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# Thermal Analysis of the System $Li_2WO_4$–$Li_4P_2O_7$–$WO_3$

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**Abstract**—The system $Li_2WO_4$–$Li_4P_2O_7$–$WO_3$ in the range of $WO_3$ contents of up to 60 mol % was studied by thermal analysis. In the examined range of the composition triangle, the crystallization fields of lithium tungstate and pyrophosphate, of congruently melting compound *D* ($Li_2WO_4 \cdot WO_3$), and of incongruently melting compound $D_2$ ($2Li_2WO_4 \cdot Li_4P_2O_7$) were revealed, and the glass formation region was established. Low-melting compositions showing promise for synthesis of lithium–tungsten oxide bronzes were revealed.

One of procedures for preparing powders of tungsten oxide bronzes, exhibiting high catalytic activity, is electrolysis of melts of systems based on alkali metal polytungstates and phosphates [1].

In this work, we performed thermal analysis of the system $Li_2WO_4$–$Li_4P_2O_7$–$WO_3$ with the aim to elucidate how the components interact in a heterogeneous medium and to reveal low-melting compositions with favorable composition and physicochemical properties for preparing lithium–tungsten oxide bronzes. The system was studied at the $WO_3$ content of up to 60 mol %, because, at a higher content of $WO_3$, glasses are formed, and such compositions are unsuitable for preparing bronzes.

**Binary systems.** The system $Li_2WO_4$–$WO_3$ was studied in numerous works; we took data for this system from [2]. According to these data, the components form lithium ditungstate *D* ($Li_2W_2O_7$, mp 745°C) and incongruently melting lithium tetratungstate $D_1$ ($Li_2W_4O_{13}$), with the peritectic point $P_1$ (67 mol % $WO_3$, 800°C).

The characteristics of the nonvariant points of this system are listed in Table 1.

The system $Li_4P_2O_7$–$WO_3$ has not been studied previously. We found that the components form an eutectic (50% $WO_3$, mp 690°C) and an incongruently melting compound $D_3$ ($Li_4P_2O_7 \cdot 3WO_3$, peritectic point $P_3$ at 68 mol % $WO_3$, 800°C).

X-ray phase analysis of the new phase $D_3$ showed that it cannot be considered as a simple adduct; formation of this compound involves anion rearrangement and can be described by Eq. (1):

$$Li_4P_2O_7 + 5WO_3 \rightleftarrows Li_2O \cdot P_2O_5 \cdot 3WO_3 + Li_2W_2O_7. \quad (1)$$

It should be noted that the system $Li_4P_2O_7$–$WO_3$ behaves in this case similarly to the related systems with sodium and potassium pyrophosphates. The mechanism of the occurring process can be explained in more detail in terms of acid–base equilibria in melts. Under the action of $WO_3$, phosphates can transform into more acidic species, and $WO_3$, into more basic species, which can be expressed in our case as follows:

$$Li_4P_2O_7 + WO_3 \longrightarrow 2LiPO_3 + Li_2WO_4. \quad (2)$$

Lithium metaphosphate and tungstate formed by reaction (2) subsequently combine with $WO_3$ to form the product of reaction (1).

The system $Li_2WO_4$–$Li_4P_2O_7$ was not studied previously either. We found that its components form an eutectic ($e_3$) containing 20 mol % $Li_4P_2O_7$ (mp 690°C) and an incongruently melting compound $D_2$ ($2Li_2WO_4 \cdot Li_4P_2O_7$, peritectic point $P_2$ at 30 mol % $Li_4P_2O_7$, 750°C).

**Ternary system.** To plot the liquidus surface of the system $Li_2WO_4$–$Li_4P_2O_7$–$WO_3$, we studied 14 internal sections and, in the examined concentration

**Table 1.** Characteristics of nonvariant points of the system $Li_2WO_4$–$WO_3$

| Designation | $WO_3$ content, mol % | mp, °C | Point type |
|---|---|---|---|
| $E_1$ | 20 | 696 | Eutectic |
| $E_2$ | 55 | 740 | " |
| $P_1$ | 65 | 800 | Peritectic |
| *D* | 50 | 745 | Distectic |

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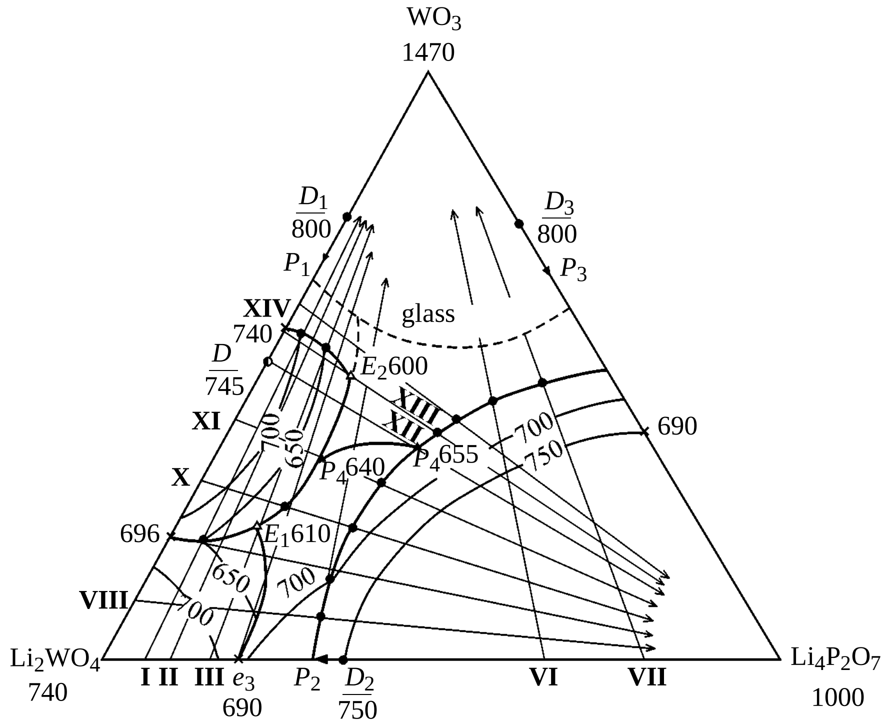


Melting diagram of the system $Li_2WO_4$–$Li_4P_2O_7$–$WO_3$ (temperatures in °C).

**Table 2.** Characteristics of nonvariant points of the system $Li_2WO_4$–$Li_4P_2O_7$–$WO_3$

| Designation | Temperature, °C | Composition, mol % | | | Point type |
|---|---|---|---|---|---|
| | | $Li_2WO_4$ | $WO_3$ | $Li_4P_2O_7$ | |
| $E_1$ | 610 | 65 | 22 | 11 | Eutectic |
| $E_2$ | 620 | 40 | 48 | 12 | " |
| $P_4$ | 655 | 34 | 36 | 30 | Transition |
| $P_5$ | 640 | 50 | 35 | 15 | " |

region of the composition triangle, revealed the crystallization fields of lithium tungstate and pyrophosphate, of congruently melting compound *D* (lithium ditungstate $Li_2W_2O_7$), and of incongruently melting compound $D_2$ ($2Li_2WO_4 \cdot Li_4P_2O_7$); also, we revealed the glass formation region (see figure).

The characteristics of the nonvariant points and interception points of the internal sections are listed in Tables 2 and 3.

Our results show that the structure of the melting diagram of the system $Li_2WO_4$–$Li_4P_2O_7$–$WO_3$ is predetermined by interaction of the components in the binary subsystems, and the compositions adjacent to the $Li_2WO_4$–$WO_3$ side, mp 650–700°C, show promise for development of an electrochemical procedure for preparing powders of lithium–tungsten oxide bronzes.

**Table 3.** Characteristics of interception points of the internal sections of the system $Li_2WO_4$–$Li_4P_2O_7$–$WO_3$

| Section no. | Initial composition, mol % | Component added, mol % | Temperature, °C | Section no. | Initial composition, mol % | Component added, mol % | Temperature, °C |
|---|---|---|---|---|---|---|---|
| **I** | 95% $Li_2WO_4$ + 5% $Li_4P_2O_7$ | 20 $WO_3$ | 650 | **IV** | 80% $Li_2WO_4$ + 20% $Li_4P_2O_7$ | 32 $WO_3$ | 630 |
| | | 55 $WO_3$ | 700 | | | 55 $WO_3$ | 670 |
| **II** | 90% $Li_2WO_4$ + 10% $Li_4P_2O_7$ | 22 $WO_3$ | 630 | **V** | 70% $Li_2WO_4$ + 30% $Li_4P_2O_7$ | 37 $WO_3$ | 650 |
| | | 55 $WO_3$ | 674 | | | 50 $WO_3$ | 660 |
| **III** | 85% $Li_2WO_4$ + 15% $Li_4P_2O_7$ | 23 $WO_3$ | 610 | **VI** | 65% $Li_2WO_4$ + 35% $Li_4P_2O_7$ | 44 $WO_3$ | 675 |
| | | 51 $WO_3$ | 650 | | | | |

**Table 3.** (Contd.)

| Section no. | Initial composition, mol % | Component added, mol % | Tempe-rature, °C | Section no. | Initial composition, mol % | Component added, mol % | Tempe-rature, °C |
|---|---|---|---|---|---|---|---|
| **VII** | 20% $Li_2WO_4$ + | 40 $WO_3$ | 680 | **XI** | 60% $Li_2WO_4$ + | $15Li_4P_2O_7$ | 640 |
| | 80% $Li_4P_2O_7$ | | | | 40% $WO_3$ | $38Li_4P_2O_7$ | 660 |
| **VIII** | 90% $Li_2WO_4$ + | $20Li_4P_2O_7$ | 670 | **XII** | 50% $Li_2WO_4$ + | $14Li_4P_2O_7$ | 660 |
| | 10% $WO_3$ | 30 $Li_4P_2O_7$ | 700 | | 50% $WO_3$ | $30Li_4P_2O_7$ | 655 |
| **IX** | 80% $Li_2WO_4$ + | $5Li_4P_2O_7$ | 650 | **XIII** | 45% $Li_2WO_3$ + | $13Li_4P_2O_7$ | 620 |
| | 20% $WO_3$ | $15Li_4P_2O_7$ | 645 | | 55% $WO_3$ | $30Li_4P_2O_7$ | 660 |
| | | $38Li_4P_2O_7$ | 700 | | | | |
| **X** | 70% $Li_2WO_4$ + | $12Li_4P_2O_7$ | 620 | **XIV** | 40% $Li_2WO_4$ + | $15Li_4P_2O_7$ | 660 |
| | 30% $WO_3$ | $20Li_4P_2O_7$ | 670 | | 60% $WO_3$ | $32Li_4P_2O_7$ | 655 |
| | | $38Li_4P_2O_7$ | 750 | | | | |

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