Phase equilibrium and synthesis in ionic melts of the system Li, Na, Pb || WO₄

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Abstract. The phase diagram of a three-component system has been studied for the first time by the method of differential thermal analysis and XRF Li,Na,Pb//WO₄. The coordinates of the invariant points are determined (42.5% Na₂WO₄, 47.5% Li₂WO₄, 10% Pb₂WO₄, 450°C), areas of crystallization of the initial components. The possibility of chemical synthesis of lead oxide tungsten bronzes in ionic melts of the studied system is shown.

1. Introduction

Interest in a comprehensive study of lead tungstate single crystals is due to its scintillation properties [1-5]. It was found that lead tungstate occupies an exceptional position in the tungstate family with a sheltie structure. Lead tungstate single crystal is a scintillation material [1], used in the Large Hadron Collider electromagnetic calorimeter and the photon detector in the ALICE experiment at CERN [1, 2]. Now we can say unequivocally that lead tungstate is the most promising scintillation material in the next decade.

The scintillation properties of lead tungstate single crystals are due to their ability to glow under the influence of ionizing radiation, which is of great theoretical and practical interest from the point of view of the possibility of registering ionizing radiation (charged particles, gamma quanta, etc.). As it turned out, due to the large charge of the lead and tungsten nuclei, and the high density (8 g / cm³), lead tungstate effectively absorbs gamma quanta.

At present, studies are continuing on the possibility of improving the scintillation properties of single crystals of d-element tungstate’s [3,4].

In the modern world, scientific and practical research based on accelerators is impossible without the use of highly efficient detecting elements capable of maintaining a high stability of their parameters under the influence of radiation for a long period of time.

That is why, in the early 1990s, the LHC program initiated a number of research projects to develop advanced detectors with improved performance. As part of the functioning of this project, the scintillation properties of lead tungstate were revealed, thanks to the joint work of scientists in the field of materials science, technologists and physicists specializing in high energy physics.

Over the past five years, the technology for the production of single crystals has grown from the release of individual samples to mass production with precisely specified characteristics and properties.

Until recently, the Bogoroditsk Plant of Technochemical Products in Russia carried out mass production of lead tungstate single crystals by the Czochralski method. Small quantities of lead tungstate
single crystals are produced by the Shanghai Institute of Ceramics (China) using the modified Bridgman method [6], Institute of Single Crystals (Kharkiv, Ukraine) [7].

In addition, the luminescent properties of lead tungstate single crystals were discovered. [8].

At the same time, the existing methods of synthesizing lead tungstate are far from perfect, require a lot of labor and energy, and pollute the environment.

Oxide tungsten bronzes are promising for the manufacture of anodes of chemical current sources, cathodes of electrolysis baths, are used as catalysts in organic synthesis, to obtain high-quality printing inks, materials for semiconductor diodes and pressure sensors. They are also used for the manufacture of electrodes used in redox titration, since they have high activity and selectivity and in some processes successfully replace platinum metals. In the molten state, they are very strong reducing agents and are used for etching laser rods. Serves as a protective coating for some metal parts, prevents oxidation of the titanium base of iridium oxide anodes.

Thus, the development of an optimal technology for the synthesis of lead tungstate and oxide tungsten lead bronzes in ionic melts of multicomponent systems are of great theoretical and practical interest.

It seems to us that the role of phase diagrams of multicomponent systems in solving the problems of finding optimal conditions for the synthesis of substances is extremely great.

The development of complexation and the presence of solid so that complicate the study of the system. This is of great methodological value, since allows you to study real systems in their morphological development and mutual influence.

Three-component systems (NaCl₂-Na₂CO₃-(NaF)₃, (KCl)₂-K₂CO₃-K₂MoO₄ and (KCl)₂-K₂CO₃-K₃WO₄) belong to the simple eutectic type. Each of them implements a single triple eutectic.

In the systems NaCl₂-(NaF)₂-Na₂WO₄, (NaCl)₂-(NaF)₂-Na₂MoO₄, (KCl)₂-(KF)₂-K₂WO₄ [9], (KF)₂-(KCl)₂-K₂WO₄, (KCl)₂-(KF)₂-K₂CO₃, (NaCl)₂-Na₂CO₃-Na₂WO₄ [10], (NaCl)₂-Na₂CO₃-Na₂MoO₄, (NaF)₂-Na₂CO₃-Na₂MoO₄, (NaF)₂-Na₂CO₃-Na₂WO₄, (KF)₂-K₂CO₃-K₂MoO₄, (KF)₂-K₂CO₃-K₂MoO₄, (KF)₂-K₃CO₃-K₃WO₄, in addition to the liquidus surfaces of the initial components, crystallization regions of double complex compounds NaCl-Na₂WO₄, NaCl-Na₂MoO₄, KF-K₂WO₄, KF-K₂MoO₄, KF-K₂CO₃, 2 NaF-Na₂MoO₄, 2NaF-Na₂WO₄.

Table 1. The phase diagrams of these systems are triangulated into phase unit blocks.

| FEBi | HBT | System |
|------|-----|--------|
| I (NaCl)₂-(NaF)₂-NaCl-Na₂WO₄ | E₅₁₃ | Na/F, Cl, WO₄ |
| II (NaCl)₂-NaClNa₂WO₄-2NaF-Na₂WO₄ | empty | "R" "R" "R" "R" "R" "R" |
| III Na₂WO₄-NaCl-Na₂WO₄-2NaF-Na₂WO₄ | E₆₅₆, P₃₂₇ | "R" "R" "R" "R" "R" "R" |
| IV (NaCl)₂-(NaF)₂-NaCl-Na₂MoO₄ | E₅₈₆ | Na/F, Cl, MoO₄ |
| V (NaF)₂-NaCl-Na₂MoO₄-2NaF-Na₂MoO₄ | empty | "R" "R" "R" "R" "R" "R" |
| VI Na₂MoO₄-NaCl-Na₂MoO₄-2NaF-Na₂MoO₄ | E₅₈₂, P₃₃₆ | "R" "R" "R" "R" "R" "R" |
| VII (KCl)₂-(KF)₂-KF-K₂WO₄ | E₅₆₅ | K/F, Cl, WO₄ |
| VIII (KCl)₂-K₂WO₄-KF-K₂WO₄ | empty | "R" "R" "R" "R" "R" "R" |
| IX (KCl)₂-(KF)₂-KF-K₂MoO₄ | E₅₄₉ | K/F, Cl, MoO₄ |
| X (KCl)₂-K₂MoO₄-KF-K₂MoO₄ | E₅₅₈ | "R" "R" "R" "R" "R" "R" |
| XI (KCl)₂-K₂CO₃-KF-K₂CO₃ | empty | K/F, Cl, CO₃ |
| XII (KCl)₂-(KF)₂-KF-K₂CO₃ | E₅₂₈, P₃₃₂ | "R" "R" "R" "R" "R" "R" |
| XIII (NaCl)₂-Na₂CO₃-[NaCl-Na₂WO₄] | E₅₈₈ | Na/F, Cl, CO₃, WO₄ |
| XIV Na₂CO₃-Na₂WO₄-[NaCl-Na₂WO₄] | E₅₆₉ | "R" "R" "R" "R" "R" "R" |
| XV (NaCl)₂-Na₂CO₃-[NaCl-Na₂MoO₄] | E₅₇₂ | Na/F, Cl, CO₃, MoO₄ |
| XVI Na₂CO₃-Na₂MoO₄-[NaCl-Na₂MoO₄] | E₅₄₈ | "R" "R" "R" "R" "R" "R" |
| XVII (NaF)₂-Na₂CO₃-2NaF-Na₂MoO₄ | empty | Na/F, Cl, CO₃, MoO₄ |
| XVIII Na₂CO₃-Na₂MoO₄-2NaF-Na₂MoO₄ | E₅₄₄, P₅₇₀ | "R" "R" "R" "R" "R" "R" |
| XIX (NaF)₂-Na₂CO₃-2NaF-Na₂WO₄ | empty | Na/F, Cl, WO₄ |
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FEBI II, VI, XII, XVII and XIX are empty, due to the migration of triple eutectics into neighboring adjacent FEBI with inversion into triple peritectics.

In the systems Na₂CO₃-Na₂MoO₄-Na₂WO₄, K₂CO₃-K₂MoO₄-K₂WO₄, belt solid solutions based on Na₂MoO₄ and Na₂WO₄, K₂MoO₄ and K₂WO₄ do not decompose.

**Three-component reciprocal systems** Na, K//F, Cl and Na, K//Cl, CO₃ irreversible reciprocal diagonal type, without complication.

Systems Na, K//F, CO₃, Na, K//F, CO₃ are reversibly reciprocal diagonal-adiagonal type with complexation.

**Table 2.** Their phase complexes are triangulated by stable diagonals and adiagons to the corresponding FEBI.

| FEBI       | HBT       | System                  |
|------------|-----------|-------------------------|
| I (KF)₂-(NaF)₂-KF-K₂CO₃ | empty     | Na, K//F, CO₃            |
| II (NaF)₂-K₂CO₃-KF-K₂CO₃ | E₆₅₅, P₆₈₄ | " " " " " " " " " " " " |
| III (NaF)₂-K₂CO₃-Na₂CO₃-KF-K₂MoO₄ | solid solution | E₆₄₈, Na, K//F, MoO₄ |
| IV (NaF)₂-(KF)₂-KF-K₂MoO₄ |            |                         |
| V (NaF)₂-K₂MoO₄-KF-K₂MoO₄ | E₆₇₂       | " " " " " " " " " " " " |
| VI (NaF)₂-K₂MoO₄-Na₂MoO₄-K₂MoO₄ | P₆₄₅     | " " " " " " " " " " " " |
| VII (NaF)₂-Na₂MoO₄-Na₂MoO₄-K₂MoO₄ | E₅₉₃, R₅₉₉ | " " " " " " " " " " " " |
| VIII (NaF)₂-(KF)₂-KF-K₂WO₄ | E₆₄₅       | Na, K//F, WO₄            |
| IX (NaF)₂-K₂WO₄-KF-K₂WO₄ | E₆₆₄       | " " " " " " " " " " " " |
| X (NaF)₂-K₂WO₄-Na₂WO₄-K₂WO₄ | empty     | " " " " " " " " " " " " |
| XI (NaF)₂-Na₂WO₄-K₂WO₄-2NaF-Na₂WO₄ | empty   | " " " " " " " " " " " " |
| XII Na₂WO₄-Na₂WO₄-K₂WO₄-2NaF-Na₂WO₄ | E₅₉₁, P₅₉₆, P₆₁₀ | " " " " " " " " " " " " |

A distinctive feature of the Na, K // F, MoO₄ system is that the compound 2NaF-Na₂MoO₄ "wedges out" and is not included in the composition of the completely crystallized alloy, due to its decomposition below the temperature of HBT R. Thus, the pole of this compound cannot be triangulating, and the point R does not belong to FEB VII. Note also that HBT E₆₄₅ migrates from FEB VII to VI, to which it belongs.

In the Na, K // F, WO₄ system, HBT P₆₁₀ and P₅₉₆ are localized in FEB XII, but belong to FEBI X and XI, respectively. Migration processes do not take place here.

The systems Na, K // Cl, MoO₄ and Na, K // Cl, WO₄ belong to reversibly reciprocal systems of the adiagonal type with complexation. In them, the chemical processes of mutual exchange are suppressed by the processes of complex formation.

**Table 3.** The compounds NaCl-Na₂MoO₄ and NaCl-Na₂WO₄ are the poles of three-beam triangulating stars, which divide the corresponding squares of the compositions by FEBI.

| FEBI       | HBT       | System                  |
|------------|-----------|-------------------------|
| I (NaCl)₂-(KCl)₂-NaCl-Na₂MoO₄ | empty     | Na, K/Cl, MoO₄          |
| II (KCl)₂-K₂MoO₄-NaCl-Na₂MoO₄ | P₁, E, P₂ | " " " " " " " " " " " " |
| III K₂MoO₄-NaCl-Na₂MoO₄-Na₂MoO₄-K₂MoO₄ | P     | " " " " " " " " " " " " |
The aim of this work is to study phase equilibria and the possibility of chemical synthesis of oxide tungsten bronzes in ionic melts of the studied system.

2. Experimental part

The object of research is the phase diagram of the three-component system Li, Na, Pb // WO₄ (table 1).

Experimental study of the phase diagram of the three-component Li, Na, Pb // WO₄ system was carried out by differential thermal analysis (DTA).

Used Pt-Pt / Rh thermocouples and platinum microcrucibles with a capacity of 0.5 g. The qualification of the starting salts is not lower than “chemically pure”. The crystallization (melting) temperature of each sample was measured twice, the difference between the crystallization and melting temperatures was no more than 3-4 °C, the measurement error of the crystallization (melting) temperature was ± 2 °C, the compositions of the eutectics were determined with an absolute accuracy.
of ± 0,5% by each component. All compositions are expressed in mol. %, and the temperature - in °C. We used the techniques of the projection thermographic method.

The chemical composition of the obtained oxide tungsten bronzes was determined by X-ray phase analysis (XRD).

In the three-component system Na2WO4-Li2WO4-Pb2WO4, only one eutectic with a melting point of 450 °C and concentration coordinates was revealed: 42,5% Na2WO4, 47,5% Li2WO4, 10% Pb2WO4. Component liquidus determined Na2WO4, Li2WO4 и Pb2WO4 (surface of primary crystallization of components, positions of monovariant lines (lines of joint crystallization of two phases - lines of double eutectics e1-E, e2-E и e3-E). Consequently, there is no chemical interaction between the components, and the system under study is a simple eutectic one.

![Figure 1](image_url)

**Figure 1.** Composition triangle of the ternary system Na2WO4-Li2WO4-Pb2WO4.

Synthesis of oxide tungsten lead bronzes in ionic melts of a three-component system Na2WO4-Li2WO4-Pb2WO4.

For us, of particular interest was the question of the possibility of chemical synthesis of oxide molybdenum lead bronzes in melts of a three-component system Na2WO4-Li2WO4-Pb2WO4.

Synthesis technique. Powders of metallic tungsten and tungsten (VI) oxide were introduced into the initial sample of the eutectic composition based on the percentage of lithium, sodium and lead tungstates in accordance with the reaction equation:

\[
3\text{Li}_2\text{WO}_4 + 2\text{WO}_3 + \text{W} = 6\text{LiWO}_3
\]

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

\[
3\text{Na}_2\text{WO}_4 + 2\text{WO}_3 + \text{W} = 6\text{NaWO}_3
\]

The resulting mixture was thoroughly mixed in a mortar, then dried at a temperature of 150-200 °C. Then the charge was transferred into a crucible, lowered into a shaft furnace and heated to the melting point. The melt was kept at this temperature for up to 30-45 minutes. Then the melt was poured into a stainless steel cuvette, and after cooling, it was thoroughly ground in a mortar and transferred into
boiling distilled water to wash the bronze from salts. After separation from the filtrate, the bronze was dried at 100 °C, weighed and the product yield was determined, which was 95.6%.

A brown multiphase mixture was obtained, in which the phases were identified by XRF: Pb0.5WO3, Pb0.45WO3, Pb0.40WO3, Pb0.35WO3, Na0.49WO3, Na0.44WO3, Na0.54WO3, NaWO3, NaWO3, Na0.54WO3, Na0.55WO3, LiWO3, Li0.51WO3.

3. Conclusions
The phase diagram of the three-component system Li, Na, Pb // WO4 and the possibility of chemical synthesis of oxide tungsten bronzes in ionic melts of the three-component system have been studied Li, Na, Pb//WO4.

It follows from the data obtained that in the three-component system Na2WO4-Li2WO4-Pb2WO4 there is no chemical interaction between the components, as evidenced by the formation of only one eutectic point.

As the results of studying the possibility of chemical synthesis of lead tungstate show, in ionic melts of a three-component system Li, Na, Pb//WO4 it is possible to synthesize highly dispersed powders of oxide tungsten bronzes with a high yield of the main product.

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