ELSEVIER

Thermochimica Acta 275 (1996) 295-300

thermochimica acta

Phase diagrams of $SmCl_3$–$ZnCl_2$ and $SmCl_3$–$ZnCl_2$–$MgCl_2$

Yifeng Zhang *, Rongjie Gao, Yan Fu

Department of Chemistry, Northeastern University, Shenyang 110006, People's Republic of China

Received 24 March 1995; accepted 26 July 1995

Abstract

The phase diagrams of molten salts of the rare earth systems $SmCl_3$–$ZnCl_2$ and $SmCl_3$–$ZnCl_2$–$MgCl_2$ have been investigated by DTA. The phase diagram of the binary system $SmCl_3$–$ZnCl_2$ displays a simple eutectic, $e_1 = 290°C$ (7.7 mol% $SmCl_3$). The phase diagram of the ternary $SmCl_3$–$ZnCl_2$–$MgCl_2$ system is also of simple eutectic type, with the ternary eutectic $E = 282°C$ (7.0 mol% $SmCl_3$, 92.5 mol% $ZnCl_2$).

Keywords: DTA; Magnesium chloride; Phase diagram; Samarium chloride; Zinc 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 these compounds and their production, utilization and materials science. However, there are only a few references in the literature related to the subject of this paper. As part of a series of investigations on the phase diagrams of rare earth chloride systems, we have determined the phase diagrams of the binary system $SmCl_3$–$ZnCl_2$ and the ternary system $SmCl_3$–$ZnCl_2$–$MgCl_2$ by DTA, which have not previously been reported in the literature.

2. Experimental

2.1. The anhydrous salts

Dehydration of the salts must take place in dry HCl, because the basic salts Zn(OH)Cl, Mg(OH)Cl and Mg(OH)Cl are easily formed when the hydrated salts

* Corresponding author. Fax: 0086-024-3891829.

Elsevier Science B.V.
SSDI 0040-6031(95)02679-7

$ZnCl_2 \cdot H_2O$ and $MgCl_2 \cdot 6H_2O$ are heated

$$ZnCl_2 \cdot H_2O \rightleftharpoons Zn(OH)Cl + HCl(g)$$

$$MgCl_2 \cdot 6H_2O \rightleftharpoons Mg(OH)Cl + HCl(g) + 5H_2O(g)$$

The melting temperature of $ZnCl_2$ is 310°C and that of $MgCl_2$ is 710°C. Sm_2O_3 (99.9 wt%, cream-yellow powder, Ultrafunction Enterprise Co., Ltd., Huizhou, Guangdong, PRC) 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. It was then vacuum-heated in dry HCl and sufficiently dehydrated step by step [1]. The melting temperature of $SmCl_3$ is 676°C.

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 weighed on a balance. The ampoules were sealed under vacuum, the samples were melted and thoroughly shaken, and annealed for 12 h at 400°C.

2.3. *DTA*

The sample tube has an insert at the bottom in which a NiCr–NiSi thermocouple was placed. The DTA apparatus was calibrated by standard substances (KNO_3, 127.7°C; Sn, 231.9°C; $KClO_4$, 299.5°C; Zn, 419.5°C; SiO_2, 573°C; K_2SO_4, 583°C; K_2CrO_4, 665°C; $BaCO_3$, 810°C) with known phase change temperatures (calibrating the heating and cooling curves at the same time). The heating rate was 10°C min^{-1}. Al_2O_3 was used as reference substance. The temperature error was ± 3°C. The liquidus temperature was determined with the aid of the cooling curve. 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 system $SmCl_3$–$ZnCl_2$*

The $SmCl_3$–$ZnCl_2$ phase diagram is shown in Fig. 1. It is a simple eutectic system, with the eutectic point at $e_1 = 290$°C (7.7 mol % $SmCl_3$).

3.2. *Studies on phase diagrams of other binary systems*

Before determining the ternary phase diagram, we studied the literature on phase diagrams of the above two binary systems. The phase diagrams of $ZnCl_2$–$MgCl_2$ and $SmCl_3$–$MgCl_2$ were reported in Refs. [2–4]. The result for $ZnCl_2$–$MgCl_2$ is shown in Fig. 2; $e_2 = 303$°C, 1.0 mol% $MgCl_2$; Ref. [2] reports $e = 271$°C, close to $ZnCl_2$. For the $SmCl_2$–$MgCl_2$ system, $e_3 = 589$°C, 38.0 mol% $MgCl_2$ is the same as in Ref. [3], but different from that in Ref. [4] (in Ref. [4] $e = 599$°C, 57.5 mol% $MgCl_2$).

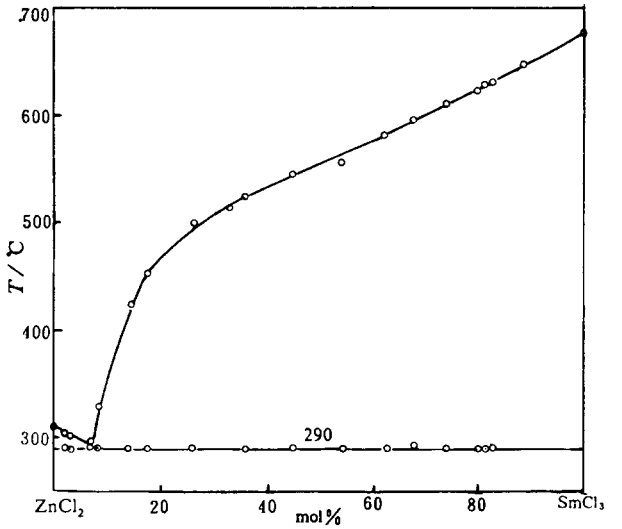

Fig. 1. Phase diagram of the $SmCl_3$–$ZnCl_2$ system.

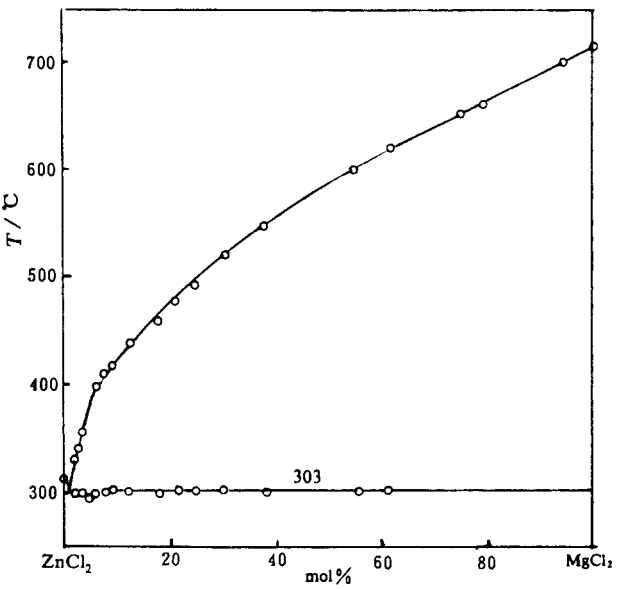

Fig. 2. Phase diagram of the $ZnCl_2$–$MgCl_2$ system.

3.3. *Construction of the phase diagram of the $SmCl_3$–$ZnCl_2$–$MgCl_2$ system*

Four vertical sections were determined, and their position in the composition triangle is shown in Fig. 3. The liquidus curves of these vertical sections are shown in

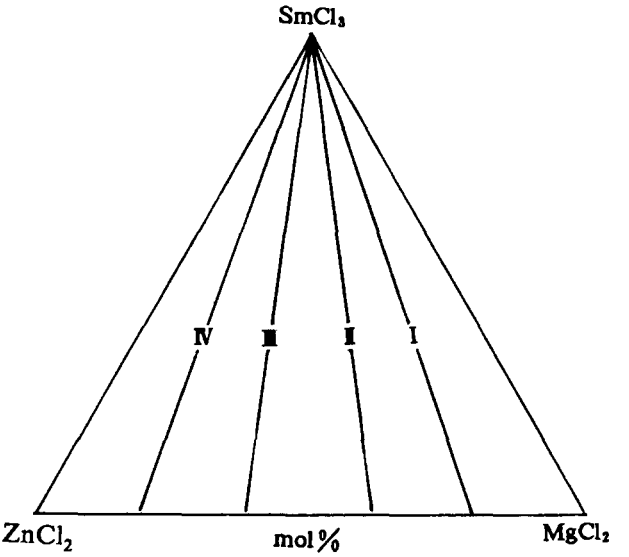

Fig. 3. Position of four vertical sections in the composition triangle.

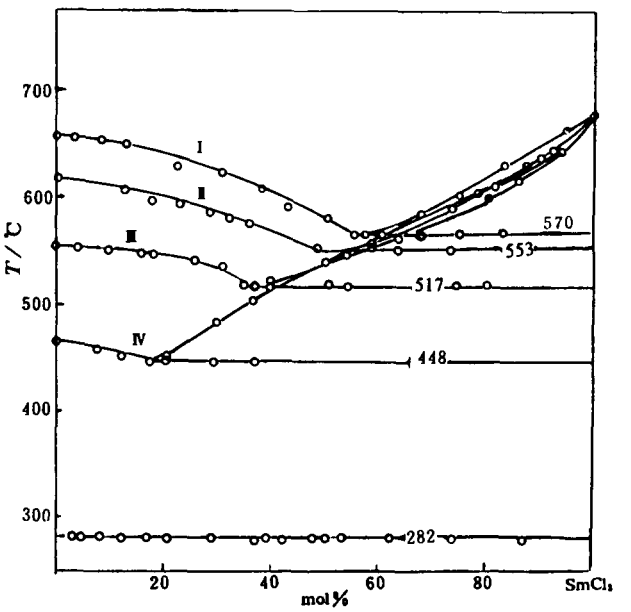

Fig. 4. Compositions and temperatures of composition triangle deflection points on the liquidus curves.

Fig. 4. The compositions and temperatures of the deflection points on the liquidus curves along various vertical sections are shown in Table 1.

The compositions and temperatures of the deflection points on the liquidus curves in the four vertical sections in Table 1 were projected orthogonally onto the base triangle.

Table 1
Compositions and temperatures of deflection points on the liquidus curves

	Section/mol%	Deflection points	
		mol% $SmCl_3$	°C
I	$ZnCl_2$ 20.3 $MgCl_2$ 79.7	57.0	570
II	$ZnCl_2$ 38.4 $MgCl_2$ 61.6	49.5	553
III	$ZnCl_2$ 61.9 $MgCl_2$ 38.1	35.0	517
IV	$ZnCl_2$ 81.4 $MgCl_2$ 18.6	17.6	448

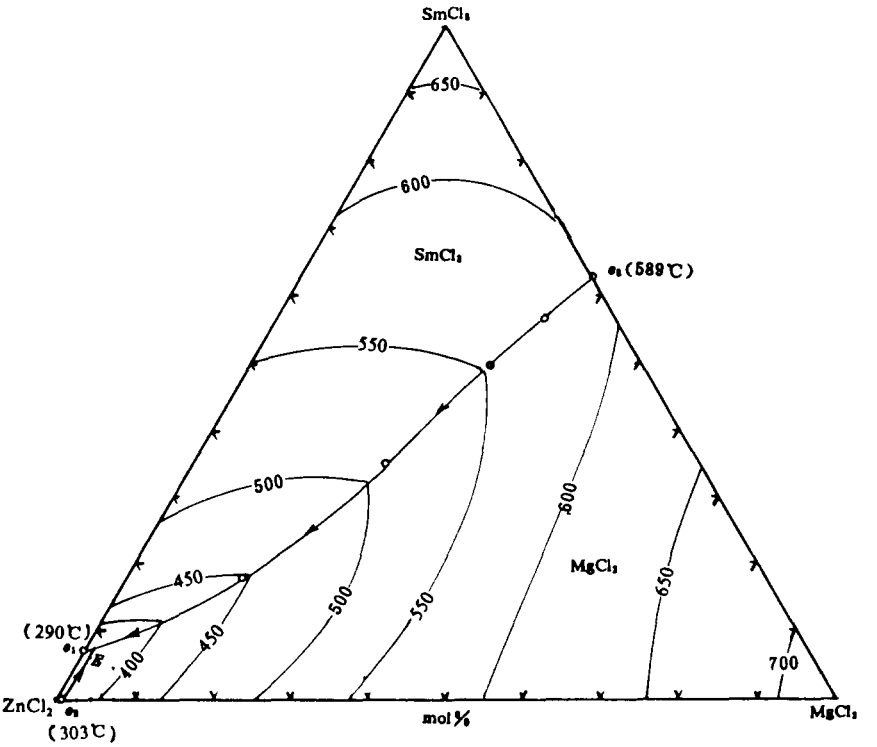

Fig. 5. Orthogonal projection of secondary crystallization lines and isothermals of the ternary system $SmCl_3$–$ZnCl_2$–$MgCl_2$.

When they are connected, they form the secondary crystallization line. We determined the ternary eutectic point at $E = 282$°C (7.0 mol% $SmCl_3$, 92.5 mol% $ZnCl_2$) by extrapolation. The projection of the liquidus surface on the Gibbs triangle of the ternary system is given in Fig. 5.

References

[1] Su Mianzeng, Chem. Bull., 4 (1979) 22 (in Chinese).
[2] O. Menge, Z. Anorg. Chem., Bd 72 (1911) 2,S. 162–218.
[3] Zhang Yifeng and Meng Bo, Acta Chimica Sinica, 50 (1992) 257.
[4] G. Vogel and A. Schneider, Inorg. Nucl. Chem. Lett., 8 (1972) 513.