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Synthesis and Structure of $KBGe_2O_6$: The First Chiral Zeotype Borogermanate with 7-Ring Channels

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Among the known zeolite topologies, odd rings are rare with the exception of 5-ring. We report here the hydrothermal synthesis and structural characterization of a novel compound, $KBGe_2O_6$, the first germanate-based zeotype material with 7-ring channels. It crystallized in the orthorhombic system, space group $P2_12_12_1$ (No. 19), $a = 4.8037(3)$ Å, $b = 10.2063(7)$ Å, $c = 10.7402(10)$ Å, $V = 526.57(5)$ Å^3, $Z = 3$. The framework topology of this compound is previous unknown with the vertex symbol $4\cdot6\cdot4\cdot6\cdot6\cdot7_2$(vertex1), $4\cdot6\cdot4\cdot6\cdot6\cdot7_2$(vertex2), and $6\cdot6\cdot6\cdot6\cdot6_2\cdot7_2$(vertex3). It is worth noting that the structure of the compound is chiral containing helices condensed from GeO_4 tetrahedra, which arrange around 2_1 screw axes. Furthermore, the K^+ ions within the channels are mobile and can be partially ion-exchanged with Na^+ at room temperature.

Great efforts have been made for the discovery of microporous solids due to their rich structural chemistry and wide application in some commercial purposes as ion exchanger, adsorbent, and catalyst.[1] Chiral zeolites are of special interest because they open a new window for the manufacture of optically pure organic compounds. To get such materials, one useful synthetic approach is the use of chiral organic amines or chiral metal complexes as structure-directing agents (SDAs) because the chirality of these SDAs can be transferred to the inorganic framework. For example, chiral (1*R*,2*R*)-(−)-1,2-diaminocyclohexane, D-glucosamine, and cobalt complexes are used in the synthesis of chiral aluminum and gallium phosphates.[2] Another approach is the selection of framework elements that can form helices, such as boron-based materials.[3] Recently, germanates attracted much attention due to their ability to form extended structures with GeO_4 tetrahedra, GeO_5 trigonal bipyramids, and GeO_6 octahedra and to the capacity of germanates to form odd membered rings, for example, germanates with 3-ring, 5-ring, 7-ring, and 9-ring have been reported.[4−7] It is expected that the combination of the borate and the germanate group in the same crystalline material may generate a new class of materials with novel framework topology and properties. However, there is little research that has been carried out on the open-framework borogermanates.[7e] This is in part due to the large difference in the radius of boron and germanium. Here, we report the synthesis and structure of the first chiral borogermanate, $KBGe_2O_6$ (denoted FJ-9). X-ray analysis revealed that the crystal structure of FJ-9 could be described as a three-dimensional open framework built of corner-sharing BO_4 and GeO_4 tetrahedra.[8]

In a typical synthesis for FJ-9, 0.219 g of $K_2B_4O_7\cdot4H_2O$ was dispersed in a mixture solution of 0.5 mL of water and

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(8) Crystal data for FJ-9: space group $P2_12_12_1$, $a = 4.8037(3)$ Å, $b = 10.2063(7)$ Å, $c = 10.7402(10)$ Å, $V = 526.57(5)$ Å^3, $Z = 3$, Mo Kα, $\theta_{max} = 25.01°$. A total of 1561 reflections (913 independent) were measured at 293 K. Final agreement indices are R1 = 5.68%, wR2 = 12.76%, GOF = 1.001.

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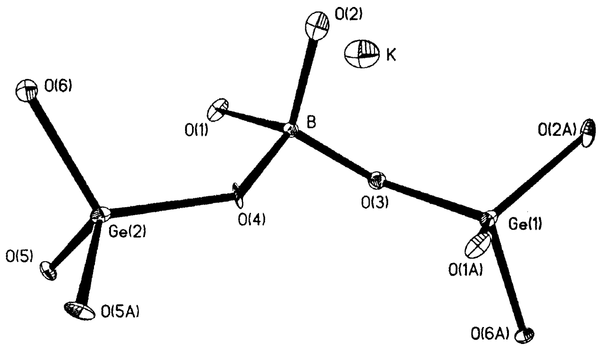

Figure 1. View of the tetrahedral coordination environments for Ge and B in the asymmetric unit of FJ-9, showing the atom-labeling scheme and 50% thermal ellipsoids. Atom labels having "a" refer to symmetry-generated atoms.

1.33 mL of ethylene glycol; then, 0.621 g of DABCO (1,4-diazabicyclo[2,2,2]octane) was added under constant stirring. To this mixture, 0.15 g of GeO_2 was added, and the resulting mixture was homogenized for 30 min at room temperature. The final mixture of the composition $GeO_2/K_2B_4O_7$/DABCO/H_2O/EG in a molar ratio of 1:0.5:2:33:16.6 was sealed in a Teflon-lined steel autoclave, heated at 170 °C for 11 days, and then cooled to room temperature. Colorless crystals were obtained which were recovered by filtration, washed with distilled water, and dried in air (70% yield based on GeO_2). The experimental and simulated X-ray powder diffraction patterns are in good accord with each other, indicating the phase purity of the sample.

The asymmetric unit consists of two unique Ge atoms and one unique B atom; all of them are tetrahedrally coordinated by oxygen atoms (Figure 1). The boron tetrahedron is connected by three $Ge(1)O_4$ and one $Ge(2)O_4$ tetrahedra, the $Ge(1)O_4$ tetrahedron is connected by three boron tetrahedra and one $Ge(2)O_4$ tetrahedron, and the $Ge(2)O_4$ tetrahedron is connected by one boron tetrahedron, one $Ge(1)O_4$ tetrahedron, and two $Ge(2)O_4$ tetrahedra, respectively. In particular, there is no B−O−B connection. The structure can be thought of as consisting of two parts. The first is a zeolite-like layer made up of $B_2Ge_2O_8$ single 4-rings(S4Rs) and Ge_2O_4 dimeric units (Figure 2). The S4Rs and the dimeric units are connected alternately to form a layer containing 7-ring channels. When all the adjacent layers are stacked in the eclipsed configuration (AAAA sequence), then the three-dimensional open framework of FJ-9 is formed. FJ-9 is the first borogermante zeotype structure with 7-ring channels, and it has a previously unknown framework topology having the vertex symbols $4{\cdot}6{\cdot}4{\cdot}6{\cdot}6{\cdot}7_2$(vertex1), $4{\cdot}6{\cdot}4{\cdot}6{\cdot}6{\cdot}7_2$(vertex2), and $6{\cdot}6{\cdot}6{\cdot}6{\cdot}6_2{\cdot}7_2$(vertex3). [9] The 7-ring channels run along the [100] direction with a $2(GeO_4)-(BO_4)-3(GeO_4)-(BO_4)$ sequence, and there are smaller 6-ring channels along the [001] direction with a $5(GeO_4)-(BO_4)$ sequence. The pore aperture and size are shown in Figure 3. Among the known zeolite topologies, the rings bounded by 7 tetrahedra are rare and present only in ZSM-18 and SSZ-23.[10] FJ-9 is the first example of germanium-based materials.

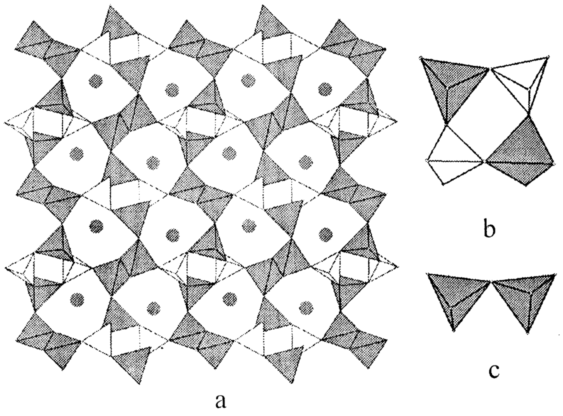

Figure 2. (a) Polyhedral representation of the structure viewed along the [100] direction illustrating the 7-ring channels connected by (b) 4-rings and (c) dimeric units: germanium tetrahedra, medium gray; boron tetrahedra, white. Potassium is represented by the medium gray spheres in the 7-ring channels.

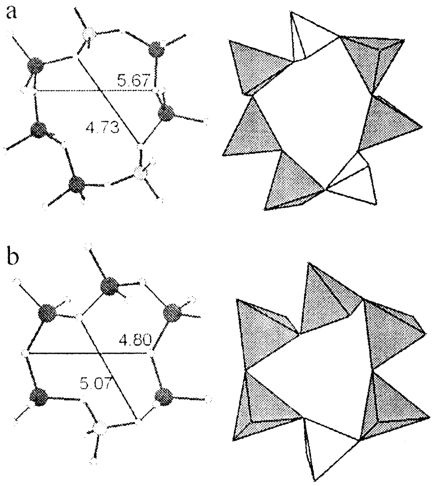

Figure 3. Ball-and-stick and polyhedral representation of the 7-ring channel and 6-ring channel of FJ-9. Distances to the centers of oxygen atoms are given.

The Ge−O distances are in the range 1.707−1.777 Å (av 1.743 Å), and the O−Ge−O bond angles are in the range 104.1−114.9° (av 109.4°), in agreement with other tetrahedral germanates.[11] The B−O distances are between 1.44(2) and 1.50(2) Å (av 1.48 Å), and the O−B−O bond angles are between 104.8° and 113.2° (av 109.4°), which are similar values to those of related materials.[3,7e] The Ge−O−Ge and B−O−Ge angles observed in FJ-9 (ca. 130°) are smaller than those found in porous silicates for Si−O−Si (ca. 145°). The small T−O−T angle favors the synthesis of germanates with 3-membered rings, which is believed to be very important for achieving very porous nets.[12] The extraframework K^+ cation resides in the 7-ring channel and is coordinated to 10 framework O sites with

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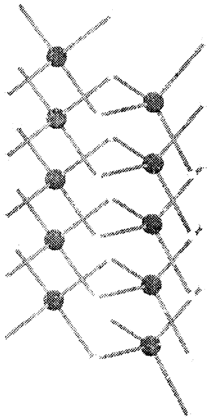

Figure 4. Ball-and-stick representation of the helical chain: germanium, dark gray; oxygen, open circle.

interatomic distances in the range 2.625(13)−3.251(13) Å. The calculated bond valence sum of 1.181 is in good agreement with the expected value of 1.0.[13]

It is worth noting that the structure is chiral (space group $P2_12_12_1$). The condensation of GeO_4 tetrahedra through common vertices leads to tetrahedral chains, which are arranged around 2_1 screw axes to form helices (Figure 4). These helices are linked by the zigzag ribbons with 4-membered ring in which BO_4 and GeO_4 tetrahedra alternate, giving a chiral 4-connected framework.

The IR spectrum of FJ-9 contains a strong band at about 1026 cm^{-1}, in good agreement with the existence of tetrahedral BO_4 in the crystal structure.[14] The bending vibration of B−O is observed at ca. 409 cm^{-1}. The peaks at 877 and 827 cm^{-1} can be assigned to an asymmetrical stretch of Ge−O of the tetrahedral germanium. The absorption bands at 552 and 587 cm^{-1} are caused by a symmetrical stretch of Ge−O. The peak at 494 and 467 cm^{-1} is due to bending vibrations of Ge−O.

An ion-exchange experiment was carried out by stirring a sample of as-synthesized crystals (150 mg) in 10 mL of 1 M $NaNO_3$ (aq) solution for 24 h at room temperature. Following this treatment, the sample was filtered out and washed thoroughly with distilled water and ethanol and followed by air-drying. The elemental analysis for the exchanged materials indicates that K^+ cations in the channels are partially exchanged with Na^+ ions. We formulate the exchanged material as $Na_xK_{1-x}BGe_2O_6{\cdot}yH_2O$ ($x \approx 0.2$, $y \approx 0.4$) on the basis of elemental analysis and thermogravimetric analysis.[15] X-ray powder diffraction patterns for the exchanged materials are in good accord with the pattern observed for as-synthesized crystals, meaning its framework keeps stable after cation exchange.

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Supporting Information Available: Experimental and simulated powder X-ray diffraction patterns of as-synthesized crystals and experimental powder X-ray diffraction patterns of Na^+-exchanged materials. X-ray crystallographic data for $KBGe_2O_6$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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