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Structural Modeling and Forecasting of New Cationic Conductors by Combinatorial Method

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***Annotation** - The main results of the combinatorial structural modeling and forecasting of composition of new cationic conductors were discussed. It has been stated that the electrical conductivity values (0,2 – 0,5 Sm/cm) and activation energy of cationic conductors with α-$RbAg_4I_5$ structure are characteristically for representatives of this structural type. For Li- and Na containing salts the value of ionic conductivity is within 10^{-7} – 10^{-4} Sm/cm at room temperature.*

The development of new compounds with ionic conductivity is evoked by the requirements of electrochemical power engineering and information science. Efficiency of the development is determined by employing not elaborated and reliable methods of structural modeling and prediction of cationic conductors.

The comprehensive combinatorial method of structural modeling was elaborated. The main principles of structure types forming by modeling are the principle of maximal compactness and the principle of fragmental structure of inorganic substances. The second principles is based on using of a compact and symmetric structural fragments, which may be received for given type of the structure from fundamental structural fragment as its modification and contains one formula unite of substance.

The modeling methodic of cationic conducting structures is includes the next stages: 1) the selection of possible non-isolated structural fragments and analysis of its compatibility with modules forming; 2) analysis of modules packing variants and determining of packing symmetry; 3) the symmetry identification of the received modular structures. Taking into account this methodic the possible cationic conducting structures with compositions $A_aB^{V-a}X_5$ and $A_aB^{V}X_4$ (a = 3, 7) were received.

For promising conducting structures (of type α-$RbAg_4I_5$ with space group $P4_332$, some tetrahedral types Cu_3VS_4, α-Ag_3PO_4, γ-Li_3PO_4 et. al.) the forecasting of chemical compositions of inorganic substances was followed by method of crystal chemical analysis on functional criteria (1).

Suppose that all cationic conductors with $A_a^{\alpha}B_b^{\beta}X_d^{\gamma}$ (α=1, a+βb+γd=0) compositions having the fixed indexes and related structure are characterized by definite intervals of

relationship between mobile cationic volume and space volume in structural channel allotted for it in the lattice as well as between size of mobile ion and minimum structural channel width. Taking into consideration that bounds of interval of relationship are geometric functional criteria characterizing the range of ionic conductor existence the prediction of new ionic conductors can be reduced to a comparative analysis of their coordinates regarding the range previously established.

In according to the results of prediction some substances with promising compositions for ionic conductivity were synthesized and physic-chemical properties were investigated (tab. 1 (2-8), tab. 2 (8-13)).

Table 1. Constants of equation $\sigma = \sigma_o \exp(-E/kT)$ and conductivity of the some ionic conductors with α-$RbAg_4I_5$ structural type

Composition of the ionic conductor	σo.103, Sm.K/sm	E, eV	Conductivity, σ, Sm/sm	
			T = 298 K	T = 498 K
	calc. exp.	calc. exp.	calc. exp.	calc. exp.
$RbCu_4Br_3I_2$	6,99 6,98	0,100 0,102	0,46 0,42*	1,25 1,19
$RbCu_4Br_{3,10}I_{1,90}$	6,90 6,78	0,100 0,103	0,44 0,40*	1,22 1,16
$RbCu_4Br_{3,35}I_{1,65}$	6,71 6,46	0,101 0,104	0,42 0,37*	1,17 1,05
$NH_4Cu_4Br_3I_2$	5,97 3,80	0,096 0,088	0,46 0,40*	1,18 0,91
$NH_4Cu_4Br_{3,10}I_{1,90}$	5,88 3,01	0,096 0,090	0,45 0,30*	1,16 0,70
$NH_4Cu_4Br_{3,15}I_{1,85}$	5,82 2,51	0,096 0,089	0,45 0,26*	1,15 0,59
$KCu_4Br_3I_2$	5,13 4,00	0,096 0,094	0,39 0,32*	1,03 0,83
$KCu_4Br_{3,06}I_{1,94}$	5,31 3,75	0,096 0,090	0,39 0,35*	1,05 0,86
$KCu_4Br_{3,125}I_{1,875}$	5,50 7,15	0,097 0,110	0,40 0,35*	1,07 1,02
$KCu_4Br_{3,25}I_{1,75}$	5,90 6,19	0,098 0,102	0,42 0,37*	1,11 1,05
$Rb_{0,5}K_{0,5}Cu_4Br_3I_2$	5,97 4,36	0,098 0,091	0,43 0,41*	1,12 0,97

Table 2. Conductivity of the ionic conductors $A_aB^{VIII-a}X_4$ (a = 3, 4) and $Li_7B^VN_4$

Composition of the ionic conductor	Probability of the ionic conductivity, Q,%	Ionic conductivity, σ, Sm/sm	T, K
Li_3SbS_4	89	2.10^{-7}	298
Li_3VS_4	77	9.10^{-5}	298
Li_3PS_4	72	10^{-5}; 3.10^{-7}	298
Na_3SbS_4	37	3.10^{-5}	298
Na_3VS_4	35	2.10^{-5}	298
K_3SbS_4	0	10^{-9}	298
K_3VS_4	0	10^{-9}	298
Li_7VN_4	82	2.10^{-4}	500
Li_7TaN_4	100	$1,2.10^{-5}$	500

It has been stated that the electrical conductivity values (0,2 – 0,5 Sm/cm) and activation energy of cationic conductors with α-$RbAg_4I_5$ structure are very fine (tab.1) that characteristically for representatives of this structural type (1,8,13,14). For Li- and Na

containing salts the value of ionic conductivity is within 10^{-7} – 10^{-4} Sm/cm at room temperature (tab.2).

References:

1. *Ivanov VV. Crystal chemical analysis of inorganic substances by geometrical criteria as a semi-empiric forecasting method of cationic conductors: Inorganic Materials, 1992, V.28, N.3; 665-667.*
2. *Ivanov VV, Kolomoetc AM. Prediction of composition of solid electrolytes on base cooper halogenides: Proceedings of the Academy of Sciences of the USSR. Inorganic Materials, 1987, V.23, N.3; 501-505.*
3. *Ivanov VV, Vybornov VF, Kolomoetc AM, Shvetcov VS. Superionic conductor $RbCu_4Br_3I_2$ and its solid state solutions: Proceedings of the Academy of Sciences of the USSR. Inorganic Materials, 1988, V.24, N.2; 299-302.*
4. *Shvetcov VS, Ivanov VV, Kolomoetc AM. Superionic conductors $KCu_4Br_{3+x}I_{2-x}$.: Electrochemistry, 1990, V.26, N.2; 183-185.*
5. *Shvetcov VS, Ivanov VV. Conductors $NH_4Cu_4Br_{3+x}I_{2-x}$ with high cooper ion transport: Proceedings of the Academy of Sciences of the USSR. Inorganic Materials, 1992, V.28, N.8; 1734-1736.*
6. *Ivanov VV. Analysis of the use isomorphism possibilities for receiving of inorganic cationic conductors: Proceedings of the Academy of Sciences of the USSR. Inorganic Materials, 1992, V.28, N.1; 344-349.*
7. *Ivanov VV. Superionic conductor $K_{0,5}Rb_{0,5}Cu_4Br_3I_2$: Inorganic Materials, 1992, V.28, N.1; 182-183.*
8. *Ivanov VV. Combinatorial Modeling of the Probable Structures of Inorganic Substances. Rostov-on-Don: Northern-Caucasian Science Center of Higher Institute of Learning, 2003; 204.*
9. *Ivanov VV, Skalozubov DM. Methodic of search of the inorganic cationic conductors by geometric criteria: Proceedings of the Academy of Sciences of the USSR. Inorganic Materials, 1990, V.26, N.11; 2383-2388.*
10. *Ivanov VV, Skalozubov DM. Complex halcogenides Na_3AX_4 as a promising ionic conductors: Proceedings of the Academy of Sciences of the USSR. Inorganic Materials, 1990, V.26, N.8; 1773-1775.*
11. *Ivanov VV, Skalozubov DM. Prognoses of the inorganic cationic conductors of $A_4B^{IV}X_4$ type by geometric criteria for $A_3B^VX_4$.: Proceedings of the Academy of Sciences of the USSR. Inorganic Materials, 1991, V.27, N.12; 2661-2663.*
12. *Ivanov VV, Skalozubov DM. Prognoses of the inorganic cationic conductors of $A_aB^{VIII-a}X_4$ (were a = 2, 5, 6) and $A_7B^VY_4$ type by geometric criteria for $A_3B^VX_4$.: Inorganic Materials, 1992, V.28, N.2; 369-362.*
13. *Ivanova IV, Ivanov VV. Forecasting of inorganic substances with required properties: Research Journal of International Studies, 2014, №11(30), Part 2; 17-20.*
14. *Ivanova IV, Ivanov VV. The forming principles of the structures of ionic conductors with structural disordering: Research Journal of International Studies, 2014, №11(30), Part 2; 22-24.*
15. *Ivanov VV. Metodologic forecasting basis of the inorganic materials with necessary for using properties: The success of modern natural science, 2015, № 11; 35-43.*