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PHYSICOCHEMICAL ANALYSIS OF INORGANIC SYSTEMS

Phase Equilibria in the Ternary System NaF–KF–CsF

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Abstract—The ternary eutectic system CsF–KF–NaF was studied by differential thermal analysis. The melting point and composition of the ternary eutectic were determined, and so was the boundary of the region of limited series of solid solutions within the composition triangle. The compositions of crystallizing phases were confirmed by X-ray powder diffraction analysis. The specific enthalpy of melting of the ternary eutectic was experimentally found.

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The compositions of various new functional liquid-phase materials and composites are studied by physicochemical analysis methods. By these methods, the relationship between the composition and properties of equilibrium systems is established, which is used for constructing the composition–property diagram (*T*–*x* diagram) [1].

Of great interest to researchers are mixtures of alkali metal halides, which have such valuable properties as high electrical conductivity, ability to work over a wide temperature range, thermal stability, and nontoxicity.

Owing to such an extensive area of applications of composites and mixtures, it is topical to study multicomponent systems based on alkali metals. Therefore, as an object of investigation in this work, the ternary system CsF–KF–NaF was chosen.

The ternary system CsF–KF–NaF was studied previously [2]. According to that study, the liquidus of the system has two crystallization fields: for sodium fluoride and for a continuous series of solid solutions based on cesium fluoride and potassium fluoride. Moreover, it was stated [2] that the binary faceting system CsF–KF is a system with a continuous series of solid solutions. However, according to [3], the CsF–KF system is eutectic with a limited solid solution based on potassium fluoride. In the monograph [4], this system was assigned to the eutectic type. Therefore, we decided to perform a more accurate study of the ternary system CsF–KF–NaF.

The faceting elements of the ternary system NaF–KF–CsF are the binary systems NaF–CsF [5], KF–CsF [5], and NaF–RF [3] of the eutectic type. The systems NaF–KF and KF–CsF have the regions of limited series of solid solutions based on the components KF(α) and CsF(β), respectively. Because all the faceting elements of the ternary system are eutectic, it is expected that, in this system, a ternary eutectic with the phases NaF + α + β forms.

OBJECTS AND METHODS OF INVESTIGATION

Phase equilibria in the ternary system NaF–KF–CsF were studied by standard differential thermal analysis [6] in platinum microcrucibles (GOST (State Standard) 13498-68). The cold junctions of thermocouples were thermostated at 0°C in a Dewar flask filled with melting ice. The rate of heating (cooling) of samples was 10–15 K/min. The indifferent substance was freshly calcined, analytically pure aluminum oxide. The thermocouples were calibrated against the melting points and polymorphic transformations of anhydrous inorganic salts. The temperature measurement accuracy was ±2.5°C at an accuracy of weighing samples on a Vibra HT analytical balance of ±0.0001 g. The compositions of all the mixtures were expressed as molar percentages, and the temperatures were measured in °C. The weight of the initial mixtures was 0.3 g. Chemically pure KF and pure CsF were used. Their melting points agreed with the literature data [6, 7]. The purity of the initial reactants and mixtures was checked against the melting points and the data of X-ray powder diffraction analysis performed with an ARL X'TRA diffractometer [8].

EXPERIMENTAL

Figure 1 presents the composition triangle of the NaF–KF–CsF system. For experimental investigation, in the NaF–KF–CsF system, we chose the polythermal section *A*(42% NaF, 58% KF)–*B*(42% NaF, 58% CsF) in the sodium fluoride crystallization field. Figure 2 shows the *T*–*x* diagram of the *AB* section. By

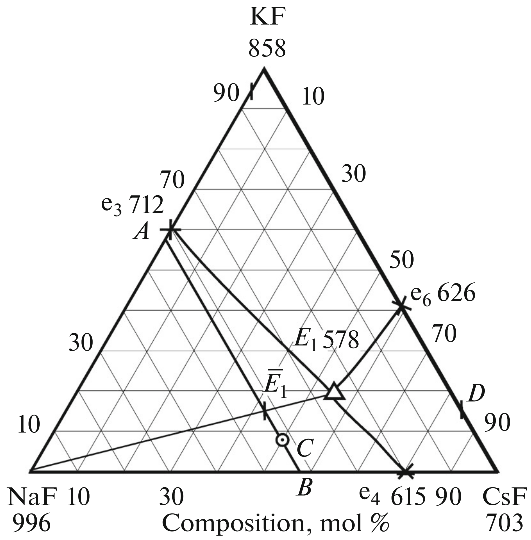

Fig. 1. Projection of the phase complex of the ternary system NaF–KF–CsF to the composition triangle.

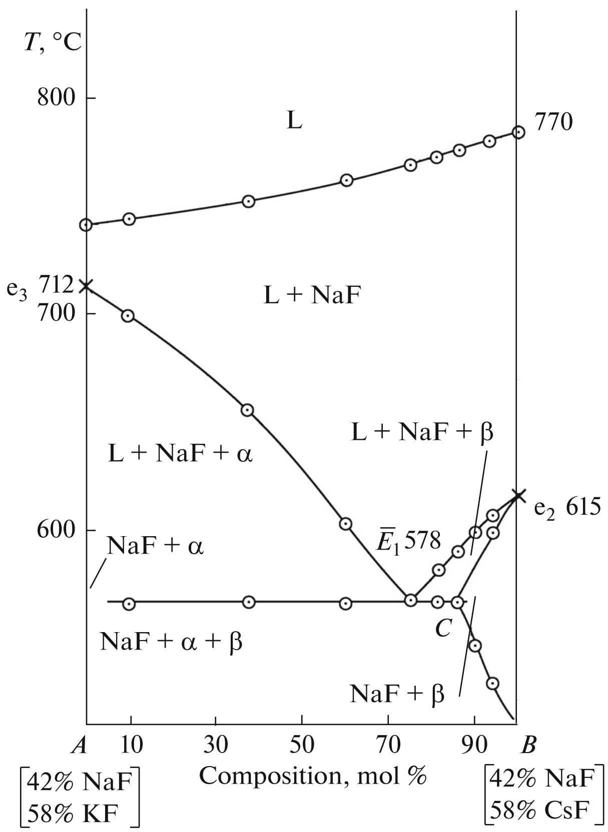

Fig. 2. *T–x* diagram of the section *AB*.

the experimental investigation of the polythermal section, we found the projection of the ternary eutectic point $\bar{E}$ to the plane of the *AB* section, the melting point of the eutectic, and the ratio between the concentrations of the components KF and CsF in the eutectic. In the polythermal section *AB*, we experimentally determined the composition corresponding to the point *C*(42% NaF, 10% KF, 48% CsF), which is the boundary of the region of solid solutions based on CsF.

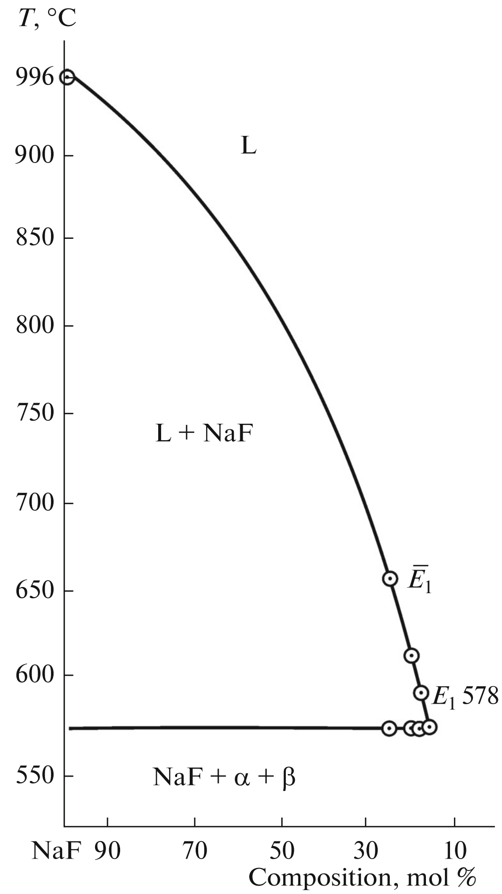

Fig. 3. *T–x* diagram of the section NaF → $\bar{E}_1$ → E_1.

By studying the polythermal section NaF → $\bar{E}_1$ → E_1 originating from the sodium fluoride composition vertex and passing through the projections of the ternary eutectic (Fig. 3), we determined the composition of the eutectic as (24% NaF + 21% KF + 55% CsF) with the melting point 578°C.

To conform the composition of crystallizing phases, X-ray powder diffraction analysis of a sample of the composition corresponding to the point E_1 was carried out (Fig. 4). The X-ray powder diffraction data confirmed that the ternary eutectic consists of three crystallizing phases: NaF and solid solutions α and β.

The liquidus of the ternary system NaF–KF–CsF is represented by three crystallization fields: for sodium fluoride and limited series of solid solutions α and β. In the ternary eutectic E_1, there is phase equilibrium L $\rightleftarrows$ NaF + α + β. In the composition triangle, the maximum crystallization field is that of high-melting sodium fluoride, and the minimal field is that

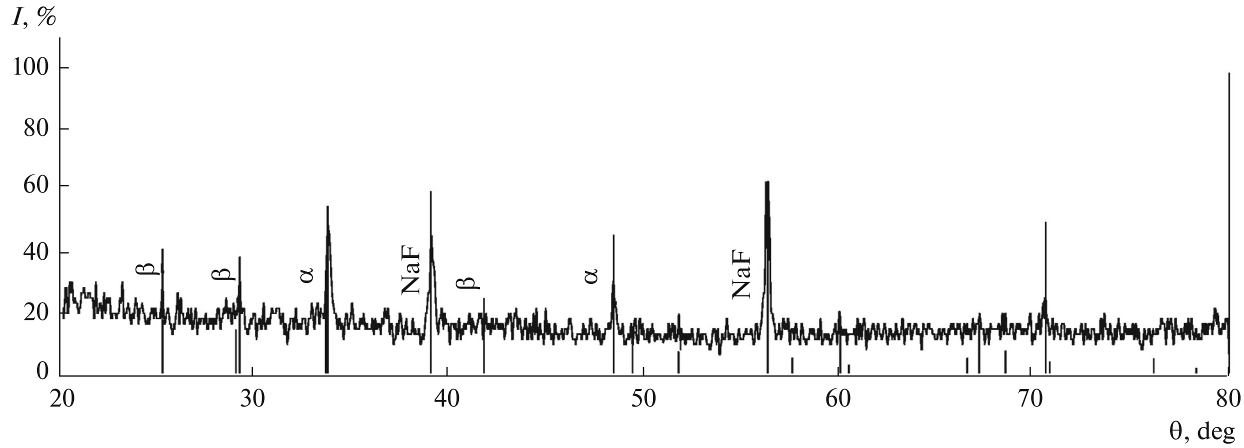

Fig. 4. X-ray powder diffraction pattern of the sample of the composition corresponding to the point E_1.

of the phase β based on lowest-melting cesium fluoride.

The specific enthalpy of melting of an alloy of the eutectic composition in the ternary system CsF–KF–NaF, which was determined by comparing withe the specific enthalpy of melting of a standard substance (LiCl, melting point 610°C, enthalpy of melting 466 kJ/kg), is 227 kJ/kg.

Thus, in this work, the ternary system NaF–KF–CsF was experimentally investigated by differential thermal analysis. The ternary eutectic E_1 was found to have the composition (24% NaF + 21% KF + 55% CsF) and the melting point 578°C. The composition corresponding to the point *C*(42% NaF, 10% KF, 48% CsF) was determined, which is the boundary of the region of solid solutions.

The X-ray powder diffraction analysis confirmed that the ternary eutectic consists of three crystallizing phases: NaF, β, and α.

The specific enthalpy of melting of an alloy of the eutectic composition is 227 kJ/kg.

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