

## Structure of the First Silicate Molecular Sieve with 18-Ring Pore Openings, ECR-34

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**Abstract:** The three-dimensional microporosity of zeolite frameworks have allowed their widespread use in industry as heterogeneous catalysts, absorbents, and ion-exchangers. While the phosphate analogues of zeolites having up to 24 tetrahedral atoms in the pore openings are known, silicate-based zeolites have, until now, been limited to 14-membered ring pore openings. We now disclose the structure and characterization of the synthetic zeolite ECR-34, which can be prepared from a mixed alkali metal reaction gel containing tetraethylammonium (TEA) cations. Its structure has been determined from powder diffraction data and shows ECR-34 to be hexagonal with the dimensions  $a, b = 21.030(1) \text{ \AA}$ ,  $c = 8.530(1) \text{ \AA}$ , containing one-dimensional, 18-ring pores with 10 Å diameter free openings. ECR-34 is stable to 800 °C and is able to absorb and ion-exchange large organic molecules. The existence of ECR-34 suggests the potential of preparing other thermally stable silicate molecular sieves with extra-large pores.

### Introduction

Zeolites dominate the catalytic conversion of crude oils to fuels and lubricants and in the synthesis and purification of petrochemicals. They are sometimes used in detergent builder systems and are of increasing interest in the synthesis of fine chemicals.<sup>1</sup> To manipulate larger molecules or support large organometallic catalytic moieties, larger pore systems than those available in conventional zeolites are required. Until recently, the pore openings of zeolites have been limited in size to 12 tetrahedral atoms. In the past 20 years, new families of aluminophosphate-<sup>2</sup> and silicoaluminophosphate-based<sup>3</sup> molecular sieves have been prepared having zeolite type frameworks and properties. Like the silicate materials, both trivalent (Fe, Ga, B, etc.) and divalent (Be, Mg, Co, Mn, Zn, etc.) metals are known to substitute for aluminum in phosphate-based molecular sieves.<sup>4</sup> The syntheses of microporous aluminophosphate materials have led to the discovery of new structures with pore openings larger than 12 tetrahedra, such as ALPO-8,<sup>2</sup> VPI-5,<sup>5</sup> and cloverite.<sup>6</sup> All of these materials contain mixed metal ion coordinations (octahedral and tetrahedral aluminum), terminal hydroxyl groups, or other nontetrahedral framework groups, such as  $-\text{OH}$ ,  $-\text{F}$ , and  $-\text{OH}_2$ , that reduce their stability.<sup>1</sup> Since these large-pore phosphate materials do not have the thermal stability

of silicates, their use in petrochemical applications has been limited. More recently, three new silicate zeolites, UTD-1,<sup>7</sup> CIT-5,<sup>8</sup> and OSB-1<sup>9</sup> containing 14-ring openings have been prepared. While the beryllium silicate, OSB-1, is thermally unstable, UTD-1 and CIT-5 represent the first thermally stable silicate zeolites having pore openings larger than 12-ring openings.

Zeolites are microporous oxides with structures of three-dimensional frameworks containing silicon and aluminum oxide tetrahedra and having uniform pore openings. Other metals capable of tetrahedral coordination such as B, Ga, Fe, Be, and Zn can substitute for aluminum in varying amounts. While there are several examples of zinc-containing microporous silicates, such as VPI-7,<sup>10</sup> VPI-8<sup>11</sup> (and the isostructural SSZ-41<sup>12</sup>), VPI-9,<sup>13</sup> and RUB-17,<sup>14</sup> and borosilicates, such as RUB-13,<sup>15</sup> having no aluminosilicate analogues, there was only one reported gallium-containing silicate zeolite, TsG-1,<sup>16</sup> (and the isostructural ECR-9<sup>17</sup>), having no aluminosilicate analogue, even though gallium is well-known to substitute into many aluminosilicates.<sup>18</sup> The synthetic zeolite ECR-34,<sup>19</sup> prepared from a mixed alkali

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**Table 1.** Sodium, Potassium, and TEA Syntheses in the Gallium Silicate System Showing Crystallization Time and Products Formed<sup>a</sup>

no.	TEA <sub>2</sub> O:Ga <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O:Ga <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O:Ga <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub> :Ga <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O:Ga <sub>2</sub> O <sub>3</sub>	time (days)	products <sup>b</sup>		
							1	2	3
1	1.73	0.67	0.80	12	180	11	ECR-34	PAU	
2	1.73	0.67	0.80	12	180	17	ECR-34		
3	2.40	0.00	0.80	12	180	3	FAU		
4	1.30	1.10	0.00	9	140	14	MER	CGS	
5	0.00	1.00	2.00	9	140	7	CGS	MER	ECR-34
6	0.80	1.60	0.60	9	140	6	LTL	CGS	
7	1.00	1.00	1.00	9	140	6	CGS	ECR-34	
8	3.00	1.85	1.85	20	300	12	CGS	ECR-34	

<sup>a</sup> All syntheses used aluminum-containing nucleant seeds such that 2% Ga was replaced by Al. <sup>b</sup> PAU = paulingite; FAU = faujasite; MER = merlinoite; LTL = zeolite L; CGS = ECR-9.

metal reaction gel containing tetraethylammonium (TEA) cations, is the second new gallosilicate. This material was originally thought to have 12-ring pores, but we have determined its structure and found it to have 18-ring pores.

## Experimental Section

**Synthesis and Characterization.** A stock potassium, sodium gallate solution was first prepared by heating KOH<sup>1/2</sup>H<sub>2</sub>O (5.23 g, 0.080 mol), NaOH (3.90 g, 0.096 mol), Ga<sub>2</sub>O<sub>3</sub> (11.0 g, 0.059 mol), and 15.0 g of H<sub>2</sub>O on a hot plate stirrer until gallium oxide dissolved. The solution was slightly cooled and H<sub>2</sub>O added to bring the weight of the solution to 38.4 g. To a plastic beaker was added colloidal silica (49.9 g duPont Ludox HS-40, 40% SiO<sub>2</sub>, 0.332 mol), 40% (TEA)OH solution (36.1 g, 0.098 mol), nucleant seeds<sup>20</sup> (3.67 g of 13.33:1:12.5:267 Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub>:SiO<sub>2</sub>:H<sub>2</sub>O, 0.00057 mol of Al<sub>2</sub>O<sub>3</sub>), potassium, sodium gallate solution (18.1 g, 0.0277 mol of Ga<sub>2</sub>O<sub>3</sub>), 48% H<sub>2</sub>SO<sub>4</sub> solution (1.44 g, 0.007 mol), and 25.8 g of H<sub>2</sub>O. The order of addition of the ingredients delays gel formation and allows for optimum homogenization. The mixture was mixed with a spatula and then transferred to a 125 mL blender and thoroughly homogenized. The gel was placed in a 125 mL Teflon bottle and reacted in an air oven at 100 °C for 17 days. The white product was filtered and washed with distilled water. The morphology of ECR-34 consists of 0.5–10 μm spherical- and irregular-shaped crystals containing terracelike steps of 50–100 nm in size. Chemical analysis was performed with a Thermo-Optics IRIS inductively coupled plasma-atomic emission spectrometer. Thermogravimetric analysis was performed with a TA Instruments 2950 TGA. A sample of ECR-34 was calcined at 650 °C for 3 h in air to remove the organic template. Temperature-resolved powder X-ray diffraction was collected with Cu Kα radiation and Bragg–Brentano geometry using a Scintag XDS-2000 diffractometer equipped with an Edmund Bühler high-temperature attachment. Gas adsorption was measured using an automated Cahn vacuum microbalance equipped with a furnace, gas inlet manifold, and MKS manometer. The calcined ECR-34 sample was first outgassed overnight at 400 °C to a pressure less than 1 × 10<sup>-4</sup> Torr before perfluorotri-*n*-butylamine uptake measurement at room temperature.

**Structure Refinement.** For Rietveld refinement a calcined/dehydrated sample of ECR-34 was sealed under vacuum at 300 °C in a 2.0 mm quartz capillary tube. The room-temperature synchrotron powder X-ray diffraction pattern was measured at Beamline X-10B at Brookhaven National Laboratory at a wavelength of 0.872 62 Å from 2 to 40.0° 2θ and a step size of 0.01°. The program GSAS<sup>21</sup> was used to perform Rietveld refinement. The framework tetrahedral atoms and oxygen atoms were constrained to have the same isotropic thermal parameters. A shifted Chebyshev<sup>22</sup> function with 16 parameters was used to fit the background, and a six-parameter pseudo-Voigt function,<sup>23</sup>

the peak profile. Soft constraints were placed on the Si–/Ga–O bonds (1.67 ± 0.02 Å) and the tetrahedral O–O distances (2.72 ± 0.05 Å). Although the relative weight of these constraints could be reduced throughout the refinement, they could not be fully removed and a final soft constraint weight factor of 5 was used. Complete removal of these constraints led to unreasonable interatomic distances and only reduced the agreement factor,  $Rwp = \{\sum w(I_o - I_c)^2 / \sum w I_o^2\}^{1/2}$  ( $I_o$  = observed intensity of each point,  $I_c$  = calculated intensity of each point, and  $w$  = weight factor), from 8.9 to 8.5%. The positions of the nonframework cations were determined by difference Fourier mapping. Non-framework cations were modeled as potassium atoms, and no attempt was made to distinguish between the potassium and sodium atoms. If unconstrained, the sum of electron density from the total occupancy of the potassium atoms was slightly higher than that expected from the sum of the sodium and potassium atoms found from elemental analysis. Therefore the sum of potassium occupancies for K1 and K2 was constrained to match the electron density found from elemental analysis for sodium and potassium. There were 3841 total observations including 40 soft constraints with a total of 70 refinable variables. The final agreement factors were  $Rw = 6.4\%$ ,  $Rwp = 8.9\%$ , and expected  $Rwp = 7.0\%$  (see Supporting Information Table S1).

## Results and Discussion

The synthesis of ECR-34 was first discovered during attempts to make the gallium version of ECR-18,<sup>24</sup> which is a low silica/alumina zeolite having the paulingite structure. It was found that three cations, sodium, potassium, and tetraethylammonium, were necessary to synthesize ECR-34. Typical impurities identified were faujasite (FAU), merlinoite (MER), zeolite L (LTL), ECR-9 (CGS), and paulingite (PAU) when the relative amounts of sodium, potassium, and TEA cations were varied from the optimum. (The three-letter mnemonics used in this paper are zeolite framework structure codes as assigned by the Structure Commission of the International Zeolite Association.<sup>25</sup>) When any of the three cations are excluded from, or are not of high enough concentration in the synthesis, it is not possible to make ECR-34 (see Table 1). For example, in the absence of potassium, faujasite is made, or when sodium or TEA is removed, ECR-9, merlinoite, or zeolite L is obtained. The SiO<sub>2</sub>:Ga<sub>2</sub>O<sub>3</sub> ratio is also important. Both lower and higher ratios bring in gallosilicate ECR-9 and other impurities. The addition of nucleant seeds prevents the formation of zeolite β and alternate silica sources such as silica gel and sodium silicate gave mixtures of faujasite, ECR-9, and merlinoite.

ECR-34 can be synthesized from low-silica, nucleant-seeded, gallia gels prepared from colloidal silica at a temperature of

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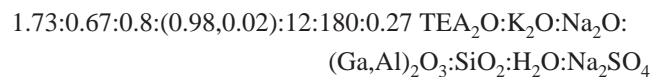
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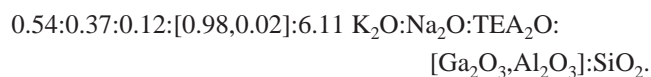
100 °C for 17 days. A relatively pure sample of ECR-34 was prepared from a gallium-containing gel of stoichiometry<sup>19</sup>



where TEA is tetraethylammonium. The calcined sodium, potassium form of ECR-34 was found to be thermally stable to > 800 °C by temperature-resolved powder X-ray diffraction (see Supporting Information Figure S1).

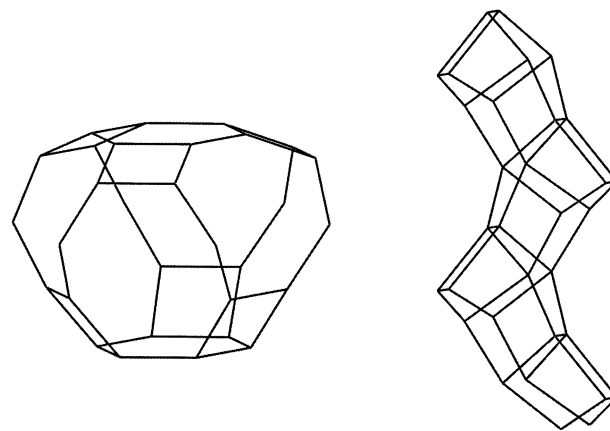
The powder X-ray diffraction pattern for as-synthesized ECR-34 was indexed with a hexagonal unit cell, dimensions  $a = 20.970(1)$  Å and  $c = 8.611(1)$  Å. Systematic absences in the X-ray diffraction pattern indicated that ECR-34 belonged to one of three possible space groups,  $P6_3mc$ ,  $P\bar{6}2c$ , or  $P6_3/mmc$ . The gallosilicate ECR-9,<sup>26</sup> which is orthorhombic and has the CGS framework, has an  $a$  dimension of 8.64 Å very close to the  $c$  dimension of 8.61 Å for ECR-34. Also, the infrared spectra of both ECR-9 and ECR-34 are almost identical in the mid-infrared region (400–1300  $\text{cm}^{-1}$ ), characteristic of the structural groups of zeolite frameworks (see Supporting Information Figure S2). These facts, and the fact that ECR-9 frequently cocrystallizes with ECR-34, strongly suggest that these two gallosilicates are structurally related, possibly containing the same secondary building units or polyhedra.

Thermogravimetric analysis showed a 4.4% organic weight loss at 365 °C and elemental analysis gave 17.8% Ga, 0.16% Al, 22.4% Si, 2.24% Na, and 5.46% K. This represents a product stoichiometry of



The TGA template weight loss at 365 °C is at a temperature typical for the loss of a tetraalkylammonium template from a large pore. A sample of ECR-34 was calcined in air for 3 h at 600 °C, and its density was measured in a pycnometer with *m*-xylene and found to be 1.93  $\text{g}/\text{cm}^3$  after correcting for the amount of *m*-xylene absorbed (6.0%) as measured by gas adsorption. This represents a framework density of about 49 T-atoms per unit cell or about 15 T-atoms/(1000 Å<sup>3</sup>).

Initial attempts to build hexagonal models of ECR-34 using the open hexagonal unit of CGS did not generate any suitable models. A method for trial framework generation which uses simulated annealing to predict low-energy configurations based upon geometric constraints derived from known silicate structures was developed by Deem and Newsam<sup>27</sup> and extended by Falcioni and Deem.<sup>28</sup> Simulated framework annealing automatically determines ways in which the required number of T-atoms can be placed within the unit cell to generate viable zeolite models. Since the space group and number of unique atoms per unit cell of ECR-34 could not be determined with certainty, multiple runs of the simulated framework annealing program were used to generate a suitable trial framework. Although many hexagonal models were generated having the correct unit cell dimensions and space group, none of the initial models had a calculated X-ray diffraction pattern close to that measured for ECR-34. Finally, a trial framework with five unique T-atoms,



**Figure 1.** Polyhedra found in ECR-34: left, *plg* cage also seen in PAU framework; right, open hexagonal prisms also seen in CGS framework.

although not the correct answer, gave a calculated pattern similar to the experimental pattern. Inspection of this model down the  $c$ -axis revealed a projection that indicated the proper way of connecting the open hexagonal prisms into a hexagonal unit cell with the correct dimensions.

The structure of ECR-34 is built of open hexagonal prisms (see Figure 1), the same secondary building unit as that found in gallosilicate ECR-9 and cobalt gallium phosphate-6,<sup>29</sup> both having the CGS structure. In the CGS framework, these secondary building units are arranged in a manner to form an orthorhombic cell with 10-ring pore openings having the dimensions of  $3.5 \times 8.1$  Å, which is too small for hydrocarbons to pass through. The structure of ECR-34 is built from the same open hexagonal prisms but arranged in a hexagonal cell to form one-dimensional channels having 18-ring openings with a diameter of 10 Å. Gallosilicate ECR-34 is the first silicate molecular sieve having 18-ring pore openings.

The coordinates of the tetrahedra atoms from the model were taken and oxygen atoms placed at positions halfway between the tetrahedral framework silicon atoms. This oxygen-containing model was then subjected to geometric distance least-squares refinement (DLS)<sup>30</sup> to optimize the coordinates using as input a Si–O distance of 1.67 Å based upon a Si/Ga ratio of 3. The DLS reliability index,  $R_{\text{DLS}} = \{\sum(w_j[D_j^0 - D_j])^2 / \sum(w_j D_j^0)^2\}^{1/2}$  ( $D_j^0$  = prescribed interatomic distance of type  $j$ ,  $D_j$  = calculated interatomic distance of type  $j$ , and  $w_j$  = weight ascribed to the interatomic distance of type  $j$ ), value of 0.0037 indicates that this model has interatomic distances and angles consistent with known silicate structures. The calcined dehydrated form has unit cell dimensions of  $a, b = 21.030(1)$  Å,  $c = 8.530(1)$  Å. The results of the DLS refinement for the ECR-34 model using these dimensions were used as initial coordinates. Final atomic coordinates and thermal parameters (with estimated standard deviations) are given in Table 2, and the comparison of the calculated and observed X-ray diffraction patterns is shown in Figure 2. The final interatomic distances and angles are given in Supporting Information Table S2, although it is noted that these values reflect the soft constraints used in the refinement. Nonetheless, the final results are consistent with other known

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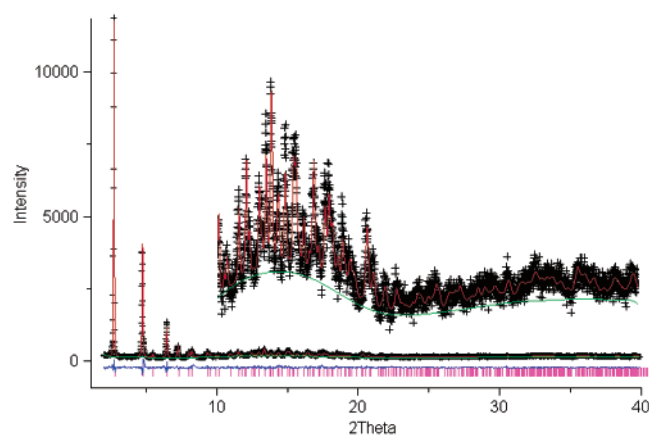
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**Table 2.** Final Atomic Coordinates and Thermal Parameters from Rietveld Refinement with Estimated Standard Deviation in Parentheses<sup>a</sup>

atom	site	x	y	z	occupancy	U <sub>iso</sub> (Å <sup>2</sup> )
Si/Ga1	12d	0.7451(6)	0.1059(6)	0.0165(29)	0.76/0.24(0)	0.017(4)
Si/Ga2	12d	0.6672(7)	0.1847(5)	0.1510(19)	0.76/0.24(0)	0.017(4)
Si/Ga3	12d	0.6416(8)	0.9720(9)	0.2287(34)	0.76/0.24(0)	0.017(4)
Si/Ga4	12d	0.6143(7)	0.0740(8)	0.4425(31)	0.76/0.24(0)	0.017(4)
O1	12d	0.7447(12)	0.0736(15)	0.8377(33)	1.0(0)	0.021(9)
O2	6c	0.8306(11)	0.1694(11)	0.0620(50)	1.0(0)	0.021(9)
O3	12d	0.6909(16)	0.1424(17)	0.0143(25)	1.0(0)	0.021(9)
O4	12d	0.7159(12)	0.0422(12)	0.156(4)	1.0(0)	0.021(9)
O5	6c	0.7253(8)	0.2747(8)	0.146(6)	1.0(0)	0.021(9)
O6	6c	0.5839(15)	0.1678(30)	0.099(5)	1.0(0)	0.021(9)
O7	12d	0.6625(17)	0.1479(13)	0.3294(0)	1.0(0)	0.021(9)
O8	12d	0.5844(15)	0.9157(12)	0.093(4)	1.0(0)	0.021(9)
O9	12d	0.5950(14)	-0.0002(12)	0.339(5)	1.0(0)	0.021(9)
O10	6c	0.5342(12)	0.0684(24)	0.491(5)	1.0(0)	0.021(9)
K1 <sup>b</sup>	6c	0.5449(16)	0.4551(16)	0.849(7)	0.62(2)	0.08(2)
K2 <sup>b</sup>	6c	0.3844(18)	0.1922(9)	0.540(6)	0.86(2)	0.12(2)

<sup>a</sup> Space group  $P6_3/mc$  (No. 186). Unit cell dimensions  $a, b = 21.030(1), c = 8.530(1)$ . <sup>b</sup> Nonframework cations were refined as potassium.

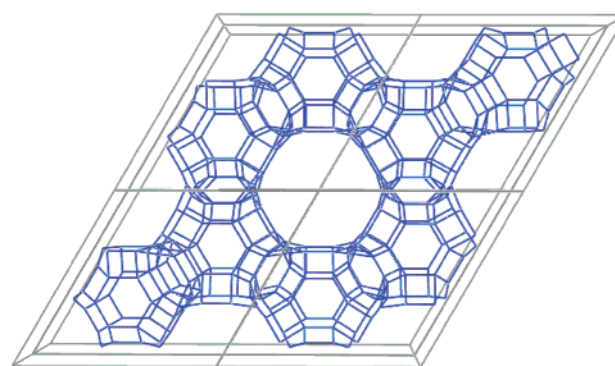


**Figure 2.** Final calculated (red line), experimental (+), and difference (blue lower) plot from Rietveld refinement of calcined/dehydrated ECR-34. Tick marks show the location of allowed reflections, and the green line is the fitted background curve. The inset pattern has a  $\times 25$  intensity scale.

framework structures, the agreement values are very good, and the simulated XRD pattern closely matches the experimental data.

The unit cell contains four unique T-atoms and 10 unique oxygen atoms. The measured density, 1.93 g/cm<sup>3</sup>, is within the experimental error of the calculated density, 1.89 g/cm<sup>3</sup>, of the final structure. The framework density is 14.7 T-atoms/(1000 Å<sup>3</sup>), lower than that found for the CGS structure (15.6 T-atoms/(1000 Å<sup>3</sup>)) and slightly higher than that for the 18-ring VFI framework (14.2 T-atoms/(1000 Å<sup>3</sup>)).

The structure of ECR-34 can be described as a three-dimensional tetrahedral framework built from open hexagonal prisms to form one-dimensional 18-ring channels as shown in Figure 3. The 18-ring channel is down the  $c$ -axis along the origin of the unit cell. These 18-ring channels are interconnected through 8-ring windows to  $plg$  cages<sup>31</sup> of the type 4<sup>6</sup>2<sup>8</sup>6 (a polyhedra containing six 4-rings, two 6-rings, and six 8-rings; see Figure 1). The actual symmetry of the  $plg$  cages in ECR-34 is reduced from the idealized,  $\bar{3}2$  symmetry to  $3m$  symmetry because of the distortion allowed by the  $P6_3/mc$  space group. The  $plg$  cage is also seen in the PAU structure along the [111] direction of the unit cell.<sup>32</sup>



**Figure 3.** Framework structure of synthetic ECR-34 viewed down the  $c$  direction showing the 18-ring channel. Framework oxygen atoms and nonframework cations are omitted for clarity.

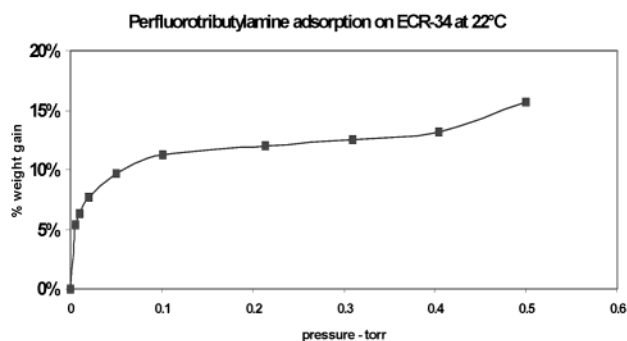
The channel walls are composed of ribbons of 4 T-atom member rings having 8-ring windows to the  $plg$  cages. The arrangement of these 4-ring ribbons is such that the walls of the channels are irregular with shallow side pockets of 10-ring windows at the channel and 8-ring openings to the  $plg$  cages. The 18-ring opening is puckered. Assuming an oxygen radius of 1.35 Å, the pore size of ECR-34 is 10.1 Å, along the  $a$  direction not quite perpendicular to the  $c$ -axis. This compares to the 12.7 Å channel of the more planar 18-ring opening of the aluminophosphate VFI-5 (VFI) structure. A perfectly planar 18-ring channel has a free diameter of approximately 15 Å.<sup>33</sup> The size of the pore was confirmed experimentally by the ability of ECR-34 to ion exchange with tetrabutylammonium cations (molecular diameter about 10 Å; data not shown) and by its ability to absorb perfluorotri- $n$ -butylamine (molecular diameter = 10 Å, Figure 4).

One cation was located in the 8-ring window of the open hexagonal prism and is similar to the location found in gallosilicate TsG-1.<sup>16</sup> This cation is coordinated to the framework O6 and O9 atoms. The other cation position, K2, was found in the 8-ring window of the  $plg$  polyhedra in the 18-ring channel and is coordinated to the O8 framework atoms. As mentioned above sodium, potassium, and TEA cations are all necessary to synthesize ECR-34, suggesting that the combinations of these cations stabilize the secondary building units of

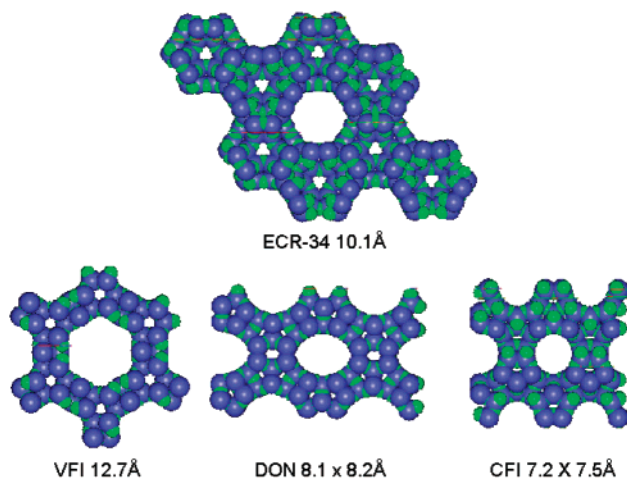
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**Figure 4.** Adsorption of perfluorotri-*n*-butylamine (kinetic diameter = 10.2 Å) on calcined/dehydrated ECR-34 at 22 °C.



**Figure 5.** Comparison of the pores of ECR-34 compared to other large-pore frameworks: VFI = VPI-5; DON = UTD-1; CFI = CIT-5.

the ECR-34 structure during crystallization. The fact that the location of K1 is similar to that found in TsG-1 indicates that potassium cations appear to stabilize the open hexagonal chains. It is also noted that these same cations are also necessary for synthesizing the PAU framework, suggesting that some combination of Na, K, and TEA helps to stabilize *plg* polyhedra found in both the PAU and ECR-34 frameworks.

A comparison of the ECR-34 pore to some other large-pore frameworks is shown in Figure 5. ECR-34 is the only molecular sieve framework with circular pores of a size midway between the 12-ring and 14-ring zeolites (7–9 Å) and the 18-ring VPI-5 molecular sieve. This 10 Å pore zeolite has potential for applications in separations and reaction chemistry not feasible with other zeolites.

### Conclusion

In conclusion, the framework structure of gallosilicate ECR-34 has been determined from a combination of simulated framework annealing and model building. Its calcined/dehydrated structure was refined from powder X-ray diffraction data using Rietveld refinement and has unit cell dimensions of  $a, b = 21.030(1)$  Å,  $c = 8.530(1)$  Å with space group symmetry  $P6_3mc$  (No. 186). Gas adsorption, ion exchange of  $TBA^+$  cations, and FTIR data are consistent with the one-dimensional, 18-ring model. The framework of ECR-34 is built from structural units of open hexagonal prisms and *plg* polyhedra, which are also present in the CGS and PAU frameworks, respectively. It may be viewed as “extended building units” producing multiple topologies within a given compositional space or as a “boundary phase” crystallization.<sup>34</sup> ECR-34 contains one-dimensional pores of diameter 10.1 Å and is the first silicate molecular sieve to contain 18-ring pore openings. The existence of thermally stable ECR-34 shows that extra-large-pore silicate frameworks are viable, which suggests the potential of preparing other silicate molecular sieves with extra-large pores.

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**Supporting Information Available:** Crystallographic data, interatomic distances and angles of ECR-34, variable temperature XRD, and IR (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA0371653

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