Arsenate Zeolite Analogues with 11 Topological Types

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While there is always a general interest in discovering new open-framework materials in novel compositional domains,[1−3] our interest in arsenates also stems from our desire to understand roles of chemical and geometrical factors of precursor molecules in determining the composition and topology of the final product. When only the geometric factor is concerned, the arsenic system should be more like the germanate system because its ionic size (As^{5+}, 0.335 Å) is much closer to Ge^{4+} (0.39 Å) than to P^{5+} (0.17 Å).[4] On the other hand, when chemical factors such as atomic charge are concerned, the arsenate system would be expected to be more like the phosphate system. Thus, the study of the arsenate system affords a unique opportunity to investigate individual roles of chemical and geometric factors and their interplay in determining the final framework composition and topology.

An examination of known arsenates and phosphates with four-connected zeolite-type topologies shows two different aspects. In the T^{2+}/T^{5+} systems such as zincoarsenates and zincophosphates (T refers to a tetrahedral atom) templated with alkali metal cations, both arsenate and phosphate structures can usually be made.[5] On the other hand, in the T^{3+}/T^{5+} system such as aluminoarsenates and aluminophosphates, few tetrahedral arsenates with open framework topologies have been made even though many $AlPO_4$ structures are known.[6−10] Thus, the first step in our overall synthetic strategy for developing tetrahedral arsenates is to combine the T^{2+}/T^{5+} and T^{3+}/T^{5+} systems and to synthesize ternary $T^{2+}/T^{3+}/T^{5+}$ four-connected arsenates. Such a strategy also addresses a fundamental parameter in the formation of four-connected open frameworks: host−guest charge density matching. From earlier work on phosphates and germanates, we observed that regardless how well the geometrical conformation of a molecular template matches the internal pore geometry of a three-dimensional framework, the framework would not form unless the host−guest charge density also matches simultaneously.[11−13]

Both gallo- and aluminoarsenates are investigated in this work, and zinc is selected as the divalent T-atom. A typical synthesis condition is as the following.[14] As_2O_5 (0.711 g) and tris(2-aminoethyl)amine (1.470 g) were added to a mixed solvent containing H_2O (5.354 g) and ethylenegloycol (2.713 g). The mixture was stirred for 1 day before $Al(NO_3)_3{\cdot}9H_2O$ (1.155 g) was added. After stirring for another day, $Zn(NO_3)_2{\cdot}6H_2O$ (0.919 g), 49% HF (0.049 g), and pyridine (0.491 g) were added. The pH of the mixture was lowered to 5.23 with 2 M HNO_3 (9.372 g). The mixture was heated in a Teflon-coated steel autoclave at 150 °C for 4 days, and clear crystals of zinc aluminoarsenate with UCSB-7 topology were recovered. Other arsenate phases can be made by a similar procedure with different amines at different pH values.

From single-crystal structural analyses, 11 four-connected topologies (ABW, ANA, CHA, EDI, GIS, KFI, LAU, SOD, THO, UCSB-7, ACP-2) have been identified (Table 1).[6,12,13] Different chemical compositions with various lattice symmetries have also been made by changing types of T^{3+} atoms (Al or Ga), T^{3+}/T^{2+} ratios, and structure-directing agents. The coexistence of T^{2+} and T^{3+} cations can be inferred by the charge neutrality role when guest molecules are located. More generally, the average T−O bond distance can be used to estimate the T^{2+}/T^{3+} ratio by comparing the T−O distance to the pure T^{2+}−O and T^{3+}−O distance. For mixed T^{2+}/T^{3+} sites, the T−O distance would be intermediate between the pure T^{2+}−O and T^{3+}−O distances.[12]

To our knowledge, $AlAsO_4$−CHA is the first and only undoped aluminoarsenate compound that has a structural analogue among aluminosilicate zeolites.[6] Because of the absence of divalent substitution, its framework is neutral like many $AlPO_4$ phases. The protonated amine molecules (i.e., pyridine) are completely ordered, and their positive charges are balanced by hydroxyl groups that are attached to one-third of Al^{3+} sites, in a fashion similar to that found in some $AlPO_4$'s such as the ultra-large pore VPI-5.[6]

The size effect of the T-atom is shown in two different ways. One is in comparison with phosphates. Because of the larger size of As^{5+}, ZnAlAs-THO (THO = Thomsonite) and ZnAlAs-2 are synthesized with 1,4-diaminobutane and 1,5-diaminopentane, whereas similar phosphate phases, ACP-THO (ACP = aluminum cobalt phosphate) and ACP-2 were made with 1,3-diaminopropane and 1,4-diaminobutane.[12] This is an interesting example that an increase in the T-atom size from P^{5+} to As^{5+} requires an extra methylene group in the structure-directing agent to have a better host−guest geometrical fit. ZnAlAs-2 has the same four-connected topology as that reported for ACP-2 and GCP-2, two cobalt phosphates substituted by Al^{3+} and Ga^{3+}, respectively.[12] Such a topology has not yet been found in either silicates or germanates.

A fundamentally different size effect is seen when a comparison is made with the germanate system. It is worth noting that the topology of UCSB-7 has not yet been found in either phosphates or silicates yet, but it frequently occurs in both germanate and arsenate systems.[13] Dozens of different amines can give rise to such a topology in either germanate or arsenate systems. This is apparently due to the similar ionic size between Ge^{4+} and As^{5+} cations. This is a very good example that shows that the stability of a given topology and the ease with which a given topology can be created are intimately related to the ionic size of the tetrahedral atom.

One benefit of working with the arsenate system over the germanate system is that the noncentrosymmetry of the UCSB-7 framework can be maintained when the framework negative charges are tuned by changing the T^{2+}/T^{3+} ratio. UCSB-7 has two helical 12-ring pore systems.[13] The two helical pore systems are left-handed and right-handed; however, they are not mirror images of each other when there are two unique, alternating T-atom sites. In the germanate system, when we attempt to enhance the framework stability by increasing the Ge/Ga ratio above 1 and decreasing the framework negative charge, the noncentrosymmetry is lost because of the disorder in T-atom sites.[13] On the other hand, As^{5+} sites and T^{2+}/T^{3+} sites are always alternating in arsenates, and the noncentrosymmetry is preserved at different framework charge density. This may have some implications as nonlinear optical materials or in their potential use as noncentric chiral hosts.

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(14) Arsenate compounds used in the synthesis may present a health or environmental hazard. Proper safety procedures and disposal rules should be followed in the handling of these compounds.

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Table 1. Summary of Crystallographic Data for New Arsenate Phases Synthesized in This Study[a]

name	formula	amine[b]	space group	a (Å)	b (Å)	c (Å)	β (deg)	$R(F)$	$2\theta_{max}$	M−O (Å)
$ZnAsO_4$-ABW	NH_4ZnAsO_4	NH_4^+	$P2_1$	8.959	5.633	9.130	90.159	4.06	56	1.950
$ZnAsO_4$-ANA	$[Zn(H_2O)]Zn_3As_3O_{12}$	NH_4^+	$I2_13$	13.853	13.853	13.853	90	6.19	56	1.918
$ZnAsO_4$-CHA	$(Zn)Zn_6As_6O_{24}$	R19	R-3	13.838	13.838	15.971	90	6.13	50	1.940
$AlAsO_4$-CHA	$(Al_3As_3O_{12})(OH)$	py	P-1	9.422	9.476	9.643	86.582	3.47	56	1.745
$ZnAsO_4$-EDI	$(NH_4)_3Zn_5As_5O_{20}$	R4	P-4	10.192	10.192	27.550	90	4.15	56	1.939
ZnGaAs-GIS	$ZnGaAs_2O_8$	TMA	$C2/c$	15.424	9.796	10.874	134.29	3.36	56	1.874
ZnAlAs-GIS	$ZnAlAs_2O_8$	DMA	$C222_1$	14.641	14.823	9.484	90	5.50	56	1.833
$ZnAsO_4$-KFI	$ZnZn_6(AsO_4)_6$	R6	Pn-3	18.965	18.965	18.965	90	4.97	56	1.961
ZnAlAs-LAU	$ZnAl_2As_3O_{12}$	py	$C2/c$	15.456	13.555	15.618	112.29	4.97	56	1.809
ZnGaAs−SOD1	$ZnGa_2As_3O_{12}$	TMA	P-43n	9.1245	9.1245	9.1245	90	2.37	56	1.872
ZnAlAs−SOD	$ZnAl_2As_3O_{12}$	TMA	P-43n	9.1343	9.1343	9.1343	90	1.38	56	1.804
ZnGaAs−SOD2	$Zn_2GaAs_3O_{12}$	pip	P-1	9.4345	9.2805	8.5418	94.972	3.64	56	1.905
ZnAlAs-THO	$Zn_4AlAs_5O_{20}$	R4	$P2_1/n$	13.453	14.661	14.666	90.197	14.4	56	1.903
ZnAlAs-2	$Zn_3AlAs_4O_{16}$	R5	$Pbcm$	9.0778	15.594	15.163	90	6.75	56	1.876
ZnGaAs−SV-1	$ZnGa_2As_3O_{12}$	TMA	$I4_132$	18.623	18.623	18.623	90	2.38	56	1.872
ZnGaAs−SV-2	$Zn_{1-x}Ga_xAsO_4$	R3	$I4_132$	18.600	18.600	18.600	90	3.69	56	1.893
ZnGaAs−SV-3	$Zn_{1-x}Ga_xAsO_4$	R4	$I4_132$	18.705	18.705	18.705	90	4.47	56	1.912
ZnGaAs−SV-4	$Zn_{1-x}Ga_xAsO_4$	dabco	$I4_132$	18.763	18.763	18.763	90	6.52	50	1.898
ZnAlAs−SV-1	$Zn_2AlAs_3O_{12}$	R14	$I4_132$	18.624	18.624	18.624	90	4.54	56	1.880
ZnAlAs−SV-2	$Zn_2AlAs_3O_{12}$	R16	$I4_132$	18.611	18.611	18.611	90	6.11	50	1.876
ZnAlAs−SV-3	$Zn_2AlAs_3O_{12}$	R20	$I4_132$	18.568	18.568	18.568	90	4.71	50	1.853
ZnAlAs−SV-4	$Zn_2AlAs_3O_{12}$	lysine	$I4_132$	18.561	18.561	18.561	90	4.45	56	1.862

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ with $F_o > 4.0\,\sigma(F)$. Single-crystal data with Mo Kα. In all formulas, $x < 0.5$. For ZnGaAs-SOD2, $\alpha = 90.950(3)°$, $\beta = 94.972(2)°$, $\gamma = 90.149(3)°$, for $AlAsO_4$-CHA, $\alpha = 76.112(1)°$, $\beta = 86.582(1)°$, $\gamma = 89.094(1)°$. M−O is the average metal−oxygen bond distance. [b] TMA = $(CH_3)_4N^+$; DMA = $(CH_3)_2NH_2^+$; pip = piperazine; py = pyridine; dabco = 1,4-diazabicyclo[2.2.2]octane; R3 = $NH_2(CH_2)_3NH_2$; R4 = $NH_2(CH_2)_4NH_2$; R5 = $NH_2(CH_2)_5NH_2$; R6 = $NH_2(CH_2)_6NH_2$; R14 = $NH_2(CH_2)_3NH(CH_2)_2NH_2$; R16 = 2-(2-aminoethylamine)ethanol, $H_2NCH_2CH_2NHCH_2CH_2OH$; R19 = 4-(aminomethyl)piperidine; R20 = *N*-(2-aminoethyl)pyrrolidine.

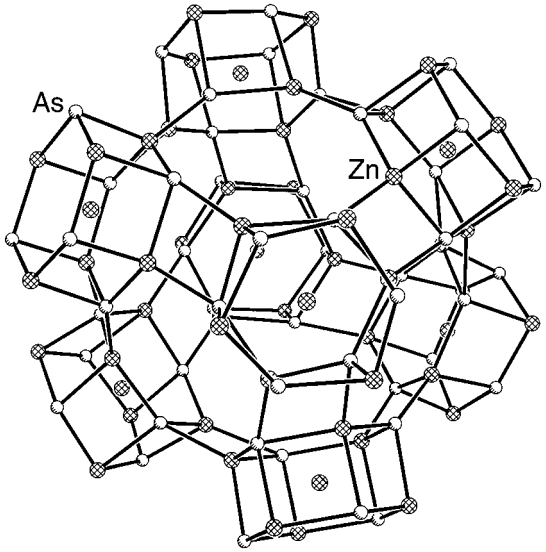

Figure 1. α-Cage surrounded by eight double six-ring units in $ZnAsO_4$-KFI. Framework oxygen atoms are omitted for clarity. Cross-hatched spheres represent Zn^{2+} sites, whereas white spheres are As^{5+} sites. Unconnected spheres are extra-framework Zn^{2+} sites.

Three sodalite analogues reported here demonstrate that principles of host−guest charge-matching and symmetry-matching developed in the phosphate and germanate systems are equally applicable in the arsenate system.[12,13] While $N(CH_3)^{4+}$ cations with the three-fold symmetry give rise to a cubic sodalite lattice, protonated piperazine molecules bring the cubic symmetry of a regular sodalite lattice all the way down to the triclinic. Many dozens of sodalite analogues with various chemical compositions are known, but rarely has the sodalite lattice undergone such a dramatic reduction as that reported here.

The synthesis of gismondine analogues in both alumino-, gallo-arsenate compositions (the structure type: GIS) and an alumino-arsenate laumontite analogue (the structure type: LAU) illustrates that the arsenate system bears some similarities to silicates and phosphates. In particular, the gismondine topology constructed from the common 4.8.8 net is a frequent occurrence in the synthesis of either silicates or phosphates. The synthesis of the gismondine analogues suggests that other 4.8.8 net-based structure types such as phillipsite and merlinoite might be accessible in the arsenate system.

Other topologies (ABW, analcime, chabazite, edintonite, and ZK-5) have been made in the zinc arsenate system. Among these, the large cage ZK-5 analogue, $ZnAsO_4$-KFI, is of particular interest because its structure is related to the commercially important zeolite A, but it has never been made before as a non-aluminosilicate despite extensive academic and industrial efforts in the exploration of phosphate-based molecular sieves.

With the exception of the ABW phase that is directed by ammonium cations only, the formation of analcime, chabazite, edingtonite, and ZK-5 phases requires the joint structure directing of two chemical species. For the edingtonite phase, both NH_4^+ cations and protonated 1,4-diaminobutane are included into the eight-ring channels. In the case of the chabazite and ZK-5 analogues, in addition to the protonated amine molecules, there is a Zn^{2+} cation located at the center of each double six-ring secondary building unit (Figure 1). Similar charge-balancing Zn^{2+} cations are also present in the analcime analogue.

In summary, it is shown that while the geometrical factor is the controlling factor in the synthesis of the four-connected UCSB-7 helical arsenate phases, the charge factor plays an important role in the synthesis of a number of structures that are analogues of phosphate phases. The interplay between the two factors allows the arsenate system to possess the structural characteristics of both phosphate and germanate systems. This explains why arsenates can adopt framework topologies that are unique either to the phosphate or germanate system. A peculiar feature of the arsenate system is the inclusion of divalent metals into structural subunits (e.g., double six-rings) of several analogues. With an enhanced understanding of various factors in the fabrication of zeolite-type frameworks, it is anticipated that more potentially useable microporous materials may be discovered by using the synthetic concept outlined here.

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Supporting Information Available: Crystallographic data for all structures listed in Table 1 including positional parameters, thermal parameters, and bond distances and angles (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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