

# Nomenclature of structural and compositional characteristics of ordered microporous and mesoporous materials with inorganic hosts(IUPAC Recommendations 2001)

**Journal Article****Author(s):**

McCusker, L. B.; Liebau, F.; Engelhardt, G.

**Publication date:**

2001

**Permanent link:**

<https://doi.org/10.3929/ethz-b-000423004>

**Rights / license:**

In Copyright - Non-Commercial Use Permitted

**Originally published in:**

Pure and Applied Chemistry 73(2), <https://doi.org/10.1351/pac200173020381>

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

PHYSICAL CHEMISTRY DIVISION

COMMISSION ON COLLOID AND SURFACE CHEMISTRY INCLUDING CATALYSIS\*

# NOMENCLATURE OF STRUCTURAL AND COMPOSITIONAL CHARACTERISTICS OF ORDERED MICROPOROUS AND MESOPOROUS MATERIALS WITH INORGANIC HOSTS

(IUPAC Recommendations 2001)

Prepared for publication by

L. B. McCUSKER<sup>1</sup>, F. LIEBAU<sup>2</sup>, AND G. ENGELHARDT<sup>3</sup>

<sup>1</sup>Laboratorium für Kristallographie, ETH, Zürich, Switzerland; <sup>2</sup>Institut für Geowissenschaften der Universität Kiel, Kiel, Germany; <sup>3</sup>Institut für Technische Chemie, Universität Stuttgart, Stuttgart, Germany

\*Membership of the Commission during the preparation of this report (1994–2001) was as follows:

**Titular Members:** J. Ralston (1994–1999; Chairman, 1994–1997); L. K. Koopal (1994–present; Chairman, 1998–present); A. M. Cazabat (Secretary, 1994–1997); I. Dékány (Secretary, 1998–present); B. Delmon (1994–1997); F. Gonzalez-Caballero (2000–2001); T. Kunitake (1998–present); Y. H. Ma (2000–present); M. Misono (1994–1997); V. N. Parmon (1998–present); J. B. Rosenholm (2000–present); R. A. Schoonheydt (1998–present); K. K. Unger (1994–1997). **Associate Members:** S. Ardizzone (1994–2000); A. M. Cazabat (1998–1999); A. Dabrowski (2000–present); I. Dékány (1994–1997); N. Furlong (1994–1997); F. Gonzalez-Caballero (1998–1999); J. Gregory (2000–present); Y. Iwasawa (1998–present); T. Kunitake (1994–1997); P. E. Laibinis (2000–present); Y. H. Ma (1998–1999); R. Miller (1998–1999); J. A. Pajares (1994–1999); G. A. Panov (1994–1995); V. N. Parmon (1996–1997); H. Rehage (2000–present); J. B. Rosenholm (1998–1999); J. F. Roth (1994–1995); B. Vincent (1994–1997).

Subcommittee on Advanced Materials: Colloid, Surface, and Catalytic Aspects

**Members (not already listed as titular members or associate members):** E. F. Barbosa (1994–1999); F. Liebau (1994–present); P. Pendleton (1994–1997); J. Ramsay (1998–2001); J. Rouquérol (1995–1997). **National Representatives:** E. F. Barbosa (Portugal, 1994–present); S. Bahaduri (India, 1996–present); L. E. Cascarini de Torre (Argentina, 1994–present); S. Chen (China, 1994–1997); Y. Chen (China, 1998–present); H. Chon (Korea, 1995–1997); P. Claesson (Sweden, 1996–present); A. Da Costa Faro, Jr. (Brazil, 1994–1999); N. A. Debacher (Brazil, 2000–present); J. Haber (Poland, 1994–1999); K. Kim (Korea, 1998–1999); M. Kocirik (Czech Republic, 2000–present); B. Lindman (Sweden, 1994–1996); J. Lyklema (The Netherlands, 1994–1995); C. T. O'Connor (South Africa, 1996–1999); J. H. Petropoulos (Greece, 1994–1995); D. Platikanov (Bulgaria, 2000–present); R. A. Schoonheydt (Belgium, 1995–1997); M. S. Scurrrell (South Africa, 1994–1995); M. Tunçay (Turkey, 1996–1997); E. van Steen (South Africa, 1998–present); M. S. Suwandi (Malaysia, 1994–1995); Y. S. Uh (Korea, 2000–present); B. Wichterlová (Czech Republic, 1994–1999); M. Zrinyi (Hungary, 2000–present).

---

Republication or reproduction of this report or its storage and/or dissemination by electronic means is permitted without the need for formal IUPAC permission on condition that an acknowledgment, with full reference to the source, along with use of the copyright symbol ©, the name IUPAC, and the year of publication, are prominently visible. Publication of a translation into another language is subject to the additional condition of prior approval from the relevant IUPAC National Adhering Organization.

# Nomenclature of structural and compositional characteristics of ordered microporous and mesoporous materials with inorganic hosts

## (IUPAC Recommendations 2001)

*Abstract:* A system of terms applicable to ordered microporous and mesoporous materials is proposed, and rules for writing a standardized crystal chemical formula for such materials are presented. The recommendations are based both on common usage and on a systematic classification scheme. The nomenclature has been developed to encompass all inorganic materials with ordered, accessible pores with free diameters of less than 50 nm. The crystal chemical formula describes the chemical composition of both the guest species and the host, the structure of the host, the structure of the pore system, and the symmetry of the material. This formula can be simplified or expanded to suit the user's requirements.

### 1. INTRODUCTION

To facilitate communication between people working in the field of ordered microporous and mesoporous materials, a system of terms, whose definitions are generally accepted, is required. In this document, such a system is proposed, and rules for writing crystal chemical formulae for these materials are recommended. The recommendations are based both on common usage and on a systematic classification of such materials that will be published shortly by Liebau [1].

Because they constitute the largest group of ordered microporous materials and because a basic nomenclature already exists for them, zeolites and zeolite-like materials, with their 3-dimensional, 4-connected inorganic frameworks, have served as a basis for this terminology [2]. However, the nomenclature has been developed with the idea of encompassing *all* ordered, microporous and mesoporous materials with inorganic hosts, including those with nonzeolitic chemical compositions, with nontetrahedral building units, and/or with host structures that do not extend in three dimensions. The only restrictions imposed are that the pores must be ordered (e.g., pillared clays are therefore not included), accessible (e.g., clathrates are not specifically considered, although the terminology could be extended to include them), and have free diameters of less than 50 nm (generally accepted range for microporous and mesoporous materials).

Terms that describe the most relevant features of such materials have been defined, and a crystal chemical formula that can be abbreviated or expanded to suit the user's need has been developed.

### 2. MATERIALS TO BE COVERED

Any material can be considered to consist of atoms linked by chemical bonds and the voids between these linked atoms. In an ordered microporous or mesoporous material, the voids between the linked atoms have a free volume larger than that of a sphere with a 0.25 nm diameter, and they are arranged in an ordered manner. For subsequent discussion, the linked atoms are called the host and the voids the pores. The pores can be empty, or they can be occupied by guest species. According to IUPAC recommendations [3], pores with free diameters of less than 2 nm are called micropores, and those in the range of 2 to 50 nm mesopores.

In most cases, the atoms of the host (and therefore the voids) are arranged periodically with long-range order (at least 10 repeats in all directions) and produce sharp maxima in a diffraction experiment. That is, the materials are crystalline. However, there are some materials for which the host displays only short-range order (i.e., is amorphous with respect to diffraction experiments), but the pores are of uniform size with long-range order and produce diffraction maxima at  $d$ -values reflecting the pore-to-pore distance. That is, the pore structure is “crystalline”. Examples of the latter include MCM-41, MCM-48 [4–6], and FSM-16 [7]. The following recommendations apply to any material in which the arrangement of the pores within the inorganic host is highly ordered. They do not apply to materials such as pillared clays, where the pores are disordered, to the large class of microporous layered compounds with continuous 2-dimensional voids (unless the layers themselves contain ordered pores), or to materials with partly or fully organic hosts.

### 3. GENERAL DEFINITIONS

An ordered microporous or mesoporous material can be described in terms of a host structure, which defines a pore structure, which may contain guest species. The terminology defined in the following sections describes the pertinent characteristics of the host and the pores. Because these materials are often used as catalysts or molecular sieves, features controlling the diffusion of guest species and the space restrictions for reaction intermediates are considered to be particularly relevant.

#### 3.1 The host

##### 3.1.1 Topology

The topology of a host structure describes the connectivity of its host atoms without reference to chemical composition or observed symmetry (including crystallographic translations).

##### 3.1.2 Symmetry

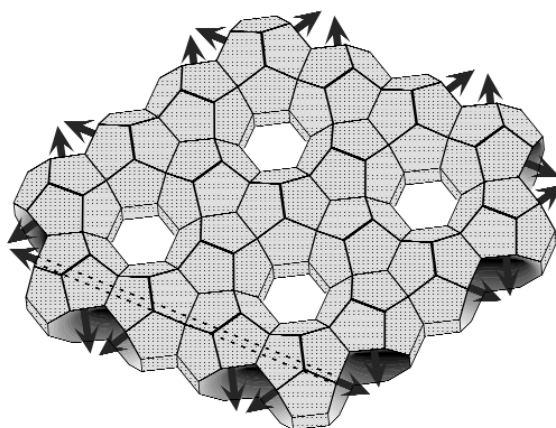
The highest possible symmetry for a host structure is the symmetry of its topology (topological symmetry). Although the symmetry of a particular material can be as high as the topological symmetry, it is often a subgroup thereof. Whatever the observed symmetry, however, the number of framework atoms in the unit cell will be an integer multiple of the number in the topological unit cell. Distortions of the host structure due to the chemical composition of the host and/or to the presence of guest species in the pores are common.

##### 3.1.3 Zeolite framework type

Microporous materials with an inorganic, 3-dimensional host structure composed of fully linked, corner-sharing tetrahedra and the same host topology constitute a zeolite framework type. Each confirmed zeolite framework type is assigned a three-letter code (e.g., **FAU** for the faujasite framework type) by the Structure Commission of the International Zeolite Association (IZA), and details of these framework types are published in the *Atlas of Zeolite Framework Types* [8], formerly entitled the *Atlas of Zeolite Structure Types* [9]. All framework types, including updates between editions of the *Atlas*, are also published on the internet at <http://www.iza-structure.org/databases/>. A three-letter code preceded by a hyphen has been assigned in a few cases to zeolite-like framework types that are not fully 4-connected (i.e., interrupted frameworks such as that of the gallophosphate cloverite [10], whose topology has the code **-CLO**). In subsequent discussion, the three-letter code will be referred to as the IZA code.

##### 3.1.4 Host dimensionality ( $D^h$ )

A host structure can extend in zero (finite), one (chain), two (layer), or three (framework) dimensions. Most known microporous and mesoporous materials have three-dimensional host structures, but it is



**Fig. 1** The precursor of the zeolite ITQ-1 [11]. An example of a two-dimensional host structure with an ordered two-dimensional channel system (indicated with arrows). The nodes are Si atoms. Bridging oxygen atoms have been left out for clarity. The D6R or  $[4^6 6^2]$  “holes” in the layer have been left unshaded to show the shape of the channel system more clearly. They are 0-dimensional cages and are too small to allow species to pass from one side of the layer to the other.

also possible for a lower dimensional host to have an ordered pore system. For example, the precursor of the high-silica zeolite ITQ-1 [11] (Fig. 1) and the mineral rhodesite [12] both have 2-dimensional host structures with ordered arrangements of channels within the layers.

### 3.1.5 Basic building units

The host structure can be constructed by linking basic building units (usually coordination polyhedra sharing corners, edges, or faces, but sometimes single atoms). In the case of zeolite structures, these basic building units (**BBU**) are tetrahedra, where the central atom ( $c_c\mathbf{H}$ ) is typically Si or Al, and the peripheral atoms ( $p_c\mathbf{H}$ ) are O. In the vast majority of microporous and mesoporous materials with inorganic hosts, the central atoms are cations and the peripheral atoms anions (e.g.,  $[\text{BO}_3]$ ,  $[\text{SiO}_4]$ ,  $[\text{AlO}_4]$ ,  $[\text{PO}_4]$ ,  $[\text{SnS}_5]$ ,  $[\text{MnO}_6]$ ). In a few cases, however, an anion is surrounded by cations (e.g.,  $[\text{OH}_4]$  in clathrate hydrates [13,14],  $[\text{SAg}_4]$  and  $[\text{SAg}_5]$  in  $\text{CsAg}_7\text{S}_4$  [15], and  $[\text{TeAg}_4]$  and  $[\text{TeAg}_7]$  in  $\text{CsAg}_5\text{Te}_3$  [16]).

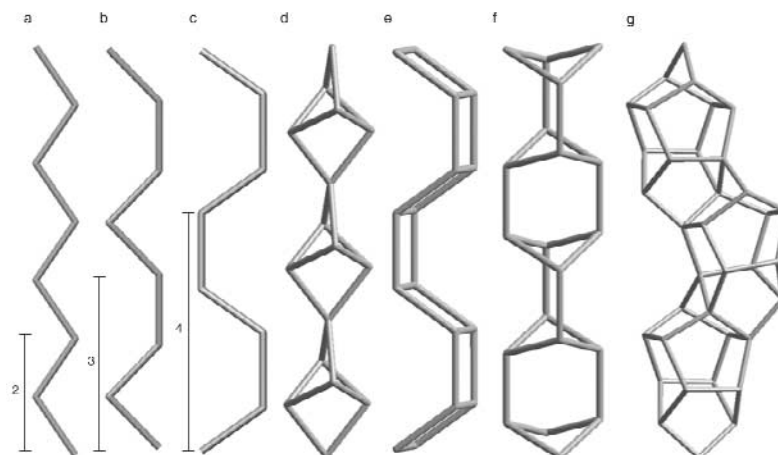
### 3.1.6 Composite building units

It is sometimes useful to combine **BBUs** to construct a larger composite building unit (**CBU**) that is characteristic of the topology. For example, single rings, single chains (Figs. 2a–d) or polyhedral building units (Fig. 3), composed of a finite or infinite number of **BBU**'s can be chosen. In some cases, more complex **CBUs**, such as the chains shown in Figs. 2e–g or the channel walls shown in Fig. 4, might be appropriate. The nodes shown in these figures are the central atoms ( $c_c\mathbf{H}$ ) of the **BBUs**. Rings are described using the notation  $n$ -ring, where  $n$  is the number of  $c_c\mathbf{H}$  atoms in the ring, and polyhedral building units using the notation  $[n_1^{m_1}]$ , where  $m$  is the number of  $n$ -rings defining the polyhedron and  $\Sigma m_i$  is the total number of faces. For example, the double 8-ring in Fig. 3 is defined by eight 4-rings and two 8-rings, so its **CBU** descriptor is  $[4^8 8^2]$ .

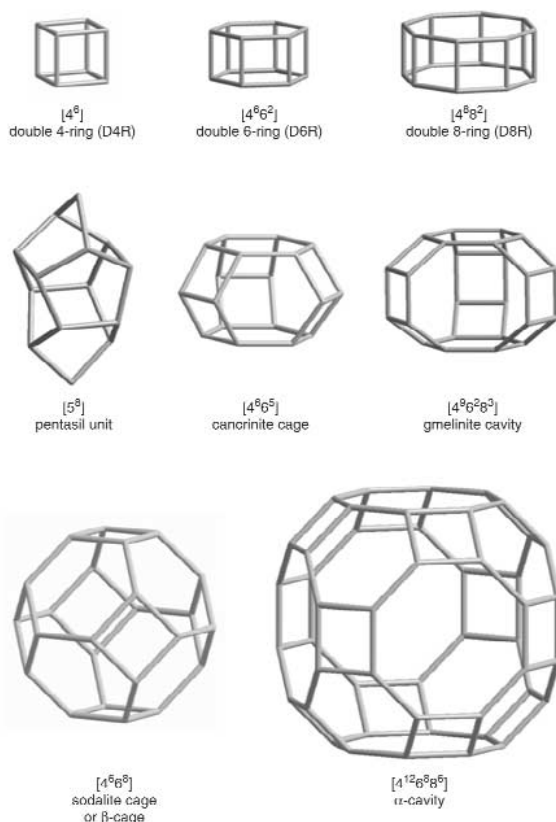
## 3.2 The pores

### 3.2.1 Windows

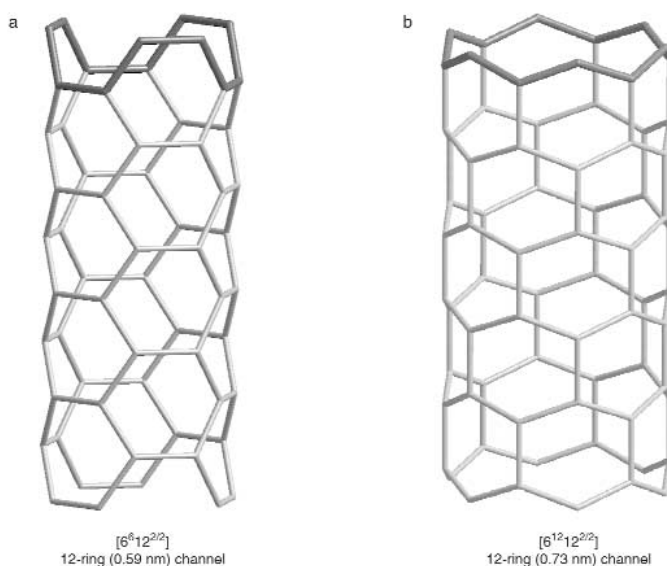
The  $n$ -rings defining the faces of a polyhedral pore are called windows.



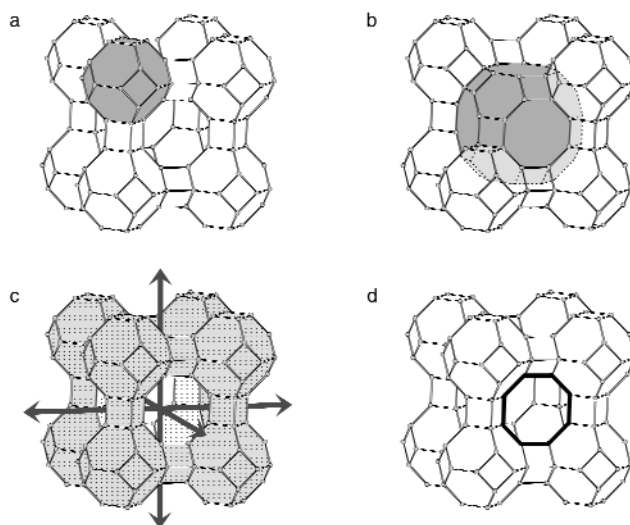
**Fig. 2** Some examples of chain composite building units (common names given in parentheses). Unbranched single chains with periodicities of (a) two (zig-zag chain), (b) three (sawtooth chain), (c) four (crankshaft chain), (d) a branched single chain (natrolite chain), (e) an unbranched double chain (double crankshaft chain), (f) a branched double chain (narsarsukite chain), and (g) a more complex chain (pentasil chain). The nodes are tetrahedrally coordinated atoms such as Si or Al. Bridging oxygen atoms have been left out for clarity.



**Fig. 3** Some examples of polyhedral composite building units with their corresponding pore symbols and common names. The nodes are tetrahedrally coordinated atoms such as Si or Al. Bridging oxygen atoms have been left out for clarity.



**Fig. 4** Two examples of chain-like composite building units. (a) The six-fold chain with a periodicity of two found in cancrinite (IZA code **CAN**), and (b) the six-fold chain with a periodicity of four found in  $\text{AlPO}_4\text{-5}$  (IZA code **AFI**). The 12-rings defining the effective widths of the channels defined by these **CBUs** have been highlighted. The corresponding pore symbols and effective topological and metrical channel widths are indicated. The nodes are tetrahedrally coordinated atoms such as Si, Al, or P. Bridging oxygen atoms have been left out for clarity.



**Fig. 5** Features of the pores in zeolite A (IZA code **LTA**): (a) the sodalite cage ( $[4^6 6^8]$ ), (b) the  $\alpha$ -cavity ( $[4^{12} 6^8 8^6]$ ), (c) the three-dimensional channel system, and (d) the 8-ring defining the 0.41 nm effective channel width. The nodes are tetrahedrally coordinated atoms such as Si or Al. Bridging oxygen atoms have been left out for clarity.

### 3.2.2 Cages

A polyhedral pore whose windows are too narrow to be penetrated by guest species larger than H<sub>2</sub>O is called a cage. For oxides ( $\rho_{\text{pe}}\mathbf{H} = \text{O}$ ), the limiting ring size is considered to be  $n = 6$ . For example, the [4<sup>6</sup>6<sup>8</sup>] polyhedron (sodalite cage) in zeolite A (see Fig. 5a) is a cage.

### 3.2.3 Cavities

A polyhedral pore, which has at least one face defined by a ring large enough to be penetrated by guest species, but which is not infinitely extended (i.e., not a channel), is called a cavity. For example, the [4<sup>12</sup>6<sup>8</sup>6<sup>6</sup>] polyhedron in zeolite A (see Fig. 5b) is a cavity.

### 3.2.4 Channels

A pore that is infinitely extended in one dimension and is large enough to allow guest species to diffuse along its length is called a channel. Channels can intersect to form 2- or 3-dimensional channel systems. For example, the channels in zeolite A (Fig. 5c) intersect to form a 3-dimensional channel system.

### 3.2.5 Effective channel width

The effective width of a channel is a fundamental characteristic of a microporous or mesoporous material that describes the accessibility of the pore system to guest species (i.e., the “bottleneck”). It is generally defined in terms of either the smallest  $n$ -ring (topological description) or the smallest free aperture (metrical description) along the dimension of infinite extension. For example, the 3-dimensional channel system in zeolite A has 8-ring pore openings (topological description) with a free diameter of ca. 0.41 nm (metrical description) in all three directions (Fig. 5d). The free diameter takes into account the size of the  $\rho_{\text{pe}}\mathbf{H}$  atoms (e.g., an ionic radius for oxygen of 0.135 nm has been assumed, so 0.27 nm has been subtracted from the O...O distance defining the pore diameter). The pore width along a channel, topologically as well as metrically, can be constant or it may undulate (e.g., if the channel consists of a series of cavities). In zeolite A, for example, the section of the channel in the center of the cavity is wider than it is at the 8-ring entrance to the cavity. However, it is the 8-ring that defines the size of guest species that can diffuse through the material (i.e., the effective channel width).



**Fig. 6** The sinusoidal channel in chiral zincophosphate (IZA code **CZP**) [16]. The distorted 12-ring defining the effective channel width and a chain showing the helical nature of the channel have been highlighted. Bridging oxygen atoms have been left out for clarity.



For channels defined by helices, by rings not perpendicular to the channel or by unusually distorted rings, the effective width must be given metrically. For example, the 1-dimensional sinusoidal channel in the chiral zincophosphate  $\text{Na}_{12}[\text{Zn}_{12}\text{P}_{12}\text{O}_{48}]$  [17,18] (IZA code **CZP**) can be described either in terms of a helical structure or in terms of a very distorted 12-ring (Fig. 6). The effective channel width is approximately elliptical with minimum and maximum dimensions of 0.38 and 0.65 nm.

### 3.2.6 Pore dimensionality ( $D^p$ )

The number of dimensions in which the pore has infinite extension is the pore dimensionality ( $D^p$ ). For cages,  $D^p = 0$ , and for channels,  $D^p = 1$ . For systems of interconnected channels,  $D^p = 2$  or 3. The dimensionality of the pore system,  $D^p$ , will always be less than or equal to the dimensionality of the host,  $D^h$ .

## 4. CRYSTAL CHEMICAL FORMULA

Since the properties of microporous and mesoporous materials are controlled principally by their chemical composition and their structures, the crystal chemical formula should describe these features in a standardized manner. Furthermore, the formula should be consistent with the recommendations of the International Union of Crystallography for the nomenclature of inorganic structure types [19], with IUPAC rules [20] and with common usage, while being flexible enough to allow the researcher to emphasize only those points that are relevant to his work.

With these guidelines in mind, a crystal chemical formula with the following scheme has been developed:

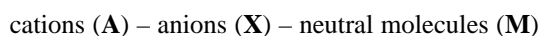


The first two terms describe the chemical composition of the guest species (between boldface vertical bars) and the host (in boldface square brackets), respectively. The next two terms (in boldface curly brackets) contain information about the structure of the host and the pores, respectively. The fifth term (in boldface round brackets) gives the (actually observed) symmetry of the material. If the host structure of the material belongs to a zeolite framework type, the sixth term (preceded by a dash) is the IZA code in boldface type.

Each of these terms has a prescribed content, which can be reduced or expanded in accordance with the detail appropriate for a specific problem. In the following sections, each term is considered in turn.

### 4.1. Chemical composition of the guest species

The chemical formulae for the various guest species present in the pores of the material are placed inside boldface vertical bars and arranged in the order



to yield the general term



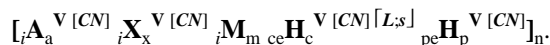
This term should reflect the chemical composition of the guest species for the complete unit cell. If the topological (or for zeolites, the framework type) unit cell of the host structure is known, the composition should be expressed in multiples (n) of that unit cell (see examples in Section 4.7).

### 4.2. Chemical composition of the host

The symbols for the atoms constituting the host are placed inside boldface square brackets and are arranged in the order

interstitial species ( ${}_i\mathbf{A}$ ,  ${}_i\mathbf{X}$  or  ${}_i\mathbf{M}$ ) – central host atoms ( ${}_{ce}\mathbf{H}$ ) – peripheral host atoms ( ${}_{pe}\mathbf{H}$ ).

An interstitial species is a non-exchangeable cation, anion, or molecule located in a void with a free diameter of less than 0.25 nm. The element symbols can be complemented in the usual way to indicate oxidation state  $\mathbf{V}$  (Roman numeral superscript) and coordination number  $\mathbf{CN}$  (Arabic number superscript within square brackets). The linkedness  $\mathbf{L}$  and connectedness  $s$  of the central host atoms, which indicate the number ( $s$ ) of neighboring  $\mathbf{BBU}$ s that share corners, edges, or faces ( $\mathbf{L} = 1, 2, \text{ or } 3$ , respectively) with the  ${}_{ce}\mathbf{H}$  under consideration [19], can also be specified within Japanese brackets ( $\lceil \rceil$ ), if desired. The general form of the term can be written as



From this, the basic building unit(s) ( $\mathbf{BBU}$ ) of the host,  $[{}_{ce}\mathbf{H}({}_{pe}\mathbf{H})_n]$ , can be deduced. As for the guest species, this term should reflect the chemical composition of the host for a complete unit cell and be expressed as multiples ( $n$ ) of the topological (or for zeolites, the framework type) unit cell, if it is known.

### 4.3. Structure of the host

The parameters describing the host structure are placed inside boldface curly brackets preceded by a subscript  $h$  and are arranged in the order

dimensionality of the host ( $\mathbf{D}^h$ ) – composite building unit ( $\mathbf{CBU}$ )

to yield the general term



The composite building unit(s) can be chosen to highlight those aspects of the host structure that are relevant to the discussion. For example, the host structure of the zeolite faujasite would be given as  ${}_h\{3 [4^6 6^2] [4^6 6^8]\}$  indicating that the framework is 3-dimensional and contains both double-6-ring and sodalite cages. If a  $\mathbf{CBU}$  is selected according to the set of hierarchical rules described by Liebau [1], it becomes a fundamental building unit ( $\mathbf{FBU}$ ), and then additional parameters that describe the host structure in terms of the  $\mathbf{FBU}$  can be added. Further details are given in ref. 1.

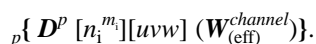
### 4.4. Structure of the pores

The parameters describing the pore system are placed inside boldface curly brackets preceded by a subscript  $p$  and are arranged in the order

dimensionality of the pore system  $\mathbf{D}^p$  – shape of the pore [ $n_i^{m_i}$ ] – direction of the channel [ $uvw$ ]

– effective channel width ( $\mathbf{W}_{(eff)}^{channel}$ )

to yield the general term



The term [ $uvw$ ] can be replaced with  $\langle uvw \rangle$  to indicate that all crystallographically equivalent directions are involved. If more than one pore system is present, the descriptions are separated by a slash (/).

### 4.5. Symmetry information

Materials with the same host topology do not necessarily have the same symmetry. If this aspect of the structure is pertinent, it can be included as the fifth term of the crystal chemical formula enclosed in boldface round brackets. Following the recommendations of the International Union of Crystallography

[21] and the International Mineralogical Association [22], this information can be given in form of the crystal system (*C* for cubic, *H* for hexagonal, *T* for trigonal, *R* for rhombohedral, *Q* for tetragonal, *O* for orthorhombic, *M* for monoclinic, and *A* for triclinic) or the space group symbol.

#### 4.6. IZA code

For zeolites and zeolite-like materials, full descriptions of the confirmed zeolite framework types are given in the *Atlas of Zeolite Framework Types* [8]. The three-letter code alone conveys a wealth of information about the host structure and the pore system, so when relevant, it should be appended to the crystal chemical formula following a dash.

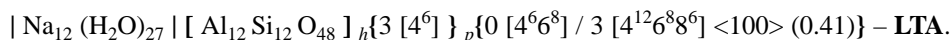
#### 4.7. Examples of the application of the crystal chemical formula

##### 4.7.1. Zeolite A (a standard case)

A typical crystal chemical formula for zeolite A [23] would be:

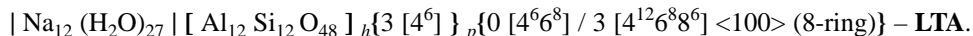


This formula can be expanded to include information about the host and pore structure:

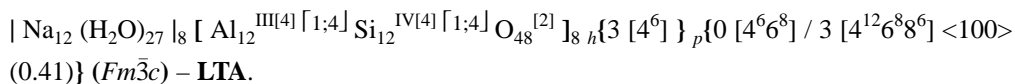


Here, the fact that the host is 3-dimensional and can be constructed by linking double 4-rings as composite building units is highlighted. The description of the pores indicates that there are sodalite cages and a 3-dimensional channel system which contains  $\alpha$ -cavities. The channels run parallel to  $\langle 100 \rangle$  (i.e., parallel to [100], [010], and [001]), and have an effective channel width of 0.41 nm.

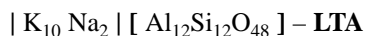
The effective pore width can be given topologically instead:



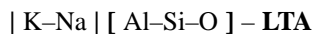
Further expansion of the formula can be used to describe the oxidation states, coordination numbers, and connectivities of the host atoms (see refs. 1,19), and to indicate that the symmetry of the material is lower and the unit cell eight times larger than that of the **LTA** framework type (space group  $Pm\bar{3}m$ ):



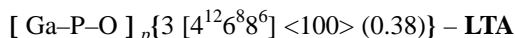
Alternatively, the formula can be simplified to highlight only those aspects of the chemical composition and/or structure that are of immediate interest. For example,



describes the cation composition (e.g., after a  $\text{K}^+$  ion exchange) within the pores of an aluminosilicate material with the **LTA** framework type,

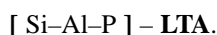


describes the same material without specifying the extent of ion-exchange, or



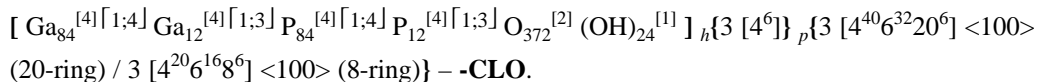
emphasizes the effective width of the channel system for the gallophosphate material with the **LTA** framework type. Note that chemical symbols are delimited with dashes if the stoichiometry is not given.

If only the framework host composition is of interest, the crystal chemical formula can be simplified even further. For example, for the silicoaluminophosphate SAPO-42, the formula could be just



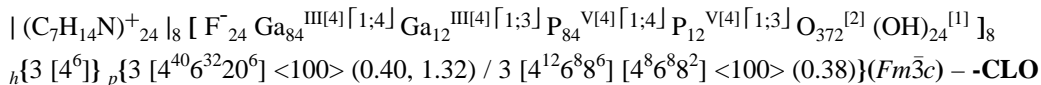
#### 4.7.2. Cloverite (with an interrupted framework host structure)

Cloverite [10] is a gallophosphate with an interrupted framework structure and an unusual pore structure, so the connectivity of the framework atoms and a description of the channel system may be of particular interest:



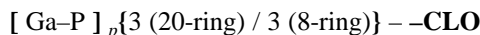
The formula indicates that the framework host is a gallophosphate with 4-coordinate Ga and P atoms (1/8 of which are only 3-connected), bridging O atoms, and terminal OH groups. The framework host is 3-dimensional, and contains double 4-rings. There are two nonintersecting 3-dimensional channel systems running parallel to  $\langle 100 \rangle$ . One system includes very large cavities and has an effective channel width defined by 20-rings, while the other has smaller cavities with an effective channel width defined by 8-rings. The zeolite framework type code is **-CLO** (hyphen indicates that the framework is interrupted).

This crystal chemical formula can be expanded further to include additional details:

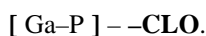


such as the presence of quinuclidinium ions in the pores, interstitial fluoride ions (in the double 4-rings), the oxidation states of the central host atoms, the fact that two different cavities make up the smaller channel system, that the observed symmetry is lower than that of the framework type, and that the unit cell is eight times as large. It is immediately apparent from the metrical effective channel width that the 20-ring has an unusual shape (minimum 0.40 nm and maximum 1.32 nm).

Of course, the formula can also be simplified to:

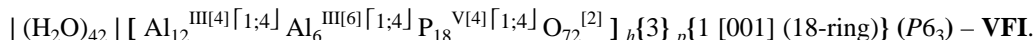


where the host is described just in terms of the identity of the central host atoms, and the pore systems are given in abbreviated form, or even just

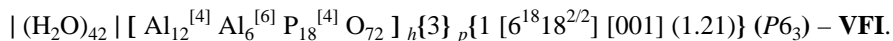


#### 4.7.3. VPI-5 (with different coordination numbers for the central host atoms)

Although VPI-5 [24] can be considered to have a 4-connected zeolite framework structure, some of the central atoms of the host also coordinate to water molecules:

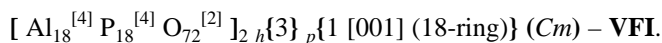


The 18-ring channel in VPI-5 is lined with 6-rings, and this information can be given in the description of the pore (given for one unit cell):



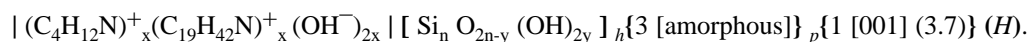
Note that although the channel is infinitely long along the [001] direction, the pore-shape descriptor is given in terms of the repeating unit, and therefore the delimiting 18-rings must be halved (i.e., only 1/2 of each terminating 18-ring "belongs" to a single repeat).

Upon dehydration of a particular VPI-5 material, the water in the pores is removed, the 6-coordinate Al becomes 4-coordinate, the unit cell doubles in size, and the symmetry is reduced to monoclinic [25]:



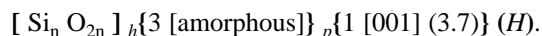
#### 4.7.4 MCM-41 (a mesoporous material with ordered pores but an amorphous host)

A typical crystal chemical formula for a member of this family of mesoporous materials (e.g., ref. 4) might be:



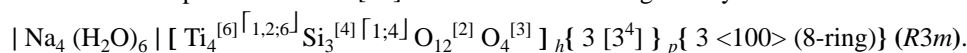
The pores are filled with tetramethylammonium and hexadecyltrimethylammonium hydroxide species, the chemical composition of the 3-dimensional but amorphous host is  $\text{SiO}_2$  with some terminal OH groups, the pore system is 1-dimensional with an effective channel width of 3.7 nm, and the channels are arranged in a hexagonal manner running parallel to [001].

Removal of the organic species from the pores by calcination would then produce:



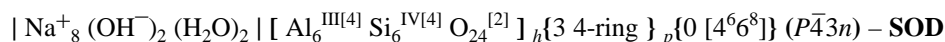
#### 4.7.5 Sodium titanium silicate (microporous material whose host is not a zeolite framework type)

This nonzeolite microporous material [26] can be described using the crystal chemical formula:



Sodium ions and water molecules are present in the pores of this rhombohedral titanosilicate host. Titanium is 6-coordinate and linked via corners and edges to six neighboring central host atoms (3 Ti and 3 Si), while silicon is 4-coordinate and shares corners with four central host atoms (Ti). Four of the 16 oxygens are 3-coordinate while the other twelve are 2-coordinate. The host is 3-dimensional and contains tetrahedral composite building units. The pore system is 3-dimensional running along the  $\langle 100 \rangle$  directions with an effective channel width defined by 8-rings.

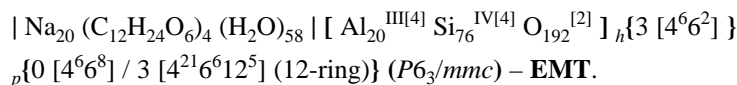
#### 4.7.6 Basic sodalite [27]



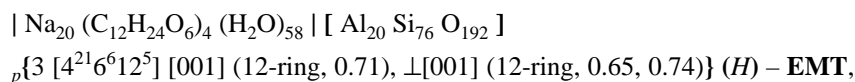
In the unit cell, there are 8  $\text{Na}^+$  ions, 2  $\text{OH}^-$  ions, and 2  $\text{H}_2\text{O}$  molecules in the pores, and 6 Al (oxidation state III), 6 Si (oxidation state IV), and 24 O in the framework host, the Al and Si atoms are all 4-coordinate, the framework O's bridge between two atoms, the observed unit cell is the same size as the topological one (even though the topological symmetry is  $Im\bar{3}m$ ), the host is 3-dimensional and can be constructed by linking 4-rings, the  $[4^6\text{8}^8]$  pores (sodalite cages) are 0-dimensional (i.e., only small windows present), the space group of the material is  $P\bar{4}3n$ , and the zeolite framework type code is **SOD**.

#### 4.7.7 Zeolite EMC-2 [28]

The structure of this hexagonal high-silica zeolite, which is synthesized in the presence of 1,4,7,10,13,16-hexaoxacyclooctadecane (crown ether 18-crown-6), is related to that of the cubic zeolite faujasite (**FAU**) in that its framework host is composed of double 6-rings and sodalite cages. Its pore system, like that of faujasite, is also 3-dimensional with effective channel widths defined by 12-rings:

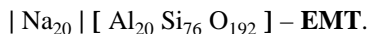


However, in EMC-2, the 12-rings are not equivalent and their shapes differ significantly. To emphasize this point, the crystal chemical formula could be written as



where the descriptions of the different channels are separated by commas and the effective channel widths are given both topologically and metrically. For further information on delimiters in more complicated formulas, see ref. 1.

As in previous examples, the formula could also be simplified somewhat to



## REFERENCES

1. F. Liebau. *Microporous Mesoporous Mater.*, submitted for publication.
2. R. M. Barrer. *Pure Appl. Chem.* **51**, 1091–1100 (1979).
3. J. Rouquérol, D. Avnir, C. W. Fairbridge, D. H. Everett, J. H. Haynes, N. Pericone, J. D. F. Ramsay, K. S. W. Sing, K. K. Unger. *Pure Appl. Chem.* **66**, 1739–1758 (1994).
4. C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck. *Nature* **359**, 710–712 (1992).
5. A. Monnier, F. Schüth, Q. Huo, D. Kumar, D. Margolese, R. S. Maxwell, G. D. Stucky, M. K. Krishnamurty, P. Petroff, A. Firouzi, M. Janicke, B. F. Chmelka. *Science* **261**, 1299–1303 (1993).
6. Q. S. Hue, D. I. Margolese, U. Ciesla, P. Feng, T. E. Gier, P. Sieger, R. Leon, P. M. Petroff, F. Schüth, G. D. Stucky. *Nature* **368**, 317–321 (1994).
7. S. Inagaki, A. Koiwai, N. Suzuki, Y. Fukushima, K. Kuroda. *Bull. Chem. Soc. Jpn.* **69**, 1449–1457 (1996).
8. Ch. Baerlocher, W. M. Meier, D. H. Olson. *Atlas of Zeolite Framework Types*, 5<sup>th</sup> ed., Elsevier, Amsterdam (2001).
9. W. M. Meier, D. H. Olson, Ch. Baerlocher. *Atlas of Zeolite Structure Types*, 4<sup>th</sup> ed., Elsevier, Amsterdam (1996).
10. M. Estermann, L. B. McCusker, C. Baerlocher, A. Merrouche, H. Kessler. *Nature* **352**, 320–323 (1991).
11. S. L. Njo, H. van Koningsveld, B. van de Graaf, Ch. Baerlocher, L. B. McCusker. In *Proc. 12th Int. Zeolite Conf.*, M. M. J. Treacy, B. K. Marcus, M. E. Bisher, J. B. Higgins, (Eds.), pp. 2519–2524, Materials Research Society, Warrendale, PA (1999).
12. K.-F. Hesse, F. Liebau, S. Merlino. *Z. Kristallogr.* **199**, 25–48 (1992).
13. G. A. Jeffrey. In *Inclusion Compounds*, Vol. 1, J. L. Atwood, J. E. D. Davies, D. D. MacNicol (Eds.), pp. 135–140, Academic Press, London (1984).
14. F. Liebau. In *The Physics and Technology of Amorphous SiO<sub>2</sub>*, R. A. B. Devine (Ed.), pp. 15–35, Plenum Press, New York (1988).
15. P. T. Wood, W. T. Pennington, J. W. Kolis. *Inorg. Chem.* **33**, 1556–1558 (1994).
16. J. Li, H.-Y. Guo, X. Zhang, M. G. Kanatzides. *J. Alloys Compd.* **218**, 1–4 (1995).
17. N. Rajic, N. Z. Logar, V. Kaucic. *Zeolites* **15**, 672–678 (1995).
18. W. T. A. Harrison, T. E. Gier, G. D. Stucky, R. W. Broach, R. A. Bedard. *Chem. Mater.* **8**, 145–151 (1996).
19. J. Lima-de-Faria, E. Hellner, F. Liebau, E. Makovicky, E. Parthé. *Acta Crystallogr.* **A46**, 1–11 (1990).
20. G. J. Leigh (Ed.). *IUPAC Nomenclature of Inorganic Chemistry (Recommendations 1990)*, Blackwell, Oxford (1990).
21. A. Guinier, G. B. Bokii, K. Boll-Dornberger, J. M. Cowley, S. Durovic, H. Jagodzinski, P. Krishna, P. M. de Wolff, B. B. Zvyagin, D. E. Cox, P. Goodman, Th. Hahn, K. Kuchitsu, S. C. Abrahams. *Acta Crystallogr.* **A40**, 399–404 (1984).
22. E. H. Nickel and J. A. Mandarino. *Amer. Mineral.* **72**, 1031–1042 (1987).
23. V. Gramlich and W. M. Meier. *Z. Kristallogr.* **133**, 134–149 (1971).
24. L. B. McCusker, Ch. Baerlocher, E. Jahn, M. Bülow. *Zeolites* **11**, 308–313 (1991).

25. J. de Oñate Martínez, Ch. Baerlocher, L. B. McCusker. *Microporous Mesoporous Mater.* **34**, 99–113 (2000).
26. M. S. Dadachov and W. T. A. Harrison. *J. Solid State Chem.* **134**, 409–415 (1997).
27. I. Hassan and H. D. Grundy. *Acta Crystallogr.* **C39**, 3–5 (1983).
28. Ch. Baerlocher, L. B. McCusker, R. Chiappetta. *Microporous Mater.* **2**, 269–280 (1994).