

Beryllsilicate Frameworks and Zeolites

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Abstract: Using inspiration derived from studying naturally occurring minerals, a series of framework beryllsilicates have been synthesized under hydrothermal conditions. These include two new zeolite topologies, a unique layered beryllsilicate, and beryllsilicate analogues of numerous aluminosilicate zeolites. Materials with the structure of the rare zeolite mineral nabesite have been synthesized for the first time, including both sodium and potassium derivatives. The structural chemistry of these beryllsilicate frameworks is discussed with reference to the networks of linked tetrahedra, which include the first instance of pentagonal, two-dimensional Cairo-tiling of silicate tetrahedra in one of the new zeolite topologies, their porosity, and their thermal stability.

1. Introduction

The synthesis of new microporous materials, in terms of both composition and framework topology, is an important target given their widespread applications in areas as diverse as catalysis, gas adsorption, including separation and storage, and ion exchange. As well as control of the pore size, factors such as site acidity and thermal stability (for catalysis), weight (for gas storage), and ion-exchange capacities are important considerations. The aluminosilicate zeolites, for example **ZSM-5**¹ and zeolite A (**LTA**),² remain the most commercially important functional materials of this type with their excellent chemical and thermal stabilities, though incorporation of alternative species into tetrahedral frameworks often yields improved functionality and new structure types. Thus, aluminophosphates are used widely in basic catalysis conditions,³ and transition-metal-doped zeolites have applications in redox catalytic reactions.⁴ One related area of high current research activity concerns the development of metal–organic frameworks (MOFs); examples of the compounds synthesized under this heading include MIL-101,⁵ covalent organic frameworks (COFs),⁶ zeolitic imidazolate frameworks (ZIFs),⁷ and lightweight beryllium-based MOFs.⁸ Potential applications for these MOF-type compounds revolve mainly around their gas and molecular adsorption properties (in hydrogen storage, carbon dioxide sequestration, and drug delivery), as their chemical and thermal

stability is distinctly lower than that of pure inorganic frameworks, making them less suitable for applications involving high temperatures (e.g., catalysis) or chemically harsh conditions (e.g., radionuclide ion exchange or gas storage in acidic or wet conditions).

For many applications, new inorganic framework materials with specific compositional and structural features are required; so for gas storage, lightweight systems are desirable, while for catalytic function, a wide variety of specific structural and compositional features have been identified as beneficial, such as Brønsted and Lewis acid sites. Beryllate-based frameworks offer both lightness and the propensity for unusual structural features, such as three-rings, but very little synthesis work has been undertaken using this building unit. Naturally occurring, beryllium-containing zeolites, include lovdarite ($\text{Na}_{12}\text{K}_4\text{[Be}_8\text{Si}_{28}\text{O}_{72}] \cdot 18\text{H}_2\text{O}$)⁹ and nabesite ($\text{Na}_2\text{BeSi}_4\text{O}_{10} \cdot 4\text{H}_2\text{O}$), and several related beryllium-containing frameworks have been discovered.¹⁰ Two synthetic beryllsilicate zeolite topologies have been very briefly described¹¹ whose frameworks contain three-rings, a fairly rare feature of topologies formed from linked tetrahedra, but known to have excellent catalytic properties. Two other synthetic beryllsilicate frameworks, gismondine¹² and lovdarite,¹³ have also been reported.

Beryllium and its compounds are widely used in applications such as lightweight alloys for aircraft structures and sports equipment, as electronic components in optical scanners and switches/relays, and in areas such as dental bridges and jewelry (e.g., emeralds), that is, in applications where low weight, refractory properties, and chemical toughness are desirable properties. *The oral toxicity of beryllium is relatively low, as*

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Table 1. Natural and Synthetic Nabesites

	nabesite type material (NAB)	synthesized Na-nabesite, LSJ-23	synthesized K-nabesite, LSJ-2
chemical formula	$\text{Na}_8[\text{Be}_4\text{Si}_{16}\text{O}_{40}] \cdot 12\text{H}_2\text{O}$	$\text{Na}_{5.28}[\text{Be}_{2.64}\text{Si}_{17.36}\text{O}_{40}] \cdot 12.5\text{H}_2\text{O}$	$\text{K}_8[\text{Be}_4\text{Si}_{16}\text{O}_{40}] \cdot 12\text{H}_2\text{O}$
crystal system	orthorhombic	orthorhombic	orthorhombic
space group	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 18)	$C222_1$ (No. 20)
cell parameters	$a = 9.748 \text{ \AA}$ $b = 10.133 \text{ \AA}$ $c = 11.954 \text{ \AA}$ $V = 1180.8 \text{ \AA}^3$	$a = 9.6889(4) \text{ \AA}$ $b = 10.0184(3) \text{ \AA}$ $c = 11.8966(4) \text{ \AA}$ $V = 1154.8 \text{ \AA}^3$	$a = 9.6631(4) \text{ \AA}$ $b = 12.2031(4) \text{ \AA}$ $c = 9.9913(4) \text{ \AA}$ $V = 1178.2 \text{ \AA}^3$
Si:Be Ratio	4:1	6.56:1	4:1

the element is very poorly absorbed from the stomach and intestines; LD50 (rats) values for most beryllium salts are in the range 20–200 mg/kg. The major toxic properties associated with beryllium derive from inhalation over a long term of lightweight particles, such as BeO, and this is avoided in the numerous current applications. The inclusion of beryllium into highly crystalline frameworks offers the potential to produce porous, lightweight structures with high thermal and chemical stability and, as a divalent cation, high Brønsted acidity.

As part of a program of work directed at deriving inspiration for new functional materials from studies of naturally occurring minerals, we have targeted framework beryllium compounds.¹⁴ During this work, we have recently synthesized several new berylliosilicate frameworks, including two new zeolite topologies, a layered berylliosilicate, the first synthetic variants of the mineral nabesite, and several beryllium-containing zeolites of known topologies, but previously unknown as berylliosilicate frameworks.

2. Experimental Methods

All berylliosilicate frameworks were synthesized using hydrothermal conditions by reaction of solutions containing beryllium and silicon sources [typically $\text{Be}(\text{OH})_2$ (City Chemical) and colloidal silica (LuDOX), $\text{SiO}_2 \cdot n\text{H}_2\text{O}$] in a strongly basic solution of an alkali metal hydroxide and a template alkylammonium ion. Due to the toxic nature of the beryllium hydroxide powder used (see Introduction), it was weighed and handled in a glovebox. The resulting solutions/gels were heated in the range 130–240 °C in 23 mL Parr, Teflon-lined hydrothermal bombs for typically 48 h. The reaction vessels were then removed from the oven and allowed to cool, and the products were retrieved by vacuum filtration. The products, mixtures of white powder and transparent single crystals, were washed with distilled water and dried at 80 °C. A systematic investigation of berylliosilicate formation as a function of Si:Be: $\text{H}_2\text{O}:\text{M}^{n+}$ ($\text{M}^{n+} = \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{Sr}^{2+}, \text{Ba}^{2+}$, and various alkylammonium cations) was undertaken (see Supporting Information, Table S1), and this generated several new compositions and structures (Tables 1–3, below). The series of products was initially labeled LSJ-*n* (Leverhulme–Southampton Joint project, reaction number *n*). We also studied high water content systems and have reproduced the syntheses of other reported berylliosilicate topologies, including OSB and OSO.¹¹

Single crystals suitable for structural analysis by X-ray diffraction were isolated from the reaction products. Data were collected using a Bruker Kappa CCD with rotating anode Mo K α radiation at 120 K. The structures were solved by direct methods followed by successive difference Fourier methods, with all calculations performed using the software program SHELX. The crystallographic results are summarized in Tables 1–3, and full details (including X-ray crystallographic files in CIF format) are given in the Supporting Information. For many of the zeolite topologies analyzed, considerable disorder in the framework beryllium and

silicon distribution was coupled with that of the nonframework cations and water molecules over partially occupied sites; however, in all cases the zeolite framework topology was well defined from these refinements.

Thermal analysis data were collected using a Stanton-Redcroft simultaneous DTA/TGA STA1500 systems, and SEM micrographs were obtained using a Jeol JSM-5910. Surface area measurements were undertaken using a Micrometrics Gemini 2375 surface area analyzer with molecular nitrogen at 77 K. Samples with new topologies, LSJ-10 and LSJ-39, were converted to porous systems for surface area analysis by ion exchange with three aliquots of aqueous 1 M NH_4Cl at 50 °C for 24 h and subsequent thermal treatment at 600 °C for 2 h.

3. Results

3.1. Nabesite. Nabesite (nat-NAB, named after its chemical composition: $\text{Na}_2\text{BeSi}_4\text{O}_{10} \cdot 4\text{H}_2\text{O}$) is a very rare berylliosilicate mineral discovered by Petersen et al. in 1999 at a unique locality on the Kvanefjeld Plateau, South Greenland, in the Ilímaussaq alkaline complex¹⁰ (Table 1).

Beryllium and silicon atoms are ordered with the SiO_4 tetrahedra forming sheets consisting of a combination of four- and eight-membered rings; these sheets are linked to each other via $[\text{BeO}_4]$ groups in two three-rings to give a spiro-5 arrangement as a secondary building unit which forms the framework. Channels within the framework are occupied by sodium ions approximately octahedrally coordinated to the framework oxygen atoms and H_2O molecules (Figure 1a).

Synthetic potassium and sodium nabesites (K-NAB, product of reaction LSJ-2, and Na-NAB, from LSJ-23) obtained in this work have the same framework topology as the natural mineral, but because of differences in the framework Be:Si ratio, and therefore levels of extraframework cations, and in the preferred coordination geometries of these cations, there are modifications to the detailed structural features. Comparison of nat-NAB and synthetic Na-NAB shows that our synthetic material has a slightly lower beryllium content, such that the central spiro-5 tetrahedral site is occupied by Be:Si in the ratio of 2:1 rather than purely by beryllium. This decreases the framework charge, reduces the level of sodium ions in the pores, and results in a significantly smaller unit cell (2.2% smaller for synthetic Na-NAB); the level of water incorporated into the pores to coordinate to sodium also falls as a consequence. In nat-NAB (Figure 1a), the sodium ions lie slightly off center in the nine-rings coordinated to three framework oxygen atoms (two from one BeO_4 tetrahedron) and three water molecules. Sodium is located on similar sites in Na-NAB and nat-NAB (Figure 1b), but these are only occupied at about the two-thirds of the level in Na-NAB, probably reflecting occupation of only sites adjacent to BeO_4 tetrahedra. A further effect of this disordering is to remove the 2_1 screw axis along the *c*-lattice direction.

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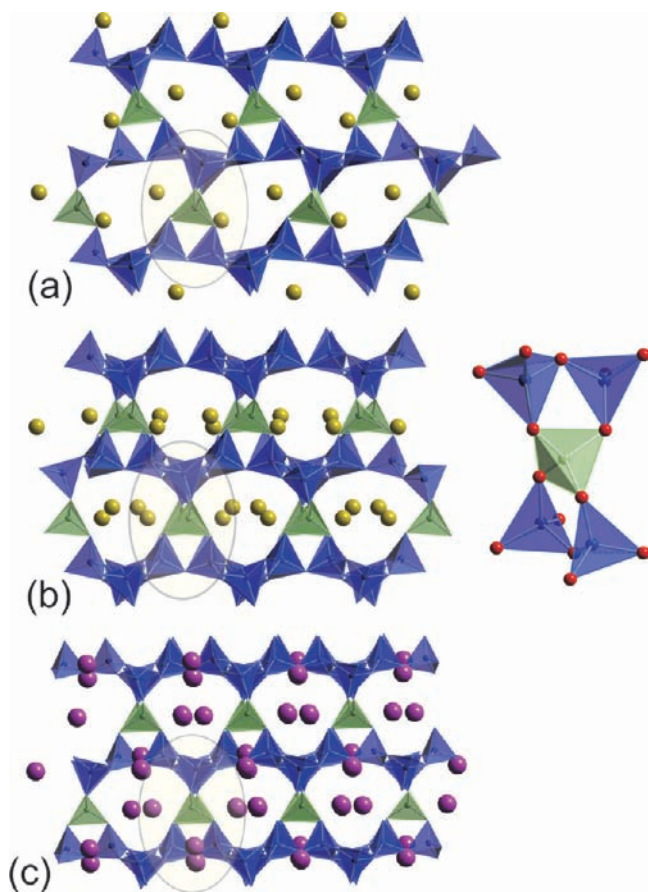


Figure 1. Comparison of the nabesite framework topologies and extra-framework cation positions. Top to bottom: natural Na-NAB, synthetic Na-NAB, and synthetic K-NAB. SiO₄ tetrahedra, blue; BeO₄ tetrahedra, pale green; sodium, yellow; and potassium, magenta. Inset: the BeO₄-centered spiro-5 ring that connects the silicate layers as highlighted in each of the NAB structures.

In synthetic K-NAB, the lattice parameters show a marked expansion in the *c* axis and minor contraction in the *a* and *b* directions compared with nat-NAB (*a*, *b*, *c* for the type material NAB = *a*, *c*, *b* for LSJ-2). The framework and pore symmetry also increases. Potassium ions occupy two distinct sites in the structure that are very different from those occupied by sodium in Na-NAB and reflect its preference for higher coordination numbers (Figure 1c). One, K1, is situated in the eight-membered rings coordinated to four oxygen atoms of SiO₄ tetrahedra and three water molecules, while K2 is sited in the center of the larger cavity formed from the intersection nine-membered-ring channels — again coordinated to four framework oxygen atoms of framework SiO₄ tetrahedra and, in this case, four water molecules.

3.2. Gismondine. The gismondine (GIS) topology is common to the minerals gismondine, garronite, gobbinsite, and amicitte. Several synthetic non-aluminosilicate variants have been reported in the literature, for example, the beryllphosphates [H₃N(CH₂)₂NH₃]_{0.5}[BePO₄]¹⁵ and (C₄H₁₂N₂)Be₂P₂O₈¹⁶ and the cobaltphosphate [H₃N(CH₂)₂NH₃]_{0.5}[CoPO₄]¹⁷ as well as novel GIS frameworks containing three distinct tetrahedral atom types,

[Al/Co/P],¹⁸ [Zn/Ga/P],¹⁹ and [Zn/B/P].²⁰ Gismondine, exemplified by the type material Ca(AlSiO₄)₂·H₂O²¹ with an Al:Si ratio of 1:1, shows that this framework can support a relatively high negative charge.

The beryllsilicate GIS obtained in this work (Table 2, LSJ-13; Figure 2), of composition Na₈[Be₄Si₁₂O₃₂]·8H₂O, was found to have a Si:Be ratio of 3:1, with beryllium randomly distributed over the two distinct T-sites in the structure. The unit cell volume (931 Å³) is significantly smaller than that of natural aluminosilicate gismondines, as would be expected as a result of the decrease in average T–O distances with Be–O (~1.62 Å) partially replacing Al–O (~1.73 Å).

3.3. Analcime. Analcime (ANA) is a well-known natural zeolite; its ideal chemical formula is NaAlSi₂O₆·H₂O, and it has a channel structure formed from distorted eight-membered rings. As well as the archetypal aluminosilicate example of the mineral analcime,²² numerous other compositions with this structure type are known, including [Ga-Ge-O]-ANA²³ and [Zn-As-O]-ANA.²⁴ Beryllium has been previously incorporated into the ANA topology as the beryllphosphate K-[Be-B-P-O]-ANA,²⁵ and it is also known as the anhydrous beryllsilicate pollucite, Cs-[Be-Si-O]-ANA, produced via a high-temperature reaction.²⁶ A hydrated ANA [Be–Si] zeolite framework has not previously been reported; Ueda and Koizumi originally described the synthesis of a beryllsilicate purported to have the analcime structure, but they did not undertake any structural analysis.²⁷

The beryllsilicate ANA obtained in this work, of composition Na₂₅Si_{35.5}Be_{12.5}O₉₆·16H₂O (Table 2, LSJ-7; Figure 2), has a single tetrahedral site Si/Be site with a random distribution of Si and Be in a ratio close to 3:1. The beryllsilicate unit cell shows a marked contraction in comparison with NaAlSi₂O₆·H₂O.

3.4. Phillipsite. The phillipsite (PHI) framework is constructed of layers formed from eight- and four-rings linked in the third dimension by four-rings, forming double crankshafts with the four-rings of the layer.²⁸ While the aluminosilicate PHI zeolite occurs naturally in large deposits, this topology is rarely found for non-aluminosilicate zeotypes, and there are only two reported compositional derivatives of this framework type: [Al-Co-P-O]-PHI¹⁹ and DAF-8.²⁹ The beryllsilicate PHI material obtained in this work, of composition K_{~5}Si_{13.32}Be_{2.68}O_{32.8}·*x*H₂O, (Table 2, LSJ-40; Figure 2), has a Si:Be ratio of 4.9:1, somewhat higher than that found for the other previously known framework topologies now obtained as beryllsilicates in this work. The extraframework electron density was distributed fairly evenly along the centers of the main channels defined by the eight-

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Table 2. New Beryllsilicate Compositions for Known Synthetic Zeolite Topologies

chemical formula	gismondine		analcime		phillipsite		merlinoite	
	aluminosilicate type material (GIS)	synthesized beryllsilicate gismondine, LSJ-13	aluminosilicate type material (ANA)	synthesized beryllsilicate analcime, LSJ-7	aluminosilicate type material (PHI)	synthesized beryllsilicate phillipsite, LSJ-40	aluminosilicate type material (MER)	synthesized beryllsilicate merlinoite, LSJ-47
crystal system	[Ca ²⁺ ₄ (H ₂ O) ₁₆][Al ₈ Si ₈ O ₃₂]	N ₈₄ [Be ₈ Si ₁₂ O ₃₂]·8H ₂ O	[Na ⁺ ₁₆ (H ₂ O) ₁₆][Al ₁₆ Si ₁₂ O ₉₆]	Na ₂₅ Si _{13.5} Be _{12.5} O ₉₆ ·16H ₂ O	[K ⁺ ₂ (Ca ²⁺ , Na ⁺) ₂](H ₂ O) ₁₂][Al ₆ Si ₁₀ O ₃₂]	[K ⁺ ₃ (Ca ²⁺ ₂ (H ₂ O) ₂₄][Al ₆ Si ₁₂ O ₆₄]	(K ⁺ _{~8} (NEt ₄) _{~2})[Be _{6,9} Si _{25,1} O ₆₄]	
space group	monoclinic	tetragonal	cubic	cubic	monoclinic	orthorhombic	tetragonal	
cell parameters	<i>a</i> = 9.832 Å <i>b</i> = 10.019 Å <i>c</i> = 10.635 Å γ = 92.417° <i>V</i> = 1047 Å ³	<i>a</i> = 9.8276(4) Å <i>b</i> = 9.8276(4) Å <i>c</i> = 9.6372(7) Å <i>V</i> = 931 Å ³	<i>a</i> = 13.72 Å <i>V</i> = 2582 Å ³	<i>a</i> = 13.318(1) Å <i>V</i> = 2362 Å ³	<i>a</i> = 9.865 Å <i>b</i> = 14.300 Å <i>c</i> = 8.668 Å β = 124.20° <i>V</i> = 1011 Å ³	<i>a</i> = 8.4812(8) Å <i>b</i> = 13.7542(7) Å <i>c</i> = 8.518(7) Å β = 109.015° <i>V</i> = 939 Å ³	<i>a</i> = 14.116 Å <i>b</i> = 14.229 Å <i>c</i> = 9.946 Å <i>V</i> = 1998 Å ³	<i>a</i> = 13.8256(3) Å <i>b</i> = 13.8256(3) Å <i>c</i> = 9.7767(2) Å <i>V</i> = 1869 Å ³
Si:Al or Si:Be ratio	1:1	3:1	2:1	2.84:1	1.7:1	2.6:1	3:64:1	

rings and could be modeled using potassium ions distributed over several sites, yielding an overall content close to that required for charge balance. Tetraethylammonium (TEA) could also be present in the channels, though for charge balance reasons the total amount required would be very low. The high level of extraframework cation disorder is likely to be the result of the random Be²⁺ and Si⁴⁺ distribution observed in the framework, which will produce significant variations in local charge densities around different channels.

3.5. Merlinoite. The mineral merlinoite (MER, K₅Ca₂-(Al₉Si₂₃O₆₄)·24H₂O) adopts an orthorhombic (*Immm*) unit cell, but the idealized topology has a tetragonal symmetry.^{30,31} An ammonium beryllphosphate with the merlinoite framework topology has been synthesized under hydrothermal conditions.³¹ A beryllsilicate zeolite of the composition [K_{~8}(NEt₄)_{~2}]-[Be_{6,9}Si_{25,1}O₆₄]·10H₂O was obtained in this study with a Si:Be ratio of 3.64:1 (Table 2, LSJ-47). Potassium ions occupy sites in the eight-ring windows, while the TEA cations are disordered on sites in the main eight-ring channels along the *c*-direction (Figure 2). TEA as a structure-directing agent for MER cages has been seen previously in an aluminophosphate (KFI) following predictions from modeling calculations.³²

3.6. LSJ-10: New Topology. LSJ-10 was prepared using the conditions summarized in Table S1 (Supporting Information). Under hydrothermal conditions the material grows as sprays of platelets up to 120 μm in length; Figure S1 in the Supporting Information shows an SEM micrograph of a typical crystal spray. This framework was only obtained from solutions containing potassium ions in combination with a large amine cation, typically the TEA cation, though lower yields were found in systems employing DABCO. The structure of LSJ-10 (Figure 3) shows features typical of beryllsilicate frameworks, with four- and eight-rings formed from SiO₄ tetrahedra cross-linked by spiro five-rings centered on BeO₄ tetrahedra. The structure solution (Table 3) was analyzed against known and theoretical zeolite topologies, demonstrating that the framework topology adopted by LSJ-10 is a new four-connected net.³³

A comparison of the topologies of the NAB and LSJ-10 frameworks shows that they have significant similarities. The individual layers in both cases consist of a square net formed from four-rings and eight-rings, as shown in Figure 4a,b; these layers are linked to each other through BeO₄ tetrahedra, as spiro five-rings, to produce the three-dimensional framework. However, in the NAB topology, alternate layers are displaced relative to each other so that a four-ring of one layer is sited directly above an eight-ring of the adjacent layer; this arrangement effectively makes the NAB pore geometry only two-dimensional—along the directions of the planes containing the BeO₄ units. However, in LSJ-10, the square nets of four- and eight-rings are aligned directly above each other, and the layers are connected through BeO₄ tetrahedra situated only above and below the small four-rings. Channels running orthogonal to each other in the plane containing the BeO₄ are constructed from nine-rings, as in NAB. This alignment of the eight-rings produces a fully three-dimensional channel structure (Figure 3)

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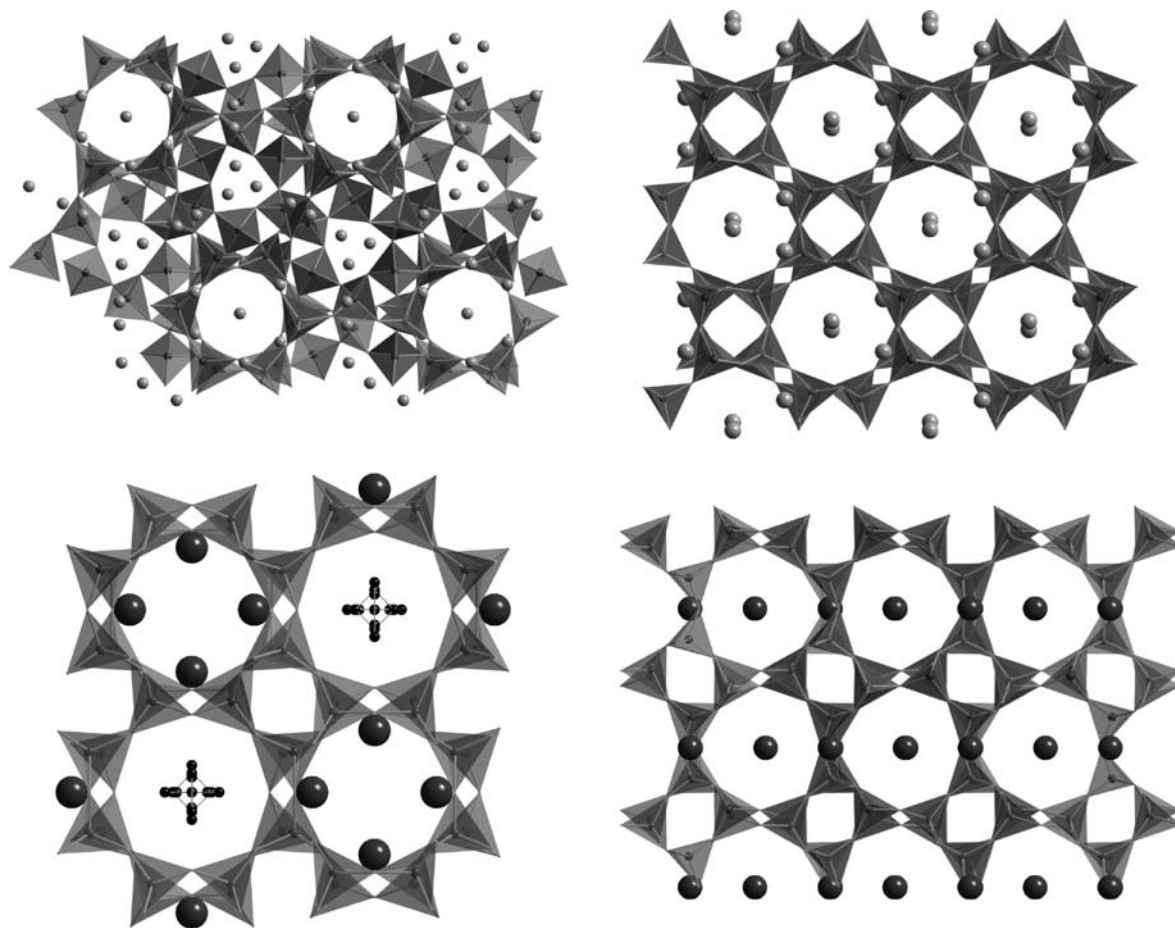


Figure 2. Beryllsilicate frameworks of known topologies. Clockwise from top left: ANA, GIS, PHI, and MER. Beryllium and silicon are disordered on all tetrahedral sites in these frameworks. Only the extraframework cations are shown for clarity.

and, at the intersections between these channels, moderate sized cavities (see Supporting Information, Figure S2). The location of electron density associated with the template molecules in the structure solution at these channel intersections indicates that a small level of TEA cations acts as a structure-directing agent during the synthesis, ensuring formation of the more open LSJ-10 topology rather than NAB. The framework density was calculated as 17.07 T atoms/1000 Å³.

Thermogravimetric and differential thermal analyses of LSJ-10, in combination with powder X-ray diffraction data collected from heated material, show that the framework integrity remains to 750 °C (see Supporting Information, Figure S3) before starting to recrystallize; water is lost from the framework pores mainly between 100 and 200 °C, and additional weight loss occurs between 200 and 350 °C, associated with TEA decomposition and further water loss. Such high-temperature stability is probably a reflection of the relatively small pore structure and strength of the short Be–O and Si–O bonds (in comparison with the longer, weaker Al–O bonds of many zeolites). Surface area measurements gave a value of 470 m²/g; it is notable that this value is enhanced slightly (by about 5%) relative to that of a material with the same framework topology but having an aluminosilicate framework composition due to the presence of a moderate level of low-atomic-mass beryllium.

3.7. LSJ-39: New Topology. Details of the reaction conditions under which LSJ-39 is formed are given in Table S1, and structure information is summarized in Table 3. The unit cell of LSJ-39 is pseudo-tetragonal, though the structure solution

was derived in P1 with a constrained framework as a result of disorder in the extraframework species. Compared to LSJ-10, LSJ-39 was obtained from a solution that was significantly lower in concentrations of beryllium, silicon, and potassium and also higher in water content. In addition, the solution contained a low concentration of Sr(OH)₂, although Sr²⁺ was apparently not, on the basis of EDAX measurements sensitive to values above ~3%, incorporated into the structure. In common with the other new synthetic beryllsilicate zeolites obtained in this work, the structure of LSJ-39 consists of layers formed purely of SiO₄ tetrahedra cross-linked by BeO₄ tetrahedra; the calculated framework density is 17.7 T atoms/1000 Å³. The structure solution (Table 3) was analyzed against known and theoretical zeolite topologies, demonstrating that the framework topology adopted by LSJ-39 is a new four-connected net.³² A remarkable feature of the tetrahedral net of the LSJ-39 structure is that the layers of connected SiO₄ tetrahedra are formed from purely five-membered rings (Figures 4c and 5). These five-rings are highly puckered, so producing irregular pentagons, when viewed from above, that form the complete layer (see Supporting Information, Figure S4). This arrangement is the well-known Cairo pentagonal tiling (named because it appears on the streets of Cairo and in many Islamic decorations), with a dual semiregular tiling of the Euclidean plane. TGA and DTA analysis, which could only be undertaken on an impure sample that contained some residual Be(OH)₂ and SiO₂·*n*H₂O (estimated at around 30% of the sample visually), showed loss of extraframework species and water from the impurities at between 50 and 350 °C; power

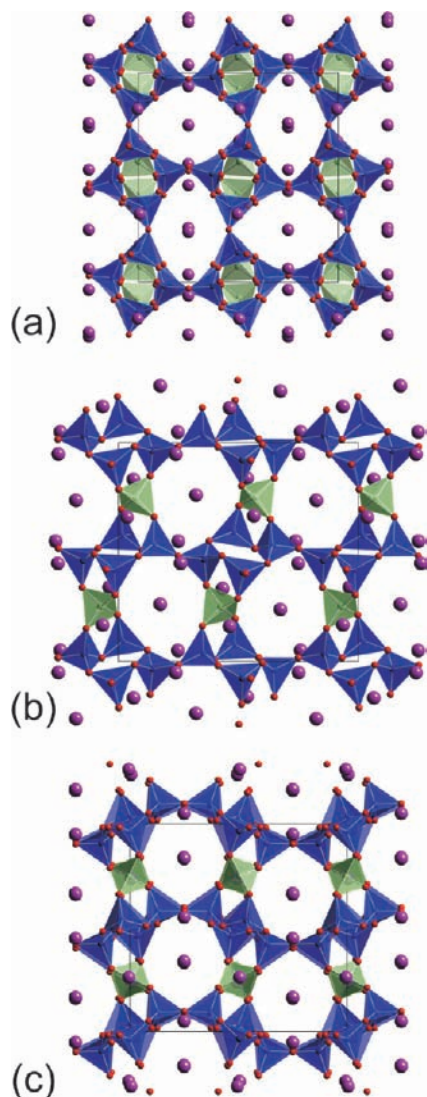


Figure 3. New framework topology denoted LSJ-10, viewed along the orthogonal cell directions *a*, *b*, and *c*, from top to bottom. SiO₄ tetrahedra are shaded blue and BeO₄ pale green. Only the extraframework cations are shown for clarity.

X-ray diffraction patterns collected from a sample heated to 650 °C showed that the framework topology retained its integrity to at least this temperature (see Supporting Information, Figure S3). Surface area measurements on the (impure) material heated at 650 °C gave a value of 365 m²/g, though this value will not represent a pure LSJ-39 topology due to contributions from small particles of SiO₂ and BeO.

3.8. Layered Structure (Potassium Hydroxyberyllosilicate), LSJ-51. At a higher temperature (220 °C) and more basic conditions, a two-dimensional (phyllo) beryllosilicate of the

Table 3. New Beryllosilicate Zeolite Topologies LSJ-10 and LSJ-39 and Layered Beryllosilicate LSJ-51

	LSJ-10	LSJ-39	LSJ-51
chemical formula	[K _(~14) (N(C ₂ H ₅) ₄) _(~2)] ₁₆ [Si ₃₂ Be ₈ O ₈₀]•4H ₂ O	K ₄ [Si ₁₂ Be ₂ O ₂₈]•(H ₂ O) ₅	K ₆ [Si ₇ Be ₃ O ₁₈ (OH) ₄
crystal system	orthorhombic	pseudo-tetragonal	monoclinic
space group	<i>Pnma</i>	<i>P1/P4</i> ₂	<i>Cc</i>
cell parameters	<i>a</i> = 12.7069(9) Å <i>b</i> = 13.2309(7) Å <i>c</i> = 13.9362(8) Å	<i>a</i> = 7.1316(4) Å <i>c</i> = 15.5209 Å	<i>a</i> = 12.1773(5) Å <i>b</i> = 7.0903(3) Å <i>c</i> = 12.8804(4) Å <i>β</i> = 104.209(2)° <i>V</i> = 1078.1(7) Å ³
Si:Be ratio	4:1	6:1	2.33:1

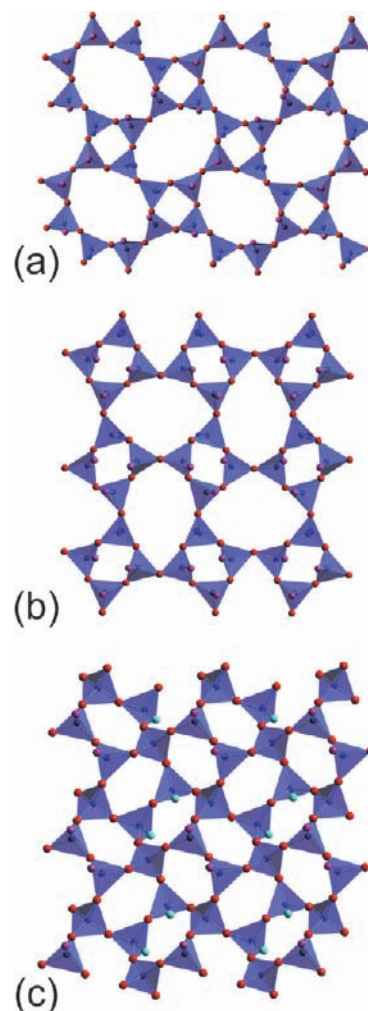


Figure 4. Comparison of the silicate layers present in the (a) NAB, (b) LSJ-10, and (c) LSJ-39 structures.

composition K₆[Si₇Be₃O₁₈(OH)₄] was isolated. The structure (Table 3, LSJ-51; Figure 6) is formed from beryllosilicate layers consisting of four-rings of SiO₄ tetrahedra cross-linked by double BeO₄-centered three-rings to produce eight-rings; these eight-rings coordinate to potassium ions. The layers are decorated with hydroxyl ions which form reasonably strong hydrogen bonds (OH⋯O distances of 1.798 and 2.095 Å) to the adjacent layers. The structure of this material is very closely related to the new LSJ-10 topology in that the layers of composition [T₁₀O₁₈(OH)₄] are identical to those that exist in a *ca* plane of the LSJ-10 topology (Figure 3). Thus, the LSJ-10 structure can be obtained by condensation of the LSJ-51 layers (by elimination of water molecules between two adjacent OH groups); this involves shifting of the layers along the *b* direction (see Figure

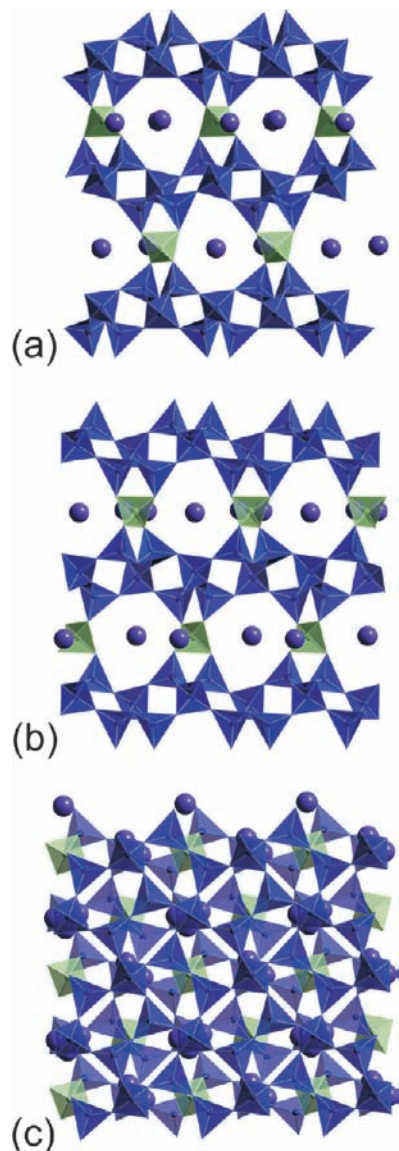


Figure 5. New framework topology denoted LSJ-39, viewed down the *a*, *b*, and *c* directions, top to bottom. SiO_4 tetrahedra are shaded blue and BeO_4 pale green. Only the extraframework potassium ions are shown for clarity.

6c), thus forming the eight-rings seen in the LSJ-10 structure viewed down *a* (Figure 3a).

The formation of simple sheets of linked tetrahedra is known for a number of systems, e.g. $\delta\text{-Na}_2\text{Si}_2\text{O}_5$ and $\text{Ba}_2\text{Si}_4\text{O}_{10}$ (sanbornite) and apophyllite, but these structure types exhibit the normal ring sizes of silicates, namely four-, six-, and eight-rings. Introduction of beryllium into these silicate layers allows the formation of three-rings, and the new layer topology of LSJ-51 is formed from a combination of three-, four-, and eight-rings.

4. Discussion

The new synthetic zeolite topologies found in this work, K- and Na-NAB, LSJ-10, and LSJ-39, as well as the layered LSJ-51, all contain three-rings as a central structural feature that is also common to the recently reported OSO and OBW zeolite topologies.¹¹ However, this structural feature is not an essential element of beryllosilicate frameworks, as evidenced by the

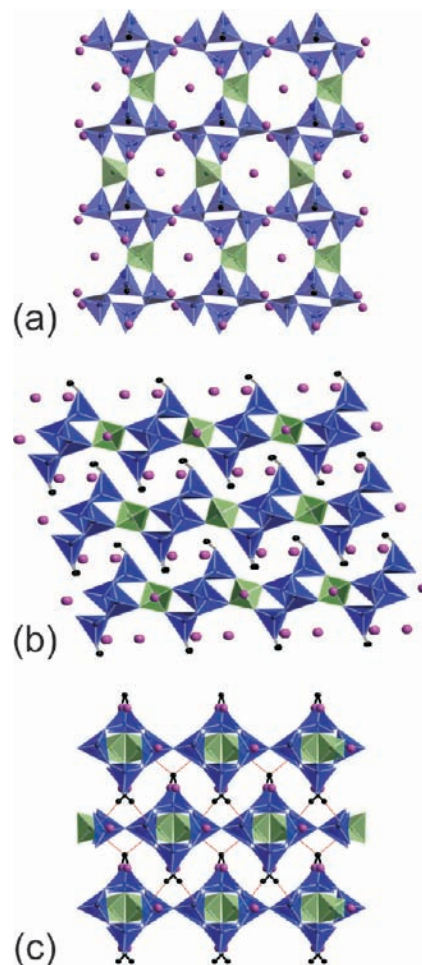


Figure 6. LSJ-51 layer structure viewed down the *a*, *b*, and *c* directions, top to bottom. Hydrogen-bonding is shown in the lower figure. The relationship of this layer structure to LSJ-10 can be seen by comparison with Figure 3.

synthesis in this work of several well-known aluminosilicate zeolite topologies, PHI, MER, ANA, and GIS, that do not contain three-rings. One clue to this variation in structural features in beryllosilicates may be the Si:Be ratio; those found in the aluminosilicate analogues generally lie in the range 2:1 to 4:1, while for the NAB, LSJ-10, and LSJ-39 structures the values are between 4:1 and 6:1. That is, under hydrothermal conditions and high beryllium concentrations, yielding relatively beryllium-rich materials with Si:Be ratios in the products below 4:1, systems crystallize with topologies having large ring sizes, four or greater, and have beryllium disordered across the structure. At lower beryllium concentrations, structures with beryllium-containing three-rings preponderate. This behavior may indicate the operation of a rule similar to Lowenstein's rule for aluminosilicates, in that assembly in solution of structural units with high levels of low-valent cations (i.e., Al^{3+} or Be^{2+}) is disfavored. That is, any secondary building units initially formed with high numbers of BeO_4 units in three-rings, and which have as a consequence a high overall negative charge on the unit, tend to re-form into more thermodynamically stable four- and eight-rings. While OSO and OBW have structures containing three-rings and lower Si:Be ratios (2.0 and 2.45, respectively), their topologies are much more open, with tetrahedral framework densities of near 13 T atoms/ 1000 \AA^3 , compared to values of 16–19 T atoms/ 1000 \AA^3 for all the other beryllosilicates reported here, so that the lower-valent beryllium

cations and associated, more negatively charged portions of the $(\text{TO}_2)_n$ framework are spatially well separated. Indeed, when the tetrahedral BeO_4 framework densities (Be atoms/1000 \AA^3) are determined for all the beryllosilicate zeotypes, the values all lie between 2.5 and 5, and the highest values for the beryllosilicates **ANA** (4.99) and **OSO** (4.49) are about half the maximum values for aluminum in aluminosilicates (e.g., 9.6 Al atoms/1000 \AA^3 in **ANA**). This indicates that frameworks with very high densities of divalent species, such as beryllium, are unlikely to form from solution due to the relative instability of intermediate species containing two or more BeO_4 units in reasonable proximity; these units will have a propensity to undergo further reaction toward more open structures and larger ring sizes.

The relationship between the template added to the reaction and the resulting zeolitic structure is less clear, though changes in pH caused by the template may influence the process. As no or only small levels of an organic template were found in any of the structures produced in this work, we believe that the sizes of the K^+ and Na^+ ions are the main factors controlling the formation of the different structures, with the former directing the formation of eight-rings, as is found for many aluminosilicates. The presence of TEA as a structure-directing agent seems to have a role in the synthesis of the beryllosilicate **MER** topology, **LSJ-39**, and possibly the **PHI** topology; in each of these reaction mixtures, the level of template was relatively high (see Table S1), and evidence of template was observed in the structure solutions of **MER** and **LSJ-39**. The template, while disordered in these structures, is located at sites at the intersections of the channels: the three orthogonal eight-ring channels in **MER** and the two orthogonal eight-ring channels in **LSJ-39**. The effect of temperature on the final crystalline product was also examined. Below 175 $^\circ\text{C}$ (at 140 $^\circ\text{C}$) the products were amorphous, and above 175 $^\circ\text{C}$ (at 220 $^\circ\text{C}$) layer structures and denser beryllosilicates such as chkalovite, $\text{Na}_2\text{Be}(\text{Si}_2\text{O}_6)$,³⁴ and not zeolitic structures, were obtained. Reaction time was also examined but was found to have little effect on the final crystalline product.

5. Conclusions

One of the original inspirations for this work derived from the observation that the beryllosilicate zeotype nabesite had not been synthesized in the laboratory. In general, beryllium frameworks have been poorly studied in terms of both reproducing the structures of beryllate minerals and the synthesis of new materials containing this unit. The structures of many beryllium minerals have been studied in detail, including our recent work combining single-crystal X-ray and powder neutron diffraction

methods,¹⁴ and show many features of interest in terms of porosity, centers that may show high catalytic activity, low density, ferroelectricity, and extraframework ion-trapping. Beryllate frameworks have also been shown to have applications in, for example, optical materials.³⁶ Therefore, developing the framework chemistry of the BeO_4 unit is of high significance in generating new functional materials, provided that any application reflects the hazardous nature of lightweight, friable beryllium compounds that could be inhaled; the new framework materials developed in this work all form as large crystallites (10–150 μm), minimizing such risks. One potential area of application of beryllium-based frameworks is in gas storage, where beryllium-based MOFs have been synthesized;⁸ in comparison with MOFs, beryllium zeolites have additional advantages of high chemical and thermal stability. Currently, the best zeolites for hydrogen storage are zeolites X and Y, with weight percent values approaching 2.5% in Li-X,³⁵ which is much less than that demanded for mobile applications. Assuming similar capacities for hydrogen adsorption, a cation-free framework of composition $[\text{Be}_2\text{O}_4]$ versus one of composition $[\text{AlSiO}_4]$ has a 50% potential increase in wt % hydrogen uptake. Furthermore, the higher framework charge of a beryllate framework may increase the strength of physisorption in such a system. Further studies of beryllosilicate frameworks are in progress with the aims of investigating their gas storage potential and activity in—because of the Be^{2+} centers—acid-catalyzed reactions.

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Supporting Information Available: Figure S1, SEM micrograph of a crystal with the **LSJ-10** structure type; Figure S2, comparisons of free internal surface areas of **NAB** and **LSJ-10**; Figure S3, thermogravimetric/differential thermal analyses data for **LSJ-10** and **LSJ-39**; Figure S4, puckered five-connected net in **LSJ-39**, highlighting the repeat unit of Cairo tiling formed from four distorted pentagons; Table S1, synthesis conditions and detailed methods of synthesis of **LSJ-10** and **LSJ-39**; crystallographic information files for beryllosilicate structures presented (**Na-NAB**, **K-NAB**, **ANA**, **GIS**, **MER**, **PHI**, **LSJ-10**, **LSJ-39**, and **LSJ-51** (KHBS)). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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