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New Inorganic Helical Chain: Synthesis, Structure, Characterization, and Interconversion of $BaGa_2O_2(OH)_4$

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A new pseudo-two-dimensional compound, $BaGa_2O_2(OH)_4$, containing pure inorganic helical chains has been synthesized under hydrothermal reaction conditions using $Ba(OH)_2 \cdot 8H_2O$, Ga_2O_3, and H_2O as reagents. Further characterizations as well as a reversible transformation reaction to $BaGa_2O_4$ and H_2O are discussed.

Naturally ocurring and synthetic helical structures are of great interest in biological or pharmacological systems as well as a variety of materials chemistry fields such as nonlinear optics, asymmetric catalysis or separations, and molecular recognitions.[1−15] These helical moieties have often been observed in materials possessing rich structural architectures such as polyoxometalates, microporous phosphates, metal−organic frameworks, and metal oxyfluorides.[16−23] Most helical structures have been synthesized through hydro(solvo)thermal reactions, where the structure-directing agents, hydrogen bonds between the guest molecules and the hosts, and spontaneous aggregation of intact ligands with metal ions seem to play significant roles in the formation of the geometry.[24−27] Elevated temperatures, autogenous pressures, and mineralizers employed would also influence the preparation of structually diverse materials. In this Communication, we report the synthesis, structure, and characterization of a new inorganic helical chain compound, $BaGa_2O_2(OH)_4$. In addition, we demonstrate that an interconversion is possible between the helical chain structure of $BaGa_2O_2(OH)_4$ and the three-dimensional $BaGa_2O_4$ materials.

$BaGa_2O_2(OH)_4$ has been synthesized hydrothermally by combining $Ba(OH)_2 \cdot 8H_2O$, Ga_2O_3, and H_2O at 230 °C for 4 days.[28] Colorless crystals have been isolated as a single phase.[29] $BaGa_2O_2(OH)_4$ crystallizes in the space group *Pbca*

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(28) $BaGa_2O_2(OH)_4$ was synthesized by combining $Ba(OH)_2 \cdot 8H_2O$ (1.893 g, 6.00×10^{-3} mol), Ga_2O_3 (0.375 g, 2.00×10^{-3} mol), and H_2O (12 mL) in a Teflon-lined stainless steel autoclave and heating the mixture to 230 °C for 4 days before cooling to room temperature at a rate of 6 °C/h. A colorless crystalline product was recovered by filtration. A yield of 78% based on gallium was observed.
(29) Crystal data: crystal size $0.02 \times 0.03 \times 0.06$ mm^3, orthorhombic, space group *Pbca* (No. 61) with $a = 12.586(2)$ Å, $b = 7.4091(14)$ Å, $c = 13.042(3)$ Å, $V = 1216.1(4)$ Å^3, $Z = 8$, $\rho_{calc} = 4.116$ g cm^{-1}, $2\theta_{max} = 56.00°$, $\lambda = 0.710\,73$ Å, $T = 298.0(2)$ K, total data 6847, unique data 1406, observed data 1406 [$I > 2\sigma(I)$], $\mu = 15.161$ mm^{-1}, 83 parameters, $R(F)/R_w(F) = 0.0255/0.0656$ on $|F^2|$.

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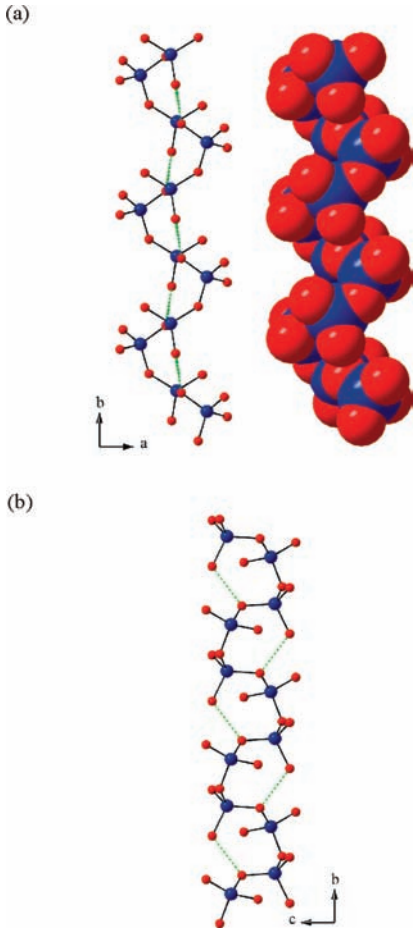

Figure 1. Ball-and-stick and space-filling models representing a helical chain structure of $BaGa_2O_2(OH)_4$ along the (a) *ab* and (b) *bc* planes. Note that the green dashed lines indicate the intrachain hydrogen bonds (blue, Ga; red, O).

(No. 61) with a structure similar to that of $BaAl_2O_2(OH)_4$.[30] $BaGa_2O_2(OH)_4$ has unidimensional helical chains that run parallel to the [010] axis (see Figure 1). Each helical chain consists of distorted $GaO_2(OH)_2$ tetrahedra that are corner-shared through O atoms. Within the chain, there are two unique Ga^{3+} cations. Each Ga^{3+} cation is bonded to two terminal OH groups as well as two bridging O atoms. While the observed distances for the bridging $Ga^{3+}-O$ bonds range from 1.811(3) to 1.830(3) Å, those of the terminal $Ga^{3+}-OH$ are longer, 1.848(3)−1.868(3) Å. As we will discuss more in detail later, the differences in the Ga−O bond lengths might be attributable to the hydrogen-bonding interactions. The $O-Ga^{3+}-O$ bond angles range from 103.79(14) to 114.33(15)°.

In order to identify the positions of H^+, the hydrogen bonds in the structure were analyzed. Bond valence sum (BVS) calculations[31,32] on these oxygen molecules reveal very similar small values of 1.076, 1.147, 1.108, and 1.119 for terminal oxygens O(3), O(4), O(5), and O(6), respectively. We also observe that strong intra- and interchain hydrogen bonds occur from terminal and adjacent O atoms [O(1)−O(4) 2.627(5) Å; O(2)−O(6) 2.733(4) Å; O(3)−O(5) 2.852(5) Å] (see dashed lines drawn in Figures 1 and 2). The intra- and interchain hydrogen-bonding interactions might be responsible for the helical chain geometry and pseudo-two-dimensional topology of $BaGa_2O_2(OH)_4$, respectively. Placing H^+ on the terminal oxygen sites is also consistent with the distances of the Ga−O bonds: the terminal Ga−O bond lengths [≤1.830(3) Å] are shorter than those of bridging Ga−O bonds [>1.848(3) Å] attributable to the hydrogen-bonding interactions. Finally, the IR spectrum confirms the presence of coordinated OH groups.

In connectivity terms, the structure may be described as a unidimensional helical chain of $[2GaO_{2/2}(OH)_{2/1}]^{2-}$, with the charge balance maintained by the Ba^{2+} cation. BVS calculations[31,32] on $BaGa_2O_2(OH)_4$ resulted in values of 1.77 and 2.96−2.98 for Ba^{2+} and Ga^{3+} cations, respectively.

The powder X-ray diffraction pattern of the ground polycrystalline $BaGa_2O_2(OH)_4$ is in good agreement with the calculated pattern from the single-crystal model (see the Supporting Information). The IR spectrum of the material shows the Ga−*O*−*H* vibrations at 3588 and 855

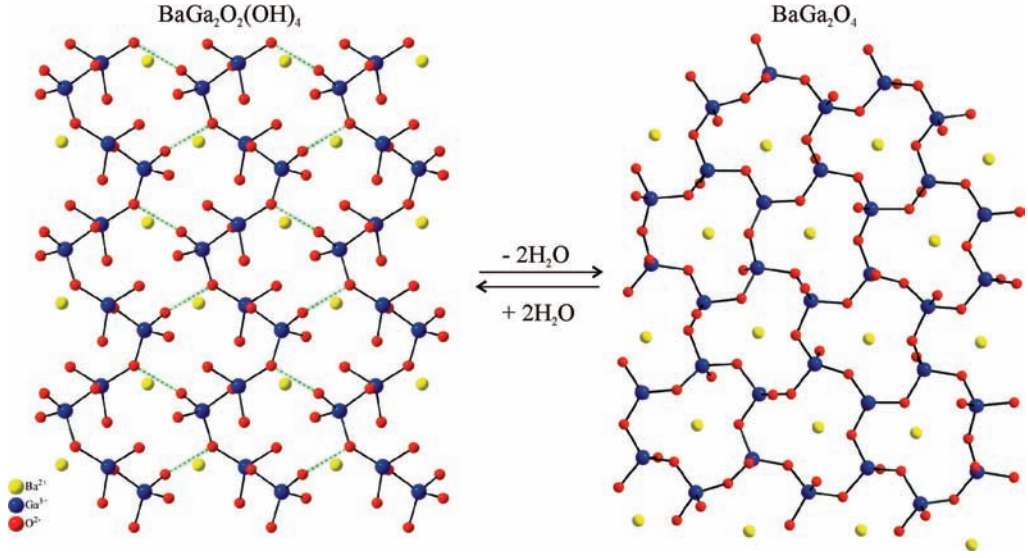

Figure 2. Ball-and-stick representations of $BaGa_2O_2(OH)_4$ and $BaGa_2O_4$. The green dashed lines indicate interchain hydrogen bonds, giving the structure a pseudo-two-dimensional topology. Note how the structures of $BaGa_2O_2(OH)_4$ and $BaGa_2O_4$ interconvert each other with the loss and gain of H_2O.

cm^{-1}. The vibrations at 718 and 667 cm^{-1} can be assigned to the *Ga−O* stretches. The assignments are consistent with those previously reported.[33] Thermal analysis indicates that the material is stable up to 240 °C. Above 240 °C, loss of H_2O molecules is observed with a total weight loss of 10.11% (calcd 9.56%).

An interesting characteristic of the material is the interconversion of $BaGa_2O_2(OH)_4$ to $BaGa_2O_4$[34] with the accompanying loss and gain of H_2O. This transformation is shown schematically in Figure 2. Once the powder samples of $BaGa_2O_2(OH)_4$ are heated up, the H_2O molecules are removed and a three-dimensional stuffed framework structure of $BaGa_2O_4$ is obtained. The powder X-ray diffraction measurement on the calcined material revealed a pattern consistent with that of $BaGa_2O_4$. Interestingly, the conversion is reversible: 100 mg of polycrystalline $BaGa_2O_4$ was transferred to a 23 mL Parr reactor with 5 mL of H_2O. The reactor was subsequently closed and heated to 200 °C. After cooling down to room temperature at a rate of 6 °C/h, colorless crystals of $BaGa_2O_2(OH)_4$ were obtained, which were identified by a powder X-ray diffraction pattern.

Attempts have been made to prepare a strontium analogue of the $BaGa_2O_2(OH)_4$ phase under the same synthesis conditions using $Sr(OH)_2$. However, colorless block-shaped crystals of $Sr_3Ga_2(OH)_{12}$[35] cubic garnet were obtained. The structural details for the new strontium−gallium hydroxide compound $Sr_3Ga_2(OH)_{12}$ are deposited in the Supporting Information.

In summary, we have successfully synthesized and characterized a new helical chain compound. Additional experiments using a variety of organic templating agents are ongoing and will be reported shortly.

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Supporting Information Available: Crystallographic data in CIF format, experimental and calculated powder X-ray diffraction patterns and thermogravimetric diagram for $BaGa_2O_2(OH)_4$, and detailed structural representations for $BaGa_2O_2(OH)_4$ and $Sr_3Ga_2(OH)_{12}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(35) Crystal data: crystal size 0.08 × 0.08 × 0.10 mm^3, cubic, space group $Ia\bar{3}d$ (No. 230) with $a = b = c = 13.1467(4)$ Å, $V = 2272.22(12)$ $Å^3$, $Z = 8$, $\rho_{calc} = 3.475$ g cm^{-1}, $2\theta_{max} = 55.84°$, $\lambda = 0.710\,73$ Å, $T = 173.0(2)$ K, total data 6903, unique data 197, observed data 197 [$I > 2\sigma(I)$], $\mu = 18.66$ mm^{-1}, 16 parameters, $R(F)/R_w(F) = 0.0466/0.1138$ on F^2.