Quaternary reciprocal system Li, K, Pb // Cl, WO4

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Abstract. There is a topology of the four-component reciprocal system Li, K, Pb // Cl, WO4, its phase diagram was triangulated and stable tetrahedra revealed, the dominant chemical reactions of mutual exchange and complexation were determined. There are chemical synthesis of lead tungstate and lead oxide tungsten bronzes in ionic melts of the Li, K, Pb // Cl, WO4 system carried out. A synthesis technology for lead tungstate in ionic melts is proposed based on the results.

1. Introduction
The lead tungstate single crystal PbWO4 is used as a scintillator since it has a high density and radiation resistance meeting the basic requirements for scintillators [1–10]. At the same time, existing methods for the synthesis of lead tungstate are not that perfect. That is why the role of state diagrams in solving problems of searching for optimal conditions for the synthesis of substances is extremely large [11–14]. In this regard, there is a great interest in mutual singular systems with mutual exchange reactions.

The study focuses on the phase diagram of the four-component reciprocal system Li, K, Pb // Cl, WO4, chemical synthesis of lead tungstate and lead oxide tungsten bronzes in ionic melts of the Li, K, Pb // Cl, WO4 system.

The aim of the study is to reveal the phase diagram of the four-component reciprocal system Li, K, Pb // Cl, WO4, to develop methods for the synthesis of lead tungstate and lead oxide tungsten bronzes in ionic melts.

The research objectives are the following:
1. Triangulation of the phase diagram of the four-component reciprocal system Li, K, Pb // Cl, WO4
2. Identification of chemical reactions of mutual exchange and complexation in the quaternary reciprocal system Li, K, Pb // Cl, WO4
3. Studying the phase diagram of the four-component system LiCl – KCl – Li2WO4 – PbWO4 and determining the coordinates of the low-melting quaternary eutectic.
4. Chemical synthesis of lead tungstate in ionic melts of the quaternary system \( Li, K, Pb \parallel Cl, WO_4 \).

5. Chemical synthesis of lead tungsten oxide bronzes in ionic melts of the four-component system \( LiCl – KCl – Li_2WO_4 – PbWO_4 \).

2. Methods and materials

All two-component systems, with the exception of the \( KCl – PbCl_2 \) system, are simple eutectic. Only in the \( KCl – PbCl_2 \) system did the interaction of components with the formation of two new compounds \( D1 \) and \( D2 \) be found.

The study is conducted using the method of a prediction of the crystallization set [11–14]. This identifies phase complexes forming quadruple invariant points of the system and their reaction based on the development of the tetrahedron (Figure 1).

Another method used in the study is the method of calculating the coordinates of invariant points using analytical models of joint crystallization surfaces of two phases [11–14]. In this case, there is a licensed program “Approximation of Phase Equilibrium States” developed in C++Builder 6.0 used to approximate all phase equilibria using first and second order equations and calculate the coordinates (temperature and concentration) of the desired invariant points based on the input information.

An experimental study of the phase equilibria of the elements of the selected systems was carried out by differential thermal analysis (DTA).

3. Results

There are six simplexes of triangulation identified:

The four-component reciprocal system \( Li, K, Pb \parallel Cl, WO_4 \) (Figure 1) refers to an irreversibly reciprocal diagonal-adiagonal type with developed complexation. It is characterized by the formation of binary compounds \( D1-D4 \), including congruently melting – \( D1, D3, D4 \) and incongruently melting – \( D2 \).

I. \( LiCl–KCl–PbWO_4–D_1 \)

II. \( LiCl–PbCl_2–PbWO_4–D_1 \)

III. \( LiCl–KCl–PbWO_4–Li_2WO_4 \)

IV. \( KCl–K_2WO_4–D_3–D_2 \)

V. \( KCl–Li_2WO_4–D_3–D_2 \)

VI. \( KCl–PbWO_4–Li_2WO_4–D_3 \)

Chemical reactions of mutual exchange and complexation in ternary \( Li, K // Cl, WO_4 \) (Figure 1) refers to an irreversibly reciprocal diagonal-adiagonal type with developed complexation. It is characterized by the formation of binary compounds \( D1-D4 \), including congruently melting – \( D1, D3, D4 \) and incongruently melting – \( D2 \).

1. System \( Li,Pb//Cl,WO_4 \):
   \( 2LiCl + K_2WO_4 = Li_2WO_4 + 2KCl \)

2. System \( K,Pb//Cl,WO_4 \):
   \( K_2WO_4 + PbCl_2 = 2KCl + PbWO_4 \)

3. System \( Li,K//Cl,WO_4 \):
   \( 2LiCl + K_2WO_4 = Li_2WO_4 + 2KCl \)

4. System \( Li,K,Pb//Cl,WO_4 \):
   \( Li_2WO_4 + K_2WO_4 + 2PbCl_2 = 2PbWO_4 + 2LiCl + 2KCl \)
Thermodynamic substantiation of mutual exchange reactions in ternary Li, K // Cl, WO₄; K, Pb // Cl, WO₄; Li, Pb // Cl, WO₄ and the quaternary reciprocal systems Li, K, Pb // Cl, WO₄ (Figure 1, Tables 1–3).

Figure 1. The prism of the quaternary reciprocal system Li, K, Pb // Cl, WO₄

The isobaric potentials of the mutual exchange reactions were calculated by the Temkin-Schwartzman method. The mathematical processing of the kinetic measurement data was calculated for temperatures of 298, 720, 820, 920 °C according to the equations of Erofeev-Kolmogorov, Sakovich, Arenius. Entropy is calculated by the formula A.F. Kapustinsky and K.B. Yatsemirsky.

Table 1. Metabolic reactions

| Metabolic reactions                              | ΔH°298, kJ/mol | S°298, kJ/mol | Cp° 298, kJ/mol |
|--------------------------------------------------|----------------|---------------|-----------------|
| K₂WO₄ + 2LiCl = Li₂WO₄ + 2KCl                     | −76.9          | −15.02        | 6.6             |
| K₂WO₄ + PbCl₂ = 2KCl + PbWO₄                     | −51.58         | 27.68         | −5.86           |
| Li₂WO₄ + PbCl₂ = PbWO₄ + 2LiCl                    | 25.32          | 39.66         | −12.46          |
| 2LiCl + 3K₂WO₄ + PbCl₂ = 6KCl + Li₂WO₄ + 2PbWO₄  | −180.06        | 43.26         | −4.52           |
| 2PbCl₂ + Li₂WO₄ + K₂WO₄ = 2PbWO₄ + LiCl + 2KCl   | −26.26         | 67.3          | −18.32          |
The obtained thermodynamic data indicate that all the presented exchange reactions are fundamentally possible and can be used for the synthesis of lead tungstate in the solid phase or in melts.

Table 2. $\Delta C_{p}^{\circ}MoT$ different temperature values

| Reactions | $T$,K | $\Delta C_{p}^{\circ}MoT$ |
|-----------|-------|--------------------------|
| $K_{2}WO_{4} + 2LiCl = Li_{2}WO_{4} + 2KCl$ | 298 | 0.26546 |
| | 720 | 1.40517 |
| | 820 | 2.03132 |
| | 920 | 2.76786 |
| $K_{2}WO_{4} + PbCl_{2} = 2KCl + PbWO_{4}$ | 298 | 0.2357 |
| | 720 | 1.24762 |
| | 820 | 1.8033 |
| | 920 | 2.43089 |
| $Li_{2}WO_{4} + PbCl_{2} = PbWO_{4} + 2LiCl$ | 298 | 0.50115 |
| | 720 | 2.65278 |
| | 820 | 3.83452 |
| | 920 | 5.16877 |
| $2LiCl + 2PbCl_{2} + 3K_{2}WO_{4} = 6KCl + Li_{2}WO_{4} + 2 PbWO_{4}$ | 298 | 0.1818 |
| | 720 | 0.92326 |
| | 820 | 1.39101 |
| | 920 | 1.87023 |
| $2 PbCl_{2} + Li_{2}WO_{4} + K_{2}WO_{4} = 2 PbWO_{4} + LiCl + 2KCl$ | 298 | 0.73685 |
| | 720 | 3.9004 |
| | 820 | 5.64392 |
| | 920 | 7.59649 |

Table 3. Isobaric potentials $\Delta G_{r}^{\circ}$ reactions in systems

| Reaction | $\Delta G_{r}^{\circ}= \varphi(T)$ | $T$,K | $\Delta G_{r}^{\circ}$ |
|----------|---------------------------------|-------|---------------------|
| $K_{2}WO_{4} + 2LiCl = Li_{2}WO_{4} + 2KCl$ | $\Delta G_{r}^{\circ}=-76.9-(-0.01202)T+\Delta C_{p}^{\circ}MoT$ | 298 | -73.053 |
| | | 720 | -66.012 |
| | | 820 | -65.012 |
| | | 920 | -63.104 |
| $K_{2}WO_{4} + PbCl_{2} = 2KCl + PbWO_{4}$ | $\Delta G_{r}^{\circ}=-51.58-0.02768T+\Delta C_{p}^{\circ}MoT$ | 298 | -59.593 |
| | | 720 | -70.262 |
| | | 820 | -72.474 |
| | | 920 | -74.615 |
| $Li_{2}WO_{4} + PbCl_{2} = PbWO_{4} + 2LiCl$ | $\Delta G_{r}^{\circ}=25.32-0.03966T+\Delta C_{p}^{\circ}MoT$ | 298 | 14.002 |
| | | 720 | 0.582 |
| | | 820 | 3.367 |
| | | 920 | 5.998 |
| $2LiCl + 2PbCl_{2} + 3K_{2}WO_{4} = 6KCl + Li_{2}WO_{4} + 2PbWO_{4}$ | $\Delta G_{r}^{\circ}=-180.06-0.04326T+\Delta C_{p}^{\circ}MoT$ | 298 | -192.77 |
| | | 720 | -210.284 |
| | | 820 | -214.142 |
| | | 920 | -217.984 |
| $2 PbCl_{2} + Li_{2}WO_{4} + K_{2}WO_{4} = 2 PbWO_{4} + LiCl + 2KCl$ | $\Delta G_{r}^{\circ}=-26.26-0.0673T+\Delta C_{p}^{\circ}MoT$ | 298 | -45.579 |
| | | 720 | -70.816 |
| | | 820 | -75.802 |
| | | 920 | -80.58 |

The study revealed the phase diagram of one of its stable tetrahedra LiCl – KCl – Li2WO4 – PbWO4 and only one quadruple eutectic in the quaternary reciprocal system Li, K, Pb || Cl, WO4, (Table 4).
The results of calculating the coordinates of the quadruple eutectic made it possible to plan an experimental study of the LiCl – KCl – Li₂WO₄ – PbWO₄ tetrahedron with a minimum number of polythermal sections.

3.1. Synthesis of lead tungstate
In accordance with the identified metabolic reaction equation:
1) System Li, Pb // Cl, WO₄: Li₂WO₄ + PbCl₂ = PbWO₄ + 2LiCl,
2) System K, Pb // Cl, WO₄: K₂WO₄+ PbCl₂ = 2KCl + PbWO₄,
3) System Li, K, Pb // Cl, WO₄: Li₂WO₄ + K₂WO₄ + 2PbCl₂ = 2PbWO₄ + 2LiCl + 2KCl.

Table 4. The calculated and experimental coordinates of the quadruple eutectic of the four-component system

| System composition | Temperature °C | Molecular composition % | Second order-type equation | Linear model | DTA |
|--------------------|---------------|--------------------------|----------------------------|--------------|-----|
| LiCl               | 317           | 50                       | 310                        | 315          | 310 |
| KCl                | 34            | 36                       | 36                         | 37           | 35  |
| Li₂WO₄             | 9             | 10                       | 10                         | 8            | 9   |
| PbWO₄              | 7             | 7                        | 7                          | 7            | 8   |

Δij * – deviation of the liquidus surface from the plane along the line connecting the double eutectics. Chemical synthesis of lead tungstate and lead tungsten oxide bronzes in ionic melts of ternary Li, Pb // Cl, WO₄; K, Pb // Cl, WO₄ and the four-component Li, K, Pb // Cl, WO₄ reciprocal systems.

The initial components taken in equivalent amounts were mixed and put in a mortar, loaded into a platinum crucible and lowered into a shaft furnace. The temperature in it was gradually raised up to 650 °C and held for 30 minutes. The melt was poured onto a steel substrate and after cooling, it was carefully ground in a mortar and PbWO₄ was washed from slag (sulfates) in hot water for 20 minutes, then it was filtered by rinsing with hot water. The obtained PbWO₄ powder was dried at 300 °C, and then calcined at 500 °C. It is very important that in this case too, soluble salts are formed in the reaction products – potassium and sodium chlorides, lead tungstate from which is easily washed.

X-ray phase analysis of the obtained samples showed that PbWO₄ does not contain impurities (Figure 2). The yield of PbWO₄ was 98–99.3 %.

Figure 2. Diffraction pattern of the PbWO₄ synthesis at temperature 650 °C according to the exchange reaction.
3.2. Chemical synthesis of lead tungsten oxide bronzes

The initial sample of the eutectic composition of the quaternary system LiCl – KCl – Li2WO4 – PbWO4 introduced the calculated amounts of tungsten powder, tungsten oxide (VI) in accordance with the reaction equation:

\[3x\text{Me}_2\text{WO}_4 + (6-4x)\text{Me}_3\text{O}_3 + x\text{Me} = 6\text{Me}_x\text{WO}_3\]

or

\[3\text{PbWO}_4 + 2\text{WO}_3 + \text{W} = 6\text{Pb}_0.5\text{WO}_3\]

The resulting mixture was thoroughly mixed in a mortar, then dried at a temperature of 150–200 °C. Next, the charge was transferred to a crucible, lowered into a shaft furnace and heated to the melting temperature. The melt was held at this temperature for up to 30–45 minutes. Then, the melt was poured into a stainless steel cuvette, and after cooling, it was carefully put in a mortar and transferred to boiling distilled water to wash the bronzes from salts. After separation from the filtrate, the bronzes were dried at 100 °C, weighed, and the product yield was determined.

A brown multiphase mixture was obtained with the identified XRD phases (Figure 3): Pb0.5WO3, Pb0.3WO3, Pb0.45WO3, Pb0.35WO3, Pb0.46WO3, Pb0.47WO3.

![Figure 3. Diffraction pattern of the synthesis product of oxide tungsten bronze lead at a temperature of 650 °C](image)

### 4. Conclusion

1. The study is focused on the topology of the quaternary reciprocal system Li, K, Pb // Cl, WO4. Its phase diagram was triangulated, stable tetrahedron revealed, dominant chemical reactions of mutual exchange and complexation were determined.

2. The phase diagram of the stable LiCl – KCl – Li2WO4 – PbWO4 tetrahedron of the four-component reciprocal system Li, K, Pb // Cl, WO4 was studied for the first time, its phase diagram was triangulated into simplexes, the crystallization tree and coordinates of the four eutectic point revealed.

   It is shown that the calculated data on the coordinates of the quadruple eutectic point are agreed with the experimental data.

3. The identified low-melting eutectic composition can 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; 4) technologies for growing single crystals of lead tungstate.

4. The chemical synthesis of lead tungstate and lead oxide tungsten bronzes in ionic melts of the quaternary reciprocal system Li, K, Pb // Cl, WO4 was carried out.

5. Based on the results obtained, a synthesis technology for lead tungstate is proposed, which can be introduced at the Bogoroditsky Plant of Technochemical Products, at OJSC North Crystals (Apatity, Murmansk Region), at the Kurchatov Institute.
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