ELSEVIER

Thermochimica Acta 254 (1995) 383–390

thermochimica acta

Note

Phase diagram of the ternary system $SmCl_3$–NaCl–$CaCl_2$

Yifeng Zhang *, Yuanshan Han, Shulan Wang

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

Received 18 April 1994; accepted 21 July 1994

Abstract

The phase diagram of molten salts of the rare earth system $SmCl_3$–NaCl–$CaCl_2$ has been investigated by DTA. For four liquidus corresponding to the primary crystallization of $SmCl_3$, NaCl, $CaCl_2$ and $2NaCl \cdot SmCl_3$, five univariant lines related to the secondary crystallization, ternary eutectic point $E = 376°C$ (33.1 mol% $SmCl_3$, 46.9 mol% NaCl) and ternary peritectic point $P = 389°C$ (29.3 mol% $SmCl_3$, 52.6 mol% NaCl) were found.

Keywords: Calcium chloride; DTA; Phase diagram; Samarium chloride; Sodium chloride; Ternary system

1. Introduction

It is obvious that investigations on phase diagrams of rare earth molten salts are very important for understanding the basic physical chemistry properties of these compounds and the electrolytic production of their metals. However, there are only a few references in the literature related to this subject. As part of the series of investigations on phase diagrams of molten salts of rare earth chloride systems, we have determined the phase diagram of the ternary system $SmCl_3$–NaCl–$CaCl_2$ by DTA, which has not previously been reported in the literature.

* Corresponding author.

SSDI 0040-6031(94)02030-2

2. Experimental methods

2.1. The anhydrous salts

NaCl (A.R.) and $CaCl_2$ (A.R.) were prepared and sufficiently dehydrated. The melting temperature of NaCl is 800°C and that of $CaCl_2$ is 775°C. Sm_2O_3 (99.9 wt%) was chlorinated with HCl (A.R.), and the resulting $SmCl_3 \cdot 6H_2O$ 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 conducted 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, and the samples were melted and thoroughly shaken, and annealed for 12 h at 400°C.

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 with known

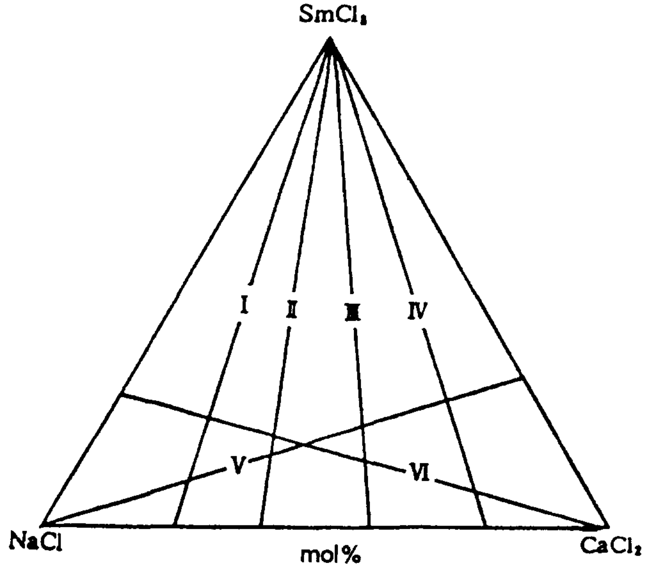

Fig. 1. Distribution of six sections on the composition triangle.

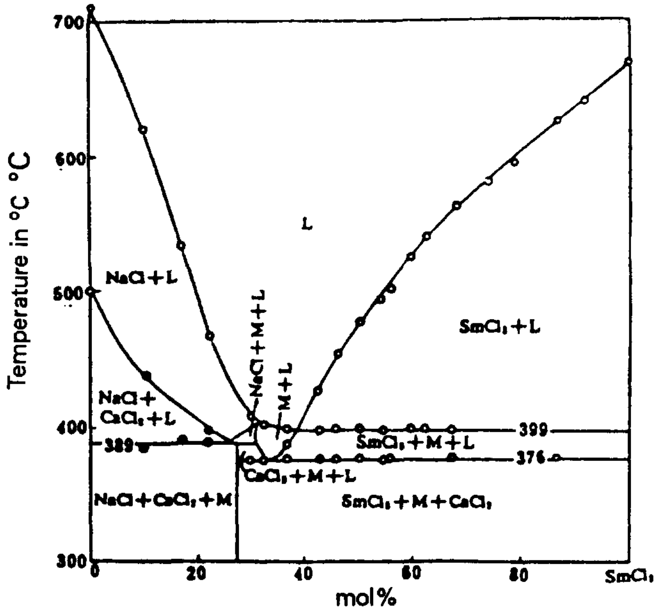

Fig. 2. Section I.

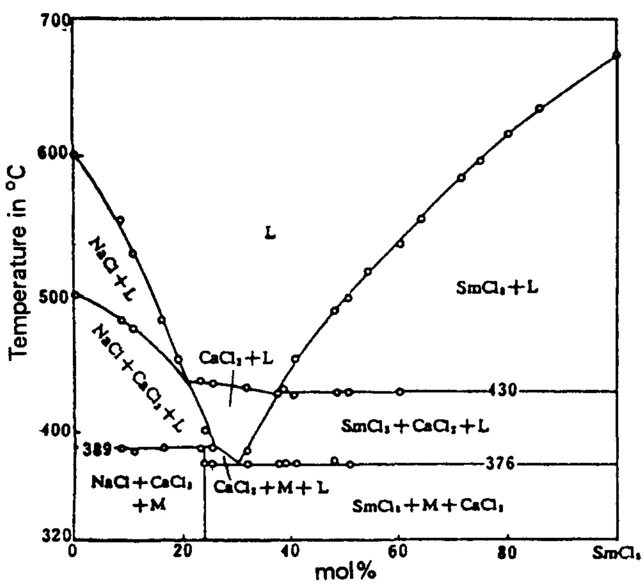

Fig. 3. Section II.

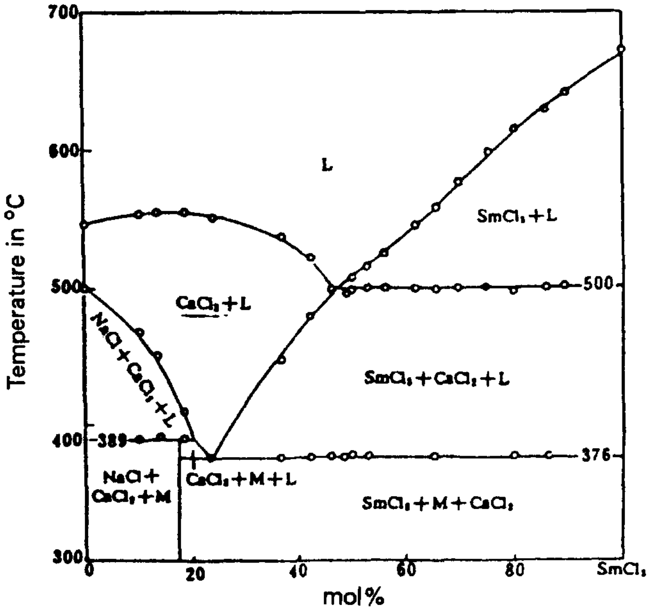

Fig. 4. Section III.

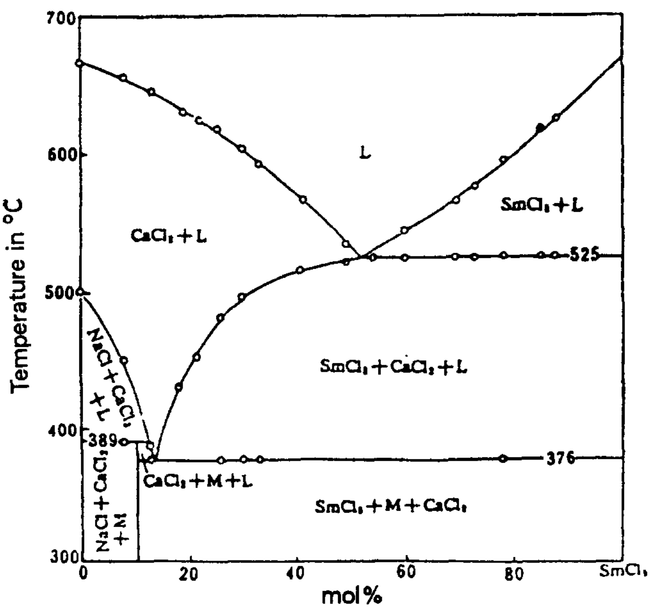

Fig. 5. Section IV.

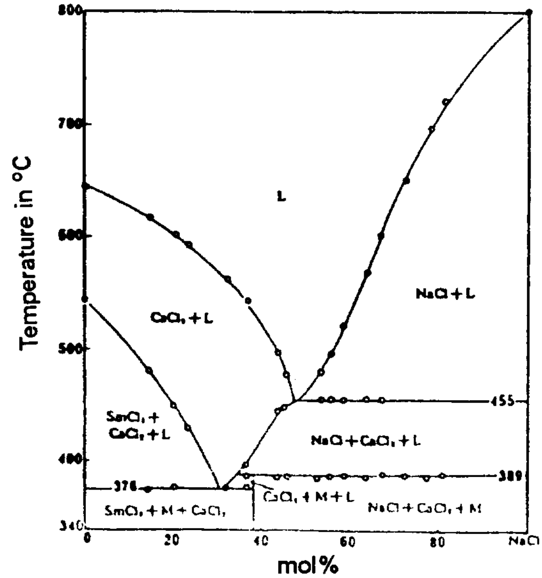

Fig. 6. Section V.

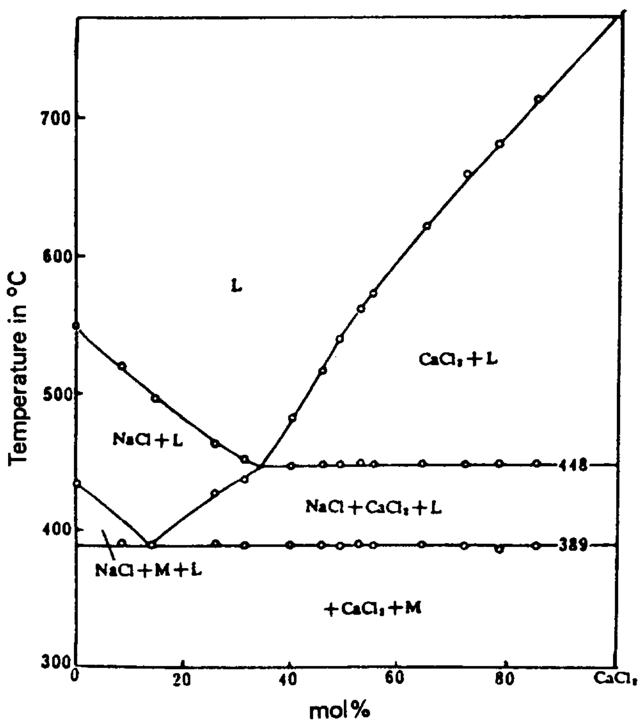

Fig. 7. Section VI.

phase change 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 $\pm 3°C$. The liquidus temperature was determined with the aid of the cooling curve; other temperatures were determined using the extended initial temperature of the peaks from the heating curve.

3. Results

3.1. Studies on related phase diagrams of binary systems

The related phase diagrams of the binary systems $SmCl_3$–NaCl, NaCl–$CaCl_2$ and $SmCl_3$–$CaCl_2$ were reported in Refs. [2]–[4]. Before determining the ternary phase diagram, we studied the literature on phase diagrams of the above two binary systems. The results for $SmCl_3$–NaCl are different from those in Ref. [2] for invariant temperatures. In the former, $e_1 = 410°C$ (50.0 mol% NaCl) and $p = 435°C$ (61.0 mol% NaCl), whereas in Ref. [2] $e_1 = 390°C$ and $p = 425°C$. Hence the invariant temperatures are higher than the values cited in the literature. Firstly, the reason may be the more effective dehydration (e.g. the melting point of $SmCl_3$ in Ref. [2] is 665°C and in this paper is 676°C); secondly, perhaps it is due to the strictly sealed conditions of the whole experimental process. The result for NaCl–$CaCl_2$ is the same as in Ref. [3], being of a simple eutectic type, i.e. $e_2 = 500°C$ (51.0 mol% $CaCl_2$). $SmCl_3$–$CaCl_2$ is also a simple eutectic system, for which $e_3 = 545°C$ (55.8 mol% $SmCl_3$).

Table 1
Compositions and temperatures of deflection points on the liquidus

Section		Mol%			Temperature in °C	Mol%	Temperature in °C
I	$CaCl_2$ NaCl	22.3 77.7	$SmCl_3$	31.5	401	38.5	399
II	$CaCl_2$ NaCl	38.2 61.8	$SmCl_3$	21.0	436	38.0	430
III	$CaCl_2$ NaCl	57.7 42.3	$SmCl_3$	46.5	500		
IV	$CaCl_2$ NaCl	78.2 21.8	$SmCl_3$	52.0	525		
V	$CaCl_2$ $SmCl_3$	68.7 31.3	NaCl	48.0	455		
VI	NaCl $SmCl_3$	72.8 27.2	$CaCl_2$	34.5	448		

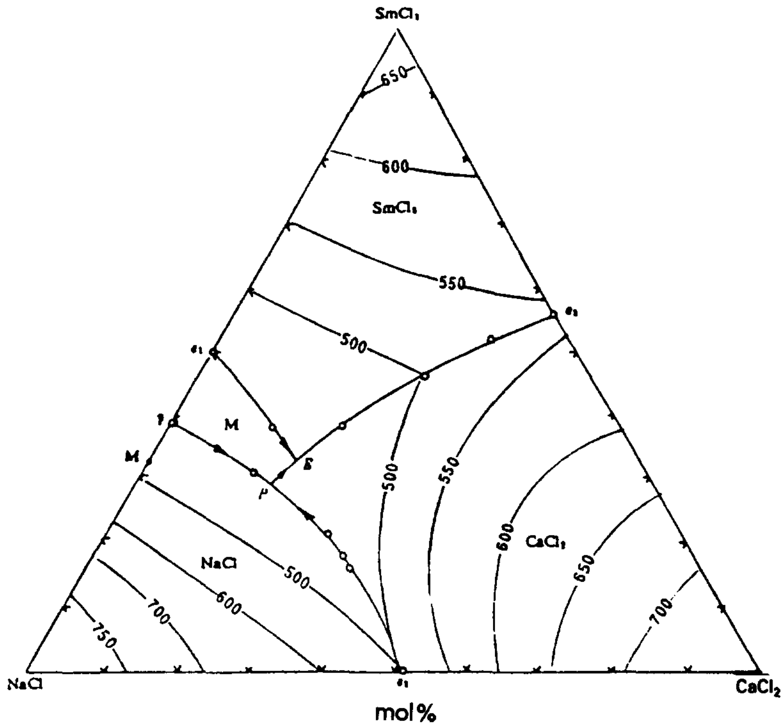

Fig. 8. Phase diagram of $SmCl_3$–NaCl–$CaCl_2$.

3.2. *Construction of the phase diagram of the $SmCl_3$–NaCl–$CaCl_2$ system*

Six vertical sections were determined, and their distribution in the composition triangle is shown in Fig. 1. The vertical sections I–VI are shown in Figs. 2–7. In these Figures L represents the liquid phase, and M represents the incongruent compound 2NaCl · $SmCl_3$. The compositions and temperatures of deflection points on the liquidus at various vertical sections are shown in Table 1.

The compositions and temperatures of the deflection points on the liquidus at the six vertical sections in Table 1 are orthogonally projected onto the base triangle. When they are connected, they form secondary crystallization lines. Extending and intersecting, and according to the calorific effect of equilibrium reactions with four phases under liquidus, we determine the ternary eutectic point $E = 376°C$ (33.1 mol% $SmCl_3$, 46.9 mol% NaCl) and the ternary peritectic point $P = 389°C$ (29.3 mol% $SmCl_3$, 52.6 mol% NaCl). The phase diagram of the ternary system is given in Fig. 8.

References

[1] Su Mianzeng, Chem. Bull., 4 (1979) 22 (in Chinese).
[2] B.G. Korshunov, Zh. Neorgan. Khim., 9 (1964) 1427.
[3] Li Ruiqing and Qiao Zhiyu, J. Univ. Sci. Technol. Beijing, 9 (1987) 114.
[4] Zhang Yifeng, Acta Metall. Sin. 27 (1991) B438.