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Cluster-precursors for structure formation of Alkali Zirconosilicates in the Systems AOH-ZrO_2-SiO_2-H_2O (A = Li-Cs): algorithm for their identification and self-assembling modeling

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The modeling of the crystal structure formation in hydrothermal systems AOH-ZrO_2-SiO_2-H_2O (A - Li-Cs) was carried out on the base of combinatorial-topological analysis of the framework A,M-silicates structures. The mechanism of successive stages of the matrix assembly of the crystal structures from suprapolyhedral structural units (SSU invariants) was suggested. Modeling is based on the theory of space symmetry, graph theory and theory of hierarchic self-organization of the systems.

1. Introduction

Crystal-chemical descriptions of the structures are usually based on the choice of some structure units, which may be absolutely different in the papers of different authors. Thus, Meier's "secondary structure units" [1, 2] or Smith's "subunits" were used for description of framework zeolites [3]. Tompson J.B. [4] used "structure polysomatic modules" in mineral structure analysis. Hawthorne F. [5] suggested "fundamental structure blocks" for sulfate and phosphate structures. In all cases the choice of such local structural groups (consisted of polyhedra), their relation to the structure as a whole were not explained.

Only the modeling of the structure on the base of such fragments and correct rules for their choice may prove the selective preference of the polyhedral fragment, which was used as precursor for structure formation.

We worked out the geometrical-topological model for the formation, selection and evolution of cluster suprastructural units taking part in non-equilibrium processes of crystal structure formation in oxide systems. For the first time there were carried out the modeling of subsequence of elementary events resulting in the cluster formation; there were formulated the criteria of the selection providing the fastest evolution of the cluster and the appearance of far ordering in the structure.

2. Modeling of the crystal structure formation

2.1. 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 [6–9] 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 [9] ("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 structural unit, 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

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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.

2.2. The simplest types of precursor SSUs

In terms of the matrix self-assembling model, the *primary elementary act* e_1 in a crystal-forming system of vacant M and T polyhedra is the transition from isolated tetrahedra and octahedra to the simplest suprastructural unit, a monomer pair (*monomer*) formed by a corner-shearing of octahedron and tetrahedron (Fig. 1), i.e., the formation of a complex with the linkage $p = 1$.Transition *e1* and all of the subsequent transitions *e1* with more complex SSUs formed from monomers by a discrete mechanism are considered as a series of consecutive transitions of the starting system, with the point and translational symmetry being the highest possible for unlinked M and T polyhedra, to a system with a lowered symmetry for SSUs, i.e., to a system in which the simplest structural units have a reduced degree of freedom.

The simplest SSU is a monomer of linked M and T polyhedra (in Fig. 1a). It is depicted (in Fig. 1b) as a vector directed from M to T. For monomers involved in random structural interactions K + K (elementary acts e_2) with one ($c = 1$) or two ($c = 2$) shared vertices, only five orientations are possible for monomers in a dimeric complex (dimer). Type A and B dimers correspond to the case of two-bonded monomer interactions, which result in ring SSUs; the other three cases are single-bonded monomer interactions and conservation of the chain types of SSUs (Fig. 1c).

The interactions considered above are five pathways of the structural evolution of a system that can be classified as A, B, C, D, and E pathways in accordance with the types of primary interactions between monomers (Fig. 1c).

2.3. 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).

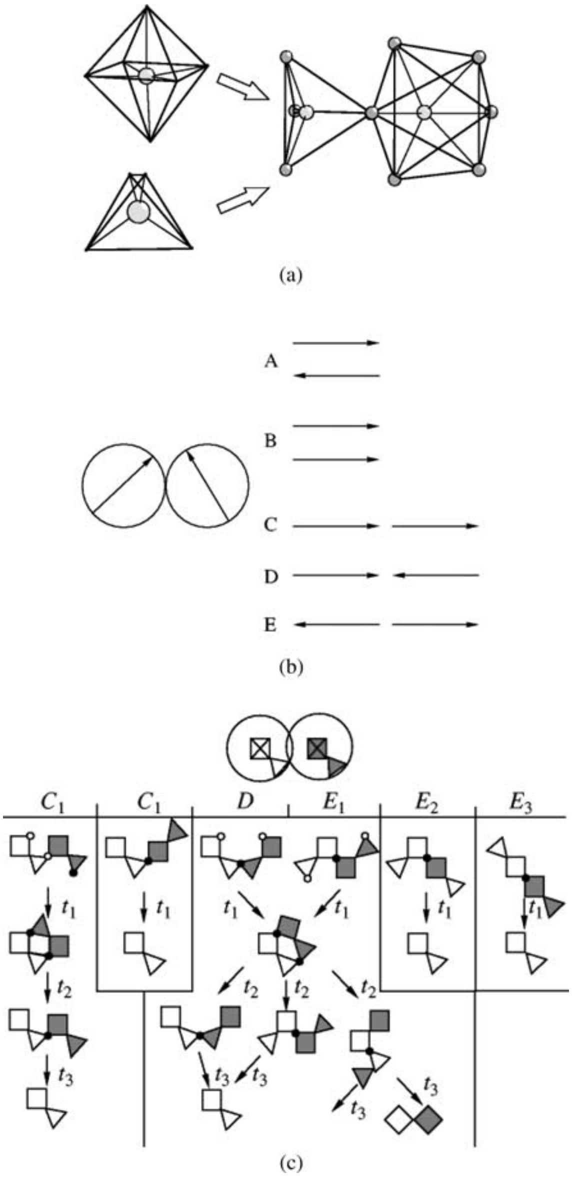
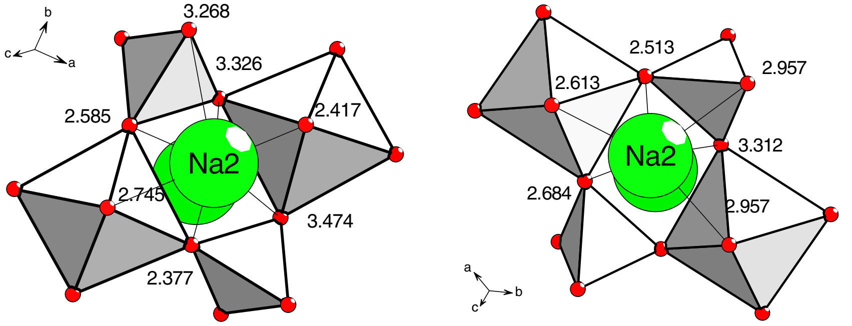


Figure 1 Panel (a): monomer formation from unlinked M octahedron and T tetrahedron; Panel (b): Orientationally possible types of monomer arrangement on a plane; Panel (c) : Topologically different types of dimers with a monomer linkage of 1 and 2; bonding vertices.

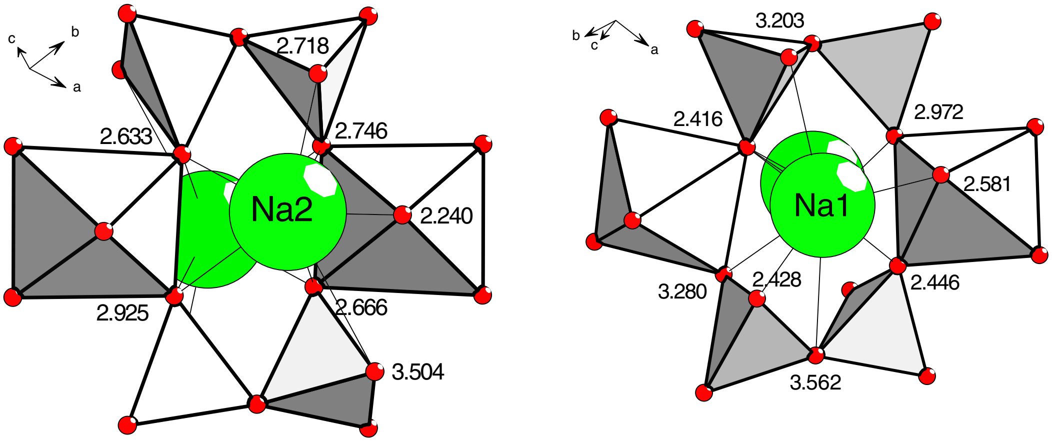
Crystallography deals with the main fundamental properties of crystal structures, among which are the primary classification of structures according to the Bravais lattice types (one of 14 translation groups). Then microstructures are described within 230 symmetry space groups *G*, which include a translation 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.



Na_2ZrSiO_5

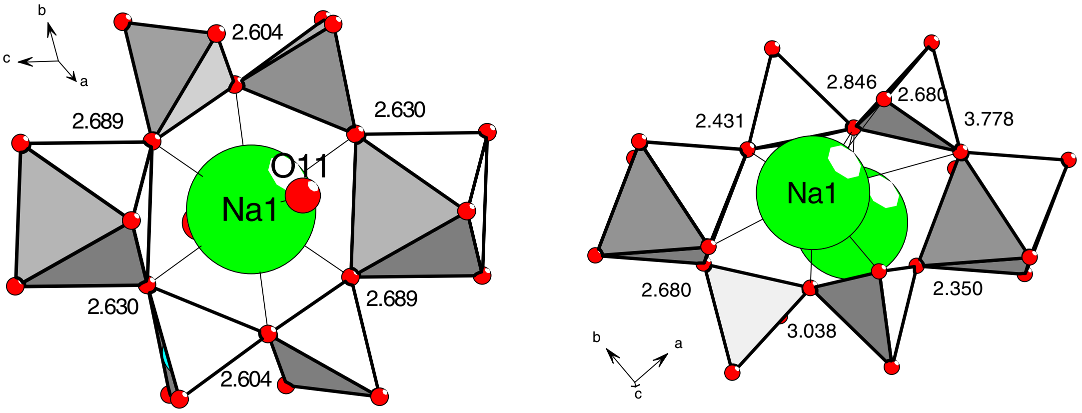
$Na_4Zr2Si_3O_{12}$ (NAS)

Figure 2 Ring type M_2T_2 of SSU-precursors for Na,Zr-silicates (A-channel of evolution).



$Na_2ZrSi_2O_7$ (KEL)

Na_4 Sn_2 Si_5O_{16} H_2O ($Na_4Zr_2Si_5O_{16}$ H_2O



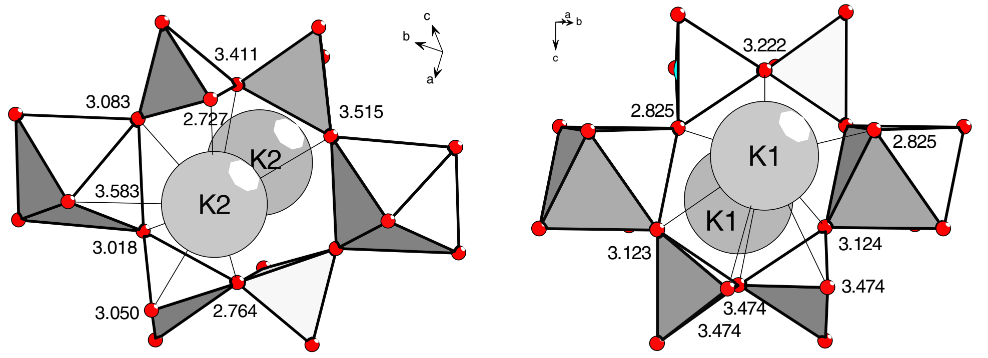
$Na_2ZrSi_3O_9$ $2H_2O$ (CAT)

$Na_2ZrSi_4O_{11}$(VLA)

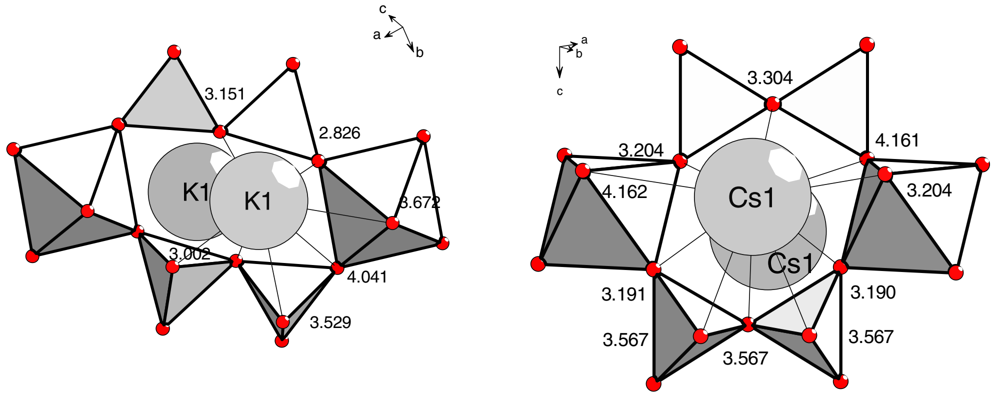
Figure 3 Ring type M_2T_4 SSU-precursors for Na,Zr- silicates (D-channel of the system evolution).

The following crystallographic definitions of the cluster precursor and the supra(super)precursor of the crystal structure are accepted [6].

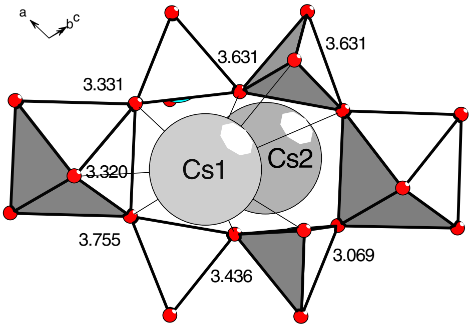
The cluster precursor of a structure is an *n*-atom cluster consisting of two or more atoms or polyhedral particles ($n \geq 2$), which is defined as a particular monomeric supraunit. Condensation of cluster precursors in all stages of self-assembly of the structure occurs by a mechanism of complementary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



$K_2ZrSi_2O_7$ (KHI) $K_2ZrSi_3O_9$ (WAD)



$K_2ZrSi_6O_{15}$ (DEL) $Cs_2ZrSi_3O_9$ (Cs-WAD)



$Cs_2ZrSi_6O_{15}$

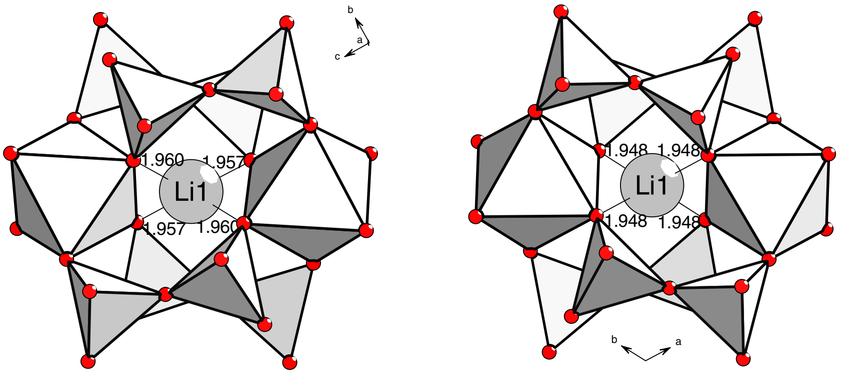
Figure 4 Ring type M_2T_4 SSU-precursors for K,Zr- and Cs,Zr-silicates (D-channel of the system evolution).

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 superprecursor 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.



Zektzerite, Na Li Zr Si6 O15

Sogdianite Li3 K1 Zr2 Si12O30

Figure 5 Ring type M_2T_8 SSU-precursors for Li-Zr-silicates (D-channel of evolution).

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 octameric structure, because each magnitude of the translation vector requires the determination of pair orientation relations of the cluster precursors in the *XYZ* three-dimensional space, which is reflected in the magnitudes of the noncoplanar vectors *a*, *b*, and *c* and the angles between them.

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.

3. Theoretical methods

3.1. Method of local crystal-structure intersection of space groups

To separate a topological invariant, we used the methods of the local (crystallo-structural) intersection of space groups *G* describing the structures of the phases considered in [6–8].

The algorithm of the search for invariants reduces to the following.

a) Stereon with V_{min} (fundamental area of group *G*) is being built in an unit cell; the number of stereons $N = V/V_{min}$ is equal to an order of group *G*.

b) Bound fragments from various combinations of basic polyhedrons are created in stereon.

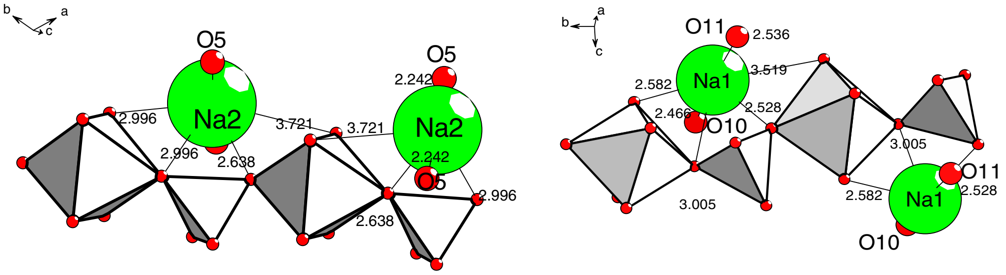
c) The sequential extension of regular systems of points with local symmetry in groups *G* is carried out; these points lay on a stereon surface (on complementary parts of stereon); stereons are connected each other by complementary parts of surfaces in accordance with a symmetry of the given group.

d) Topology of a constitution of a new bound fragments from polyhedrons with $V = 2V_{min}$ is analyzed.

The further transfer of basic dimer to higher level of structural organization (from dimer- to tetramer- and from tetramer- to octamer-level) is inspected by a symmetry and connectedness between dimers.

a) In a unit cell, all symmetrically possible SSU-tetramers from dimers are built within the framework of group symmetry *G*.

b) The indexes of a connectedness of SSU are defined for transformation of dimers into tetramers (and tetramers into octamers).



$Na_2ZrSi_3O_9 \cdot 3H_2O$ (HIL)

$Na_2ZrSi_3O_9 \cdot 2H_2O$ (GAI)

Figure 6 Chain type MTMT SSU-precursors for $Na_2ZrSi_3O_9$ $3H_2O$ and $Na_2ZrSi_3O_9$ $2H_2O$ (C-channel of evolution).

c) The basic SSU with a maximal connectedness are chosen.

3.2. Method of two-color decomposition of structure graphs into the primary and secondary contours

For the planar networks, the existence of a cluster substructure can be revealed by the two-color decomposition into elementary cycles [6].

Within the framework of this method, planar networks consisting of SU-nodes are considered as packings of equivalent N-link cyclic SSU clusters (N is the number of structural units). The structure of a planar network can be represented as a packing of cyclic clusters if any node of the network can belong to one and only to one SSU.

If a network (chemical graph) can be completely decomposed into equivalent elementary cycles (main contours of the network), these cycles marked by different colors can be regarded as isolated islands.

These methods give the possibility to identify the topological type of precursors in three-dimensional chemically close structures.

4. Experimental

Hydrothermal crystallization of zirconosilicates was studied with molar ratio $ZrO_2/SiO_2 = 1:1 = 1:6$ in starting nutrient and concentration AOH(AX) = 2,5 – 35 mas.%. Runs were performed at t 300–550°C, p 0.05–0,1 GPa (fill coefficient $f = 0.4, 0.6$) in Cu- or Ag-lines autoclaves with capacity ∼40 and ∼ 130 cm^3. Starting components were hardly soluble monoclinic ZrO_2 or as-prepared well soluble nanocrystalline ZrO_2, well soluble silicagel SiO_2: the mass ratio of solid to liquid phase was 1 : 3–1 : 4. Temperature gradient along the vertical axis of the autoclave was 1.5–2.0 degree/cm. The duration of hydrothermal treatment was 240 h. The analytical methods of crystallization product study were XRD, DTA, TGA.

5. Results and discussion

Twenty one A,Zr-silicates structural type (including natural minerals) are characteristic for the systems under study [10]. We synthesized 17 types under hydrothermal conditions (T 300–500°C) (Tables I and II).

Developed procedures permits to follow the subsequent stages of the construction of A,M-silicates three-dimensional structures from invariant local domains, which were found in their MT- framework (M-octahedron ZrO_6, T-tetrahedron SiO_4). The suprapolyhedral invariants as local regions with compositions M_2T_2 and M_2T_4 are found in the AZr-silicate structures.

Twenty one A,Zr-silicates [10] divided into four groups depending on topological types of invariant predecessors.

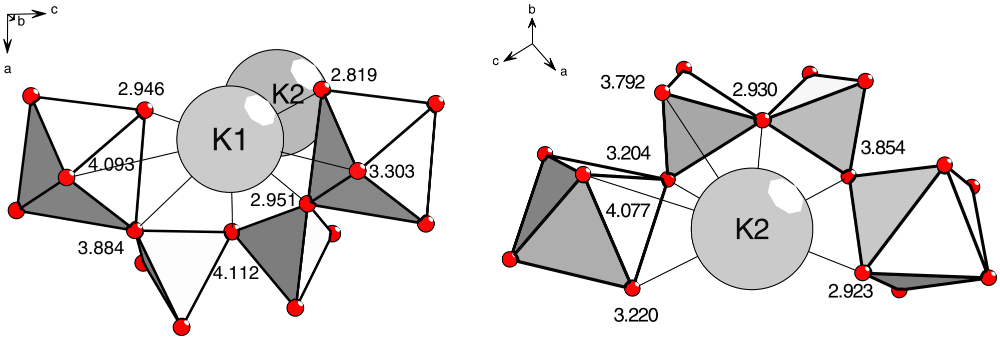
First group: the structures contain the M_2T_2 cyclic four-polyhedron precursor SSUs formed by two ZrO_6 octahedra and two SiO_4 tetrahedra (Fig. 2); they are Na_2ZrSiO_5 (having MT-analog of $NbPO_5$), $Na_4Zr_2Si_3O_{12}$($Nb_2P_3O_{12}$), $Na_3HZrSi_2O_8$ [$Zr(HPO_4)^2$ H_2O].

TABLE I Phase compositions of crystallization products in the system with rank of chemical complexity $R = 5$

Systems	$T_{cryst.}$	Phase compositions
$LiOH$-ZrO_2-SiO_2-H_2O	500°C	$ZrSiO_4$ (ZIR), $Li_2Si_2O_5$, Li_2SiO_3, SiO_2
$NaOH$-ZrO_2-SiO_2-H_2O	>450–500°C	$Na_8ZrSi_6O_{18}$(LOV), $Na_3HZrSi_2O_8$ (SYN-1), $Na_4Zr_2Si_3O_{12}$ (NAS), Na_2ZrSiO_5.
$NaOH$- ZrO_2(nanocryst.)-SiO_2-H_2O	>450°C	$Na_8ZrSi_6O_{18}$(LOV), $Na_4Zr_2Si_5O_{16}$ H_2O(SYN-2), $Na_3HZrSi_2O_8$(SYN-3), $Na_4Zr_2Si_3O_{12}$ (NAS).
KOH- ZrO_2-SiO_2-H_2O	400°C	$K_2ZrSi_6O_{15}$(DEL), $K_2ZrSi_3O_9$ (BAD), $K_2ZrSi_2O_7$ (KHI)
KOH-$ZrSiO_4$ -H_2O	400°C	$ZrSiO_4$, $K_2ZrSi_2O_7$ (KHI)
KOH-ZrO_2(nanocryst.)-SiO_2-H_2O	400°C	$ZrSiO_4$(ZIR), $K_2ZrSi_3O_9$ (BAD), $K_2ZrSi_2O_7$ (KHI), $K_2ZrSi_3O_9$ H_2O-1(UMB), $K_2ZrSi_3O_9$ H_2O-2 (KOS)
$RbOH$-ZrO_2-SiO_2-H_2O	500°C	$Rb_2ZrSi_3O_9$(Rb-BAD)
$CsOH$-ZrO_2-SiO_2-H_2O	500°C	$Cs_2ZrSi_3O_9$(Cs-BAD)

TABLE II Phase compositions of crystallization products in the system with rank of chemical complexity $R = 6$ at 400–500°C

Systems	$T_{cryst.}$	Phase compositions
Na_2CO_3-ZrO_2(nanocryst.)-SiO_2-H_2O	450°C	$Na_2ZrSi_6O_{15}\cdot 3H_2O$ (ELP)
Na_2CO_3 -ZrO_2-SiO_2-H_2O	450°C	$ZrSiO_4$(ZIR), $Na_2ZrSi_6O_{15}\cdot$ $3H_2O$(ELP), $Na_2ZrSi_3O_9\cdot 2H_2O$(CAT), $Na_4Zr_2Si_5O_{16}\cdot H_2O$(SYN-2)
Na_2CO_3-ZrO_2-SiO_2-H_2O	500°C	$Na_2ZrSi_4O_{11}$(VLA), $Na_2ZrSi_2O_7$(KEL), $Na_4Zr_2Si_3O_{12}$(NAS)
KF-ZrO_2-SiO_2-H_2O	400°C	$ZrSiO_4$(ZIR), $K_2ZrSi_6O_{15}$(DEL), $K_2ZrSi_3O_9$(BAD), K_3ZrF_7
$CsCl$-ZrO_2-SiO_2-H_2O	400°C	$ZrSiO_4$(ZIR), $Cs_2ZrSi_6O_{15}$ (SYN-4)



$K_2ZrSi_3O_9 \cdot H_2O$-1 (UMB)

$K_2ZrSi_3O_9$ H_2O-2 (KOS)

Figure 7 Chain type MTTM SSU-precursors for $K_2ZrSi_3O_9$ H_2O-1 and $K_2ZrSi_3O_9 \cdot$ H_2O-2 (D-channel of evolution).

Second group: the structures contain the M_2T_4 cyclic six-polyhedron precursor SSUs formed by two ZrO_6 octahedra and four SiO_4 tetrahedra with two (or one) A atoms in the center of the complex (Figs 3 and 4); they are $Na_2ZrSi_2O_7$, $Na_4Zr_2Si_5O_{16} \cdot$ H_2O, $Na_2ZrSi_3O_9 \cdot 2H_2O$, $Na_2ZrSi_4O_{11}$, $Na_2ZrSi_6O_{15} \cdot 3H_2O$, $Na_8ZrSi_6O_{18}$, $Na_4H_4ZrSi_6O_{18}$, $K_2ZrSi_2O_7$, $K_2ZrSi_6O_{15}$, $A_2ZrSi_3O_9$,(A-K,Rb,Cs), $Cs_2ZrSi_6O_{15}$.

Phase $Li_2ZrSi_6O_{15}$ (Fig. 5) (as against $Li_2SnSi_6O_{15}$, ZEK) is not obtained because of preferable crystallization of $ZrSiO_4$ with cyclic four-polyhedron precursor SSUs (two ZrO_8 dodecahedra and two SiO_4 tetrahedra).

Third group: the structures contain the M-T-M-T chain precursor formed by four-polyhedrons (two ZrO_6 octahedra and four SiO_4 tetrahedra with one Na atom (Fig. 6); they are $Na_2ZrSi_3O_9 \cdot$ $2H_2O$ (gaidonnayite) and $Na_2ZrSi_3O_9$ $3H_2O$ (hilerite). These phases are the low-temperature minerals and they did not synthesized.

Fourth group: the structures contain the M-T-T-M chain precursor consisted of four-polyhedrons (two ZrO_6 octahedra and four SiO_4 tetrahedra with two K atom}; they are $K_2ZrSi_3O_9$ H_2O-1 (umbite), $K_2ZrSi_3O_9$ H_2O-2> (kostilevite). These phases crystallize only at temperatures less 400°C (Fig. 7).

Comparison of crystal structures of the silicates synthesized has shown that several types of SSU-precursors arise in the growth media. As a result compounds constructed from such SSU are formed. Reconstruction of the mechanism of matrix assembling from SSU invariants with their transition to a higher level of structural organization (successive formation of chains, layers, and frameworks) is performed by selecting (among the set of possible complexes) the MT complexes with a value of the subunit connectivity index. The MT frameworks of different compounds are formed due to the bifurcation of SSU evolution pathways in crystal-forming media; i.e., cluster formation and evolution (in the sequence of elementary events: cluster-chain-layer-framework).

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References

1. W. M. MEIER, in "Molecular Sieves". (London: Society of Chem. and Industry, 1968). p. 10.
2. Atlas of Zeolite Structure Types. 4th ed., edited by Meier W. M., Olson D. H. (Baerlocher C. Amsterdam: Elsevier, 1996).
3. J. V. SMITH, *Chem. Rev.* **88** (1988) 149.
4. J. B. TOMPSONJr., *J. Am. Miner.* **63** (19780) 239.
5. A. C. HAWTHORN, *Z. Kristallographie* **192** (1990) 1.
6. G. D. ILYUSHIN, in "Modeling of Self-Organization Processes in Crystal-Forming Systems," (Editorial URSS, Moscow, 2003) pp. 376 (in Russian).
7. G. D. ILYUSHIN and L. N. DEMIANETS, Proceedings of the Institute of Crystallography. Physics of Crystallization, Nauka, Fizmalit, Moscow, 2002), 82 (in Russian).
8. G. D. ILYUSHIN and L. N. DEMIANETS. "Germanates of Tetravalent Metals". (VINITI, Moscow, 1989) pp. 176 (in Russian).
9. J.-M. LEHN. "Supramolecular Chemistry. Concepts and Perspectives" (VCH, Weinheim—New York—Bales—Cambridge—Tokio, 1995).
10. G. D. ILYUSHIN and B. A. BLATOV, *Acta Cryst.* **B 58** (2002) 198.

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