

K_{5.76}Ga_{5.76}Si_{10.24}O₃₂·3.4H₂O, a gallo-silicate with the zeolite gismondine topologyAkhilesh Tripathi,^{a*} John B. Parise,^{a,b} Sun Jin Kim,^b
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The title compound, K–GaSi–GIS, potassium gallium silicon oxide hydrate, was synthesized hydrothermally and its crystal structure was determined from data collected on a single crystal of dimensions 10 × 10 × 8 μm at a synchrotron X-ray source. The compound, which has the aluminosilicate (AlSi) zeolite gismondine (GIS) topology, Ca₄[Al₈Si₈O₃₂]·16H₂O, crystallizes in the tetragonal space group *I*₄₁/*a*. A disordered distribution of the framework Si/Ga sites leads to higher symmetry of the GIS-type network compared with the usual monoclinic symmetry in AlSi–GIS. Framework Ga substitution for Al in AlSi–GIS leads to substantial distortion of the crankshaft chains, reducing the effective pore dimensions and suggesting the possibility of pore-dimension control *via* partial framework-cation substitution.

Comment

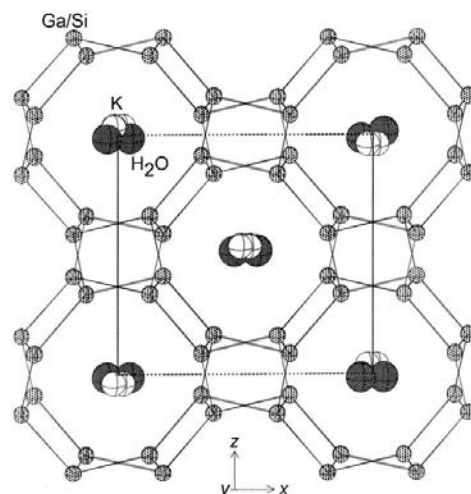
The present synthesis and structure determination is part of ongoing studies on the structural modifications induced upon heteroatom substitution in zeolites. The high flexibility of the GIS framework, evident from its accommodation of different chemical compositions, is of interest to us. In the case of framework substitution of Si by Ge of an aluminogermanate gismondine (AlGe–GIS), we observed a unique ordered Na and a usual disordered K form (Tripathi *et al.*, 2000). Further, some gallosilicate framework structures show unique behavior in their ability to catalyze cyclization reactions and NO reduction with methane, such as Ga–H–ZSM-5 (Li & Armor, 1994).

Recently, the synthesis of a gallosilicate (TNU-2) with the GIS topology was reported (Cho *et al.*, 2000). The chosen space group *I*₄ was based on preliminary indexing of the powder diffraction pattern. However, in the case of K–GaSi–GIS, a symmetry check using the program *PLATON* (Spek, 2000; Le Page, 1987, 1988) revealed that after applying an

origin shift in the non-centrosymmetric disordered structure model, pairs of atoms related by inversion and translation can be found. These fulfill the symmetry requirements of a centrosymmetric (*I*₄₁/*a*) structure model within a maximal deviation of about 4 s.u.'s.

The structure of K–GaSi–GIS consists of two double crankshaft chains of disordered [(Si,Ga)O₄] tetrahedra (*T* atoms), connected at right angles to each other, forming a framework. Its pores are interconnected through a three-dimensional channel system with eight-ring openings along the *a* and *b* axes. As a consequence of this arrangement of *T* atoms, a gismondine-like cage is formed by four eight-membered and six four-membered rings (Meier *et al.*, 1996).

Tetrahedral Si–O and Ga–O bond distances in oxides are 1.61 and 1.82 Å, respectively (Shannon, 1976). The average *T*–O distance of 1.697 Å in K–GaSi–GIS (Table 1) matches closely with the calculated mean distance of 1.685 Å obtained from the refined Si/Ga ratio of 1.78 and the established empirical formula (K₆Ga₆Si_{10.5}O₃₆) from the electron probe microanalysis (EPMA). The mean *T*–O distance and the Si/Ga distribution in a ratio of 1.78 along the 4₁ screw axis rules out an ordered arrangement. Further, the calculated valence sum of 3.50 v.u for the *T* site confirms its disordered nature (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991). The most evident difference between the three K–GaSi–GIS, K–AlSi–GIS (Bauer & Baur, 1998) and K–AlGe–GIS (Tripathi *et al.*, 2000) GIS topologies results from the *T*-atom ratio. Unlike the Si(Ge)/Al ratio of 1 observed for the AlSi and AlGe frameworks, a ratio of 1.78:1 is observed for Si/Ga in K–GaSi–GIS. Accordingly, whereas in the AlGe–GIS and AlSi–GIS topologies, maximum ordering on the *T* sites results in the lower symmetry monoclinic space group, a disordered *T*-atom distribution allows the higher tetragonal symmetry for K–GaSi–GIS. The disordered distribution of *T* atoms in K–GaSi–GIS is similar to the framework model of partially dehydrated Ca-garronite, Ca_{2.83}Al_{5.66}Si_{10.34}O₃₂·13H₂O, which has a similar *T*-atom ratio (Schröpfer & Joswig, 1997).

**Figure 1**

Projection along [010] for K–GaSi–GIS. Small empty spheres represent K ions and large filled gray spheres represent water molecules.

A true comparison of the volume change and the average $T-O-T$ angles upon Ga substitution of Si is not possible with K-AlSi-GIS or Ca-garronite since the hydration levels and extra framework cations are different. However, the observed contraction of the $T-O-T$ angle upon substitution with the larger heteroatom (Ga) is consistent with other isotopic substituted zeotypes, such as AlGe-NAT [Tripathi *et al.* (2000); NAT is a three-letter code assigned by the International Zeolite Association to the zeolite Natrolite (Meier *et al.*, 1996)] and GaSi-NAT (Lee *et al.*, 2000). The mean $T-O-T$ angle of 135.6° in K-GaSi-GIS is 3.4° smaller than that in K-AlSi-GIS and 9.95° smaller than that in Ca-garronite. Such a contraction leads to changes in ellipticity of the eight-rings and a twist in the double crankshaft chains. The ratio of the longest (L) to the shortest diagonals (S) of an eight-ring defines the ellipticity with values of L/S ratios close to one for circular eight-rings. The eight-rings in K-GaSi-GIS were found to be 6.4% more elliptical compared with K-AlSi-GIS. The distortions in K-GaSi-GIS can be more closely observed from the twist in the double crankshaft chains. In the hydrated modification of Ca-garronite or other isotopic GIS with a zero twist case, the four-rings have their normals approximately parallel to either (100) or (010). Upon dehydration, the normals to the rings come at modified angles off these planes. In the case of K-GaSi-GIS, the normals to the rings come alternatively about $+15.3$ or -15.3° off these planes. The *ex situ* heating studies of K-GaSi-GIS indicate that the GIS topology is retained up to *ca* 1173 K. Consistent with the behavior in Ca-garronite, where the ellipticity and twisting of the crankshaft chains increases until dehydration, K-GaSi-GIS is also likely to show higher distortion and twist upon dehydration.

The Ga/Si tetrahedra are regular with a deviation from the ideal tetrahedral angle (109.47°) of 1.56° . The extra-framework K^+ cations and H_2O molecules reside close to the center of eight-ring channels along [100] and [010] (Fig. 1). The K1 site is coordinated to five framework O atoms and three partially occupied H_2O molecules with interatomic distances in the ranges 2.676 (8) to 3.178 (8) Å, and 2.76 (4) to 2.89 (3) Å, respectively. The interatomic distance of 1.927 Å between two of the partially occupied H_2O sites suggests a coordination sphere of seven for the K1 site. The calculated bond valence sum of 1.02 v.u., assuming seven coordination for the K1 site, is in good agreement with the expected value of 1.0 v.u. (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991). The observed range of K-O bond lengths also compares well with those observed in other GIS topologies, such as K-AlGe-GIS [range 2.74 (1)–3.31 (2) Å]. The OW1 site is coordinated to three K sites, with interatomic distances in the range 2.76 (4)–2.89 (3) Å, consistent with K-AlSi-GIS and Ca-garronite. The slightly higher values of the isotropic displacement parameters for K1 (7.74 \AA^2) and OW1 (4.65 \AA^2) are not unprecedented for a disordered structure with partial occupancies (Tracey *et al.*, 1996). The largest components of the anisotropic displacement parameters for K1 and OW1 are in the direction of the a axis. This is one of the most open parts of the structure with eight-ring channels.

Experimental

The K-GaSi-GIS single crystals were synthesized hydrothermally from the gel of composition $0.3Li_2O:7.0K_2O:1.0Ga_2O_3:10SiO_2:170H_2O$. KOH (2.99 g) and Ga_2O_3 (0.624 g) were dissolved in deionized water (6.4 g), heated at at 383 K for 16 h and cooled to room temperature. LiOH· H_2O (0.086 g) and colloidal silica (Ludox AS 40, 5.0 g) were then added to this solution. After being stirred for 24 h, the resultant solution was heated for 5 d at 383 K. The product was filtered, washed with deionized water, and dried at room temperature. Octahedrally shaped colorless crystals were obtained. The sample was characterized to establish phase identity and purity using a Scintag PAD-X automated X-ray powder diffractometer. Upon comparing the peak positions in the XRD pattern with the peak positions in Ca-garronite, the sample was found to be phase pure (Tracey *et al.*, 1996). Wavelength-dispersive EPMA was carried out with a Cameca electron microprobe using 15 kV accelerating potential and a beam current of 10 nA. Single-crystal data were collected at the SUNY X3A1 beamline of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL).

Crystal data

$K_{5.76}Ga_{5.76}Si_{10.24}O_{32} \cdot 3.4H_2O$	$\lambda = 0.6430 \text{ \AA}$
$M_r = 1484.3994$	Cell parameters from 5045 reflections
Tetragonal, $I4_1/a$	$\theta = 2.62\text{--}30.62^\circ$
$a = 9.9639 (6) \text{ \AA}$	$\mu = 5.196 \text{ mm}^{-1}$
$c = 9.3806 (9) \text{ \AA}$	$T = 298 (5) \text{ K}$
$V = 931.3 (1) \text{ \AA}^3$	Octahedral, colorless
$Z = 1$	$0.010 \times 0.008 \times 0.008 \text{ mm}$
$D_x = 2.647 \text{ Mg m}^{-3}$	
Synchrotron radiation	

Data collection

Bruker SMART CCD area-detector diffractometer	749 reflections with $I > 2\sigma(I)$
φ scans	$R_{\text{int}} = 0.094$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$\theta_{\text{max}} = 30.62^\circ$
$T_{\text{min}} = 0.949$, $T_{\text{max}} = 0.959$	$h = -15 \rightarrow 15$
5111 measured reflections	$k = -15 \rightarrow 15$
939 independent reflections	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0460P)^2 + 15.7958P]$
$R[F^2 > 2\sigma(F^2)] = 0.067$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.156$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.131$	$\Delta\rho_{\text{max}} = 1.19 \text{ e \AA}^{-3}$
939 reflections	$\Delta\rho_{\text{min}} = -0.97 \text{ e \AA}^{-3}$
47 parameters	

Table 1

Selected geometric parameters (Å, °).

Ga1—O1 ⁱ	1.673 (5)	K1—OW1 ⁱⁱⁱ	2.76 (4)
Ga1—O2 ⁱⁱ	1.684 (4)	K1—OW1 ^{iv}	2.84 (3)
Ga1—O2	1.686 (5)	K1—O1 ⁱⁱⁱ	2.852 (8)
Ga1—O1	1.688 (5)	K1—OW1 ^v	2.89 (3)
K1—O2	2.676 (8)	K1—O1 ^v	3.066 (11)
K1—O2 ⁱⁱⁱ	2.697 (7)	K1—O2 ^{vi}	3.178 (8)
O1 ⁱ —Ga1—O2 ⁱⁱ	108.0 (2)	O2 ⁱⁱ —Ga1—O1	109.7 (3)
O1 ⁱ —Ga1—O2	113.0 (3)	O2—Ga1—O1	104.6 (2)
O2 ⁱⁱ —Ga1—O2	107.5 (3)	Si1 ^{vii} —O1—Ga1	135.8 (3)
O1 ⁱ —Ga1—O1	113.8 (4)	Si1 ^{vi} —O2—Ga1	135.4 (3)

Symmetry codes: (i) $\frac{3}{4} - y, \frac{1}{4} + x, \frac{1}{4} - z$; (ii) $\frac{3}{4} - y, \frac{1}{4} + x, \frac{1}{4} + z$; (iii) $\frac{1}{4} - y, x, \frac{3}{4} - z$; (iv) $\frac{3}{4} - y, \frac{3}{4} + x, -\frac{1}{4} - z$; (v) $y - \frac{3}{4}, \frac{3}{4} - x, -\frac{1}{4} - z$; (vi) $y - \frac{1}{4}, \frac{3}{4} - x, z - \frac{1}{4}$; (vii) $y - \frac{1}{4}, \frac{3}{4} - x, \frac{1}{4} - z$.

A monochromatic beam was selected using an Si(111) single crystal. The wavelength was calibrated by measuring the cell dimension of the ruby standard crystal. Data were collected by fixing the detector while rotating the crystals in φ with a 0.3° step interval. The intensity of the incident beam was normalized based upon the counts from a beam monitor. Initial cell parameters were determined using sets of reflections with $I > 15\sigma(I)$ from 400 frames measured in φ from 0 to 120° . The intensities were integrated using the *SAINTE* program (Sheldrick, 1996). During the integration, the cell parameters were refined, and the orientation matrix was optimized every 50 frames. Corrections for Lorentz–polarization effects were made, and absorption corrections were applied using *SADABS* (Sheldrick, 1996). The space groups were determined by examining the systematic absences. Structural models were determined and refined using the *SHELXTL* program (Sheldrick, 1997). No H-atom positions were determined.

Data collection: *SMART* (Bruker, 1996); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *CrystalMaker Software* (Palmer, 2000); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1009). Services for accessing these data are described at the back of the journal.

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