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PKU-10: A New 3D Open-Framework Germanate with 13-Ring Channels

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PKU-10, a germanate with the formula $[(CH_3)_4N]_3Ge_{11}O_{19}(OH)_9$, is synthesized under hydrothermal conditions, and its structure is determined by single-crystal X-ray diffraction data. PKU-10 possesses 3D intersected 13-ring channels and presents a new 6-connectedness linkage mode of the Ge_7 cluster, T^3P^2O, forming a *pcu* topological network. Each Ge_7 cluster is, in fact, surrounded by eight Ge_7 clusters in a nearly perfect cube because the hydrogen bonds between Ge_7 clusters are also taken into account. The structure-directing agent tetramethylammonium (TMA^+) ions, locating in the channels, can be partially exchanged by Li^+ with retention of the germanate framework. The germanate framework collapses with decomposition of the TMA^+ ions at temperatures higher than 240 °C.

Introduction

Crystalline oxide materials with extra-large pores, generally larger than 12-ring, have attracted considerable attention because of their potential in catalysis and the separation of larger molecules such as those species in heavy oils.[1−3] The design of crystalline porous inorganic structures from molecular building units is one of the effective approaches, as demonstrated by recent progress in the synthesis of porous germanates.[4−6] Besides the structural similarity to silicon with tetrahedral geometry, which has led to a number of novel germanate zeolite frameworks,[7,8] germanium exhibits more diverse coordination geometries, such as square pyramid or trigonal bipyramid (GeO_5) and octahedron (GeO_6) because of the larger radius of Ge^{4+}. More interestingly, the Ge-centered polyhedra tend to form polymetallic clusters, such as Ge_7,[9,10] Ge_8,[8] Ge_9,[12] and Ge_{10}.[13] In many newly found porous germanates, these polymetallic clusters act as secondary building units, which are assembled either by direct linkage or

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via additional building units, forming diversified large-pore frameworks.[11] SU-M, for instance, is a mesoporous germanate with crystalline pore walls consisting of Ge_{10} clusters.[11b] SU-MB, on the other hand, consists of both Ge_{10} and Ge_7, in which the Ge_7 clusters fill one set of the two gyroidal channels in SU-M and thus shows channel chirality.[11b] The Ge_7 cluster, which is built by one octahedron, two trigonal bipyramids, and four tetrahedra, is, in fact, one of the most frequently appearing species in various germanate structures, forming 1D chains,[9h,i,10] 2D layers,[9e,f] and 3D frameworks.[9a−d]

Here in this paper, we report a new germanate, $[(CH_3)_4N]_3Ge_{11}O_{19}(OH)_9$ (PKU-10). It is a 3D porous framework structure constructed by the Ge_7 clusters and additional GeO_4 tetrahedra. A simplified polyhedron of the Ge_7 cluster, where each vertex corresponds to a Ge atom, is applied to show the 13MR channels of the framework.

Experimental Section

Materials and Methods. All reagents are of analytical grade and were used as obtained from commercial sources without further purification. PKU-10 was synthesized under hydrothermal conditions from a homogeneous mixture of germanium dioxide (GeO_2) and tetramethylammonium hydroxide (TMAOH). Solid GeO_2 and aqueous TMAOH were mixed and stirred until a clear solution was obtained. The water content was controlled by evaporation of the mixture at 65 °C in an oven. The molar ratio of the starting gel was 1:0.6:2.5−4.5 GeO_2/TMAOH/H_2O. The gel was transferred to a Teflon-lined stainless autoclave and heated at 175 °C for 14 days. After cooling to room temperature, transparent crystals were obtained. The product was filtered, washed with deionized water and acetone, and then dried at 65 °C. Anal. Calcd for $Ge_{11}O_{28}H_{45}C_{12}N_3$ (fw 1478.00): C, 9.75; H, 3.08; N, 2.84. Found: C, 9.76; H, 3.17; N, 2.80. The IR spectrum showed peaks (cm^{-1}; the intensity character is indicated following the position) at 3384m, 3221m, 3036m, 2452w, 1640w, 1448m, 1419w, 1384w, 1115w, 1019w, 956m, 847s, 815vs, 787vs, 768vs, 718m, 703m, 583m, 541m, 504m, 488m, and 452m.

The purity of the products was examined by using powder X-ray diffraction on a Rigaku D/Max-2000 diffractometer with a Cu Kα radiation source ($\lambda = 1.5418$ Å) and a graphite monochromator at the secondary beam. Thermogravimetric analysis (TGA) of the samples was done on the instrument TGA Q50 V20.6 with a heating rate of 10 °C·min^{-1} from 25 to 900 °C under an air flow. Elemental analysis of carbon, nitrogen, and hydrogen was carried out with an Elementar Vario EL III microanalyzer. The elemental contents of Ge^{IV} and Li^{I} in the Li^+-ion-exchanged PKU-10 were measured by using the inductively coupled plasma (ICP) method on an ESCALAB2000 analyzer. IR spectroscopy was performed on a Nicolet Magna-IR 750 FTIR spectrophotometer in the region of 4000−400 cm^{-1}.

The Li^+-ion-exchanged sample (Li-PKU-10) was obtained by heating a mixture of PKU-10 and $LiAc\cdot 2H_2O$ with the molar ratio 1:10 at 85 °C for 2 h, in which $LiAc\cdot 2H_2O$ was in a molten state. Then the mixture was cooled and washed with ethanol to move the unreacted $LiAc\cdot 2H_2O$, and the product was dried at 65 °C. The elemental analysis result (%) for the product Li-PKU-10 was C 6.99, H 2.62, and N 1.96, while the ICP result shows that the ratio of Ge to Li is 10.3. We can deduce that some of the TMA^+ ions (about 30%) were exchanged by Li^+ ions. The exchange by Li^+ in an aqueous solution was not successful.

Crystallographic Studies. Single-crystal ($0.2 \times 0.15 \times 0.12$ mm^3) X-ray diffraction data of PKU-10 were collected on a Bruker SMART X-ray diffractometer, equipped with an APEX-CCD area detector and using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) at 298 K. The data absorption correction was based on symmetry-equivalent reflections using the *ABSOR* program. The structure was solved by the direct method and refined on F^2 with full-matrix least-squares methods using the *SHELX-97* program. All Ge, O, and N atoms were refined anisotropically, while the C atoms from the structure-directing agent were refined isotropically. H atoms were added in the riding model and refined isotropically with C−H = 0.96 Å and O−H = 0.94 Å. Crystallographic data and structure refinement results are summarized in Table 1. The corresponding CIF file is supplied in the Supporting Information.

Table 1. Crystallographic Data and Structure Refinement Results for PKU-10

chemical formula	$Ge_{11}O_{28}C_{12}H_{45}N_3$
fw	1478.00
temperature/K	298(2)
cryst syst	orthorhombic
space group	$P2_12_12_1$
a/Å	12.4827(12)
b/Å	17.3115(14)
c/Å	18.5392(21)
cell volume/Å^3	4006.2(16)
Z	4
D_c/g·cm^{-3}	2.450
μ(Mo Kα)/mm^{-1}	8.219
cryst size/mm^3	$0.20 \times 0.15 \times 0.12$
2θ range/deg	1.97−33.51
no. of reflns measd	38 870
no. of indep reflns	14 944
R_{int}	0.0596
no. of obsd reflns	12 648
final R indices [$I > 2\sigma(I)$]	0.0455, 0.1014
R indices (all data)	0.0578, 0.1067
GOF	1.028

Results and Discussion

Structure Description. PKU-10 crystallizes in the orthorhombic space group $P2_12_12_1$ with lattice constants a = 12.4827(12) Å, b = 17.3115(14) Å, and c = 18.5392(21) Å. An asymmetric unit in PKU-10 contains 11 crystallographically independent Ge atoms, 28 O atoms, and 3 TMA^+ ions (12 C and 3 N atoms). As shown in Figure 1a, a Ge_7 cluster and four additional GeO_4 tetrahedra form the fundamental building unit of the germanate framework. The displacement parameters are regular for Ge atoms but show a considerably wide range for O atoms; the displacement parameters of the hydroxyl O atom are about 2 or 3 times larger than those of the bridging O atoms; the O1 atom, which is at the center of the Ge_7 cluster and bonds to three Ge atoms, has very small displacement parameters. The bond distances and angles in PKU-10 are all coincident with the previously reported data (Table S1 in the Supporting Information).[9−13] The Ge−O distances are in the range of 1.696(4)−1.764(4) Å in Ge tetrahedra and 1.767(4)−2.059(3) Å in octahedra and trigonal bipyramids. The Ge−O−Ge angles can be divided into two groups: the Ge−O−Ge angles within one Ge_7 cluster are in the range of 91.44−135.25°, which reflects the relatively "rigid" connection of the groups inside the cluster, while the Ge−O−Ge angles related to the linkage of the Ge_7 cluster with additional tetrahedra can vary from 121.05(19) to 140.9(2)°.

The Ge_7 cluster (Figure 1b) has seven apical O atoms that can combine with other atoms. In PKU-10, they all connect to additional GeO_4 tetrahedra: Ge(8)O_4, Ge(10)O_4, Ge(11)O_4, and Ge(9)O_4. Among these tetrahedra, Ge(8)O_4, Ge(10)O_4, and Ge(11)O_4 are intergroups that cross-link two adjacent Ge_7 clusters and appear as $GeO_2(OH)_2$ units, while Ge(9)O_4 only connects to one Ge_7 cluster through the Ge(6)O_4 group and resides as a terminal

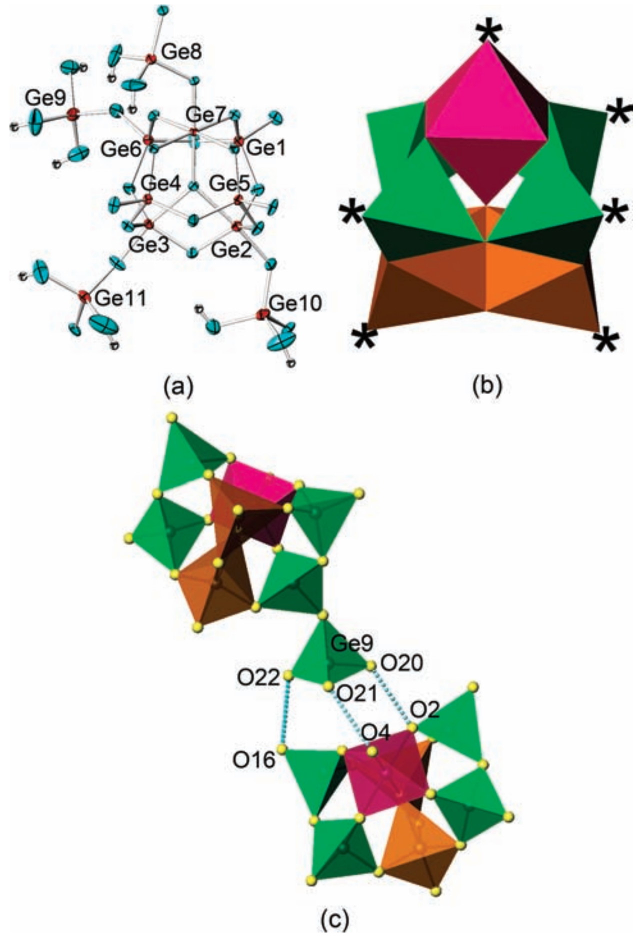

Figure 1. (a) The germanate asymmetric unit of PKU-10; (b) the Ge_7O_{16} cluster with one GeO_6 octahedron (pink), two GeO_5 trigonal bipyramids (orange), and four GeO_4 tetrahedra (green); the asterisk symbols indicates the polyhedra joining to extend the framework; (c) the terminal GeO-$(OH)_3$ group toward an adjacent Ge_7 cluster, forming three hydrogen bonds.

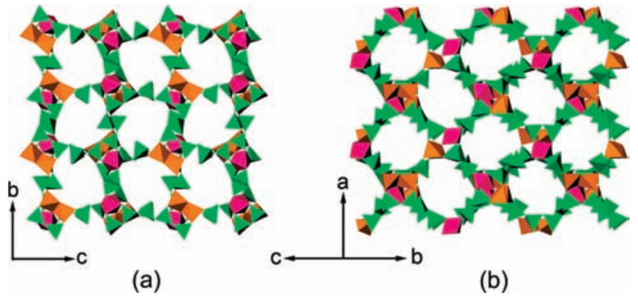

Figure 2. Structures of PKU-10: (a) viewed along [100]; (b) viewed along [011].

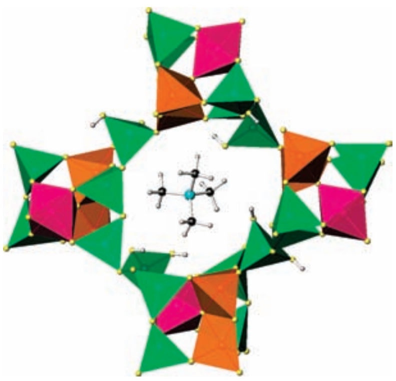

Figure 3. Location of the TMA^+ ion in the 13-ring channels of PKU-10.

$GeO(OH)_3$ unit. Interestingly, this $GeO(OH)_3$ unit points toward another adjacent cluster, forming three hydrogen bonds with O−H−O distances of 2.65, 2.75, and 2.95 Å, as shown in Figure 1c. As a consequence, the distance between the two clusters is nearly the same as the distance between clusters connected through a $GeO_2(OH)_2$ unit. From the view of the connections by covalent bonds, the Ge_7 cluster in PKU-10 can be regarded as a 6-connected building unit, which combines with six neighboring Ge_7 clusters through $GeO(OH)_2$ groups. However, considering the Ge_7 cluster in the whole structure, the Ge_7 cluster is surrounded by eight clusters, where the two additional clusters are related by hydrogen bonds. The terminal O atoms of these four additional tetrahedra, i.e., two on the cross-linked tetrahedra $[Ge(8)O_4$, $Ge(10)O_4$, and $Ge(11)O_4]$ and three on $Ge(9)O_4$, are all hydroxyl groups, thus giving rise to a framework formula of $[Ge_{11}O_{19}(OH)_9]^{-3}$ for PKU-10. We can define the connection linkage of the Ge_7 cluster in PKU-10 according to the nomination by Yu et al.[10] Each Ge_7 cluster connects to seven GeO_4 tetrahedra, but there are only six tetrahedra involved in the extension of the 3D germanate framework. The linkage mode of the Ge_7 cluster in PKU-10 can be assigned as T^3P^2O, as shown in Figure 1b, which is a new one with the 6-connectedness. The other two known modes are T^4P^2 and T^4PO, which appear together with the Ge_9 cluster in the structures of SU-44 and SU-8.[11c]

Figure 2 shows the polyhedral presentation of the PKU-10 structure framework. With hexadentate connectivity, Ge_7 clusters are cross-linked by GeO_4 tetrahedra, forming a very open structure with 3D intersecting channel systems, along the directions [100], [011], and [0−11], respectively. The 13-ring channel along the [100] direction (Figure 2a) has an effective open window with the size of 5.2 Å × 5.4 Å. The other two 13-ring channels are identical, which are perpendicular to the 13-ring channel along the [100] direction (Figure 2b). The 13-rings are formed by the surrounding of eight GeO_4, three GeO_5, and two GeO_6. The Ge_7 cluster works as a node for extension of the structure and constructs the channels in combination with the bridging GeO_4 tetrahedra. The framework density of PKU-10 is very low, 11.0 Ge atoms per 1000 $Å^3$. Three TMA^+ ions, which act as structure-directing agents as well as counterions, are located within the 13-ring channels (Figure 3). Two cations (N1 with C1−C4 and N3 with C9−C12) arrange alternately in the middle of the channels along the *a* axis, while the third one (N2 with C5−C8) locates in the cross of the channels of the [011] and [0−11] directions.

Though the structure of PKU-10 has been described above by the polyhedral expression, it is still somehow difficult to get a straightforward view of the structure feature, owing to the complexity of the Ge_7 cluster. The connections of Ge_7 clusters via the GeO_4 tetrahedra in PKU-10 can be expressed concisely with the aid of the scale chemistry concept.[5,6] We can define a simplified polyhedron (or pseudopolyhedron), which only takes the geometrical configuration of the center atoms (Ge) into account.

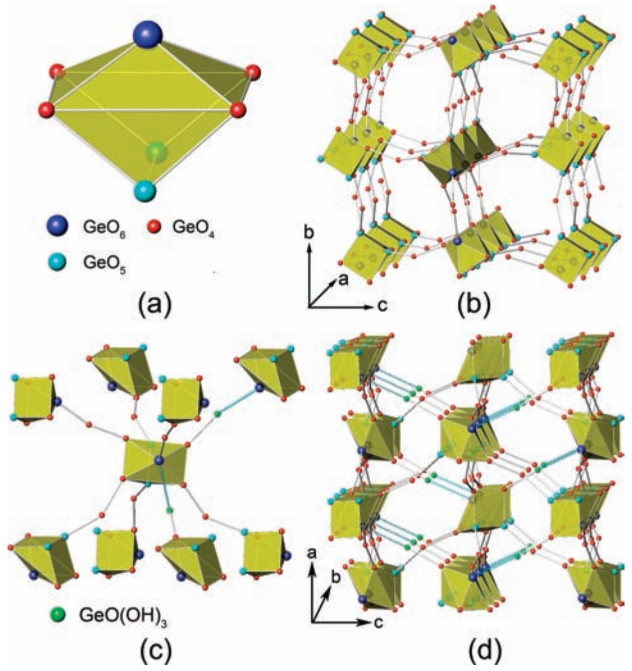

Figure 4. (a) Ge_7 cluster represented as a simplified polyhedron in which each vertex corresponds to a Ge atom. (b) Framework structure of PKU-10 by simplified polyhedra, showing the 13MR channels. (c) Each Ge_7 cluster surrounded by eight neighbors in a cubic environment. (d) Interaction between $GeO(OH)_3$ tetrahedra and Ge_7 clusters by hydrogen bonds as indicated by blue dashed lines.

The Ge_7 cluster can be drawn out as a convex polyhedron composed of a triangular prism and a tetragonal pyramid by sharing faces, as shown in Figure 4a. The drawing of the structure by the simplified polyhedra is shown in Figure 4b. It clearly shows that the hexadentate connectivity of the Ge_7 cluster enables it to extend in 3D space in a *pcu* topology,[14] although the irregularness of the "brick" results in a seriously twisted network. By a simplified polyhedral presentation, the 13-ring channel along the [100] direction can be recognized, and it is also easy to see that each Ge_7 cluster is surrounded by eight neighbors in a nearly perfect cube, as shown in Figure 4c. The interaction between Ge_7 clusters and $GeO(OH)_3$ groups by hydrogen bonds is drawn by blue dashed lines. Thus, the Ge_7 cluster can be regarded as an 8-connected species where the GeO_6 octahedron provides two branches (Figure 4c): one is connected to a bridging $GeO(OH)_2$ group, and the other is linked to a $GeO(OH)_3$ group by hydrogen bonds. Figure 4d shows the germanate framework including extension by the hydrogen bonds. The $GeO(OH)_3$ groups and its connections to adjacent Ge_7 clusters block the channels along the *b* direction.

IR Spectrum. Figure S1 in the Supporting Information shows the IR spectrum of PKU-10. The peaks at 3400−3200 and ~1000 cm^{-1} correspond to the stretching and bending vibrations of the −OH groups, respectively. The absorption bands at 1488 and 1419 cm^{-1} correspond to the C−H bending vibrations of the TMA^+ ions. The absorption bands at 847, 815, 787, 768, 718, and 703 cm^{-1} can be assigned to the asymmetric stretching vibrations of the Ge−O bonds. The peaks at 583 and 541 cm^{-1} are attributed to the symmetrical stretch of the Ge−O bonds, and the absorptions at 504, 488, and 452 cm^{-1} are related to Ge−O bending vibrations.[9d]

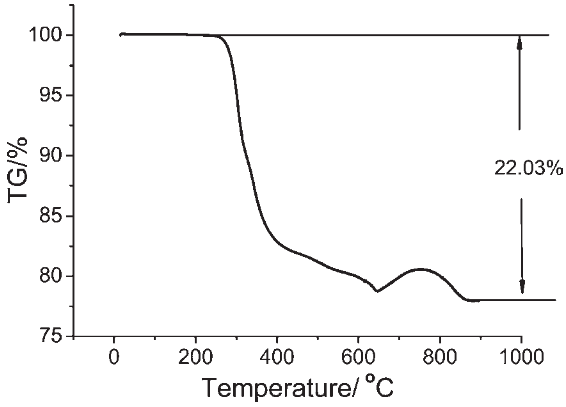

Figure 5. TGA of PKU-10.

Thermal Stability. TGA for PKU-10 shows a weight loss of 22.03% between 250 and 850 °C, as shown in Figure 5, which agrees well with the expected value (22.16%) of the removal of all TMA^+ ions from the structure. Interestingly, an unexpected peak occurs at about 780 °C, indicating an intermediate phase change during decomposition. To understand the reaction process, the powder X-ray diffraction patterns were recorded after heating treatment at different temperatures (Figure 6). The results clearly show that the structure of PKU-10 collapses with degradation of the TMA^+ ions at about 250 °C. An amorphous phase forms at 250−630 °C, and it transforms to GeO_2 after further treatment at 700, 780, and 900 °C under atmospheric condition. Although we do not know the exact composition of the amorphous phase, the unexpected weight increase indicates the formation of the low-valent germanium species. It was reported that GeO might be formed in an amorphous state, which is volatile but could be caught by charcoal.[15] The removal of organic species and dehydration of the hydroxyl groups from PKU-10 are complex, giving out various species including charcoal, CO, CO_2, and H_2O by combining oxygen from the air flow. Apparently, Ge^{IV} can be reduced by C or CO in situ. Thus, we can infer that GeO was formed in the decomposition process of the TMA^+ ions at ~300−500 °C. GeO is caught by charcoal from decomposition of the TMA^+ cations. With an increase of the temperature, GeO can be reoxidized by oxygen to GeO_2, which is accompanied by a weight increase. Meanwhile, the residual charcoal also can be oxidized to gaseous CO and/or CO_2, which corresponds to a weight loss. In the temperature range of 630−780 °C, reoxidation of GeO to GeO_2 dominates, while at the stage of 780−850 °C, the removal of carbon is the main action. To further confirm the reduction of Ge^{IV} in the process by C or CO, we treated PKU-10 at 900 °C under a nitrogen atmosphere, which led to the formation of elementary germanium as shown in Figure 6b.

Ion-Exchange Property. The structure-directing-agent TMA^+ cations in the channels can be partially exchanged

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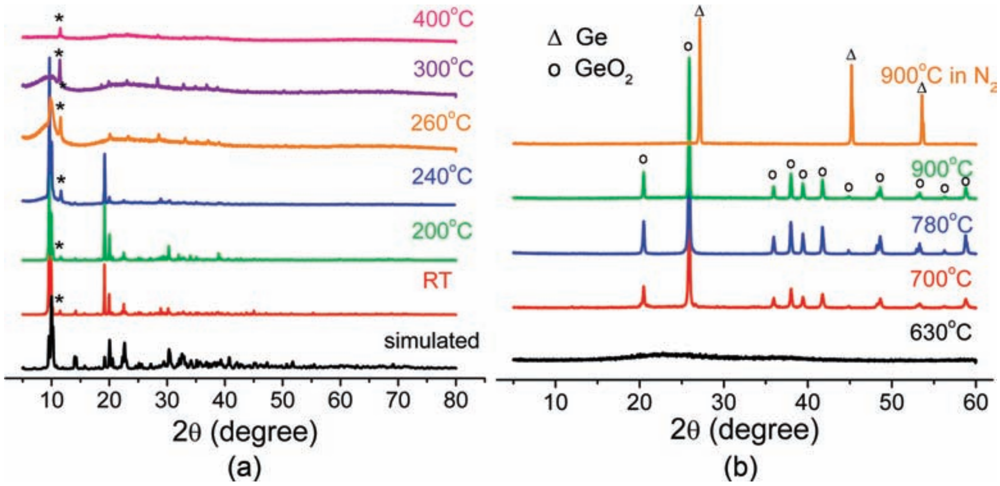

Figure 6. Powder X-ray diffraction patterns of PKU-10 calcined under atmospheres except the one marked with "in N_2": (a) from the room temperature (RT) to 400 °C; (b) from 630 to 900 °C. The peaks marked by asterisks are from the impurity $Li_3HGe_7O_{16}$.

by Li^+ in a melt of $LiAc \cdot 2H_2O$ at 85 °C. Elemental analysis and the ICP result revealed that nearly 30% of the TMA^+ ions were exchanged by the Li^+ ions. The reaction time needs to be controlled carefully. With the prolonging of the exchange time to 4 h, the framework of PKU-10 collapsed and transferred partly to pharmacosiderate $Li_3HGe_7O_{16}$. The higher temperature also accelerated the formation of $Li_3HGe_7O_{16}$ and caused the loss of crystal water molecules from $LiAc \cdot 2H_2O$, which then affected the exchange reaction activity. The powder X-ray diffraction profile of Li-PKU-10 is shown in Figure S2 in the Supporting Information. Profile fitting reveals that the lattice constants of the exchanged product are $a = 12.487(1)$ Å, $b = 17.309(2)$ Å, and $c = 18.529(1)$ Å, almost no change compared with those of the as-synthesized PKU-10. This means that the partial exchange of TMA^+ ions by Li^+ ions has little effect on the germanate framework, while the remaining ~70% of the TMA^+ ions still support the structure well.

Conclusion

PKU-10 is a porous germanate with a low framework density, 11.0 Ge per 1000 Å^3. The structure of PKU-10 is built by the connections of Ge_7 clusters with additional tetrahedra, possessing 3D intersecting 13-ring channels. TMA^+ ions work as structure-directing agents and reside in the channels. The Ge_7 cluster adopts a new 6-connected linkage mode, T^3P^2O, forming a *pcu* topological network. The simplified polyhedral presentation, where the Ge_7 cluster is drawn as a convex polyhedron composed of a triangular prism and a tetragonal pyramid by sharing faces, shows the porous structure concisely. Some of the TMA^+ ions can be exchanged by Li^+ ions with retention of the germanate framework. The germanate framework collapses with decomposition of the TMA^+ ions at temperatures higher than 240 °C. The removal of organic species and dehydration of the hydroxyl groups from PKU-10 is complex, and the weight increase at about 630−780 °C in the TGA curve is assigned as reoxidation of GeO formed from the reduction of Ge^{IV} in situ by the reductive species from TMA^+ cations.

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Supporting Information Available: Crystallographic data in CIF format, selected bond distances and angles, an IR spectrum, and the peak profile fitting result of Li-PKU-10. This material is available free of charge via the Internet at http://pubs.acs.org.