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Phase diagram of $SmCl_3$–$PbCl_2$–$MgCl_2$

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Abstract

The phase diagram of the rare-earth system $SmCl_3$–$PbCl_2$–$MgCl_2$ has been investigated by DTA. The results of the ternary system are as follows: four liquidus surfaces corresponding to the primary crystallization of $SmCl_3$, $PbCl_2$, $MgCl_2$ and $PbSm_3Cl_{11}$, respectively, five secondary crystallization lines, the ternary eutectic point $E = 695$ K (25.0 mol% $SmCl_3$, 57.0 mol% $PbCl_2$), and the ternary peritectic point $P = 713$ K (31.5 mol% $SmCl_3$, 48.0 mol% $PbCl_2$). The reactions between four equilibrium phases are:

$$L_P + SmCl_3 \rightleftharpoons PbSm_3Cl_{11} + MgCl_2$$

$$L_E \rightleftharpoons PbSm_3Cl_{11} + PbCl_2 + MgCl_2.$$

Keywords: DTA; Lead chloride; Magnesium chloride; Phase diagram; Samarium chloride

1. Introduction

It is obvious that investigations on phase diagrams of rare-earth salts are very important for understanding the basic physicochemical properties of rare-earth compounds, the electrolytic production of rare-earth metals and material science. However, there are only few references in the literature related to this subject. As part of the series of investigations on the phase diagrams of rare-earth chloride systems, we have determined the phase diagram of the ternary system $SmCl_3$–$PbCl_2$–$MgCl_2$ by DTA, which has not been previously reported in the literature.

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2. Experimental methods

2.1. The anhydrous salts

$PbCl_2$ (A.R) was heated at 573 K for a long time. The melting temperature of $PbCl_2$ is 773 K. Dehydration of $MgCl_2$ must be carried out in dry HCl because the basic salt Mg(OH)Cl is easily formed when the hydrated salt $MgCl_2{\cdot}6H_2O$ is heated:

$$MgCl_2{\cdot}6H_2O \rightleftharpoons Mg(OH)Cl + HCl_{(g)} + 5H_2O_{(g)}$$

The melting temperature of $MgCl_2$ is 983 K. Sm_2O_3 (99.9 wt% cream-yellow powder) was chlorinated with HCl (A.R), and the resulting $SmCl_3{\cdot}6H_2O$ was placed in a drying vessel in P_2O_5 and dehydrated for the first time, then it was vacuum-heated to dehydrated

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step by step in dry HCl [1]. The melting temperature of $SmCl_3$ is 949 K.

2.2. Preparation of samples

The operation was performed in a P_2O_5 drying box. Samples of about 150 mg were placed in silica ampoules and accurately weighted on a balance. The ampoules were sealed under vacuum. The samples were melted, thoroughly shaken and annealed for 12 h at 673 K.

2.3. DTA

The sample tube has a hole at the bottom in which a NiCr–NiSi thermocouple was placed. The DTA apparatus was calibrated by standard substances (KNO_3, 400.7 K; Sn, 504.9 K; $KClO_4$, 572.5 K; Zn, 692.5 K; SiO_2, 846 K; K_2SO_4, 856 K; K_2CrO_4, 938 K; $BaCO_3$, 1083 K) with known transition temperatures (calibrating the heating and cooling curves at the same time). The heating rate was 10 K min^{-1}. Al_2O_3 was used as reference substance. The temperature error was ± 3 K. The liquidus temperature was determined with the aid of the cooling curve. (We determined it with the aid of both of the heating curve and the cooling curve when the undercooling phenomena occurred.) Other temperatures were determined using the extrapolated initial temperature of the peaks from the heating curve.

3. Results

3.1. Studies on phase diagrams of the binary systems

The phase diagrams of binary system $SmCl_3$–$PbCl_2$ has been reported [2], which contains the compound $PbSm_3Cl_{11}$, the eutectic point of which was found at $e_1 = 725$ K (67.0 mol% $PbCl_2$) and the peritectic point at $p_1 = 738$ K (58.0 mol% $PbCl_2$). The phase diagrams of binary system $SmCl_3$–$MgCl_2$ has been previously investigated [3,4], and the eutectic point of which was found at $e_3 = 862$ K (38.0 mol% $MgCl_2$). The phase diagram of system $PbCl_2$–$MgCl_2$ was reported in literature [5,6]. Before determining the ternary phase diagram, we studied the literature on

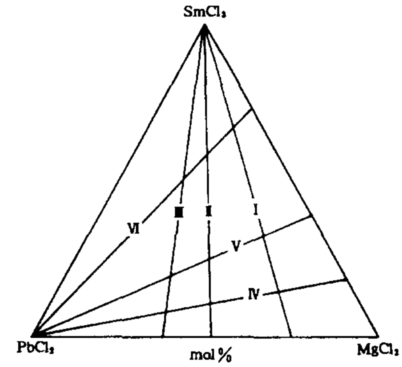

Fig. 1. Position of six vertical sections on the composition triangle.

phase diagram of the $PbCl_2$–$MgCl_2$ system. The result is similar to Ref. [6], $e_2 = 731$ K (16.0 mol% $MgCl_2$) (in Ref. [6], $e = 729$ K, 17.0 mol% $MgCl_2$).

3.2. Construction of the phase diagram of the $SmCl_3$–$PbCl_2$–$MgCl_2$ ternary system

Six vertical sections were determined and their position in the composition triangle is shown in Fig. 1. The vertical sections I, IV and VI are shown in Figs. 2–4. (Sections II, III are similar to I, Section V is similar to IV, so they were omitted.)

In these figures, L presents liquid phase and M the incongruent melting compound $PbSm_3Cl_{11}$. The compositions and temperatures of the deflection points on liquidus of these vertical sections are shown in Table 1.

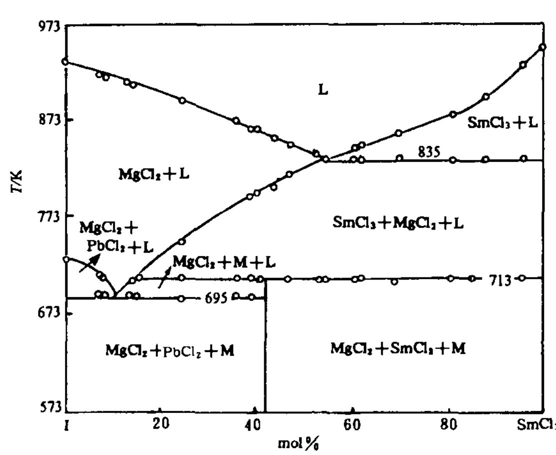

Fig. 2. Section I.

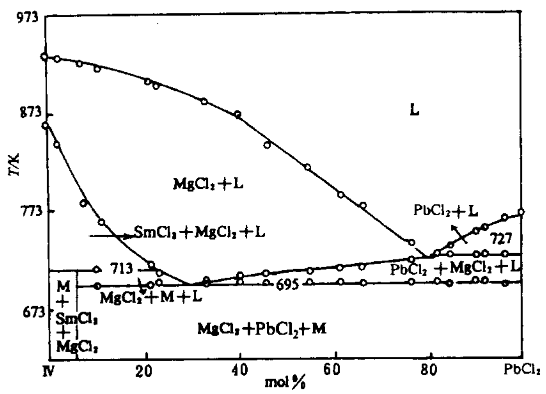

Fig. 3. Section IV.

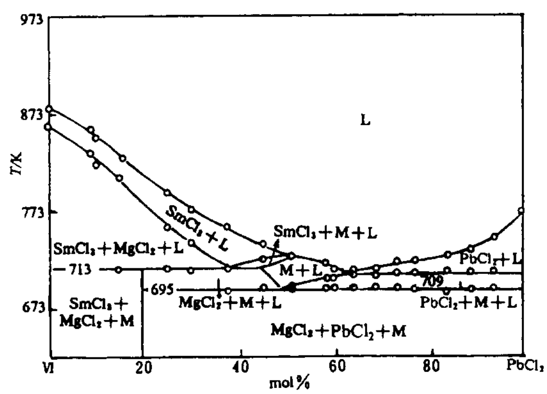

Fig. 4. Section VI.

Table 1
Composition and temperature of deflection points on the liquidus

	Section	mol%	Deflection point	mol%	Temperature (K)
I	$PbCl_2$	25.06			
	$MgCl_2$	74.94	$SmCl_3$	54.0	835
II	$PbCl_2$	48.34			
	$MgCl_2$	51.66	$SmCl_3$	45.0	773
III	$PbCl_2$	62.00			
	$MgCl_2$	38.00	$SmCl_3$	38.0	743
IV	$SmCl_3$	18.48			
	$MgCl_2$	81.52	$PbCl_2$	81.0	727
V	$SmCl_3$	39.00			
	$MgCl_2$	61.00	$PbCl_2$	73.8	716
VI	$SmCl_3$	73.04	$PbCl_2$	51.0	727
	$MgCl_2$	26.96	$PbCl_2$	61.0	709

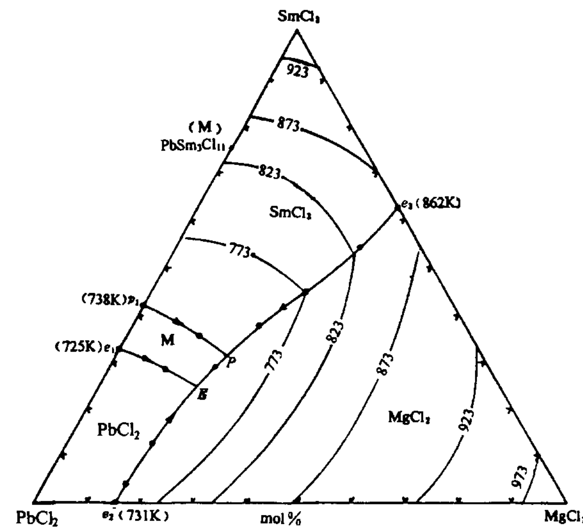

Fig. 5. Phase diagram of $SmCl_3$–$PbCl_2$–$MgCl_2$.

The compositions and temperatures of the deflection points on the liquidus of the six vertical sections in Table 1 are orthogonally projected onto the Gibbs triangle. When they are connected, they form the secondary crystallization lines. We determined the ternary eutectic point $E = 695$ K (25.0 mol% $SmCl_3$, 57.0 mol% $PbCl_2$) and the ternary peritectic point $P = 713$ K (31.5 mol% $SmCl_3$, 48.0 mol% $PbCl_2$). The phase diagram of the ternary system is given in Fig. 5.

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