Research Article

Synthesis, Structure, and Characterization of Keggin-Type Germanate

Ya-feng Li,^{1,2} Xiao-lin Qin,¹ Yue Xu,¹ Wen-yuan Gao,¹ and Yue Gao¹

¹ School of Chemical Engineering, Changchun University of Technology, Changchun 130012, China

² College of Chemistry, Jilin University, Changchun 130023, China

Correspondence should be addressed to Ya-feng Li; fly012345@sohu.com

Received 13 June 2012; Revised 20 September 2012; Accepted 18 October 2012

Academic Editor: Cengiz Soykan

Copyright © 2013 Ya-feng Li et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

A novel Keggin-type germanate, $(\text{NH}_4)_9[\text{Ge}_7\text{O}_{14}\text{F}_3]_3 \cdot 1.75\text{H}_2\text{O}$ (I), is hydrothermally synthesized and structurally characterized by X-ray single-crystal diffraction, elemental analysis, XRD, and TG. (I) is tetragonal system with space group $I4/mmm$ and unit cell: $a = 28.280(4) \text{ \AA}$, $c = 24.881(5) \text{ \AA}$, $V = 19899(6) \text{ \AA}^3$, $D_c = 1.632 \text{ g/cm}^3$, $\mu(\text{Mo K}\alpha) = 6.309 \text{ mm}^{-1}$, $Z = 2$, $R_1 = 0.1141$ for 2576 reflections with $F_o > 2(F_\sigma)$. $\text{Ge}_7\text{O}_{14}\text{F}_3$ entry is defined as the cluster including one octahedron, two edge-sharing trigonal bipyramids, and four tetrahedra. Every $\text{Ge}_7\text{O}_{14}\text{F}_3$ entry links adjacent four $\text{Ge}_7\text{O}_{14}\text{F}_3$ entries by four tetrahedra. Twelve $\text{Ge}_7\text{O}_{14}\text{F}_3$ entries construct a cage with all octahedra of $\text{Ge}_7\text{O}_{14}\text{F}_3$ pointing inside, which can be simplified into Keggin-type cage through $\text{Ge}_7\text{O}_{14}\text{F}_3$ as the node. The solvent experiment proves that (I) is stable in the water and sensitive to base and acid. The result of XRD shows that the structural water of (I) is easily lost to drop the crystalline. The thermal study indicates that the Keggin-type cage of (I) begins to partly collapse at 200°C and finally changes into GeO_2 .

1. Introduction

Over the two decades, more efforts have been focused on synthesis of germanates because germanates could not only form the zeolites or molecular sieves [1, 2] but also achieve more openness than silicates owing to smaller rings and lower framework density based on the flexible Ge–O–Ge of $\sim 130^\circ$ [3–5]. It is hard for germanium to condense itself into zeolite due to the limitation of synthesis method. Only several examples have been found as BEC, ASV, and UOZ [6–8], and more instances can be accessible by germanium and the other tetrahedral elements—B, Al, Ga, Si, and so on [5, 9–17]. As a result of the large atomic radii of germanium conforms higher five- and six-coordination rather than four-coordination, the clusters comprised of the mixed coordinations give rise to large porous and extra porous frameworks [18–23]. The mixed 4-, 5- and 6-coordination $\text{Ge}_7\text{O}_{14}\text{F}_3$ cluster is discussed in detail as robust building unit of 2D and 3D nets [24–27]. In recently reported tubular germanate [22], $[(\text{C}_5\text{N}_2\text{H}_{14})_4(\text{C}_5\text{N}_2\text{H}_{13})(\text{H}_2\text{O})_4][\text{Ge}_7\text{O}_{12}\text{O}_{4/2}(\text{OH})\text{F}_2][\text{Ge}_7\text{O}_{12}\text{O}_{5/2}(\text{OH})\text{F}]_2[\text{GeO}_{2/2}(\text{OH})_2]$,

twelve $\text{Ge}_7\text{O}_{14}\text{F}_3$ clusters form a cage which mimics the Keggin structure with respect to $\text{Ge}_7\text{O}_{14}\text{F}_3$ cluster as the node. Interestingly, this Keggin-type germanate cage possesses $5.3 \text{ \AA}$ aperture and $8.3 \text{ \AA}$ cavity, which is bigger than Keggin-type POM- $\text{PMo}_{12}\text{O}_{40}^{3-}$. In this work, we have aimed to crystallize Keggin-type germanate, $(\text{NH}_4)_9[\text{Ge}_7\text{O}_{14}\text{F}_3]_3 \cdot 1.75\text{H}_2\text{O}$ —CCUT-8 (denoted as the Changchun University of Technology) and furthermore studied the solvent and thermal stabilities of Keggin-type cage.

2. Experimental Section

2.1. Materials and Instrument. All of the reagents were of analytical grade and used as received. The deionized water was used in all the experiments.

The infrared (IR) spectra were recorded within the $400\sim 4000 \text{ cm}^{-1}$ region on a BRUKER Vertex 70 FTIR spectrometer using KBr pellets. The elemental analyses were performed on

a PerkinElmer 2400 element analyzer. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX PC2200 diffractometer for Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), with a scan speed of $5^\circ/\text{min}^{-1}$. The thermal gravimetric analyses (TG) were performed on Pyris Diamond TG/DTA instrument used in an atmospheric environment with a heating rate of $10^\circ\text{C}/\text{min}$.

2.2. Synthesis. The colorless crystals of $(\text{NH}_4)_9[\text{Ge}_7\text{O}_{14}\text{F}_3]_3 \cdot 1.75\text{H}_2\text{O}$ were obtained under solvothermal condition. GeO_2 (0.25 g) was firstly dispersed in H_2O (1 mL). Then pyridine (4 mL), 2-methylpiperazine (0.95 g), and hydrofluoric acid (0.5 mL) were successively added under vigorous stirring. The clear solution with molar ratio of 1 GeO_2 :4 (2-methylpiperazine):50 pyridine:58.3 H_2O :4.8 HF was stirring for 4 hours and then it was transferred into 15 mL stainless steel autoclave and heated at 438 K for 14 days. After naturally cooled to room temperature, colorless product was collected as a single phase. All the crystals were washed by water and alcohol. The resultant crystals were dried naturally before single-crystal X-ray diffraction. $\text{H}_{158}\text{F}_{36}\text{Ge}_{84}\text{N}_{36}\text{O}_{175}$ (10245.60): H 1.54, N 4.92; found H 1.74, N 5.32.

2.3. Spectra of FTIR. The peaks at 3254 and 1590 cm^{-1} were attributed to the stretching and bending vibrations of NH_4^+ ; the peaks at 3446 and 1454 cm^{-1} were assigned to stretching and bending vibrations of H_2O ; the peaks at 860 , 831 , 578 , 460 cm^{-1} were due to vibrations of Ge–O or Ge–F.

2.4. Thermal Stability. The results of thermal gravimetric analyses showed that the total weight loss was 15.3% from room temperature to 600°C , corresponding to structural water and decomposition of ammonia and fluoride (calculated value: 15.6%), respectively, (Figure 1). CCUT-8 experienced the two weight losses from room temperature to 600°C and gave rise to final residues (GeO_2). The gradual part from 100°C to 250°C was assigned to structural water, and the sharp part from 300°C to 350°C was attributed to the decomposition of ammonia and fluoride.

The crystalline and thermal stability were investigated through the XRD (Figure 2). The broad and weak peak of (I) in XRD pattern of room temperature indicated that the crystalline of (I) decreased owing to fast loss of the structure water. Furthermore, we made an attempt to fuse the separated Keggin-type cage of (I) by condensing the oxygen of adjacent cage to build the solid structure. However, the XRD of the samples treated at 200°C and 300°C for 3 hrs in the air showed that Keggin-type cage of (I) began to partly collapse at 200°C and basically changed into the GeO_2 at 300°C , which consisted with the results of TG.

2.5. X-Ray Single-Crystal Diffraction. X-ray diffraction data were collected at 293 K from a suitable single crystal sealed in glass capillary on a Rigaku R-AXIS RAPID diffractometer equipped with graphite-monochromatized Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by the direct-method routine of SHELXS-97 and refined by full-matrix

FIGURE 1: TG analyses of I.

FIGURE 2: The XRD patterns of I. (a) simulated; (b) experimental; (c) treated at 200°C for 3 hrs; (d) treated at 300°C for 3 hrs.

least-squares on F^2 using SHELXL-97. The heavy atoms (Ge) were firstly located by the direct method, and then the light atoms (N, O, and F) were identified from the different Fourier maps. All nonhydrogen atoms were refined anisotropically. CCDC 903319 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

A summary of experiment data and refinement parameters of I is given in Table 1. The atomic coordinates and selected bond distances and angles of I are given in Tables 2 and 3.

2.6. The Solvent Experiments. 10 mg of I was added to 10 mL water, 10 mL base (1 M NaOH), and 10 mL acid (1 M HCl) overnight, respectively. The experimental results show that I was insoluble in the water and soluble in the base and acid.

FIGURE 3: The $\text{Ge}_7\text{O}_{14}\text{F}_3$ cluster containing one octahedron, two edge-sharing trigonal bipyramids, and four tetrahedra.

(a)

(b)

FIGURE 4: (a) Keggin-type I with the cavity bearing two kinds of apertures defined as 6 MR and 12 MR; (b) the simplified I with $\text{Ge}_7\text{O}_{14}\text{F}_3$ cluster as node.

3. Results and Discussion

I may be designated to the Keggin-type cage of which the MO_6 octahedron in $\text{POM-PMo}_{12}\text{O}_{40}^{3-}$ is replaced with

TABLE 1: The crystallographic data and structural refinement for I.

Empirical formula	H158 F36 Ge84 N36 O175
Formula weight	10245.60
Temperature/K	293(2) K
Wavelength/nm	0.71073 Å
Crystal system, space group	Tetragonal, $I4/mmm$
Unit cell dimensions	$a = 28.280(4)$ Å $c = 24.881(5)$ Å
V/nm^3	$19899(6)$ Å ³
$Z, D_c/(\text{Mg}\cdot\text{m}^{-3})$	2, 1.632 Mg/m ³
μ/mm^{-1}	6.309
$F(000)$	9324
Crystal size	0.17 mm × 0.18 mm × 0.20 mm
Range of θ	3.06° to 25.00°
Limiting indices	$-33 \leq h \leq 33, -33 \leq k \leq 33, -29 \leq l \leq 27$
Reflections collected/unique	72989/4806 [$R(\text{int}) = 0.2021$]
Completeness to $\theta = 25.00^\circ$	99.3%
Absorption correction	Semiempirical from equivalents
Max. and min. transmission	0.41 and 0.38
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4806/0/224
Goodness-of-fit on F^2	1.319
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0946, wR_2 = 0.2277$
R indices (all data)	$R_1 = 0.1638, wR_2 = 0.2514$
Largest diff. peak and hole	1.970 and -1.090 e/Å^3

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}.$$

$\text{Ge}_7\text{O}_{14}\text{F}_3$ cluster. The mixed-coordination $\text{Ge}_7\text{O}_{14}\text{F}_3$ cluster has been considerably studied [24–27], which consists of one octahedron, two edge-sharing trigonal bipyramids, and four tetrahedra (Figure 3). The distances of Ge–O (1.703(9) Å~2.168(13) Å) and Ge–F (1.736(14) Å~1.797(15) Å) and bond angles of O–Ge–O(88.6(6)° ~ 178.0(6)°) and Ge–O–Ge(87.5(7)° ~ 136.3(3)°) are consistent to the reported results [24].

In Keggin-type $\text{PMo}_{12}\text{O}_{40}^{3-}$ anion cage, twelve MoO_6 octahedra can be fallen into 4 entities in which three edge-sharing MoO_6 octahedra are integrated by an oxygen in PO_4 tetrahedron. The Keggin cage is formed by vertex-sharingly connecting 4 entities, showing the T_d molecular symmetry. In cage of I, twelve $\text{Ge}_7\text{O}_{14}\text{F}_3$ clusters surround the cavity of 8.3 Å with two kinds of apertures defined as 6 MR and 12 MR. The larger 12 MR aperture gives rise to 5.3 Å pore. Like Keggin $\text{PMo}_{12}\text{O}_{40}^{3-}$ anion, when three $\text{Ge}_7\text{O}_{14}\text{F}_3$ clusters by which 6 MR aperture is surrounded are looked as an entity, I mimics the T_d Keggin structure (Figure 4). In the case of JLG-5 in which the tetrahedral GeO_2 units link the adjacent Keggin-type cage into the infinite structure, I becomes the

TABLE 2: Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for I.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U _{eq}
Ge(1)	2343(1)	1584(1)	920(1)	67(1)
Ge(2)	1635(1)	0	1913(1)	64(1)
Ge(3)	1618(1)	1618(1)	0	64(1)
Ge(4)	1610(1)	816(1)	2731(1)	67(1)
Ge(5)	2354(1)	814(1)	1853(1)	68(1)
Ge(6)	2841(1)	0	2440(1)	76(1)
Ge(7)	2137(1)	0	3306(1)	78(1)
Ge(8)	2845(1)	2110(1)	0	81(1)
F(1)	1177(4)	0	1416(4)	71(3)
F(2)	1178(3)	1178(3)	0	72(5)
F(3)	3461(4)	0	2555(6)	97(4)
F(4)	3474(5)	2196(5)	0	115(5)
F(5)	2232(6)	0	3995(6)	125(5)
O(1)	1302(3)	470(3)	2294(4)	71(3)
O(2)	2593(3)	1242(3)	1431(4)	77(3)
O(3)	1251(4)	1251(4)	2997(5)	73(4)
O(4)	1812(4)	536(3)	3311(4)	81(3)
O(5)	2080(3)	1091(3)	2396(4)	74(3)
O(6)	1945(3)	1275(3)	530(4)	70(3)
O(7)	2850(3)	1769(3)	592(4)	72(3)
O(8)	2065(3)	2065(3)	1236(5)	71(4)
O(9)	2093(4)	2093(4)	0	64(5)
O(10)	1955(3)	465(3)	1512(4)	67(3)
O(11)	2121(5)	0	2435(5)	66(4)
O(12)	2712(5)	2712(5)	0	88(7)
O(13)	2867(3)	535(3)	2061(4)	72(3)
O(14)	2749(5)	0	3154(6)	84(4)
O(1W)	0	0	0	58(10)
O(2W)	0	5000	0	160(19)
O(3W)	1542(6)	5000	0	78(7)
N(1)	474(4)	474(4)	554(6)	60(4)
N(2)	1024(4)	1024(4)	1206(7)	77(5)
N(3)	2517(5)	-359(3)	4395(4)	69(4)
N(4)	1567(9)	0	315(12)	63(9)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

0D separated cage because the excessive HF impedes the formation of GeO₂ unit.

4. Conclusions

Keggin-type I has been solvothermally obtained. The structural determination shows that in cage of I, twelve Ge-O₁₄F₃ clusters surround the cavity of 8.3 Å with two kinds of apertures defined as 6 MR and 12 MR. The thermal studies show that Keggin-type cage of I begins to partly collapse from 200°C to finally change into GeO₂.

TABLE 3: Selected bond lengths (Å) and bond angles (°) for I.

Ge(1)–O(6)	1.723(9)	Ge(5)–O(10)	1.724(8)
Ge(1)–O(7)	1.731(9)	Ge(5)–O(13)	1.730(9)
Ge(1)–O(2)	1.747(9)	Ge(5)–O(2)	1.738(9)
Ge(1)–O(8)	1.759(7)	Ge(5)–O(5)	1.744(9)
Ge(2)–F(1)	1.792(10)	Ge(6)–F(3)	1.778(12)
Ge(2)–O(10) ⁱⁱ	1.881(9)	Ge(6)–O(13) ⁱⁱ	1.785(9)
Ge(2)–O(10)	1.881(9)	Ge(6)–O(13)	1.785(9)
Ge(2)–O(1) ⁱⁱ	1.883(10)	Ge(6)–O(14)	1.795(15)
Ge(2)–O(1)	1.883(10)	Ge(6)–O(11)	2.034(13)
Ge(2)–O(11)	1.891(12)	Ge(7)–F(5)	1.736(14)
Ge(3)–F(2)	1.759(14)	Ge(7)–O(14)	1.771(16)
Ge(3)–O(6) ⁱⁱⁱ	1.880(10)	Ge(7)–O(4) ⁱⁱ	1.774(10)
Ge(3)–O(6) ^{iv}	1.880(10)	Ge(7)–O(4)	1.774(10)
Ge(3)–O(6) ⁱ	1.880(10)	Ge(7)–O(11)	2.168(13)
Ge(3)–O(6)	1.880(10)	Ge(8)–O(12)	1.745(11)
Ge(3)–O(9)	1.900(17)	Ge(8)–O(7) ⁱⁱⁱ	1.761(9)
Ge(4)–O(1)	1.703(9)	Ge(8)–O(7)	1.761(9)
Ge(4)–O(3)	1.728(5)	Ge(8)–F(4)	1.797(15)
Ge(4)–O(4)	1.742(9)	Ge(8)–O(9)	2.127(13)
Ge(4)–O(5)	1.749(9)		
O(6)–Ge(1)–O(7)	115.5(5)	F(3)–Ge(6)–O(13) ⁱⁱ	92.5(4)
O(6)–Ge(1)–O(2)	113.2(5)	F(3)–Ge(6)–O(13)	92.5(4)
O(7)–Ge(1)–O(2)	100.1(4)	O(13) ⁱⁱ –Ge(6)–O(13)	116.0(7)
O(6)–Ge(1)–O(8)	110.6(5)	F(3)–Ge(6)–O(14)	89.0(7)
O(7)–Ge(1)–O(8)	110.3(5)	O(13) ⁱⁱ –Ge(6)–O(14)	121.9(3)
O(2)–Ge(1)–O(8)	106.4(5)	O(13)–Ge(6)–O(14)	121.9(3)
F(1)–Ge(2)–O(10) ⁱⁱ	88.9(4)	F(3)–Ge(6)–O(11)	171.1(6)
F(1)–Ge(2)–O(10)	88.9(4)	O(13) ⁱⁱ –Ge(6)–O(11)	92.2(4)
O(10) ⁱⁱ –Ge(2)–O(10)	88.6(6)	O(13)–Ge(6)–O(11)	92.2(4)
F(1)–Ge(2)–O(1) ⁱⁱ	89.2(4)	O(14)–Ge(6)–O(11)	82.1(6)
O(10) ⁱⁱ –Ge(2)–O(1) ⁱⁱ	90.8(4)	F(5)–Ge(7)–O(14)	93.5(8)
O(10)–Ge(2)–O(1) ⁱⁱ	178.0(4)	F(5)–Ge(7)–O(4) ⁱⁱ	94.2(4)
F(1)–Ge(2)–O(1)	89.2(4)	O(14)–Ge(7)–O(4) ⁱⁱ	120.5(4)
O(10) ⁱⁱ –Ge(2)–O(1)	178.0(4)	F(5)–Ge(7)–O(4)	94.2(4)
O(10)–Ge(2)–O(1)	90.8(4)	O(14)–Ge(7)–O(4)	120.5(4)
O(1) ⁱⁱ –Ge(2)–O(1)	89.7(6)	O(4) ⁱⁱ –Ge(7)–O(4)	117.5(7)
F(1)–Ge(2)–O(11)	179.7(6)	F(5)–Ge(7)–O(11)	172.3(7)
O(10) ⁱⁱ –Ge(2)–O(11)	90.9(4)	O(14)–Ge(7)–O(11)	78.8(6)
O(10)–Ge(2)–O(11)	90.9(4)	O(4) ⁱⁱ –Ge(7)–O(11)	89.8(4)
O(1) ⁱⁱⁱ –Ge(2)–O(11)	91.0(4)	O(4)–Ge(7)–O(11)	89.8(4)
O(1)–Ge(2)–O(11)	91.0(4)	O(12)–Ge(8)–O(7) ⁱⁱⁱ	122.5(3)
F(2)–Ge(3)–O(6) ⁱⁱⁱ	89.0(3)	O(12)–Ge(8)–O(7)	122.5(3)
F(2)–Ge(3)–O(6) ^{iv}	89.0(3)	O(7) ⁱⁱⁱ –Ge(8)–O(7)	113.5(7)
O(6) ⁱⁱⁱ –Ge(3)–O(6) ^{iv}	90.9(6)	O(12)–Ge(8)–F(4)	94.6(7)
F(2)–Ge(3)–O(6) ⁱ	89.0(3)	O(7) ⁱⁱⁱ –Ge(8)–F(4)	93.8(4)
O(6) ⁱⁱⁱ –Ge(3)–O(6) ⁱ	178.0(6)	O(7)–Ge(8)–F(4)	93.8(4)
O(6) ^{iv} –Ge(3)–O(6) ⁱ	89.1(6)	O(12)–Ge(8)–O(9)	78.8(6)
F(2)–Ge(3)–O(6)	89.0(3)	O(7) ⁱⁱⁱ –Ge(8)–O(9)	89.8(3)
O(6) ⁱⁱⁱ –Ge(3)–O(6)	89.1(6)	O(7)–Ge(8)–O(9)	89.8(3)
O(6) ^{iv} –Ge(3)–O(6)	178.0(6)	F(4)–Ge(8)–O(9)	173.5(6)
O(6) ⁱ –Ge(3)–O(6)	90.9(6)	Ge(4)–O(1)–Ge(2)	118.1(5)

TABLE 3: Continued.

F(2)–Ge(3)–O(9)	180.0(7)	Ge(5)–O(2)–Ge(1)	131.9(5)
O(6) ⁱⁱⁱ –Ge(3)–O(9)	91.0(3)	Ge(4) ⁱ –O(3)–Ge(4)	133.6(8)
O(6) ^{iv} –Ge(3)–O(9)	91.0(3)	Ge(4)–O(4)–Ge(7)	123.5(6)
O(6) ⁱ –Ge(3)–O(9)	91.0(3)	Ge(5)–O(5)–Ge(4)	120.5(5)
O(6)–Ge(3)–O(9)	91.0(3)	Ge(1)–O(6)–Ge(3)	117.0(5)
O(1)–Ge(4)–O(3)	110.8(6)	Ge(1)–O(7)–Ge(8)	123.5(5)
O(1)–Ge(4)–O(4)	115.8(5)	Ge(1)–O(8)–Ge(1) ⁱ	119.5(8)
O(3)–Ge(4)–O(4)	101.4(5)	Ge(3)–O(9)–Ge(8) ^{iv}	136.3(3)
O(1)–Ge(4)–O(5)	109.8(5)	Ge(3)–O(9)–Ge(8)	136.3(3)
O(3)–Ge(4)–O(5)	108.2(6)	Ge(8) ^{iv} –O(9)–Ge(8)	87.5(7)
O(4)–Ge(4)–O(5)	110.3(5)	Ge(5)–O(10)–Ge(2)	117.0(5)
O(10)–Ge(5)–O(13)	115.8(4)	Ge(2)–O(11)–Ge(6)	137.0(7)
O(10)–Ge(5)–O(2)	110.9(4)	Ge(2)–O(11)–Ge(7)	134.5(7)
O(13)–Ge(5)–O(2)	99.9(4)	Ge(6)–O(11)–Ge(7)	88.5(5)
O(10)–Ge(5)–O(5)	110.3(4)	Ge(8)–O(12)–Ge(8) ^{iv}	114.9(11)
O(13)–Ge(5)–O(5)	110.2(5)	Ge(5)–O(13)–Ge(6)	120.6(5)
O(2)–Ge(5)–O(5)	109.1(5)	Ge(7)–O(14)–Ge(6)	110.6(7)

Symmetry transformations used to generate equivalent atoms: ⁱ y, x, z ; ⁱⁱ $x, -y, z$; ⁱⁱⁱ $x, y, -z$; ^{iv} $y, x, -z$.

Acknowledgment

This work was supported by the Scientific Research Foundation for the Returned Overseas Team, Chinese Education Ministry.

References

- [1] D. W. Breck, *Zeolite Molecular Sieves: Structure, Chemistry and Use*, Wiley & Sons, New York, NY, USA, 1974.
- [2] J. Cejka, A. Corma, and S. Zones, *Zeolites and Catalysis: Synthesis, Reactions and Applications*, Wiley-VCH, Weinheim, Germany, 2010.
- [3] G. O. Brunner and W. M. Meier, "Framework density distribution of zeolite-type tetrahedral nets," *Nature*, vol. 337, no. 6203, pp. 146–147, 1989.
- [4] M. O'Keeffe and O. M. Yaghi, "Germanate zeolites: contrasting the behavior of germanate and silicate structures built from cubic T_8O_{20} units ($T = \text{Ge or Si}$)," *Chemistry*, vol. 5, no. 10, pp. 2796–2801, 1999.
- [5] J. Jiang, J. L. Jorda, M. J. Diaz-Cabanas, J. Yu, and A. Corma, "The synthesis of an extra-large-pore zeolite with double three-ring building units and a low framework density," *Angewandte Chemie*, vol. 49, no. 29, pp. 4986–4988, 2010.
- [6] T. Conradsson, M. S. Dadachov, and X. D. Zou, "Synthesis and structure of $(\text{Me}_3\text{N})_6[\text{Ge}_{32}\text{O}_{64}] \cdot (\text{H}_2\text{O})_{4.5}$, a thermally stable novel zeotype with 3D interconnected 12-ring channels," *Microporous and Mesoporous Materials*, vol. 41, no. 1–3, pp. 183–191, 2000.
- [7] H. Li and O. M. Yaghi, "Transformation of germanium dioxide to microporous germanate 4-connected nets," *Journal of the American Chemical Society*, vol. 120, no. 40, pp. 10569–10570, 1998.
- [8] Y. Mathieu, J.-L. Paillaud, P. Caullet, and N. Bats, "Synthesis and characterization of IM-10: a new microporous silicogermanate with a novel topology," *Microporous and Mesoporous Materials*, vol. 75, no. 1–2, pp. 13–22, 2004.
- [9] J. Su, Y. Wang, Z. Wang, and J. Lin, "PKU-9: an aluminogermanate with a new three-dimensional zeolite framework constructed from CGS layers and *spiro*-5 units," *Journal of the American Chemical Society*, vol. 131, no. 17, pp. 6080–6081, 2009.
- [10] A. Corma, M. J. Diaz-Cabanas, J. L. Jorda, F. Rey, G. Sastre, and K. G. Strohmaier, "A zeolitic structure (ITQ-34) with connected 9- and 10-ring channels obtained with phosphonium cations as structure directing agents," *Journal of the American Chemical Society*, vol. 130, no. 49, pp. 16482–16483, 2008.
- [11] Y. Lorgouilloux, M. Dodin, J. L. Paillaud et al., "IM-16: a new microporous germanosilicate with a novel framework topology containing *d4r* and *mtw* composite building units," *Journal of Solid State Chemistry*, vol. 182, no. 3, pp. 622–629, 2009.
- [12] X. Bu, P. Feng, T. E. Gier, D. Zhao, and G. D. Stucky, "Hydrothermal synthesis and structural characterization of zeolite-like structures based on gallium and aluminum germanates," *Journal of the American Chemical Society*, vol. 120, no. 51, pp. 13389–13397, 1998.
- [13] D. L. Dorset, K. G. Strohmaier, C. E. Klierer et al., "Crystal structure of ITQ-26, a 3D framework with extra-large pores," *Chemistry of Materials*, vol. 20, no. 16, pp. 5325–5331, 2008.
- [14] L. Tang, L. Shi, C. Bonneau et al., "A zeolite family with chiral and achiral structures built from the same building layer," *Nature Materials*, vol. 7, no. 5, pp. 381–385, 2008.
- [15] T. E. Gier, X. Bu, P. Feng, and G. D. Stucky, "Synthesis and organization of zeolite-like materials with three-dimensional helical pores," *Nature*, vol. 395, no. 6698, pp. 154–157, 1998.
- [16] J. Sun, C. Bonneau, A. Cantin et al., "The ITQ-37 mesoporous chiral zeolite," *Nature*, vol. 458, no. 7242, pp. 1154–1157, 2009.
- [17] Y. F. Li and X. D. Zou, "SU-16: a three-dimensional open-framework borogermanate with a novel zeolite topology," *Angewandte Chemie*, vol. 44, no. 13, pp. 2012–2015, 2005.
- [18] X. Zou, T. Conradsson, M. Klingstedt, M. S. Dadachov, and M. O'Keeffe, "A mesoporous germanium oxide with crystalline pore walls and its chiral derivative," *Nature*, vol. 437, no. 7059, pp. 716–719, 2005.
- [19] M. V. Peskov and X. Zou, "Germanates built from $\text{Ge}_{10}(\text{O}, \text{OH})_{27-28}$ and $\text{Ge}_7(\text{O}, \text{OH}, \text{F})_{19}$ secondary building units: from systematic study of reported compounds to rational design of novel structures," *Journal of Physical Chemistry C*, vol. 115, no. 15, pp. 7729–7739, 2011.
- [20] B. Guo, A. K. Inge, C. Bonneau et al., "Investigation of the GeO_2 -1,6-diaminohexane-water-pyridine-HF phase diagram leading to the discovery of two novel layered germanates with extra-large rings," *Inorganic Chemistry*, vol. 50, no. 1, pp. 201–207, 2011.
- [21] C. Bonneau, J. Sun, R. Sanchez-Smith et al., "Open-framework germanate built from the hexagonal packing of rigid cylinders," *Inorganic Chemistry*, vol. 48, no. 21, pp. 9962–9964, 2009.
- [22] Q. Pan, J. Li, K. E. Christensen et al., "A germanate built from a 6^812^6 cavity cotemplated by an $(\text{H}_2\text{O})_{16}$ cluster and 2-methylpiperazine," *Angewandte Chemie*, vol. 47, no. 41, pp. 7868–7871, 2008.
- [23] Y. Han, Y. Li, J. Yu, and R. R. Xu, "A gallogermanate zeolite constructed exclusively by three-ring building units," *Angewandte Chemie*, vol. 50, no. 13, pp. 3003–3005, 2011.
- [24] J. Plévert, T. M. Gentz, T. L. Groy, M. O'Keeffe, and O. M. Yaghi, "Layered structures constructed from new linkages of $\text{Ge}_7(\text{O}, \text{OH}, \text{F})_{19}$ clusters," *Chemistry of Materials*, vol. 15, no. 3, pp. 714–718, 2003.

- [25] H. Li, M. Eddaoudi, D. A. Richardson, and O. M. Yaghi, "Porous germanates: synthesis, structure, and inclusion properties of $\text{Ge}_7\text{O}_{14.5}\text{F}_2 \cdot [(\text{CH}_3)_2\text{NH}_2]_3(\text{H}_2\text{O})_{0.86}$," *Journal of the American Chemical Society*, vol. 120, no. 33, pp. 8567–8568, 1998.
- [26] J. Plévert, T. M. Gentz, A. Laine et al., "A flexible germanate structure containing 24-ring channels and with very low framework density," *Journal of the American Chemical Society*, vol. 123, no. 50, pp. 12706–12707, 2001.
- [27] L. Shi, C. Bonneau, Y. Li, J. Sun, H. Yue, and X. Zou, "SU-22 and SU-23: layered germanates built from 4-coordinated Ge_7 Clusters exhibiting structural variations on the 4^4 topology," *Crystal Growth & Design*, vol. 8, no. 10, pp. 3695–3699, 2008.