A Four-Component Reciprocal System of Tungstate and Sulfates of Lithium, Sodium, and Lead

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Abstract. The topology of the phase diagram of the four-component mutual system Li,Na,Pb//WO_4,SO_4 has been analyzed. It is shown that it is saturated with the formation of double compounds, as well as triple bonding. Triangulation of the phase diagram into stable elements has been carried out by the graph method and the main chemical reactions of exchange by the conversion method have been revealed. The phase diagram of the internal stable section Li_2SO_4 -Na_2SO_4 -$PbWO_4$ was studied by the differential thermal analysis, the coordinates of the three ternary nonvariant points, including eutectics, peritectics and transition point of wedging were revealed. The possibility of chemical synthesis of lead oxide tungsten bronzes in eutectic melts of the three-component system Li_2SO_4 -Na_2SO_4 -$PbWO_4$ has been shown.

1 Introduction

Lead tungstate has scintillation properties [1-2], which is due to its high density and radiation resistance. It is successfully used in the Large Hadron Collider and in the electromagnetic calorimeter detector PANDA [3]. In addition, lead tungstate is a photoconductor [5], a luminophore, a photocatalyst, a catalyst for oxidative dehydrogenation of propane [6], etc. Of practical and theoretical interest are the so-called oxide tungsten bronzes of lead and alkali metals as promising materials for the manufacture of anodes of chemical current sources and cathodes of electrolysis baths. They are used as catalysts in organic synthesis, for production of high-quality printing inks, materials for semiconductor diodes and pressure sensors [7-9], for production of electrodes used in redox titration, since they possess high activity and selectivity and, in some processes, they successfully substitute platinum metals [10]. In the molten state oxide tungsten bronzes are very strong reducing agents and are used for etching laser rods [11]. They serve as protective coatings on some metal parts [12-14].

The aim of the work is to study the phase diagram of the four-component mutual system Li,Na,Pb//WO_4,SO_4 and to determine the possibility of chemical synthesis of lead oxide tungsten bronzes.

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The objectives of the study are:

1.Topological analysis of the phase diagrams of the facet elements of the three-component mutual systems: Li, Na//WO_4, SO_4, Li, Pb//WO_4, SO_4, Na, Pb//WO_4, SO_4 and threecomponent systems: Li_2SO_4 -Na_2SO_4 -$PbSO_4$ and Li_2WO_4-Na_2WO_4-$PbWO_4$.

2.Triangulation of the phase diagram of the four-component mutual system Li,Na,Pb//WO_4,SO_4.

3.Differential thermal analysis of the three-component system Li_2SO_4 -Na_2SO_4 -$PbWO_4$.

2 Research Methodology

Experimental study of the phase diagram of the three-component system Li2SO4 -Na2SO4 -PbWO4 was carried out by differential thermal analysis (DTA).

Pt-Pt/Rh thermocouples and 0.5 g platinum microtubes were used. The qualification of the initial salts was not lower than "pure chemical". Crystallization (melting) temperature of each sample was measured twice, the difference between the crystallization temperature and melting temperature was not more than 3-4oC, the error in measuring the temperature of crystallization (melting) was ±2oC, compositions of eutectics were determined with absolute accuracy 0,5% for each component. All compositions are expressed in mol%, and temperature - in oC. Methods of projection thermographic method were used.

The chemical composition of the obtained oxide tungsten bronzes of lead and alkali metals was determined by X-ray diffraction analysis (XRD).

3 Results and Discussions

Chemical synthesis of oxide tungsten bronzes of lead

For us of particular interest was the question about the possibility of chemical synthesis of oxide tungsten bronzes of lead in the melts of three-component system

Li2WO4–Na2WO4–PbWO4.

Chemical synthesis of bronzes in the eutectic melt system Li2SO4 -Na2SO4 -PbSO4 (Fig. 2) was carried out as follows. Powders of metallic tungsten and tungsten oxide (VI) were introduced into the initial sample of eutectic composition E according to the percentage content of lead tungstate in the sample according to the reaction equations:

3PbWO4 + 2WO3 + W = 6Pb0.5WO3.

The resulting mixture was thoroughly stirred in a mortar, then dried at 150-200 °C. Then the charge was transferred into a crucible, lowered into a shaft furnace and heated to the melting temperature. The melt was kept at this temperature up to 30-45 minutes. Then the melt was poured into a stainless-steel cuvette, and after cooling was thoroughly grinded in a mortar and transferred into boiling distilled water to wash the bronze from salts. After separation from the filtrate, the bronzes were dried at 100 °C, weighed and the product yield determined. Oxide tungsten bronzes of the composition Pb0.5WO3 of brown color were obtained, with a yield of 91%.

Three-component systems (Fig. 1, 2).

The system Li2WO4–Na2WO4–PbWO4 is simple eutectic, studied by DTA by us [15,16].

The system Li2SO4 -Na2SO4 -PbSO4 [17] was studied earlier, it is characterized by the crystallization fields of double incongruent compounds and the crystallization field of triple incongruent compound.

The reciprocal system Li,Na//WO4,SO4 studied earlier [18] is saturated with double incongruent melting compounds: Li2SO4.Na2SO4, Li2SO4.2Na2SO4, 2Li2WO4.Na2WO4, 2Na2WO4.Na2SO4, Na2WO4.Na2SO4. The system belongs to the diagonal type of mutually reversible systems, two triple eutectics (E1 and E2), peritectic point (P1) and three points of wedging (R1, R2, R3) are revealed in it. The reciprocal system of Na,Pb//WO4, SO4 was studied earlier [18], repeatedly by us, saturated with double incongruent melting compounds: 2Na2WO4.Na2SO4, Na2WO4.Na2SO4. The system belongs to the diagonal type of mutually irreversible systems, the triple eutectics (E3) and two peritectics (P2, P3) are revealed in it. Mutual system Li, Pb // WO4, SO4 studied earlier [18], characterized by two double eutectics (E4, E5), refers to the diagonal type of mutual irreversible systems.

Three-component system Li2SO4 -Na2SO4 -PbWO4.

We first studied the three-component system Li2SO4 -Na2SO4 -PbWO4 (Fig. 2). In order to determine coordinates of nonvariant points we studied polythermal sections A-B, PbWO4–Ē–E and PbWO4 – P. Coordinates of triple eutectics (E), triple peritectics (P) and the point of wedging (R) were revealed: E: 500o, 35% Na2SO4; 7,5% PbWO4; 57,5% Li2SO4;

P: 530o, 42% Na2SO4; 8,5% PbWO4; 49,5% Li2SO4; R: 550o, 45% Na2SO4; 5% PbWO4; 50% Li2SO4.

As can be seen (Fig. 2) double incongruent compound Li2SO4.2Na2SO4 decays above the temperature of 550o, as evidenced by the wedging point (R).

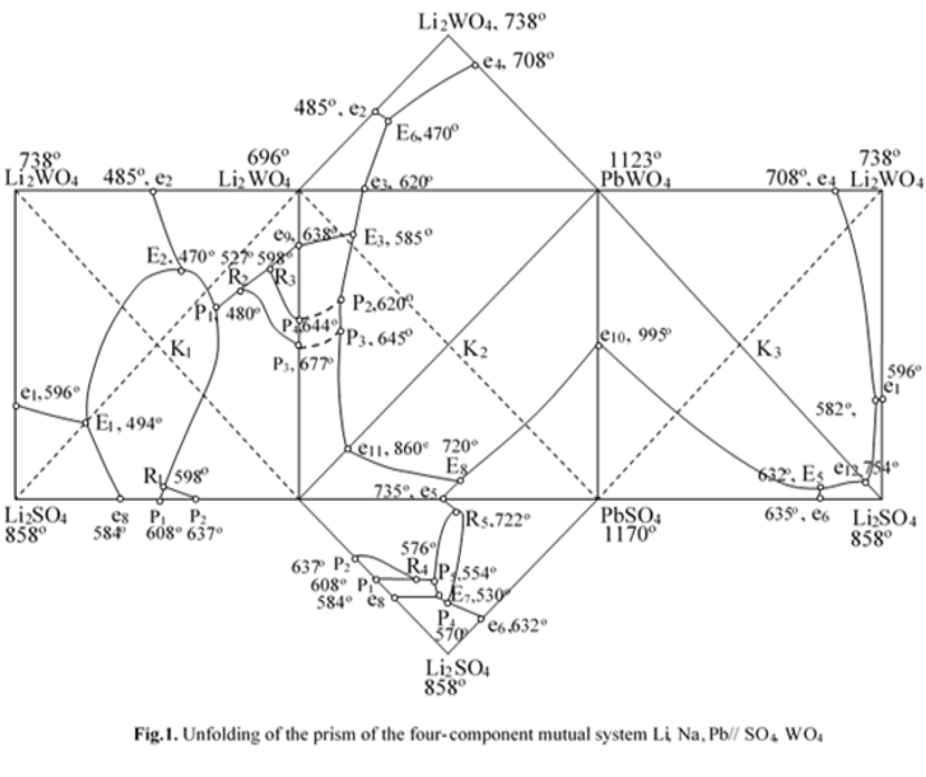

Fig.1. Unfolding of the prism of the four-component mutual system Li, Na, Pb// SO4, WO4

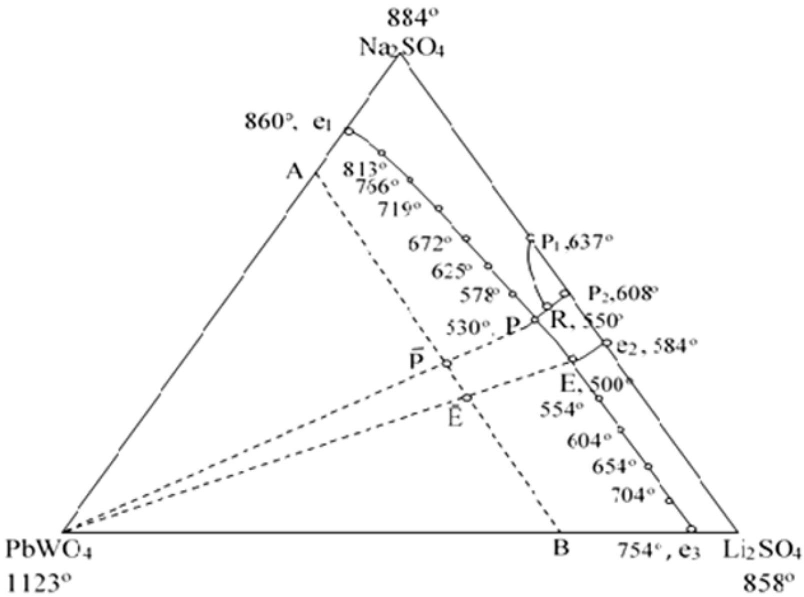

Fig. 2. A three-component system $PbWO_4$ - Na_2SO_4 - Li_2SO_4

4 Conclusions

Topological analysis of the phase diagram of the four-component mutual system Li, Na, Pb//WO4, SO4 showed that it is saturated with the formation of double compounds as well as triple compounds. The method of graphs has been triangulated the phase diagram on the stable elements and identified the main chemical reactions of exchange by conversion method. The phase diagram of the internal stable section Li2SO4 -Na2SO4 -PbWO4 was studied by the differential thermal analysis, the coordinates of the three ternary nonvariant points, including eutectics, peritectics and transition point of wedging were revealed. The possibility of chemical synthesis of lead oxide tungsten bronzes in eutectic melts of the three-component system Li2SO4 -Na2SO4 -PbWO4 has been shown.

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