LETTERS

A mesoporous germanium oxide with crystalline pore walls and its chiral derivative

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Microporous oxides are inorganic materials with wide applications in separations, ion exchange and catalysis[1–3]. In such materials, an important determinant of pore size is the number of M (where M = Si, Ge and so on) atoms in the rings delineating the channels[1]. The important faujasite structure exhibits 12-ring structures while those of zeolites[4,5], germanates[6–8] and other[9] materials can be much larger. Recent attention has focused on mesoporous materials with larger pores of nanometre scale[9–11]; however, with the exception of an inorganic–organic hybrid[11], these have amorphous pore walls, limiting many applications. Chiral porous oxides are particularly desirable for enantioselective sorption and catalysis[12]. However, they are very rare in microporous[14,15] and mesoporous[16] materials. Here we describe a mesoporous germanium oxide, SU-M, with gyroidal channels separated by crystalline walls that lie about the G (gyroid) minimal surface as in the mesoporous MCM-48 (ref. 9). It has the largest primitive cell and lowest framework density of any inorganic material and channels that are defined by 30-rings. One of the two gyroidal channel systems of SU-M can be filled with additional oxide, resulting in a mesoporous crystal (SU-MB) with chiral channels.

We first describe the framework structure of SU-M, which was prepared by standard hydrothermal methods without using surfactants, but with an organic amine as the structure-directing agent, similar to conventional zeolite synthesis (see Methods). SU-M is cubic and has a unit cell of $a = 51.3$ Å. Similar to MCM-48, SU-M has symmetry $Ia\bar{3}d$—the most complex cubic symmetry characterized by non-intersecting rotation axes, and glide rather than mirror planes—and structures with this symmetry are notoriously hard to illustrate[17]. The volume of the primitive cell is 67,640 Å^3; searches of the Cambridge Crystallographic (http://www.ccdc.cam.ac.uk) and Inorganic Crystal (http://icsdweb.fiz-karlsruhe.de) Structure Databases found only one inorganic material, a molybdenum oxide cluster compound[18], with a larger primitive cell.

SU-M is built from a unique $Ge_{16}O_{24}(OH)_3$ cluster (Fig. 1a) with O atoms singly coordinated to Ge corresponding to OH. The cluster consists of a central core of four octahedrally coordinated Ge atoms and six tetrahedrally coordinated Ge atoms. Each cluster is linked to five other clusters (Fig. 1b) via Ge–O–Ge bonds to form a three-dimensional framework with overall stoichiometry $Ge_{16}O_{20.5}(OH)_3$. There are 96 $Ge_{16}O_{24}(OH)_3$ clusters per unit cell that build crystalline walls about the G minimal surface, and that correspond to the amorphous walls in MCM-48[9]. A (111) slab of the structure shown in Fig. 1c demonstrates a complex system of linked $Ge_{16}O_{24}(OH)_3$ clusters forming big cavities (>20 Å, see Fig. 1c). The big cavities are at positions 16*b* (with coordinates 1/8, 1/8, 1/8 and their symmetry equivalents). Each cavity is connected to three other cavities through windows of 30 GeO_4/GeO_5 polyhedra (30-rings) (Fig. 1d) to form giant gyroidal channels. SU-M contains two such channels of opposite chirality (see Supplementary Video 1); the largest opening between the two channels is a 12-ring formed by six $Ge_{10}O_{24}(OH)_3$ clusters that are located around the positions 16*a* (the origin of the unit cell and its symmetry equivalents) (Fig. 1c).

The gyroidal channels can be described as three-coordinated nets with vertices at the centres of the big cavities and edges connecting the nearest cavities of the channels, as shown in Fig. 2a. Each channel forms such a three-coordinated net, well known as the net of the Si

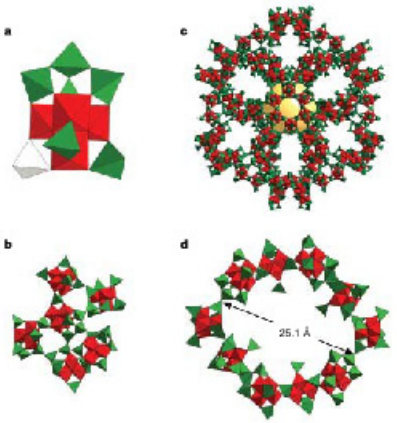

Figure 1 | Linkage of $Ge_{16}O_{24}(OH)_3$ clusters in SU-M. a, The $Ge_{16}O_{24}(OH)_3$ cluster built from six GeO_4 tetrahedra (green) and four GeO_6 octahedra (red). The white tetrahedron belongs to an adjacent cluster. **b**, A $Ge_{16}O_{24}(OH)_3$ cluster as in **a** linked to five neighbouring clusters. **c**, A 30-Å-wide slab with a big cavity at the centre. The yellow ball represents an oblate spheroid at the centre of the cavity that does not touch the centre of any framework atom. It has an equatorial diameter of 26.2 Å and a polar diameter of 18.6 Å and a volume equal to that of a sphere of diameter23.4 Å. **d**, A 30-ring window formed by ten $Ge_{16}O_{24}(OH)_3$ clusters. The free diameter of the 30-ring is 10.0 × 22.4 Å, assuming the van der Waals diameter of oxygen 2.7 Å. The big cavity at the centre in **c** is connected to three other big cavities (upper-left, upper-right and below) through the 30-ring windows.

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atoms in the $SrSi_2$ structure, with symbol **srs** (for a database of nets, see ref. 19). The repeat unit ('tile') of the **srs** net[20] is composed of three 10-rings (the red unit in Fig. 2b). This net is one of the five regular three-periodic nets[21]; it is the only chiral one (with space group $I4_132$). The **srs** net has the property that it can intergrow with its enantiomorph in such a way that all the 10-rings of one net are catenated with the 10-rings of the other. The combined structure has symmetry $Ia\bar{3}d$ (Fig. 2a). Now imagine the nets uniformly inflated as suggested in Fig. 2c, until they meet at a surface. This continuous periodic surface of negative curvature is known as the G (gyroid) minimal surface[21] and is the underlying structure of the walls of mesoporous materials SU-M and MCM-48 (ref. 9).

The crystalline wall of SU-M can be described as a 5-coordinated net with vertices at the centres of the $Ge_{16}O_{24}(OH)_3$ clusters. The net is a two-dimensional (2D) tiling of the G surface, with vertex symbol $3^2.4.3.6$, forming an infinite polyhedron[22], as shown in Fig. 2e. This net is known as **fcz**[19] and can be described also in terms of a 3D tiling of space[23] by tiles (Fig. 2f): a 'small' tile with face symbol[20] $[3^4.4^3.10^2]$ (Fig. 3a) and a 'big' tile with face symbol $[6^3.10^3]$ (Fig. 3b). The big tiles (16 per unit cell), with symmetry 32 (D_3) are centred at the vertices of the two interpenetrating **srs** nets, and correspond to

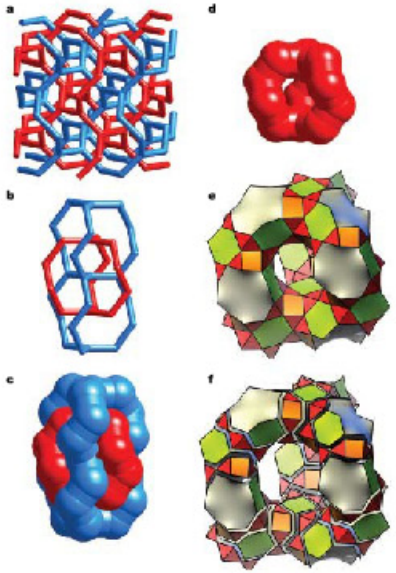

Figure 2 | Hierarchical description of the fcz net[19]. a, Two interpenetrating **srs**[20] nets—positions 16*b* of $Ia\bar{3}d$. **b**, A fragment of **a**. The red unit outlines a tile[19] for one of the nets. **c**, The same as **b** but inflated so the two parts meet at a common surface, the *G* surface. **d**, The inflated red unit alone. **e**, The net **fcz** as an infinite polyhedron forming a 2D tiling $3^2.4.3.6$ of the *G* surface. **f**, The same fragment of the structure shown as an exploded 3D tiling of space by big and small tiles. Notice that not all the tiles are shown—the full set of tiles completely fills space.

Table 1 | Comparison of the faujasite, SU-12 and SU-M structures

Structure	Net[20]	Cluster	Framework density (atoms nm^{-3})	Largest ring	Available V	Occupiable V
Faujasite[13]	fau	Si	13.45	12	0.544	0.295
SU-12[9]	fee	Ge_4	8.58	24	0.701	0.411
SU-M	fcz	Ge_{16}	7.10	30	0.746	0.508

'Cluster' is the number of metal atoms per vertex of the underlying net. Framework density and volumes (V) are reported as fractions of the total volume. 'Available V' is the volume not occupied by spheres with van der Waals radius centred on the framework atoms. 'Occupiable V' was calculated for a probe sphere of radius 1.5 Å exploring the framework as described by Connelly[24] and implemented in the Cerius-2 computer program.

the big cavities in SU-M (Fig. 1c and 3d). The small tiles are at the centres of the links and correspond to the 30-ring windows of SU-M (Fig. 1d and 3c). The structure of SU-M can be built by replacing the vertices of the **fcz** net with $Ge_{16}O_{24}(OH)_3$ clusters. This last step is an example of 'scale chemistry'[25], as illustrated in Fig. 4.

SU-MB is a chiral derivative of SU-M, prepared in the presence of hydrofluoric acid (see Methods below). In the structure of SU-MB, one half of the big tiles (big cavities) are filled with additional (Ge, O, F) clusters. These clusters, formulated as $Ge_7O_{16}F_3$, are familiar from other germanium oxide frameworks[25] including ASU-16 (ref. 6) and SU-12 (ref. 8). Six of these clusters (144 additional atoms, Fig. 5b) fit inside one big tile (big cavity), with three of them connected to each 12-ring window of the main framework through the terminal atoms of the $Ge_{16}O_{24}(OH)_3$ clusters (Fig. 5a). The occupied big tile and its contents (that is the unit shown in Fig. 5a) now has composition $Ge_{222}X_{51.6}$ (where X = O, OH or F). The most remarkable aspect of SU-MB is, however, the fact that only half of the cavities are filled (see Supplementary Video 1), specifically all those of one hand, and the symmetry is reduced to $I4_132$. The system of empty pores and channels is accordingly chiral and corresponds to one of the red or blue nets of Fig. 2a: that is, the topology of the chiral net **srs**[20]. We note that a chiral zeolite structure, UCSB-7, with a similar pore system has been reported[14]; however, in UCSB-7 the chirality is induced by ordering of the framework atoms, rather than by blocking

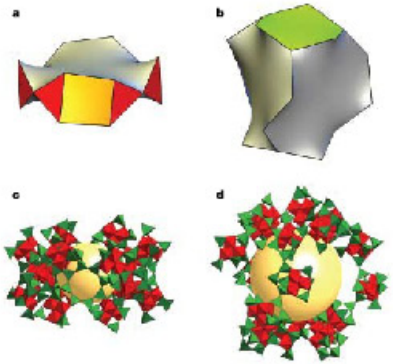

Figure 3 | The tiles of SU-M. a, A small tile of Fig. 2 and **c** the same tile in SU-M with each original vertex decorated with $Ge_{16}O_{24}(OH)_3$ clusters. The shortest ring around the perimeter in **c** involves 30 Ge atoms (see Fig. 1). **b**, A big tile of Fig. 2; **d**, the same tile in SU-M with the vertices similarly decorated. The yellow balls correspond to the largest sphere that fits inside each tile. The radius of the ball is 13.1 Å in **c** and 18.6 Å in **d**.

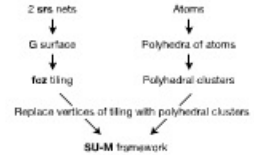

Figure 4 | The hierarchical nature of the structure of the SU-M framework.

one set of channels. We note also that the unit-cell volume of SU-MB ($a = 50.8$ Å) is over twenty times that of UCSB-7 ($a = 18.6$ Å), and the pores are much larger. As many as 336 (Ge, O, F) polyhedra can be incorporated into one of the gyroidal channels per unit cell. The chiral mesoporous silica[16] is also very different as it consists of rifled parallel channels arranged as in MCM-41. At this point we are unable to account for the formation of chiral material in SU-MB and note that it will be a significant challenge to produce enantiopure material, presumably using chiral templates in the synthesis.

The germanium oxide framework is charged, with a formal charge of -4 per $Ge_{16}O_{24}(OH)_3$ cluster in SU-M and an additional charge of -3 per $Ge_7O_{16}F_3$ cluster in SU-MB. The counter charge is provided by a protonated aliphatic diamine (2-methylpentamethylenediamine, MPMD), although in the crystal structures these amines and included water are incompletely resolved because of disorder. The chemical composition of SU-M is accordingly written $|(H_2MPMD)_2(H_2O)_n|[Ge_{16}O_{16.5}(OH)_3]$. For SU-MB the corresponding formulation is $|(H_2MPMD)_{3.5}(H_2O)_n|[(Ge_{16}O_{11}(OH)_2)_2 \cdot [Ge_7O_{14}F_3]]$.

Given the large scale of SU-M, it is interesting to compare it with other low-density materials. The faujasite framework[25] (Fig. 5) is often cited as the paradigm of a low-density zeolite framework. ASU-16 (ref. 6), specifically in its lower density conformation SU-12 (ref. 8), had the previous record for low framework density for an oxide material. Some properties related to density and porosity are listed for these three materials in Table 1. We note that in SU-M over 50% of the total volume is accessible to a probe sphere of radius 1.5 Å (appropriate for a molecule like water), in contrast to faujasite, in which less than 30% of the total volume is accessible.

Despite the presence of counterions and solvent, we have shown in preliminary experiments on as-synthesized SU-M that the material has permanent porosity, as shown by the observation of reversible type-I nitrogen adsorption isotherm, with a pore diameter of 12 Å deduced by non-local density functional theory[27] (see Supplementary Fig. 1). The BET (Brunauer–Emmett–Teller) surface area was 214 $m^2 g^{-1}$ (note that because of the larger atomic weight of Ge compared to Si this would correspond to 368 $m^2 g^{-1}$ for a silicate). One might also expect significant increase when post-synthetic treatment of the material is optimized. Energy dispersive spectroscopy showed that the MPMD cations in SU-M could be completely exchanged by Cs^+, K^+ and Na^+. The structure of the ion-exchanged SU-M was maintained, but with a slightly smaller unit cell, as shown by both single-crystal X-ray diffraction and X-ray powder diffraction. The crystallinity of SU-M was maintained when heated up to 320 °C in air, indicated by the *in situ* X-ray powder diffraction (see Supplementary Fig. 2). Thermogravimetric analysis of SU-M in N_2 showed three steps of weight loss (see Supplementary Fig. 3), corresponding to surface water (10%, 20–100 °C), crystal water (8%, 150–250 °C) and partial decomposition of the protonated MPMD (6%, 320–450 °C).

A mesoporous GeO_2 has recently been made by a surfactant templating method[28]; it has a thermal stability very similar to that of SU-M, but less than that of silica-based materials. However, we have previously shown[6] that replacement of tetrahedral Ge in Ge cluster oxides by Si can significantly enhance stability, and this is a strategy worth pursuing for SU-M as well. This mesoporous material has a hexagonal array of parallel channels of the MCM-41 type but is otherwise amorphous. In contrast, the preparation of SU-M (see Methods) involves no surfactant. We believe it is significant that we have also found (work to be published elsewhere) that an ordered crystalline germanium oxide of the MCM-41 type constructed from clusters very similar to those in SU-M can also be made by a surfactant-free process. These observations open up the possibility that there may be more general routes to ordered mesoporous materials, including ones with chiral channel systems, of which the ones reported here are just the first.

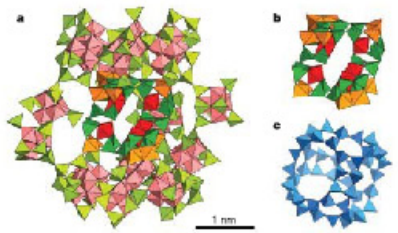

Figure 5 | Cavities in SU-MB and faujasite. **a**, The filled big tile in SU-MB. **b**, The six $Ge_7O_{16}F_3$ clusters in the interior of **a**; orange polyhedra are trigonal bipyramids. **c**, A faujasite supercage on the same scale. Note the 1-nm scale marker.

METHODS

Synthesis. Both SU-M and SU-MB were synthesized under hydrothermal conditions from a homogenous solution of germanium dioxide, MPMD and water with the molar ratios of 1:8–10:38–40. In addition, hydrofluoric acid with a molar ratio of GeO_2:HF = 1:1.5 was added for the synthesis of SU-MB. The solutions were heated at 165 °C in Teflon-lined Parr autoclaves under autogenous pressure and the synthesis time was seven days for SU-M and 11 days for SU-MB. Octahedral crystals, with sizes of $160 \times 160 \times 160\ \mu m^3$ for SU-M and $80 \times 80 \times 80\ \mu m^3$ for SU-MB, were obtained (see Supplementary Fig. 4).

Crystallographic studies. X-ray diffraction data were collected at 170 K on a STOE IPDS diffractometer equipped with an image plate and graphite-monochromatized MoKα radiation (λ = 0.71073 Å) from a rotating anode. The structures were solved by direct methods and refined by full-matrix least-squares techniques against F^2.

For SU-M, 134,976 reflections, of which 8,922 were unique, were collected in the region $4.34° < 2\theta < 48.18°$. The space group is $Ia\bar{3}d$ and the unit-cell dimensions are $a = 51.335(3)$ Å, $Z = 96$, $V = 135,282(14)$ Å^3. All framework atoms, all nitrogen and more than half of the carbon from MPMD cations were located. Several water oxygen atoms were also located. All non-hydrogen framework atoms were refined anisotropically. $R_1 = 0.0744$ for 6,519 reflections with $I > 2\sigma(I)$ and 0.1057 for all 8,922 reflections; $wR_2 = 0.2362$ and S (the goodness of fit on F^2) = 1.013. Crystal data and details of structure determination are given in Supplementary Table 1. Atomic coordinates and equivalent isotropic displacement parameters are given in Supplementary Table 2.

For SU-MB, 34,928 reflections, of which 11,888 were unique, were collected in the region $7.94° < 2\theta < 42.98°$. The space group is $I4_132$ and the unit-cell dimensions are $a = 50.873(3)$ Å, $Z = 48$, $V = 131662(13)$ Å^3. Owing to the relatively small crystal size, more than half of the reflections have intensities less than $2\sigma(I)$. The structure was solved by direct methods. All framework atoms and some of the nitrogen and carbon from MPMD cations were located. Several water oxygen atoms were also located. Only the germanium atoms were refined anisotropically. $R_1 = 0.0838$ for 6,403 reflections with $I > 2\sigma(I)$ and 0.1678 for all 11,888 reflections; $wR_2 = 0.2309$ and $S = 0.966$. Crystal data and details of structure determination are given in Supplementary Table 3. Atomic coordinates and equivalent isotropic displacement parameters are given in Supplementary Table 4.

***In situ* X-ray powder diffraction.** *In situ* X-ray powder diffraction was performed on a Huber Guinier camera 670 equipped with an imaging plate, using synchrotron radiation at Beamline 711, Max-lab, Lund University, Sweden. The as-synthesized SU-M was heated in air from 20 to 340 °C with an average heating rate of 7 °C min^{-1}. X-ray powder diffraction data were collected at every 50 °C up to 200 °C and every 20 °C from 200 to 340 °C.

Ion exchange. The ion exchange was performed in solutions of CsCl (1 M), KCl (1 M) and NaCl (1 M) at 20 °C for 20 h. The ion-exchanged crystals were first washed with water, then ethanol, and finally dried at 80 °C for 2 h.

Adsorption study. Nitrogen adsorption and desorption isotherm of as synthesized SU-M was measured at 77 K on a Micromeritics ASAP 2020 system. The sample was degassed first at 297 K for 5 h and then at 357 K for 5 h.

Received 26 April; accepted 28 July 2005.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

Acknowledgements We thank S. Lidin for help and discussions, A. Chizmeshya for the volume data reported in Table 1, K. E. Christensen for checking ion-exchanged samples and A. Garcia-Bennett for the N_2 isotherm. L. Q. Tang and E. Karlsson participated in the synthesis. The project is supported by the Swedish Science Research Council, M.O'K. acknowledges support from the US National Science Foundation. X.D.Z. is a Research Fellow of the Royal Swedish Academy of Sciences, supported by a grant from the Alice and Knut Wallenberg Foundation.

Author Information The additional crystallographic data for SU-M (CCDC-278829) and SU-MB (CCDC-278830) can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Reprints and permissions information is available at npg.nature.com/reprintsandpermissions. The authors declare no competing financial interests. Correspondence and requests for materials should be addressed to X.D.Z. (zou@struc.su.se).