Lanthanide Germanate Cluster Organic Frameworks Constructed from {Ln8Ge12} or {Ln11Ge12} Cage Cluster Building Blocks

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Open-framework materials have been extensively studied because of their widespread applications in catalysis, ion exchange, and separation.[1] Since the discovery of the first open-framework germanate in 1991,[2] the interest in germanates has been growing steadily.[3−5] Recently, one area of increasing attention is introducing heteroatoms into germanate backbones to make novel open frameworks containing main-group elements and transition metals.[6] However, except for several lanthanide germanates obtained by both the flux-growth method and a high-temperature, high-pressure hydrothermal method in supercritical water,[7] no systematic investigation of lanthanide germanates has been carried out under mild hydrothermal conditions. This is because of the fact that the conditions for solubility of germanium dioxide (GeO_2, a traditional germanium source) and lanthanide oxide (Ln_2O_3) are incompatible: acidic and basic solutions are favorable reaction systems for Ln_2O_3 and GeO_2, respectively. Recently, we have been extending our interest from B−Ge−O to Ln−Ge−O systems for making novel lanthanide germanate frameworks built from Ge−O and Ln−O or mixed Ln−Ge−O cluster units under mild hydrothermal conditions. Because of the flexible coordination geometries of Ge and Ln atoms, their ability to form Ge−O[3,4] and Ln−O[8] frameworks under rational conditions, and their unique cluster structural units, the Ln−Ge−O system is likely to provide novel structures with new topological frameworks.

To make open-framework lanthanide germanates under mild hydrothermal conditions, three approaches have been tried with the Ln−Ge−O system in our lab: (1) replacing Ln_2O_3 with lanthanide salts in basic solution; (2) replacing GeO_2 with soluble germanium alkoxides in acidic solution; and (3) using lanthanide salts and germanium alkoxides in acidic solution. However, the first approach failed because the lanthanide salts (oxide salts or alkoxides) were all hydrolyzed to form nondissolving Ln_2O_3 in basic solution, which could not further react with GeO_2; the latter two methods were also fruitless because of the very poor crystallization of the product, although germanium alkoxides and Ln_2O_3 (or lanthanide salts) have good solubility in acidic solution.

In previous work, we have successfully made a series of Ln−O cluster organic frameworks in which formation of the Ln−O cluster unit is induced by carboxyl groups of the ligand. Accordingly, another type of organogermanium source, bis(carboxyethylgermanium) sesquioxide, $(HOOCCH_2CH_2)_2Ge_2O_3$ ($H_2E_2Ge_2O_3$, $E = -CH_2CH_2COO^-$; Scheme S1 in the Supporting Information), was chosen as the multifunctional ligand for the following reasons: (1) $H_2E_2Ge_2O_3$ with hydrophilic tails has good solubility in water, forming a highly acidic aqueous solution (pH 4) that may dissolve Ln_2O_3. (2) $H_2E_2Ge_2O_3$ contains two carboxyls and a Ge_2O_3 ($O=Ge-O-Ge=O$) core with two $Ge=O$ bonds and thus not only offers the possibility for structural derivatives but also is an effective precursor for making extended frameworks. (3) The carboxyls may induce Ln ions to aggregate into Ln−O clusters, and the Ge_2O_3 core can further polymerize to form a Ge−O cluster when the $Ge=O$ double bonds are

opened; thus, frameworks containing Ge−O and Ln−O clusters might be obtained. Here we report the systematic syntheses, structures, and properties of five lanthanide germanate frameworks under hydrothermal conditions, $[Nd_8Ge_{12}(\mu_3\text{-}O)_{24}E_{12}(H_2O)_7] \cdot 13H_2O$ (**FJ-19**) and $[Ln_{11}Ge_{12}(\mu_3\text{-}O)_{24}E_{12}(pa)_6(H_2O)_{10}] \cdot (Cl,2OH) \cdot nH_2O$ [Hpa = 2-picolinic acid; Ln = Pr (**FJ-20a**), Nd (**FJ-20b**), Eu (**FJ-20c**), Gd (**FJ-20d**); n = 19 (Pr, Nd), 15 (Eu), 14 (Gd)], containing the high-nuclearity cage-shaped lanthanide germanate clusters (LGCs) $[Nd_8Ge_{12}(\mu_3\text{-}O)_{24}(H_2O)_7]^{24+}$ (Nd_8Ge_{12}) for **FJ-19** and $[Ln_{11}Ge_{12}(\mu_3\text{-}O)_{24}(H_2O)_{10}]^{33+}$ ($Ln_{11}Ge_{12}$) for **FJ-20**, which act as building blocks that link to each other via the E groups, forming novel 3D lanthanide germanate cluster organic frameworks (LGCOFs) (Figure 1). **FJ-19** is a twofold-interpenetrating enantiomorphic pair of nets, while the members of the **FJ-20** series are noninterpenetrating LGCOFs.
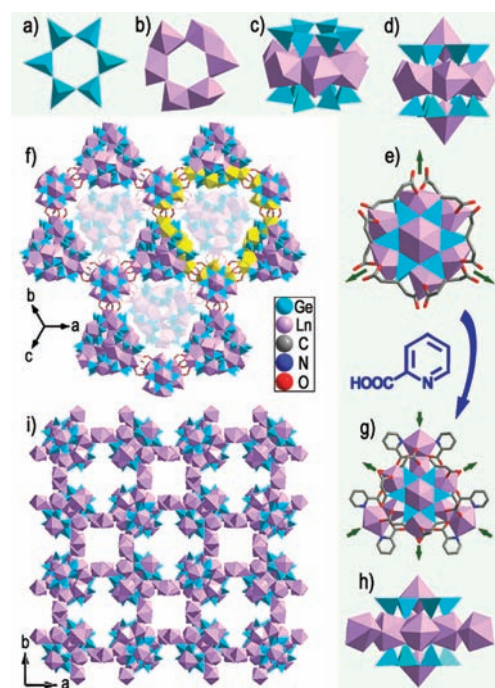

Figure 1. (a−c) View of the Ge_6 and Nd_6 rings and the linking mode. (d) Side view of the Nd_8Ge_{12} cage. (e) Top view of the Nd_8Ge_{12} cage surrounded by 12 E groups, in which the arrows show the linking modes with three adjacent Nd_8Ge_{12} cages. (f) Interpenetrating enantiomorphic pair of (10,3)-a nets possessing threefold helices with opposite chirality along the [111] direction in **FJ-19**. One of the nets is shown lighter. (g) Top view of the $Pr_{11}Ge_{12}$ cage surrounded by six pa ligands and 12 E groups, in which the arrows show its linking modes with six adjacent $Pr_{11}Ge_{12}$ cages. (h) Side view of the $Pr_{11}Ge_{12}$ cage. (i) View of the two types of channels along the [100] direction in **FJ-20a**.

Crystals of **FJ-19** and **FJ-20** were made by hydrothermal reaction of $H_2E_2Ge_2O_3$ and Nd_2O_3 in water in the presence of HNO_3 (pH 3) for **FJ-19**, while for **FJ-20a−d**, $H_2E_2Ge_2O_3$ reacted with Pr_6O_{11}, Nd_2O_3, Eu_2O_3,

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and Gd_2O_3, respectively and Hpa in the presence of HCl (pH 3).[9a] X-ray crystal structure analyses revealed that **FJ-19** and **FJ-20** crystallize in the high-symmetry cubic space groups $Ia\bar{3}$ and $I\bar{4}3m$,[9b] respectively.

In **FJ-19**, there are two kinds of wheel-shaped clusters with six-membered Ge_6 (Figure 1a and Figure S5) and Nd_6 (Figure 1b and Figure S6) rings. Three $E_2Ge_2O_3^{2-}$ moieties are polymerized to form each Ge_6 ring built by six corner-sharing Ge tetrahedra, with the E groups radiating out of the Ge_6 ring. Each Nd_6 ring built from three dimers is sandwiched between two Ge_6 rings via 12 $Ge-\mu_3$-O$-$Nd bridges to form a sandwich-type Nd_6Ge_{12} cluster with two six-membered-ring windows (Figure 1c) that are further capped by two Nd ions, resulting in a spindle-shaped Nd_8Ge_{12} cage cluster with dimensions of $13 \times 14 \times 14$ Å^3 (Figure 1d). Of the 24 O_{COO} atoms of the 12 E groups radiating out of the LGC (Figure 1e), 12 O_{COO} atoms are flexed inward and link back to the Nd_6 ring to stabilize the Nd_8Ge_{12} cage, while the other 12 O_{COO} atoms point out from the Nd_8Ge_{12} cage, with three pairs free and the other three pairs bound to three adjacent Nd_8Ge_{12} cages (Figure S7), giving rise to a 3D LGCOF (Figure 1f and Figure S8) with a (10,3)-a network and a $SrSi_2$ (srs) topology.[10a] The extra-large channels of $15.0 \times 15.0/16.8 \times 16.8$ Å in the (10,3)-a network cannot be stabilized by sufficient solvent molecules, so a second net of the same type but opposite chirality interpenetrates the first one (Figure 1f).

In order to avoid interpenetration, a rigid chelating ligand, Hpa, was introduced into the reaction system. Not only would the considerable steric hindrance of Hpa occupy enough space to avoid the formation of the interpenetrating networks, but also Hpa would stabilize new the LGC formed in situ through the chelating coordination modes. As expected, a series of isostructural and noninterpenetrating LGCOFs, **FJ-20**, were made. Here, only **FJ-20a** is described in detail. The 23-atom $Pr_{11}Ge_{12}$ unit (Figure 1g,h) is derived from the 20-atom Ln_8Ge_{12} unit (Figure 1d) with three added Pr5 atoms linked to the Pr_6 ring (Figure S11). In **FJ-20a**, 12/6 inward-/outward-pointing O_{COO} atoms of the 12 E groups play an important role in stabilizing the $Pr_{11}Ge_{12}$ cluster, while of the remaining six outward-pointing O_{COO} atoms, three are free and three link to three adjacent $Pr_{11}Ge_{12}$ units in a monodentate fashion (Figure S12). In addition, three adjacent $Pr_{11}Ge_{12}$ units also join the central $Pr_{11}Ge_{12}$ cage through three outward-pointing O_{COO} atoms. Therefore, each $Pr_{11}Ge_{12}$ cage is a six-connecting node joined to six adjacent nodes to form a 3D LGCOF (Figure 1i) with α-Po (pcu) topology.[10b] Although the pyridyl rings of the pa ligands and the organic E groups are trapped inside the two types of channels, their free diameters are still up to 7.1×7.1 and 4.2×4.2 Å, respectively (Figure S13). The accessible void volume of the channels in **FJ-20a** is 11496.5 Å^3, which occupies 34.2% of the whole unit cell volume. According to the elemental and thermogravimetric (TG) analyses, there are three counteranions (one Cl$^-$, two OH$^-$) and 19 solvent water molecules located in the channels of **FJ-20a**, but these could not be unambiguously located by X-ray analysis.[4c,g]

The solid-state luminescence of **FJ-20c** was investigated at room temperature. **FJ-20c** displays intense red luminescence ($\lambda_{ex} = 278$ nm) and exhibits the characteristic transitions of the Eu^{3+} ion, with the peaks at 578, 594, 619, 651, and 700 nm are attributed to the $^5D_0 \rightarrow {}^7F_J$ ($J = 0-4$) transitions, respectively. The $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions correspond to the magnetic-dipole and electric-dipole transitions, respectively. The former is fairly insensitive to the coordination environment of the Eu^{3+} ion, while the latter, which corresponds to the strongest emission at 619 nm, is hypersensitive to the environment of the Eu^{3+} ions. The narrow peak at 578 nm is assigned to the $^5D_0 \rightarrow {}^7F_0$ transition corresponding to the symmetry-forbidden emission, which is strictly forbidden in a field of symmetry. Thus, the above results reveal that the Eu^{3+} ions in **FJ-20c** occupy sites with low symmetry and without an inversion center. Notably, the $I({}^5D_0 \rightarrow {}^7F_2)/I({}^5D_0 \rightarrow {}^7F_1)$ intensity ratio is

$\sim$3.7, which further confirms that the Eu^{3+} ions are not in an inversion center.[11] This is also in agreement with the results of the single-crystal X-ray analysis. The sorption of Ar gas by **FJ-20b** at 87 K displays a type-I isotherm, as expected for microporous materials. The BET surface area is 94.4 m^2 g^{-1}, which is close to that of NTHU-2 (112 m^2 g^{-1}).[12]

In summary, a series of novel 3D LGCOFs has been successfully made under mild hydrothermal conditions using an organogermanium compound as germanium source. The key points of the synthetic procedures have been well-established, which indicates that this strategy not only offers an effective and feasible way of making novel LGCOFs but also opens a new avenue for making metal germanate hybrid materials. Work in progress includes making novel functional LGCOFs by using larger rigid N-containing carboxylate ligands and metal germanate hybrid materials by using various metals salts under hydrothermal conditions. It is reasonable to believe that the present work will be important in expanding the study of germanates with open frameworks.

Supporting Information Available: Two schemes, 17 figures, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Cheetham, A. K.; Férey, G.; Loiseau, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 3268. (b) Davis, M. E. *Nature* **2002**, *417*, 813.

(2) (a) Cheng, J.; Xu, R. *J. Chem. Soc., Chem. Commun.* **1991**, 483. (b) Cheng, J.; Xu, R.; Yang, D. *J. Chem. Soc., Dalton Trans.* **1991**, 1537.

(3) (a) Gier, T. E.; Bu, X.; Feng, P.; Stucky, G. D. *Nature* **1998**, *395*, 154. (b) Bu, X.; Feng, P.; Gier, T. E.; Zhou, D.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 13389. (c) Cascales, C.; Gutiérrez-Puebla, E.; Iglesias, M.; Monge, M. A.; Ruíz-Valero, C. *Angew. Chem., Int. Ed.* **1999**, *38*, 2436.

(4) (a) Li, H.; Eddaoudi, M.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 653. (b) Bu, X.; Feng, P.; Stucky, G. D. *Chem. Mater.* **2000**, *12*, 1811. (c) Plévert, J.; Gentz, T. M.; Laine, A.; Li, H. L.; Young, V. G.; Yaghi, O. M.; O'Keeffe, M. *J. Am. Chem. Soc.* **2001**, *123*, 12706. (d) Zhou, Y.; Zhu, H.; Chen, Z.; Chen, M.; Xu, Y.; Zhang, H.; Zhao, D. *Angew. Chem., Int. Ed.* **2001**, *40*, 2166. (e) Lin, Z.-E.; Zhang, J.; Zhao, J.-T.; Zheng, S.-T.; Pan, C.-Y.; Wang, G.-M.; Yang, G.-Y. *Angew. Chem., Int. Ed.* **2005**, *44*, 6881. (f) Pan, Q.; Li, J.; Christensen, K. E.; Bonneau, C.; Ren, X.; Shi, L.; Sun, J.; Zou, X.; Li, G.; Yu, J.; Xu, R. *Angew. Chem., Int. Ed.* **2008**, *47*, 7868. (g) Christensen, K. E.; Bonneau, C.; Gustafsson, M.; Shi, L.; Sun, J.; Grins, J.; Jansson, K.; Sbille, I.; Su, B.; Zou, X. *J. Am. Chem. Soc.* **2008**, *130*, 3758.

(5) Zou, X.; Conradsson, T.; Klingstedt, M.; Dadachov, M. S.; O'Keeffe, M. *Nature* **2005**, *437*, 716.

(6) (a) Pan, C.-Y.; Liu, G.-Z.; Zheng, S.-T.; Yang, G.-Y. *Chem.—Eur. J.* **2008**, *14*, 5057. (b) Liu, G.-Z.; Zheng, S.-T.; Yang, G.-Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 2827.

(7) (a) Chen, P.-L.; Chiang, P.-Y.; Yeh, H.-C.; Chang, B.-C.; Lii, K.-H. *Dalton Trans.* **2008**, 1721. (b) Emirdag-Eanes, M.; Krawiec, K.; Kolis, J. W. *J. Chem. Crystallogr.* **2002**, *31*, 281.

(8) (a) Ghosh, S. K.; Bureekaew, S.; Kitagawa, S. *Angew Chem., Int. Ed.* **2008**, *47*, 340. (b) Cheng, J.-W.; Zhang, J.; Zheng, S.-T.; Zhang, M.-B.; Yang, G.-Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 73.

(9) (a) A mixture of Nd_2O_3 (0.087 g), $H_2E_2Ge_2O_3$ (0.088 g), H_2O (10 mL), and HNO$_3$ (0.1 mL) was stirred for 2 h (pH 3), sealed in a 30 mL Teflon-lined bomb at 165 °C for 7 days, and then cooled to room temperature (pH 6). Purple polyhedral crystals of **FJ-19** were recovered by filtration, washed with distilled water, and dried in air. For **FJ-20**, a similar procedure was used, but Hpa (0.10 g) and HCl (0.1 mL) were introduced into the reaction systems with Ln_2O_3 (0.088 g of Pr_6O_{11}, 0.087 g of Nd_2O_3, 0.091 g of Eu_2O_3, and 0.094 g of Gd_2O_3. Yield: 25 and 27% for **FJ-19** and the **FJ-20** series, respectively, based on $H_2E_2Ge_2O_3$. Prismatic crystals: **FJ-20a** (green), **FJ-20b** (purple), **FJ-20c** (colorless), and **FJ-20d** (colorless). Elemental-analysis, IR, TG, powder X-ray diffraction, luminescence, and crystal data for **FJ-19** and **FJ-20** are given in the Supporting Information (Figures S14−17). (b) Crystal data for **FJ-19**: cubic; space group $Ia\bar{3}$; $a = 34.1837(3)$ Å; $V = 39944.5(6)$ Å^3; $Z = 16$; GOF = 1.093; R1 (wR2) = 0.0513 (0.1438). For **FJ-20a**: cubic; space group $I\bar{4}3m$; $a = 32.2786(11)$ Å; $V = 33631(2)$ Å^3; $Z = 8$; GOF = 1.096. R1 (wR2) = 0.056 (0.1504).

(10) (a) Friedrichs, O. D.; O'Keeffe, M.; Yaghi, O. M. *Acta Crystallogr.* **2003**, *A59*, 22. (b) O'Keeffe, M.; Hyde, B. G. *Crystal Structures I: Patterns and Symmetry*; Mineralogical Society of America: Washington DC, 1996.

(11) Zhao, B.; Chen, X.; Cheng, P.; Liao, D.; Yan, S.; Jiang, Z. *J. Am. Chem. Soc.* **2004**, *126*, 15394.

(12) Liao, Y.-C.; Liao, F.-L.; Chang, W.-K.; Wang, S.-L. *J. Am. Chem. Soc.* **2004**, *126*, 1320.

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