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Synthesis and Characterization of $\mathrm{NaGaTe_2O_6{\cdot}2.4H_2O}$: A New Open-Framework Tellurite Related to Zemannite

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Three-dimensional open-framework oxide materials are of current interest owing to their widespread application in catalysis, energy storage, sorption, and ion exchange.[1,2] Zeolites, or aluminosilicates, encompass a specific class of these materials. An enormous effort has been expended to understand not only their syntheses and structures but also their physical properties.[3] A related research area concerns synthesizing new non-aluminosilicate zeolitic materials. Beginning with the aluminum phosphates, i.e., AlPO's,[4] this chemistry has been extended to encompass a variety of transition and main group elements.[5−10] Despite these efforts, open-framework tellurites are extremely rare; in fact, only one naturally occurring open-framework tellurite mineral, zemannite $\mathrm{Mg_{0.5}[(Zn,Fe)_2(TeO_3)_3]{\cdot}4.5H_2O}$, has been found.[11,12] To the best of our knowledge, only one instance of synthetic zemannite has been reported.[13] In this communication we report the synthesis and structure of $\mathrm{NaGaTe_2O_6{\cdot}2.4H_2O}$, an open-framework tellurite with a zemannite-like structure.[14−18]

$\mathrm{NaGaTe_2O_6{\cdot}2.4H_2O}$ is a three-dimensional material consisting of distorted trigonal pyramidal $\mathrm{Te^{4+}O_3}$ groups linked to $\mathrm{Ga^{3+}O_6}$ octahedra, through corner-shared oxygen atoms. If the structure is viewed down the [001], the similarity to zemannite is apparent (see Figure 1). As with zemannite, this 12-membered ring (12-MR) is composed of alternating $[\mathrm{TeO_{3/2}}]^+$ cations and, in our case, $[\mathrm{GaO_{6/2}}]^{3-}$ anions. Each $[\mathrm{GaO_{6/2}}]^{3-}$ anion is linked to two $[\mathrm{TeO_{3/2}}]^+$ cations, whereas each $[\mathrm{TeO_{3/2}}]^+$ cation is connected to a $[\mathrm{GaO_{6/2}}]^{3-}$ anion and an additional $[\mathrm{TeO_{3/2}}]^+$ cation. However, unlike zemannite $\mathrm{NaGaTe_2O_6{\cdot}2.4H_2O}$ does not contain any face-shared octahedra. Owing to the lack of face-shared octahedra, $\mathrm{NaGaTe_2O_6{\cdot}2.4H_2O}$ contains channels along the [100] and [010] directions (see Figure 2). These eight-membered-ring (8-MR) channels intersect the 12-MR pores and consist of four $[\mathrm{TeO_{3/2}}]^+$ cations and four $[\mathrm{GaO_{6/2}}]^{3-}$ anions that alternate around the ring. The pore sizes for the three channels are 5.0 Å × 5.0 Å (12-MR) and 2.1 Å × 3.6 Å (for both 8-MR), taking into account the atomic radii for oxygen.[19]

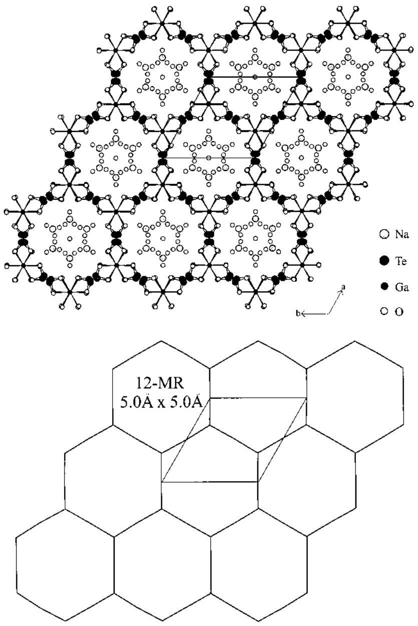

Figure 1. Ball-and-stick and wire representations of $\mathrm{NaGaTe_2O_6{\cdot}2.4H_2O}$ showing the 12-MR channels.

An interesting feature of $\mathrm{NaGaTe_2O_6{\cdot}2.4H_2O}$ is the occurrence of a $[\mathrm{Na_3{-}5H_2O}]^{3+}$ "cluster" (see Figure 3). The Na atoms form an equilateral triangle with Na−Na distances of 3.336(3) Å. Coplanar with this triangle are three $\mathrm{H_2O}$ molecules that equatorially bridge the Na atoms ($\mathrm{Na{-}H_2O_{eq}}$: 2.37(1) Å). The two remaining $\mathrm{H_2O}$ molecules are observed directly above and below the $\mathrm{Na_3}$ triangle interacting with all three Na atoms at a distance of 2.62(1) Å. Between the "clusters", along the *c*-axis, are the

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(14) $\mathrm{NaGaTe_2O_6{\cdot}2.4H_2O}$ was synthesized under supercritical hydrothermal conditions by combining 2.6 M NaOH (0.513 mL), $\mathrm{Ga_2O_3}$ (0.0310 g, 1.65×10^{-4} mol), and $\mathrm{TeO_2}$ (0.1066 g, 6.68×10^{-4} mol) in a gold tube (length = 7.5 cm and inner diameter = 0.47 cm). The tube was sealed and placed in a 27 mL Leco Tem-Press autoclave filled with 16 mL of $\mathrm{H_2O}$ (60% fill). The autoclave was heated to 425 °C for 72 h and cooled to room temperature at 6 °C $\mathrm{h^{-1}}$. The gold tube was opened, and colorless hexagonal columnar crystals were recovered, by filtration, in 20% yield based on tellurium.

(15) A colorless prismatic crystal (0.05 mm × 0.08 mm × 0.2 mm) was glued onto a glass fiber. Single-crystal data were collected on a Siemens SMART diffractometer equipped with a 1K CCD area detector using graphite-monochromated Mo Kα radiation at 293 K. The data were integrated using the Siemens SAINT[16] program, with the intensities corrected for Lorentz, polarization, air absorption, and absorption attributable to the variation in the path length through the detector faceplate. A ψ-scan absorption correction was applied. The structure was solved by direct methods using SHELXS-97[17] and refined using SHELXL-93.[18] Crystal data for $\mathrm{NaGaTe_2O_6{\cdot}2.4H_2O}$: trigonal, $P\bar{3}1c$ (No. 165), $a = b = 9.216(7)$ Å, $c = 16.711(15)$ Å, $V = 1229.2(2)$ Å^3, $Z = 3$, $R(F) = 0.017$, $R_w(F^2) = 0.043$. Powder X-ray diffraction, using Cu Kα radiation, on the product is in good agreement with the generated pattern from the single-crystal data (see Supporting Information). Attempts to synthesize the material under subcritical conditions at similar reaction times produced a mixture of starting reagents. Infrared data: $\nu_{\mathrm{H_2O}}$: 3200, 1655 cm^{-1}, $\nu_{\mathrm{Ga-O}}$: 780 cm^{-1}; $\nu_{\mathrm{Te-O}}$: 703, 665 cm^{-1}.

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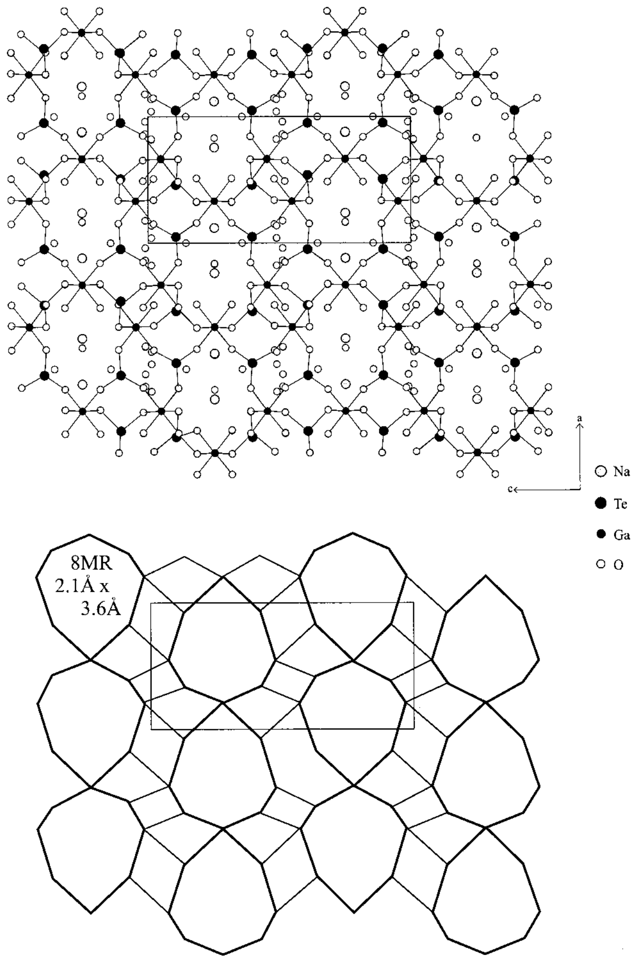

Figure 2. Ball-and-stick and wire representations of $NaGaTe_2O_6{\cdot}2.4H_2O$ showing the 8-MR channels.

remaining H_2O molecules. Thus there are three different types of H_2O molecules in the structure, "equatorial", "axial", and "free" (see Figure 3). (The "free" H_2O molecules interact through O−H···O hydrogen bonding with each other, the "equatorial" H_2O molecules, and framework oxide atoms.) The dehydration and, in one instance, rehydration of $NaGaTe_2O_6{\cdot}2.4H_2O$ can be understood by taking into account the environments of the H_2O molecules. TGA experiments revealed three weight losses at 180, 260, and 350 °C, consistent with the removal of 0.4 H_2O, 1 H_2O, and 1 H_2O, respectively (see Supporting Information).[20] The first dehydration step is completely reversible, indicative of the de- and rehydration of the "free" H_2O: the H_2O molecules observed between the "clusters", along the *c*-axis (see Figure 3). Powder XRD measurements, after this step, revealed that the material completely retained its crystallinity (see Supporting Information). The second dehydration step, occurring between 180 and 260 °C, is consistent with the loss of the "axial" H_2O molecules on the $[Na_3{-}5H_2O]^{3+}$ "cluster". This step is irreversible and results in a decrease of crystallinity. The final dehydration step occurs between 260 and 350 °C and indicates the loss of the "equatorial" H_2O molecules in the "cluster". This step is also irreversible, and powder XRD measurements revealed a complete loss of crystallinity. Therefore we suggest that the "free" H_2O molecules are lost first, then the axial ($Na{-}H_2O_{ax}$: 2.62(1) Å), and finally the equatorial H_2O molecules ($Na{-}H_2O_{eq}$: 2.37(1) Å). Thus, the three loss events are consistent with the degree of interaction of the H_2O molecules with the Na^+ cations. Interestingly, if $NaGaTe_2O_6{\cdot}2.4H_2O$ is heated above 400 °C, a new crystalline material is observed (see Supporting Information). Powder XRD measurements reveal a pattern that may be indexed on a primitive tetragonal cell, with $a = b = 9.58$ Å and $c = 9.29$ Å. Future work involving the structure of this material is in progress. Initial ion-exchange experiments indicate that the Na^+ cations can be exchanged for Li^+. We are currently exploring the exchange of other cations including H^+ with $NaGaTe_2O_6{\cdot}2.4H_2O$.

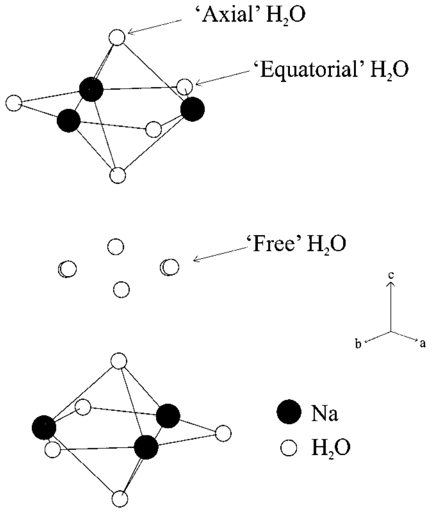

Figure 3. Ball-and-stick representation of the $[Na_3{-}5H_2O]^{3+}$ "cluster" showing the "axial", "equatorial", and "free" water molecules.

In summary, we have synthesized and characterized a rare example of an open-framework tellurite material that is related to the mineral zemannite. The utilization and flexibility of GaO_6 and TeO_3 groups as "building blocks" suggests that a large family of open-framework zemannite-type materials are possible. We have very recently synthesized other open-framework tellurites and will be reporting on them shortly.

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Supporting Information Available: ORTEP diagram, X-ray powder diffraction patterns (observed, calculated, and variable temperature), thermogravimetric data, and complete crystallographic data in CIF format for $NaGaTe_2O_6{\cdot}2.4H_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Thermogravimetric experiments were carried out on a SIEKO TG/DTA 320 instrument. The sample was heated at a rate of 5 °C min^{-1} under a flowing argon atmosphere. For the rehydration experiments, the sample was cooled under a flow of wet air.