T-x-y-z Diagram Prediction for the Quaternary System Li,Na,Ca,La||F

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Abstract. The prediction of the geometric structure of the LiF-NaF-CaF2-LaF3 quaternary system T-x-y-z diagram has been carried out on the basis the data about the binary systems and the 3D computer models of the T-x-y diagrams of boundary ternary systems, designed earlier; and its prototype has been constructed. Correctness of the prediction may be confirmed (or rejected) by the experiments only.

1. Introduction

In the literature are given the diverse Variants of the potential fuel of IV generation nuclear reactors, both calculated thermodynamically and studied experimentally, are given in literature [1-7]. However, the represented information about the geometrical structure of the corresponding phase diagrams is limited only by the visualization of the liquidus surfaces and (not always) a certain number of isothermal sections and isopleths. Whereas it is necessary for obtaining the information about the results of interaction of initial components the complete model of diagram, which includes phase regions with the liquid and solid-phase regions.

The developed 3D and 4D computer models of T-x-y and T-x-y-z diagrams of ternary and quaternary systems, correspondingly, serve both for the visualization of their geometrical structure and are the source of obtaining information about the crystallization stages and formation of microstructure, give possible to qualitatively and quantitatively evaluate the relations of phases for the assigned composition [8, 9]. This complex study of the fluoride systems properties gives the possibility to optimize the selection of fuel and to predict its properties, and also is the theoretical basis for the experimental investigations.

The compositions, obtained from the LiF-NaF-CaF2-LaF3 system тоже are investigated in connection with the development of IV generation nuclear reactors [1]. Fluoride of lanthanum (LaF3) serves as a proxy-compound for fluoride of plutonium (PuF3), since the direct use of fluoride of plutonium (PuF3) would cause enormous experimental difficulties.

2. 3D computer models of T-x-y diagrams for systems forming four-component system of lithium, sodium, calcium and lanthanum fluorides

The surfaces of the phase diagrams formed by the fluorides of lithium, sodium, calcium, and lanthanum are not complicated. But the geometric structure of these diagrams becomes more complicated by the formation of the binary NaLaF4 compound and polymorphism of CaF2 [4].

Before designing a computer 3D (and 4D too) model, it is necessary to discuss the boundary systems, as well as to make a formal indication of the considered quaternary system, that is, to indicate the LiF-NaF-CaF2-LaF3 system as A-B-C-D (Fig. 1), and to give the necessary indication of all phase transformations [10]. For example, two polymorphic modifications of CaF2 are involved in the formation of the LiF-NaF-CaF2-LaF3 (A-B-C-D) diagram and they received the appropriate indicators: C and C1.
Figure 1. 3D компьютерные модели T-x-y диаграмм LiF-NaF-CaF₂ (A-B-C) (a), LiF-NaF-LaF₃ (A-B-D) (b), LiF-CaF₂-LaF₃ (A-C-D) (c), NaF-CaF₂-LaF₃ (B-C-D) (d).

2.1. T-x diagrams of binary systems
The systems LiF-NaF (A-B), LiF-LaF₃ (A-D) and CaF₂-LaF₃ (C-D) are the eutectic ones, but the last is characterized more over by the eutectoid reaction C→C₁+D because of the polymorphism of calcium fluoride.

The LiF-CaF₂ (A-C) and NaF-CaF₂ (B-C) systems are also of eutectic type, but the allotropy of calcium fluoride (CaF₂) is the reason of the polymorphic transition in the form of the metatectic reaction (C→C₁+L).

The NaF-LaF₃ (B-D) system has a typical T-x diagram with the peritectic pDR: L+D→R reaction of forming the incongruently melting NaLaF₄ (R) compound and eutectic eBR: L→B+R reaction.

2.2. T-x-y diagrams of ternary systems
The LiF-NaF-CaF₂ (A-B-C) ternary system is characterized by eutectic invariant reaction E₁: L→A+B+C₁ and the univariant polymorphic C→C₁+L transition between two CaF₂ modifications.
The LiF-NaF-LaF$_3$ (A-B-D) system with the NaLaF$_4$ (R) binary incongruently melting compound includes the quasi-peritectic Q$_1$: L$\rightarrow$A+D+C and eutectic E$_2$: L$\rightarrow$A+B+R invariant reactions.

It seems that the LiF-CaF$_2$-LaF$_3$ (A-C-D) and the LiF-NaF-LaF$_3$ (A-B-D) systems are similar. Except the eutectic reaction E$_3$: L$\rightarrow$A+D+C the A-B-D system includes one additional invariant reaction. It is called a quasi-peritectic reaction in [1] and is written as L$\rightarrow$C$\rightarrow$C1+D. However, it is not. Because of the polymorphous transfer in the LiF-CaF$_2$ (A-C) binary system the V$_1$: C$\rightarrow$C1+D+L polymorphic transition also takes a place with the passive role of the L and LaF$_3$ (D). More details on ternary systems with allotropy of components, including a similar case, are described in the paper [11].

Construction of the 3D computer model of the T-x-y diagram begins with the 3D scheme of univariant and invariant states [11, 12]. This is a 3D variant of well-known scheme of phase reactions (planar Sheil scheme) [13], supplemented by the concentrations of phases, which participate in three-phase transformations. This very important addition opens wide possibilities for describing all surfaces and phase regions of the T-x-y diagram (as it is shown in previous slides for the system, formed by fluorides of sodium, calcium and lanthanum.

The polymorphic transition V$_2$: C$\rightarrow$C1+R+L is intermediate between two invariant reactions: the quasi-peritectic Q$_2$: L+D$\rightarrow$C+R and the eutectic E$_4$: L$\rightarrow$B+R+C1 in the NaF-CaF$_2$-LaF$_3$ (B-C-D) system. So, its scheme leads to the third invariant reaction E$_5$: C$\rightarrow$C1+D+R of the eutectoid type.

The scheme of univariant and invariant states allows to define all unruled ruled surfaces, horizontal planes, according to invariant reactions, and all phase regions with liquid and without liquid.

Thus, a 3D computer model provides an excellent opportunity to get a complete and comprehensive view of the T-x-y diagram, either its geometric structure or the options for its melts crystallization. In addition, 3D models are very useful for their structures understanding and for the 4D model designing of the four-component system T-x-y-z diagram, formed by them.

Each spatial computer model is a prototype of a phase diagram, which is able to become a perfect model of a real system after the experimental or calculated parameters (concentrations and temperatures of binary and ternary points, curvature characteristics of surfaces, according to isothermal sections and isopleths) input.

3. 4D computer model of the predicted T-x-y-z diagram

The same approach is applied to design the 4D computer model of the T-x-y-z diagram. As for the LiF-NaF-CaF$_2$-LaF$_3$ (A-B-C-D) system, the logic of the bi-, uni- and invariant state schemes leads to the only possible scheme of the phase reactions of the quaternary system (Table 1) [14].

From the scheme it follows those three invariant reactions can be expected the polymorphic transition CaF$_2$$\rightarrow$CaF$_2$$'+$LaF$_3$+NaLaF$_4$+L (or $\nu$: C$\rightarrow$C1+D+R+L) between two modifications of calcium fluoride (C and C1) in the presence of liquid L, LaF$_3$ (D) and NaLaF$_4$ (R) compound at temperatures below 985 K, the quasi-peritectic reaction L+LaF$_3$$\rightarrow$LiF+CaF$_2$$'+$NaLaF$_4$ ($\pi$: L+D$\rightarrow$A+C1+R) below 869 K and the eutectic reaction L$\rightarrow$LiF+NaF+CaF$_2$$'+$NaLaF$_4$ ($\varepsilon$: L$\rightarrow$A+B+C1+R) below 854 K (Fig. 2-3).

In general, the T-x-y-z diagram includes: 6 hypersurfaces of liquidus and 6 - of solidus ones; 11 pairs of solvus hypersurfaces (total - 22); 2 hypersurfaces of the transus; 22 triads of ruled hypersurfaces with a generated line (66 in total); 52 ruled hypersurfaces with a generated plane; 3 complexes, corresponding to the invariant transformations $\nu$, $\pi$, $\varepsilon$, each of them consists of five horizontal (isothermal) hyperplanes.

All these 169 hypersurfaces serve as the boundaries of 62 phase regions: 6 single-phase regions I (A, B, C, C1, D, R) and 6 two-phase regions L$\rightarrow$I; 12 two-phase regions I$\rightarrow$J without liquid (A+B, A+C1, A+D, A+R, B+C1, B+R, C+D, C+R, C+C1, C1+D, C1+R, D+R) and 12 three-phase regions with liquid L$\rightarrow$I+J; 10 three-phase regions I$\rightarrow$J+K without liquid (A+B+C1, A+ B+R, A+C1+D, A+C1+R, A+D+R, B+C1+R, C+C1+D, C+C1+R, C+D+R, C1+D+R) and 10 four-phase regions with liquid L$\rightarrow$I+J+K; 3 four-phase regions without liquid A+B+C1+R, A+C1+D+R, C1+D+R, and 3 five-phase regions, degenerated into planar hyperplanes, L$\rightarrow$A+B+C1+R, L$\rightarrow$A+C1+D+R, L$\rightarrow$C+C1+D+R.
Table 4. The phase reactions scheme of the LiF-NaF-CaF$_2$-LaF$_3$ (A-B-C-D) T-x-y-z diagram with the incongruently melting compound NaLaF$_4$ (R) (Fig. 2-3), $D>C>\varepsilon \rightarrow \pi \rightarrow \pi \rightarrow \varepsilon$

| A-B-C  | A-B-C-D  | A-B-D  | A-C-D  | B-C-D  |
|--------|----------|--------|--------|--------|
|        |          |        |        |        |

Figure 2. Liquidus prototype 4D model: x-y-z projection of the LiF-NaF-CaF$_2$-LaF$_3$ (A-B-C-D) T-x-y-z diagram.
4. Summary

The T-x-y-z diagram, based on the T-x-y diagrams 3D models [14], has been predicted and the 4D model of its prototype has been constructed. It includes the polymorphic transition between two modifications of calcium fluoride with the passive role of liquid, LaF$_3$ and the NaLaF$_4$ compound, the quasi-peritectic and eutectic invariant reactions. In general, the T-x-y-z diagram may consist of 169 hypersurfaces and 66 phase regions.

When designing spatial computer models of phase diagrams of ternary, quaternary, and more complex systems, it should be paid more attention to updating the data on their edges, including information about the initial components and compounds. In the 4D model of the LiF-NaF-CaF$_2$-LaF$_3$ diagram, considered in this paper and forming it 3D models of ternary systems, it is necessary in the future to take into account the decomposition of the binary compound NaLaF$_4$ in the sub-solidus at 330°C, which is not mentioned in [15], where a binary system has been limited from below by the temperature of 600 K.
This 4D model is based on data from [1] with CaF$_2$ allotropy. However, this property of calcium fluoride is not taken into account in [10-12]. It is possible that the authors of these papers [15-17]. It is possible that the authors of these papers were not interested, for practical reasons, in such high temperatures (1420 K) and they did not take into account the high-temperature modification of calcium fluoride, stable at atmospheric pressure [18].

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