INVESTIGATION ON PHASE DIAGRAM OF SYSTEM $LaCl_3$-$BaCl_2$-NaCl ①

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ABSTRACT On the basis of reinvestigation of related binary systems, the phase diagram of system $LaCl_3$-$BaCl_2$-NaCl was determined by DTA. There are 5 liquid surfaces corresponding to $LaCl_3$, NaCl, α-$BaCl_2$, β-$BaCl_2$ and Ba_2LaCl_7 respectively and 6 univariant curves corresponding to the secondary crystallization and eutectic point E (69.0% $LaCl_3$, 2.0% $BaCl_2$, 29.0% NaCl, 509 ℃) and peritectic point P (52.0% $LaCl_3$, 22.0% $BaCl_2$, 26.0% NaCl, 550 ℃).

Key words phase diagram $LaCl_3$-$BaCl_2$-NaCl $LaCl_3$

1 INTRODUCTION

Either for a deeper insight into the physico-chemical properties of compounds containing RE, or for improvement of the technology of preparation of RE metals studies on the phase diagrams of system containing RE-molten salts are of considerable significance. A series of phase diagrams containing rare earth molten salts have been studied[1].

Although the present ternary system itself has not yet been reported, the related binary systems are well known in literature. The $LaCl_3$-NaCl[2] and $BaCl_2$-NaCl[3] belong to simple eutectic type. The eutectics of them are 70.4% $LaCl_3$, (540 ℃) and 29.6% NaCl, (650 ℃) respectively. Vogel[4] reported that the $LaCl_3$-$BaCl_2$ is of peritectic type with eutectic point at 70.0% $LaCl_3$, (730 ℃) and peritectic point P at 51.6% $LaCl_3$, (806 ℃). We have reinvestigated these systems and found that the results are in agreement with them. We use these data in the paper.

On the basis of reinvestigation of the related binary systems, the phase diagram of the ternary system $LaCl_3$-$BaCl_2$-NaCl was determined. 5 polythermal sections were determined.

2 EXPERIMENTAL

Materials: La_2O_3 was with the purity of 99.99%; $BaCl_2 \cdot 2H_2O$, NaCl and others were analytical reagents.

Dehydration of salts: $BaCl_2 \cdot 2H_2O$ was heated directly to dehydrate and then the temperature was raised to 700 ℃ and kept constant for 10 h. M. P. of the product was 960 ℃. La_2O_3 was first converted to $LaCl_3 \cdot 6H_2O$ with HCl. Then $LaCl_3 \cdot 6H_2O$ was dehydrated stepwise[5] under an atmosphere of HCl at low pressure. Its M. P. was 875 ℃. NaCl was dehydrated by slow heating to melt. Melting point of NaCl was 800 ℃.

Sample preparation: The operation was carried out in a dry box with P_2O_5. The salt mixtures in appropriate proportions were loaded into quartz ampules and weighed on the analytical balance. The weight of each sample was about 150 mg. The ampules were sealed in vacuum and the samples were homogenized by annealing.

DTA: At the bottom of each ampule an indentation was made to fit the NiCr-NiAl thermocouple. The thermoanalyzer was calibrated against some standard substances of known melting points. Two curves of calibration were ob-

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tained (on cooling and heating). The heating rate was 10 ℃/min. and pure Al_2O_3 was used as reference. The heat effects on liquids were determined by the cooling curves and the calibration curve on cooling was corrected accordingly. The temperatures of the heat effects were estimated by means of extrapolation.

3 RESULTS

Five vertical sections are shown in Fig. 1 (a), (b), (c), (d) and (e), in which " L " means liquid phase; " X " – Ba_2LaCl_7. The composition and temperatures of points of deflection on liquidus are listed in Table 1.

Project these point of 5 sections liquidus deflection on the composition triangle orthogonally and joint the projection which are interrelated. One obtains curves of secondary crystallization of the system. Extensions of these curves intersect at the eutectic point E and peritectic point P of the system, which have the following values:

E (69.0% $LaCl_3$, 2.0% $BaCl_2$, 29.0% NaCl, 509 ℃)

P (52.0% $LaCl_3$, 22.0% $BaCl_2$, 26.0% NaCl, 550 ℃)

Two ternary reactions occur in the system:

$L + \beta\text{-}BaCl_2 = Ba_2LaCl_7 + NaCl$

$L = LaCl_3 + Ba_2LaCl_7 + NaCl$

4 DISCUSSION

Some regular alterations in phase diagrams of systems $RECl_3$-$BaCl_2$-NaCl (RE = La, Pr, Nd), as melting point of $RECl_3$, temperature of invariant points of binary and ternary systems are listed in Table 2, 3.

It can be seen that along with the increase

Table 1 Composition and temperatures of points of deflection on liquidus

Sections	First point		Second point		Third point	
	Composition/% $LaCl_3$	t/℃	Composition/% $LaCl_3$	t/℃	Composition/% $LaCl_3$	t/℃
Ⅰ (90.0NaCl-10.0$BaCl_2$)-$LaCl_3$	71.5	544	68.0	547		
Ⅱ (70.0NaCl-30.0$BaCl_2$)-$LaCl_3$	71.0	575	60.0	535		
Ⅲ (45.0NaCl-55.0$BaCl_2$)-$LaCl_3$	71.0	632	52.0	653	46.0	595
Ⅳ (20.0NaCl-80.0$BaCl_2$)-$LaCl_3$	70.0	665	51.0	702		
Ⅴ Ba_2LaCl_7-NaCl	25.0(NaCl)	625				

Table 2 Cited data of binary system

RE	$r_{RE^{3+}}$ /nm	$RECl_3$ M.P. t/℃	$RECl_3$-$BaCl_2$				$RECl_3$-NaCl	
			E		P			
			$RECl_3$/%	t/℃	$RECl_3$/%	t/℃	$RECl_3$ /%	t/℃
La	0.1032	875	70.0	730	51.6	806	70.4	540
Pr	0.099	768	68.2	664	49.3	766	71.3	468
Nd	0.0983	765	70.0	633	54.0	743	76.0	438

Table 3 Ternary systems $RECl_3$-$BaCl_2$-NaCl

RE	E				P				Ref.
	C/%			t/℃	C/%			t/℃	
	$RECl_3$	$BaCl_2$	NaCl		$RECl_3$	$BaCl_2$	NaCl		
La	69.0	2.0	29.0	509	52.0	22.0	26.0	550	Present
Pr	68.5	1.5	30.0	451	62.0	14.0	24.0	510	[6]
Nd	74.0	1.6	24.4	430	57.0	19.1	23.9	508	[7]

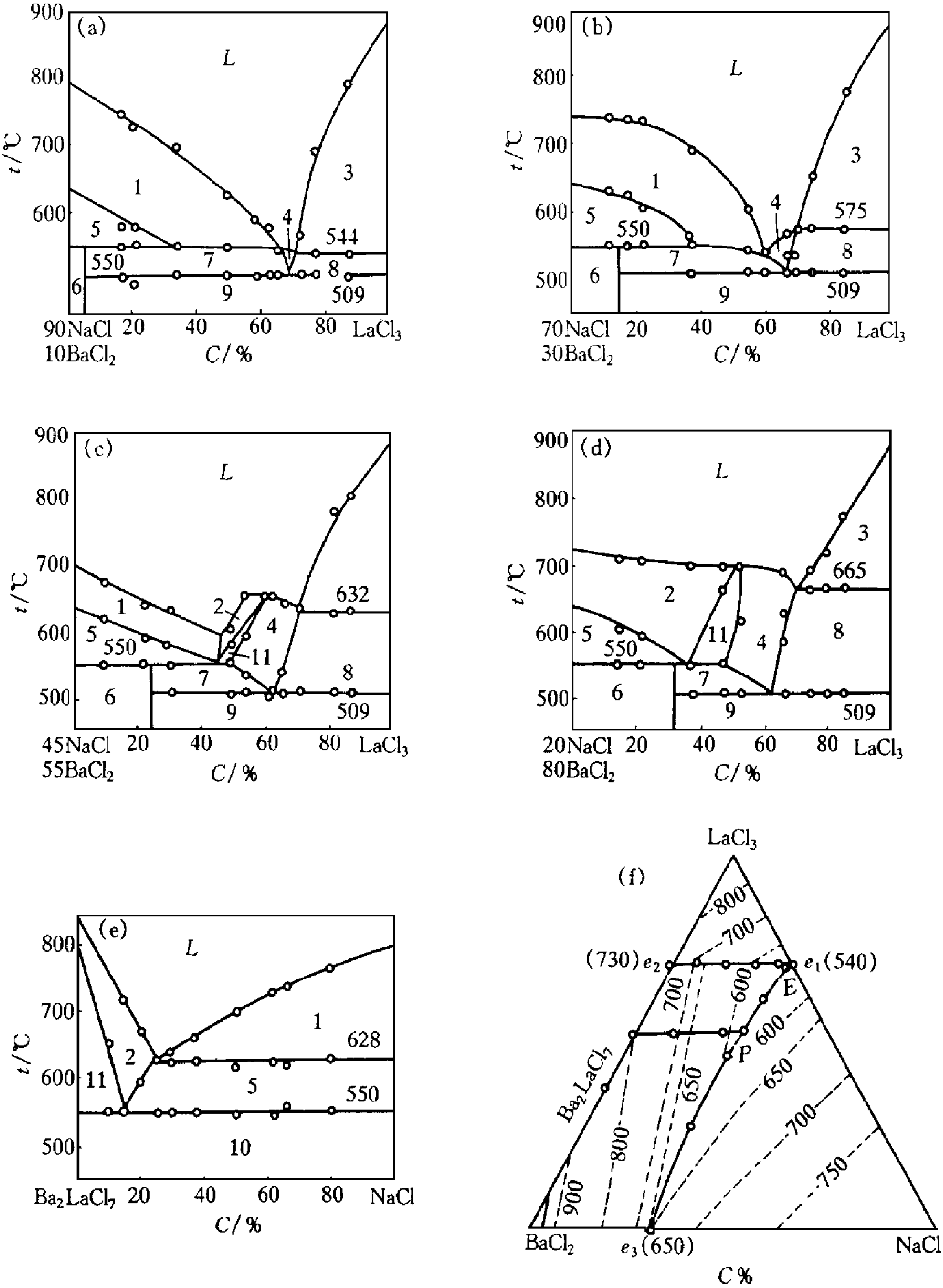

Fig. 1 Phase diagram of system $LaCl_3$-$BaCl_2$-NaCl

(a) —section Ⅰ; (b) —section Ⅱ; (c) —section Ⅲ; (d) —section Ⅳ;
(e) —section Ⅴ; (f) —phase diagram of system $LaCl_3$-$BaCl_2$-NaCl
1 —*L* + NaCl; 2 —*L* + β-$BaCl_2$; 3 —*L* + $LaCl_3$; 4 —*L* + *X*;
5 —*L* + NaCl+ β-$BaCl_2$; 6 —NaCl+ *X* + β-$BaCl_2$; 7 —*L* + NaCl+ *X*;
8 —*L* + X+ $LaCl_3$; 9 —NaCl+ *X* + $LaCl_3$; 10 —NaCl+ *X*; 11 —*L* + β-$BaCl_2$+ *X*

of atomic number Z of RE, the melting point of $RECl_3$, the temperatures of eutectics as well as the peritectic point decrease gradually (Table 2, 3). Modern theory of chemical bond believes "Pure" ionic bond is scarcely encountered in real crystals. There is always a certain amount of covalency in ionic bonds. The higher the covalent percentage, the more stable the chemical bond within the molecule and the weaker the attractive force between the molecules. In consequence, the melting point of crystals will be lowered. In $RECl_3$ crystals, with the increase of the atomic number Z of RE, the ionic radii R diminishes and the polarizing effect of RE^{3+} becomes even stronger, and the covalent character of the bonding increases. Eventually, the melting points of the compounds decrease regularly from 875 ℃($LaCl_3$) to 765 ℃($NdCl_3$). The temperatures of eutectics and peritectic point in systems $RECl_3$-$BaCl_2$, $RECl_3$-NaCl, as well as $RECl_3$-$BaCl_2$-NaCl (RE= La, Pr, Nd) decrease. Similarly, an unstable new phase, formed in the solid state, was found in the systems $RECl_3$-$BaCl_2$-NaCl (RE= Pr[5] or Nd[6]). But, there is not any new phase in this system $LaCl_3$-$BaCl_2$-NaCl. Because the increase of atomic number Z of lanthanide even more prominent influence of chemical bonds upon phase diagrams will affect the formation of new phases and their stability[1]. It is because the "Lanthanide Contraction", effective ionic radii of RE^{3+} decrease regularly from 0.1031 nm (La^{3+}) to 0.0983 (Nd^{3+}) with increasing atomic number Z. This means that when the anion (Cl^-) keeps unchanged, along with the increase of Z, the polarizing force (RE^{3+} on Cl^-) is to be strengthened. So, It is easy to form $[RECl_n]^{-(n-3)}$ complex ion as well as the coordination compound $M_n[RECl_m]$ (M = Ba, Na).

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