MWW

MWW.1 Zeolite framework type and topology

The designation of the FTC refers to the type material **M**CM-t**W**enty-t**W**o (MCM-22, Mobil Composition of Matter with sequence number twenty-two), first synthesized by [90Rub1]. The crystal structure was solved by [94Leo1] in space group $P\,6/mmm$. The authors state that the real symmetry might be lower to avoid T-O-T angles of 180°. However, attempts to refine the structure in $Cmmm$ failed. Molecular-mechanics calculations [97Njo1] indicated a $P\,6/m$ symmetry for the MCM-22 topology which does contain straight T-O-T angles. Straight angles Si-O-Si of 180° have been repeatedly observed in crystal structures of experimentally well determined silicates and silicon dioxide polymorphs [80Bau1].

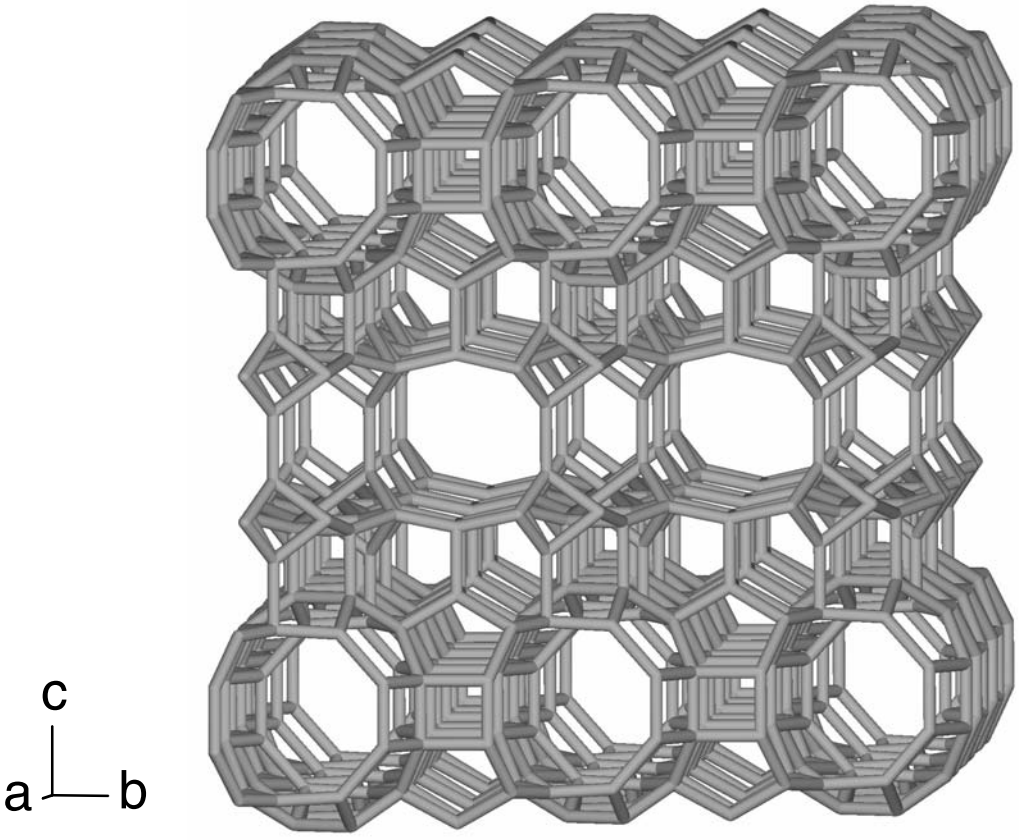


Fig. MWW.1.1. The framework structure of MWW-type compounds in the highest possible topological symmetry $P\,6/mmm$ (MWW1998a01, 98Cam1). View parallel [100] rotated by 2° about [120] and [001].

The framework structure (Figs. MWW.1.1 and MWW.1.2) consists of pillars in 0, 0, *z* formed by an alternating sequence of *bb34* ($5^{12}6^{12}6^{2}10^{6}$) and *hpr* ($4^{6}6^{2}$) units (Fig. MWW.1.5) crosslinked by *bb35* ($4^{2}5^{4}5^{4}10^{2}$), *mel* ($4^{1}5^{2}6^{2}$), and *kzd* (4^{3}) units as shown in Figs. MWW.1.3 to MWW.1.6. The 10-ring channels parallel **a** (and **b**) are formed by *bb34* units in *x*, 0, 0 (Fig. MWW.1.7) and by *bb35* units in *x*, ½, ½ (Fig. MWW.1.8).

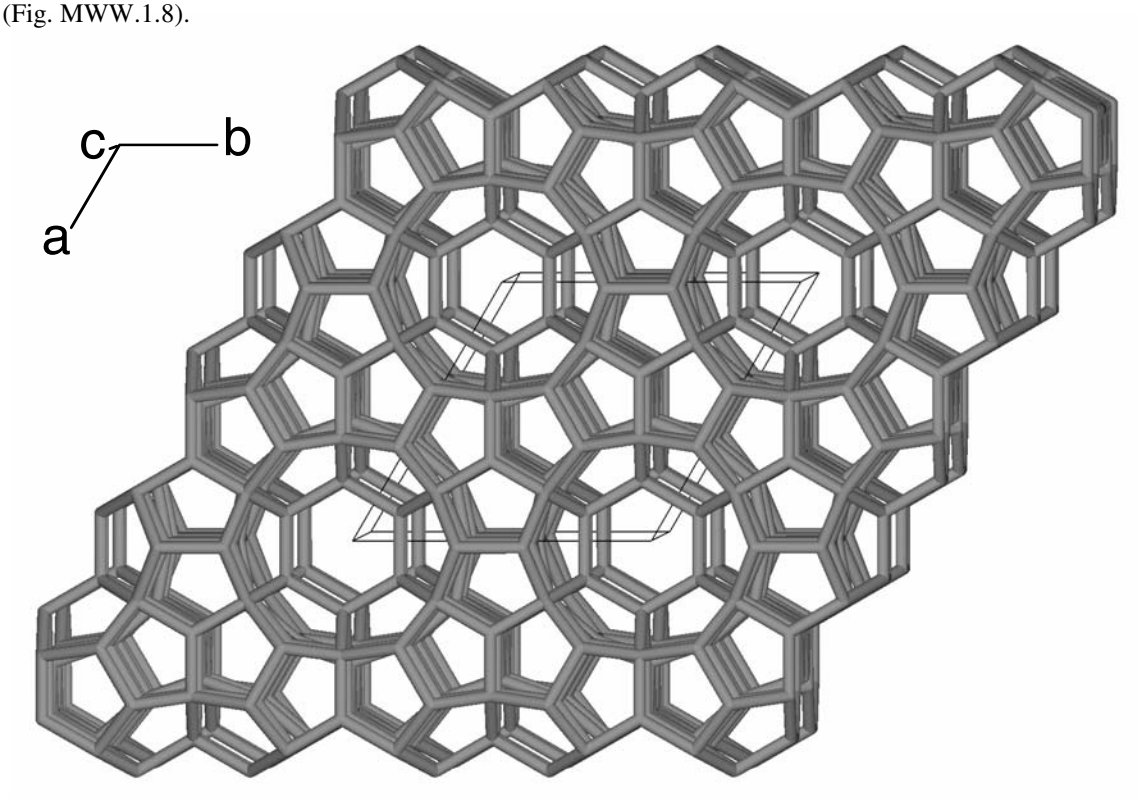
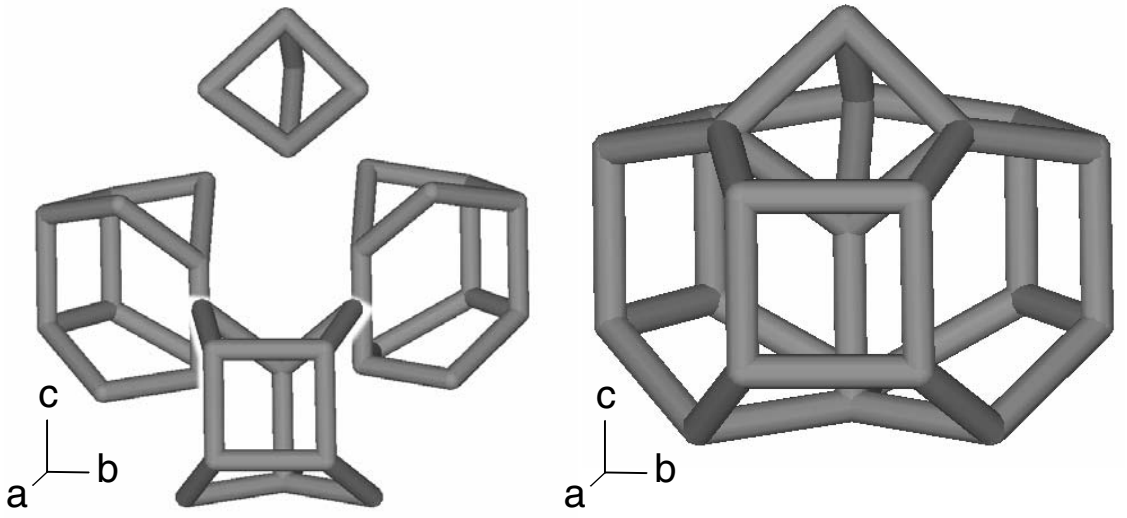


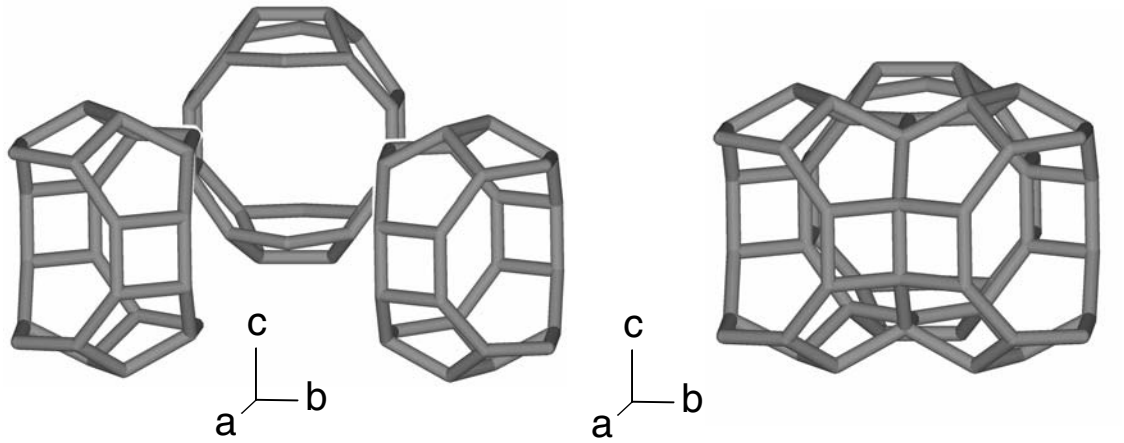
Fig. MWW.1.2. The framework structure shown in Fig. MWW.1.1 projected parallel [001] rotated by 1° about [010] and 2° about [210].



a Linkage of *mel* and *kzd* units.

b The whole assemblage shown in a). The outer faces correspond to the *doo* ($4^{3}5^{6}6^{3}$) unit.

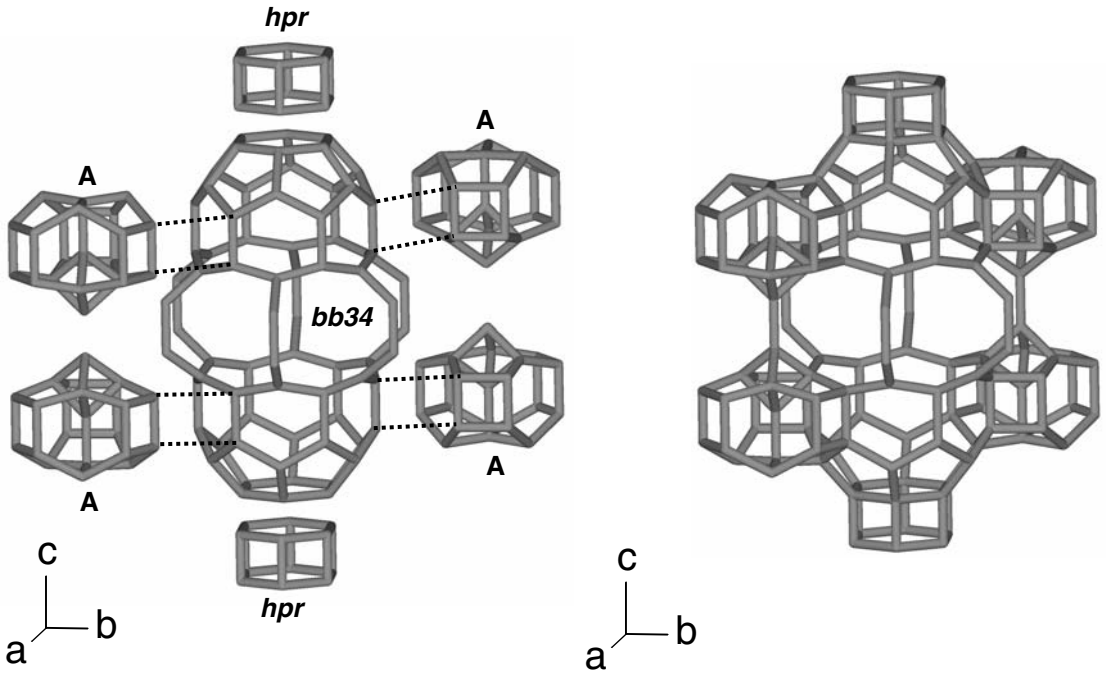
Fig. MWW.1.3. Composite unit A formed by three *mel* units and one *kzd* unit. View parallel [210] rotated by 10° about [010] and 5° about [001].



a Linkage of *bb35* units.

b The whole assemblage shown in a).

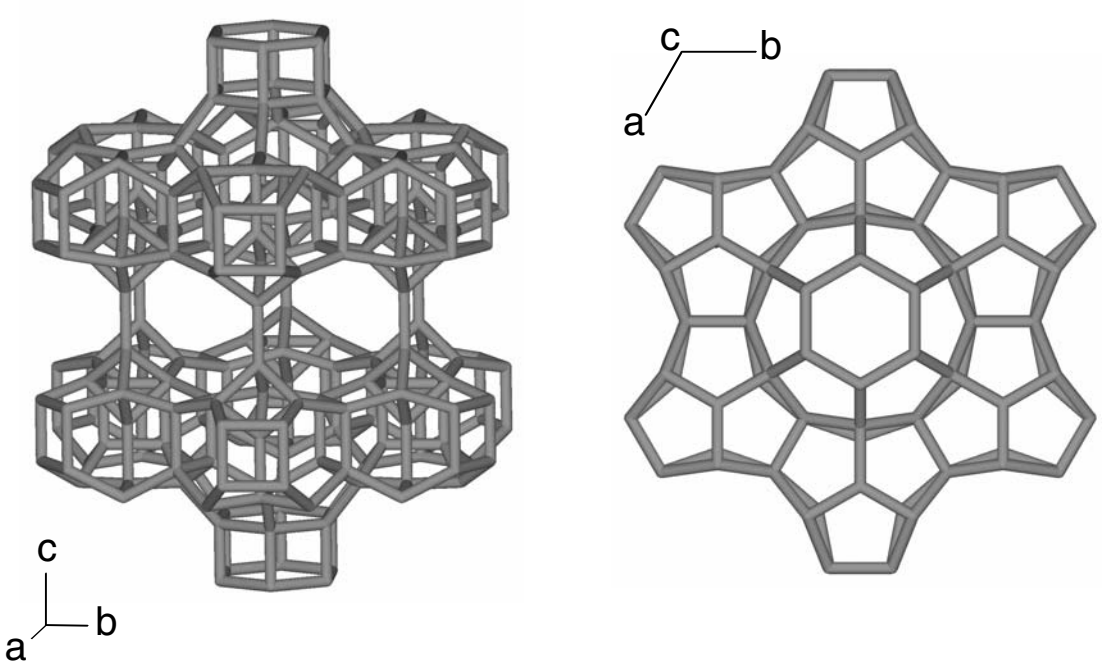
Fig. MWW.1.4 Composite unit B formed by three *bb35* units. View parallel [210] rotated by 10° about [010] and 5° about [001].



a Linkage of *bb34* unit with *hpr* unit and composite A units (Fig. MWW.1.2). View parallel [210] rotated by 10° about [010] and 5° about [001].

b The whole assemblage shown in a).

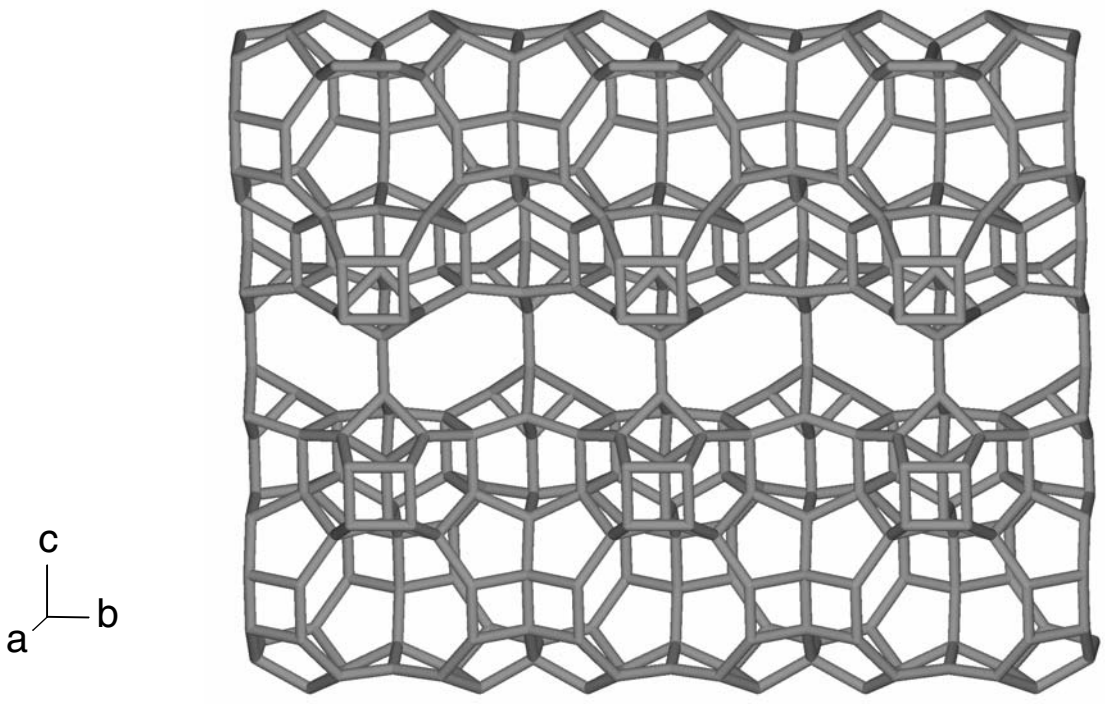
Fig. MWW.1.5. Linkage of units around the *bb34* unit.



c The assemblage shown in b) with all composite A units around the 6-fold axis.

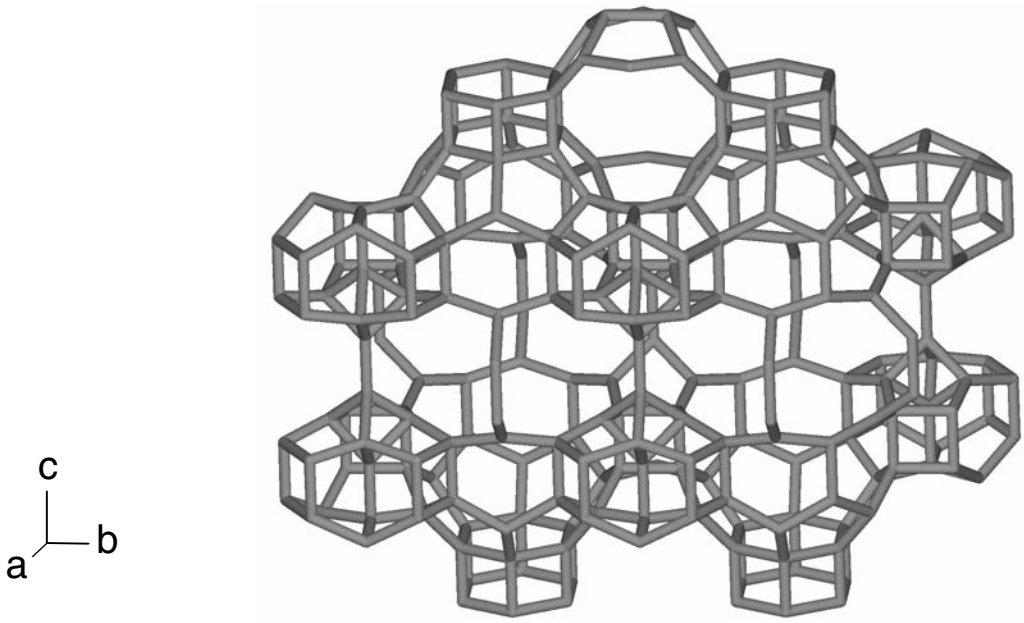
d Top view of the assemblage shown in c) parallel [001].

Fig. MWW.1.5 (continued) Linkage of units around the *bb34* unit.

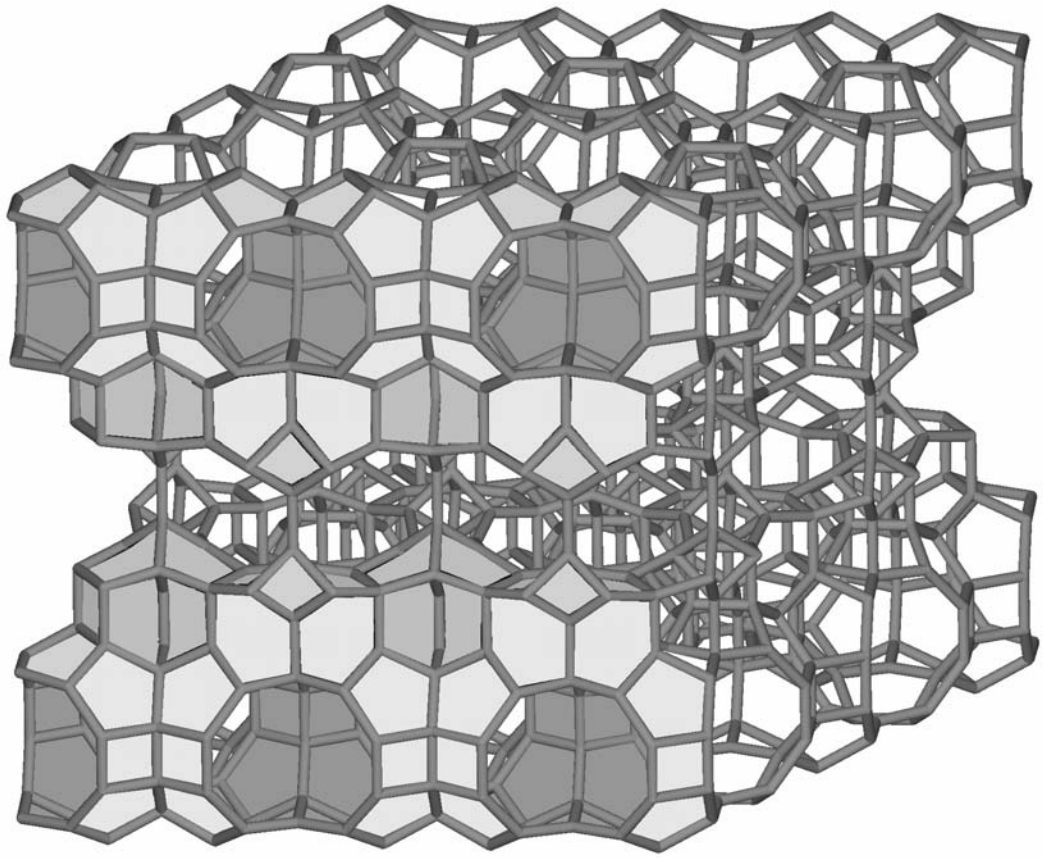


a Linkage in the (100) plane at x = -½.

Fig. MWW.1.6 The framework structure viewed parallel [210] rotated by 20° about [010] and 5° about [001].



b Linkage in the (100) plane at $x = 0$.



c The complete framework structure. The 4-, 5-, and 6-rings of the front units are shown nontransparently.

Fig. MWW.1.6 (continued) The framework structure viewed parallel [210] rotated by 20° about [010] and 5° about [001].

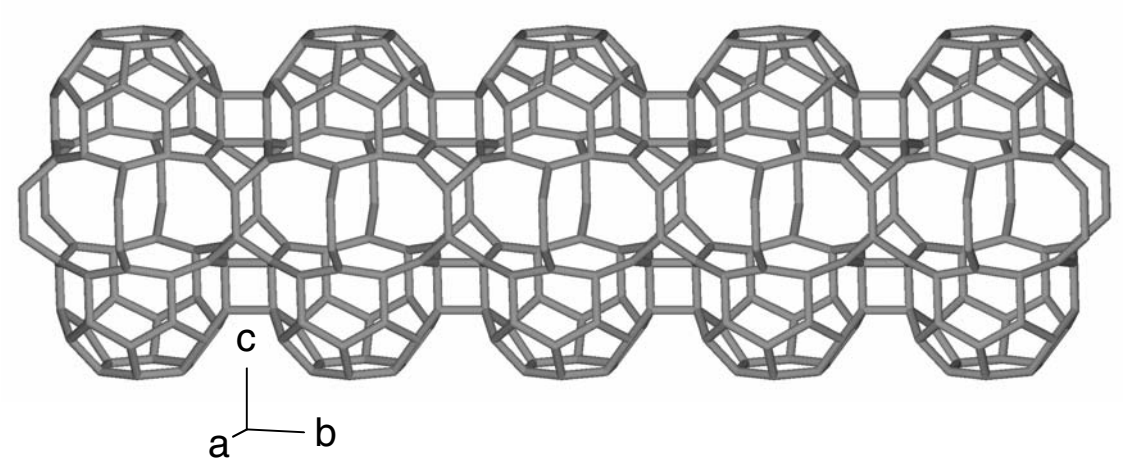


Fig. MWW.1.7 The 10-ring channel formed by *bb34* units in *x*, 0, 0 (here 0, *y*, 0). View parallel [210] rotated by 10° about [010] and [001].

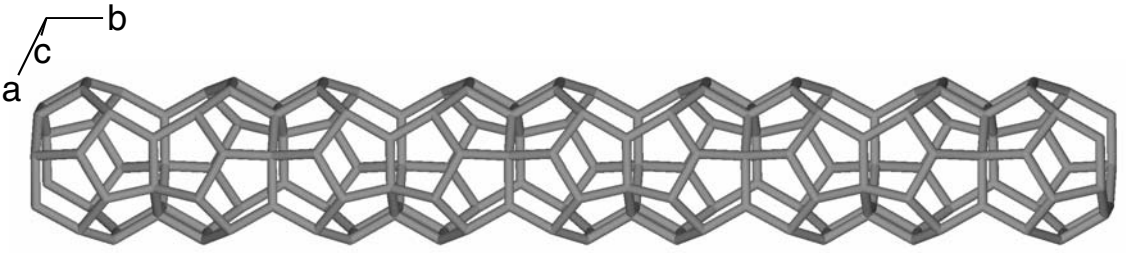


Fig. MWW.1.8 The 10-ring channel formed by *bb35* units in *x*, ½, ½ (here ½, *y*, ½). View parallel [001] rotated by 10° about [010] and 5° about [210].

MWW.2 Compounds and crystal data

Table MWW.2.1 Chemical data.

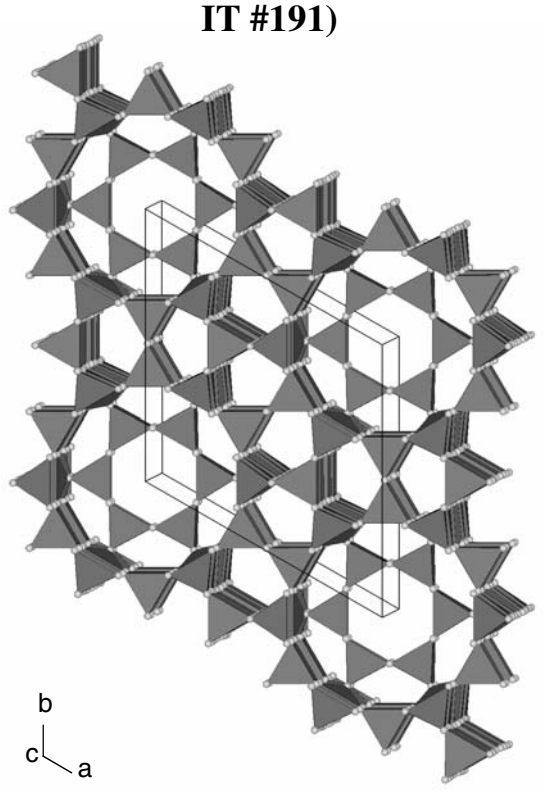
FD = framework density CE = cation exchange TT = thermal treatment REF = reference
SM = source of material SR = sorbate T = temperature of thermal treatment [K]

Code	chemical composition	compound	FD	SM	CE	SR	TT	T	REF
MWW-I ***P 6/m m m***									
MWW1994a01	$H_{2.4}Na_{3.1} \cdot Al_{0.36}B_{5.11}Si_{66.53}O_{144} \cdot 23H_2O$	MCM-22	16.8	S	-	H_2O	C	813	94Leo1
MWW1998a01	$Si_{72}O_{144}$	ITQ-1	16.5	S	-	-	C	853	98Cam1

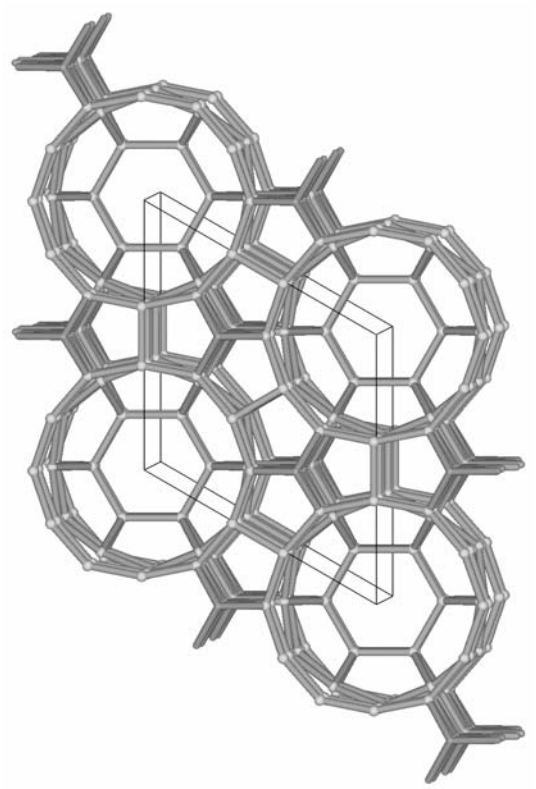
Table MWW.2.2 Structural parameters of MWW-type compounds.

code	*a* [Å]	*c* [Å]	*V* [Å^3]	*T* [K]	reference
MWW-I ***P 6/m m m***					
MWW1994a01	14.1145(8)	24.882(2)	4293	n.s.	94Leo1
MWW1998a01	14.2081(1)	24.945(2)	4361	n.s.	98Cam1

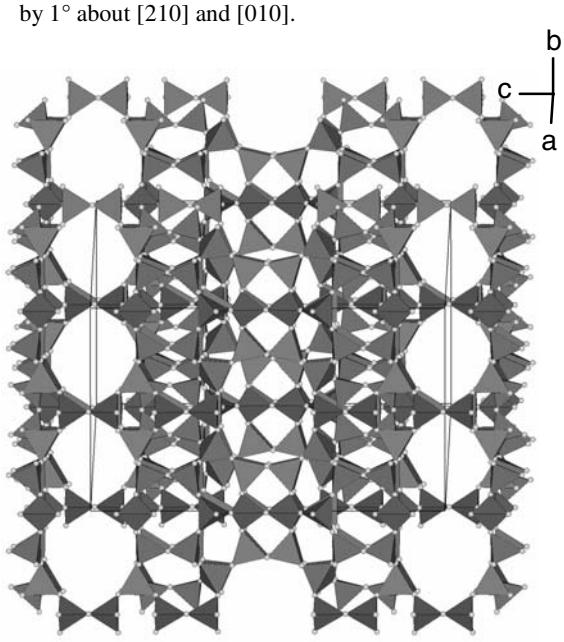
MWW.3 Framework structure of MWW-I compound (*P* 6/*m m m*, IT #191)



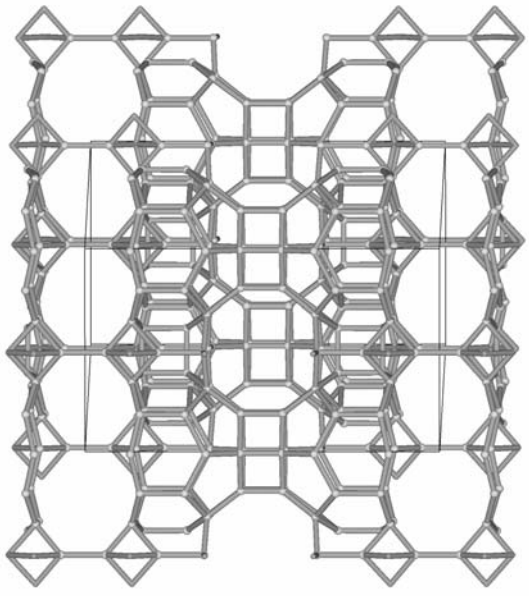
a Polyhedral representation. View parallel [001] rotated by 1° about [210] and [010].



b Ball and stick model corresponding to a).



c Polyhedral representation. View parallel [210] rotated by 2° about [010] and [001].



d Ball and stick model corresponding to a).

Fig. MWW.3.1 Projections of the MWW-I crystal structure of MCM-22, $Si_{72}O_{144}$ (MWW1998a01, 98Cam1).

Table MWW.3.1 Atomic coordinates and site definitions for MWW-I, MCM-22, $Si_{72}O_{144}$ (MWW1998a01, 98Cam1).

atom	*x*	*y*	*z*	B_{eq} [Å^2]	site symmetry	Wyckoff position	no. of atoms in unit cell
Si1	0.2342(2)	2*x*	0.1356(3)	1.11(8)	. *m* .	12(o)	12
Si2	0.2107(2)	2*x*	0.3470(2)	1.11(8)	. *m* .	12(o)	12
Si3	0.1272(2)	2*x*	0.4407(2)	1.11(8)	. *m* .	12(o)	12
Si4	0.3904(4)	0	0.1607(3)	1.11(8)	. . *m*	12(n)	12
Si5	0.3895(4)	0	0.2872(3)	1.11(8)	. . *m*	12(n)	12
Si6	1/3	2/3	0.0633(3)	1.11(8)	3 *m* .	4(h)	4
Si7	1/3	2/3	0.2108(4)	1.11(8)	3 *m* .	4(h)	4
Si8	1/3	2/3	0.3404(4)	1.11(8)	3 *m* .	4(h)	4
O1	0.3942(5)	0.1048(4)	0.1348(3)	1.5(2)	1	24(r)	24
O2	0.3945(6)	0.1063(5)	0.3116(3)	1.5(2)	1	24(r)	24
O3	0.2735(3)	2*x*	0.3638(4)	1.5(2)	. *m* .	12(o)	12
O4	0.1768(4)	2*x*	0.4014(4)	1.5(2)	. *m* .	12(o)	12
O5	0.2706(3)	2*x*	0.0822(4)	1.5(2)	. *m* .	12(o)	12
O6	0.2726(3)	2*x*	0.1882(4)	1.5(2)	. *m* .	12(o)	12
O7	0.3763(9)	0	0.2239(3)	1.5(2)	. . *m*	12(n)	12
O8	0.1835(6)	0	0.4300(5)	1.5(2)	. . *m*	12(n)	12
O9	0.1508(7)	2*x*	1/2	1.5(2)	*mm*2	6(m)	6
O10	1/2	0	0.1449(7)	1.5(2)	2*mm*	6(i)	6
O11	1/2	0	0.3021(7)	1.5(2)	2*mm*	6(i)	6
O12	1/3	2/3	0.2755(4)	1.5(2)	3 *m* .	4(h)	4
O13	1/3	2/3	0	1.5(2)	$\bar{6}$ *m* 2	2(c)	2

Table MWW.3.1 Selected interatomic distances and angles for MWW-I, MCM-22, $Si_{72}O_{144}$ (MWW1998a01, 98Cam1).

	T - O [Å]	T - O - T [°]		T - O [Å]	T - O - T [°]
Si1 - O1	1.599(9)	139.6(5)	Si2 - O4	1.594(11)	160.4(8)
Si1 - O1	1.599(9)	139.6(5)	Si2 - O3	1.599(9)	143.2(7)
Si1 - O5	1.604(11)	140.8(7)	Si2 - O2	1.600(9)	164.7(5)
Si1 - O6	1.617(11)	146.4(7)	Si2 - O2	1.600(9)	164.7(5)
mean	1.605	141.6	mean	1.598	158.3
Si3 - O4	1.566(11)	160.4(8)	Si4 - O7	1.589(11)	166.0(8)
Si3 - O9	1.590(8)	137.1(12)	Si4 - O1	1.599(8)	139.6(5)
Si3 - O8	1.591(6)	159.3(9)	Si4 - O1	1.599(8)	139.6(5)
Si3 - O8	1.591(6)	159.3(9)	Si4 - O10	1.606(6)	151.6(13)
mean	1.584	154.0	mean	1.598	149.2
Si5 - O7	1.590(11)	166.0(8)	Si6 - O13	1.579(7)	180.0(4)
Si5 - O2	1.597(9)	164.7(5)	Si6 - O5	1.616(8)	140.8(7)
Si5 - O2	1.597(9)	164.7(5)	Si6 - O5	1.616(8)	140.8(7)
Si5 - O11	1.613(6)	153.4(13)	Si6 - O5	1.616(8)	140.8(7)
Mean	1.599	162.2	Mean	1.606	150.6

Table MWW.3.1 (continued)

	T - O [Å]	T - O - T [°]		T - O [Å]	T - O - T [°]
Si7 - O6	1.566(11)	146.4(7)	Si8 - O3	1.585(9)	143.2(7)
Si7 - O6	1.590(8)	146.4(7)	Si8 - O3	1.585(9)	143.2(7)
Si7 - O6	1.591(6)	146.4(7)	Si8 - O3	1.585(9)	143.2(7)
Si7 - O12	1.591(6)	180.0(9)	Si8 - O12	1.619(14)	180.0(4)
mean	1.601	154.8	mean	1.594	152.4

MWW.4 Chemical composition

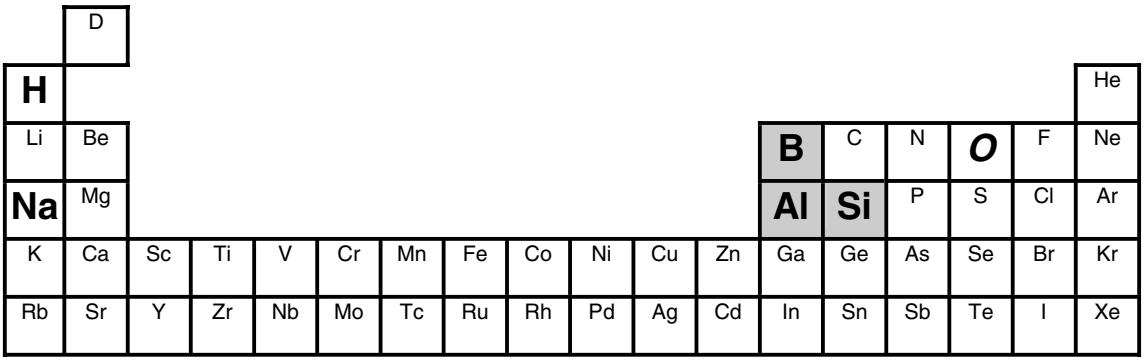


Fig. MWW.4.1 Chemical elements (highlighted) occurring in MWW-type compounds. Framework cations are in grey fields.

MWW.5 Flexibility and apertures

There is insufficient information to judge the flexibility of the MWW-type framework.

The 10-ring openings in the framework of MWW have free diameters ranging from about 4.0 Å to about 5.5 Å. This means that they are rather compressed and buckled compared with the openings in the MFI-type framework, which measure between 5.0 Å and 5.5 Å.

MWW.6 Other information

MWW-type catalysts have been commercially applied to the production of ethylbenzene [97Maz1], as quoted in [2001Zon1]. The interest in MWW-type compounds is great. At the 2005 conference of the Federation of European Zeoliyte Associations in Prague numerous papers dealt with MCM-22 (Studies in Surface Science and Catalysis, vol. 158). For recent reports on the catalytic activity of MWW-type compounds see [2000Cor1, 2004Hua1]. In addition to MCM-22 and ITQ-1 the compounds called ITQ-2 [2000Cor1] and SSZ-25 [2001Zon1] are related to MWW.

MWW.7 References

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