Modeling of self-organization processes in crystal-forming systems. Structural mechanism of self-assembly of zirconosilicate $Na_2ZrSi_2O_7$ from suprapolyhedral clusters

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Topological analysis of the crystal structure of $Na_2ZrSi_2O_7$ (parakeldyshite, space group $P\bar{1}$) with an MT framework, where M are ZrO_6 octahedra and T are SiO_4 tetrahedra, was carried out by the method of coordination sequences (TOPOS.3.2 program package), and the self-organization of this structure was modeled. The cyclic-type suprapolyhedral cluster precursor $Na_2M_2T_4$ with the local symmetry $\bar{1}$ was identified by bicolor decomposition of the 4**6**46+**6**64 net. The cluster is composed of six polyhedra with two Na atoms located in the center. The precursors control the evolution of high-level crystal-forming clusters. The cluster coordination number is six. The centers of eight cluster precursors in the superprecursor of the $Na_2ZrSi_2O_7$ structure are related by translation vectors.

Key words: modeling, crystal structure, template self-assembly, suprapolyhedral precursors, zirconosilicate $Na_2ZrSi_2O_7$, zirconogermanate $Na_2ZrGe_2O_7$.

Modeling of self-organization processes in chemical systems at the atomic level is an extensively researched area, which integrates advances in various fields of sciences (mathematics, physics, biology, and chemistry).[1—10] Self-organization is taken to mean the spontaneous formation of ordered three-dimensional structures in nonequilibrium open systems.

The problem of self-organization of nonequilibrium atomic systems is universal for systems of different physicochemical nature. Among systems of this type are crystal-forming systems characterized by the spontaneous appearance of the long-range order in the arrangement of structural units of any nature (micro- and macromolecules, clusters) that initially occur as a random mixture. This process is called crystallization.

Solid crystalline bodies formed in a system have a global structure or possess large-scale coherence in the arrangement of the particles. The appearance of the simplest (one-dimensional) and more complex (two- and three-dimensional) periodicities in different stages of evolution, which reflects the fundamental nature of the crystalline state, is difficult to unambiguously predict. In particular, the establishment of long-range order in atomic crystal-forming systems is not evident from analysis of interactions between the simplest constituent particles at the lowest level of structural organization of the system.

The appearance of single crystals in a system allows one, in principle, to read (by determining the atomic structure of the solid body by diffraction methods) the symmetry-topological code of the processes of structure assembly, which occurs at the supra(super)atomic level (nanometer scale, 1 nm = 10 Å), and make conclusions about the nature and properties of crystal-forming cluster precursors.

One of the problems of the theory of the condensed state (and natural sciences as a whole) is to model self-organization processes in nonequilibrium systems and, finally, to explain these processes at the microscopic, cluster level in the context of the model of complementary highly selective self-assembly of crystal structures from microtemplate precursors (clusters with a topologically specific structure).[6—8]

Until recently, there have been no general analytical methods and approaches, which allow one to explain the observed structural topology of three-dimensional networks of bonds between atoms in the crystal structures of various compounds, including metal oxides and complex oxides (for example, framework silicates).[6]

On the one hand, this situation is associated with the lack of algorithmic methods for decoding the symmetry-topological code of the formation of the existing macrostructures of the crystals studied by diffraction methods.

On the other hand, when performing direct successive modeling of all stages of crystal nucleation and growth, it is necessary to state the criteria for selecting special solutions (physically universal in their nature) from an ex-

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tremely large set of microstructural solutions (based on the connectednesses and symmetry types). Specific clusters characterized by a block-diagonal form of the matrices of connectedness of the simplest structural units (SU) were revealed.[6] These types of clusters characterized by a sectional or hierarchical partition were determined as precursors of crystal structures, which can most rapidly evolve giving rise to a long-range order in the structures.

Main stages of self-organization of chemical system

In modeling of the structural behavior of evolving systems, when self-organization gives rise to atomic structures with a crystal lattice, researchers introduced terms,[6] such as a crystal-forming "cluster precursor," "self-assembly" of the structure, an "evolution channel" of the system, *etc*.

Three partially overlapping stages of self-organization of the system (small-, medium-, and large-scale fluctuations), which are accepted in physical models of order—disorder kinetic transitions,[6] were related to those introduced in supramolecular chemistry[1] ("template" stage, "self-organization" of a system, and "self-assembly"). Small-scale fluctuations belong to the "template" stage, which includes the formation of the simplest associates from atomic clusters or molecules and decomposition of these associates (minimum degree of complementary connection of the simplest SU). Medium-scale fluctuations are responsible for the stage of "self-organization" of the system, which includes the formation of more long-lived (stable) cluster ensembles as short chains, microlayers, and microframeworks (in a special case of molecular systems, the complementary formation of two- or three-dimensional associates as supramolecular ensembles from molecules). Large-scale fluctuations (autocatalysis) belong to the stage of "self-assembly" of the system, which includes the complementary three-dimensional condensation of cluster superprecursors or super(supra)molecular ensembles (formation of global crystal structures).

This scheme is used for analyzing processes of hierarchical self-organization of crystal-forming systems.[6]

The above-described general scheme of self-organization and new concepts, which are introduced for detailed description of crystal-forming inorganic systems of different nature, are universal. Among these concepts are a cluster precursor and a superprecursor.

Definition of precursors of crystal structures

Let us define the concept of a cluster precursor of a crystal structure in the context of crystallography (physical theory of the formation of crystal structures[31]).

Crystallography deals with the main fundamental properties of crystal structures, among which are the primary classification of structures according to the Bravais lattice types (one of 14 translation groups). Then microstructures are described within 230 symmetry space groups G, which include a translation group as a subgroup. The factor group of any space group with respect to the translation subgroup is always isomorphous to the crystallographic point group (or its group in magnitude).

The definition of the cluster precursor of the crystal structure should include the crystal lattice as a fundamental concept.

The following crystallographic definitions of the cluster precursor and the supra(super)precursor of the crystal structure are accepted.[6] The cluster precursor of a structure is an n-atom cluster consisting of two or more atoms or polyhedral particles ($n \geq 2$), which is defined as a particular monomeric supraunit. Condensation of cluster precursors in all stages of self-assembly of the structure occurs *via* a mechanism of complementary connection and is controlled by triple selection based on translation symmetry.

Modeling of the crystal structure includes the determination of the hierarchical sequence of the self-assembly mechanism in the crystallographic space.[6—8] Initially, the mechanism of formation of a primary chain of the structure (first level of self-organization of the system) from zero-level cluster precursors (corresponding to the template stage of the system) is examined. Then, self-assembly of a layer from the chain (second level) and self-assembly of a three-dimensional microframework of the structure from the layer (third level) are studied. Simultaneously, the relations between all magnitudes of translation vectors with linear sizes of the cluster precursor are considered.[6—8]

The supra(super)precursor of the structure is a high-level supercluster structure (superprecursor, supercluster), which is revealed by algorithmic modeling of the process of complementary self-assembly of the crystal structure from cluster precursors.

The minimum number of zero-level cluster precursors, which form a three-dimensional superprecursor of a framework-type crystal structure, is eight. This superprecursor has an eight-dimensional structure, because each magnitude of the translation vector requires the determination of the pair orientation relations of the cluster precursors in the three-dimensional XYZ space, which is reflected in the magnitudes of the noncoplanar vectors a, b, and c and the angles between these vectors.

The hierarchical relations between the cluster precursor and the superprecursor of the crystal structure are evident. The former is a zero-level precursor for a third-level superprecursor.

Eight types of the simplest suprapolyhedral structural units composed of two M octahedra and two T tetrahedra, *i.e.*, cluster precursors corresponding to the template stage of the system, were revealed[6] by graph theory methods. These structural units have topological symmetry and allow several symmetrically different representations (characterized by point and translation symmetries).[6—8]

The topological type and symmetry of cluster precursors, which determine the architecture of the crystal structures of elemental compounds (including fullerenes) and simple and complex oxides (silicates and germanates), were identified[6—8] by the following methods: the local crystal-structural intersection of symmetry groups,[6—8] the bicolor decomposition of structural graphs into primary and secondary contours,[6,7] and the determination of equivalent coordination sequences.[6,12]

The algorithm of self-assembly of a three-dimensional structure that occurs *via* a universal mechanism of complementary connection of cluster precursors in going to a higher level of structural self-organization of the system has been considered in detail in the studies.[6,7]

General characterization of the crystal structures of Na-Zr silicates

The formation of polyhedral SU as tetrahedra and octahedra is typical of most structures of alkali A-M silicates (germanates), where M is polyvalent metal.

There is a large crystal-chemical family of alkali A(1+),Zr and alkaline-earth B(2+),Zr silicates (~30 structural types)[15] available in the Inorganic Crystal Structure Database (ICSD-2002).[16] Among these compounds, the family of Na-Zr silicates is unique in regard to the number of representatives. In the NaOH—ZrO_2—SiO_2—H_2O system, twelve individual compounds can be synthesized.[17—21]

All structures of Na-Zr silicates[15] are formed from polyhedral structural units, *viz.*, the ZrO_6 octahedra (M octahedra) and SiO_4 tetrahedra (T tetrahedra), sharing only vertices. Eleven Na-Zr silicates have three-dimensional MT frameworks, and only zirconosilicate $Na_3HZrSi_2O_8$ has a two-dimensional layered MT structure.

Five Na-Zr silicates are anhydrous phases, and seven Na-Zr silicates are hydrated compounds. The parameters characterizing the chemical composition of the framework Na—Zr silicates $Na_pZrSi_qO_z \cdot nH_2O$ vary within broad ranges: $p = 2—8$, $q = 1—6$, and $n = 0—3$. The order of the values of q (minimum and maximum values and their increments) in the formula of the framework zirconosilicates MT_qO_m remains to be explained. For Na-Zr silicates (minerals and synthetic phases), the following seven values are known: q = 1, 1.5, 2, 2.5, 3, 4, and 6. Three topological types correspond to the MT_3O_9 composition ($q = 3$). Only one topological type is known for MT_2O_7 ($q = 2$). For $q > 6$ and $q < 1$, no framework structures occur.

The $Na_2ZrSi_2O_7$ structure with the MT_2O_7 framework ($q = 2$) is of considerable importance for an understanding of crystallization processes of Na—Zr silicates in the NaOH—ZrO_2—SiO_2—H_2O system.

First, the structural topology of the first three phases of the Na-Zr-silicate family (arranged in order of increasing q), *viz.*, orthosilicates with compositions Na_2ZrSiO_5 ($q = 1$),[21] $Na_4Zr_2Si_3O_{12}$ ($q = 1.5$),[22] and $Na_3HZrSi_2O_8$ ($q = 2$),[23] as the three-dimenisonal MTO_5 and $M_2T_3O_{12}$ frameworks and the two-dimensional MT_2O_8 layer is reproduced in the alkali-free phases $NbPO_5$,[25] $Nb_2P_3O_{12}$,[26] and $Zr(HPO4)_2 \cdot H_2O$,[27] respectively.

Second, nine framework phases (q = 2—6) beginning with $Na_2ZrSi_2O_7$ ($q = 2$)[28] are T-condensed structures and have no alkali-free structural analogs among MT-framework structures.

Third, the MT framework of phosphate ZrP_2O_7 [29] (which remains constant for all M from Si to U)[16] and the MT framework ($ZrSi_2O_7$) of silicate $Na_2ZrSi_2O_7$, in spite of the fact that their structues involve octahedra and diortho groups, are topologically different. This is associated with a radical change in the mechanism of formation of a suprapolyhedral cluster precursor of cubic phosphate ZrP_2O_7 (characterized by the P—O—P bond angle of 180°) compared to that of triclinic silicate $Na_2ZrSi_2O_7$ (Si—O—Si angle decreases to 126°). The difference is that Na atoms play a considerable role in the formation of the precursor of the $Na_2ZrSi_2O_7$ structure.

Fourth, the type of the cluster precursor, which was identified, is retained in the series of framework structures with a high percentage of silicon atoms (q = 2.5—6). The $Na_2ZrSi_2O_7$ structure lies at the basis of the homologous series of Na-Zr silicates.

In the present study, topological analysis and modeling of the template self-assembly of the $Na_2ZrSi_2O_7$ structure were carried out. To reveal the maximum possible topological symmetry of the M, T, and O atoms, the representation of the MT framework as network structures (graphs)[6,15,30—35] was used. The coordination sequences of the nodes of the network were calculated using the geometric and topological TOPOS.3.2 program package.[35,36] The suprapolyhedral cluster precursor was identified by bicolor decomposition of structural graphs. Modeling of the complementary self-assembly of the structure[6—8] revealed the topology of bonds and the connectednesses of cluster precursors in the crystal structure.

The present study was undertaken in continuation of investigations[6—8,11—15,17,30] of the geometric and topological structural features and modeling of self-organization processes of silicate and germanate systems at the suprapolyhedral level, involving the development of new algorithms of analysis and experimental validation of theoretical conclusions.

Main concepts and conventional notions

The primary structural unit (SU) is the simplest polyhedral structural unit of the MT framework composed of the M octahedron and T tetrahedra.

The cluster precursor of the crystal structure is the suprapolyhedral cluster M_2T_2 belonging to one of eight types with topological symmetry.[6—8]

The high-level suprapolyhedral structural units are suprapolyhedral clusters, which contain complementary connected precursors in an integrated form.

The connectedness of clusters in the microensemble that formed is the number of shared O atoms on the complementary surfaces of the low-level precursors upon the assembly of high-level precursors.

The stereon is a fundamental (independent) region of the symmetry space group G in the unit cell; elements with point symmetry are located at the boundaries of the unit cell.[31]

The MTO and MT networks are topological representations of the MT framework as network structures (graphs) consisting of corners (Zr, Si, O and Zr, Si atoms as nodes) and edges (bonds) between these corners.[15]

The coordination sequence for the MTO network consists of a set of $\{N_k\}$, where N_k is the number of nodes in the k-th coordination sphere of the atom chosen as the central one.[15,30,32—35]

The polyhedral microensemble (PME) M-PME, which is a taxonomic cluster of MT frameworks composed of the central M octahedron and six polyhedra on its surface, is the geometric interpretation of the calculated sequences $\{N_k\}$ for the M nodes within three coordination spheres.[15]

The cluster coordination number (CCN) is the number of the adjacent cluster precursors, which share bonds between the oxygen atoms.

Calculation procedure

Geometric and topological analysis of the crystal structure of $Na_2ZrSi_2O_7$ was carried out with the use of the method of coordination sequences,[6,15,30,32—35] which allows one to reveal the maximum possible topological symmetry of the M, T, and O atoms in MT frameworks represented as network structures (graphs). The determination of the topological symmetry of the nodes in 3D networks using the TOPOS.3.2 program package[35,36] enables one to either confirm the high crystallographic complexity of the $Na_2ZrSi_2O_7$ structure revealed by X-ray diffraction analysis[28] or come to analysis of its more simple topological model. For this purpose, the topological equivalence of the atoms located in the M and T positions was revealed by calculation of the coordination sequences $\{N_k\}$ without visualization of the structure, and the O atoms were additionally differentiated into three types of possible bridging atoms that link pairs of the polyhedral structural units in M—O—M, T—O—T, and M—O—M combinations (O atoms differ in the values of $\{N_k\}$ already in the second coordination sphere).

The algorithm for the search for the structural—genetic relationships and topological analysis of the crystal structure of $Na_2ZrSi_2O_7$ using the TOPOS.3.2 program package[6,15,30,35,36] involved the following steps:

1) compilation of the crystal-structural database for compounds of the $A_2MT_2X_7$ type available in the ICSD-2002 with the aim of revealing all structures (of silicates, germanates, phosphates, and arsenates) characterized by the pKEL topology of the framework,[15] *i.e.*, with the $ZrSi_2O_7$ framework of $Na_2ZrSi_2O_7$;

2) calculation of the matrix of connectedness for $A_2MT_2X_7$ using the *AutoCN* program[36] (strong contacts between atoms, to which the "main" faces of the Voronoi—Dirichlet polyhedra with solid angles larger than 5% of the total solid angle of 4π steradians correspond, were taken into account; in calculations of the matrix of connectedness by the method of intersecting sectors, the system of Slater atomic radii was used);

3) calculation of the coordination sequences $\{N_k\}$ for all topological representations of the $A_2MT_2X_7$ structure using the *IsoTest* program[36] (to determine the individual topological characteristics of the nodes in the MT frameworks, the A atoms were removed from the structure and the sequences $\{N_k\}$ were calculated only for the framework atoms M, T, and O).

Results and Discussion

Of 120 $A_2MT_2X_7$ compounds (available in the ICSD-2002), 11 compounds were extracted and classified into three families with different symmetry groups:

— structure type of parakeldyshite $Na_2ZrSi_2O_7$ [28] with the triclinic space group $P\bar{1}$, the order of group is 2;[37]

— structure type of khibinskite $K_2ZrSi_2O_7$ [38] with the monoclinic space group $P112_1/b$, the order of group is 4;[37]

— type of the high-pressure phase $Na_2Si^{VI}Si_2O_7$ [39] with the monoclinic space group $C12/c1$, the order of group is 8.[37]

The representatives of the families are alkali silicates (germanates) and phosphates (arsenates) with M(4+) = Si, Zr; M(2+) = Mn, Cd, Ca, Sr, Ba; and A are only large atoms, Na, K, Rb Cs.

It was found that the structure type of triclinic parakeldyshite is retained only upon the replacement of the Si atoms in the $Na_2ZrSi_2O_7$ structure with Ge.[40] It should be noted that there is a misprint in the y coordinate of the O_5 atom of germanate $Na_2ZrGe_2O_7$ available in the ISCD-2002 data base (Collection Code CC=20402); according to the data reported in the original study,[40] the correct value of this coordinate has a minus sign.

Table 1. Changes in the chemical composition of the coordination spheres of atoms in the MTO networks

Node in the network	Coordination spheres N_k (k = 1—5)				
	1	2	3	4	5
M	O	{T,T} or {M,T}	O	{M,T} and {T,T}	O
T	O	{M,T} or {T,T}	O	{M,T} and {T,T}	O
O	{M,T} or {T,T}	O	{M,T} and {T,T}	O	{M,T} and {T,T}

Table 2. Calculated parameters of the coordination sequences N_k for the atoms of the $ZrSi_2O_7$ framework ($ZrGe_2O_7$) in $Na_2ZrSi_2O_7$ ($Na_2ZrGe_2O_7$)*

Node in the network	Atoms in the structure	Coordination sequences N_k (k = 1—10)									
		1	2	3	4	5	6	7	8	9	10
M	Zr(1)	6	6	18	12	42	30	102	50	122	74
T	Si(1), Si(2) (Ge(1), Ge(2))	4	4	18	15	48	27	78	49	156	76
O (T—O—M)	O(1), O(3)—O(7)	2	8	8	26	19	62	38	114	61	164
O (T—O—T)	O(2)	2	6	6	30	24	60	30	102	68	198

* Topologically equivalent framework atoms are characterized by the identical sets N_k. The atomic numbering scheme corresponds to the structural data.[28,40]

The differentiated compositions of the coordination spheres of the atoms of the MT framework, in which the O atoms or different combinations of the M and T atoms alternate in sequence, are given in Table 1. The sequences $\{N_k\}$ for the M, T, and O atoms are listed in Table 2. The codes of the O atoms are divided into two groups depending on $\{N_k\}$ in the second coordination sphere (see Table 2): (1) the {2,6} code signifies that there is a local region of the framework as a cluster containing the central O atom (which is used as the starting point for the calculations), which links two T atoms (in the first coordination sphere), and six atoms (in the second sphere); the composition of the cluster is Si_2O_7 (O_3—Si—O—Si—O_3); (2) the {2,8} code corresponds to a cluster containing the central O atom, which links the T and M atoms (in the first sphere), and eight O atoms (in the second sphere); the composition of the cluster is $ZrSiO_9$ (O_3—Si—O—Zr—O_5).

Interpolyhedral bonds of two types, *viz.*, M—O—T and T—O—T, were revealed in the local regions of the MT framework. Since there are no M—O—M bonds in the framework, only four (of eight theoretically possible) simplest types of cluster precursors with composition M_2T_2 can occur: the MTMT cluster of the cyclic A type (*cis*-type closed chain) and the MTMT clusters, which retain a chain structure (*trans*- and *cis*-type C1 and C2, respectively) and the D-type MTTM chains. The B and E1, E2, E3 types are absent.[6]

General structural features of $Na_2ZrSi_2O_7$

Geometric model. The lattice parameters for the $Na_2ZrSi_2O_7$ and $Na_2ZrGe_2O_7$ structures are given in Table 3.[28]

Table 3. Lattice parameters of the $Na_2ZrSi_2O_7$ and $Na_2ZrGe_2O_7$ structures

Parameter	$Na_2ZrSi_2O_7$	$Na_2ZrGe_2O_7$
a/Å	6.66(3)	5.630(1)
b/Å	8.83(4)	6.677(2)
c/Å	5.42(2)	9.108(5)
α/deg	92.75	70.60(4)
β/deg	94.25	88.85(4)
γ/deg	72.33	87.04(2)
V/Å	302.76	322.51
Z	2	2

The changes in the lattice parameters in going from the silicate to the germanate have anomalies. The total change in the unit-cell volume of the germanate (V_{Ge} : V_{Si}) is 1.065, whereas the linear expansions along the equivalent crystallographic directions arranged in increasing order are as follows:

6.677 Y_{Ge} : 6.66 X_{Si} = 1.002 (Δ = 0.017 Å),
9.108 Z_{Ge} : 8.83 Y_{Si} = 1.031 (Δ = 0.278 Å),
5.630 X_{Ge} : 5.42 Z_{Si} = 1.038 (Δ = 0.210 Å),

i.e., there are virtually no changes in the germanate structure along the Y direction (which corresponds to the X direction in the silicate), whereas the maximum change is observed along the X direction (or the Z direction in the silicate). The layers located parallel to the XY and YZ planes are the most rigid fragments in the structures of silicate $Na_2ZrSi_2O_7$ and germanate $Na_2ZrGe_2O_7$, respectively. It should be noted that it is the XY plane along which the characteristic polysynthetic twinning of the single crystals of $Na_2ZrSi_2O_7$ is observed.[41,42]

The architecture of the 3D structure of $Na_2ZrSi_2O_7$ can be described as consisting of ZrO_6 octahedra (M octahedra) linked to each other through the SiO_4 ortho groups and the Si_2O_7 diortho groups (Fig. 1). The Na(1) and Na(2) atoms occupy the MT cavities.

The projection of the MT layer of silicate $Na_2ZrSi_2O_7$ onto the XY plane is shown in Fig. 2. The polyhedral composition of the layer is T : M = 2, which corresponds, on the whole, to the MT composition of the three-dimensional framework of $ZrSi_2O_7$ (q = 2). Two crystallo-

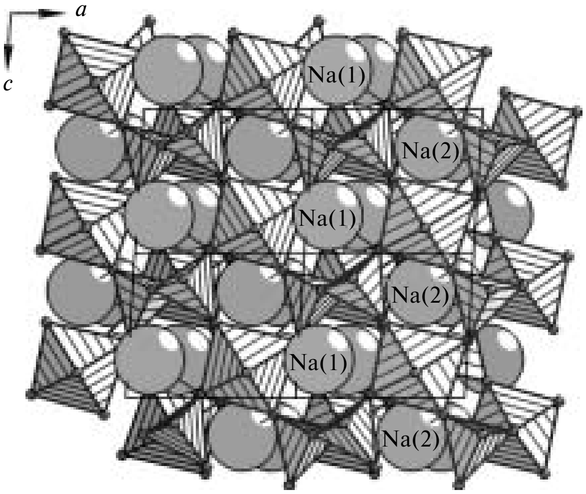

Fig. 1. Framework of the $Na_2ZrSi_2O_7$ structure consisting of the ZrO_6 octahedra (M octahedra) linked to each other by the SiO_4 ortho groups and the Si_2O_7 diortho groups; the Na(1) and Na(2) atoms are located in the MT cavities.

graphically independent Na atoms are located above and below the plane of the layer.

The Wyckoff sequence[37] for the crystal structures of silicate $Na_2ZrSi_2O_7$ and germanate $Na_2ZrGe_2O_7$ is i^{12}, *i.e.*, twelve atoms (one M, two T, two Na, and seven O) are located in the stereon (asymmetric unit cell) and occupy the general *i* positions; all eight centrosymmetrical positions at the boundary of the stereon possible for the space group $P\bar{1}$ are vacant. Since the stereon contains one M octahedron, the MT fragments built in the symmetrized stereons[6—8] contain centrosymmetrical pairs of M octahedra, which are linked to each other through either the SiO_4 ortho groups or the Si_2O_7 diortho groups depending on the crystallographic direction.

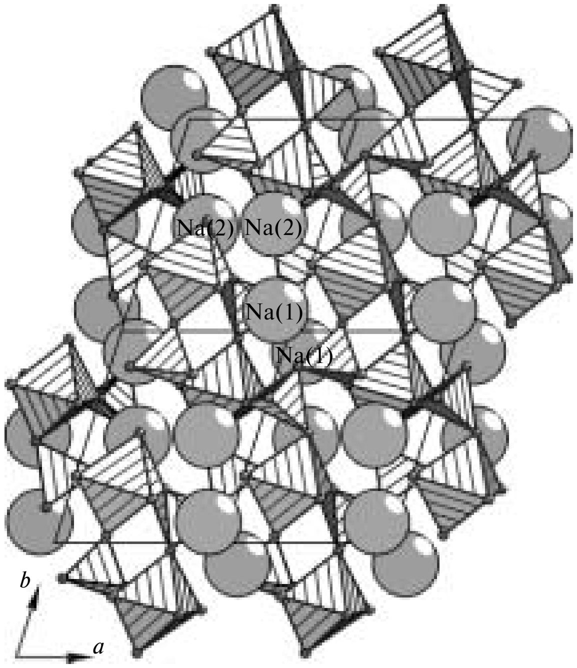

Fig. 2. Projection of the MT layer of silicate $Na_2ZrSi_2O_7$ onto the *XY* plane. The Na(1) and Na(2) atoms are marked in the center of the figure.

Structure of taxonomic M-PME of $Na_2ZrSi_2O_7$. The first-level taxonomic polyhedral microensemble M-PME[15] distinguished in the local region of the $Na_2ZrSi_2O_7$ structure is shown in Fig. 3. Such polyhedral microensembles consisting of seven polyhedra[15] characterize the type of the local environment of the M octahedron by six adjacent polyhedra. In the general case, the T atoms on the surface of the M octahedron can be linked to each other to form T—O—T fragments. In the study,[15]

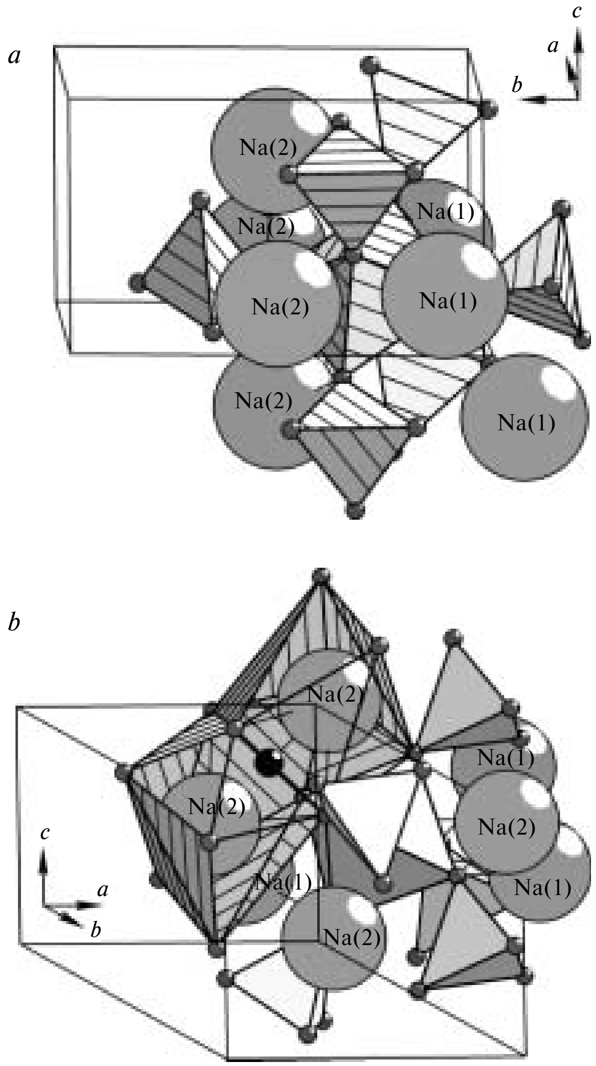

Fig. 3 Taxonomic polyhedral microensemble M-PME of the $Na_2ZrSi_2O_7$ structure characterizing the local region of the MT framework. Seven sodium atoms, which form bonds with the oxygen atoms of the ZrO_6 octahedron, are additionally included in the composition of the cluster.

twelve topological types of M-PME were classified using the graph theory.

Topologically equivalent MT frameworks in compounds with chemical composition $A_2MT_2X_7$ were searched for in the ICSD database with consideration for the high-level topological type of M-PME using the TOPOS.3.2 program package[35,36] (based on the complete coincidence of the calculated coordination sequences for the M nodes up to the tenth coordination sphere). The MT structures of 93 zirconosilicates and their analogs were classified into 12 M-PME, which are topologically different in the third coordination sphere.[15]

The structure of the first-level M-PME for $Na_2ZrSi_2O_7$ with no bonds between the T tetrahedra, was found in eight of the twelve structures of Na-Zr silicates.

The microensemble M-PME containing additionally sodium atoms, which form bonds with the O atoms of the M octahedron, was considered (Fig. 3, *a*).

Of four Na(2) atoms and three Na(1) atoms, only one Na(2) atom was demonstrated to be involved in three bonds with the O atoms, which form the face of the M octahedron (corresponding "Zr-face + Na-face" contact is shown in Fig. 3, *b*). In the silicate and the germanate, the Na(2)—Zr(1) distance remains virtually constant (3.41(6) and 3.35(1) Å, respectively).

The above-considered Na(2) atom is also related to another Na(2) atom by a center of symmetry. These atoms share four bonds formed by the O atoms (in Fig. 3, *b*, the centrosymmetrical "Na-face + Na-face" contact is represented by a small solid ball located in the special position *1e* at the boundary of the stereon).

Topological model of the MT framework of the $Na_2ZrSi_2O_7$ structure. The coordination sequences $\{N_k\}$ for the framework atoms of silicate $Na_2ZrSi_2O_7$ (see Table 2) are indicative of the topological supersymmetry of six out of seven O atoms as well as of both Si atoms. In their own groups of atoms, these atoms possess the same coordination sequences. In addition, all seven oxygen atoms are differentiated according to N_k into terminal atoms (through which the M and T polyhedra are linked to each other) and bridging atom (through which the T tetrahedra are linked to form diortho groups). The atomic numbering scheme in Table 2 corresponds to the data from X-ray diffraction studies of $Na_2ZrSi_2O_7$ [28] and $Na_2ZrGe_2O_7$.[40]

Therefore, only four topologically different types of nodes were revealed for the 3D framework of $ZrSi_2O_7$ containing ten crystallographically different atoms in the MTO network. The groups composed of six O atoms and two T atoms fulfill the same functions in the self-assembly process (are functionally equivalent). In the presence of equivalent two-dimensional cross-sections (planar layers containing the M and T nodes linked to each other) in the 3D network of the framework, the topological symmetry of the T nodes is retained.

The above-described data (see Table 2) demonstrate that the crystallographic symmetry of $ZrSi_2O_7$ is substantially lowerer than the topologically possible symmetry. There is desymmetrization of the bonds of the atoms in the M and T polyhedra as well as of the T polyhedra in the MT framework.

Hierarchical structure of silicate (identification of cluster precursor)

Let us consider the structural features of the MT layer located parallel to the *XY* plane in the structure of silicate $Na_2ZrSi_2O_7$ (see Fig. 2).

To simplify primary analysis of the structure of the MT layer, let us remove the O atoms located on the bond lines between the Zr and Si atoms with retention of all bonds between the Zr and Si atoms. As a result, the MTO layer is transformed into the planar binodal Zr,Si network consisting of two types of the linked Zr and Si nodal atoms (Fig. 4).

For planar networks, the cluster structure can be revealed by bicolor decomposition into elemental rings.[6,7] In the context of this method, planar networks composed of SU nodes are considered (at a higher, cluster level of structural self-organization) as packings of cluster precursors giving rise to equivalent *n*-membered cyclic clusters (where *n* is the number of SU in the cluster). The structure of the planar network can be represented as a packing of cyclic clusters only in the event that they share no corners, *i.e.*, if any node of the network can belong to only one cluster precursor. In the case of complete decomposition, the network cannot contain nodes, which do not belong to the cluster precursor.

In Fig. 4, the type of the planar binodal network with composition $ZrSi_2$ has the Schlafli's notation 4646 (for the Zr node) + 664 (for any Si(1) or Si(2) node), *i.e.*, four polygons (two tetragons and two hexagons) form a Zr node and three polygons (two hexagons and one tetragon) form topologically equivalent Si nodes. This can be demonstrated for the 2D network (as in the case of the 3D network) by direct calculations of the coordination sequences.

The bicolor decomposition of the planar $ZrSi_2$ networks revealed the following characteristic features of their structures:

1. Type of the 4646 + 664 net (1 : 2) is derived by condensation of six nodal cyclic clusters as hexagons, which form the primary contour of the net[6] (in Fig. 4, *a*, these clusters as islands are shaded, and the net with the highlighted cluster generator takes the form 4**6**46 + **6**64 (1 : 2)).

2. Topology of the bonds in the secondary contours of the 4**6**46 + **6**64 net (1 : 2), which reflect the characteristic features of the mechanism of direct condensation of the primary contours, is represented as tetragons and hexagons (they are located between the hexagons highlighted

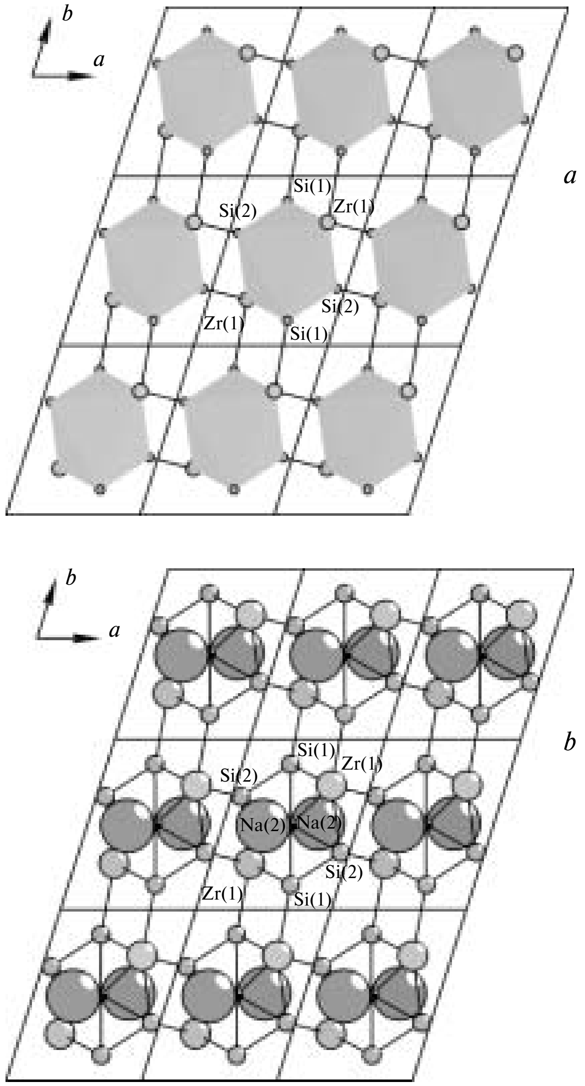

Fig. 4. Binodal network composed of the M and T nodes linked to each other. (*a*) Cyclic six-node Zr,Si clusters (network generators) are highlighted. These clusters have a hexagonal shape, and their center has the coordinates (0.5; 0.5). The clusters are related by translations. The secondary contours between the Zr,Si clusters as hexagons and tetragons are located between the highlighted hexagons. (*b*) The centers of the clusters are represented by solid balls. The Na(2) atoms are located above and below the centers of the clusters.

in Fig. 4, *a* and are involved in the notations of the nodes of the network).

3. Cyclic cluster generator in the 4**6**46 + **6**64 net (1 : 2) shares bonds with four adjacent clusters, the cluster coordination number in the *XY* plane is 4.

4. Centers of the clusters related to each other form a crystallographic Shubnikov network[6] with the 4444 topology. The distance between the centers of the clusters corresponds to the magnitudes of the translation vectors **a** and **b** (see Fig. 4).

Therefore, the cyclic cluster generator was revealed in the $ZrSi_2$ network 4**6**46 + **6**64 (1 : 2), and the mechanism of translation connection along two crystallographically different directions was elucidated.

Structure of a suprapolyhedral cluster precursor. First, it should be noted that the TO_4—SiO_4 orthotetrahedra, like GeO_4, serve as geometric templates containing a virtually undeformable system of the tetrahedral T—O bonds. However, these groups, which are linked to each other to form a diortho group, have considerable possibilities to be involved in complementary connections in the space of rigidly fixed pairs of corners. These groups can be geometrically adjusted if the distance between the pair of corners, which was estimated as described above, is no larger than the upper limit of 5.34 Å.

1. The Si—O and Ge—O bond lengths are substantially (up to 10%) different in isostructural phases. In the simplest framework modifications of SiO_2 and GeO_2 (in the tetrahedral structures of the cristobalite and quartz types[16]), the average Si—O and Ge—O distances are 1.60 and 1.75 Å, respectively. The lengths of the O—O edges are in the ranges of 2.636—2.668 and 2.734—3.100 Å, respectively. The difference in the length of the edges of the polyhedra can be as large as 0.4 Å.

2. In the Si_2O_7 diortho group with the O—O distance of 2.67 Å (for the SiO_4 orthotetrahedron), twice the distance ($2 \cdot 2.67$ Å = 5.34 Å) determines the maximum possible distance between the O atoms in the Si_2O_7 diortho group.

3. The minimum possible distance between the O atoms in the diortho group is 2.67 Å. This situation is observed in the case of formation of the three-membered ring $Si_2O_7 + SiO_4 = Si_3O_9$ from the diortho group and the orthotetrahedron.

The Na(1) and Na(2) atoms are located in the centers of clusters **1** and **2** (Fig. 5). The connectednesses of these atoms with six polyhedra that form clusters **1** and **2** are also different.

In cluster **1**, the distance between the O atoms in the diortho group is 4.919 Å (Fig. 5, *a*), which is close to the upper limit. In cluster **2**, this distance is ~2 Å shorter (2.909 Å; Fig. 5, *b*). As a consequence, the Na(1) atom in cluster **1** shares one edge and one corner with the Zr octahedra. In cluster **2**, the Na(2) atom forms a specific contact by sharing one edge and one face (Fig. 5, *a* and *b*).

The geometric parameters (distances and angles in the diortho groups) of the cluster precursors of the $Na_2ZrSi_2O_7$ and $Na_2ZrGe_2O_7$ structures (Fig. 6) and their changes upon the replacement of the smaller Si atom with the larger Ge atom are predominantly determined by the rigid system of bonds between the O atoms shared by two Na(2) atoms and two M octahedra in the cyclic precursor. Analysis of the changes in these parameters demonstrated that the replacement of the Si atom with Ge has virtually no effect on the distance between the atoms of the diortho

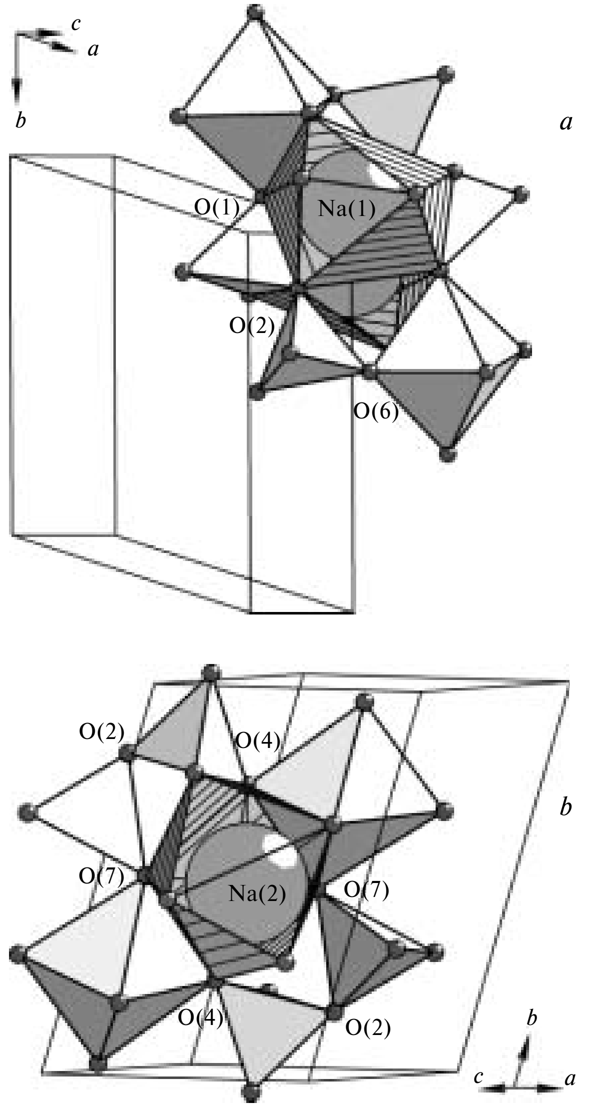

Fig. 5. Polyhedral atomic clusters $Na_2M_2T_4$. The crystallographically different Na(1) and Na(2) atoms are located above and below the centers of clusters **1** (*a*) and **2** (*b*).

groups (O(3)—O(7) are 3.29(1) and 3.25(5) Å in the Si- and Ge-containing phases, respectively); for another pair of the atoms, the O(4)—O(7) distances are 2.90(1) and 3.24(5) Å (for Si and Ge, respectively).

In the cluster precursor of $Na_2ZrSi_2O_7$, the Si(1)—O(2)—Si(2) angle is 126.75°. The deviation of the Ge(2)—O(2)—Ge(1) angle in the diortho group from 180° increases to 121.18° to compensate an increase in the Ge—O bond length compared to the Si—O bond length.

In the cyclic cluster precursor with composition M_2T_4, two M octahedra are linked to each other through the Si_2O_7 diortho groups (see Figs. 5 and 6). The Na(2) atoms are located in the center above and below the plane of the M_2T_4 ring. In the crystal structure of silicate $Na_2ZrSi_2O_7$ (see Fig. 6, *a*), the $Na_2M_2T_4$ clusters retain the center of symmetry $\bar{1}$ and occupy the vacant *1e* positions in the unit cell with the coordinates (1/2, 1/2, 0). In the crystal structure of germanate $Na_2ZrGe_2O_7$, the equivalent 1*g* position has the coordinates (0, 1/2, 1/2) (Fig. 6, *b*).

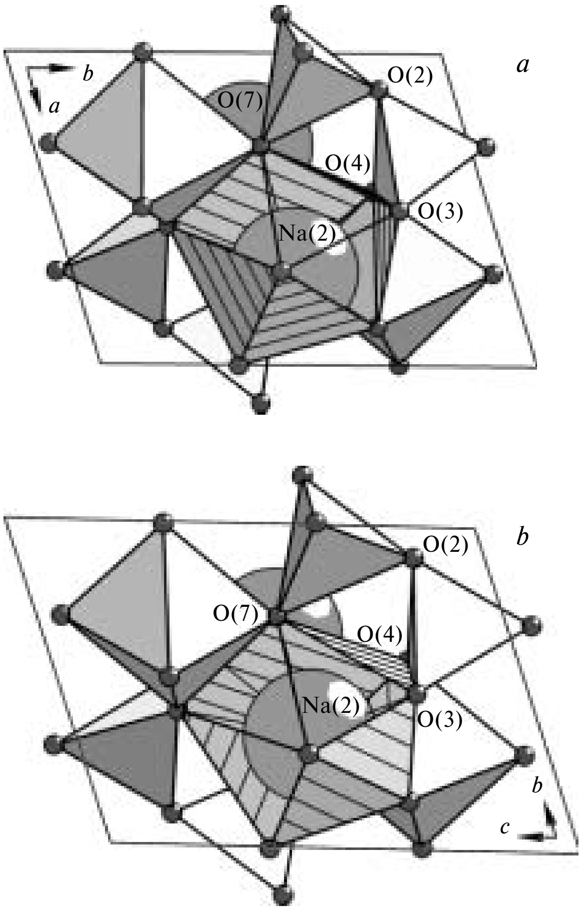

Fig. 6. Suprapolyhedral cluster precursors of the crystal structures of silicate $Na_2ZrSi_2O_7$ (*a*) and germanate $Na_2ZrGe_2O_7$ (*b*).

The maximum symmetry of the cluster precursor M_2T_4 is described by the orthorhombic point group D_{2h} = 2/*m* 2/*m* 2/*m*, the order of group is 8. The total number of free corners (centers of condensation) is 16.

Two Na atoms in the center of the $Na_2M_2T_4$ cluster (see Figs. 5 and 6) play an important role in the formation and stabilization of the cyclic structure of the precursor. The Na(2) atoms share faces (four common bonds between O atoms, Fig. 3, *b*) and share a face and an edge (three and two bonds between O atoms, respectively) with the M octahedra in the cluster. The topological features of the connection of the polyhedra in the cluster precursors $Na_2M_2T_4$ are completely retained upon the replacement of the smaller Si atom with the larger Ge atom (see Fig. 6).

The stable cyclic cluster precursors $Na_2M_2T_4$ control all processes of subsequent evolution of the suprapolyhedral crystal-forming MT cluster, *i.e.*, provide the formation of high-level superprecursors of the structural self-organization of the system.

Template self-assembly of the structure of silicate $Na_2ZrSi_2O_7$

The cation composition of the cluster precursor with the ratio between the polyhedra 2 ZrO_6 : 4 SiO_4 = 1 : 2 is identical to the atomic ratio Zr : Si = 1 : 2 in the three-dimensional structure of $Na_2ZrSi_2O_7$, which indicates that their packing by a mechanism of self-assembly most rapidly reproduces the topology of the structure as a whole.

The mechanism of reconstruction of the global (three-dimensional) topology from the local region of the sturcture as a result of complementary connection of the cluster precursors with each other involves the following steps: self-assembly of the primary MT chains of the framework, self-assembly of an MT layer of the framework, and self-assembly of the MT framework.

Self-assembly of primary MT chains of the framework. One-dimensional MT chains are formed from the precursors $Na_2M_2T_4$, which share two corners and are related to each other by a center of symmetry (Fig. 7). The distance between the centers of the cluster precursors determines the magnitude of the vector **a**, $|\mathbf{a}| = 6.66$ Å. The coordinates of the crystallographic *1c* position, which relates two precursor, are (0, 1/2, 0). The local symmetry of the position is $\bar{1}$. The index of complementary connection of the precursors upon the formation of the primary chain is 2.

Self-assembly of an MT layer of the framework. Condensation of MT chains in the same *XZ* plane along the *Y* direction gives rise to a layer composed of four $Na_2M_2T_4$ clusters (see Fig. 8). The index of complementary connection of the short chains consisting of two cluster precursors is 4. The distance between the centers of the precursors belonging to the parallel chains (see Fig. 8) determines the magnitude of the second translation vector in the structure of the silicate: $|\mathbf{b}| = 8.83$ Å.

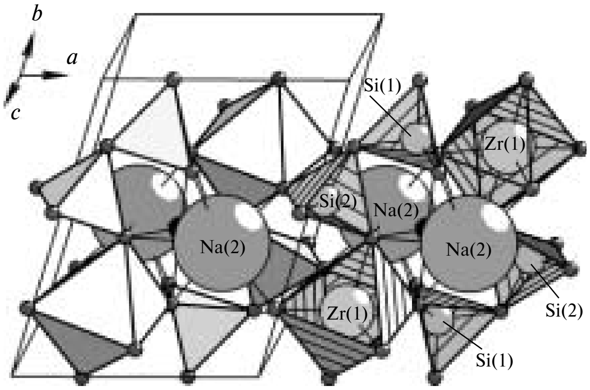

Fig. 7. Self-assembly of the primary MT chain of silicate $Na_2ZrSi_2O_7$ from the cluster precursors $Na_2M_2T_4$ by sharing two vertices. Hereinafter, the solid balls (centers of the clusters) occupy the (vacant) centrosymmetrical positions in the unit cell.

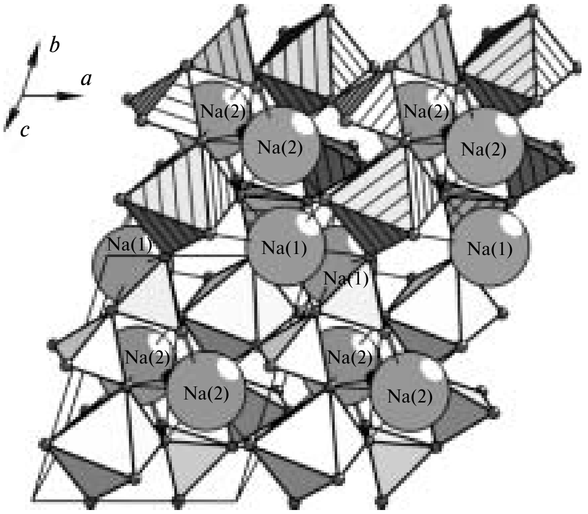

Fig. 8. Self-assembly of a microlayer of silicate $Na_2ZrSi_2O_7$ from two primary MT chains. The Na(1) atoms are located between the MT chains.

Filling of the cavities (between the MT chains) in the MT layer of the framework by the Na(1) atoms changes the chemical composition of the layer. Four Na(1) atoms, which are located between the MT chains, are shown in Fig. 8. In the case of complete filling of all Na(1) positions, the composition of the $Na_4M_2T_4$ layer (2 : 1 : 2) is identical to the composition of silicate $Na_2ZrSi_2O_7$ (2 : 1 : 2).

Self-assembly of the MT framework. Along the *Z* axis, the index of complementary connection of the planar layers containing four precursors each is 12 (Fig. 9). The

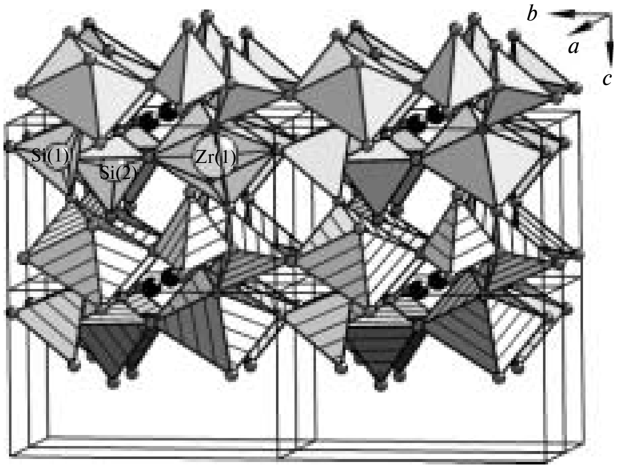

Fig. 9. Superprecursor (octamer) of the crystal structure of $Na_2ZrSi_2O_7$ consisting of eight complementary-connected cluster precursors.

distance between the centers of the precursors belonging to the parallel layers determines the magnitude of the third translation vector: $|\mathbf{c}| = 5.42$ Å.

Multiple condensation of the superprecursor, *viz.*, a suprapolyhedral cluster consisting of eight complementary connected precursors (see Fig. 9), leads to self-assembly of the 3D macrostructure of silicate $Na_2ZrSi_2O_7$.

Topologically, the related centers of the clusters form a three-dimensional network of the metallic-polonium type. The cluster coordination number of the cluster precursor is six. Four equivalent clusters lie in a layer, one cluster is located above the layer, and one cluster is located below the layer. The cluster coordination number is determined by the number of vacant corners in the cyclic cluster precursor (eight corners of two M octahedra and eight corners of four T tetrahedra), which are involved in complementary (pair) interactions along six directions $(X, -X)$, $(Y, -Y)$, $(Z, -Z)$. All cluster precursors in the 3D structure are related to each other by translations.

Therefore, the $Na_2ZrSi_2O_7$ structure with the MT framework MT_2O_7 composed of M octahedra and T tetrahedra, which crystallizes at high temperature[18] (500 °C and 1 kbar) in the hydrothermal Na_2CO_3—ZrO_2—SiO_2—H_2O system, is most rapidly formed as a results of self-assembly from the cluster precursors $Na_2M_2T_4$. The chemical composition of the precursor $Na_2M_2T_4$ with $M : T = 1 : 2$ determines the lower limit of the silicon content in the homologous series of the three-dimensional framework structures of Na,Zr silicates; $q = Si/Zr = 2$.

It should be noted that the revealed type of the 4**6**46 + **6**64 net (1 : 2) is reproduced in the MT_2O_8 framework structure of germanate $Li_2Ge^{VI}Ge^{IV}{}_2O_6(OH)_2$ (in which the OH corners of the Ge octahedra are partially unshared) with the polyhedral composition $T : M = 2$ analogous to that in $Na_2ZrSi_2O_7$.[43] Five MT structures of germanates $Li_2Ge^{VI}Ge_6{}^{IV}O_{15}$, $Li_4Ge^{VI}{}_2Ge^{IV}{}_7O_{20}$, $Li_2Ge^{VI}Ge^{IV}{}_3O_9$, $Li_2Ge^{VI}Ge^{IV}{}_2O_6(OH)_2$, and $Li_4Ge^{VI}{}_3Ge^{IV}{}_2O_{12}$ belong to a structurally homologous series.[13,44,45] Their structures are based on the topologically equivalent type of the cyclic cluster precursor $Li_2M_2T_4$ analogous to that observed in $Na_2ZrSi_2O_7$. This series originates from germanate $Li_2Ge^{VI}Ge^{IV}{}_2O_6(OH)_2$, whose structure can be described as a direct packing of the hexapolyhedral cluster precursors $Li_2M_2T_4$. Stability of the only hydrated phase $Li_2Ge^{VI}Ge^{IV}{}_2O_6(OH)_2$ (of five structures formed in the LiOH—GeO_2—H_2O system at 500 °C) characterized by OH discontinuities in the MT framework was explained[44] in the context of the model of template self-assembly of the crystal structures of framework Li—Ge germanates from invariant suprapolyhedral structural units. In $Li_2Ge^{VI}Ge^{IV}{}_2O_6(OH)_2$, the direct packing of invariant cluster precursors occurs without the involvement of additional GeO_4 polyhedra, unlike all other MT-framework structures of Li germanates. It was hypothesized[44] that the highest rate of formation of MT chains and an MT layer from the cluster precursors suppresses other channels of evolution of the precursors in the Li—Ge system at high temperatures (500 °C) and pressure of 1 kbar.

* * *

To summarize, the problems of identifying the type of a suprapolyhedral cluster precursor and elucidating the mechanism of structural evolution of high-level precursors, which form a three-dimensional periodic structure of silicate (germanate) as a result of template self-assembly, are of considerable importance for the geometric and topological modeling of self-organization processes of chemically complex (multicomponent) silicate (germanate) systems.

In the present study, the cyclic cluster precursor $Na_2M_2T_4$, which consists of two M octahedra, four SiO_4 octahedra, and the central Na atoms located above and below the center of the ring, was revealed for $Na_2ZrSi_2O_7$ by the methods of geometric and topological analysis.[6—8] All suprapolyhedral cluster precursors in the 3D structure of the silicate are related by translations.

Earlier, a cluster consisting of three polyhedra, *viz.*, one octahedron and two orthotetrahedra (in *cis* positions), has been proposed[47] as the fundamental structural block for the minerals parakeldyshite $Na_2ZrSi_2O_7$ and keldyshite $(Na, H_2O)ZrSi_2O_7$ (structural analog of parakeldyshite,[46] which differ only in that the Na(1) atoms weakly bound to the framework are partially absent). These clusters[47] were related by the symmetry operation 2_1 along the Z axis to form a polar MT chain. Since the structure of the precursor was analyzed without considering the Na atoms,[47] the choice of two particular tetrahedra (in *cis* positions) out of six tetrahedra linked to the M octahedron (see the representation of the local region of the M-PME structure consisting of M + 6T in Fig. 3) and, as a consequence, the choice of the direction, along which the primary MT chain is formed, were not substantiated. It should also be noted that the symmetry operation 2_1 responsible for the formation of the MT chain[47] does not belong to the symmetry operations of the space group $P\bar{1}$. The symmetry operations at the boundary of the stereon are centrosymmetrical operations of the $\bar{1}$ type.

To reveal the physically meaningful crystal-forming cluster precursor and the high-level superprecursor for self-organization of the system, successive combinatorial and topological analysis of the $Na_2ZrSi_2O_7$ structure was carried out, and the mechanism of its formation with the involvement of the Na(2) atom in the formation of the cluster precursor was elucidated.

Due to the fact that the polyhedral composition of the precursor with $2ZrO_6 : 4\ SiO_4 = 1 : 2$ is identical to $Zr : Si = 1 : 2$ in the three-dimensional structure of $Na_2ZrSi_2O_7$, the phase having a high crystallization temperature[18] in the Na_2CO_3—ZrO_2—SiO_2—H_2O system (500 °C and 1 kbar) maximum rapidly reproduces the topology of the superprecursor by a mechanism of self-assembly. In the superprecursor, the pair relations for the cyclic cluster precursors along all (three) crystallographically different directions are rigidly determined. It was found that the cluster coordination number of the precursors is six (four equivalent clusters lie in a layer, one cluster is located above the layer, and one cluster is below the layer).

The chemical composition of the cluster precursor $Na_2M_2T_4$ with M : T = 1 : 2 determines the lower limit of the silicon content in the series of the three-dimensional framework structures of Na,Zr silicates q = 2—6. The topological type of the cyclic precursor is retained in most structures of Na-Zr silicates with a high silicon content q = 2.5—6. Correspondingly, for each representative of the series originated from $Na_2ZrSi_2O_7$, one can determine the level of structural self-organization of the NaOH—ZrO_2—SiO_2—H_2O system, at which bifurcations of the evolution paths of invariant precursors occur, *i.e.*, the points of structural branching in the course of formation of three-dimensional topologically different structures of Na-Zr silicates. As in the case of Li germanates with three-dimensional MT frameworks formed in the LiOH—GeO_2—H_2O system,[43—45] analogous bifurcations occur both in the step of formation of the cluster precursor and the step of self-assembly of a primary chain and two-dimensional layers involving additional SiO_4 tetrahedra and Si_2O_7 diortho groups at different levels of self-organization of the silicate system.

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References

1. J.-M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives*, VCH, Weinheim—New York—Bales—Cambridge—Tokio, 1995.
2. J. S. Nicolis, *Dynamics of Hierarchical Systems*, *An Evolutionary Approach*, Springer, Heidelberg—New York—Tokio, 1986.
3. M. Eigen, *Selforganization of Matter and the Evolution of Biological Macromolecules*, Springer, Heidelberg—New York, 1971.
4. Yu. D. Tret´yakov, *Usp. Khim.*, 2003, **72**, 731 [*Russ. Chem. Rev.*, 2003, **72** (Engl. Transl.)].
5. V. S. Pervov, I. D. Mikheikin, E. V. Makhonina, and V. D. Butskii, *Usp. Khim.*, 2003, **72**, 852 [*Russ. Chem. Rev.*, 2003, **72** (Engl. Transl.)].
6. G. D. Ilyushin, *Modelirovanie protsessov samoorganizatsii v kristalloobrazuyushchikh sistemakh* [*Modeling of Self-Organization Processes in Crystal-Forming Systems*], Editorial URSS, Moscow, 2003, 440 pp. (in Russian).
7. G. D. Ilyushin and L. N. Dem´yanets, in *Trudy instituta kristallografii. Fizika kristallizatsii* [*Proceedings of the Institute of Crystallography. Physics of Crystallization*], Nauka, Fizmalit, Moscow, 2002, 82 (in Russian).
8. G. D. Ilyushin and L. N. Dem´yanets, *Germanaty chetyrekhvalentnykh metallov* [*Germanates of Tetravalent Metals*], VINITI, Moscow, 1989, 176 pp. (in Russian).
9. G. Nicolis and I. Prigogine, *Self-Organization in Non-Equilibrium Systems*, Wiley, New York, 1977.
10. N. A. Bul´enkov and D. L. Tymik, *Izv. Akad. Nauk, Ser. Khim.*, 2001, **3**, 1 [*Russ. Chem. Bull. Int. Ed.*, 2001, **3**, 1].
11. G. D. Ilyushin, *Kristallografiya*, 2003, **48**, 6 [*Crystallogr. Repts.*, 2003, **48** (Engl. Transl.)].
12. G. D. Ilyushin and L. N. Dem´yanets, *Zh. Neorg. Khim.*, 2002, **47**, 8, 1480 [*Russ. J. Inorg. Chem.*, 2002, **47** (Engl. Transl.)].
13. G. D. Ilyushin and L. N. Dem´yanets, *Kristallografiya*, 2001, **46**, 654 [*Crystallogr. Repts.*, 2001, **46** (Engl. Transl.)].
14. G. D. Ilyushin and L. N. Dem´yanets, *Zh. Neorg. Khim.*, 2002, **47**, 1699 [*Russ. J. Inorg. Chem.*, 2002, **47** (Engl. Transl.)].
15. G. D. Ilyushin and B. A. Blatov, *Acta Crystallogr., Sect. B*, 2002, **58**, 198.
16. *Inorganic Crystal Structure Database (ICSD)*, Gmelin-Institut für *a*norganische Chemie & FIZ Karlsruhe, 2002.
17. G. D. Ilyushin, *Zh. Neorg. Khim.*, 2003, **48** [*Russ. J. Inorg. Chem.*, 2003, **48** (Engl. Transl.)].
18. G. D. Ilyushin, L. N. Dem´yanets, V. V. Ilyukhin, and N. V. Belov, *Dokl. Akad. Nauk SSSR,* 1983, **271**, 1133 [*Dokl. Phys. Chem.*, 1983, **271** (Engl. Transl.)].
19. A. I. Bortun, L. N. Bortun, and A. Clearfield, *Chem. Mater.*, 1997, **9**, 1854.
20. S. R. Jale, A. Ojo, and F. R. Fitch, *Chem. Commun.*, 1999, **5**, 411.
21. P. Ferreira, A. Ferreira, J. Rocha, and M. R. Sousa, *Chem. Mater.*, 2001, **13**, 355.
22. E. N. Treushnikov, V. V. Ilyukhin, and N. V. Belov, *Dokl. Akad. Nauk SSSR,* 1970, **190**, 334 [*Dokl. Phys. Chem.*, 1970 (Engl. Transl.)].
23. H. Kohler, H. Schulz, and O. K. Mel´nikov, *Mater. Res. Bull.*, 1983, **18**, 589.
24. N. A. Nosyrev, E. N. Treushnikov, V. V. Ilyukhin, and N. V. Belov, *Dokl. Akad. Nauk SSSR,* 1974, **218**, 830 [*Dokl. Phys. Chem.*, 1974, **218** (Engl. Transl.)].
25. D. L. Serra and S.-J. Hwu, *Acta Crystallogr., Sect. C*, 1992, **48**, 733.
26. A. Leclaire, M. M. Borel, A. Grandin, and B. A. Raveau, *Acta Crystallogr., Sect.C*, 1989, **45**, 699.
27. A. Clearfield and D. Smith, *Inorg. Chem.*, 1969, **8**, 431.
28. A. A. Voronkov, N. G. Shumyatskaya, and Yu. A. Pyatenko, *Zh. Strukt. Khim.,* 1970, **11**, 932 [*J. Struct. Chem. (USSR)*, 1970, **11** (Engl. Transl.)].
29. N. Khosrovani, V. C. Korthuis, A. W. Sleight, and T. Vogt, *Inorg. Chem.*, 1996, **35**, 485.
30. G. D. Ilyushin, B. A. Blatov, and Yu. A. Zakutkin, *Acta Crystallogr., Sect. B*, 2002, **58**, 948.
31. B. K. Vainshtein, *Modern Crystallography*, Springer-Verlag, Berlin—New York, 1981.

32. A. F. Wells, *Three-Dimensional Nets and Polyhedra*, Intersci., New York, 1977.
33. G. O. Brunner and F. Laves, *Techn. Univ. Dresden*, 1971, **20**, 387.
34. W. M. Meier and H. J. Moeck, *J. Solid State Chem.*, **27**, 1979, 349.
35. V. A. Blatov, *Acta Crystallogr., Sect. A*, 2000, **56**, 178.
36. V. A. Blatov, A. P. Shevchenko, and V. N. Serezhkin, *J. Appl. Crystallogr.*, 1999, **32**, 377.
37. *International Tables for X-Ray Crystallography, Vol. 1. Symmetry Group.*, Eds N. F. M. Henry and K. Lonsdale, Birmingham Kynoch Press, 1952.
38. A. N. Chernov, B. A. Maksimov, V. V. Ilyukhin, and N. V. Belov, *Dokl. Akad. Nauk SSSR,* 1970, **193**, 1293 [*Dokl. Phys. Chem.*, 1970, **193** (Engl. Transl.)].
39. M. E. Fleet and G. S. Henderson, *Physics and Chemistry of Minerals (Germany)*, 1995, **22**, 383.
40. G. D. Ilyushin, A. A. Voronkov, L. N. Dem´yanets, V. V. Ilyukhin, and N. V. Belov, *Dokl. Akad. Nauk SSSR,* 1982, **263**, 877 [*Dokl. Phys. Chem.*, 1982, **263** (Engl. Transl.)].
41. A. P. Khomyakov, *Dokl. Akad. Nauk SSSR,* 1977, **237**, 703 [*Dokl. Phys. Chem.*, 1977, **237** (Engl. Transl.)].
42. G. Raade and M. H. Mladeck, *Canadian Mineralogist*, 1977, **15**, 102.
43. G. D. Ilyushin, *Neorg. Mater.*, 2002, **38**, 1241 [*Inorg. Mater.*, 2002, **38** (Engl. Transl.)].
44. G. D. Ilyushin and L. N. Dem´yanets, *Neorg. Mater.*, 2002, **38**, 843 [*Inorg. Mater.*, 2002, **38** (Engl. Transl.)].
45. G. D. Ilyushin and L. N. Dem´yanets, *Zh. Neorg. Khim.,* 2002, **47**, 1699 [*Russ. J. Inorg. Chem.*, 2002, **47** (Engl. Transl.)].
46. A. D. Khalilov, A. P. Khomyakov, and S. A. Mamedov, *Dokl. Akad. Nauk SSSR,* 1978, **238**, 573 [*Dokl. Phys. Chem.*, 1978, **238** (Engl. Transl.)].
47. F. C. Hawthorne, *Amer. Mineralogist.*, 1985, **70**, 455.

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