

# AN INVESTIGATION ON PHASE DIAGRM OF TERNARY SYSTEM $\text{CeCl}_3$ - $\text{BaCl}_2$ - $\text{LiCl}$ <sup>1</sup>

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## ABSTRACT

The phase diagram of ternary system  $\text{CaCl}_3$ - $\text{BaCl}_2$ - $\text{LiCl}$  was researched by DTA and X-ray analysis. There were 5 liquid surfaces corresponding to  $\text{CeCl}_3$ ,  $\alpha$ - $\text{BaCl}_2$ ,  $\beta$ - $\text{BaCl}_2$ ,  $\text{LiCl}$  and  $\text{Ba}_3\text{CeCl}_9$  respectively and 6 univariant curves corresponding to the secondary crystallization and eutectic point  $E$  (65.8 wt.-%  $\text{CeCl}_3$ , 2.5 wt.-%  $\text{BaCl}_2$ , 33.2 wt.-%  $\text{LiCl}$ , 452 °C) and peritectic point  $P$  (50.0 wt.-%  $\text{CeCl}_3$ , 22.8 wt.-%  $\text{BaCl}_2$ , 27.2 wt.-%  $\text{LiCl}$ , 480 °C). At the same time an unstable compound was found in solid state and decomposed at 110 °C.

**Key words:** system phase diagram  $\text{CeCl}_3$ - $\text{BaCl}_2$ - $\text{LiCl}$

## 1 INTRODUCTION

A knowledge of the phase diagram of molten salts is of primary importance for investigating their physicochemical properties and for electrolytic preparation of corresponding metals. Up to now, however, the phase diagram of ternary system  $\text{CeCl}_3$ - $\text{BaCl}_2$ - $\text{LiCl}$  has not been reported in literature. Therefore, for some practical purposes we determined the phase diagram of this ternary system.

The phase diagrams of the three relevant binary systems have been reported.  $\text{CeCl}_3$ - $\text{LiCl}$ <sup>[1]</sup> and  $\text{BaCl}_2$ - $\text{LiCl}$ <sup>[2]</sup> systems are both of simple eutectic type. In the former with eutectic point  $E$  at 68.3 wt.-%  $\text{CeCl}_3$ , 494 °C. As to the latter system, ГРОМОВ found  $e$  at 13.3 wt.-%  $\text{LiCl}$ , 512 °C, but we checked the result and found that  $e$  was at a higher temperature 520 °C<sup>[3]</sup>. About the system  $\text{CeCl}_3$ - $\text{BaCl}_2$ , Nishihara<sup>[4]</sup> reported that it is of simple eutectic type with  $e$  at 65.0 mol.-%  $\text{CeCl}_3$ , 672 °C, but the purity of sample  $\text{CeCl}_3$  used is 89 wt.-%  $\text{CeCl}_3$ ; Фам Нрок Тьен<sup>[5]</sup> reported that it is of peritectic type with eutectic point  $e$  at 71.5 wt.-%  $\text{CeCl}_3$ , 700 °C and peritectic point  $p$  at 55.2 wt.-%  $\text{CeCl}_3$ , 800 °C. We have reinvestigated this system

and found that the result is in agreement with Ref. [5]. We use above data in this paper.

On the basis of investigation on the related binary systems, the phase diagram of the ternary system  $\text{CeCl}_3$ - $\text{BaCl}_2$ - $\text{LiCl}$  was determined. 5 polythermal sections were determined in the paper.

The distribution of these sections in the composition-triangle is shown in Figs. 1—5.

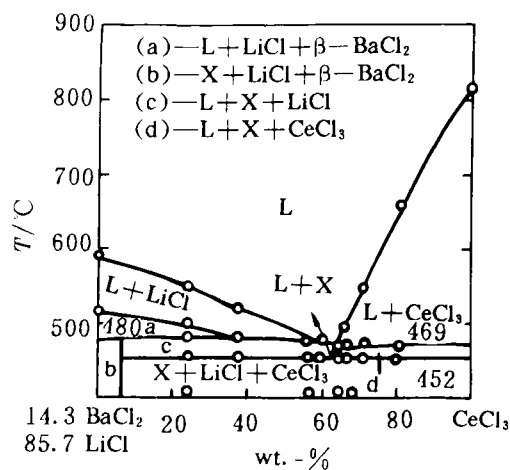


Fig. 1 Section I

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## 2 EXPERIMENTAL

**Materials:**  $\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$  99.5% pure.  $\text{LiCl}$ ,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and others were analytical reagents.

**Dehydration of salts:** The  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  was heated directly to dehydrate and then the temperature was raised to 700 °C and kept constant for 8–10 h. M. P. of the product was 960 °C.  $\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{LiCl}$ , with some moisture, were dehydrated stepwise under an atmosphere of  $\text{HCl}$  at low pressure. The M. P. of  $\text{CeCl}_3$  and  $\text{LiCl}$  were 810 °C and 612 °C respectively. The products were put into  $\text{H}_2\text{O}$  and found that the solution was transparent, meaning that there is not any hydrolysate in the samples. Therefore, the samples were pure enough.

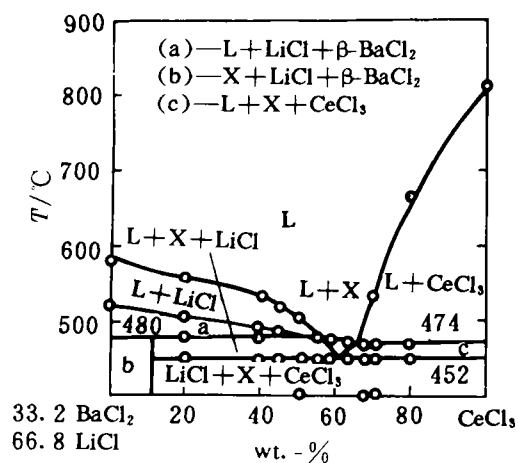


Fig. 2 Section II

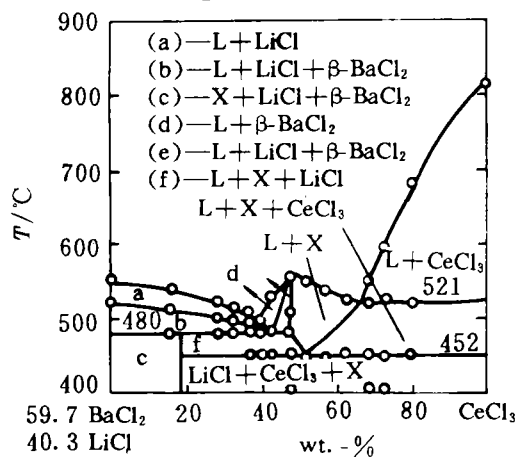


Fig. 3 Section III

**Sample preparation:** The operation carried out in a drybox with  $\text{P}_2\text{O}_5$ . The salt mixtures in appropriate proportions of the components were loaded into quartz ampules and weighed on an analytical balance. Weight of each sample was about 150 mg. The ampules were sealed in vacuum and the samples were homogenized by annealing.

**Differential Thermal Analysis (DTA):** At the bottom of each ampule an indentation was made to fit the  $\text{NiCr-NiAl}$  thermocouple. The thermoanalyzer was calibrated against some standard substances of known melting points. Two curves of calibration were obtained (on cooling and heating). The heating rate was 10 K/min. and pure  $\text{Al}_2\text{O}_3$  was used as reference. When the heat effects on liquidus were to be determined, the cooling curves

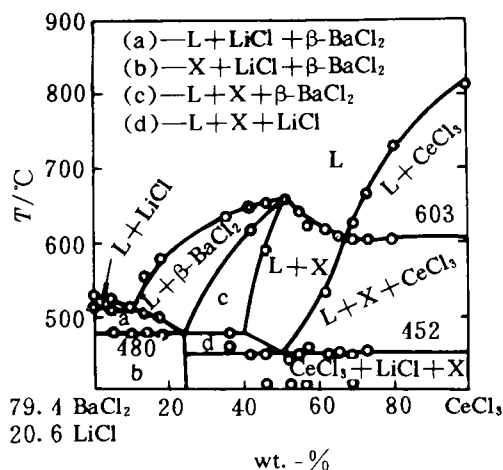


Fig. 1 Section IV

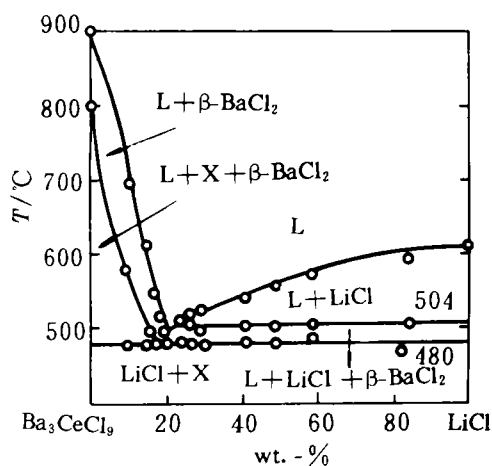


Fig. 5 Section V

were employed and the calibration curve on cooling was referred to accordingly. The other heat effects were determined by heating curves. The temperatures of the heat effects were estimated by means of extrapolation.

**X-ray Diffraction Analysis:** Powder diffraction analysis was carried out on an X-ray diffractometer of BD-74.  $\text{CuK}\alpha$  radiation and Ni filter were used. The sample was sealed in a hermetic capsule with a window of thin membrane.

### 3 RESULTS AND DISCUSSION

Five vertical sections are shown in Fig. 1—5, in which "L" means liquid phase; "X"— $\text{Ba}_3\text{CeCl}_9$ .

Project these points of 5 sections liquidus deflection on the composition-triangle orthogonally and joint the projections 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;

**Table 1 Composition and temperatures of points of deflection on liquidus**

Section		Comp	First point		Second point		Third point	
			wt.-%		wt.-%		wt.-%	
			$T/^\circ\text{C}$		$T/^\circ\text{C}$		$T/^\circ\text{C}$	
I	14.3 $\text{BaCl}_2$	$\text{CeCl}_3$	62.0	474	65.0	469		
	85.7 $\text{LiCl}$							
II	33.2 $\text{BaCl}_2$	$\text{CeCl}_3$	56.0	476	66.0	471		
	66.8 $\text{LiCl}$							
III	59.7 $\text{BaCl}_2$	$\text{CeCl}_3$	40.0	496	18.5	556	67.0	521
	40.3 $\text{LiCl}$							
IV	79.4 $\text{BaCl}_2$	$\text{CeCl}_3$	11.0	513	52.0	653	69.0	603
	20.6 $\text{LiCl}$							
V	$\text{Ba}_3\text{CeCl}_9$	$\text{LiCl}$	21.0 ( $\text{LiCl}$ )	504				

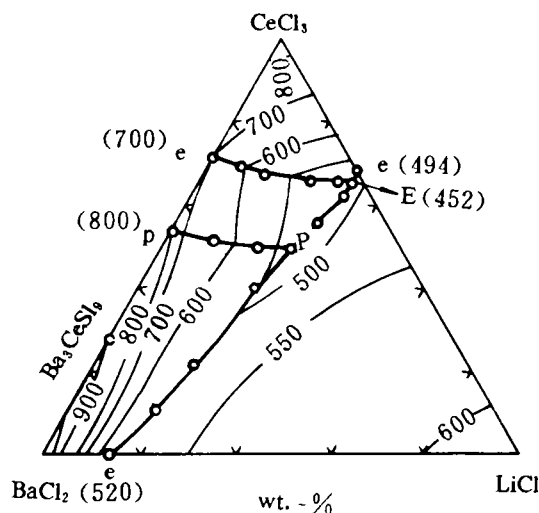
*E* (65.8 wt.-%  $\text{CeCl}_3$ , 2.5 wt.-%  $\text{BaCl}_2$ , 33.2 wt.-%  $\text{LiCl}$ ; 452  $^\circ\text{C}$ )

*P* (50.0 wt.-%  $\text{CeCl}_3$ , 22.8 wt.-%  $\text{BaCl}_2$ , 27.2 wt.-%  $\text{LiCl}$ ; 480  $^\circ\text{C}$ )

The projection and isotherms are shown in Fig. 6.

The formation of compound in the solid state; We observed that the unstable compound *Y*, which decomposed at 430  $^\circ\text{C}$  and 427  $^\circ\text{C}$  respectively,

seemed to form beneath the ternary eutectic in systems  $\text{RECl}_3\text{-BaCl}_2\text{-LiCl}$  ( $\text{RE}=\text{Pr}^{+6}, \text{Nd}^{+3}$ ). It was found that there was a peak of heat effect on the DTA curves at 410  $^\circ\text{C}$  in the region  $\text{CeCl}_3\text{-LiCl-Ba}_3\text{CeCl}_9$ . Though small, the peak was evident and appeared repeatedly in many different samples. The DTA curves of pure substances  $\text{CeCl}_3$ ,  $\text{BaCl}_2$ ,  $\text{LiCl}$ ,  $\text{Ba}_3\text{CeCl}_9$  were scrutinized, and the possibility of their polymorphism was excluded. To confirm the formation of a new phase, we took the X-ray diffraction patterns of  $\text{CeCl}_3$ ,  $\text{LiCl}$ ,  $\text{Ba}_3\text{CeCl}_9$  and B (60.0 wt.-%  $\text{CeCl}_3$ , 25.0 wt.-%  $\text{BaCl}_2$ , 15.0 wt.-%  $\text{LiCl}$ ) in the triangle  $\text{CeCl}_3\text{-LiCl-Ba}_3\text{CeCl}_9$ . It was found that besides those lines of  $\text{CeCl}_3$ ,  $\text{LiCl}$ , and  $\text{Ba}_3\text{CeCl}_9$ , there were evidently feeble lines due to a new phase in the sample B. So, the formation of a new phase has been confirmed. Consequently we supposed that, analogous to that described in ref. [6], the new phase *Y* must be a compound formed in ternary solid state. This compound seemed to form by diffusion in solid phases a process by which equilibrium could hardly be reached. Moreover, due to the reverse process of decomposition the compound was unstable. Therefore, in spite of all attempts made, we failed to get the new phase in pure state, and its composition and structure were still left to be studied.



**Fig. 6 Phase diagram of ternary system  $\text{CeCl}_3\text{-BaCl}_2\text{-LiCl}$**

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other hand, if vacuum distillation proceeds at 1100—1200 °C, molten residue is discharged. Slag in this molten residue is separated from alloy. We may take off the slag, roast the alloy in air.

## 6 CONCLUSIONS

Dearsenication from cobalt-arsenic concentrate by vacuum distillation is feasible to improve the previous pyrometallurgical process. At 950—1050 °C, bulk solid residue is discharged while at 1

100—1200 °C molten residue is discharged. Refined arsenic can be obtained after vacuum redistillation which contains 99.7% arsenic.

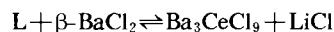
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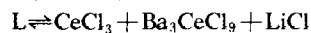
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## 4 CONCLUSIONS

(1) The phase diagram of the ternary system  $\text{CeCl}_3$ - $\text{BaCl}_2$ - $\text{LiCl}$  was determined. There were 5 liquidus surfaces corresponding to  $\text{CeCl}_3$ ,  $\alpha$ - $\text{BaCl}_2$  ( $\alpha$  type of  $\text{BaCl}_2$ ),  $\beta$ - $\text{BaCl}_2$  ( $\beta$  type of  $\text{BaCl}_2$ ),  $\text{LiCl}$  and  $\text{Ba}_3\text{CeCl}_9$  respectively and 6 univariants curves corresponding to the secondary crystallization. Two ternary reactions occur in the system:



$P$  (50.0 wt.-%  $\text{CeCl}_3$ , 22.8 wt.-%  $\text{BaCl}_2$ , 27.2 wt.-%  $\text{LiCl}$ ; 480 °C)



$E$  (65.8 wt.-%  $\text{CeCl}_3$ , 2.5 wt.-%  $\text{BaCl}_2$ , 32.2 wt.-%  $\text{LiCl}$ ; 452 °C)

(2) According to the results of DTA and X-ray diffraction Analysis (XRD), it was found that

an unstable compound was formed in solid state and decomposed at 410 °C.

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