Stable Tetrahedron NaCl – KCl – PbCl2 – PbWO4 in the quaternary reciprocal system Na, K, Pb // Cl, WO4

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Abstract. The phase diagram of the stable tetrahedron NaCl – KCl – PbCl2 – PbWO4 of the quaternary reciprocal system Na, K, Pb // Cl, WO4 was first studied using methods of differential thermal analysis. Its phase diagram was triangulated and stable triangulating internal sections of NaCl – PbWO4 – KCl.2PbCl2, NaCl – PbWO4–2KCl.PbCl2 and obtained tetrahedra NaCl – PbCl2 – PbWO4 – KCl.2PbCl2, NaCl – KCl – PbWP4, and NaCl – KCl – PbWP4. There are coordinates of three quadruple invariant points revealed.

1. Introduction

The tungstates of d- and some p-elements (CdWO4, ZnWO4, PbWO4, etc.) are widely used as heavy scintillators in new-generation electromagnetic calorimeters capable of working in the field of intense radiation [1]. Among them, it is lead tungstate that has the most optimal characteristics, close to the requirements for heavy scintillation materials [2]. Single crystals of lead tungstate have a high density and radiation resistance [2, 3]. That is why PbWO4 is used in the electromagnetic calorimeter of the Large Hadron Collider (LHC) [4, 5] and the PANDA detector [6–10].

Thus, the development of a fundamentally new technology for the tungstate synthesis and the single crystals development in low-temperature melts of multicomponent reciprocal systems is considered a great theoretical and practical interest [11, 12].

The aim of the research is to study the phase diagram of the quaternary system NaCl – KCl – PbCl2 – PbWO4, which is a stable tetrahedron of the quaternary reciprocal system Na, K, Pb // Cl, WO4.

The objectives of the study are the following:
1) the triangulation of the phase diagram of the quaternary system NaCl – KCl – PbCl2 – PbWO4;
2) identification of the crystallization tree of the quaternary system NaCl – KCl – PbCl2 – PbWO4;
3) calculation of coordinates of the quadruple invariant points of the quaternary system NaCl – KCl – PbCl2 – PbWO4;
4) determination of the coordinates of the quadruple invariant points of the quaternary system NaCl – KCl – PbCl2 – PbWO4 by differential thermal analysis (DTA).

References in the text are made in square brackets in the following form: [5, 6, 10] or [5–9] or [1, 3, 9–11] or [6]

2. Methods and materials

All bicomponent systems, with the exception of the KCl – PbCl2 system, are simple eutectic. Only the KCl – PbCl2 system has the interaction of components with the formation of two compounds: KCl2PbCl2 (D1) – congruent melting and 2KCl. PbCl2 (D2) – congruent melting. The KCl – PbWO4 system (Figure 1, Table 1) is a stable diagonal of the three-component reciprocal system K, Pb // Cl, WO4, studied and characterized in the research for the first time [11].

The NaCl – PbCl2 system (Figure 1) was studied in the research for the first time [11], as well as the coordinates of the double eutectic revealed (Table 1).

The NaCl – KCl system (Figure 1) was previously studied repeatedly by different researchers [13–16]; the results show the formation of double solid solutions with a minimum at a component ratio of 1: 1. The NaCl – PbCl2 system (Figure 1) was studied previously studied in different researches as well.

The KCl – PbCl2 system (Figure 1) was studied by the method of visual polythermal analysis [13–16], there were revealed compositions of compounds D1, D2 and the coordinates of three invariant points, including two eutectics and one peritectic (Table 1).

The three-component system NaCl – KCl – PbWO4 (Figure 1) was studied by us; it is an internal section of the four-component reciprocal system Na, K, Pb // Cl, WO4. It was shown that double solid solutions based on sodium and potassium chlorides decompose with the formation of the e6 eutectic (Table 1). The three-component system NaCl – PbCl2 – PbWO4 (Figure 1) was studied by us as part of the three-component reciprocal system Na, Pb // Cl, WO4 [12], and a triple eutectic E3 was revealed (Table 1).

| Table 1. Double and triple invariant points of the NaCl – KCl – PbCl2 – PbWO4 system |
| Nonvariant point | Composition in % | t, °C |
|-----------------|-----------------|-----|
|                 | NaCl | KCl | PbCl2 | PbWO4 |     |
| TP (ε1)         | 50   | 50  | –     | –     | 645 |
| ε2             | 75   | –   | –     | –     | 692 |
| ε3             | 28.4 | –   | 76.1  | –     | 410 |
| ε4             | –    | 23  | 77    | –     | 424 |
| ε5             | –    | 48  | 52    | –     | 410 |
| p              | –    | 63.5| 36.5  | –     | 490 |
| ε6             | –    | 80  | –     | –     | 650 |
| ε7             | –    | 30.5| 60.5  | 9     | 428 |
| ε8             | 17   | 27  | 56    | –     | 400 |
| ε9             | –    | –   | 91    | 9     | 487 |
| E1             | –    | 21  | 70    | 9     | 410 |
| E2             | –    | 46  | 48    | 6     | 400 |
| P1             | –    | 56  | 34    | 10    | 468 |
| E3             | 27.5 | –   | 65    | 7.5   | 398 |
| E4             | 18   | 11  | 71    | –     | 383 |
| E5             | 16   | 36  | 48    | –     | 387 |
| P2             | 20   | 46  | 34    | –     | 448 |
The three-component system NaCl – KCl – PbCl2 (Figure 1) was studied earlier [13], the crystallization fields of the components and two compounds D1 and D2, there were revealed coordinates of three invariant points, including two triple eutectics and one triple peritectic (Table 1).

We studied the three-component system KCl – PbCl2 – PbWO4 (Figure 1) as part of the three-component reciprocal system K, Pb l Cl, WO4 [11], revealed the crystallization fields of the components and two compounds D1 and D2, the coordinates of three invariant points, including two triple eutectics and one triple peritectics (Table 1).

We used the method of a priori prediction of the crystallization tree [17, 18], which makes it possible to identify phase complexes forming quadruple invariant points of the system and their relationship based on the development of the tetrahedron (Figure 1).

The method of calculating the coordinates of invariant points using analytical models of the joint crystallization surfaces [17, 18]. In this case, we used the licensed program “Approximation of phase equilibrium states” developed in C ++ Builder 6.0, which allows on the basis of input information (melting points of the initial components, coordinates of double and triple invariant points, coordinates of points on joint crystallization mono-variant lines of two and three phases), approximate all phase equilibria by equations of the first and second order and calculate the coordinates (temperature and concentration) of the desired invariant points.

Used the method of differential thermal analysis (DTA).

During the experimental study of the phase diagram of the NaCl – KCl – PbCl2 – PbWO4 system, the methods of the projection thermographic method were used [19–21].

3. Results

As can be seen, the NaCl – KCl – PbCl2 – PbWO4 tetrahedron (Figure 1) is triangulated by two internal sections of NaCl – PbWO4 – D1 and NaCl – PbWO4 – D2 into three trimming simplices: NaCl – PbCl2 – PbWO4 – D1, NaCl – KCl – PbWO4 – PbCl2 and NaCl – PbWO4 – D1 – D2.

By the method of a priori forecasting of the crystallization tree, the crystallization tree was revealed (Figure 2). As can be seen from the scattering of the NaCl – KCl – PbCl2 – PbWO4 tetrahedron (Figure 1), the crystallization volume of potassium chloride is limited by the phase equilibria e1E6e6P1pP2 (double, triple invariant points and corresponding monovariant lines), they also form a quadratic peritectic point at NaCl + KCl + D2 + PbWO4 + W phases. Similarly, the crystallization volume of lead chloride is limited by phase equilibria e3E3e9E1e4E4 (double, triple invariant points and corresponding monovariant lines), they also form a quadruple eutectic point in which the phases NaCl + D1 + PbCl2 + PbWO4 are in equilibrium. Finally, there is a quadratic eutectic between two quadruple invariant points (NaCl + PbWO4 + D1 + D2), into which the triple eutectics E2 and E5 are translated (Figure 2).

The identified crystallization tree (Figure 2) calculated the coordinates of the quadruple eutectics and peritectics of the quaternary system NaCl – KCl – PbCl2 – PbWO4 (Table 2).

The results of the coordinate calculating of the quadruple eutectics revealed an experimental study of the tetrahedron NaCl – KCl – PbCl2 – PbWO4 with a minimum number of polythermal sections.

According to the projection-thermographic method, the crystallization volume of PbWO4 takes the two-dimensional A – B – C section (Figs. 1, 3). There are central projections of double and triple invariant points obtained. The vertices of the obtained triangle A – B – C are represented by two-component systems and projections of the double eutectics ē2, ē6 and ē9, and the sides are represented by three-component systems and projections of the triple invariant points Ė1, Ė2, Ė3 Ė6. According to the crystallization set, these triple invariant points are translated into the corresponding quadruple invariant points (Figure 2).

First, a specific composition was expressed through A, B, and C, and then the same composition was found on the matrix, expressed already through the initial components: Z1 = NaCl, Z2 = PbWO4, Z3 = PbCl2, Z4 = KCl.
Figure 1. Scanning of the NaCl – KCl – PbCl2 – PbWO4 tetrahedron: 1) dashed and solid lines — triangulation lines; 2) dash-dotted lines show the selected ABC section and the central projections of triple invariant points (Δ) on it; 3) (°) — double invariant points

Figure 2. Crystallization set of the four-component system NaCl – KCl – PbCl2 – PbWO4 and phases crystallizing at invariant points.

At invariant points, phases crystallize the following way:
E1: PbCl2 + PbWO4 + D1; E2: PbWO4 + D1 + D2;
E3: NaCl + PbCl2 + PbWO4; E4: NaCl + PbCl2 + D1;
E5: NaCl + D1 + D2; E6: NaCl + KCl + PbWO4;
E10: NaCl + PbCl2 + D1; P1: KCl + PbWO4 + D2;
P2: NaCl + KCl + D2; P3: NaCl + PbCl2 + PbWO4 + D1;
P4: NaCl + PbWO4 + D1 + D2; P5: NaCl + KCl + PbWO4 + D2.
Table 2. The calculated and experimental coordinates of the quadruple invariant points of the NaCl – KCl – PbCl₂ – PbWO₄ system

| System components | Temperature, °C | Composition % | DTA |
|-------------------|----------------|---------------|-----|
|                   | Δ\text{ij}^* = 0 | Δ\text{ij}^* ≠ 0 | Platitude |
| t (t₁): NaCl      | 430            | 435            | 440 | 430 |
|                  | 19             | 18             | 17  | 18.2 |
|                  | 41             | 43             | 44  | 42.8 |
|                  | 30             | 31             | 28  | 30  |
|                  | 10             | 08             | 11  | 09  |
| t (t₂): NaCl      | 385            | 375            | 370 | 380 |
|                  | 18             | 17             | 16  | 17  |
|                  | 10             | 09             | 12  | 11  |
|                  | 62             | 65             | 66  | 65  |
|                  | 10             | 09             | 06  | 07  |
| t (t₃): NaCl      | 380            | 380            | 380 | 380 |
|                  | 15             | 18             | 14  | 17  |
|                  | 32             | 29             | 32  | 30  |
|                  | 47             | 49             | 48  | 47  |
|                  | 06             | 04             | 06  | 06  |

Δ\text{ij}^* – the liquidus surface deviation from the plane along the line with double eutectics.

During the experimental study of the selected two-dimensional cross-section A – B – C, all compositions were determined using the composition matrix:

\[
\begin{align*}
Z_1 & = 40 \\
Z_2 & = 60 \\
Z_3 & = 0 \\
Z_4 & = 0
\end{align*}
\]

Figure 3. Two-dimensional ABC section: 1) dashed lines – studied polythermal sections; 2) ė₂ – ė₁₀ – ė₇ – triangulating section; 3) (Δ) and (□) – projections of triple and quadruple invariant points, respectively; ė₁ – projections of double eutectics.
To determine the coordinates of the central projection of the quadruple invariant points on the two-dimensional section A – B – C (Figure 1.3), the most informative polythermal section D – K (Figure 3) was selected and studied, on the phase diagram of which (Figure 4) double projections of quadruple invariant points. The presence of a maximum on the line — tertiary crystallization in the D – K polythermal section at the ratio B: C = 1: 2 (KCl.2PbCl2) indicates that compound D1 and the internal section NaCl – PbWO4 – D1 split the tetrahedron NaCl – KCl – PbCl2– PbWO4 into two more tetrahedron NaCl – PbCl2 – PbWO4 – D1 and NaCl – KCl – PbWO4 – D1 with four invariant points.

The coordinates of the double projections of the quadruple invariant points found on the phase diagram of the D – K section determine the direction of the sections A–, A–, and A–. The coordinates of the quadruple invariant projections points is to be revealed (Figure 3). Therefore, the polythermal sections A–, A–, and A– were further studied (Figure 3), on the phase diagrams of which single projections of quadruple invariant points are reflected and primary crystallization of PbWO4, secondary joint crystallization of NaCl + PbWO4, quaternary joint crystallizations NaCl + D1 + PbCl2 + PbWO4, NaCl + PbWO4 + D1 + D2 and NaCl + KCl + D1 + D2 + PbWO4. During the experimental study of the selected crossed sections, all compositions were determined using the composition matrix given above.

The coordinates of the quadruple invariant points projection determine the directions to the quadruple invariant points, and the tetrahedron from the crystallization pole PbWO4. Therefore, the polythermal sections PbWO4–, PbWO4–, and PbWO4– were further studied, the primary crystallization of PbWO4, quaternary crystallization lines and quadruple invariant points are reflected on the phase diagrams (Table 2).

As seen (Table 2), the calculated data on the coordinates of the quadruple eutectics obtained by the equations of the first and second order are agreed with the experimental data obtained by the DTA method.

4. Conclusion
The topology of the quaternary system NaCl – KCl – PbCl2 – PbWO4 was studied for the first time. There is a phase diagram triangulated into simplexes and a crystallization set revealed.

The study shows the calculated data on the quadruple invariant points coordinates are agreed with experimental data.

Low melting eutectic compositions have been identified to be used in the development of:
1) energy-intensive phase-transition heat-accumulating materials of non-traditional energy sources;
2) the optimal technology for the chemical synthesis of lead tungsten oxide bronzes;
3) methods of electrochemical synthesis of metallic tungsten and lead tungstate.

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