Symmetrical and Topological Self-Assembly Code of the Crystalline Structure of a New Aluminosilicate Zeolite ISC-1 from Templated *t-plg* Suprapolyhedral Precursors

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Abstract—In 2008, V.Ya. Shevchenko and S.V. Krivovichev built the zeolites series related to paulingite based on the inorganic gene concept and predicted a new zeolite named ISC-1 (Institute of Silicate Chemistry-1) [1]. The structure and composition of ISC-1 are described in detail in [2]. The found chemical formula of the new zeolite ISC-1 is $Na_{14}K_{24}Al_{38}Si_{202}O_{48} \cdot nH_2O$. Further research on the principles of assembly of zeolites and prediction of another previously unknown zeolite, ISC-2 (Institute of Silicate Chemistry-2), and the conditions of its formation are presented in [3–5]. The combinatorial-topological analysis of the crystal structure of the new aluminosilicate zeolite ISC-1 with cubic cell parameters $a = 25.039$ Å, $V = 15\,699$ Å^3, and spatial group $Im\bar{3}m$ is performed by computer-based methods (ToposPro software package) [6]. The topological type of the framework composed of bonded $T–(Si,Al)O_4$ tetrahedra is characterized by a combination of polyhedral tilings: *t-grc* (48 T-atoms), *t-pau* (32 T-atoms), *t-plg* (30 T-atoms), *t-opr* (16 T- atoms), and *t-oto* (16 T- atoms). A framework-forming precursor for zeolites of 30 T-tetrahedra, which corresponds to the *t-plg* tile and contains an organic template Me_2-DABCO (N,N'-dimethyl-1,4-diazabicyclo[2.2.2]octane), is established by the complete decomposition of the 3D atomic lattice into cluster structures. *t-plg* nanoclusters with the symmetry $g = \bar{3}m$ are characterized by 4-, 6-, and 8-rings and the *n*-hedral symbol [$4^6. 6^2. 8^6$]. Na-spacers statistically occupy neighboring positions in the 8-ring and between the 4-rings of the neighboring *t-plg* clusters. The basic 3D lattice type indicative of *t-plg* clusters center-of-gravity positions correspond to a simple cubic lattice with CN = 6. The self-assembly code of the 3D structure from complementary bonded nanoclusters-precursors is simulated in its entirety: primary chain → microlayer → framework. The doubled distance between *t-plg* clusters centers corresponds to the cubic cell translation vector $a = 25.039$ Å.

Keywords: templated cluster-precursor *t-plg*, self-assembly of crystal structure, new aluminosilicate zeolite ISC-1

INTRODUCTION

The tetrahedral structures of cubic (ISC-1) and hexagonal (ISC-2) zeolites were simulated in [1–5]. The unit cell parameters, spatial symmetry groups, and coordinates of framework-forming atoms were determined. In the case of ISC-1, variants of the Na and K atoms' positions in the tiles—polyhedral voids of the framework—were investigated.

Aluminosilicate zeolites of the ISC-1 type with a narrow crystallization range were synthesized in [6]. Me_2-DABCO (N,N'-dimethyl-1,4-diazabicyclo[2.2.2]-octane) was used as the template in the ISC-1 synthesis, as well as the Na and K cations. Substitution of Me_2-DABCO by tetraethylammonium (TEA) in the reactive mixture led to crystallization of CHA (chaba-zite) + ERI (erionite) zeolites only. The decrease of the H_2O/SiO_2 ratio value from 26.7 to 13.3–20.0 resulted in the cocrystallization of ISC-1 + PAU (paulingite) + PHI (phillipsite). The increase of the H_2O/SiO_2 value up to 33.3 was followed by the formation of an X-ray amorphous phase. It was established that the framework structure of the SC-1 zeolite pertained not only upon annealing but also after conversion into a protonated form.

In the present study, the combinatorial-topological analysis of the crystal structure of an ISC-1 zeolite was performed by computer-based methods (ToposPro software package [7]). The symmetrical and topological code of the process of the cluster self-assembly of the crystal structure from templated clusters was

Table 1. Coordination sequences of Si atoms in ISC-1 tetrahedral framework

Atom	Coordination sequences									
	N_1	N_2	N_3	N_4	N_5	N_6	N_7	N_8	N_9	N_{10}
Si(1)	4	9	18	32	48	66	89	116	146	180
Si(2)	4	9	18	31	47	68	91	116	147	182
Si(3)	4	9	17	29	45	65	89	116	146	180

Table 2. Variants of cluster representation of framework structure of ISC-1 zeolite. Crystallographic positions, which corresponded to centers of voids of polyhedral clusters, were marked as ZA1, ZA2, and ZA3. Central atom of polyhedral cluster, number of its shells (first braces), and number of atoms in each shell (second braces) were indicated

Variant 1	Variant 2	
Cluster1 (0@30), 2c position, $g = -3m$	Cluster1 (0@12), 2f position, $g = -4m2$	Cluster2 (0@48), 2a position, $g = m - 3m$
6Si1	4Si1	48Si3
12Si2	8Si2	
12Si3		
Total 30 atoms	Total 12 atoms	Total 48 atoms

established in the following form: primary chain $S_3^1 \rightarrow$ microlayer $S_3^2 \rightarrow$ framework S_3^3.

The present study represents a follow-up of the works [1–5, 8–15] in the field of self-organization of systems on the suprapolyhedral level and the geometrical and topological analysis of crystal structures with the application of advanced computer-based methods.

METHODS OF ANALYSIS

The geometrical-topological analysis of zeolites was carried out the TermosPro software package [7], which allowed performing a multipurpose examination of the crystal structure automatically by representing structures as folded graphs (factor graphs).

The algorithm of the automated geometrical and topological analysis by the TermosPro software package consisted of the following stages: calculation of incidence matrices and isolation of the simplest polyhedral structural units by the AutoCN program; calculation of the coordinating sequences $\{N_k\}$ for all the free atoms by the IsoTest program; and representation of the tetrahedral framework as 3D 4-bonds lattices of T-atoms (Al, Si) with the removed oxygen atoms.

As a result, the 3D structures were represented as a 3D non-oriented graph in which atoms were identified as the graph's peaks and interatomic bonds were identified as its edges.

A new computer-based method was applied for the analysis of zeolites of any complexity: it was based on the complete decomposition of the three-dimensional graph (3D factor graph) into cluster substructures in accordance with the following principles. A structure was formed as a result of the self-assembly of nanoclusters, which can be either cyclic or polyhedral groups of T-tetrahedra. In the zeolite three-dimensional framework, the rings corresponded to cyclic groups, whereas the tiles corresponded to polyhedral groups (generalized polyhedra, which could contain double-bonded peaks and curved edges). The nanoclusters did not exhibit common (shared) T-tetrahedra. The nanoclusters included all the T-tetrahedra of the crystal structure's framework.

The latter two principles were equivalent to the condition that each T-tetrahedron was shared by only one particular nanocluster. In order to derive nanoclusters-precursors which formed the zeolite framework, all independent rings and tiles ought to be determined first. A nanocluster was included in the set if it did not have any common T-tetrahedron with the equivalent nanoclusters or with nanoclusters which were included in the set (condition 2). The set was extended until all the independent T-tetrahedra of the framework were included.

The coordinating sequences values, according to which the framework structure type was classified, are provided in Table 1.

Variants of the cluster representation of the zeolite framework structure are provided in Table 2.

RESULTS AND DISCUSSION

As a result of the complete decomposition of the tetrahedral framework with 240 tetrahedra per unit cell into tiles, its structure can be represented as an ensemble consisting of five geometrically different nanocluster types containing from 16 to 48 T-tetrahedra (the linear size of the nanoclusters ranged from 12 to 18 Å, respectively). Nanoclusters *t-grc* (48 T-atoms), *t-pau* (32 T-atoms), *t-plg* (30 T-atoms), *t-opr* (16 T-atoms), and *t-oto* (16 T-atoms) represented topologically different localized areas of the tetrahedral T-framework and explicitly determined the topological specifics of the framework structure. The computer-based analysis demonstrated that the framework could be explicitly decomposed into *t-plg* clusters with the symmetry $g = \overline{3}m$ and centers located at positions 8c. Eight *t-plg* clusters were located in the unit cell and contained 8×30 T-tetrahedra in total, i.e., 240 T-tetrahedra corresponding to the total composition of the cell.

Self-Assembly of Crystalline Structure

The simulation method applied to the crystalline structure was based on the determination of the hierarchic sequence of its self-assembly in the crystallographic space [8, 9]. At the first stage of the system's self-organization, the mechanism was determined for the formation of the structure's primary chain from nanoclusters of the 0-level formed at the template stage of chemical evolution of the system; further, the mechanism of self-assembly from the microlayer
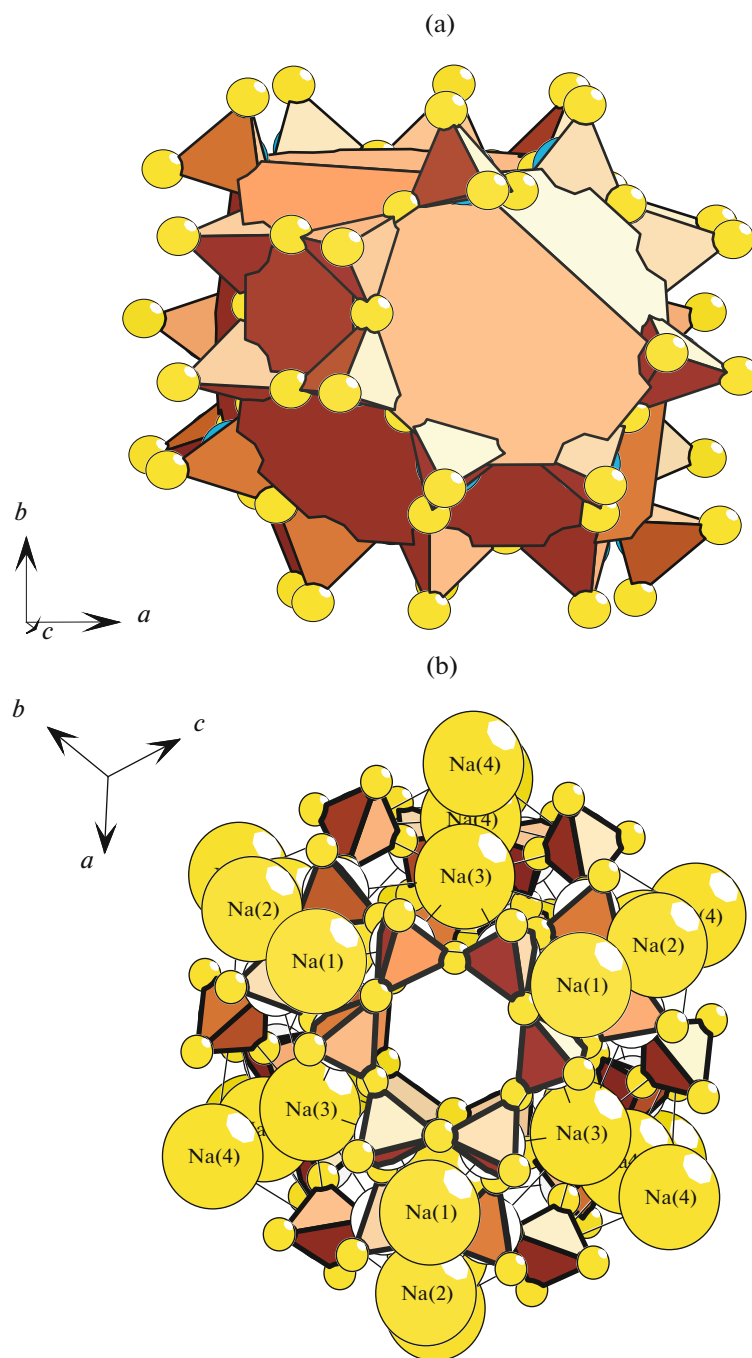
(a)

(b)

Fig. 1. Nanocluster-precursor of 30 T-tetrahedra with 4T-, 6T-, 8T-rings on surface in form of tile (a) and bonded tetrahedra and Na atoms, located on 8- and 4-rings (b).

chain (2nd level) and then from the three-dimensional microframework were determined from the microlayer (3rd level).

Crystallographic data of ISC-1. Cubic cell parameters (ISC-1): $a = 25.039$ Å, $V = 15699$ Å^3, and space group $Im\overline{3}m$ (229) [6]. The space group was characterized by elements with the point symmetry: $g = m -$

$3m$ ($2a$), $4/mmm$ ($6b$), $-3m$ ($8c$), $-4m2$ ($12d$), $4mm$ ($12e$), $3m$ ($16f$), etc.

Nanocluster-precursor. The framework-forming nanocluster-precursor t-plg of 30 T-tetrahedra was characterized by 4T-, 6T-, and 8T-rings on the surface (the edge symbol of a cluster [$4^6.6^2.8^6$]) and contained an organic template Me$_2$-DABCO in the bulk and Na atoms on the surface (Fig. 1). Na-spacers statistically
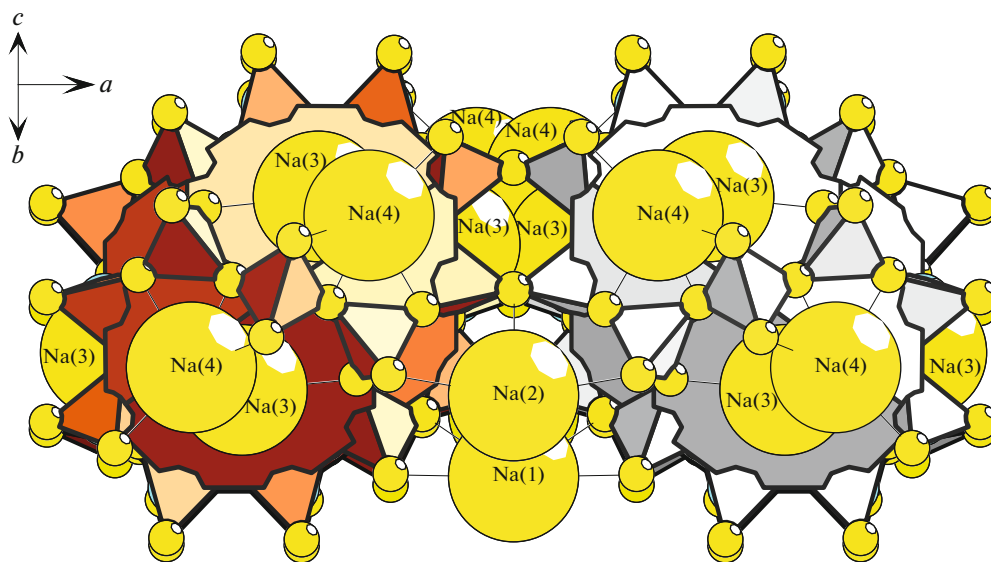
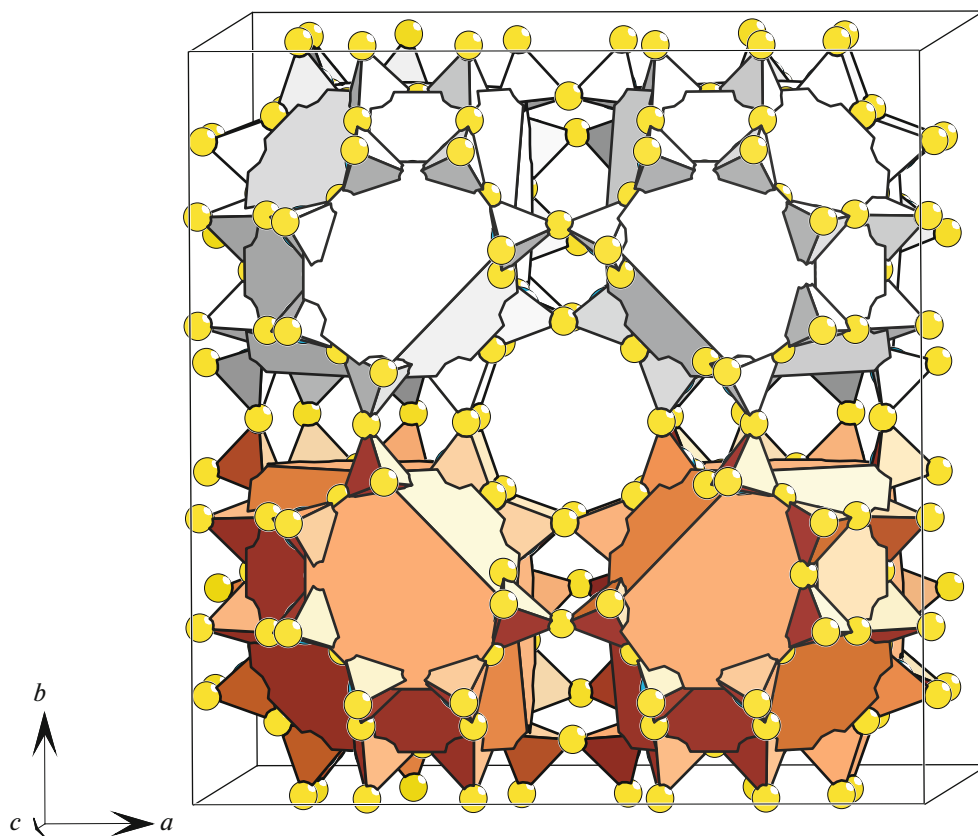**Fig. 2.** Self-assembly of primary chains of T30 clusters.

Fig. 3. Self-assembly of microlayer of primary chains.

occupied the neighboring positions in the 8-ring and between 4-rings of the neighboring clusters (Fig. 2). The *t-plg* nanocluster was characterized by the point symmetry $g = \bar{3}m$. The nanocluster center in the unit cell was located in position 8*c*. The basic 3D lattice type

indicative of *t-plg* clusters' center-of-gravity positions corresponded to a simple cubic lattice with CN = 6.

Primary chain. The self-assembly of the primary chains from *t-plg* clusters proceeded towards [100] (Fig. 2). There were six T−O−T bonds between clus-
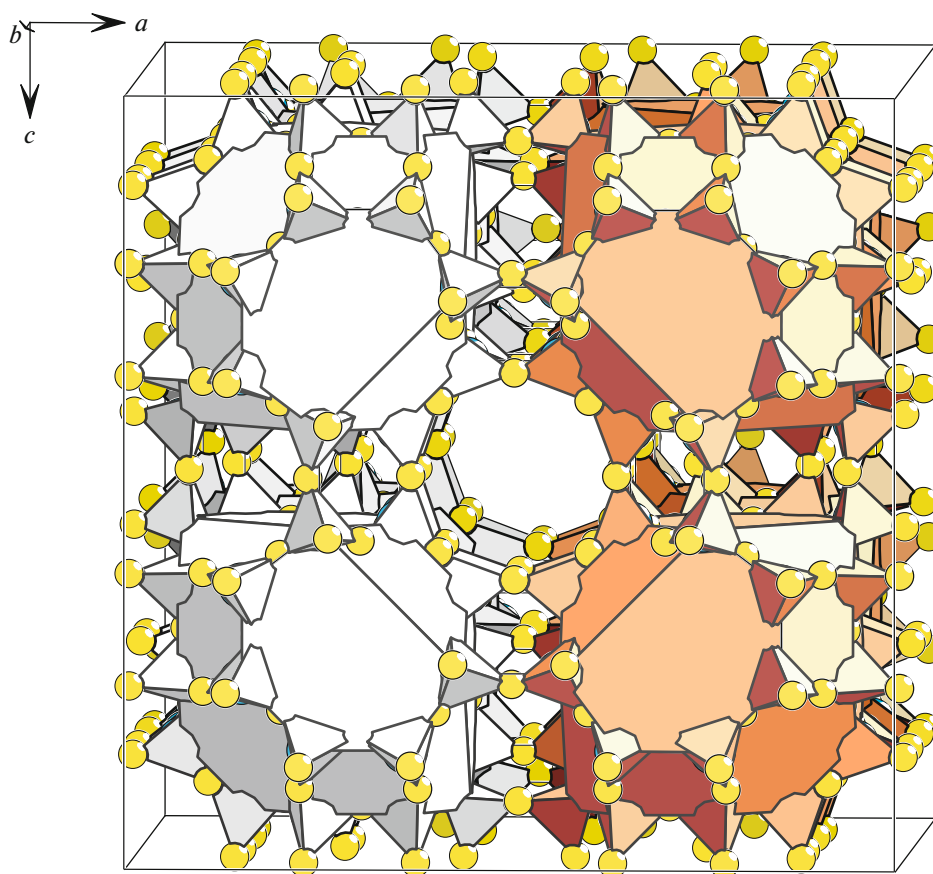
Fig. 4. Self-assembly of framework from microlayers.

ters. At this stage of self-assembly, two atoms-spacers (Na1 and Na2) were localized between the *t-plg* clusters. The doubled distance between the *t-plg* clusters' centers corresponded to the translation vector of the cubic cell $a = 25.039$ Å.

Self-assembly of a microlayer. The formation of the S_3^2 microlayer occurs upon the complementary bonding of the clusters from the neighboring primary chains (Fig. 3). The distance between centers of *t-plg* clusters from the neighboring ones corresponded to the translation vector of the cubic cell $b/2 = 25.039$ Å/2.

Self-assembly of the microframework. The microframework of the S_3^3 structure was formed upon the bonding of two microlayers (Fig. 4). The doubled distance between the centers of *t-plg* clusters from the neighboring layers corresponded to the cubic cell translation vector $c = 25.039$ Å.

CONCLUSIONS

A new type of framework-forming nanocluster-precursor of 30 T-tetrahedra containing an organic Me$_2$-DABCO template has been established by the complete decomposition of the 3D atomic lattice into cluster structures.

The framework tetrahedral structures of cubic (ISC-1) and hexagonal (ISC-2) structures have been simulated. The unit cells' parameters, symmetry space groups, and coordinates of framework-forming atoms have been determined. The aluminosilicate zeolite ISC-1 was synthesized by the authors of [6] in 2018 and has been named PST29.

The complete compliance of the structural-chemical data means that the first published name of this zeolite ought to remain primary. The synthesis of the ISC-2 zeolite is highly likely in the nearest future.

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