# Syntheses and Characterization of Two Novel Germanium Dioxide Frameworks with Occluded Ethylenediamine (EDA) and 1,3-Propylenediamine (1,3-PDA)

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Two novel germanium dioxide frameworks with occluded ethylenediamine and 1,3-propylenediamine have been hydrothermally synthesized, denoted as EDA–$GeO_2$ and 1,3-PDA–$GeO_2$ and characterized by means of X-ray powder diffraction (XRD), IR spectra and thermal analyses; the chemical compositions of EDA–$GeO_2$ and 1,3-PDA–$GeO_2$ are $GeO_2$ : 0.3 EDA : 0.6 $H_2O$ and $GeO_2$ : 0.22 (1,3-PDA) : 0.44 $H_2O$, respectively and the two compounds show similar XRD patterns.

A variety of amines and quaternary ammonium salts believed to act as templates can be encapsulated by frameworks of silica, aluminosilicate and aluminophosphate.[1] Each sort of framework can exist as various geometrical and topological structures because of the different templates being used. On calcination, the template molecules may be removed from the host lattices, and as a result the lattices become microporous and can be viewed as molecular sieves. Recently, a number of gallophosphates,[2] alumino- and gallo-arsenates[3] and metal sulphides[4] with an occluded amine or quaternary ammonium have been synthesized and received much attention. Ge is adjacent to the five elements Al, Ga, Si, P and As in the periodic table, but so far all the reported crystals composed of Ge and O do not include amines or quaternary ammonium salts. So whether the germanium dioxide framework is able to occlude these species remains an interesting question. In this communication, we describe the syntheses and characterization of two novel germanium dioxides with occluded ethylenediamine (EDA) and 1,3-propylenediamine (1,3-PDA) which are denoted as EDA–$GeO_2$ and 1,3-PDA–$GeO_2$, respectively and are the first two germanium dioxide inclusion compounds with occluded organic amines.†

Under an optical microscope, both EDA–$GeO_2$ and 1,3-PDA–$GeO_2$ appear to be pure phases. The X-ray powder diffraction (XRD) patterns of the two compounds reveal that

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† Preparation of EDA–$GeO_2$: germanium dioxide (1 equiv.), EDA organic template (8 equiv.) and water (50 equiv.) were mixed and the mixture was stirred until homogeneous, sealed in a Teflon-lined autoclave and heated at 180 °C for 7 days. Then the crystalline product was filtered off, washed with distilled water and dried at ambient temperature.

Preparation of 1,3-PDA–$GeO_2$: germanium dioxide, 1 equiv. 1,3-PDA organic template (2 equiv.) and water (50 equiv.) were mixed and the subsequent synthetic procedure was the same as that described for EDA–$GeO_2$.

Elemental analyses were performed on a P-240 element analyser, X-ray powder diffraction on a Rigaku 3DX diffractometer with Cu-Kα radiation, IR spectra on a Nicolet 5DX spectrometer and thermal analyses on a Perkin-Elmer DTA instrument.

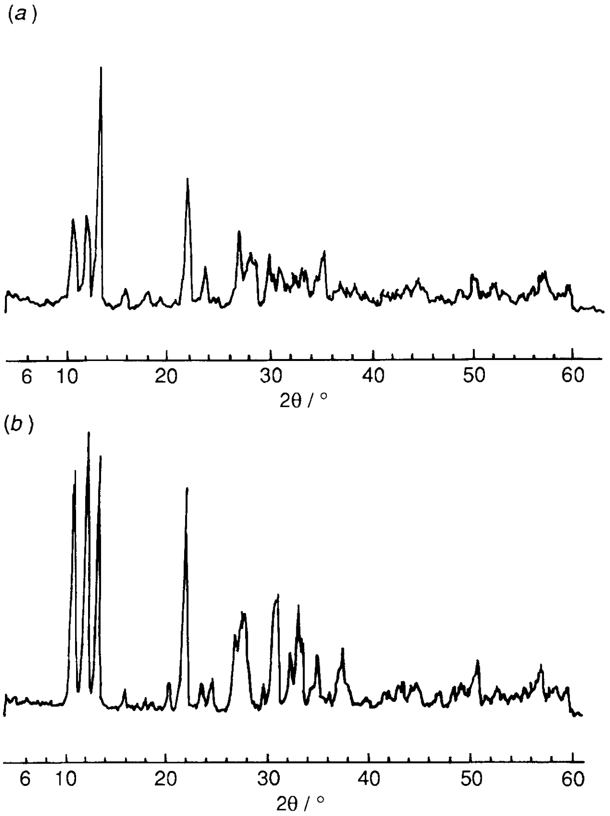

**Fig. 1** X-ray powder diffraction pattern of (*a*) EDA–$GeO_2$; (*b*) 1,3-PDA–$GeO_2$

**Table 1** The main IR absorption assignments of hexagonal $GeO_2$, $Ge_6O_{12}OHNMe_4$, EDA–$GeO_2$ and 1,3-PDA–$GeO_2$

| Name | $\nu_{as}$(Ge–O–Ge)/ $cm^{-1}$ | $\nu_s$(Ge–O–Ge)/ $cm^{-1}$ | Ge–O Bond length/Å |
|---|---|---|---|
| Hexagonal $GeO_2$ | 879.65 | 553.64 | 1.734–1.741 |
| | | 516.99 | (ref. 8) |
| $Ge_6O_{12}OHNMe_4$ | 837.21 | 567.14 | 1.768 (average) |
| | | 520.85 | |
| EDA–$GeO_2$ | 769.70 | 580.65 | |
| | 707.97 | 499.63 | |
| 1,3-PDA–$GeO_2$ | 775.48 | 497.70 | |

they are new compounds probably with similar and novel structures (Fig. 1). The empirical formulae of EDA–$GeO_2$ and 1,3-PDA–$GeO_2$ derived from the elemental analyses were $GeO_2$:0.3 EDA:0.6$H_2O$ and $GeO_2$:0.22 (1,3-PDA):0.44 $H_2O$, respectively.

To synthesize EDA–$GeO_2$, the optimum batch composition was 4–8 EDA:$GeO_2$:30–60 $H_2O$. High EDA content was found to increase the rate of crystallization and often resulted in irregular crystal morphology. An EDA:$GeO_2$ ratio lower than 2 readily resulted in a dense $GeO_2$ phase. The synthetic range suitable for 1,3-PDA–$GeO_2$ was 2–10 (1,-PDA):$GeO_2$:30–60 $H_2O$. Although the XRD pattern of 1,3-PDA–$GeO_2$ is similar to that of EDA–$GeO_2$, the morphologies of 1,3-PDA–$GeO_2$ crystals are often irregular and the crystals are often smaller.

The IR spectra of EDA–$GeO_2$ and 1,3-PDA–$GeO_2$ are shown in Fig. 2. By referring to the IR spectra of the Ge-containing zeolites[5] and talcs[6] and comparing their IR spectra with those of the dense phase hexagonal $GeO_2$ and $Ge_6O_{12}OHNMe_4$,[7] which was also first synthesized in our laboratory and whose asymmetric unit was verified to consist of five $GeO_4$ tetrahedra and one $GeO_5$ trigonal bipyramid by a

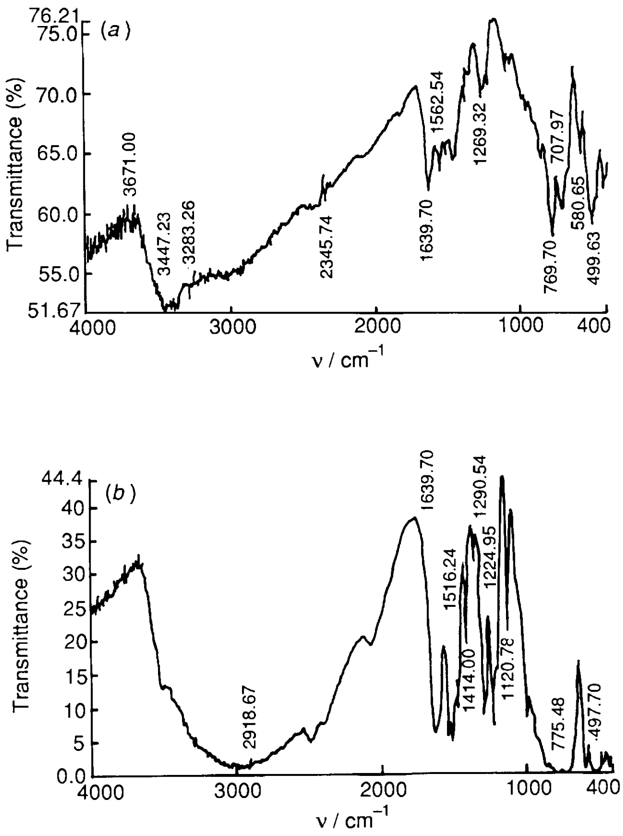

**Fig. 2** IR spectra of (*a*) EDA–$GeO_2$; (*b*) 1,3-PDA–$GeO_2$

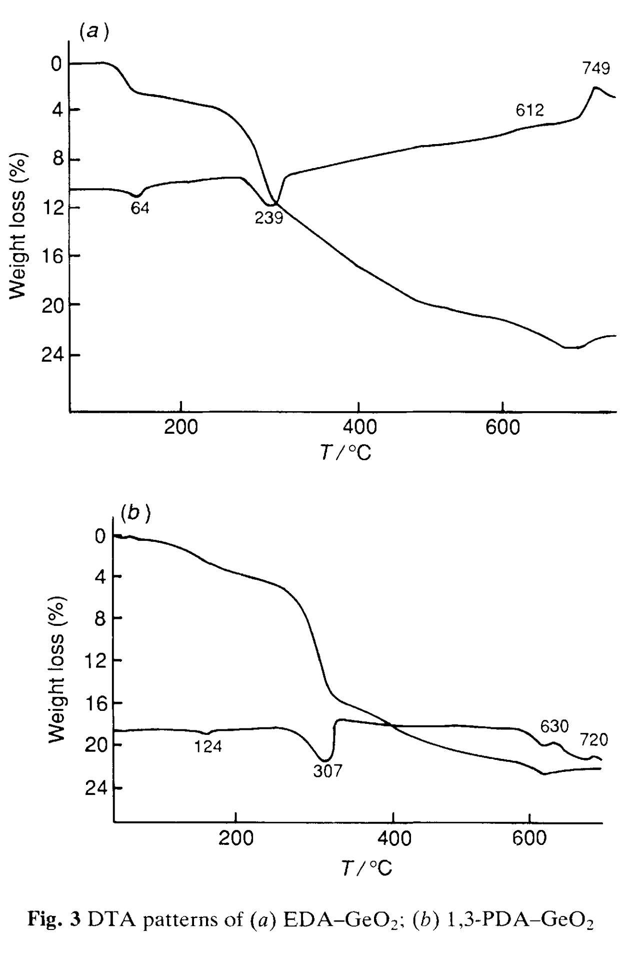

**Fig. 3** DTA patterns of (*a*) EDA–$GeO_2$; (*b*) 1,3-PDA–$GeO_2$

single crystal X-ray study (Table 1), we believe that the characteristic IR absorptions of EDA–$GeO_2$ and 1,3-PDA–$GeO_2$ at 769.70 and 775 $cm^{-1}$, respectively can be attributed to the Ge–O asymmetric stretch vibration of the $TO_n$ (T = Ge, n = 4–6) coordination polyhedron. The absorption for EDA–$GeO_2$ (1,3-PDA–$GeO_2$) is about 110 $cm^{-1}$ (104 $cm^{-1}$) lower than that of the dense phase hexagonal $GeO_2$ and about 68 $cm^{-1}$ (62 $cm^{-1}$) lower than that of $Ge_6O_{12}OHNMe_4$, which suggests that the Ge–O bond lengths of EDA–$GeO_2$ and 1,3-PDA–$GeO_2$ are longer than that of hexagonal $GeO_2$ and $Ge_6O_{12}OHNMe_4$ and that the framework is constructed by the $TO_n$ polyhedron whose coordination number $n$ may be higher than that of the hexagonal $GeO_2$ and that of $Ge_6O_{12}OHNMe_4$.

The differential thermal analysis (DTA) results of the two compounds are shown in Fig. 3. The DTA results of EDA–$GeO_2$ revealed a small endotherm at 64 °C, with a weight loss of 2.6%; at 239 °C, an endotherm was also observed with a total weight loss of 11.79% and from 239 to 749 °C, the total weight loss reached 24.6% which exceeded the theoretical EDA and water content of EDA–$GeO_2$. The DTA result of 1,3-PDA–$GeO_2$, at 124 °C, showed a very small endotherm with a weight loss of 2.2%; at 301 °C, an endotherm peak with total weight loss of 15.5% was observed and from 300 to 636 °C the total weight loss reached 21.4% which also exceeded the theoretical 1,3-PDA and water contents of 1,3-PDA–$GeO_2$. These phenomena can probably be explained in terms of the decomposition of EDA or 1,3-PDA accompanied by reduction of the $GeO_2$ framework to GeO or Ge by EDA, 1,3-PDA or products of their decomposition. At 749 °C, the DTA of EDA–$GeO_2$ showed an exotherm with an increased weight of 1.5%; at 720 °C the DTA of 1,3-PDA–$GeO_2$ also showed an exotherm, with an increased weight of 0.9%. These results may be explained by the air oxidation of GeO or Ge to $GeO_2$ or GeO, the Ge resulting from the disproportionation $GeO \rightarrow Ge + GeO_2$.[9] However, the DTA results of the two compounds require further studies.

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