PHASE DIAGRAMS OF THE BINARY SYSTEMS $TbCl_3$–MCl_n (M = Li, Mg, Ca, Pb; n = 1 or 2)①

Zheng, Chaogui Zhao, Zhongdong Wang, Siqiang
Peking University, Beijing 100871, China

ABSTRACT

The phase diagrams of the binary systems $RECl_3$–MCl_n (M = Li, Mg, Ca, Pb; n = 1 or 2) were investigated by means of DTA and X–ray diffraction analysis. It was found that they are of simple eutectic type with eutectic points 50.1 Mol.–% $TbCl_3$(445 ℃), 67.5Mol.–% $TbCl_3$ (589 ℃), 65.9Mol.–% $TbCl_3$ (563 ℃) and 35.6 Mol.–% $TbCl_3$ (445 ℃) respectively. Unstable compounds, formed in the solid state, are $MgTbCl_7$, $CaTb_2Cl_8$, $LiTb_2Cl_7$ and $PbTbCl_5$. Their decomposition temperatures are 388 ℃ with a phase transition at 352, 500 and 521 ℃ with a phase transition at 483 and 405 ℃ respectively. Some rules of the phase diagrams were explored.

Key words: $TbCl_3$ $TbCl_3$— LiCl $TbCl_3$— $MgCl_2$ $TbCl_3$— $CaCl_2$ $TbCl_3$— $PbCl_2$ system phase diagram Rule of phase diagram

1 INTRODUCTION

It is important to investigate the phase diagrams for systems containing chloride for understanding the physico-chemical properties of RE compounds, exploring the rules of phase diagrams, and developing solid coordination compounds. No phase diagram on systems $TbCl_3$–MCl_n(M = Li, Mg, Ca, Pb; n = 1 or 2) have been reported in the literature. As part of a series of study of phase diagrams of systems containing rare earth chloride, the phase diagrams of the above 4 binary systems have been determined by means of DTA and X–ray diffraction analysis.

2 EXPERIMENTAL

LiCl(A.R.), $CaCl_2$ (A.R.) and $PbCl_2$(99.5%), with a little moisture, were dehydrated. Their melting points are 614, 772 and 500 ℃ respectively. Tb_4O_7 (99.5%) was chlorinated with HCl (A.R.) and the resulting $TbCl_3 \cdot 6H_2O$ and $MgCl_2 \cdot 6H_2O$ were respectively placed in P_2O_5 drying vessels and dehydrated for the first time. Then they were vacuum heated respectively in a dry HCl atmosphere and sufficiently dehydrated step by step[1]. Their melting points were determined to be 616 and 724 ℃.

Samples precisely weighed on an analytical balance were put into quartz ampoules under a dry atmosphere. After evacuation and sealing of the ampoules, the samples were melted and carefully shaken to bring about homogenization. Then they were kept at 400 ℃ for 4 h, and left for use in DTA. The thermoanalyzer was calibrated against conventional substances of known melting points. Two calibration curves (heating and cooling) were obtained. The rate of heating was 10 ℃ / min, and Al_2O_3 was used as the reference. The thermal effects on liquids were determined by referring to cooling curves, while for others heating curves were employed. The temperature of the point at which the base line intersects the extrapolation line of the peak was taken

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as the temperature of the heat effect.

The samples for X–ray diffraction analysis were prepared as above. Then the samples were homogenized at 350℃ for two days. Powder diffraction analysis was carried out on an X–ray diffractometer of D/max–YA, Japan. CuKα radiation and Ni filter were used. The sample was sealed in a hermetic capsule with thin membrane window.

The four unstable compounds, formed in the solid state, were determined by means of DTA and X–ray diffraction analysis. In the former, the identification was based on the composition corresponding to the largest heat effect in Tamman's triangle. As to the latter, a new phase was confirmed by a set of X–ray diffraction pattern belonging to the new phase. Meanwhile the composition corresponding to a set of the strongest diffraction peak intensities belongs to the new phase. The experiments confirmed that the results from the two methods are in good agreement.

3 RESULTS

3.1 $TbCl_3$–$LiCl$ *System*

A phase diagram of the $TbCl_3$–$LiCl$ system is shown in Fig. 1. It was found that it is of a simple eutectic type with a eutectic point at 50.1 mol.%(445 ℃). Its eutectic reation is

$$L \xrightleftharpoons{445℃} LiCl_{(s)}+TbCl_{3(s)} \quad (1)$$

The unstable compound $LiTb_2Cl_7$, formed in the solid state, decomposed at 388 ℃ with a phase transition at 352 ℃. Their reactions are

$$LiCl_{(s)}+2TbCl_{3(s)} \xrightarrow[388\sim445\,℃]{<388\,℃} LiTb_2Cl_{7(s)} \quad (2)$$

$$\alpha\text{–}LiTb_2Cl_{7(s)} \xrightarrow[<352℃]{352\sim388\,℃} \beta\text{–}LiTb_2Cl_{7(s)} \quad (3)$$

3.2 $TbCl_3$–$MgCl_2$ *System*

phase diagram of the $TbCl_3$–$MgCl_2$ system is shown in Fig.2. It was found that it is of simple eutectic type with eutectic point at 67.5-mol.–%$TbCl_3$(589℃). The unstable compound Mg_2TbCl_7, formed in the solid state, decomposed at 500 ℃, its reaction is

$$2MgCl_{2(s)}+TbCl_{3(s)} \xrightarrow[500\sim589\,℃]{<500℃} Mg_2TbCl_{7(s)} \quad (4)$$

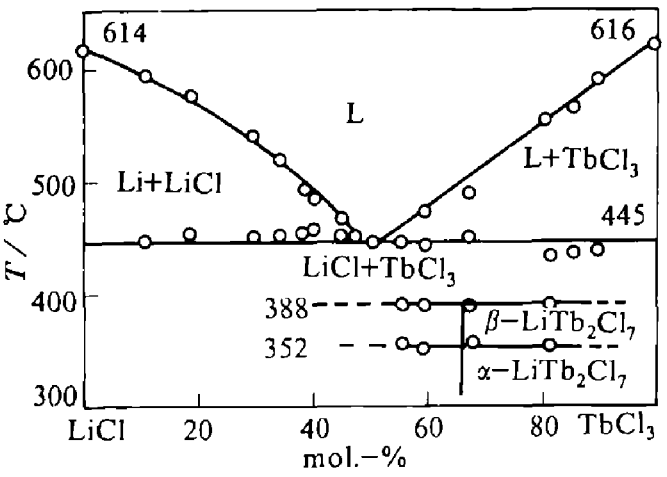

Fig. 1 Phase diagram of $TbCl_3$–$LiCl$ system

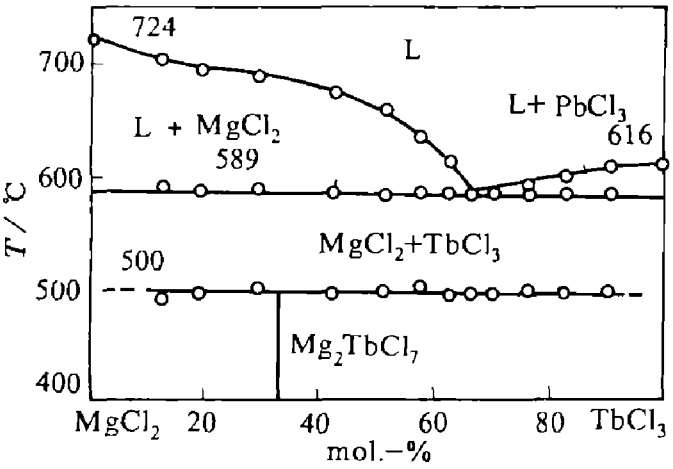

Fig. 2 Phase diagram of the $TbCl_3$–$MgCl_2$ system

3.3 $TbCl_3$–$CaCl_2$ *System*

The phase diagrams of the $TbCl_3$–$CaCl_2$ system is shown in Fig.3, having a eutectic point at 65.9mol.–% $TbCl_3$(563 ℃) in the system. The unstable compound $CaTb_2Cl_8$, formed in the solid state, decomposed at 521 ℃ with a phase transition at 483 ℃. Their reactions are

$$CaCl_{2(s)}+2TbCl_{3(s)} \xrightarrow[521\sim563\,℃]{<521℃} \beta\text{–}CaTb_2Cl_{8(s)} \quad (5)$$

$$\alpha\text{–}CaTb_2Cl_{8(s)} \xrightarrow[<483\,℃]{483\sim521\,℃} \beta\text{–}CaTb_2Cl_{8(s)} \quad (6)$$

This system was not necessarily of a simple eutectic type but possessed a peritectic line over the $CaCl_2$-rich region. Unfortunately, the peritectic compound could not be specified as was the case in the systems $GdCl_3$–$MgCl_2$[2], $GdCl_3$–$CaCl_2$[3], $YbCl_3$–$SrCl_2$[4].

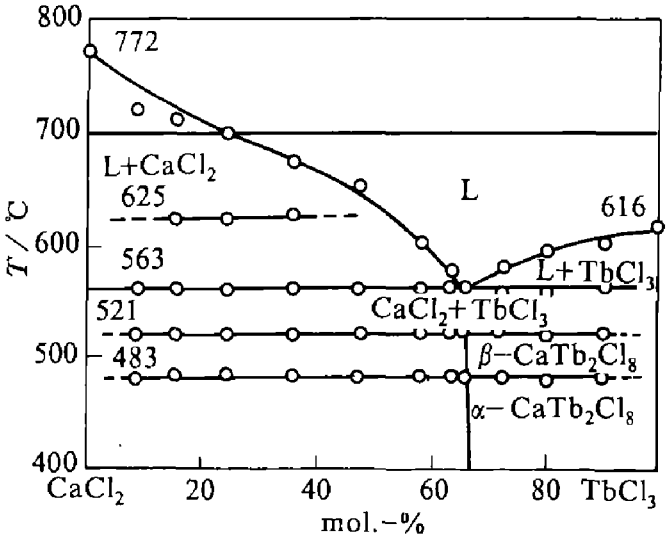

Fig. 3 Phase diagram of $TbCl_3$–$CaCl_2$ system

3.4 $TbCl_3$–$PbCl_2$ *System*

The phase diagram of the $TbCl_3$–$PbCl_2$ system is shown in Fig. 4. It was found that it is of a simple eutectic type with eutectic point at 35.6 mol.–% $TbCl_3$ (445 ℃). An unstable compound $PbTbCl_5$, formed in the solid state, decomposed at 405 ℃. Its reaction is

$$PbCl_{2(s)}+TbCl_{3(s)} \xrightarrow[405\sim445\ ℃]{<405℃} PbTbCl_{5(s)} \qquad (7)$$

4 COUNTER–POLARIZATION FOR THE INFLUENCE OF PHAES DIAGRAM TYPE

In 1987, Zheng–Ye[5]proposed that the accuracy of phase diagram determination could be improved by careful design of experimental procedures and strict treatment of the obtained data. And thus, more precise data, which provide a scientifc basis for drawing thermodynamic information from phase diagrams and for judging the reliability of phase diagram calculation, could be obtained. In 1988[6] attempts were also made to explore the rule governing the alteraton in the phase diagrams containing rare earth chloride, the formation of compounds and their stabilities using the concepts of polarization and counter-polarization. Systems $RECl_3$–$MgCl_2$–LiCl[7] and $RECl_3$––$SrCl_2$–$CaCl_2$[8] (RE = La, Ce, Pr, Nd) were determined, and some rules were explored. This paper explores counter-polarization for the influence of phase diagram type between $RECl_3$–$SrCl_2$ and $RECl_3$–$PbCl_2$.

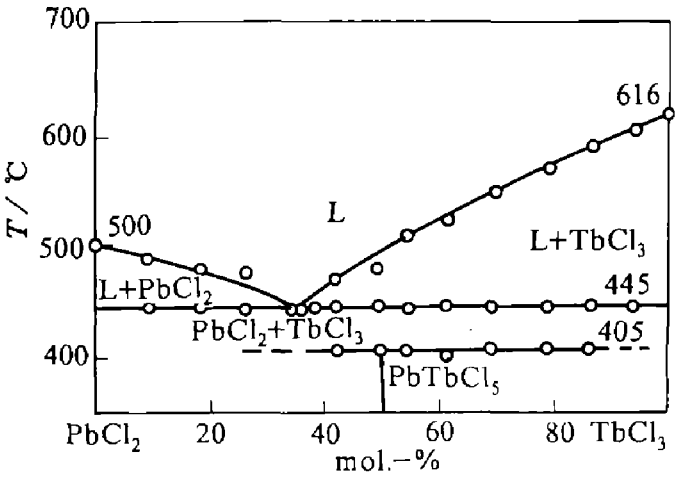

Fig. 4 Phase diagram of $TbCl_3$–$PbCl_2$ system

It is shown in Table 1 that the $RECl_3$–$SrCl_2$ system are of peritectic of complicated type, except $RECl_3$–$SrCl_2$ (RE = La, Ce are of simple eutectic type). Increasing the atomic number of Re leads to an increase in the numbers of Compounds . When RE = Gd and Yb, the number of compounds increases to 2 and 3 respectively; $RECl_3$–$PbCl_2$ systems are of a simple eutectic type. The unstable compound $REPbCl_5$, formed in the solid state, decomposed at about 400 ℃.

The effective ionic radii of $Sr^{2+}$and Pb^{2+} (of coordination number 6) are 0.118 nm and 0.119 nm respectively. They are almost equal in radius. But the types of phase diagrams are quite diferenent from each other. Sr belongs to group 2 in the Periodic Table, and its ionic configuration is of 8 electron-group-state, $\{[Ar]3d^{10}\}4s^24p^6$. However Pb^{2+} is a noble electron pair-group-state, $\{[Xe]4f^{14}\}5d^{10}6s^2$. According to the concept

Table 1 Comparison of phase diagram types for the $RECl_3$—$SrCl_2$ and $RECl_3$—$PbCl_2$ systems

RE	R_{RE}^{3-} / nm	$RECl_3$—$SrCl_2$[8]		$RECl_3$—$PbCl_2$	
		Type	compounds	Type	compounds
La	0.1031	Eutectic	Sr_2LaCl_7 formed in the solid	Eutectic	$LaPbCl_5$ formed in the solid
Ce	0.101	Eutectic	$xCeCl_3 \cdot ySrCl_2$ formed in the solid	Eutectic	$CePbCl_5$ formed in the solid
Pr	0.099	Peritectic	Sr_3PrCl_9 melt incongruently	Eutectic	$PrPbCl_5$ formed in the solid
Nd	0.0983	Peritectic	Sr_3NdCl_9melt incongruently	Eutectic	$NdPbCl_5$ formed in the solid
Gd	0.0938	Complicated	Sr_2GdCl_7	Eutectic	$GdPbCl_5$ formed in the solid
Tb	0.0923		Sr_4GdCl_{11}	Eutectic	$TbPbCl_5$ formed in the solid
Yb	0.0868	Complicated	3 compounds	Eutectic	$YbPbCl_5$ formed in the solid

of polarization, ion configurations with 2 electron group states, 18 electron group states and noble electron pair group state have unusual polariza- tions.

In the $Mn[RECl_m]$ molecule, the attraction of RE^{3+} to Cl^- is called as a polarization of RE^{3+} to Cl^-. The attraction of M^{p+}, which exists in the outside of the complex ion $[RECl_m]^{(m-3)-}$, to Cl^- is called as counter-polarization of M^{p+}, which exist in the outside of the complex ion $[RECl_m]^{(m-3)-}$, to Cl^- is called a counter polarisation of $M^{p+}(Pb^{2+})$. With increasing the counter-polarization of $M^{p+}(Pb^{2+})$, the stabillity of formed $MCl_p(PbCl_2)$ increase, the stability of complex ion$[RECl_m]^{(m-3)-}$and coordination compound $Mn(RECl_m]$ decrease. The numbers of compounds formed decrease, so that the compound could not be formed or only formed very unstable compounds in the solid state. So the types of phase diagrams tend to simple eutectic type. This illustrates that counter- polarization is also an important factor influencing phase diagram types.

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