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Note

Phase diagrams of the systems $NaF-Na_3AlF_6-Na_3FSO_4$ and $NaCl-Na_3AlF_6-Na_3FSO_4$. Experimental study and calculation

P. Fellner *, J. Gabčová, V. Danielik

Department of Inorganic Technology, Slovak Technical University, CS-812 37 Bratislava, Slovak Republic

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Abstract

Experimental data on solid–liquid phase equilibria in the ternary systems $NaF-Na_3AlF_6-Na_3FSO_4$ and $NaCl-Na_3AlF_6-Na_3FSO_4$ are presented. The experimental phase diagrams are compared with calculations based on a model of molten salt mixtures. The influence of composition on the thermal dissociation of anions in the melts is discussed.

Keywords: Chloride; Cryolite; Fluoride; Halide; Phase; SLE; Ternary system

1. Introduction

Phase diagrams of the systems $NaF-Na_3AlF_6-Na_3FSO_4$ and $NaCl-Na_3AlF_6-Na_3FSO_4$ are presented. These ternary systems contain substances (Na_3AlF_6 and Na_3FSO_4) which partly thermally dissociate on melting. No data on the solid–liquid phase equilibria of these systems are available in the literature.

In Ref. 1, we discussed the phase diagram of the system $LiF-Na_3AlF_6-Na_3FSO_4$. Lithium fluoride brings lithium cations into the system. This cation influences the thermal dissociation of the complex anions AlF_6^{3-} and FSO_4^{3-}. In the present paper, we will discuss the thermodynamic behaviour of the molten systems NaF–

* Corresponding author.

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Na_3AlF_6–Na_3FSO_4 and NaCl–Na_3AlF_6–Na_3FSO_4. Sodium fluoride is a product of the thermal dissociation of both Na_3AlF_6 and Na_3FSO_4. The system NaCl–Na_3AlF_6–Na_3FSO_4 contains sodium chloride that brings chloride anions into the melt. These anions may react with the complex anions AlF_6^{3-} and FSO_4^{3-}. All these reactions influence the composition of the melt and the Gibbs energy of mixing of the species present. Comparison of the experimental and calculated phase diagrams allows the concept of molten salt mixtures, outlined in Ref. 1, to be tested.

2. Experimental

The solid–liquid phase equilibria were studied by the "cooling curves" method. The temperature was measured by a PtRh10–Pt thermocouple. The cooling rate was 1.0–2.5 K min^{-1} and the thermoelectric voltage of the thermocouple was sampled at 10 s intervals and stored in the computer memory. The "cooling curves" obtained were treated numerically and the reproducibility in the determination of the equilibrium temperature was about 0.3 K. The thermocouples were calibrated using the melting temperatures of pure salts. Experimental details can be found in Ref. 1.

3. Results and discussion

The experimental phase diagrams of the ternary systems NaF–Na_3AlF_6–Na_3FSO_4 and NaCl–Na_3AlF_6–Na_3FSO_4 are plotted in Figs. 1 and 2, respectively. Nine sections of the first order (constant ratio of two components) and nine sections of the second order (constant content of one component) were investigated. (Numerical data will be supplied by the authors on request.)

The ternary eutectic point of the system NaF–Na_3AlF_6–Na_3FSO_4 has the parameters $\theta(\text{eut}) = 764°\text{C}$; $x(\text{NaF}) = 0.210$, $x(Na_3AlF_6) = 0.150$, $x(Na_3FSO_4) = 0.640$. Phase diagrams of the binary systems Na_3AlF_6–Na_3FSO_4, NaF–Na_3AlF_6 and NaF–Na_3FSO_4 have been published by Fellner and Gabčová [1], Holm [2], and Koštenská and Malinovský [3], respectively.

The ternary eutectic point of the system NaCl–Na_3AlF_6–Na_3FSO_4 has the parameters $\theta(\text{eut}) = 617°\text{C}$, $x(Na_3AlF_6) = 0.045$, $x(Na_3FSO_4) = 0.275$, $x(\text{NaCl}) = 0.680$.

Phase diagrams of the binary systems Na_3AlF_6–Na_3FSO_4 and NaCl–Na_3AlF_6 have been published by Fellner and Gabčová [1] and Holm [2], respectively. The phase diagram of the system NaCl–Na_3FSO_4 has been studied as a part of the ternary system NaCl–NaF–Na_2SO_4 by Mukimov [4] and Wolters [5]. The data published in the cited papers are in good agreement with this work.

The temperature of the primary crystallization can be calculated according to the Le Chatelier–Shreder equation

$$\ln a_{\text{A,l}} = \frac{\Delta H_{\text{m}}^{\ominus}}{R}\left(\frac{1}{T_{\text{m}}} - \frac{1}{T}\right) \qquad (1)$$

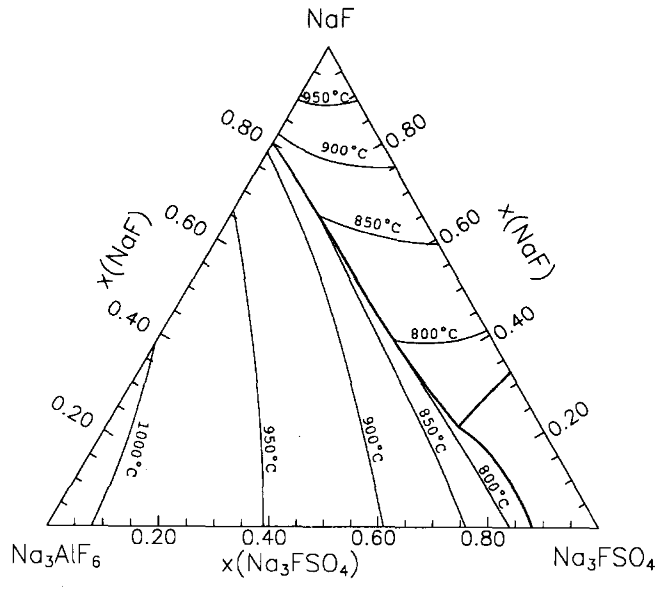

Fig. 1. Experimental phase diagram of the system $NaF-Na_3AlF_6-Na_3FSO_4$.

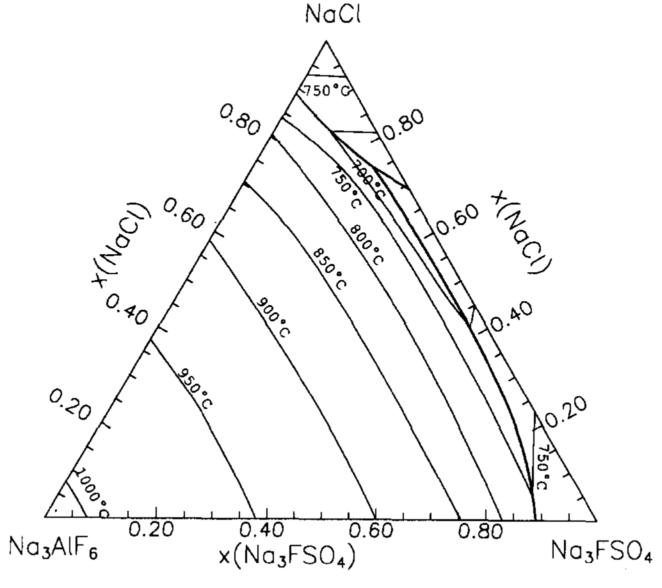

Fig. 2. Experimental phase diagram of the system $NaCl-Na_3AlF_6-Na_3FSO_4$.

where $\Delta H_m^{\ominus}$ is the standard molar enthalpy of melting of pure substance A, T_m/K is the temperature of melting of the pure component, and T is the equilibrium temperature of primary crystallization of A. It is assumed that the difference in heat capacity between solid and liquid A is so small that it can be neglected. (This is a reasonable assumption when $T_m - T < 100$ K.) In those cases where A forms a solid solution with other components, the expression on the left-hand side of Eq. (1) is replaced by $\ln(a_{A,l}/a_{A,s})$.

It follows that for calculation of the equilibrium temperature of primary crystallization it is necessary to know the activity of the components in a particular molten mixture.

It is assumed that, in the first approximation, the activity equals the model mole fraction of a given component and the ideal thermodynamic behaviour of the molten mixtures $NaF-Na_3AlF_6-Na_3FSO_4$ and $NaCl-Na_3AlF_6-Na_3FSO_4$ can be described under the following assumptions.

(i) The molten mixtures consist of the ionic assemblies $Na^+ \cdot F^-$, $3Na^+ \cdot AlF_6^{3-}$, $3Na^+ \cdot FSO_4^{3-}$, $Na^+ \cdot AlF_4^-$, $2Na^+ \cdot SO_4^{2-}$, and $Na^+ \cdot Cl^-$, $Na^+ \cdot F^-$, $3Na^+ \cdot AlF_6^{3-}$, $3Na^+ \cdot FSO_4^{3-}$, $Na^+ \cdot AlF_4^-$, $2Na^+ \cdot SO_4^{2-}$, respectively.

(ii) In an ideal molten mixture the ionic assemblies mix randomly.

(iii) The model mole fractions can be calculated from the equilibria of reactions between ionic assemblies in the molten state (for simplicity, the components are written in molecular form).

The same equilibrium constants as in Ref. 1 were used, i.e. for $Na_3AlF_6 = NaAlF_4 + 2NaF$, $K_1 = 0.06$; for $Na_3FSO_4 = Na_2SO_4 + NaF$, $K_2 = 1.123$.

The temperature dependence of the equilibrium constants was neglected in this approximation. Further details of the model and the calculation procedure can be found in Ref. 1.

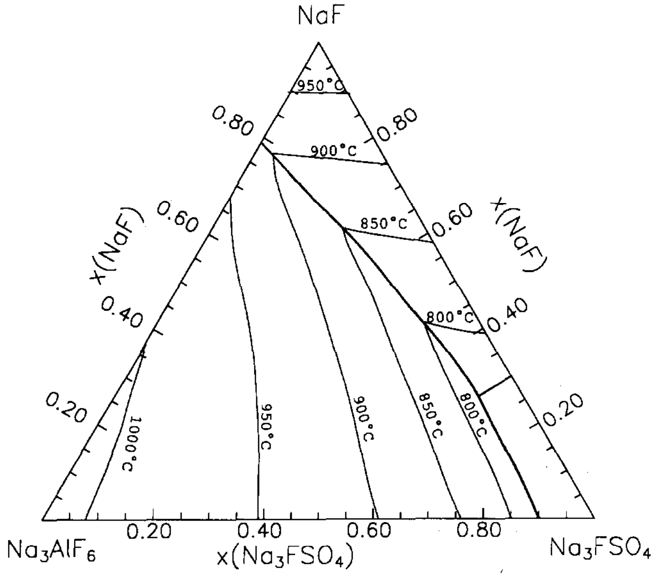

Fig. 3. Calculated phase diagram of the system $NaF-Na_3AlF_6-Na_3FSO_4$.

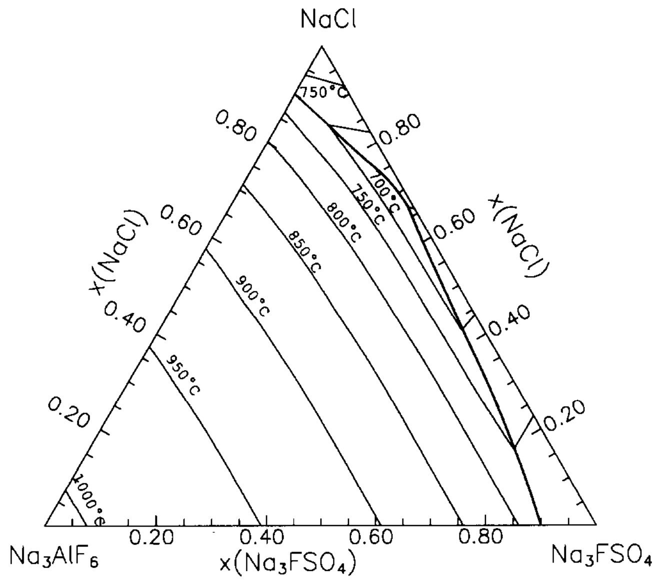

Fig. 4. Calculated phase diagram of the system $NaCl-Na_3AlF_6-Na_3FSO_4$.

The calculated phase diagrams of the ternary systems $NaF-Na_3AlF_6-Na_3FSO_4$ and $NaCl-Na_3AlF_6-Na_3FSO_4$ are plotted in Figs. 3 and 4, respectively. It follows that the experimental and calculated phase diagrams are in reasonably good agreement. No correction for deviation from thermodynamically ideal behaviour was made. As the proposed thermodynamic model was able to describe successfully the behaviour of the system $LiF-Na_3AlF_6-Na_3FSO_4$ [1], it is not surprising that it can also be used for calculation of the phase diagram of the system $NaF-Na_3AlF_6-Na_3FSO_4$.

The thermodynamic behaviour of the system $NaCl-Na_3AlF_6-Na_3FSO_4$ was described under the assumption that sodium chloride does not react with the complex anions present in the melt. Good agreement between the experimental and calculated data suggests that sodium chloride behaves as an "inert" addition in the melts containing AlF_6^{3-} or FSO_4^{3-} ions.

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