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Thermal Analysis of Pseudoternary Systems $Me_4P_2O_7$–WO_3–MeCl (Me = Na, K)

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Abstract — Thermal analysis of the pseudoternary systems $Na_4P_2O_7$–WO_3–NaCl and $K_4P_2O_7$–WO_3–KCl was performed, and the crystallization fields were revealed of sodium and potassium pyrophosphates, incongruently melting compounds $Na_4P_2O_7 \cdot 3WO_3$ and $K_4P_2O_7 \cdot 3WO_3$, and of products formed by reactions of WO_3 with NaCl and KCl. Low-melting compositions were revealed, which are of interest for preparing Na(K)–W oxide bronzes.

Powders of tungsten oxide bronzes can be prepared both chemically and electrochemically from melts based on polytungstates and alkali metal phosphates [1, 2].

Therefore, to reveal compositions with optimal physicochemical properties, we performed in this work the thermal analysis of the pseudoternary systems $Na_4P_2O_7$–WO_3–NaCl and $K_4P_2O_7$–WO_3–KCl.

Binary systems. Although data on the systems $Na_4P_2O_7$–NaCl and $K_4P_2O_7$–KCl are available [3], we have studied them anew. The components of these systems form eutectics with the compositions 20 mol % NaCl and 11 mol % KCl and melting points 565 and 738°C, respectively (Figs. 1, 2).

The systems $Na_4P_2O_7$–WO_3 and $K_4P_2O_7$–WO_3 were studied in [4–6]. The components of these sys-

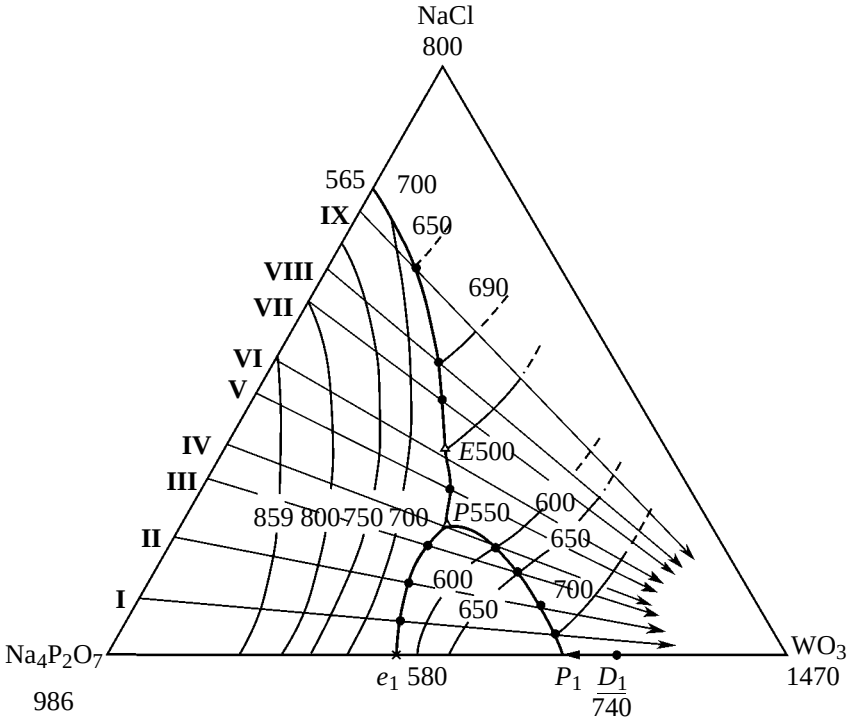

Fig. 1. Melting diagram of the system $Na_4P_2O_7$–WO_3–NaCl (the temperatures are in °C).

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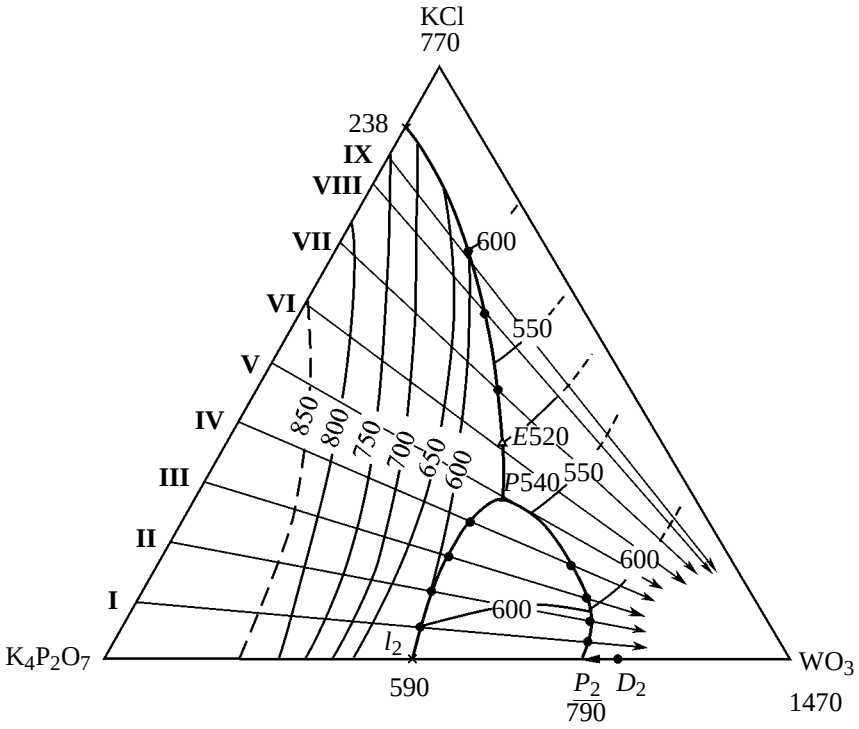

Fig. 2. Melting diagram of the system $K_4P_2O_7$–WO_3–KCl (the temperatures are in °C).

tems form incongruently melting compounds D_1 $Na_4P_2O_7 \cdot 3WO_3$ and D_2 $K_4P_2O_7 \cdot 3WO_3$ with the peritectic points P_1 (66 mol % WO_3, 740°C) and P_2 (70 mol % WO_3, 790°C).

In these systems, there are eutectic points with the compositions e_1 42 mol % WO_3 and e_2 45 mol % WO_3 and melting points 580 and 590°C, respectively.

Table 1. Characteristics of nonvariant points of the pseudoternary systems $Na_4P_2O_7$–WO_3–NaCl and $K_4P_2O_7$–WO_3–KCl

Designation	Composition, mol %			Temperature, °C	Point
	$Na_2P_2O_7$ or $K_2P_2O_7$	WO_3	NaCl or KCl		
		$Na_2P_2O_7$–WO_3–NaCl			
E	33	32	35	560	Eutectic
P	40	40	20	550	Transition
P_1	–	66	–	740	Peritectic
		$K_2P_2O_7$–WO_3–KCl			
E	23	40	37	520	Eutectic
P	27	43	30	540	Transition
P_1	–	70	–	690	Peritectic

X-ray diffraction study of the new phases D_1 and D_2 formed in these systems shows that the process is considerably more complex than mere adduct formation and involves rearrangement of anions in the initial compounds:

$$Na_4(K_4)P_2O_7 + 5WO_3 \rightleftarrows Na_2(K_2)O \cdot P_2O_5 \cdot 3WO_3 + Na_2(K_2)W_2O_7. \quad (1)$$

The reaction mechanism can be interpreted in more detail in terms of acid–base interactions in melts. In the reaction with WO_3, phosphates transform into more acidic forms, and WO_3, into a more basic form:

$$Na_4(K_4)P_2O_7 + WO_3 \longrightarrow 2Na(K)PO_3 + Na_2(K_2)WO_4. \quad (2)$$

The products of reaction (2), sodium (or potassium) metaphosphate and tungstate, combine to form the product of reaction (1).

The systems NaCl–WO_3 and KCl–WO_3 were studied previously [7]. In these systems WO_3 reacts with NaCl or KCl to form alkali metal tungstate and tungsten oxychlolride, e.g.,

$$2Na(K)Cl + 3WO_3 \longrightarrow Na_2(K_2)WO_4 + WO_2Cl_2.$$

Therefore, the systems studied in this work should be regarded as pseudoternary systems.

Table 2. Characteristics of interception points of internal sections of the pseudoternary systems $Na_4P_2O_7$–WO_3–NaCl and $K_4P_2O_7$–WO_3–KCl

Section no.	Initial composition, mol %	WO_3 added, mol %	Temperature, °C
	$Na_4P_2O_7$–WO_3–NaCl		
I	90%$Na_4P_2O_7$ + 10%NaCl	40	590
		65	700
II	80%$Na_4P_2O_7$ + 20%NaCl	40	580
		60	680
III	70%$Na_4P_2O_7$ + 30%NaCl	32	570
		55	640
IV	65%$Na_4P_2O_7$ + 35%NaCl	40	550
		48	600
V	55%$Na_4P_2O_7$ + 45%NaCl	37	540
VI	50%$Na_4P_2O_7$ + 50%NaCl	32	550
VII	40%$Na_4P_2O_7$ + 60%NaCl	28	520
VIII	35%$Na_4P_2O_7$ + 65%NaCl	25	600
		36	530
IX	25%$Na_4P_2O_7$ + 75%NaCl	12	650
		38	550
	$K_4P_2O_7$–WO_3–KCl		
I	90%$K_4P_2O_7$ + 10%KCl	43	600
		72	670
II	80%$K_4P_2O_7$ + 20%KCl	42	580
		70	600
III	70%$K_4P_2O_7$ + 30%KCl	40	570
		65	590
IV	60%$K_4P_2O_7$ + 40%KCl	42	560
		60	570
V	50%$K_4P_2O_7$ + 50%KCl	43	540
VI	40%$K_4P_2O_7$ + 60%KCl	40	520
VII	30%$K_4P_2O_7$ + 70%KCl	40	530
		55	540
VIII	20%$K_4P_2O_7$ + 80%KCl	45	545
		30	560
IX	15%$K_4P_2O_7$ + 85%KCl	20	600

Ternary systems. To construct the liquidus surfaces of the pseudoternary systems $Na_4P_2O_7$–WO_3–NaCl and $K_4P_2O_7$–WO_3–KCl, we studied for each system nine internal sections and revealed the crystallization fields of sodium and potassium pyrophosphates, incongruently melting compounds D_1 $Na_4P_2O_7 \cdot 3WO_3$ and D_2 $K_4P_2O_7 \cdot 3WO_3$, and products of reactions of NaCl and KCl with WO_3 (Figs. 1, 2).

A particular mention should be made of the field of unstable state of the reaction products of WO_3 and NaCl or KCl. This field does not correspond to any definite phase, because, as mentioned above, the initial components react to give sodium (or potassium) tungstate and tungstent oxychloride.

The characteristics of the nonvariant points and interception points of the internal sections of the systems are given in Tables 1 and 2.

Our results show that the structure of the melting diagrams of the systems under consideration is determined by interaction of the components of the binary subsystems, and the phase equilibria should be considered with due regard to the reactions occurring in the system.

Also, low-melting compositions in the vicinity of ternary eutectics (mp 500–550°C) can be used for preparing Na(K)–W oxide bronzes.

EXPERIMENTAL

Thermal analysis was performed by visual polythermal and, in part, by thermographic (DTA) methods.

The initial sodium and potassium pyrophosphates and chlorides (analytically pure grade) were recrystallized and dried at 250–300°C. Tungsten oxide was of ultrapure grade.

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