpy interaction parameters in liquid mixtures of ACl-YCl_3 (A: Li, Na, K,Rb, Cs) systems
1: Power series in mole fraction
2: Power series in equivalent fraction
3: Modified quasichemical model
(Experimental data from G. N. Papatheodorou et al., Acta Chem. Scand. A33(1979) No. 3 pp. 173-178)

enthalpies of mixing are evaluated with power series in more or equivalent fraction and modified quasi-chemical model, the V-shaped curves can be described. But, the compositions of the maximum negative values are a little different each other and the V-shape curves with modified quasi-chemical model are more sharp. As shown in Fig.2, the curves of measured enthalpy interaction parameter ($\lambda^M = \Delta H^M/(X_1 \cdot X_2)$) also exhibit V-shape peaks, except the YCl_3-LiCl system, and the compositions of the maximum negative values exist in X_{YCl3}=0.21-0.25. Also, in Fig.2 the curves fitted with power series in mole fraction are straight lines. However, if the curves fitted with power series in equivalent fraction and just taking α=1, β=3 in eq. (4), the characteristic V-shaped curves of measured enthalpies interaction parameters are well displayed. But, the composition of maximum ordering a little deviats from the measured one. Moreover, in the case of using modified quasi-chemical model, the calculated composition of the maximum ordering exists in X_{YCl3}=0.25 nearby, which agrees better with measured one.

3.1.4 Sufficient and necessary condition for reasonably choosing thermodynamic model

The agreement between calculated and measured phase diagram is a necessary condition for reasonably choosing thermodynamic model. But, the sufficient condition should include the agreement between calculated and measured thermodynamic data. Take YCl_3-ACl binary systems for example, although measured phase diagrams agreed well with calculated ones by using either of the three models discussed above to describe the enthalpies of mixing in these systems, the enthalpies of mixing optimized by power series in mole fraction can not reveal the maximum ordering characteristics in the binary YCl_3-ACl (A∴Li) systems. However, if using power series in equivalent fraction and modified quasi-chemical model, the fit is much better, just as discussed above.

3.2 Thermodynamic criterion for judging the symmetry of ternary systems

It is well known that geometric models for predicting thermodynamic properties of ternary systems from the three sub-binary ones can be reasonably divided into two types: symmetric and asymmetric. In order to improve the accuracy of calculation in using geometric models, it is very important to reasonably identify the symmetry of ternary systems, in other words, to correctly choose the model, symmetric or asymmetric. For ternary molten salt systems, charge-asymmetry has been used as the criterion for identifying the symmetry in most previous work and for ternary oxide systems the acid-base asymmetry[8] has been used. As a matter of fact, the above-mentioned criteria are not essential and for a large number of $RECl_3$-$AECl_2$-ACl (RE: rare earth metal, AE: alkali earth metal, A: alkali metal) systems it is impossible to determine the asymmetric component according to the charge-asymmetry. Therefore, from a thermodynamic point of view we propose a thermodynamic criterion for reasonably identifying the symmetry of a ternary system.

Based on the interaction among all species in ternary system, a thermodynamic criterion for identifying the symmetry of ternary systems (from energy-asymmetry) was proposed as follows. If the thermodynamic behaviors of the three sub-binary systems are similar to each other, the ternary system is symmetric. Otherwise, if the deviations of the binary systems A-B and B-C from ideal solution are similar but differ markedly from that of the binary system A-C, the A-B-C ternary system is an asymmetric one. In the asymmetric system, the common component in two sub-binary system with thermodynamic similarity should be chosen as the asymmetric component.

Consider for example, the $PrCl_3$-$CaCl_2$-$MgCl_2$ system. From the excess molar Gibbs energy of the three binary systems, the $CaCl_2$-$MgCl_2$ and $PrCl_3$-$MgCl_2$ systems are thermodynamically similar and different from the $PrCl_3$-$CaCl_2$. Hence, according to the present thermodynamic criterion, $MgCl_2$ is to be taken as the asymmetric component in the ternary system. Thus, using Toop model to predict thermodynamic properties and to calculate the phase diagram of the $PrCl_3$-$MgCl_2$-$CaCl_2$ system, the best fit to experimental data was obtained and shown in Table I, which summarizes the calculated phase diagram results of a series of rare earth involving ternary chloride systems using Toop model to predict thermodynamic properties and then to calculate phase diagrams. It is obvious that the errors of calculation based on the present criterion to determine the asymmetric component are minimum. The proposed thermodynamic criterion for judging the symmetry of ternary systems has been successfully used in a large number of molten salt and alloy systems. From thermodynamic point of view it is very reasonable and simple and of great significance in improving the calculated accuracy in predicting thermodynamic properties of ternary solution phase from the sub-binary ones. But, it is still overlooked by several investigators, while using geometric models in the molten salt and slag and alloy systems.

Table I Analysis of asymmetric component in the ternary rare earth involving chloride systems

System		1st component			2rd component			3rd component		
		comp.	δ,mol%	ΔT,℃	comp.	δ,mol%	ΔT,℃	comp.	δ,mol%	ΔT,℃
$CeCl_3$-$CaCl_2$-LiCl	E:	$CeCl_3$	2.52	23	LiCl*	1.13	18	$CaCl_2$	1.39	20
$PrCl_3$-$CaCl_2$-LiCl	E:	$PrCl_3$	4.09	15	LiCl*	3.47	8	$CaCl_2$	3.47	10
$NdCl_3$-$CaCl_2$-LiCl	E:	$NdCl_3$	3.91	7	LiCl	2.44	7	$CaCl_2$*	1.94	2
	P:		9.31	-2		7.59	-7		10.40	-17
$PrCl_3$-$SrCl_2$-LiCl		$PrCl_3$*	———	———	LiCl	———	———	$SrCl_2$		
	E:		4.15	5		5.51	-7		7.21	-20
	P:		9.15	6		10.60	11		9.94	-26
$NdCl_3$-$SrCl_2$-LiCl		$NdCl_3$*	———	———	LiCl	———	———	$SrCl_2$		
	E:		2.08	5		5.72	8		7.82	-23
$PrCl_3$-$CaCl_2$-$MgCl_2$	E:	$PrCl_3$	2.88	12	$CaCl_2$	2.45	15	$MgCl_2$*	0.99	14

* thermodynamic asymmetric component.

Note: $\delta = \frac{1}{n}\sqrt{\sum_{i=1}^{n}\left(X_i - X_i'\right)^2} \times 100$, $\Delta T = T - T'$

where X_i and X_i' as well as T and T' represent calculated and measured mole fractions as well as ternary eutectic (E) or peritectic (P) temperatures, respectively.

4. RESULTS

4.1 Binary systems

The thermodynamic parameters of the $RECl_3$-$AECl_2$ (RE: Y, La, Ce, Pr, Nd; AE: Ba, Ca, Sr, Mg), $RECl_3$-LiCl and SmI_2-AI (A: alkali metals) binary systems, whose thermodynamic behaviours deviate not far from ideal solution, were optimized by means of power series in mole fraction. Take the YCl_3-$AECl_2$ systems as an example. The phase diagram of the YCl_3-$SrCl_2$ system[6], which was not been reported in literature, was measured by means of DTA method, and a new incongruently melting compound YSr_3Cl_9 in this system was observed by X-ray diffraction. The peritectic temperature is 560 ℃ and the eutectic point is located at 497 ℃, X_{YCl3}=0.6. The phase diagrams and thermodynamic properties of the YCl_3-$AECl_2$ systems were assessed and optimized. The optimized phase diagrams agreed well with experimentally measured ones[6] and a set of self-consistent thermodynamic parameters were given as shown in Table II and III.

Table II Calculated values of excess enthropy and mixed enthalpy of YCl_3-$AECl_2$ systems

$$\Delta H_m^M = x_A x_B (h_{11} + h_{12} x_A) \qquad (J/mol)$$

$$^E S_m = x_A x_B (s_{11} + s_{12} x_A) \qquad (J/mol \cdot K)$$

System	h_{11} (10^{-3})	h_{12} (10^{-3})	s_{11}	s_{12}
YCl_3-$MgCl_2$	13.305	1.685	12.615	7.601
YCl_3-$CaCl_2$	-5.804	-0.485	0	0
YCl_3-$SrCl_2$	-36.474	-32.112	-48.113	-24.714
YCl_3-$BaCl_2$	-20.011	-6.250	-16.998	10.551

The YbI$_2$-AI[2] and the YCl$_3$-ACl[7] systems having maximum ordering in liquid were optimized by power series in equivalent fraction and modified quasi-chemical model. The enthalpies of mixing and excess entropies as well as thermodynamic properties of intermediate compounds of the YCl$_3$-ACl systems optimized by power series with equivalent fraction were shown in Table 4 and 5. The calculated and measured phase diagrams agreed very well[7].

4.2 Ternary system

The excess molar Gibbs energies of the ternary rare earth involving chloride systems can be predicted from those of three sub-binary systems by using the geometric model chosen according to the thermodynamic criterion mentioned above. Based on the equality of the partial molar Gibbs energy for each component in all the coexisting phases, the ternary phase diagram can be calculated by TERNFIG program. The calculated phase diagrams of the ternary RECl$_3$-SrCl$_2$-LiCl (RE: La, Ce, Pr, Nd)[12], RECl$_3$-CaCl$_2$-LiCl (RE: Y, La, Ce, Pr, Nd) [13,14], RECl$_3$-SrCl$_2$-MgCl$_2$ (RE: La, Ce, Pr, Nd)[12] and RECl$_3$-CaCl$_2$-MgCl$_2$ (RE: Y, La, Ce, Pr, Nd)[14,15] systems were systematically calculated and reported. From a part of calculated Phase diagrams shown in Table VI, the agreement between calculated and measured results is good enough and the reasonable fact that the ternary eutectic temperature decreases with decrease of RE^{3+} ion radius is observed.

Table III Thermodynamic properties of intermediate compounds in YCl$_3$-AECl$_2$ systems

System	Inter. comp.	T_f ,℃	$\Delta G_f^0 = a + bT$, J / mol	
			a × 10^{-3}	b
YCl$_3$-MgCl$_2$	—	—	—	—
YCl$_3$-CaCl$_2$	Y$_6$CaCl$_{20}$	* 575	-32.115	32.439
YCl$_3$-SrCl$_2$	YSr$_3$Cl$_9$	* 560	-29.649	30.229
YCl$_3$-BaCl$_2$	YBa$_3$Cl$_9$	* 664	-43.783	39.833

Note: * peritectic temperature.

Table IV Excess enthalpies and entropies of the ACl-YCl$_3$ systems

$$H_m^M = (x_A + 3x_B)(h_{11}Z_AZ_B + h_{12}Z_AZ_B^2 + h_{13}Z_AZ_B^3) \quad (\mathrm{J/mol})$$

$$^E\mathrm{S_m} = (x_A + 3x_B)(s_{11}Z_AZ_B + s_{12}Z_AZ_B^2 + s_{13}Z_AZ_B^3) \quad (\mathrm{J/mol \cdot K})$$

System	h$_{11}$ × 10^{-3}	h$_{12}$ × 10^{-3}	h$_{13}$ × 10^{-3}	s$_{11}$	s$_{12}$	s$_{13}$
LiCl-YCl$_3$	-5.12	-11.63	17.19	-5.59	0.02	21.65
NaCl-YCl$_3$	-16.05	-55.34	57.83	3.10	-61.12	107.80
KCl-YCl$_3$	-28.36	-100.23	88.98	2.39	-28.07	50.27
RbCl-YCl$_3$	-32.79	-120.76	103.69	-2.46	-36.43	59.11
CsCl-YCl$_3$	-32.94	-152.85	124.60	34.97	18.22	0.00

Table V Thermodynamic properties of intermediate compounds

System	Inter. Comp.	T$_f$,℃	$\Delta G_f^0 = a + bT$, J / mol	
			a × 10^{-3}	b
LiCl-YCl$_3$	3LiCl · YCl$_3$	* 492	-12.814	8.990
NaCl-YCl$_3$	3NaCl · YCl$_3$	*520	-28.656	17.399
	NaCl · 9YCl$_3$	* 584	-54.325	52.648
KCl-YCl$_3$	3KCl · YCl$_3$	824	-35.542	8.223
	KCl · 2YCl$_3$	* 512	-45.289	30.010
RbCl-YCl$_3$	3RbCl · YCl$_3$	860	-45.624	15.538
	RbCl · 2YCl$_3$	610	-51.358	30.992
CsCl-YCl$_3$	3CsCl · YCl$_3$	890	-67.409	11.538
	2CsCl · YCl$_3$	* 613	-69.175	16.283
	CsCl · 2YCl$_3$	640	-47.504	9.657

Note: *, peritectic temperature; without * , congruently melting temperature.

Table VI Comparison between calculated and measured eutectic points of $RECl_3$-$CaCl_2$-LiCl and $RECl_3$-$CaCl_2$-$MgCl_2$ phase diagrams

System	Calculated			Measured		
	$RECl_3$ (mole percentage)	$CaCl_2$ (mole percentage)	T /℃	$RECl_3$ (mole percentage)	$CaCl_2$ (mole percentage)	T /℃
$LaCl_3$-$CaCl_2$-LiCl	14.5	30	445			
$CeCl_3$-$CaCl_2$-LiCl	17.0	20.1	439	17.2	18.7	420[16]
$PrCl_3$-$CaCl_2$-LiCl	23.0	19.0	430	27.0	23.0	420[17]
$NdCl_3$-$CaCl_2$-LiCl	23.0	18.5	419	18.1	22.3	408[18]
YCl_3-$CaCl_2$-LiCl	34.0	15.8	383			
$LaCl_3$-$CaCl_2$-$MgCl_2$	19.2	45.8	582			
$CeCl_3$-$CaCl_2$-$MgCl_2$	26.5	38	577	22.6	39.4	527
$PrCl_3$-$CaCl_2$-$MgCl_2$	26.0	41.5	560	26	39.4	546[19]
$NdCl_3$-$CaCl_2$-$MgCl_2$	30.0	26	548			
YCl_3-$CaCl_2$-$MgCl_2$	45.1	43.3	505			

5. CONCLUSION

(1) The agreement between calculated and measured phase diagrams and all thermodynamic data is a necessary and sufficient condition for reasonably choosing thermodynamic model to describe the Gibbs energy in each phase in the system under study. For describing the Gibbs energy of rare earth involving halide liquid phase, the power series in mole or equivalent fraction is a simple and effective model for the $RECl_3$-$AECl_2$, $RECl_3$-LiCl and the REI_2-AI systems as well as the power series in equivalent fraction and modified quasi-chemical model are effective and powerful models for the $RECl_3$-ACl systems, which belong to the ordering molten salt systems.

(2) Based on thermodynamic consideration a thermodynamic criterion for judging the symmetry of ternary systems was proposed and successfully used in a large number of rare earth involving halide ternary systems. It is of great significance in improving the calculated accuracy in predicting thermodynamic properties and phase diagrams of ternary systems from the sub-binary ones.

(3) CALPHAD technique in combination with limited accurate measurements is the best and powerful way to construct phase diagrams of numerous rare earth involving halide systems, especially ternary and high order systems.

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REFERENCES

1. Qiao Zhiyu et al., "Measurement and Calculation of the SmI_2-AI(A=Na, K, Rb, Cs) Phase Diagrams", J. of Alloys and Compounds, Vol.201, 1993, pp.217-221

2. Qiao Zhiyu et al., "Measurement and Calculation of the YbI_2-AI(A=Na, K, Rb, Cs) Phase Diagrams", J. of Solid State Chemistry, Vol.114, 1995, pp.146-150

3. CALPHAD Journal, Computer Coupling of Phase Diagram and Thermochemistry, Ed. Dinsdal A T, Pergamon, 1977-1996

4. Qiao Zhiyu et al., "Phase Diagram Optimization and Calculation of the Systems Containing Rare Earth Chlorides", Progress in Natural Science, Vol.5, No.4, Aug.1995, pp.463-470

5. Qiao Zhiyu et al., "Determination of $PrCl_3$-NaCl-LiCl Phase Diagram", Acta Metallurgica Sinica (English Edition), Series B, Vol.3, No.1, Feb.1990, pp.15-19

6. Yuan Wenxia et al., " A Study on the YCl_3-$AECl_2$(AE=Mg, Ca, Sr, Ba) Binary Phase Diagrams", Ibid, Vol.32, No.2, Feb.1996, pp.139-143

7. Qiao Zhiyu, Zhuang Weidong, Su Mianzeng, "Computer Coupled Thermodynamic and Phase Diagram Analysis of the Alkali and Yttrium chloride Systems", Science in China, Series A, (English edition) Vol.35, No.8, Aug.1992, pp.957-964

8. A.D.Pelton and M.Blander, "Thermodynamic Analysis of Ordered Liquid Solutions by a Modified Quasichemical Approach Application to Silicate

Slags", Metall. Trans. B, Vol.17B, No.2, 1986, pp.805-815

9. A.D.Pelton and M.Blander, "Least Square Optimization Technique for the Analysis of Thermodynamic Data in Ordered Liquids", CALPHAD, Vol.12, No.1, Jan.1988, pp.97- 108

10. Qiao Zhiyu, Zhuang Weidong, "Modified Quasichemical Theory and Its Application in the System of $KCl-YCl_3$", J. Univ. of Sci. & Tech. Beijing, Vol.14, No.6, 1992, pp.612- 616

11. G. N. Papatheodorou, O. Waernes, T. Φstvold, "Thermodynamic Studies of Binary Charged Unsymmetrical Fused Salt Systems — Calorimetric and Electromotive Force Measurements of Yttrium (III) Chloride-Alkali Chloride Mixtures", Acta Chemica Scandinavica, Vol.A33, 1979 pp.173-178

12. Xing Xianran, Master thesis, Univ. of Sci. and Tech. Beijing, 1992, Beijing

13. Qiao Zhiyu et al., "Calculation of $RECl_3-CaCl_2-LiCl$ (RE: La, Ce, Pr, Nd) Phase Diagrams", J. of Rare Earths, Vol.12, No.2, 1994, pp.5-12

14. Qiao Zhiyu et al., "$RECl_3-CaCl_2-MgCl_2$ (RE: La, Ce, Pr, Nd) Ternary Phase Diagrams", Transactions of Nonferrous Metals Society of China, (English edition) Vol.3, No.2, May 1995, pp.27-31

15. Yuan Wenxia et al., "A Study on the Chloride Phase Diagrams involving YCl3", Modelling and Simulation in Metallurgical Engineering and Materials Science, Metallurgical Industry Press, Beijing, 1996, pp.241-244

16. Chai, C. G. Zheng, Y. P. Ye, "Study on the $CeCl_3-LiCl$ Phase diagram and Ternary Liquidus of the $CeCl_3-CaCl_2-LiCl$ System", J. Chin. Rare Earth Soc, 8(1),1990, pp.92-93

17. Trikhonov, "$PrCl_3-CaCl_2-LiCl$ Phase Diagram", Izv. Vuz. Ts. M, 28(2), 1983, pp.60-63

18. Zheng, J. Jin, J. I. Chen, Y.P. Ye, "Liquidus Study on the $NdCl_3-CaCl_2-LiCl$ System", Chinese Science Bulletin 34(14) 1989, pp.1230-1233

19. Zheng, H. P. Liu, Z-Y. Qiao, Y. P.-Ye, "Phase Diagram of Ternary System $PrCl_3-CaCl_2-MgCl_2$", Acta Metallurgica Sinica Ser B 3(4) 1990, pp.284-286

20. Zheng, X. L. Chang, Z-Y. Qiao, Y. P.-Ye, "Study on the Ternary $CeCl_3-CaCl_2-MgCl_2$ Phase Diagram", Acta Chemica, 4(2), 1992, pp.32-33