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# *Phase Equilibria in NaBr-($Li_2WO_4$)-$V_2O_5$ Systems*

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***Abstract*—Phase equilibria in two-component systems NaBr-($Li_2WO_4$)-$V_2O_5$ were studied for the first time by physical and chemical analysis. The corresponding state diagrams are constructed. It was found that the systems are eutectic and are characterized by congruent ($2Li_2WO_4{\cdot}3V_2O_5$, $3V_2O_5{\cdot}NaBr$) and incongruent ($Li_2WO_4{\cdot}V_2O_5$) complexation based on initial compounds that can be used in the development of new working materials for high-temperature thermal batteries, as well as electrolytes for electrochemical deposition of tungsten and its compounds of the "bronze" type.**

***Keywords*—phase equilibrium, diagram, differential thermal analysis, lithium tungstate and vanadium pentoxide, eutectic, solid solutions, melts***

## I. Introduction

The polyfunctional materials include non-stoichiometric compounds of the "bronze" type on the basis of vanadium oxides that are used as catalyzing environments in some processes of organic and petrochemical synthesis to obtain semiconductor materials. The industry urgently needs resistant materials that are able to conduct electric current [1-6]. Therefore, the multilateral study of various properties and methods of alkaline bronze separation of transition metals is an urgent task. The study of systems based on vanadium oxides with alkali metal salts in melts is necessary for systematic and scientifically based selection of electrolytes for the synthesis of bronzes.

The creation of new materials with a set of valuable properties is the most important scientific direction in chemistry. High requirements to the quality of oxide and oxide-salt composite materials-powders, ceramics, films, coatings, glasses and fibers led to the development of fundamentally new methods of their production. One of them is the physical-chemical design based on multicomponent systems, which has been widely developed in recent years. Its application is tested in the world practice for many branches of engineering and inorganic materials science. This method is used, in particular, for the production of ferroelectric, piezo- and dielectrics, solid electrolytes, heat-resistant materials, membranes, protective decorative coatings, and films with special optical and electrophysical characteristics, catalysts, high-temperature superconductors and heat accumulators, etc.

The choice of the objects of study of alkaline metal salt systems – vanadium oxide (V) is caused by the fact that molten halides and nitrates are the most promising for certain technological processes in medium-temperature conditions. Due to fusibility and good electrical conductivity, they are increasingly used in metallurgy, energy and other fields as heat carriers, electrolytes of chemical current sources, etc. In the molten state, alkali metal nitrates are completely dissociated and form bronzes in the presence of transition metal oxides, which is critical for applied chemistry with regard to catalysts and anticorrosive coatings.

In order to select electrolytes and build complex systems for experimental study, we conducted a thorough analysis of a number of oxide-salt systems with alkali metal salts and vanadium oxide (V).

In particular, thermal analysis of binary systems of alkali metal nitrate-vanadium oxide (V) showed that [9-12].: the processes of phase formation in them are eutectic and peritectic in nature; the NVP temperature is relatively low and makes 250-450 °C; the minimum (but sufficient) vanadium oxide content (2-10 mol.%); the ease of achieving phase homogeneity and thermal decomposition of mixtures of these systems allows making conclusions on their potential use for thermo- and electrochemical synthesis of bronze catalysts, etc.

Alkaline bronze vanadium with one or two alkali metals, but with a different structure for each type of "bronze" can be synthesized by the electrolysis of melts of these systems. The production and properties of alkaline vanadium bronzes with two different alkali metal cations in the crystal lattice are poorly understood, however, they are of interest from the point of view of the solubility of alkaline bronzes in each other. In the formation of bronzes of any structure, alkali metal ions do not occupy all vacant lattice sites, which is the reason for their variable composition. Vanadium oxide bronzes are solid solutions of the introduction phase type, which have such properties as high electrical conductivity, high chemical resistance to alkalis and acids, high mechanical strength, which led to their wide application [9].

An important task of modern technology is to obtain new inorganic materials, including mono- and polysilicic oxide vanadium bronzes. In solving this problem, phase diagrams are of great importance, which help in finding melts with optimal physical and chemical properties for thermo- and electrochemical syntheses [1-3].

The study of physical and chemical properties of vanadium bronzes allowed understanding the chemical nature of this class of compounds, alongside with possible areas of their practical use. Vanadium bronze may be formed in the process of preparing a contact mass on the basis of vanadium oxide (V) and salts of alkali metals, which are used as oxidation catalysts [4-5, 9-12].

This paper presents the results of the study on phase equilibria in NABR-($LI_2WO_4$)-$V_2O_5$ systems, which have not been previously studied.

## II. Methods and Materials

Differential thermal analysis was performed at the installation of a synchronous thermal analyzer modification STA 409C (thermal analyzer) by the German company NETZSCH designed to measure the thermodynamic characteristics (temperature and enthalpy of phase transitions, heat capacity) and to record changes in the mass of solid and powdered materials in a wide temperature range (from +25 to +1500°C). The measurement progress was monitored by a built-in processor connected to a personal computer. The studies were conducted at a rate of heating and cooling of 5 deg/min in inert atmosphere (helium) and platinum crucibles.

## III. Results

Two-component $Li_2WO_4$-NaBr system. The results of thermal analysis revealed that it implements eutectic at 45 mol. % NaBr with the melting point of 596°C (Table 1). The liquidus of the system is represented by two crystallization fields belonging to initial components ($Li_2WO_4$, NaBr) (Fig.1).

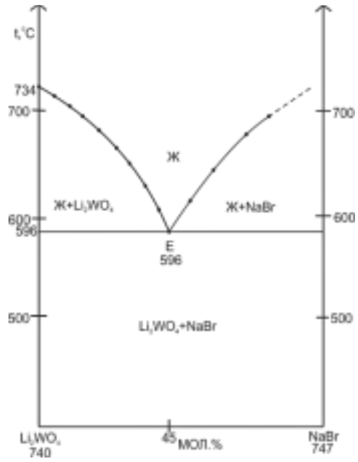


Fig. 1. State diagram of $Li_2WO_4$-NaBr system.

The formation of D ($3V_2O_5 \cdot NaBr$) congruent type of melting and two eutectic compounds was revealed in the $V_2O_5$-NaBr system (Table 1, Fig. 2). Consequently, the primary crystallization line is represented by four segments: $V_2O_5 \rightarrow E_1$; $E_1 \rightarrow D$; $D \rightarrow E_2$; $E_2 \rightarrow NaBr$. Secondary (non-invariant) equilibrium processes correspond to the following equations: $Ж \leftrightarrow V_2O_5 + D(E_1)$; $Ж \leftrightarrow 3V_2O_5 \cdot NaBr(D)$; $Ж \leftrightarrow D +$ NaBr ($E_2$).

TABLE I. NVP CHARACTERISTICS OF NABR-($LI_2WO_4$)-$V_2O_5$ SYSTEM

| **System** | **NVP** | | **Composition, mol. %** | | | **T, °C** | **Crystallizing phases** |
|---|---|---|---|---|---|---|---|
| | ***Symbol*** | ***Nature of melting*** | ***NaBr*** | ***$Li_2WO_4$*** | ***$V_2O_5$*** | | |
| $Li_2WO_4$-aBr | E | Eutectic | 45.0 | 55.0 | | 596 | $Li_2WO_4$+NaBr |
| $V_2O_5$-NaBr | $E_1$ | Eutectic | 10.0 | - | 90.0 | 640 | $V_2O_5$+D |
| | $E_2$ | Eutectic | 50.0 | - | 50.0 | 528 | D+ NaBr |
| | D | Detectice | 25.0 | - | 75.0 | 670 | $3V_2O_5 \cdot NaBr$ |
| $V_2O_5$-$i_2WO_4$ | $E_1$ | Eutectic | - | 17.5 | 82.5 | 624 | $V_2O_5$+D |
| | $E_2$ | Eutectic | - | 32.5 | 67.5 | 594 | D+S |
| | P | Peritectic | - | 45.0 | 55.0 | 686 | S+$Li_2WO_4$ |
| | D | Detectice | - | 40.0 | 60.0 | 720 | $2Li_2WO_4 \cdot 3V_2O_5$ |

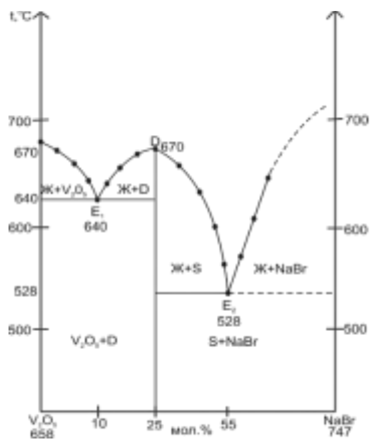


Fig. 2. State diagram of $V_2O_5$-NaBr system.

$V_2O_5$-$Li_2WO_4$ system. According to the thermal analysis, the phase diagram of the system is characterized by the implementation of four nonvariant points (NVP), including two eutectics, peritectics and distectics (Table 1). On its phase diagram (Fig. 3) the primary crystallization line is represented by five segments, including: $V_2O_5 \rightarrow E_1$; $E_1 \rightarrow D$;

D→P; P→$E_2$; $E_2$→ $Li_2WO_4$. The equations reflecting nonvariant phase equilibria, i.e. secondary crystallization processes, have the following form: Ж↔ $V_2O_5$+D($E_1$); Ж↔$2Li_2WO_4 \cdot 3V_2O_5$(D); Ж↔D+S(P); Ж↔S+ $Li_2WO_4$($E_2$). Consequently, as a result of solid-phase interaction at temperatures 680-710°C congruent and incongruent binary compounds of composition 3:2 (D) and 1:1 (S) are formed in this system, according to the equations, respectively:

$$2Li_2WO_4+3V_2O_5 \leftrightarrow 2Li_2WO_4 \cdot 3V_2O_5 \ (Li_4V_6W_2O_{23}) \ D);$$
$$Li_2WO_4+ V_2O_5 \leftrightarrow Li_2WO_4 \cdot V_2O_5 \ (Li_2V_2WO_9) \ (S).$$

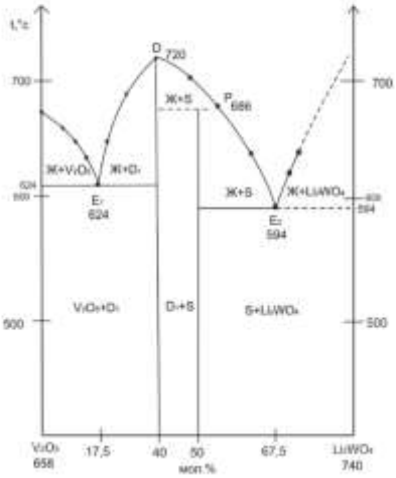


Fig. 3. State diagram of $V_2O_5$- $Li_2WO_4$ system.

### *3.1. Thermo- and electrochemical synthesis of vanadium sodium bronzes*

Sodium-vanadium bronzes were obtained from the melts of the sodium bromide – vanadium oxide (V) system at thermos- and electrochemical deposition, according to the following scheme:

$$2xNaBr+V_2O_5 \rightarrow 2Na_xV_2O_5+ xBr_2\uparrow.$$

During the electrolysis of melts, bronze is released at the cathode and at the anode-chlorine. The quantitative composition ($0.1 \le x \le 0.65$) and properties of bronze are regulated by the ratio of initial components and according to phase diagrams of the system and its cutting elements. The temperature mode of bronze production makes 550-750°C for electrolysis and 650-850°C for thermochemical synthesis.

Thus, vanadium bronze is used in production as a semiconductor material for thermistors, switches, memory elements, displays, etc. The obtained data coincide well with the fundamental theory and literature sources and confirm the potential of melts of these systems as: working materials for chemical current sources; electrolytes-solvents; background electrolytes in electrochemical production of pure and oxide bronzes; sources of electrolyte and precipitated material in electrochemical application of anticorrosive coatings, in particular, vanadium, which reduces vanadium losses. At the same time, low melting temperatures of melts also create cost-effective conditions for their use.

In thermo- and electrochemical modes, lithium and sodium vanadium bronzes can be obtained from melts of the systems. These bronzes have the following properties that determine their polyfunctionality and wide application: intense color, which is changing with composition; high electrical conductivity; significant area of homogeneity; variety of crystal structures, the formation of which depends on the production method; manifestation of properties of dielectrics and catalysts with high activity and selectivity and in some processes successfully replacing platinum.

## IV. Conclusions

Thus, the experimental study of two-component systems $Li_2WO_4$-NaBr, $V_2O_5$-NaBr and $V_2O_5$-$Li_2WO_4$ the phase equilibrium is determined, the crystallization fields of phases are specified, the compositions and the melting temperature of NVP are set.

Melts of these systems can be recommended for use as electrolytes in chemical and technological systems during high-temperature processes. The advantage against eutectic counterparts is a wide range of concentrations of compounds with similar melting points, which greatly simplifies the task of the electrolyte selection.

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