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Structural Characterization of the Gallosilicate TsG-1, $K_{10}Ga_{10}Si_{22}O_{64}\cdot 5H_2O$, with the CGS Framework Topology

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Aluminosilicate zeolites represent an important class of molecular sieves. Their unique structures, consisting of frameworks containing periodic and molecular-sized pores and channels, impart on these materials shape and size selective acid catalytic properties.[1,2] These properties can be further modified by substitution of framework aluminum and/or silicon by other tetrahedral atoms such as Ga and Ge. The substitution of Al by Ga is common and has been proposed, for example, as a means to control pore dimension[3,4] and increase para-selectivities for the alkylation of ethylbenzene[5] and for other gallium-promoted catalysis[6] such as the conversion of *n*-hexane.[7] The modification of existing aluminosilicate frameworks, or the complete substitution of Al with Ga in known aluminosilicate frameworks, is widely reported.[8] There are however few reports of microporous materials unique to gallosilicate chemistry.

A novel gallosilicate framework was reported by Krutskaya et al. while studying the phase diagrams of the $K_2O-Ga_2O_3-SiO_2-H_2O$ system at 200 °C.[9,10] This material apparently had no aluminosilicate analogue and was named TsG-1. Although the cell parameters and the water sorption properties of this material were described, the structure of TsG-1 was not reported. We report here the structure of microporous TsG-1.

TsG-1 was synthesized in the $K_2O-Ga_2O_3-SiO_2-H_2O-NH_4F$ system. A mixture of 0.625 g of Ga_2O_3 (3.33 mmol), 2.992 g of KOH (46.6 mmol), and 6.4 mL of H_2O was heated at 110 °C for 16 h in a polypropylene bottle and cooled to room temperature. The solution was added to 5 g of colloidal silica (40% SiO_2) and 0.126 g of NH_4F (3.33 mmol) as a mineralizing agent, and after stirring for 24 h, the resulting clear solution was transferred into a Teflon-lined vessel and heated at 150 °C for 5 days. The Si/Ga ratio of the original gel could be varied between 2.5 and 5.0 to produce the same material.

The structure of TsG-1 was determined from single-crystal X-ray diffraction data.[11] Following its solution, it became clear that the structure of TsG-1 is related to the CGS framework[12] and possesses the ideal topological symmetry, *Pnma*. This contrasts with the cobalt−gallium phosphate analogue[12] which exhibits an alternation of MO_4 (M = Co, Ga) and PO_4 tetrahedra throughout the framework[12] and has $P2_1/c$ symmetry. For the TsG-1 framework, however, it was found that Ga and Si atoms are disordered throughout the tetrahedral sites with the idealized Ga-to-Si ratio of 1 to 2.2. To confirm the correct cell, monoclinic symmetry was tested during the data integration by varying the unique axis choice, which resulted in either statistically equivalent or poorer agreements between symmetry equivalent reflections, compared with the orthorhombic cell choice.[11] Ab Initio indexing of the powder diffraction pattern of TsG-1 was also consistent with the choice of orthorhombic symmetry, in agreement with the single crystal study (Figure 1).[13]

TsG-1 has an interpenetrated double 6-ring building unit ($4^{10}6^38^2$) (Figure 2), which is unique to the CGS framework.[12] This building unit is closely related to the double 6-ring of group 4 zeolites[14] such as CHA, GME, FAU, ZK-5, and AEI, but has not been observed in

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(11) Crystal structure of TsG-1: $K_{10}Ga_{10}Si_{22}O_{64}\cdot 5H_2O$, $M = 1942.8(7)$, orthorhombic, *Pnma*, Z[1] = 8, $a = 8.613(2)$ Å, $b = 13.813(3)$ Å, $c = 16.330(3)$ Å, was studied using a needle-shaped crystal (10 × 12 × 150 μm) at 293(2) K. All experiments were carried out at the SUNY X3A beamline at the National Synchrotron Light Source (NSLS). A 0.643 Å X-ray beam monochromated by a Si(111) crystal was used. The data collection was performed on a Huber diffractometer equipped with a BRUKER SMART 1K CCD area detector. The cell parameters were determined from 963 reflections with $I > 20\sigma(I)$ from 600 frames measured in ϕ from 0° to 180°. The data were collected by fixing the detector at $2\theta = 20°$ while oscillating the crystal (ϕ axis) from 0° to 360° with a 0.3° step interval and 7 s counting times per frame. The incident beam intensity was normalized on the basis of the counts from a beam monitor. The intensities were integrated and merged using SAINT[19] and SORTAV[20] programs, respectively. During the integration, the orientation matrix was optimized every 50 frames. LP factor corrections were made, and absorption corrections were applied using SADABS.[21] By rejecting outliers (7.8% of the total 18307 reflections), a R_{int} of 5.75% was obtained based on 16 888 reflections, which represented 4.3 overall average measurement multiplicity. Attempts to integrate with a monoclinic cell gave R_{int} of 6.26%, 6.34%, and 6.12% for the unique axis choices of *a*, *b*, and *c* axis, respectively. The space group was determined from examination of the systematic absences. The structure was determined and refined using the SHELXTL program.[22] Refinement was based on full-matrix least-squares techniques on F^2, and standard discrepancy indexes for the final model were $R_1 = 0.0501$, ${}_wR_2 = 0.1353$, and GOF = 1.076 with 2560 reflections ($I > 2\sigma(I)$). Anisotropic temperature factors were included except for the split pairs of potassium ions, for which constrained isotropic temperature factors were used. Water molecules were also refined using isotropic temperature factors.

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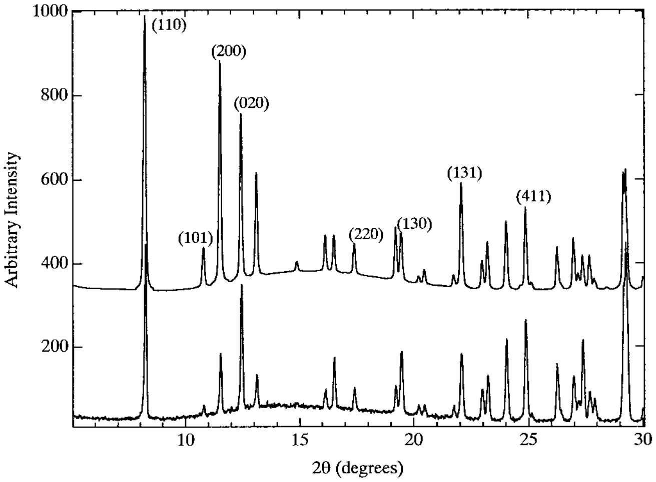

Figure 1. Observed (bottom) and calculated (top) X-ray powder diffraction patterns for TsG-1. Data collection was performed on a Scintag PAD-X automated diffractometer using Cu Kα radiation. All the reflections can be indexed, some of which are marked with their indices, without any crystalline impurities (background from the sample holder).

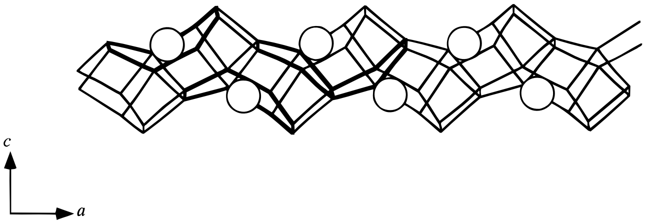

Figure 2. A skeletal representation of the sinusoidal array of the interpenetrated double 6-rings generated by sharing the intergrown 6-rings. Nodes represent the centers of Si/Ga tetrahedra and straight line sections represent the T−O−T linkages (T = Si/Ga). Potassium ions are illustrated as circles at the buckled 8-ring openings. Other potassium positions and waters are omitted for clarity. Some of the buckled 8-rings and intergrown 6-rings are emphasized with bold lines.

another 4-connected net. By replacing one of the 4-ring walls of the double 6-ring with another 6-ring, a modified scoop-shaped building unit is generated, which is composed of a pair of intergrown 6-rings, a buckled 8-ring, and five 4-ring walls ($4^5 6^2 8^1$) (Figure 2). These scoop-shaped building units are connected to each other by sharing the intergrown 6-rings, resulting in a sinusoidal array of the interpenetrated double 6-rings (Figure 2), as is observed in the CGS framework.[12] A 3D framework is constructed by connecting the sinusoidal arrays of the interpenetrated double 6-rings via 4-rings to form channels of s-shaped 10-rings and elliptical 8-rings along the [100] and [010] directions, respectively (Figure 3), following the CGS topology.[12] These channels intersect each other to form three-dimensional networks of cavities with the s-shaped 10-ring and elliptical 8-ring openings.

Unlike the cobalt−gallium phosphate analogue,[12] where template cations are disordered at the pore intersections, extraframework cations and water molecules are found along the intracrystalline channels and cavities of TsG-1. The buckled 8-ring site is fully occupied by potassium ions with coordination distances to framework oxygens in the range of 2.732(7) − 3.226(6) Å (Figure 2). Three partially occupied potassium sites, two of which split by 0.79(2) Å, were found at the pockets of the s-shaped 10-ring (coordination distances to the framework oxygens in the range of 2.78(2)−3.21(2) Å). Two other split sites partially occupied by potassium ions were found along the 2-fold axis of the elliptical 8-ring, separated from each other by 0.67(2)−1.00(1) Å. These cations coordinate to the framework oxygens at distances ranging from 2.65(2) to 3.26(1) Å. The coordinations of potassium ions in these less-symmetric ring environments are analogous with previous observations. For example, potassiums exhibited a site preference of the puckered 8-ring, while larger cesium ions were found at the flat 8-ring site in the γ cage of ZK-5.[15] The water molecules in hydrated TsG-1 partially populate four different sites bound to the potassium ions along the s-shaped 10-ring channels with K−H_2O distances in the range of 2.54(6)−3.23(4) Å.

The thermal stability and dehydration characteristics of TsG-1 were investigated using an in situ synchrotron X-ray powder diffraction technique.[16−18] Preliminary results indicate a rapid contraction along the *b*-axis during the initial dehydration ramp to 100 °C. Crystallinity is preserved throughout the course of the entire thermal ramp to 600 °C, and no intermediate phases are formed, consistent with the results from Krutskaya et al.[9,10]

The open structure of TsG-1 suggests its potential for ion exchange. Preliminary results show that Na^+, Rb^+, Cs^+, Sr^{2+}, and NH_3^+ ions can all exchange K^+ ions successfully without framework collapse. Studies are underway to detail ion exchange isotherms and ion selectivities.

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(13) Powder X-ray diffraction data of TsG-1 were measured using a Scintag PAD-X automated diffractometer and Cu Kα radiation. Indexing was performed using the GSAS suite of programs[23] to give an orthorhombic cell of a = 8.665(1) Å, b = 14.193(1) Å, and c = 16.342(1) Å. The difference in the *b*-axis of the unit cell between the models from single crystal and powder data can be related to the difference in hydration level under which each sample was prepared and the data were collected. The results from the in situ dehydration experiment[16] are consistent with this phenomenon and show the *b*-axis is most sensitive to the hydration level. Structural studies related to the dehydration behavior of TsG-1 are ongoing.

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(16) In situ synchrotron X-ray powder diffraction was performed at beamline X7B of the NSLS. A powdered sample of TsG-1 was loaded into a 0.5 mm quartz capillary connected to a vacuum (<5 mTorr), and a heater[24] was placed below the sample position. A monochromatic beam was obtained using a channel-cut Si(111) monochromator, and the wavelength of 0.9511(3) Å was calibrated using a LaB_6 standard material (a = 4.1569(1) Å). A translating imaging plate (TIP) detector recorded the diffraction pattern behind a steel screen with a 3 mm vertical slit at a step interval of 20 s while the temperature was ramped from room temperature to 600 °C for 4 h and back to room temperature for 1 h.

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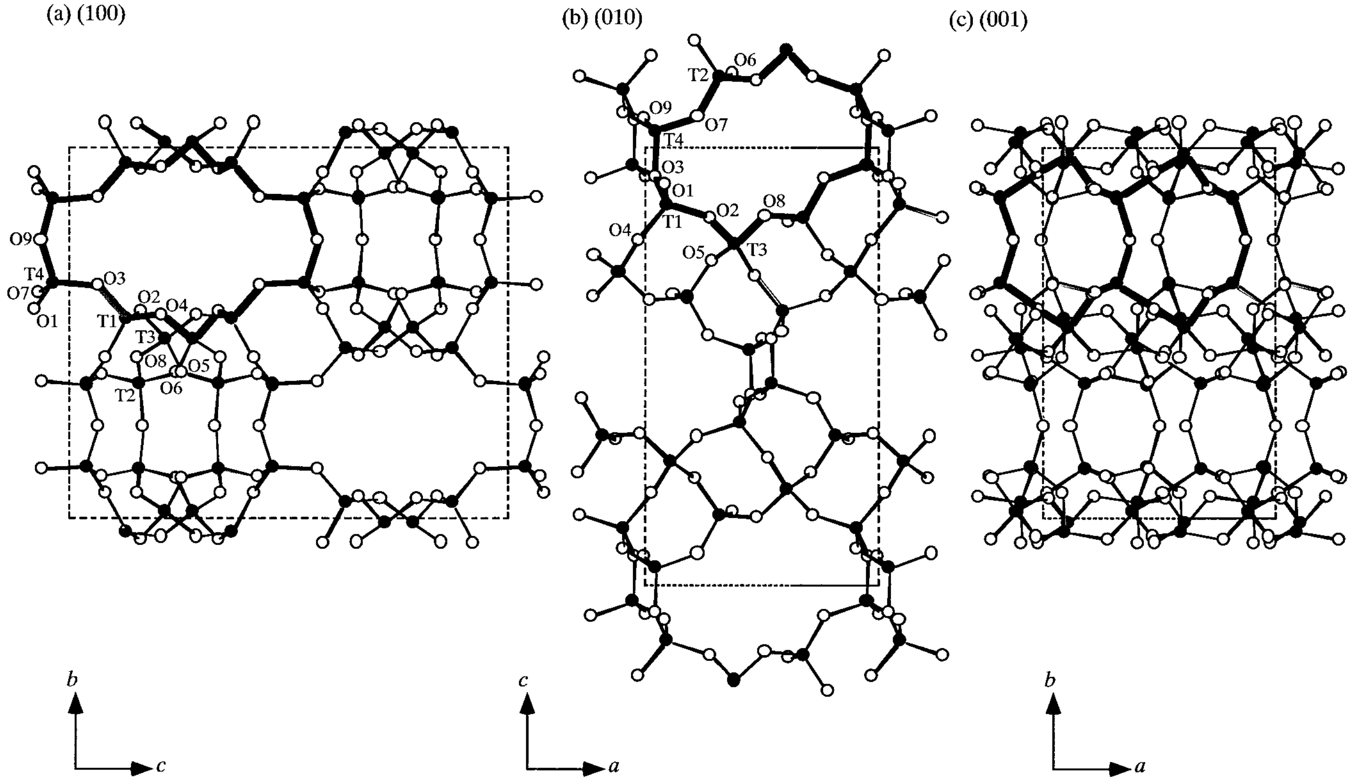

Figure 3. (a) A ball-and-stick model view down (100) of a unit cell of TsG-1 ($K_{10}Ga_{10}Si_{22}O_{64}\cdot 5H_2O$). Black circles represent the centers of Si/Ga tetrahedra and hollow circles represent the bridging oxygen atoms. Potassium ions and water molecules are not shown for clarity. Dashed lines define a unit cell. A 10-ring channel is emphasized with bold lines. The size of the 10-ring (11.15 × 6.02 Å) was determined from O9−O9 and O2−O4 distances. (b) a ball-and-stick model view down (010) of a unit cell of TsG-1. An 8-ring channel is emphasized with bold lines. The size of the 8-ring (8.88 × 5.34 Å) was determined from O3-O3 and O8-O8 distances. (c) A ball-and-stick model view down (001) of a unit cell of TsG-1. A pair of intergrown 6-rings of TsG-1 is emphasized with bold lines.

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Supporting Information Available: Crystal data, structure refinement, structure factors, and an ORTEP drawing for TsG-1. This material is available free of charge via the Internet at http://pubs.acs.org.

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