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$K_2[Ge(B_4O_9)]\cdot 2H_2O$: A Unique 3D Alternating Linkage Mode of a B_4O_9 Cluster and GeO_4 Unit in Borogermanate with Two Pairs of Interweaving Double Helical Channels

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The first noncentrosymmetric potassium templated borogermanate, $K_2[Ge(B_4O_9)]\cdot 2H_2O$, has been solvothermally synthesized and characterized by IR, SEM, powder X-ray diffraction (PXRD), TGA, energy dispersive spectroscopy (EDS), single crystal X-ray diffraction, and second harmonic generation (SHG) activity, respectively. This compound crystallized in the monoclinic space group *Cc* with $a = 6.793(1)$ Å, $b = 12.0699(3)$ Å, $c = 11.895(3)$ Å, $\beta = 91.156(4)°$, $V = 975.1(4)$ Å^3, and $Z = 4$. Interestingly, the structure possesses a unique 3D alternating linkage mode of B_4O_9 clusters and GeO_4 units and contains two pairs of interweaving double helical channels with a 10-membered ring. In one, the right- and left-handed helices couple each other, and in the other, the left- and right-handed helices couple together. The compound exhibits distinct nonlinear optical (NLO) properties because it lacks a symmetric center. Furthermore, the framework of the title compound not only displays high thermal stability but also can be recoverable to a large degree during a dehydration–hydration cycle.

Microporous and other functional materials have been investigated intensively because of the potential of these materials in widespread applications, such as molecular sieves, catalysts, adsorption, and nonlinear optical (NLO) devices. The construction of inorganic frameworks with novel topological structures offers great challenges and opportunities in terms of framework-forming elements.[1] Much of this work has so far been focused on the following systems: Al−Si−O,[2] Al−P−O,[3] Ga−P−O,[4] M−P−O (M = transition metal),[5] B−P−O,[6] as well as Ge−O.[7] To date, no systematic investigation across the B−Ge−O system has been carried out.[8] Because of the flexible coordination geometries for Ge and B atoms, and the ability to form Ge−O[7b−7d,9−11] and B−O clusters[12] as well as the special NLO properties for borates, the B−Ge−O system is likely to provide new functional materials that possess specific properties and desired features. Herein we report a novel borogermanate, $K_2[Ge(B_4O_9)]\cdot 2H_2O$ (**1**), which not only displays the first double helical structure in the borogermanate family but also exhibits distinct NLO and thermal properties.

Colorless crystals of **1** were obtained by the solvothermal reaction of $K_2B_4O_5(OH)_4\cdot 2H_2O$, GeO_2, pyridine, and H_2O

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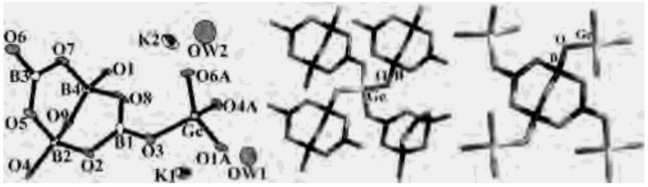

Figure 1. The structure of **1** (left), showing the local coordinaion geometry. Atom labels A refer to symmetry-generated atoms. View of the linkages of B_4O_9 and GeO_4 units (middle and right), showing each B_4O_9 (GeO_4) unit is bridged by four GeO_4 (B_4O_9) groups to 12 other B_4O_9 (GeO_4) units.

in the presence of diethylenetriamine (DETA) in basic conditions. In a typical synthesis of **1**, GeO_2 (0.104 g) was added to a stirring colorless solution of pyridine (4.8 mL) and water (0.78 mL) in the presence of diethylenetriamine (0.68 mL). After a few minutes, $K_2B_4O_5(OH_4)\cdot 2H_2O$ (0.22 g) was then added to the mixture, and the mixture continued stirring for 4 h. The final mixture with pH = 8.5 was heated in a Teflon-lined stainless steel autoclave at 170 °C for 7 days under autogenous pressure, and then it cooled to room temperature. The pure, colorless, prismlike crystals of **1** suitable for X-ray analysis were obtained by filtration, washed with water, alcohol, and acetone, and dried in air (78% yield based on Ge). Here, the pyridine was used as reaction solvent, and the water was used for dissolving $K_2B_4O_5(OH)_4\cdot 2H_2O$. It is noteworthy that the DETA used in the synthetic process not only adjusts the pH of the reaction system but also apparently plays a key role in the formation of **1** since attempts to make **1** without it were unsuccessful. The experimental and simulated powder X-ray diffraction patterns are in good accordance with each other, indicating the phase purity of the sample. The energy dispersive spectroscopy (EDS) analysis is consistent with the stoichiometry. Anal. Calcd: Ge 19.41%; K 20.90%. Found: Ge 19.02%; K 20.17%. IR (KBr pellet): 896 cm^{-1} (GeO_4), 1054 cm^{-1} (BO_4), 1399 cm^{-1} (BO_3), 3549 cm^{-1} (OH).

The title compound crystallizes in a noncentrosymmetric monoclinic space group *Cc*[13] and consists of B_4O_9 cluster units bridged by four GeO_4 tetrahedra. Figure 1 illustrates the coordination environment of the central B and Ge atoms and the connectivity of the B_4O_9 and GeO_4 units. Four unique boron atoms in the B_4O_9 unit are bridged by three and four oxygen atoms to give two triangular BO_3 (B1 and B3) and two tetrahedral BO_4 (B2 and B4) groups in which the B−O distances are from 1.346(15) to 1.395(15) Å and 1.441(14) to 1.526(15) Å, and the O−B−O bond angles are 115(1)−124(1)° and 104.6(9)−113.1(9)° for BO_3 and BO_4 groups, respectively. The Ge−O bond distances vary from 1.732(7) to 1.770(8) Å. Angles of O−Ge−O are between 106.1(3)° and 115.4 (4)°. The BO_3 and BO_4 units are connected alternately through μ_2-O, and two BO_4 groups are further linked by a μ_2-O(9) atom, resulting in a B_4O_9 unit containing two approximately perpendicular three-membered rings of polyhedra, each of which contains one BO_3 triangle and two BO_4 tetrahedra. Such an arrangement was also present in some hydrated borates of $Cs_2[B_4O_5(OH)_4]\cdot 3H_2O$,[14a] $K_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$,[14b] $K_2[B_4O_5(OH)_4]\cdot 2H_2O$,[14c] and $NaRbB_4O_5(OH)_4\text{-}\cdot 3H_2O$.[14d] In these four borates, the $[B_4O_5(OH)_4]^{2-}$ unit only exists in isolated form because the four terminal hydroxyls prevent the $[B_4O_5(OH)_4]^{6-}$ from spreading further connections, whereas in **1**, the B_4O_9 unit connects to GeO_4 groups by four shared μ_2-O atoms (Figure 1). Each B_4O_9 unit is connected to 12 others through four bridging GeO_4 tetrahedra. Like the B_4O_9 unit, each GeO_4 tetrahedron is also connected to 12 other GeO_4 tetrahedra through four bridging B_4O_9 units, resulting in no Ge−O−Ge connection in the structure.

The alternate connectivity between the B_4O_9 and the GeO_4 through their vertices gives rise to the 3D macroanionic $[Ge(B_4O_9)]_n^{2n-}$ framework with 10-, 9-, and 9-membered rings channels in the *bc*, *ab*, and *ac* planes, respectively (Figure S5, Supporting Information). The 10-membered ring channels consist of three GeO_4, three BO_4, and four BO_3 groups, while the 9-membered ring channels contain three GeO_4, four BO_4, and two BO_3 units. The charge of a macroanionic $[Ge(B_4O_9)]_n^{2n-}$ framework is balanced by K^+ cations. $K1^+$ is 10-coordinate, with seven framework oxygen (O_f) atoms and three water molecules (O_w), and $K2^+$ is eight-coordinate, with two O_w and six O_f atoms. The K−O distances are in the ranges 2.704(8)−3.269(8) Å and 2.667(9)−2.298(13) Å for $K1^+$ and $K2^+$, respectively. In the structure, there are weak hydrogen bonds between the O_w and the O_f atoms, with O···O distances from 3.017(1) to 3.192(3) Å.

The most interesting aspect for **1** is that the structure possesses two pairs of double helical channels with an unclosed 10-membered ring aperture in the [100] direction (Figure 2). One pair consists of B1, Ge, B2, and B3 atoms, and another contains B1, Ge, B4, and B3 atoms. The unclosed −B2−O−B3−O−Ge−O−B1−O−B2−O−B3−O−Ge−O−B2−O−B1−O−Ge− linkage gives rise to two types of helices with opposite chirality (Figure 2b). The right- and left-handed helices couple with each other to form the 3D framework with helical channels in the [100] direction where the K^+ cations and water molecules reside. Interestingly, another helical channel along the unclosed linkage of −B4−O−B3−O−Ge−O−B1−O−B4−O−B3−O−Ge−O−B4−O−B1−O−Ge− is in the [100] direction (Figure 2c), which is different from those shown in Figure 2b not only in shape and size, but also in the sequence of opposite chirality. The double helices containing B2 atoms interweave with another double helix consisting of B4 atoms by the μ_2-O(9) atoms, forming the combination of two pairs of helical channels with 10-membered rings (Figure 2a). It is worth

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(13) The structure determination follows: A colorless prismlike crystal with dimensions of 0.20 × 0.20 × 0.18 mm^3 was performed on a Bruker Smart CCD diffractometer with graphite-monochromated Mo Kα radiation at 298 K in the range $3.38° \leq \theta \leq 25.06°$ using ω and φ scans. The structure was solved by direct methods and refined using SHELXL 97 software. Crystal data for **1** follow: monoclinic, *Cc*, M_r = 374.06, a = 6.793(1) Å, b = 12.0699(3) Å, c = 11.895(3) Å, β = 91.156(4)°, V = 975.1(4) $Å^3$, Z = 4, μ = 4.046 mm^{-1}, ρ_{calcd} = 2.521 $g\cdot cm^{-3}$, GOF = 1.063, R1(wR2) = 0.0448(0.1023). There were 1553 reflections measured, 1072 unique (R_{int} = 0.0310).

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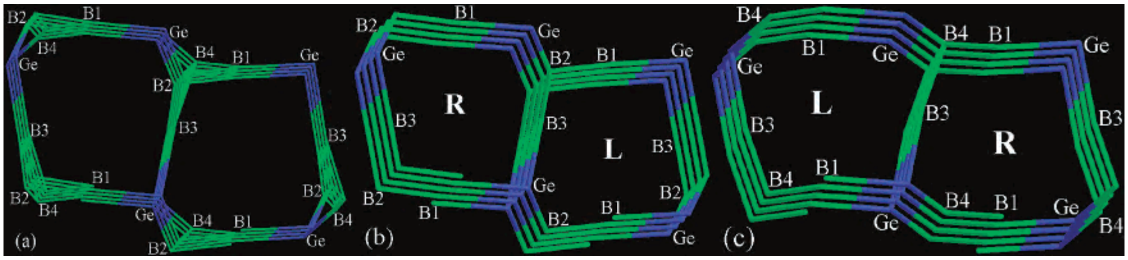

Figure 2. (a) View of the 10-membered ring channels in the structure of **1** down the [100] direction showing the combination of two pairs of 10-membered ring helical channels containing B2 and B4 atoms. (b) View of one pair of helical channels R (right-handed) and L (left-handed) containing B2 atoms. (c) View of another pair of helical channels L (left-handed) and R (right-handed) containing B4 atoms.

noting that the B_4O_9 cluster unit plays a key role in the formation of two pairs of helical channel structure.

The TGA of **1** also revealed some interesting features. For instance, there was only one step of weight loss from 30 °C to about 210 °C corresponding to the removal of two water molecules per formula unit. (Found: 10.38%. Calcd: 9.63%.) Powder X-ray diffraction patterns show that the structure of **1** can almost be retained after loss of water molecules through heating. In addition, the results of high-temperature powder XRD indicate that the structure has not changed with increasing temperature from about 210 to 1000 °C. Interestingly, although the colorless prismatic crystals after dehydrating the sample were poor quality, some good quality crystals were obtained again when these crystals were exposed to air for 5 days. A single crystal X-ray structure analysis was performed on a crystal obtained after rehydrating the heated sample, and the result indicated nearly unaltered cell constants and unchanged framework.[15]

In order to confirm its acentricity as well as to evaluate its potential as second-order nonlinear optical material, **1** has been studied by the quasipowder second-harmonic generation (SHG) measurements[16] at room temperature. Preliminary experimental results show that the intensity of the green light (frequency-doubled output: $\lambda = 532$ nm) produced by **1** powder is about 2.0 times higher than that of potassium dihydrogen phosphate (KDP) powder, and **1** represents the first NLO active bulk solid based on a three-dimensional borogermanate assembled by alternating B_4O_9 clusters and GeO_4 units with two pairs of interweaving double helical channels.

In summary, we have successfully obtained the first 3D borogermanate with two pairs of double helical channels constructed by a B_4O_9 cluster and GeO_4 group. The compound exhibits distinct NLO properties because it lacks a center of symmetry. The successful synthesis of **1** shows it is possible to synthesize other new borogermanates using Ge−O clusters in combination with B−O clusters[17] or borogermanate materials for NLO devices using Ge−O clusters in combination with asymmetric B−O clusters. Furthermore, the structure recovery process that was observed in **1** reveals an interesting phenomenon whose nature and possible application deserve further investigation. As a major research interest and aim, we are now using other B−O clusters and Ge−O clusters as building block units to make new borogermanates with open framework. Further investigation on this work is in progress.

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Supporting Information Available: Crystallographic data in CIF format. Additional 10 plots including SEM, IR, TGA, PXRD in PDF format. This material is available free charge via the Internet at http://pubs.acs.org.

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(15) Cell constants for a crystal obtained after rehydrating the heated sample follow: monoclinic, *Cc*, $a = 6.7822(3)$ Å, $b = 12.0490(6)$ Å, $c = 11.8637\,(2)$ Å, $\beta = 91.220(3)°$, $V = 969.27(7)$ Å^3, R1(wR) = 0.0485 (0.1117).

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(17) During the preparation of this Communication, another borogermanate constructed by 8-MR Ge_8O_{24} cyclic cluster and B_2O_7 cluster was obtained as single crystals. X-ray structure analysis reveals that the structure is an organically templated 3D borogermanate with large 12-MR channels.