

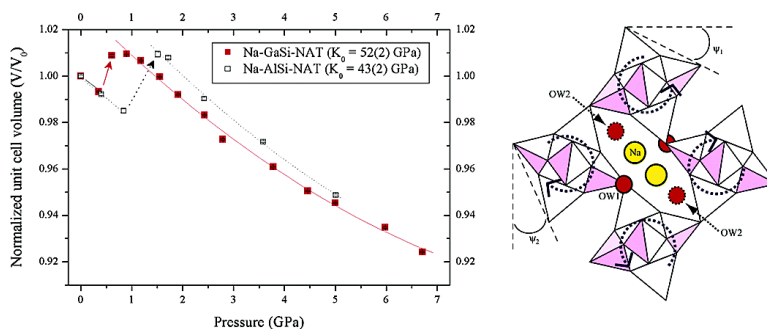
Communication

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## Pressure-Induced Hydration at 0.6 GPa in a Synthetic Gallosilicate Zeolite

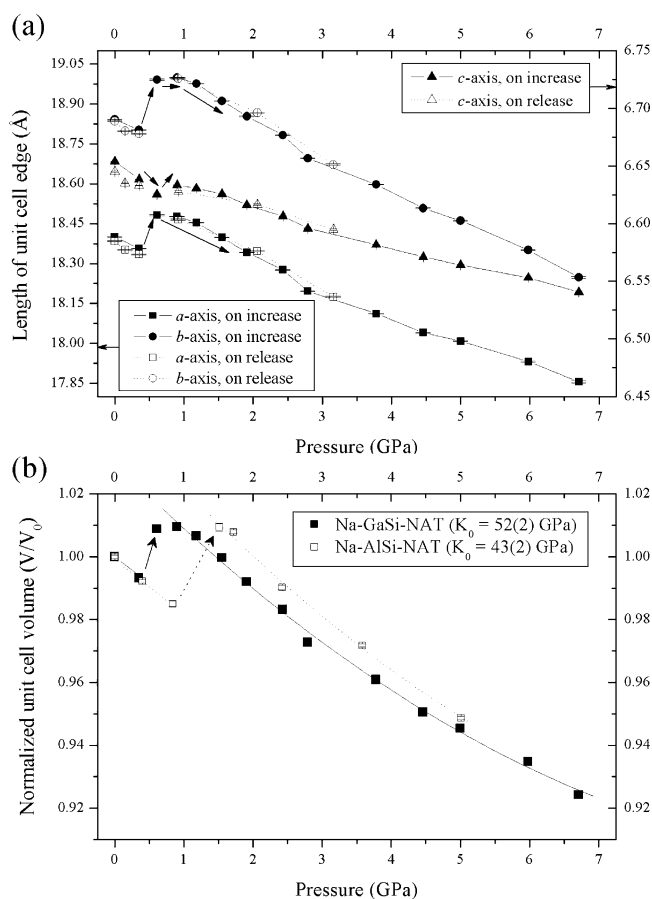
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We have recently identified the unique role of pressure in controlling the zeolitic water content, i.e., the pressure-induced hydration (PIH) and subsequent volume expansion in zeolite natrolite above 1.2 GPa caused by the selective sorption of water molecules from a pressure-transmitting fluid.<sup>1</sup> The reversibility of the PIH depends on the composition of both the framework and nonframework cations.<sup>1,2</sup> Naturally, it is important for any practical applications to lower the pressure where PIH occurs and possibly even control the degree of PIH. Here we report that a synthetic sodium gallosilicate, an isostructural analogue of the mineral sodium aluminosilicate natrolite,<sup>3</sup> has an onset of PIH between 0.3 and 0.6 GPa.<sup>4</sup>

The changes of the unit cell parameters of the sodium gallosilicate form of natrolite (Na–GaSi–NAT) as a function of pressure reveal abrupt expansions of the *a*-*b*-axes and a slight contraction of the *c*-axis at 0.61(5) GPa (Figure 1a). This gives rise to a volume expansion of ca. 1.5%, 34 Å<sup>3</sup> (Figure 1b). Further increase in pressure to 0.90(5) GPa results in a slight expansion of the *c*-axis and marginal changes in the *a*- and *b*-axes. Above 0.90(5) GPa, the unit cell parameters and volume show the normal contraction under increasing pressures up to 6.7(1) GPa. This process is reversed upon pressure release (Figure 1a). The volume expansion of Na–GaSi–NAT thus occurs at much lower pressures (between 0.35(5) and 0.61(5) GPa) than that of sodium aluminosilicate natrolite (Na–AlSi–NAT) and the behavior of Na–GaSi–NAT at 0.61(5) GPa is similar to that of Na–AlSi–NAT near 1.2 GPa.<sup>1</sup> At these pressures, both materials show two-dimensional swelling indicated by the abrupt increases in the *a*-*b*-axes lengths and the continued reduction of the *c*-axis. In Na–AlSi–NAT, an intermediate pseudo-orthorhombic phase with a partial occupancy of a new water site was claimed to precede the fully pressure-hydrated phase above 1.5 GPa.<sup>1</sup> In Na–GaSi–NAT, our imaging plate data do not show any indication of a symmetry-lowering from the orthorhombic phase although the peaks become slightly broader than those before and after the 0.61(5) GPa expansion. The bulk moduli of the PIH states are different, with that of Na–GaSi–NAT being slightly larger than that of Na–AlSi–NAT, 52(2) and 43(2) GPa, respectively (Figure 1b).<sup>5</sup> A consequence of this is that despite the original differences in cell volumes, the values appear to be converging at higher pressures. The refined value of *V*<sub>0</sub> for the PIH state of Na–GaSi–NAT, 2365(4) Å<sup>3</sup>, is 58 Å<sup>3</sup> larger than that observed for the normal state. This is an estimate of the additional space that must be created, in addition to existing void volume, to incorporate the extra water molecules.

The structural changes in Na–GaSi–NAT were determined using the in situ high-pressure synchrotron X-ray powder diffraction data and Rietveld refinements.<sup>6</sup> The PIH of Na–GaSi–NAT is characterized by a partial occupancy of a new water site (OW2) at 0.61-



**Figure 1.** (a) Pressure dependence of the unit cell edge lengths of Na–GaSi–NAT. (b) Comparison of the pressure dependence of the normalized unit cell volume in Na–GaSi–NAT (filled squares) and Na–AlSi–NAT (unfilled squares). Solid curve represents a fit of bulk modulus on *V/V*<sub>0</sub> for Na–GaSi–NAT and dotted curve for Na–AlSi–NAT.

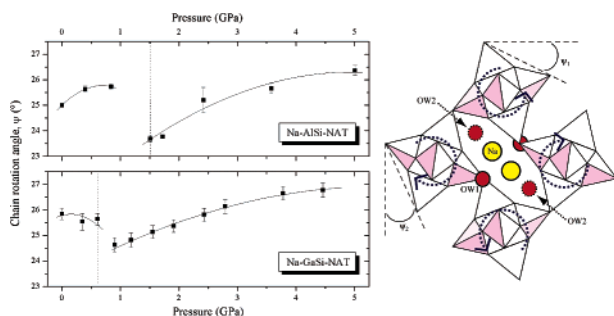
(5) GPa, which is subsequently fully occupied above 0.90(5) GPa (Figure 2, Supporting Information Tables). This gives rise to an increase of the zeolitic water contents from 16 H<sub>2</sub>O per unit cell below 0.35(5) GPa, to 28.6(5) H<sub>2</sub>O at 0.61(5) GPa, and then to 32 H<sub>2</sub>O above 0.90(5) GPa. Interestingly, the arrangements of the new water molecules at the OW2 site with respect to the original ones at the OW1 site lead to a dimensional evolution of a new hydrogen-bonded water nanostructure as the PIH progresses with increasing pressures. Before PIH, there is no hydrogen bonding between water molecules at the OW1 site. At 0.61(5) GPa, the new water molecules at the OW2 site form hydrogen bonds to the OW1 waters in such a way that the strongest OW1–OW2 interaction occurs across the channel (2.86(6) Å) rather than within the channel (3.03(5) and 3.26(8) Å, see Supporting Information Tables). Upon the full occupancy of the OW2 site at 0.90(5) GPa, the hydrogen

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**Figure 2.** Comparison of the pressure dependence of the overall chain rotation angle ( $\psi$ ) in Na–GaSi–NAT (lower) and Na–AlSi–NAT (upper). Solid curves are polynomial fits to guide the eye. Vertical dotted lines represent the pressure where PIH is first seen during the experiments (Na–GaSi–NAT at 0.61 GPa and Na–AlSi–NAT at 1.5 GPa). A polyhedral representation of the Na–GaSi–NAT structure is shown in the right to illustrate the effect of  $\psi$  angle on the channel opening for PIH.

bonds become more evenly distributed, with the interchannel OW1–OW2 distance increasing and one of the intrachannel OW1–OW2 distances decreasing to the same separation distances (2.99–(3) Å). As a result, chains of hydrogen-bonded water molecules form across the channel walls along the [101] direction. This one-dimensional, two-connected water nanochain evolves into a three-dimensional network of three-connected water molecules near 2.79(5) GPa when the OW1–OW2 separation distances of a water molecule to all three neighboring water molecules become the same within two standard deviations (2.99(3)–3.02(4) Å). This gives rise to the formation of two sets of water nanotubes across and inside the natrolite channels, with the latter being similar to the helical water nanotube observed in Na–AlSi–NAT upon PIH near 1.5 GPa.<sup>1</sup> The three-dimensional network of water molecules in Na–GaSi–NAT at 2.79(5) GPa is thus built of interconnected water nanotubes so that the smaller four-ring helices of water nanotube enclose the sodium cations and the larger eight-ring water nanotubes enclose the fibrous chains of tetrahedra of the natrolite framework.

Insights into the underlying mechanisms of the onset of PIH can be gained by comparing the structural responses of the respective host lattices. As pointed out previously, the synthetic Na–GaSi–NAT is an isostructural analogue of Na–AlSi–NAT derived by the isomorphous substitution of the ordered Al with larger Ga.<sup>3</sup> Under ambient conditions, both materials show the same distribution of the nonframework sodium cations and water molecules, which are located at the fully occupied sites along the natrolite channels.<sup>7,8</sup> In both Na–AlSi–NAT and Na–GaSi–NAT, PIH does not cause any major redistribution of the sodium cations but takes place at the same OW2 site along the channels (Supporting Information Tables). As a result, the PIH in both materials changes the sodium coordination polyhedra from a distorted trigonal prism (by four framework oxygen and two water molecules) to a pentagonal bipyramid (by four framework oxygen and three water molecules). In both cases, PIH results in an abrupt increase of the average sodium-to-framework oxygen distance, whereas the average sodium-to-nonframework OW1 oxygen distance show a marginal increase up to 5 GPa (Supporting Information Tables). Given the relatively fixed location of sodium during PIH, the abrupt increase of the sodium-to-framework oxygen distance and concomitant overbonding of the nonframework cation is mainly a consequence of the changes in the framework composition and geometry. A useful measure of the distortion of the natrolite framework from the ideal geometry is the overall rotation angle of the fibrous chain of tetrahedra,  $\psi$ , which is the mean of the angles between the sides of the quadrilateral around the  $T_5O_{10}$  tetrahedral building unit projected on the *ab*-plane.<sup>7,9</sup> Compared to that in Na–AlSi–NAT,

the  $\psi$  angle in Na–GaSi–NAT does not show an increase before PIH, and its overall change during PIH is reduced to  $\sim 1^\circ$  (Figure 2). This suggests that the entrance to the helical eight-ring channel in Na–GaSi–NAT is favorable, rather than a limiting step for PIH, due to the substitution of Al by the larger Ga and the resulting increase of the framework flexibility, especially the chain bridging T–O(2)–T angle (Supporting Information Tables). In fact, the ellipticity of the helical eight-ring channel in Na–GaSi–NAT decreases by 1.0% before PIH, whereas in Na–AlSi–NAT, it increases by ca. 5.9%. This facilitates the uptake of water into the channel and is responsible for the lower onset of PIH in Na–GaSi–NAT. As other chemical substitutions are possible to further modify the flexibility of the host lattice, yet lower pressures of PIH than the one observed in Na–GaSi–NAT and unusual physical properties are likely to be observed in future exploratory work.

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**Supporting Information Available:** Selected refinement results (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (a) Na–GaSi–NAT was synthesized using a hydrothermal method from a gel with the composition of 3.0 Na<sub>2</sub>O:1.0 Ga<sub>2</sub>O<sub>3</sub>:5.0 SiO<sub>2</sub>:200 H<sub>2</sub>O. A mixture of 1.874 g of Ga<sub>2</sub>O<sub>3</sub> (Alfa, 99.99%), 2.474 g of NaOH (Aldrich, 97%), and 30.96 g of deionized water was heated at 110 °C for 16 h in a Teflon bottle. After cooling to room temperature, 7.5 g of colloidal silica (Ludox AS 40, Aldrich) was added to the solution while stirring. After 24 h, the resultant gel was transferred into a Teflon-lined vessel and heated at 150 °C for 5 days. The product was recovered by filtration, washed with deionized water, and dried at room temperature. (b) Experiments were performed using a diamond anvil cell (DAC) and a powder sample of Na–GaSi–NAT at the X7B beamline of the National Synchrotron Light Source at Brookhaven National Laboratory. A mixture of 16:3:1 by volume of methanol:ethanol:water was used as a pressure medium. The DAC is based on a modified Merrill–Bassett design (HPDO–MBIBe) and employs beryllium supports. The pressure at the sample was measured by detecting the shift in the R1 emission line of the included ruby chips. More details regarding the high-pressure experiments are given elsewhere.<sup>1</sup> Diffraction data were collected using 200  $\mu$ m-size monochromatic synchrotron X-rays ( $\lambda = 0.9192(1)$  Å) and an imaging plate detector (Mar-345). The two-dimensional data were processed using the FIT2D suite of programs (Hammersley, A. P. *FIT2D: V9.129 Reference Manual V3.1*; ESRF Internal Report, ESRF98HA01T, European Synchrotron Radiation Facility, Cedex, France, 1998), and the structural evolution of Na–GaSi–NAT up to 4.5 GPa was determined using the Rietveld method and the GSAS suite of programs (Larson, A. C.; VonDreele, R. B. *GSAS: General Structure Analysis System*; Report LAUR 86-748, Los Alamos National Laboratory, New Mexico, 1986; Toby, B. H. *J. Appl. Crystallogr.* **2001**, *34*, 210–213). The refinement results including atomic parameters and selected bond distances and angles are listed in Supporting Information.
- Equations of state were determined by using EOSFIT 5.2 (Angel, R. J. *Equations of State*. In *High-Pressure, High-Temperature Crystal Chemistry*; Hazen, R. M., Downs, R. T., Eds. *Rev. Mineral. Geochem.* **2001**, *41*, 35–60). Both  $K_0$  and  $V_0$  were treated as variables, and several different formalisms were tried including Murnaghan, Birch–Murnaghan, Vinet and Finite Strain. Fits were tried with  $K'_0$  fixed at 4 or refined. In all cases, the values were not significantly different than those obtained using the simplest Murnaghan formalism ( $V_0 = 2365(4)$  Å<sup>3</sup>,  $K_0 = 52(2)$  GPa) and this was adopted with  $K'_0$  fixed. This is as expected given the small pressure range, with  $V/V_0$  always greater than 0.9.
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