Acta Crystallographica Section B
Structural
Science
ISSN 0108-7681

Analysis of ion-migration paths in inorganic frameworks by means of tilings and Voronoi–Dirichlet partition: a comparison

Nataly A. Anurova and Vladislav A. Blatov*

Samara State University, Ac. Pavlov St. 1, Samara 443011, Russia

Correspondence e-mail: blatov@ssu.samara.ru

Received 30 January 2009
Accepted 25 May 2009

Two methods using Voronoi–Dirichlet polyhedra (*Voronoi–Dirichlet partition*) or tiles (*tiling*) based on partitioning space are compared to investigate cavities and channels in crystal structures. The tiling method was applied for the first time to study ion conductivity in 105 ternary, lithium–oxygen-containing compounds, $\mathrm{Li}_aX_b\mathrm{O}_z$, that were recently recognized as fast-ion conductors with the Voronoi–Dirichlet partition method. The two methods were found to be similar in predicting the occurrence of ionic conductivity, however, their conclusions on the dimensionality of conductivity were different in two cases. It is shown that such a contradiction can indicate a high anisotropy of conductivity. Both advantages and restrictions of the methods are discussed with respect to fast-ion conductors and zeolites.

1. Introduction

The geometrical analysis of void and channel systems is an important part of the crystal chemistry of porous substances. Since the net of voids and channels is dual to the atomic net to some extent, the methods for studying both the ‘empty’ space (*void space*) and the space of atoms in crystals are similar in many respects; this motivated Blatov & Shevchenko (2003) to introduce the term ‘*dual*’ crystal chemistry. Recently, ‘grid’ methods (Thomas, 1991; Adams & Swenson, 2002; Küppers *et al.*, 2006) as well as the methods based on the Voronoi–Dirichlet partition of crystal space (Blatov *et al.*, 2006) have been developed to analyze void space. In the ‘grid’ methods the voids and channels are modeled by a set of points of a sufficiently dense grid embedded into the crystal space so that the distance from every point to the nearest atom is not smaller than the atom radius. The results of the analysis depend on the grid pitch and on the chosen system of atomic radii. The ‘grid’ method is implemented in the program *PLATON* (Spek, 2009) and is being applied both to inorganic and to organic crystals.

When using the Voronoi–Dirichlet partition, the centers of voids are assumed to be the vertices of Voronoi–Dirichlet polyhedra, while the channel lines connecting the voids coincide with the edges of the Voronoi–Dirichlet polyhedra. This method does not require any system of atomic radii; it has been realised in the program package *TOPOS* (Blatov, 2006) and has been successfully applied to analyze migration paths in fast-ion conductors. Thus, Anurova *et al.* (2008) treated all X-ray investigated ternary and quaternary lithium-containing inorganic compounds (822 $\mathrm{Li}_aX_b\mathrm{O}_z$ and 1349 $\mathrm{Li}_aX1_bX2_c\mathrm{O}_z$, where X, $X1$ and $X2$ are any elements) and determined the periodicity of channel systems providing the transport of lithium cations. For all the substances the migration maps characterizing systems of conducting channels were constructed and 26 potentially novel fast-ion conductors were revealed.

Quite recently, Delgado-Friedrichs *et al.* (2003) proposed one more method of 'dual' crystal chemistry resting upon a special space partition, *tiling*. The tiling consists of generalized polyhedra, *tiles*, which, unlike Voronoi–Dirichlet polyhedra, are not necessarily convex and may have nonplanar faces. The most important type is *natural tiling* that is unique for the net and contains information on all the voids and channels in the crystal structure. Until recently, the tiling applications for crystals had only been provided for high-symmetry nets (Delgado-Friedrichs *et al.*, 2003). However, after developing the appropriate software (Blatov *et al.*, 2007) the natural tilings were built for all known topological types of zeolites (*Atlas of Zeolite Frameworks*[1]).

The Voronoi–Dirichlet partition method as well as 'grid' methods can be called *geometrical* since they are essentially based on the space metrics and interatomic distances, while the tiling method is mainly *topological* and treats the topological properties of the net when searching for cavities and channels. These methods have never been compared with each other. In this study the tiling method is applied for the first time to analyze lithium-cation migration paths in ternary compounds $\mathrm{Li}_aX_b\mathrm{O}_z$, and the conclusions on conductivity are compared with earlier results by Anurova *et al.* (2008) obtained with the Voronoi–Dirichlet partition method. We will discuss both advantages and restrictions of the methods.

2. Terminology and definitions

In this section we summarize some basic notions which will be used hereafter. A more detailed list of definitions concerning the use of atomic nets in crystal chemistry was given by Delgado-Friedrichs & O'Keeffe (2005).

Net is a special type of infinite graph that is *simple* (it has no loops or multiple or directed edges) and *connected* (any pair of vertices is connected by a chain of edges); the vertices of the graph are also called *nodes* of the net. *Embedding* of the net is a distinct way to allocate the nodes in space. In this work, when exploring voids and channels we always use the embedding that corresponds to the structure of a given compound, not the most symmetrical one as has been done earlier (Blatov *et al.*, 2007, and references therein).

The *Voronoi–Dirichlet polyhedron* of a node is the convex polyhedron formed by perpendicular planes passing through the midpoints of the lines connecting the node with the neighboring ones. Voronoi–Dirichlet polyhedra of all nodes produce a normal (face-to-face) *Voronoi–Dirichlet partition* of space (Fig. 1). The Voronoi–Dirichlet partition is unique for a given net embedding. The vertices and edges of Voronoi–Dirichlet polyhedra correspond to the centers of voids and channel lines, and form the *Voronoi–Dirichlet graph.* A subgraph of the Voronoi–Dirichlet graph corresponds to the system of voids and channels (*migration map*) where the mobile ions (*conducting component*) migrate. A more detailed list of terms used in the analysis of the Voronoi–Dirichlet partition for ionic compounds (including fast-ion conductors) has been given by Anurova *et al.* (2008).

Tile is a generalized polyhedron, in which any vertex can be incident not only to three or more vertices, but also to two vertices. The faces of the tile are fragments of a minimal surface confined by a ring of the net edges; the faces have no common internal points. As Voronoi–Dirichlet polyhedra, tiles fill the space forming a normal partition, *tiling* (Fig. 2). The set of tiling's vertices and edges forms a net (*cf.* Voronoi–Dirichlet graph), and thus the notions of tiling and nets are closely related. Although any tiling carries the net, the contrary is not true in general: not all nets admit tiling in even one of its possible embeddings. On the other hand, while tiling always carries one (and only one) net, the net can admit many tilings.

The most important is *natural tiling* to be defined as follows (Blatov *et al.*, 2007):

(i) the symmetry of the tiling must coincide with the symmetry of the net;

(ii) the tile faces are confined only by *strong rings, i.e.* by rings which are not the sum of the smaller ones;

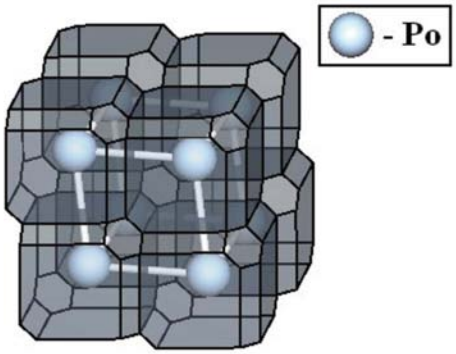


Figure 1
Fragment of Voronoi–Dirichlet partition for the crystal structure of β-Po.

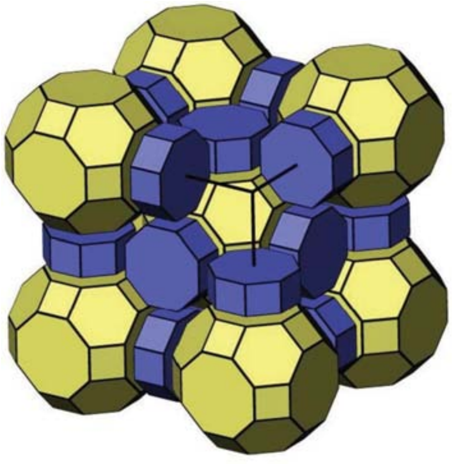


Figure 2
Tiling for the framework of the zeolite RHO.

---

[1] http://www.iza-structure.org/databases/.

(iii) all other strong rings of the net have crossings (common internal points of the corresponding fragments of minimal surfaces);

(iv) if more than one tiling obeys rules (i)–(iii), the single tiling has to be constructed as a union of tiles of different tilings.

As a result, natural tiling is always unique (if the net does admit a tiling). In general it is a non-trivial task to find natural tiling, however, there is an algorithm and its implementation in the program package *TOPOS* (Blatov *et al.*, 2007) allows the construction of natural tilings for nets of any complexity. Currently, the best tool to draw tilings and to compute their topological parameters is the *3dt* program,[2] which was used to prepare all the tiling images in this paper. The tile can be designated by its *face symbol* $[A^a{\cdot}B^b{\cdot}C^c\ldots]$, where the integrals $A, B, C, \ldots$ determine the sizes of the tile faces, and $a, b, c, \ldots$ are equal to the number of faces of size $A, B, C, \ldots$. Tiling as a whole is described by the *signature* $k_1[A^a{\cdot}B^b{\cdot}C^c\ldots] + k_2[D^d{\cdot}E^e{\cdot}F^f\ldots] + \ldots$, where the coefficients $k_1, k_2, \ldots$, show the ratios of tile numbers in the tiling. An important factor of the tiling topological complexity is the *transitivity pqrs*, where integrals p, q, r and s are the numbers of inequivalent nodes, edges, tile faces and tiles, respectively. Thus, the tiling shown in Fig. 2 consists of two types of tiles corresponding to two kinds of cavities in zeolite RHO and having face symbols $[4^8{\cdot}8^2]$ (blue tiles) or $[4^{12}{\cdot}6^8{\cdot}8^6]$ (yellow tiles). The tiling signature is $3[4^8{\cdot}8^2] + [4^{12}{\cdot}6^8{\cdot}8^6]$, *i.e.* the ratio of tile numbers is 3:1; the transitivity is 1242. Any tiling has a *dual net*, whose nodes and edges correspond to the centers of tiles and 'windows', respectively (Fig. 3).

The following properties of natural tilings determine their significance for crystal chemistry (Blatov *et al.*, 2007):

(i) Natural tiling contains all the 'topological' voids of the net, *i.e.* the space domains confined by 'windows' (strong rings of connected atoms), irrespective of the domain shape and size. For any net embedding, one can decide which voids are geometrically significant (for instance, which can hold atoms or molecules of a given size), however, the total set of the voids is predetermined by the tiling.

(ii) The faces of the natural tiles determine the complete set of 'windows' corresponding to the channels between the voids.

(iii) Natural tilings provide additional ways to classify nets; topologically equal tiles in the nets to be compared can indicate some structural similarity.

(iv) Exploring the methods of gluing tiles can be useful for crystal design and to elaborate on strategies to synthesize new porous materials.

(v) The net that admits the tiling describes the ordered part of the fast-ion conductor (we will call it *framework*), while a subnet of its dual net describes the migration map (Blatov *et al.*, 2007).

The tiling approach is, to some extent, dual to the Voronoi–Dirichlet approach. The tiles represent cavities, while the tile vertices coincide with atoms; in the Voronoi–Dirichlet partition the relations are opposite: polyhedra embrace atoms, while their vertices are allocated in the centers of voids. However, these two approaches are not mirror copies; in general (and as a rule), the Voronoi–Dirichlet graph is not isomorphic to the tiling dual net. Moreover, the topology of the Voronoi–Dirichlet graph strongly depends on the structure metrics, while tiling and its dual net are mostly determined by the atomic net topology and are not very sensitive to the net embedding method. That is why the approaches can complement each other and can be independently applied in crystal chemistry.

We emphasize that, in general, cavities and channels obtained with tiling and Voronoi–Dirichlet partitions differ from each other in two ways:

(i) Voronoi–Dirichlet cavities are mainly tetrahedral (three-dimensional simplexes) except in some highly symmetrical cases, because any vertex in the Voronoi–Dirichlet graph is equidistant to at least four atoms, while tiles can be topologically very complicated;

(ii) Voronoi–Dirichlet 'windows' are mainly triangular because any edge in the Voronoi–Dirichlet graph belongs to at least three Voronoi–Dirichlet polyhedra, while the faces of natural tiles can have any number of vertices.

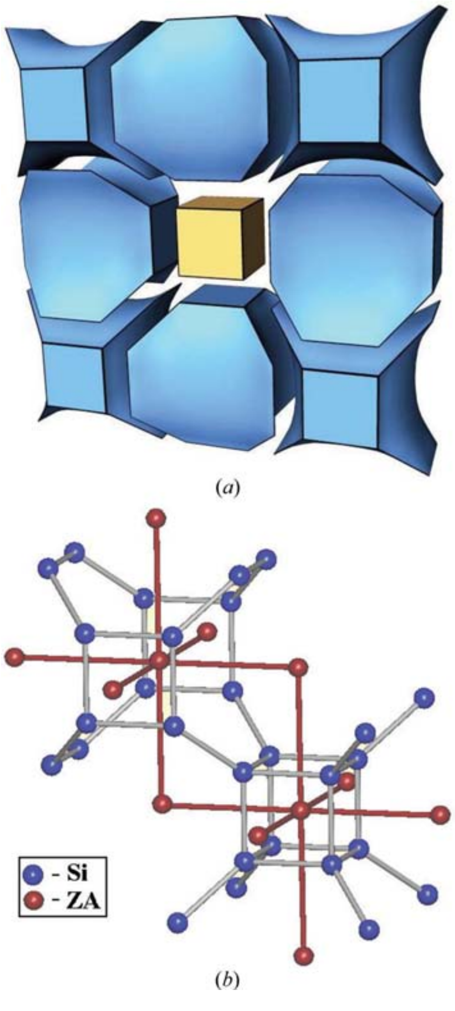


Figure 3
(*a*) Tiling and (*b*) dual net (ZA nodes) in the zeolite ACO.

---

[2] http://www.gavrog.org.

This is the reason why the dual net of tiling is, in general, simpler than the Voronoi–Dirichlet graph. However, if we consider *all* interatomic contacts (both valence and non-valence) as the net edges, the tiling becomes simpler (composed of tetrahedra), and the tiling dual net coincides with the Voronoi–Dirichlet graph. In this case both approaches give the same migration map.

3. Principles of analysis and their computer implementation

The algorithm for building and analyzing migration maps for ions by means of the Voronoi–Dirichlet partition was described in detail by Anurova *et al.* (2008) and includes the following steps:

(i) Constructing Voronoi–Dirichlet polyhedra for all inequivalent atoms, *i.e.* forming the Voronoi–Dirichlet partition of the crystal space. Note that no information on chemical bonds is required since to build the Voronoi–Dirichlet polyhedron only information on atomic coordinates is needed, not on bonds.

(ii) Determining coordinates for all inequivalent vertices and edges of the Voronoi–Dirichlet polyhedra and, as a result, allocating all elementary voids and channels, respectively, as well as computing their geometrical parameters.

(iii) Retrieving significant elementary voids and channels by comparing their geometrical parameters with the criteria specified for the task to be solved.

(iv) Building the migration map, visualizing the system of voids and channels, allocating the most probable positions of mobile ions.

Thus, the whole analysis of the void space is automated. An important point is the choice of criteria for selecting significant voids and channels. Anurova *et al.* (2008) screened and proved these criteria for lithium-conducting oxygen-containing compounds by analysing their crystal structures.

Below we propose and illustrate the three-step algorithm for constructing a migration map by the tiling method.

(i) Determining a three-periodic[3] net corresponding to the framework. While the information on the topology of the atomic net is not important to build the Voronoi–Dirichlet partition, it is crucial to find the strong rings (tile faces) and hence to construct the natural tiling. In the case of zeolites, there is a distinct framework of SiO_4 tetrahedra and the net can be unambiguously chosen (Blatov *et al.*, 2007). Fast-ion conductors do not necessarily have a three-periodic valence-bonded framework, but can consist of molecular ions, chains or layers. Thus, out of 105 ion-conducting ternary $Li_aX_bO_z$ compounds only 20 have three-periodic nets of valence bonds (Anurova *et al.*, 2008). For instance, α-$LiIO_3$ has a distinct three-periodic net of vertex-connected IO_6 octahedra (Fig. 4). If the three-periodic net cannot be built with valence bonds, the weaker oxygen–oxygen contacts as the net edges should be considered. The main problem at this stage is that the natural tiling is unambiguously determined by the net topology, therefore, treatment of different sets of non-valence interactions gives rise to different tilings.

(ii) Building natural tiling and dual nets for the framework net according to the rules of Blatov *et al.* (2007).

Let us analyze how the natural tiling changes when weak interatomic contacts are added to the initial valence-bonded net using β-Li_2SO_4 as an example. If we ignore the bonds with Li atoms, the structure is composed of isolated SO_4 tetrahedra (Ivanov-Schitz & Murin, 2000). To obtain a three-periodic net one has to link them by non-valence contacts. We have

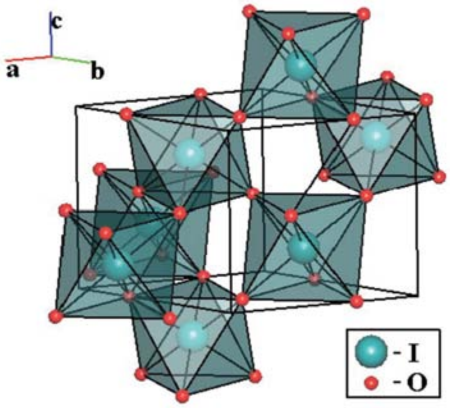
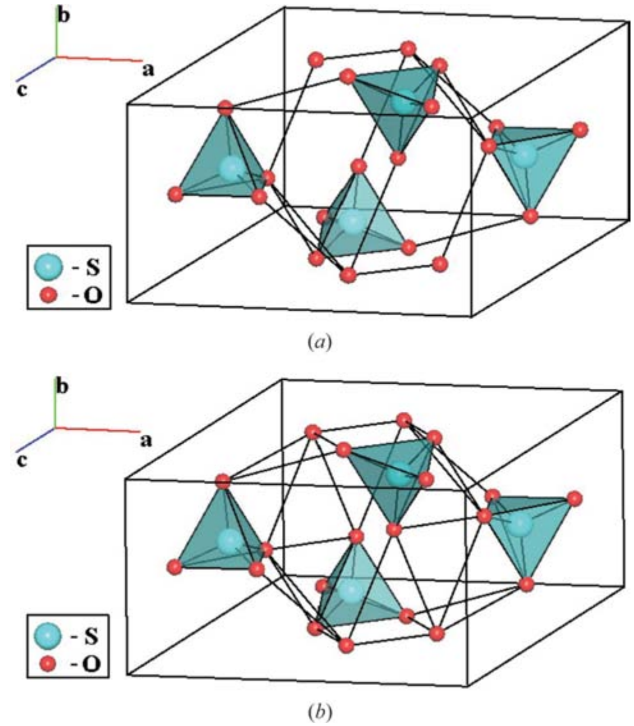


Figure 4
Framework in the α-$LiIO_3$ crystal structure.



(*a*)

(*b*)

Figure 5
The nets in the crystal structure of β-Li_2SO_4 built with non-valence contacts (*a*) $R(O-O) \leq 3.2$ Å and (*b*) $R(O-O) \leq 3.3$ Å.

---

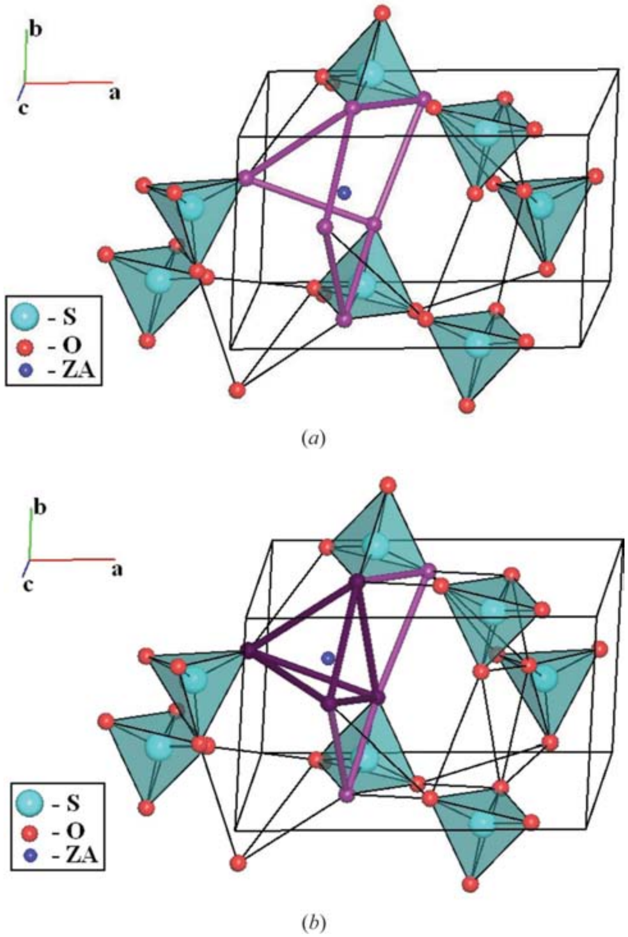
[3] In the literature, the term *n*-periodic is often confused with the term *n*-dimensional, but they are quite different. A net can be, say, two-periodic but three-dimensional *etc.*; see Delgado-Friedrichs & O'Keeffe (2005) for details.

Table 1
Shortest distances (Å) between Li atoms and nodes (ZA) of dual nets in the crystal structure of β-Li$_2$SO$_4$.

	Shortest distance Li—*ZA* (Å) in the net with			
Li atoms	$R(\mathrm{O-O}) \le 3.2$ Å	$R(\mathrm{O-O}) \le 3.3$ Å	$R(\mathrm{O-O}) \le 3.4$ Å	$R(\mathrm{O-O}) \le 3.5$ Å
Li1	0.61	0.07	0.07	0.07
Li2	1.49	0.95	0.95	0.13

constructed four nets including the contacts $R(\mathrm{O-O}) \le 3.2$, 3.3, 3.4 or 3.5 Å. For all the nets natural tilings and dual nets were also found.

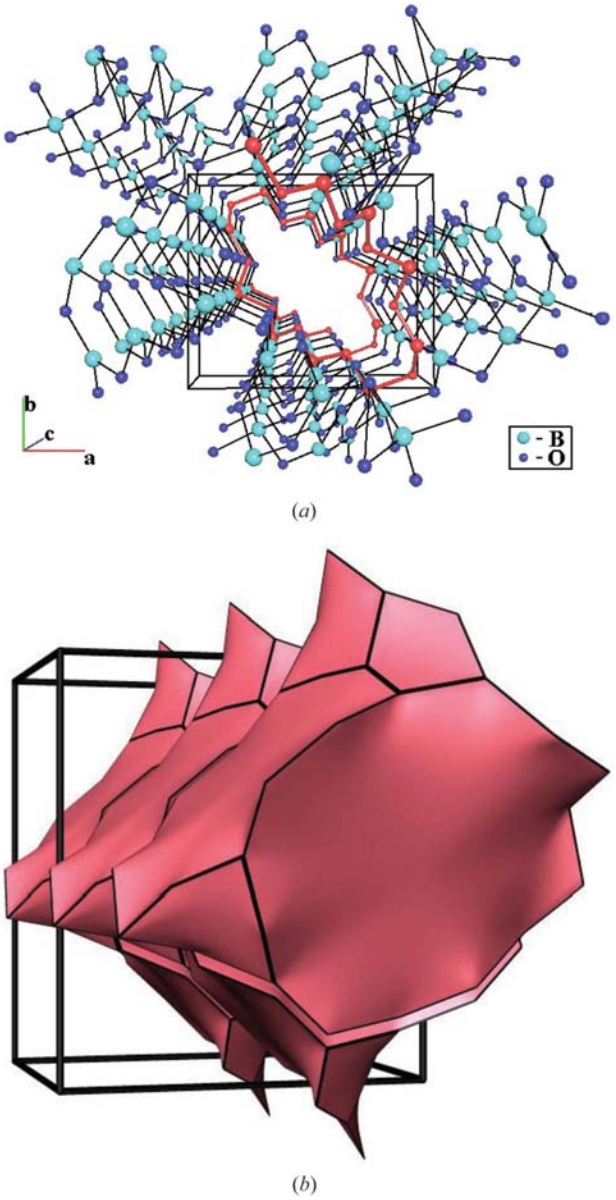
Let us compare the results obtained for the first [$R(\mathrm{O-O}) \le 3.2$ Å] and second [$R(\mathrm{O-O}) \le 3.3$ Å] nets (Fig. 5). The natural tiling for the first net consists of seven types of tiles; its signature is $2[4.5^2] + 8[3^4] + 2[3^2{\cdot}4^2] + 2[3^2{\cdot}5^2] + 2[3.5.7^2] + 2[3.5^3{\cdot}6^2] + [4^2{\cdot}7^4]$. One of them embraces the allocation place of the Li1 atom (the distance between the tile center, ZA, and the Li1 atom is 0.61 Å, Fig. 6*a*). The second net admits the natural tiling $4[4.5^2] + 10[3^4] + 8[3^2{\cdot}5^2] + [3^2{\cdot}5^6] + [3^{10}{\cdot}4^2{\cdot}5^2]$ with five types of tiles. Since the number of edges and rings increases from the first net to the second owing to additional interatomic contacts, one of the tiles $[4.5^2]$ of the first net is split into three parts: new tile $[3^4]$ and two fragments $[3^2{\cdot}4]$ belonging to other tiles (Fig. 6*b*). The distance from the center of the tile $[3^4]$ to the Li1 atom is 0.07 Å, *i.e.* the tile fits the lithium position much better. A further complication of the nets with $R(\mathrm{O-O}) \le 3.4$ Å and $R(\mathrm{O-O}) \le 3.5$ Å gives rise to an even more detailed description of voids (Table 1); in fact, adding new edges to the initial net results in splitting large cavities into smaller fragments. The channels in the more complicated net are also more detailed; they are represented by chains of edges of the corresponding dual net. In fact, this



(*a*)

(*b*)

Figure 6
(*a*) Tile $[4.5^2]$ (violet) and (*b*) tile $[3^4]$ (deep violet) built for the nets shown in Figs. 5(*a*) and (*b*), respectively. ZA balls coincide with the tiles centers.



(*a*)

(*b*)

Figure 7
(*a*) Three-periodic framework $[\mathrm{B_3O_5}]^-$ in the crystal structure of Li[B$_3$O$_5$]; the helical chain forming the [001] channel is shown in red; (*b*) a stacking of tiles that visualizes the channel.

complication breaks the channel lines by adding new nodes to them; as a result, a crooked channel can be better represented.

If the valence-bonded net is three-periodic, but does not admit any tiling, the addition of some non-valence contacts can fix the problem. Thus, the $[B_3O_5]^-$ framework in $Li[B_3O_5]$ is three-periodic (Ivanov-Schitz & Murin, 2000), however, the [001] channels are formed by infinite helical chains of B—O bonds (Fig. 7*a*); there are no 'windows' (strong rings) in this direction and, hence, finite cavities (tiles) cannot be separated in the channels. However, even adding weak O—O interactions with $R < 3.0$ Å allows the channels to be represented as a sequence of disk-shaped tiles; the corresponding tiling is isohedral (it consists of one type of tile, $[5^2.6^4.13^2.15^2]$, where 13- and 15-rings depict the 'windows' inside the channel, Fig. 7*b*). Let us emphasize that the separation of finite cavities (tiles) is relative: indeed, there are infinite cavities (channels) in the structure, and splitting them into finite parts is merely a method for visualizing. The corresponding dual net represents the channels as infinite chains of the edges conforming to 13- and 15-rings of the initial net.

As was mentioned in §2, when we consider all the non-valence contacts, the results should coincide with the Voronoi–Dirichlet approach. However, in this case the initial net becomes highly coordinated, the number of rings increases sharply, and the procedure of tiling construction becomes time-consuming and useless.

(iii) Simplifying the dual net by removing those cavities (nodes) and channels (edges) that cannot provide the transport of lithium cations owing to geometrical restrictions. To find such channels we have applied the criterion proposed by Anurova *et al.* (2008): cavities and channels with radii not exceeding 1.38 and 1.8 Å, respectively, should be removed. After removing the nodes and edges according to these criteria, one should remove the nodes of the dual net, in which only one edge or no edges meet, since the corresponding voids cannot participate in migration paths. As a result a subnet of the dual net has been obtained, and it is the subnet that describes the migration map. Thus, simplifying the four dual nets describing the void space in the β-Li_2SO_4 crystal structure at different R(O—O) gives rise to three-periodic migration maps. This conforms to the experimental data and the results of the Voronoi–Dirichlet partition method (Anurova *et al.*, 2008), but the system of voids and channels is detailed differently in the two methods (Figs. 8*a*–*c*). In special cases, the simplified dual net can be split into finite isolated graphs or may even disappear; this indicates that the ions cannot migrate in the structure.

Table 2
Three crystal structures of lithium fast-ion conductors for which the periodicities of the Voronoi–Dirichlet graph and the dual net are different (for the complete list of 105 studied crystal structures see supplementary materials).

	Periodicity		
Compound	Voronoi–Dirichlet graph	Dual net	ICSD collection code
α-LiB_3O_5	1	3	39106
$Li_2W_2O_7$	1	2	1897

Thus, if information on only the periodicity of the migration map is required, the simplest three-periodic net built with only valence contacts can be used. If the allocation places of ions should be determined, the net can be complicated by a successive accounting of the strongest non-valence contacts.

As another example let us consider the crystal structure of α-$LiIO_3$ that possesses rather high ionic conductivity (Ivanov-Schitz & Murin, 2000). The anisotropy of conductivity was experimentally proved; there are tunnels passing along [001] (Fig. 9*a*). The migration map obtained by the Voronoi–Dirichlet partition method (Anurova *et al.*, 2008) consists of one-periodic [001] channels, which agrees with the experi-

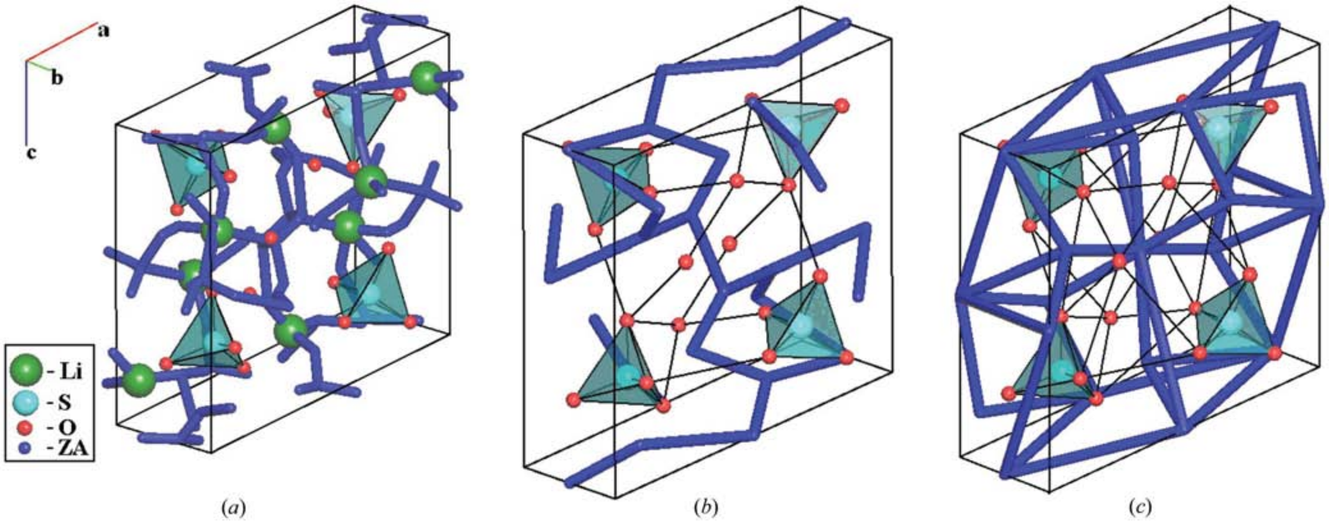


Figure 8
(*a*) The migration map in the crystal structure of β-Li_2SO_4 obtained with the Voronoi–Dirichlet partition, and the dual nets corresponding to three-periodic nets of SO_4 tetrahedra connected by the links with (*b*) R(O—O) ≤ 3.2 Å and (*c*) R(O—O) ≤ 3.5 Å.

mental data (Fig. 9*b*). As was mentioned above, the framework in this structure is formed by IO_6 octahedra sharing vertices, so there is no need to consider non-valence contacts while constructing the net. The natural tiling $[8^3] + [8^3{\cdot}12^2]$ consists of two types of tiles and, hence the dual net is binodal. After simplifying the dual net it becomes one-periodic and corresponds to [001] channels (Fig. 9*c*).

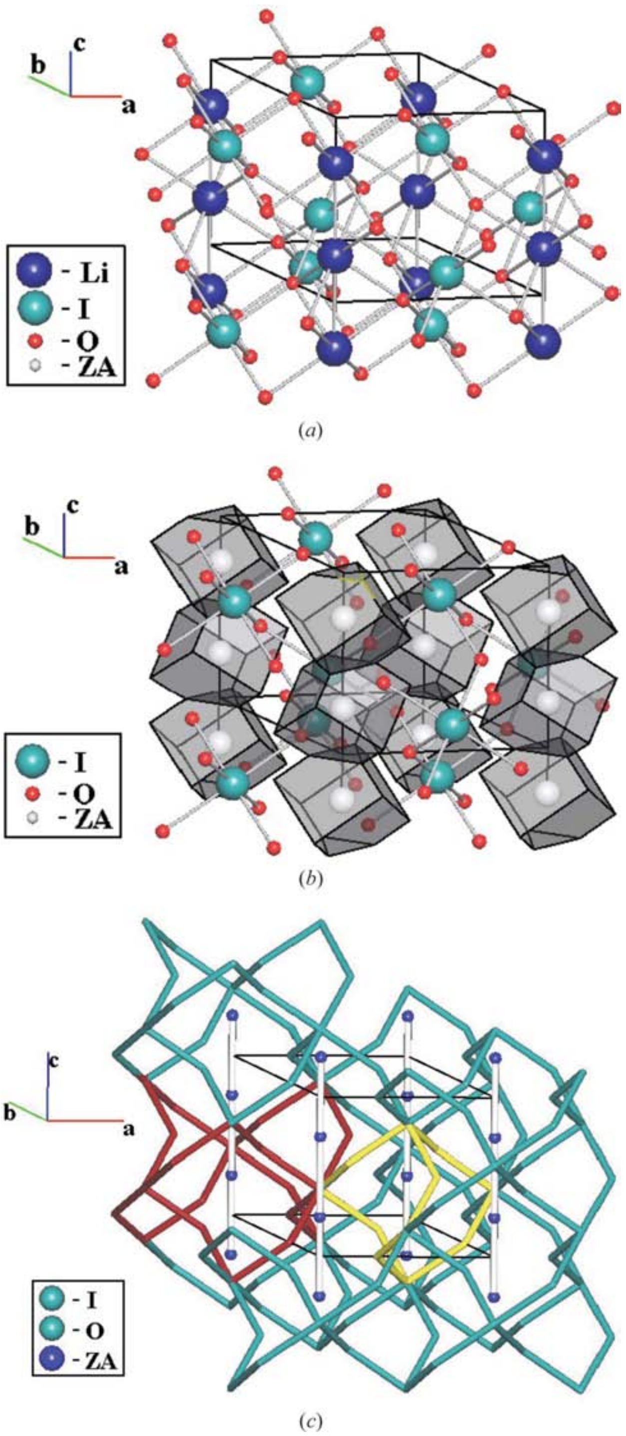


Figure 9
α-$LiIO_3$: (*a*) crystal structure and (*b*) migration map obtained with the Voronoi–Dirichlet partition; the vertices of the Voronoi–Dirichlet polyhedra coincide with lithium cations, the [001] channels are given in the polyhedral representation (Blatov & Shevchenko, 2003); (*c*) framework net with tiles $[8^3{\cdot}12^2]$ (red) and $[8^3]$ (yellow). The nodes ZA of the simplified dual net coincide with the centers of the tiles $[8^3{\cdot}12^2]$ as well as with Li atoms.

This algorithm was implemented into the program *ADS* of the *TOPOS* package. Recently, the Voronoi–Dirichlet partition method was also realised within *TOPOS* (Anurova *et al.*, 2008) which allowed us to use both methods and to compare their results when studying void space in crystals.

4. Analysis of migration maps in ternary compounds $Li_aX_bO_z$ with the tiling method

As was mentioned above, with the Voronoi–Dirichlet partition method, Anurova *et al.* (2008) found 105 crystal structures containing infinite (one-, two- or three-periodic) migration maps among 822 ternary $Li_aX_bO_z$ compounds. Below we compare these results with the migration maps built for the 105 crystal structures using the tiling method to compare the two approaches. We emphasize that for 'dense' structures where the Voronoi–Dirichlet partition method does not find cavities available for migrating cations and hence no conductivity, the tiling method also leads to the same conclusion. Checking 35 structures randomly chosen from the 822–105 = 717 non-conducting ternary compounds proved this statement.

Natural tilings were found for 90 crystal structures; for the structures without a three-periodic valence-bonded net we added the shortest non-valence O—O contacts until a three-periodic net was formed. In the remaining 16 cases natural tilings could not be constructed in a reasonable time; there is a high probability that these nets have no natural tiling. This reveals one more disadvantage of the tiling method: some nets do not admit tilings or have topology which is too complicated (large transitivity *pqrs* and/or high coordination). At the same time, the complexity of the net topology is insignificant in the Voronoi–Dirichlet partition method.

After simplifying the dual nets for the 90 natural tilings we found that the periodicity of the migration paths (dimensionality of conductivity) coincides with the results of the Voronoi–Dirichlet approach in all but two cases; in both exceptions the dual net has a higher periodicity than the Voronoi–Dirichlet graph (Table 2). For the crystal structure of $Li_2W_2O_7$ the tiling method gives a two-periodic migration map (100) consisting of distinct one-periodic chains interconnected by long (7.1 Å) rectangular channels [010] (Fig. 10*a*) with an effective radius of 1.91 Å. The Voronoi–Dirichlet partition method ignores these channels, since it splits each of them into two triangular elementary channels (Fig. 10*b*) of a smaller effective radius (1.69 Å). In this case we can expect a strong anisotropy of conductivity: even if it is two-dimensional, the conductivity magnitudes along [010] and [001] should be quite different. The same situation occurs in α-LiB_3O_5: one-periodic channels [001] are interconnected in the tiling dual net by long (4.5 Å) links that result in a three-dimensional migration map (Fig. 10*c*). The links correspond to rectangular channels of effective radius 1.92 Å, while in the Voronoi–Dirichlet graph the link is represented by two triangular elementary channels

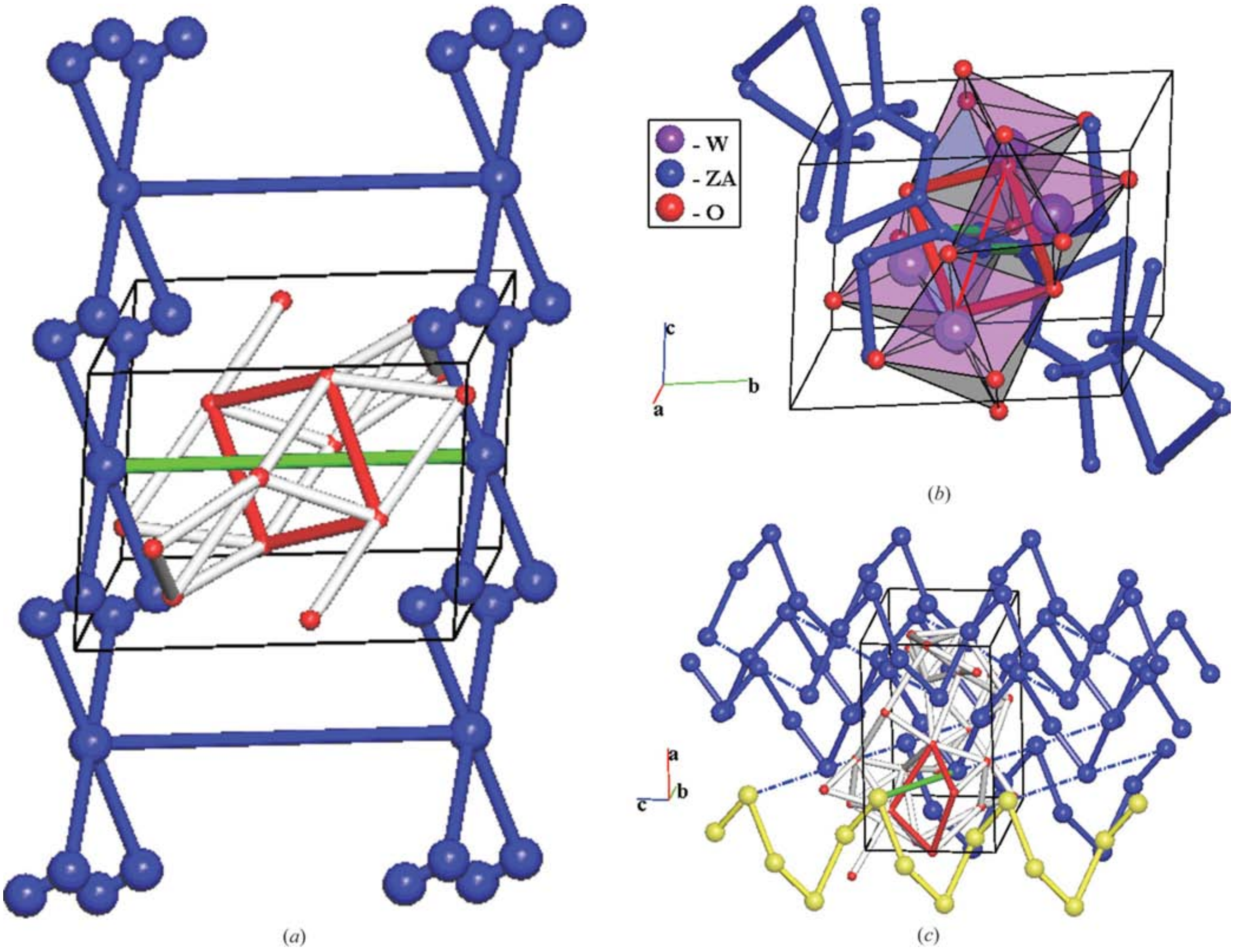


Figure 10
Fragments of (*a*) dual net of natural tiling and (*b*) the Voronoi–Dirichlet graph in the crystal structure of $Li_2W_2O_7$. Rectangular 'window' corresponding to the [010] channels is shown in red, the lines of one rectangular channel (*a*) and two triangular channels (*b*) passing through the 'window' are shown in green. (*c*) Dual net of natural tiling in the crystal structure of α-LiB_3O_5. The links between channels [001] are shown as dashed lines, one of the links, passing through the red rectangular 'window', is green; one [001] channel is yellow.

of radii 1.67 and 1.73 Å. Obviously, the conductivity magnitude along [001] is expected to be larger than in other directions. Thus, the tiling method more correctly describes large polygonal 'windows' in the net.

5. Conclusions

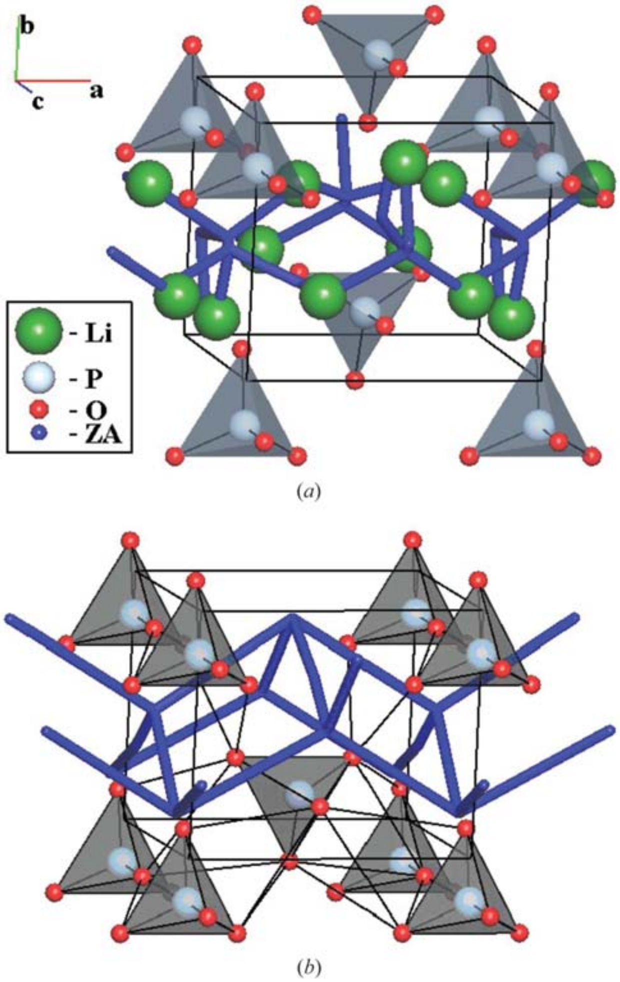
Let us summarize the main advantages and restrictions of both methods in exploring the void space in crystals.

(i) Despite different algorithms, both methods describe the same void space and, hence, have common features. In particular, the number of voids obtained with the tiling method is never larger than obtained with the Voronoi–Dirichlet partition. The reason is that the large and/or strongly distorted cavities can be represented by a conglomerate of vertices of Voronoi–Dirichlet polyhedra, while in the tiling method any cavity contains a single node of the dual net. At the same time, the complete coincidence of the migration maps obtained by both methods occurs only occasionally (we have found seven such cases in the same group of Li_8MO_6 compounds, see supplementary materials[4]).

(ii) Ordinarily, the tiling method gives a simpler conductive pattern which is easier to interpret, whereas the Voronoi–Dirichlet partition is better able to identify the most probable positions for mobile cations and describes the crooked channels in more detail. Thus, in γ-Li_3PO_4 the Voronoi–Dirichlet graph accurately defines the positions of lithium cations and the paths of their motion, while the dual net only outlines the channel system (Fig. 11). We have not found conflicting examples, where one method would predict high conductivity while the other method would not. The methods occasionally result in contradictory conclusions regarding the dimensionality of conductivity; this can indicate a high anisotropy of

---

[4] Supplementary data for this paper are available from the IUCr electronic archives (Reference: HW5002). Services for accessing these data are described at the back of the journal.



(*a*)

(*b*)

Figure 11
γ-Li_3PO_4: (*a*) migration map obtained with the Voronoi–Dirichlet partition, and (*b*) dual net built for the three-periodic net of PO_4 tetrahedra connected by the oxygen–oxygen links with $R \leq 3.2$ Å.

conductivity. Such cases require careful experimental verification.

(iii) For some complicated nets it is very time-consuming to find the natural tiling; moreover, some nets do not admit natural tiling, whereas a Voronoi–Dirichlet partition can be constructed for the crystal structure of any compound in reasonable time.

(iv) When dealing with microporous structures that contain large cavities, such as zeolites, the Voronoi–Dirichlet graph can contain conglomerates of vertices in the centers of the cavities. These conglomerates do not have a clear physical interpretation and require a special procedure for contracting (Blatov & Shevchenko, 2003), while the tiling method provides the single node of the dual net for each cavity.

In summary, we would recommend the Voronoi–Dirichlet partition method for detailed exploration of the void space in the substances containing the pores of atom size (1–5 Å) and small, preferably trigonal, windows. The tiling method can be used for micro- and mesoporous substances as well as for structures with small pores if a more schematic description is suitable. If possible, both methods should be used and their results compared; all contradictions should be carefully explored.

This work was supported by a Cariplo Fellowship to V. A. Blatov issued by Cariplo Foundation & Landau Network, Centro Volta (Como, Italy). We are grateful to Professor D. M. Proserpio for fruitful discussions on applications of the tiling approach, as well as to an anonymous referee whose comments helped us to improve the method.

References

Adams, S. & Swenson, J. (2002). *Solid State Ion.* **154–155**, 151–159.
Anurova, N. A., Blatov, V. A., Ilyushin, G. D., Blatova, O. A., Ivanov-Schitz, A. K. & Dem'yanets, L. N. (2008). *Solid State Ion.* **179**, 2248–2254.
Blatov, V. A. (2006). *IUCr CompComm Newsl.* **7**, 4–38.
Blatov, V. A., Delgado-Friedrichs, O., O'Keeffe, M. & Proserpio, D. M. (2007). *Acta Cryst.* A**63**, 418–425.
Blatov, V. A., Ilyushin, G. D., Blatova, O. A., Anurova, N. A., Ivanov-Schits, A. K. & Dem'yanets, L. N. (2006). *Acta Cryst.* B**62**, 1010–1018.
Blatov, V. A. & Shevchenko, A. P. (2003). *Acta Cryst.* A**59**, 34–44.
Delgado-Friedrichs, O. & O'Keeffe, M. (2005). *J. Solid State Chem.* **178**, 2480–2485.
Delgado Friedrichs, O., O'Keeffe, M. & Yaghi, O. M. (2003). *Acta Cryst.* A**59**, 22–27.
Ivanov-Schitz, A. K. & Murin, I. V. (2000). *Solid State Ionics*. St. Petersburg Press. (In Russian.)
Küppers, H., Liebau, F. & Spek, A. L. (2006). *J. Appl. Cryst.* **39**, 338–346.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Thomas, N. W. (1991). *Acta Cryst.* B**47**, 588–597.