

Filipenko O.S.* , Leonova L.S.* , Shilov G.V.* , Tkachev N.S.* , Ponomaryov V.I. Crystal chemistry of net-work sodium- and potassium-conductive solid electrolytes. Cation conductivity of natural analcime.**

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A basis for the layered structure of the common sodium-conductive solid electrolyte (SE) β -alumina of stoichiometric composition $\text{Na}_2\text{O}\cdot 11\text{Al}_2\text{O}_3$ is two-dimensional spinel blocks. Mobile ions are situated between the blocks occupying about 35 % of available positions. The first SE, alternative to β -alumina, NASICON of composition $\text{Na}_{1-x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$, where $1.8 < x < 2.2$, is an ancestor of a wide family of MT-network SE, whose structure contains an anionic fragment $[\text{M}_2(\text{TO}_4)_3]$, composed of isolated TO_4 -tetrahedra and MO_6 -octahedra. The network of $\text{Na}_5\text{LnSi}_4\text{O}_{12}$ consists of metasilicate 12-member rings and isolated Ln-octahedra and is an ancestor of SE containing the MT-networks, which are the most appropriate for production of SE with mobile larger cations K^+ , Cs^+ , Rb^+ . New SE of composition $\text{K}_6\text{Ln}_2\text{Si}_6\text{O}_{18}$, where Ln are La – Yb, with high sodium conductivity are produced [1]. The conductive properties of some synthetic analogs of vlassovite and carnegieite are well known, but their conductivity is relatively low.

The network structures of different topology usually contain 3D cavities, occupied by uni-charged with possibility of formation of channels for conductivity. Following to the analysis of SE structures, perfectly conductive with

respect to alkalis, we propose a scheme for classification of networks of complex SE, which is based on distinguishing of the most appropriate type of joining of network-forming polyhedron. This optimal type is heterodesmic bridges T-O-M. A conventional title of the network (tetrahedral, mixed, condensed, dodecahedral) reflects a presence of a specific complex, distinguishing the given type of the network from other and corresponding to the regular substitution of one conductive cation by another. The first type of coordination polyhedron is tetrahedron TO_4 with covalent bonding, where T = Si, Ge, Al, P, B, S, which could be either isolated T^0 or condensed T^k , forming rings and chains. Such ortho- and metatetrahedrons have “free” oxygen apexes, which serve for the formation of heterodesmic bridges with polyhedrons of another type.

The second type of polyhedra A, formed by typical metals, is present in SE as isolated structural fragments: tetrahedrons, octahedrons, trigonal dodecahedrons. As a rule, tetrahedrons T^A contain Zn, Mg, Cu, Fe, Co, Cd; octahedrons O^A are presented by complexes ZrO_6 , HfO_6 , ScO_6 , LnO_6 ; in the trigonal dodecahedra D^A , REE are complex-forming atoms. Along with the variability in bonding and specification of polyhedrons A, the following feature is significant: commensurability of the structural fragments of the network with the conductive ion. In this sense, there are lithic, sodic, potassic etc. networks. A combination of two different polyhedrons, which serve as both a stable basis and active modifying addition and designated as T^0 , T^k , T^A , O^A , D, provides a variation of heterodesmic bridges $\text{T}^0\text{-O-T}^A$, $\text{T}^0\text{-O-O}^A$, $\text{T}^k\text{-O-O}^A$, and $\text{T}^k\text{-O-D}$. Such bonding is known in four types of networks of SE (Table 1).

Table 1. Types of networks of compounds with conductivity with respect to alkalis

Network type	Cation	Solid electrolyte	σ at 300°C, (om cm) ⁻¹
Tetrahedral $\text{T}^0 - \text{T}^0_A$	Li	$\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$	0.11
	Na	$\text{Na}_2\text{ZnSiO}_4$	$2 \cdot 10^{-3}$
Mixed $\text{T}^0 - \text{O}^A$	Na	$\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$	0.22
	Li	$\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$	0.05
Condensed $\text{T}^k - \text{O}^A$	Na	$\text{Na}_5\text{GdSi}_4\text{O}_{12}$	0.20
	K	$\text{K}_6\text{Ho}_2\text{Si}_6\text{O}_{18}$	0.04
Dodecahedral $\text{T}^k - \text{D}$	Rb	$\text{RbNdP}_4\text{O}_{12}$	$5 \cdot 10^{-4}$
	Cs	$\text{CsNdP}_4\text{O}_{12}$	$1.4 \cdot 10^{-4}$

Table 2. Specific conductivity σ (Ohm⁻¹cm⁻¹) of the samples 1 and 2 in dependence on temperature

Sample	σ			
	200°C	300°C	400°C	500°C
1	$4.2 \cdot 10^{-5}$	$4.1 \cdot 10^{-4}$	$1.9 \cdot 10^{-3}$	$6.5 \cdot 10^{-3}$
2	$1.2 \cdot 10^{-5}$	$1.8 \cdot 10^{-4}$	$9.3 \cdot 10^{-4}$	$2.9 \cdot 10^{-3}$

The networks can contain different sub-types, that is supported by the presence of the conductive properties of analcime. Similarity of topology and dimensions of the network in $\text{K}_6\text{Ln}_2\text{Si}_6\text{O}_{18}$ with the structure of analcime-leucite, as well as such structural features as incomplete occupation of alkaline positions, mixed sub-type of filling in the Al-Si-oxygen tetrahedrons ($\text{T}^{0,a} - \text{T}^{0,a}$) and geometric factors (intercationic distances, shape of channels) al-

lows suggestion of high cation-conductive properties of analcime.

XRD and electrochemical studies were performed for 3 large monocrystals of analcime from the R. Galliulin's collection (Eastern Siberia) of 1-4 cm in size. XRD study showed that the rhombic analcime crystals (space group *Ibca*) show the closest similarity of the unit cell parameters and atom coordinates with one (№4) from seven analcime samples of [3].

The monocrystals were crushed for the electrochemical study. The material, preliminary heated up to 500°C, was pressed under pressure 250 MPa to form tablets of 5 mm in diameter and 1.5 mm in thickness. The tablets were sintered at 920°C during four hours to form ceramics with density of 2.2 g/cm³. Subsequently, silver past was doped onto the surface of the tablets. A total conductivity was measured by the method of impedance using the impedancemeter VM-507 and sensor RLC-819 within the interval of frequencies 500000-10 Hz with the subsequent analysis of the dispersion of frequencies. The total conductivity is mostly ionic. A value of electronic constituent, measured with constant current voltampermetry, is below 1% of the total conductivity. A specific conductivity σ of two samples is characterized by single activation energy 0.59±0.02 eV, but the value of σ is different (Table 2). Difference in conductivity is related to the presence of nepheline along with analcime in the sample 2, whereas the sample 1 is practically monophase.

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