

Comparative Study of Topology and Phase Formation in $n\text{MNO}_3 - \text{V}_2\text{O}_5$ (MoO_3 , Ta_2O_5) (M - K, Rb, Cs; $n=1, 2$) within Systems

Maglaev D.Z.

Laboratory of High-Molecular Compounds
Kh. Ibragimov Complex Institute of the Russian Academy
of Sciences
Department of General and Inorganic Chemistry
Grozny State Oil Technical University named after
Academician M.D. Millionshchikov
Grozny, Russia
maglaev.d@mail.ru

Gamataev T.Sh.

Research Institute of General and Inorganic Chemistry
Dagestan State Pedagogical University
Makhachkala, Russia
gamataeva.bariyat@mail.ru

Gasanaliev E.A.

Department of Chemistry
Dagestan State Pedagogical University
Makhachkala, Russia
gamataeva.bariyat@mail.ru

Daudova A.L.

Department of General and Inorganic Chemistry
Grozny State Oil Technical University named after
Academician M.D. Millionshchikov
Grozny, Russia
maglaev.d@mail.ru
ataeva_amina@mail.ru

Ataeva A.A.

Department of General and Inorganic Chemistry
Grozny State Oil Technical University named after
Academician M. D. Millionshchikov
Grozny, Russia

Gamataeva B.Yu.

Department of Chemistry
Dagestan State Pedagogical University
Makhachkala, Russia
gamataeva.bariyat@mail.ru

Mutsalova S.Sh.

Department of General and Inorganic Chemistry
Grozny State Oil Technical University named after
Academician M. D. Millionshchikov
Grozny, Russia
maglaev.d@mail.ru

Gasanaliev A.M.

Research Institute of General and Inorganic Chemistry
Dagestan State Pedagogical University
Makhachkala, Russia
gamataeva.bariyat@mail.ru

Abstract – The methods of physical and chemical analysis was used to study the phase formation in oxide-salty systems and the following conclusions were made: – similarity of crystal structures and small distinction of cation sizes (K^+ , Rb^+ , Cs^+) in binary systems $\text{KNO}_3 - \text{CsNO}_3$ and $\text{RbNO}_3 - \text{CsNO}_3$ of $2\text{K}/\text{A}$ type (K – cation, A – anion) leads to the formation of continuous series of substitutional solid solutions of $\text{M}_x\text{Cs}_{1-x}\text{NO}_3$ and $\text{Cs}_x\text{M}_{1-x}\text{NO}_3$ type with a minimum, which indicates complete miscibility of components in a solid state; – the study of phase balances in three-component systems $\text{KNO}_3 - \text{CsNO}_3 - \text{MoO}_3$ and $\text{RbNO}_3 - \text{CsNO}_3 - \text{MoO}_3$ made it possible to establish that solid solutions formed in binary systems with the introduction of the third component different in the structure of crystals and ion radius decay in case of MoO_3 with the formation of initial components (KNO_3 , CsNO_3 , RbNO_3); – monovariant lines of co-crystallization ($\text{KNO}_3 + \text{CsNO}_3$, $\text{KNO}_3 + \text{MoO}_3$; $\text{CsNO}_3 + \text{MoO}_3$; $\text{RbNO}_3 + \text{CsNO}_3$, $\text{RbNO}_3 + \text{MoO}_3$,

$\text{CsNO}_3 + \text{MoO}_3$ converge in three-component eutectic points; – the surface of a liquidus of the studied three-component systems represents crystallization fields of initial components (MNO_3 (M – K, Rb, Cs), MoO_3). The fused electrolysis of these systems can be used to synthesize oxide molybdenum bronze with one or two alkaline metals, but with various structure for each bronze type.

Keywords – phase formation; solid solutions; liquidus; nonvariant points; eutectics; oxide bronze.

I. INTRODUCTION

At present, scientists show a growing interest in oxide materials with semiconductor, magnetic, ferroelectric, piezoelectric, pyroelectric and superconductor properties, as

well as materials with high mixed (electronic and ionic or metal) conductivity, especially in micro and nanostructural states, which synthesis is possible in the form of powders, coatings, films, mono- and polycrystals. Such materials include complex oxide bronze-like phases synthesized via topo- and electrochemical methods in oxide-salt systems, where low-melting salts act as background electrolytes and sources of introduced ions of alkali metals, and oxides of transition metals serve as a matrix [1, 6, 10, 11, 16, 19, 20].

If until now only certain alkaline oxide bronzes with one cation were generally studied, then, in our opinion, their combination in one compound represents a particular theoretical and practical interest [20].

Due to the above, the purpose of this study is to conduct the thermal analysis of topology and phase formation in systems $n\text{MNO}_3 - \text{V}_2\text{O}_5$ ($\text{MoO}_3, \text{Ta}_2\text{O}_5$) ($M - \text{K, Rb, Cs; } n=1, 2$) and to select compositions for micro- and nanostructural synthesis of their bronze.

II. METHODS AND MATERIALS

The fusibility curves were studied via thermal analysis methods well described in literature [2–4, 17, 24].

III. RESULTS

Phase formation in $M, \text{Cs}/\text{NO}_3$ ($M - \text{K, Rb, Cs}$) and $\text{MNO}_3 - \text{V}_2\text{O}_5$ ($\text{MoO}_3, \text{Ta}_2\text{O}_5$) ($M - \text{K, Rb, Cs;}$) systems.

Continuous series of substitutional solid solutions $\text{M}_x\text{Cs}_{1-x}\text{NO}_3$ and $\text{Cs}_x\text{M}_{1-x}\text{NO}_3$ with a minimum are formed in nitrate systems $M, \text{Cs}/\text{NO}_3$ ($M - \text{K, Rb, Cs}$). We studied phase diagrams in $\text{KNO}_3 - \text{MoO}_3, \text{RbNO}_3 - \text{MoO}_3, \text{CsNO}_3 - \text{MoO}_3$

systems. These systems are characterized by the eutectics in the range of temperatures 289–370°C. The thermal gravimetric analysis of mixes within $\text{MNO}_3 - \text{MoO}_3$ ($M - \text{K, Rb, Cs}$) systems showed that nitrogen oxide (IV) is released at temperatures higher than 330, 300, 400°C, respectively:



Therefore, during the thermal analysis the molten systems were not heated above the specified temperatures (Table 1) [15–24]. The oxide-salt binary systems $\text{MNO}_3 - \text{V}_2\text{O}_5$ ($\text{MoO}_3, \text{Ta}_2\text{O}_5$) ($M - \text{K, Rb, Cs}$) are characterized as eutectic systems, in which solid solutions in salt nitrate systems (Table 1) are split up with the introduction of the third component into three-component systems, i.e. transition metal oxides ($\text{V}_2\text{O}_5, \text{MoO}_3, \text{Ta}_2\text{O}_5$) [5, 7–9, 12, 14, 15, 21–23].

We also studied three-component systems: $\text{KNO}_3 - \text{CsNO}_3 - \text{MoO}_3, \text{RbNO}_3 - \text{CsNO}_3 - \text{MoO}_3$. For $\text{KNO}_3 - \text{CsNO}_3 - \text{MoO}_3$ system we studied a number of internal sections, which allowed identifying the liquidus surface (Figure 1-3.). Monovariant curves converge in a three-component eutectics. The projection crystallization polyterms of this system to a dual side of $\text{KNO}_3 - \text{CsNO}_3$ allowed specifying crystallization fields of initial components and structure of the eutectics. The refractory component of molybdenum oxide (VI) occupies the dominating crystallization field (about 90%). At the concentration of at least 5 mol % MoO_3 in a mixture the complete solubility is observed, and above – complete insolubility. At the temperature above 350°C the release of nitrogen oxide (IV) is observed due to decomposition of nitrates. Molybdenum oxide (VI) shall be added into a cooled melt and the temperature shall be slowly increased thus mixing it to achieve a phase balance.

TABLE I. CHARACTERISTICS OF NONVARIANT POINT (NVP) OF $M, \text{Cs}/\text{NO}_3$ ($M - \text{K, Rb, Cs}$) И $\text{MNO}_3 - \text{V}_2\text{O}_5$ ($\text{MOO}_3, \text{TA}_2\text{O}_5$) ($M - \text{K, Rb, Cs}$) SYSTEMS

System	NVP				Method:	Crystallization phases	Reference
	Type	Symbol	Composition, mol. %	t, °C			
$\text{CsNO}_3 - \text{RbNO}_3$	continuous series of solid solution	min	80 RbNO_3	288	TGA, XFA, DTA, DSC	$\text{Cs}_x\text{Rb}_{1-x}\text{NO}_3, \text{Rb}_x\text{Cs}_{1-x}\text{NO}_3$	[13-15]
$\text{CsNO}_3 - \text{KNO}_3$	Eutectics	e	60 KNO_3	222		$\text{CsNO}_3, \text{KNO}_3$	[7,13-15]
$\text{CsNO}_3 - \text{V}_2\text{O}_5$			95 CsNO_3	390		$\text{CsNO}_3, \text{V}_2\text{O}_5$	Studied by us [20-24].
$\text{CsNO}_3 - \text{MoO}_3$			7 MoO_3	370		$\text{CsNO}_3, \text{MoO}_3$	
$\text{KNO}_3 - \text{MoO}_3$			6 MoO_3	324		$\text{KNO}_3, \text{MoO}_3$	
$\text{CsNO}_3 - \text{Ta}_2\text{O}_5$			10 Ta_2O_5	403		$\text{CsNO}_3, \text{Ta}_2\text{O}_5$	
$\text{KNO}_3 - \text{Ta}_2\text{O}_5$			4 Ta_2O_5	320		$\text{KNO}_3, \text{Ta}_2\text{O}_5$	
$\text{RbNO}_3 - \text{MoO}_3$			2 MoO_3	289		$\text{RbNO}_3, \text{MoO}_3$	

The phase formation in $\text{RbNO}_3 - \text{CsNO}_3 - \text{MoO}_3$ system was studied to check the solubility of MoO_3 in nitrate melts and stability of their solid solutions. For this purpose, 8 internal sections, which allowed identifying the crystallization fields of initial components, were studied. It was established that with the introduction of molybdenum oxide (VI), the double solid

solutions break up with the formation of the eutectics. The projection of crystallization surface polyterm on the dual side of $\text{RbNO}_3 - \text{CsNO}_3$ made it possible to define the structure of the eutectics (Figure 4-6.). Using the thermal gravimetric analysis of melts, we found out that at a temperature of above 400°C the decomposition is observed.

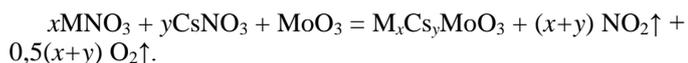
Analyzing the above results of phase formation in oxide-salt systems, which are quite coherent with the physical and chemical analysis, it is possible to draw the following conclusions:

- similarity of crystal structures and small distinction of cation sizes (K^+ , Rb^+ , Cs^+) in binary systems $KNO_3 - CsNO_3$ and $RbNO_3 - CsNO_3$ of 2K//A type (K – cation, A – anion) leads to the formation of continuous series of substitutional solid solutions of $M_x Cs_{1-x} NO_3$ and $Cs_x M_{1-x} NO_3$ type with a minimum, which indicates complete miscibility of components in a solid state;
- the study of phase balances in three-component systems $KNO_3 - CsNO_3 - MoO_3$ and $RbNO_3 - CsNO_3 - MoO_3$ made it possible to establish that solid solutions formed in binary systems with the introduction of the third component different in the structure of crystals and ion radius decay in case of MoO_3 with the formation of initial components (KNO_3 , $CsNO_3$, $RbNO_3$);
- monovariant lines of co-crystallization ($KNO_3 + CsNO_3$, $KNO_3 + MoO_3$; $CsNO_3 + MoO_3$ (Figure 1); $RbNO_3 + CsNO_3$, $RbNO_3 + MoO_3$, $CsNO_3 + MoO_3$ (Figure 2)) converge in three-component eutectic points (Table 1);
- the surface of a liquidus of the studied three-component systems represents crystallization fields of initial components (MNO_3 (M – K, Rb, Cs), MoO_3).

The results of VPA, DTA, DSC, TGA, XFA [7, 8, 9, 14, 23] methods, as well as the literature data [5, 12, 13, 21, 22] confirm that despite the molar composition of the initial mixture in these systems $MNO_3 - MoO_3$ (M – K, Rb, Cs), normal molybdates are originally formed, which form polymolybdates by interacting with a surplus of molybdenum oxide (VI). The release of nitrogen oxide (IV) and formation of molybdates take place according to the following equations:



The electrolysis of melts of these systems may be used to synthesize the molybdenum oxide bronze with one or two alkaline metals [12, 13, 5, 15], but with different structure for each bronze type. They are received according to the following schemes:



The production and properties of molybdenum oxide bronze with two different cations of alkali metals in a crystal grid are

poorly studied, however, they are of interest in terms of solubility of alkaline bronze in each other. Ions of alkali metals occupy not all vacant nodes of a crystal grid during the formation of bronze of any structure, which is the reason of their variable structure. The molybdenum oxide bronze represents solid solutions of interstitial phase type, which have such properties as high conductivity, high chemical resistance to alkalis and acids, high mechanical strength [15], which justifies their broad application.

The analysis of literature and our pilot studies showed that as a result of partial and complete interaction of reagents the $M_2V_6O_{16}$, $M_2V_8O_{20,8}$, $K_2V_2O_{13,3}$, MVO_3 , MV_6O_{15} , $M_2V_5O_{13,3}$ compounds are formed in $nMNO_3 - V_2O_5$ ($1 \leq n \leq 2$, M-alkali metals) depending on quantitative ratios and confirmed by the DTA, TGA and XRF methods. The temperature of these reactions fluctuate in the range from 276 to 600°C. All these compounds have “bronze” nature, except for MVO_3 -metavanadates. Nitrogen oxides (N_2O_5 , NO_2) and oxygen are the products of reactions.

The analysis of physical and chemical transformations in three systems of $nMNO_3$ -type – Ta_2O_5 (M = K, Cs) (Figure 7) showed that their phase diagrams are eutectic, and polymorphic transformations ($\alpha \leftrightarrow \beta$; $\beta \leftrightarrow \gamma$; $\gamma \leftrightarrow \alpha$) are typical for individual components.

Phase formation in $CsNO_3$ - $RbNO_3$ - V_2O_5 system (Figure 8-10.). Three two-component systems are part of the studied system: $RbNO_3$ - V_2O_5 ; $CsNO_3$ - $RbNO_3$; $CsNO_3$ - V_2O_5 . Two of them – $RbNO_3$ - V_2O_5 ; $CsNO_3$ - $RbNO_3$ – are studied earlier. The processes of phase formation in a system $CsNO_3$ - V_2O_5 are studied via VPA and DTA methods. This system is eutectic. The melting temperature of the eutectics is 390°C and contains 5 mol % V_2O_5 .

Table 2 shows characteristics of NVP of three-component systems. Eutectic systems and eutectics (E) melt in the range of 217-275°C, and initial components are presented in solid phases. Topological models: plane (Figure 1-8) and volume (Figure 10) phase charts are built according to literature and pilot studies.

The analysis of physical and chemical interaction in solid and liquid phases in $nMNO_3 - V_2O_5$ (MoO_3 , Ta_2O_5) (M- K, Rb, Cs; $n=1, 2$) systems via physical and chemical analysis suggests the use of the following in low-temperature chemical and technological systems, namely: methods of electrochemical synthesis of alkaline bronze of vanadium, molybdenum, tantalum; methods of anticorrosion coatings by chemical heat treatment of a surface of metals and alloys (vanadium, molybdenum); methods of topo- and electrochemical production of complex oxide phases containing transitional metals, including vanadium (V^{+5}) and (V^{+4}) with mono- and dications of alkaline metals (K, Rb, Cs).

TABLE II. CHARACTERISTICS OF NVP SYSTEMS $\text{NMNO}_3 - \text{V}_2\text{O}_5$ ($\text{MOO}_3, \text{TA}_2\text{O}_5$) (M- K, RB, CS; N= 2)

System	NVP	Composition*	t, °C	Solid phase
$\text{CsNO}_3 - \text{KNO}_3 - \text{MoO}_3$	E	38-60,5-1,5	217	$\text{CsNO}_3, \text{KNO}_3, \text{MoO}_3$
$\text{CsNO}_3 - \text{RbNO}_3 - \text{MoO}_3$	E	21-77,5-1,5	275	$\text{CsNO}_3, \text{RbNO}_3, \text{MoO}_3$
$\text{CsNO}_3 - \text{KNO}_3 - \text{Ta}_2\text{O}_5$	E	39-59-2	224	$\text{CsNO}_3, \text{KNO}_3, \text{Ta}_2\text{O}_5$
$\text{CsNO}_3 - \text{RbNO}_3 - \text{V}_2\text{O}_5$	E	19,5-78,5-2	254	$\text{CsNO}_3, \text{RbNO}_3, \text{V}_2\text{O}_5$

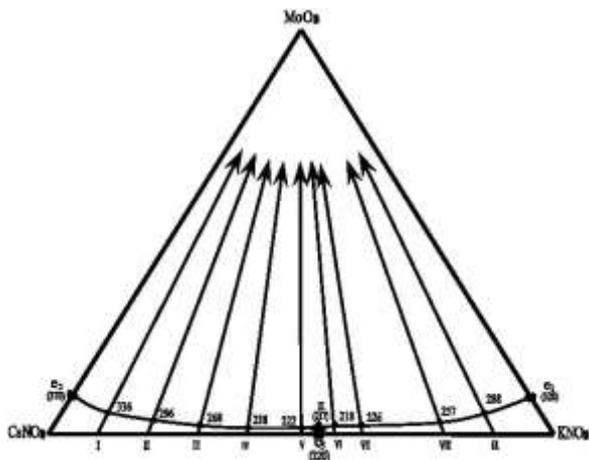


Fig. 1. Diagram of $\text{CsNO}_3 - \text{KNO}_3 - \text{MoO}_3$ system components

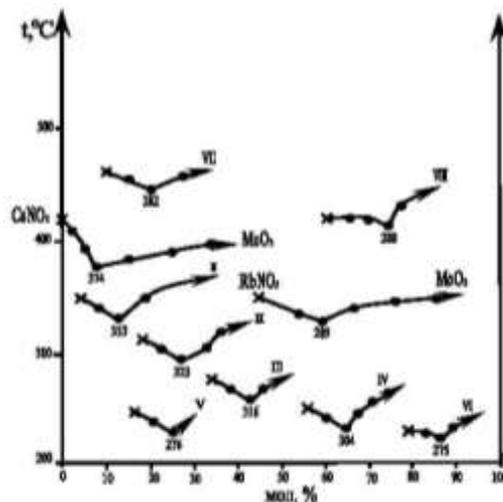


Fig. 3. Projection of crystallization polytherm of $\text{CsNO}_3 - \text{KNO}_3 - \text{MoO}_3$ to the side $\text{CsNO}_3 - \text{KNO}_3$

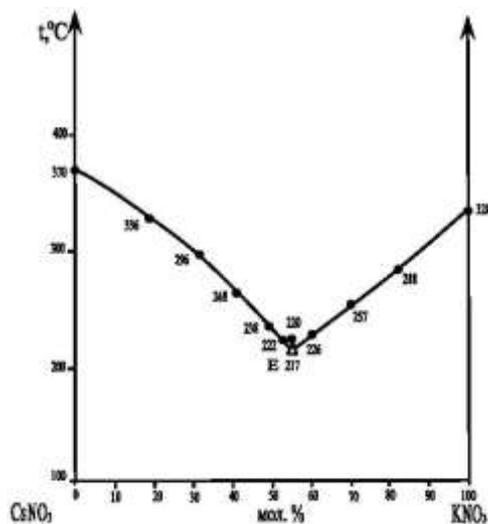


Fig. 2. Binary systems and internal sections of triple system $\text{KNO}_3 - \text{CsNO}_3 - \text{MoO}_3$.

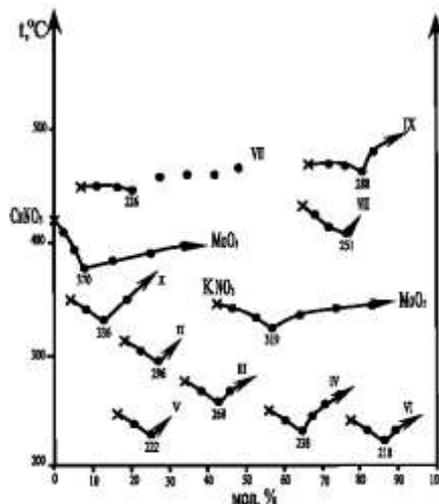


Fig. 4. Binary systems and internal sections of triple system $\text{RbNO}_3 - \text{CsNO}_3 - \text{MoO}_3$

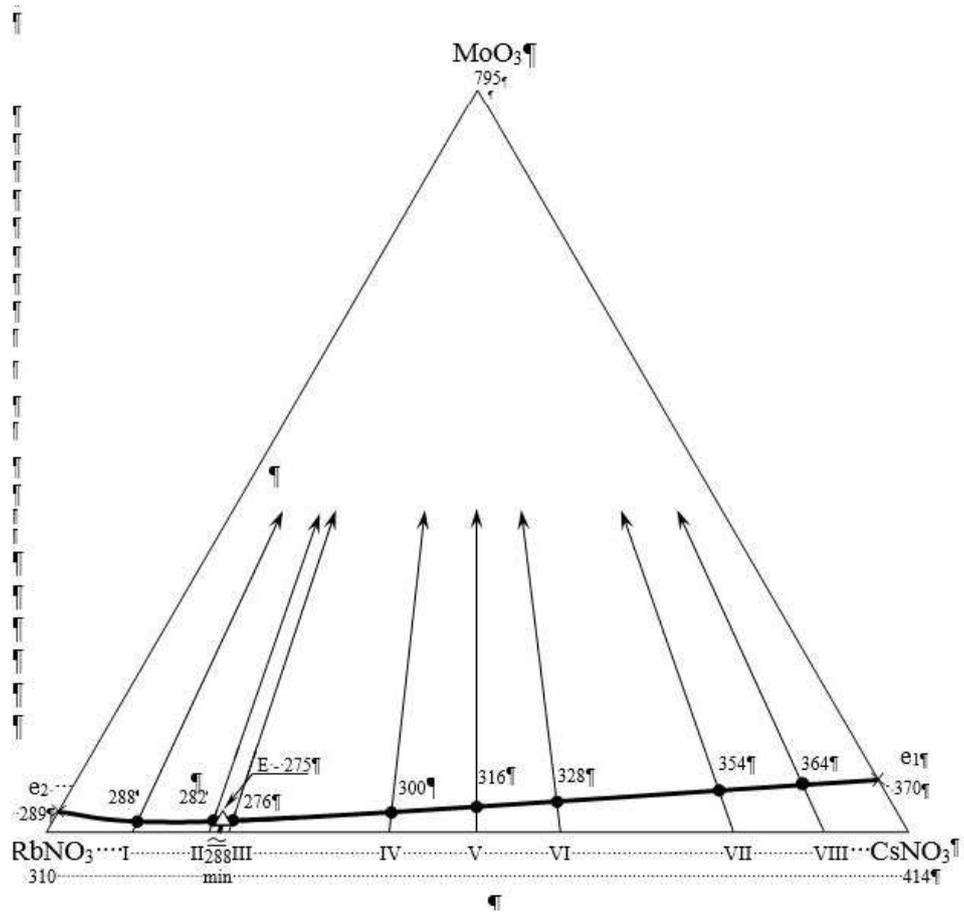


Fig. 5. Triple system $\text{CsNO}_3\text{-KNO}_3\text{-MoO}_3$

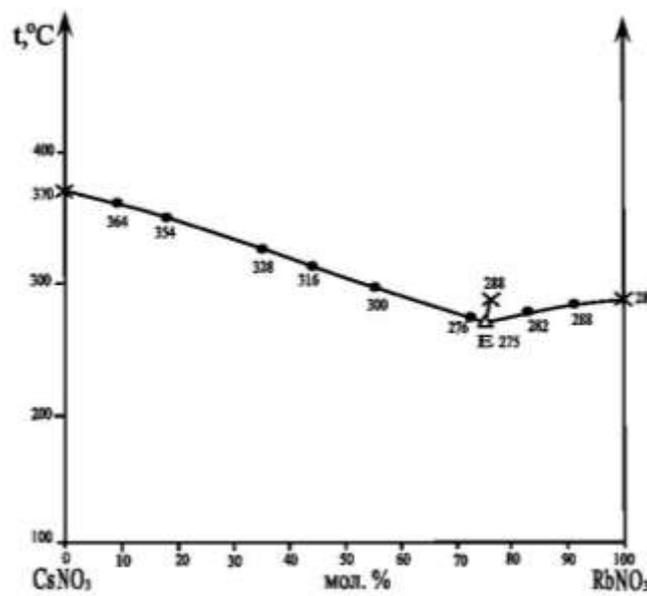


Fig. 6. Projection of crystallization polytherm of $\text{CsNO}_3\text{-RbNO}_3\text{-MoO}_3$ to the side $\text{CsNO}_3\text{-RbNO}_3$.

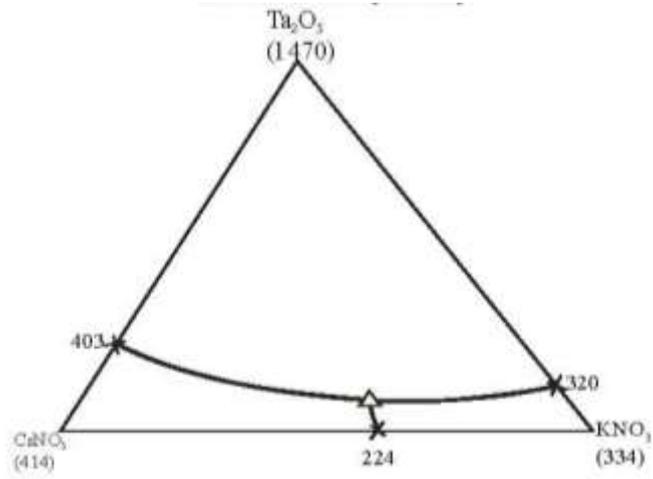


Fig. 7. Diagram of CsNO₃ – KNO₃ – Ta₂O₅ system components

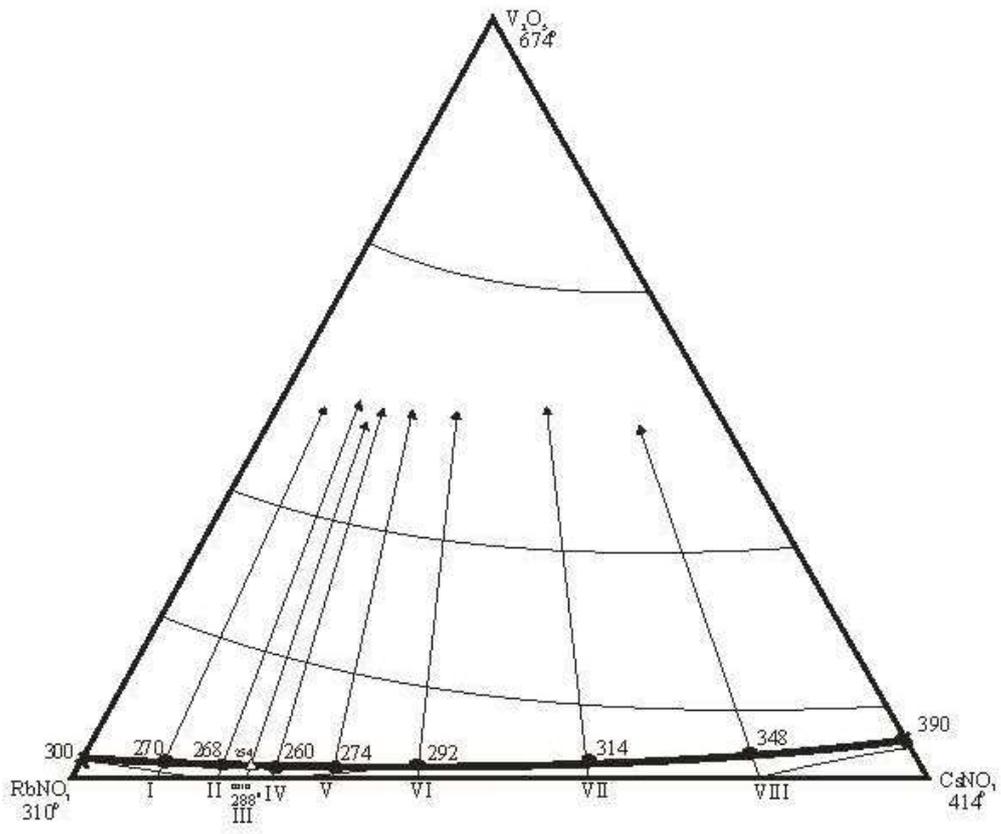


Fig. 8. Diagram of RbNO₃-CsNO₃-V₂O₅ system components

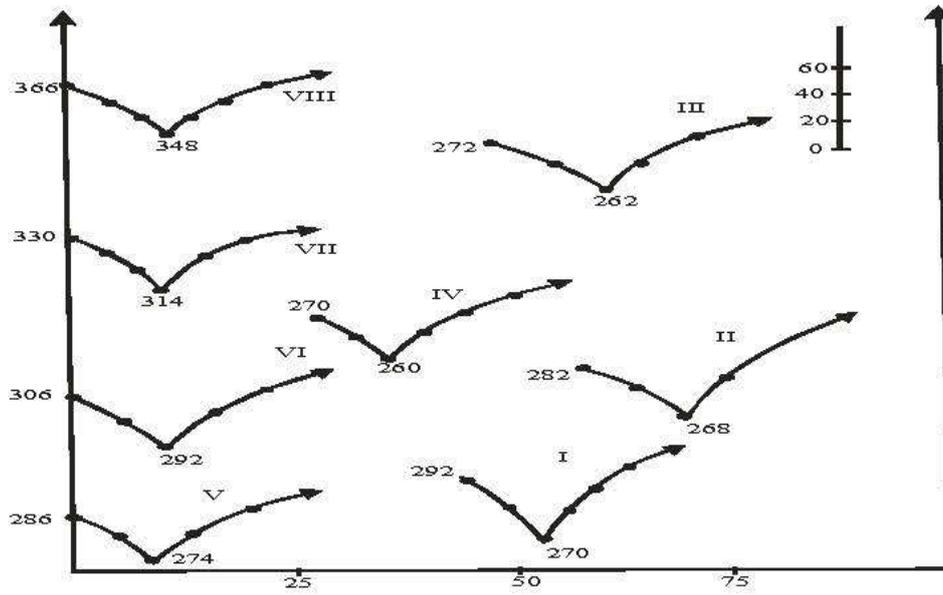


Fig. 9. Internal section of $\text{RbNO}_3\text{-V}_2\text{O}_5\text{-CsNO}_3$ system

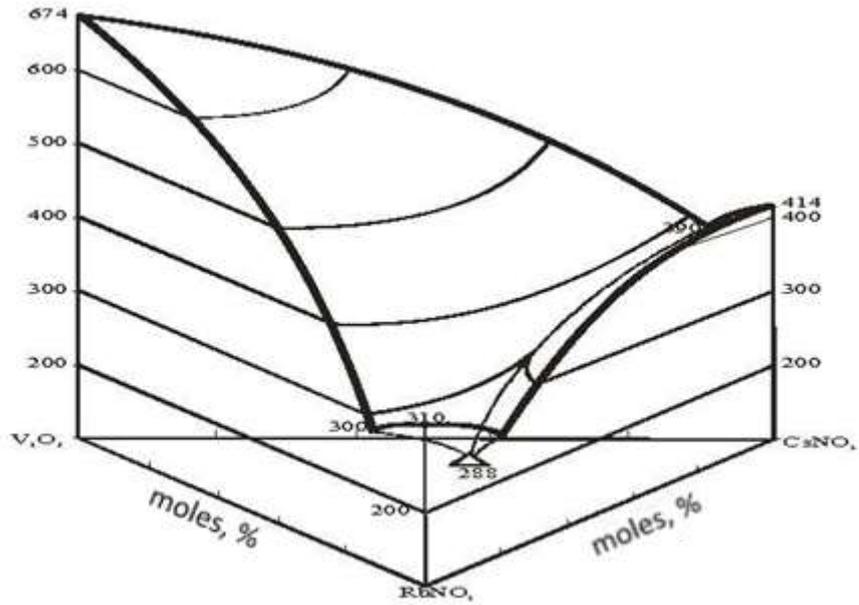


Fig. 10. 3D phase diagram of three-component system $\text{CsNO}_3\text{-RbNO}_3\text{-V}_2\text{O}_5$

References

- [1] A.N. Baraboshkin, *Electrochemistry. Electrocrystallization of metals from molten salts*. Moscow: Nauka, 1976, pp. 132–157.
- [2] A.G. Bergman, Polythermal method of complex salt systems, *Materials of the All-Union Mendeleev Congress on General and Applied Chemistry*, vol. 2, iss. I, pp. 631.
- [3] L.G. Berg, *Introduction to thermography*. Moscow: Nauka, 1969, pp. 396.
- [4] R.A. Giller, *Interplanar spacing tables*. Moscow: Nedra, 1966, pp. 362.
- [5] E.V. Danilenko, Yu.F. Rybkin, B.G. Zaslavsky, “Influence of cations and anions on surface potential of molten sodium nitrate”, *Electrochemistry*, no. 11, pp. 1714–1715, 1972.
- [6] G.A. Morachevsky, *Reference on molten salts*, vol. 1. Conductivity, density and viscosity of individual molten salts. Leningrad: Chemistry, 1971, pp. 104–107, 111.
- [7] D.Z. Maglaev, T.Sh. Gamataeva, E.A. Gasanaliev, B.Yu. Gamataeva, A.M. Gasanaliev, “Synthesis stoichiometrical and non-stoichiometrical phases in systems $\text{NMNO}_3\text{-V}_2\text{O}_5$ (N = 1, 2; M - K, RB, CS) and specific conductivity of $\text{NMNO}_3\text{-V}_2\text{O}_5$ (M-RB, K; N=1.2) systems”, *Scientific works of Kh. Ibragimov Complex Institute of the Russian Academy of Sciences*, no. 6, pp. 57–61, 2013.
- [8] D.Z. Maglaev, B.Yu. Gamataeva, E.A. Gasanaliev, A.M. Gasanaliev, “Phase formation in systems $\text{MNO}_3\text{-CsNO}_3\text{-MoO}_3$ (Ta_2O_5 , V_2O_5) (M-K,Rb,Cs)”, *Materials of interregional Paguoshsky symposium “Science and higher school of Chechen Republic: prospects of development of interregional and international scientific and technical cooperation”*, pp. 320–322, 2010.
- [9] D.Z. Maglaev, B.Yu. Gamataeva, E.A. Gasanalieva, A.M. Gasanaliev, “Conductivity of eutectic mixes $\text{KNO}_3\text{-CsNO}_3\text{-MoO}_3(\text{Ta}_2\text{O}_5)$ ”, *Materials of interregional Paguoshsky symposium “Science and higher school of Chechen Republic: prospects of development of interregional and international scientific and technical cooperation”*, pp. 322–324, 2010.
- [10] *Oxide vanadium bronze*. Under the editorship of Spitsyn. Nauka. 1982, pp. 3–18.
- [11] V.I. Posypayko, E.A. Alekseeva, N.A. Vasina, *Fusibility curves of salt systems. Part III. Reference book*. Moscow: Metallurgy, 1979, pp. 89–84.
- [12] P.I. Protsenko, A.Ya Malakhova, “Density and molar volumes of melts of nitrites and nitrates of potassium and barium mutual system”, *Magazine of inorganic chemistry*, no. 7, pp. 1662–1671, 1961.
- [13] N.P. Popovskaya., P.I Protsenko, “Interaction of metal nitrates of the first group of the Mendeleev’s periodic system with cadmium nitrate in melts”, *Journal of General Chemistry*, no. 2, pp. 207–211, 1954.
- [14] N.P. Popovskaya, P.I. Protsenko, “Temperature dependence of conductivity of nitrates and their mixes in melts”, *Journal of Inorganic Chemistry*, no. 9, pp. 2237–2240, 1962.
- [15] I.V. Radchenko, N.A. Ponyatenko, “Orientation interaction and rotary motion of NO_3 ion in melts of monovalent nitrates”, *Optics and spectroscopy*, no. 6, pp. 645–651, 1969.
- [16] D.A. Tkalenko, *Electrochemistry of nitrate melts*. Kiev: Nauka. 1983, pp. 76–114.
- [17] V.K. Trunov, L.M. Kovba, *X-ray phase analysis*. Moscow: MSU, 1976, pp. 232.
- [18] A.N. Baraboshkin, *Electrochemistry. Electrocrystallization of metals from molten salts*. Moscow: Nauka, 1976, pp. 132–157.
- [19] A.I. Efimov, et al., *Properties of inorganic compounds*. Leninkgrad: Chemistry, 1983, pp. 130, 160, 184.
- [20] *Electrochemistry. Last thirty and next thirty years*. Under the editorship of Blum G. and Guttman F. Moscow: Higher school, 1982, pp. 57–84.
- [21] A.A. Pharmakovskaya, I.A. Brovkina, M.V. Smimov, V.A. Khokhlov, “Connection of transport properties with the structure of binary molten mixes of lithium, sodium, potassium perchlorates and nitrates”, *Physical chemistry and electrochemistry of molten and solid electrolytes*. Sverdlovsk: URC USSR AS, 1973, pp. 30–32.
- [22] S.D. Shargorodsky, O.I. Shor, “Study of thermal decomposition of nitrates and carbonates of beryllium, calcium, strontium and barium”, *Ukrainian chemical journal*, no. 4, pp. 357–362, 1954.
- [23] B.Yu. Gamataeva, M.I. Gasanov, E.A. Gasanaliev, A.M. Gasanaliev, Zh.A. Kochkarov, “Phase formation in $\text{MNO}_3\text{-CsNO}_3\text{-MoO}_3$ (M = K, RB) systems”, *Journal of Inorganic Chemistry*, no. 3, pp. 483–487, 2008.
- [24] *Index Pauder Diffraction Fili*. N-York; Pennsylvania, ASTM, 1975.