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Thermochimica Acta 254 (1995) 383–390

thermochimica
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Note

Phase diagram of the ternary system $\text{SmCl}_3\text{--NaCl--CaCl}_2$

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Received 18 April 1994; accepted 21 July 1994

Abstract

The phase diagram of molten salts of the rare earth system $\text{SmCl}_3\text{--NaCl--CaCl}_2$ has been investigated by DTA. For four liquidus corresponding to the primary crystallization of SmCl_3 , NaCl , CaCl_2 and $2\text{NaCl}\cdot\text{SmCl}_3$, five univariant lines related to the secondary crystallization, ternary eutectic point $E = 376^\circ\text{C}$ (33.1 mol% SmCl_3 , 46.9 mol% NaCl) and ternary peritectic point $P = 389^\circ\text{C}$ (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 $\text{SmCl}_3\text{--NaCl--CaCl}_2$ by DTA, which has not previously been reported in the literature.

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2. Experimental methods

2.1. The anhydrous salts

NaCl (A.R.) and CaCl₂ (A.R.) were prepared and sufficiently dehydrated. The melting temperature of NaCl is 800°C and that of CaCl₂ is 775°C. Sm₂O₃ (99.9 wt%) was chlorinated with HCl (A.R.), and the resulting SmCl₃ · 6H₂O placed in a drying vessel in P₂O₅ 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 SmCl₃ is 676°C.

2.2. Preparation of samples

The operation was conducted in a P₂O₅ 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

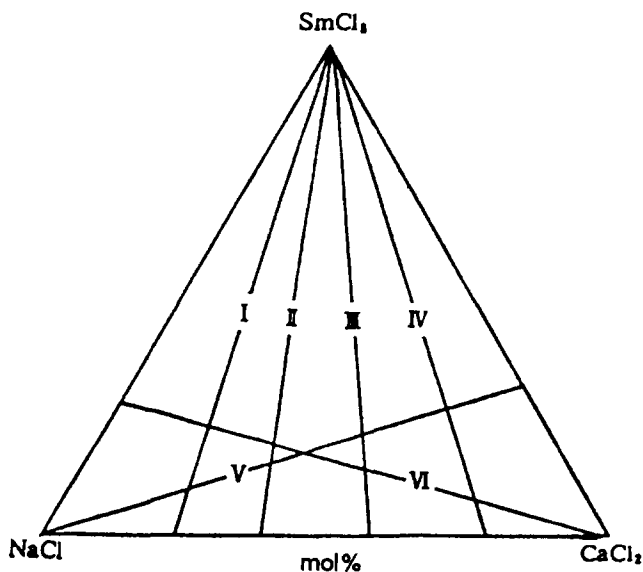


Fig. 1. Distribution of six sections on the composition triangle.

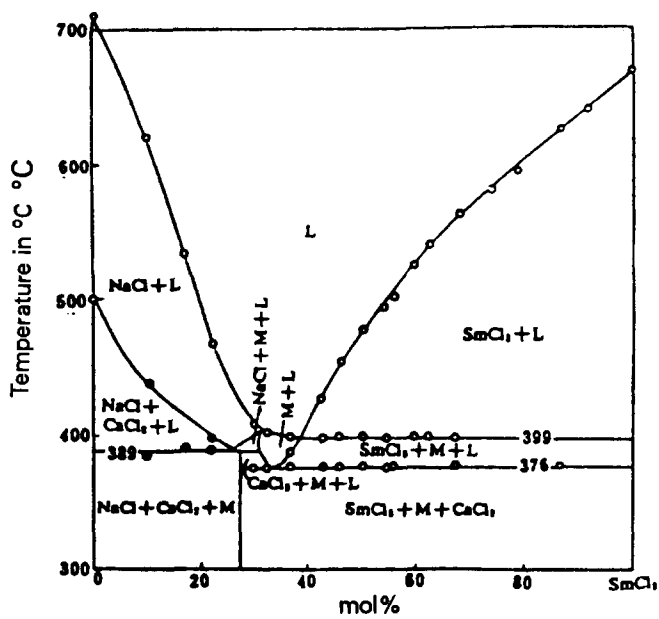


Fig. 2. Section I.

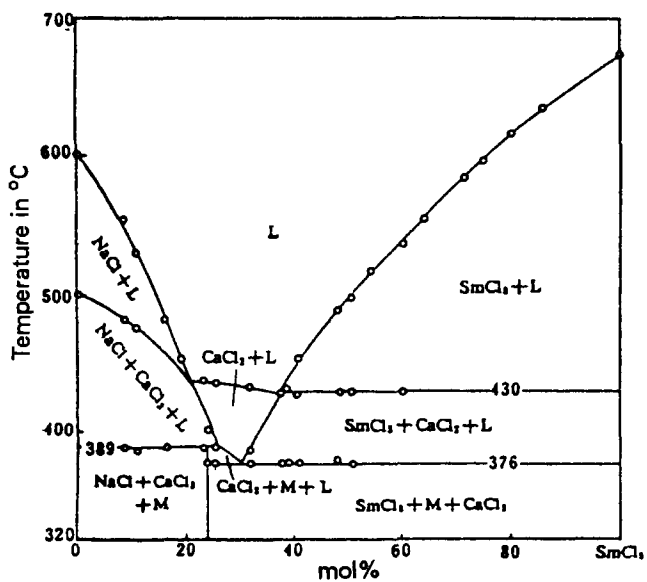


Fig. 3. Section II.

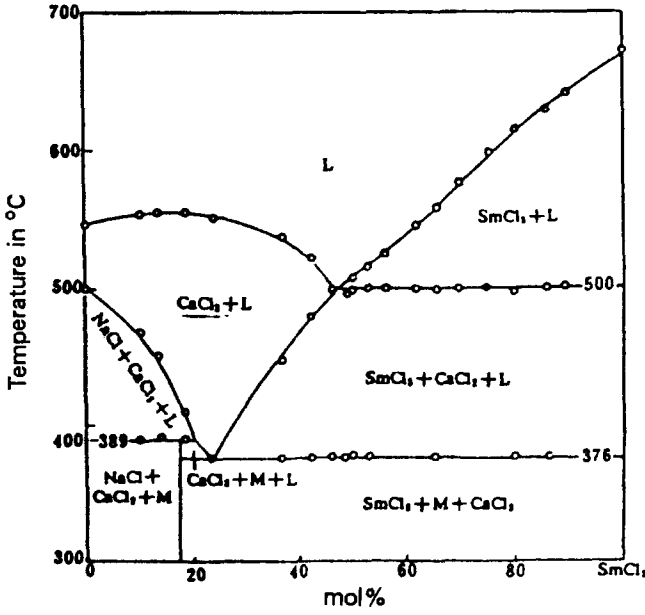


Fig. 4. Section III.

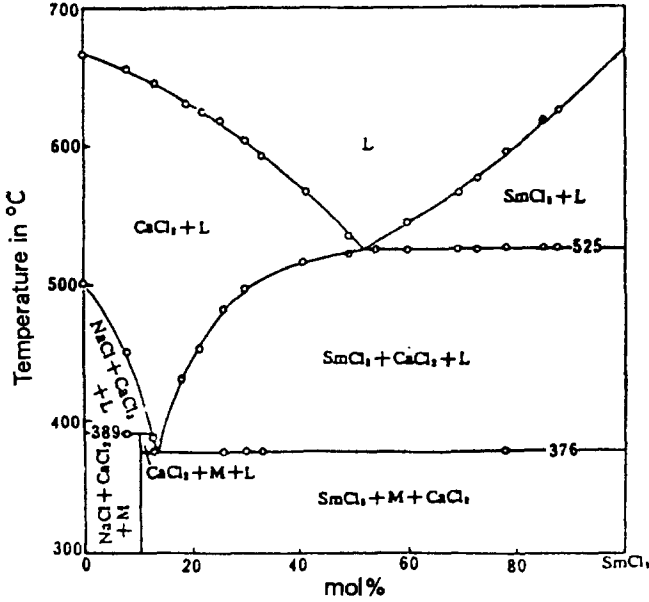


Fig. 5. Section IV.

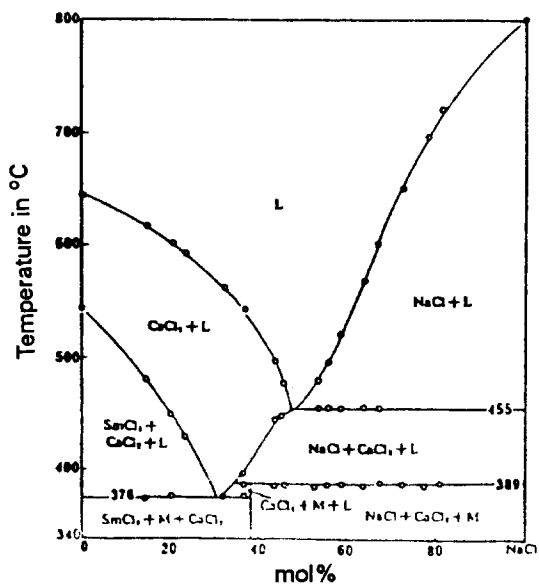


Fig. 6. Section V.

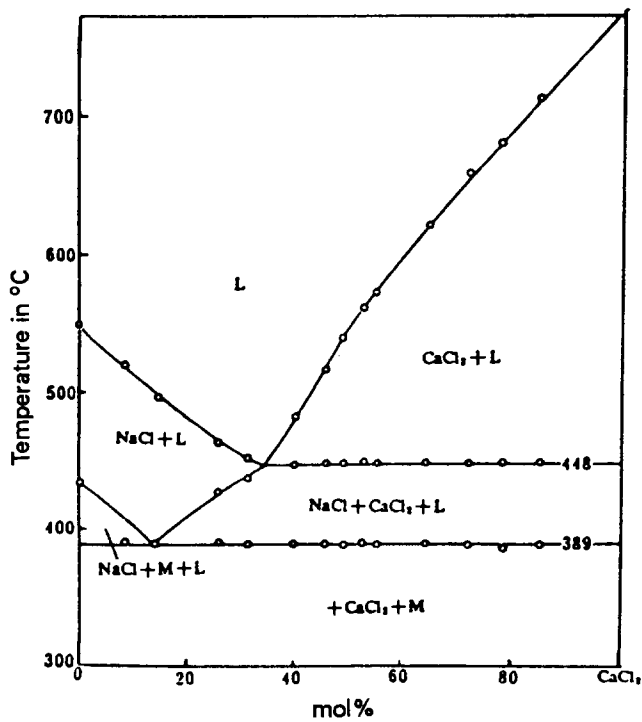


Fig. 7. Section VI.

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 $\pm 3^\circ\text{C}$. 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 $\text{SmCl}_3\text{--NaCl}$, NaCl--CaCl_2 and $\text{SmCl}_3\text{--CaCl}_2$ 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 $\text{SmCl}_3\text{--NaCl}$ are different from those in Ref. [2] for invariant temperatures. In the former, $e_1 = 410^\circ\text{C}$ (50.0 mol% NaCl) and $p = 435^\circ\text{C}$ (61.0 mol% NaCl), whereas in Ref. [2] $e_1 = 390^\circ\text{C}$ and $p = 425^\circ\text{C}$. 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. $e_2 = 500^\circ\text{C}$ (51.0 mol% CaCl_2). $\text{SmCl}_3\text{--CaCl}_2$ is also a simple eutectic system, for which $e_3 = 545^\circ\text{C}$ (55.8 mol% SmCl_3).

Table 1
Compositions and temperatures of deflection points on the liquidus

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

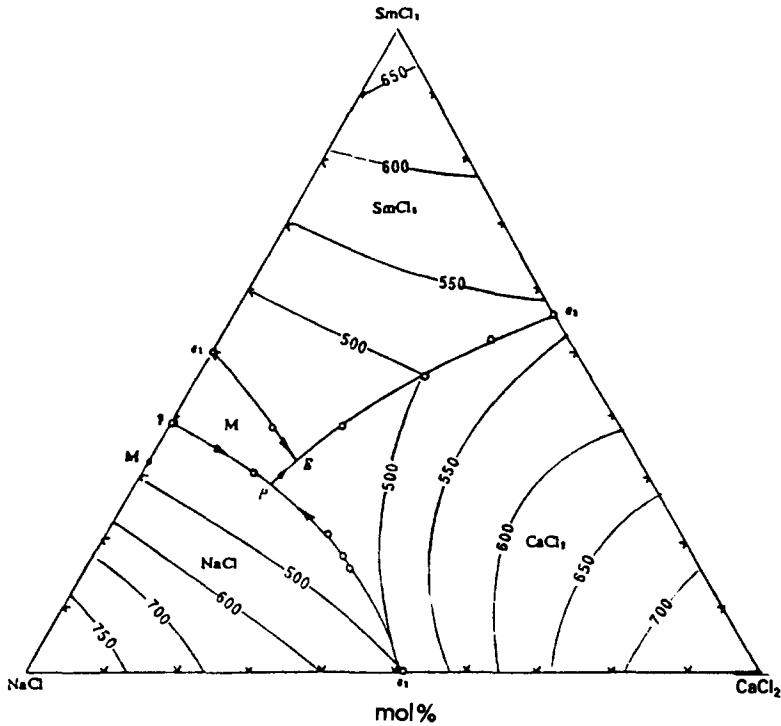


Fig. 8. Phase diagram of SmCl_3 - NaCl - CaCl_2 .

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 $2\text{NaCl} \cdot \text{SmCl}_3$. 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 $E = 376^\circ\text{C}$ (33.1 mol% SmCl_3 , 46.9 mol% NaCl) and the ternary peritectic point $P = 389^\circ\text{C}$ (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.