MTW

MTW.1 Zeolite framework type and topology

The designation of the FTC refers to the type material ZS**M**-**TW**elve (ZSM-12, Zeolite Socony Mobil with sequence number twelve), first synthesized by [74Ros1]. The crystal structure was solved by [85LaP1] in space group $C2/m$ by DLS model building. Subsequent refinements (see Tables MTW.2.1 and MTW.2.2) showed that ZSM-12 crystallizes in the lower symmetry $C2/c$ with doubled c lattice constant. The framework structure (Fig. MTW.1.1) consists of *bb46* ($5^4 6^4 12^2$) units (extended *bb19* ($6^4 6^2 12^2$) units) forming the 12-ring channels (**zzi** units, Fig. MTW.1.3) parallel [010], crosslinked by *eun* ($5^4 6^2$), *lai* (6^6) and *lau* ($4^2 6^4$) units as shown in Fig. MTT.1.2.

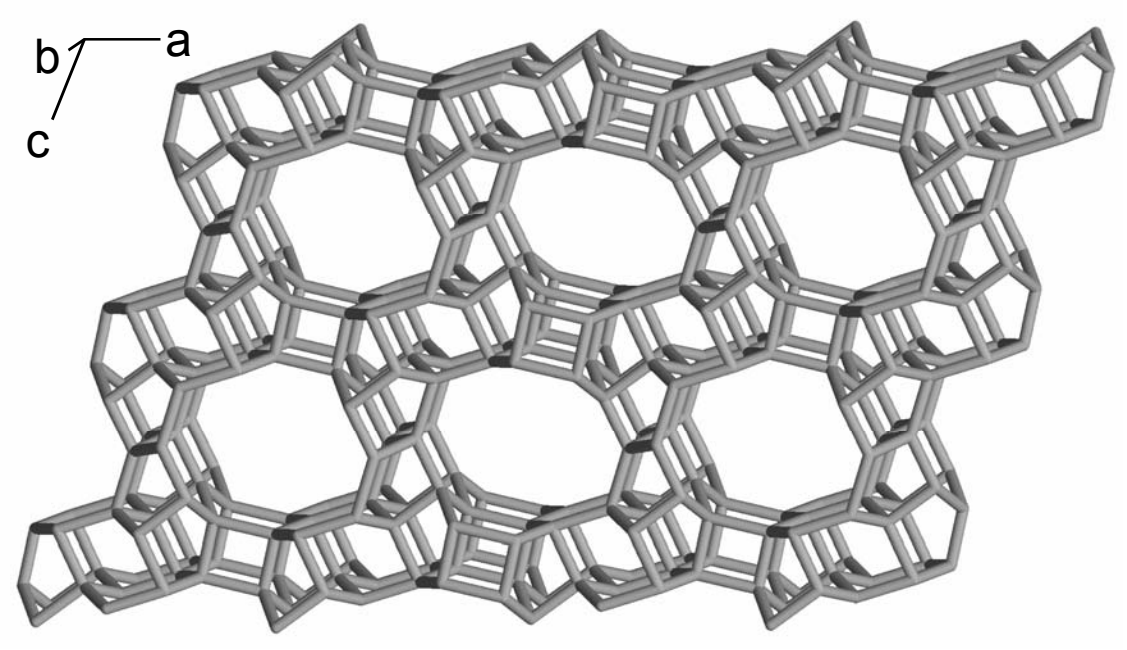
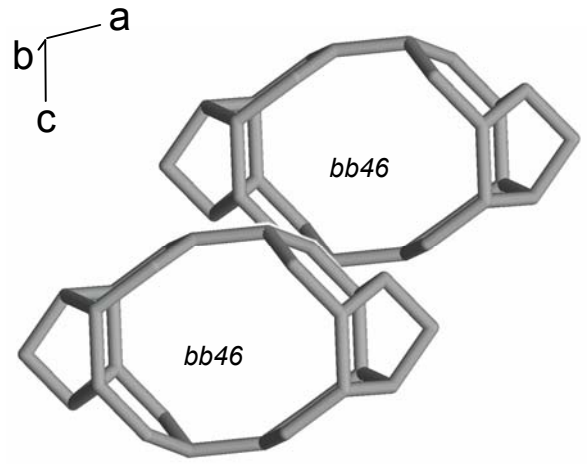
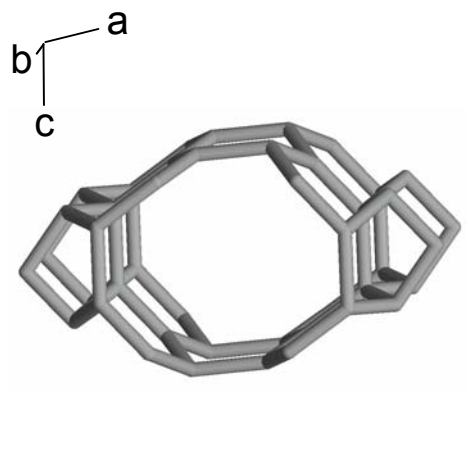


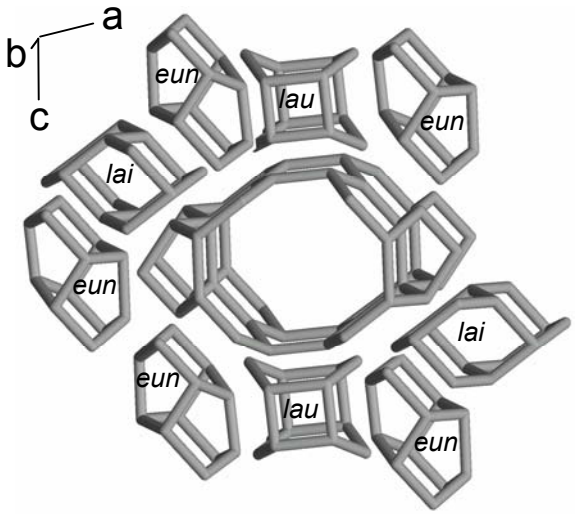
Fig. MTW.1.1. The framework structure of MTW-type compounds in the highest possible topological symmetry $C2/m$. View parallel **b** rotated by 8° about **a** and **a**×**b**.



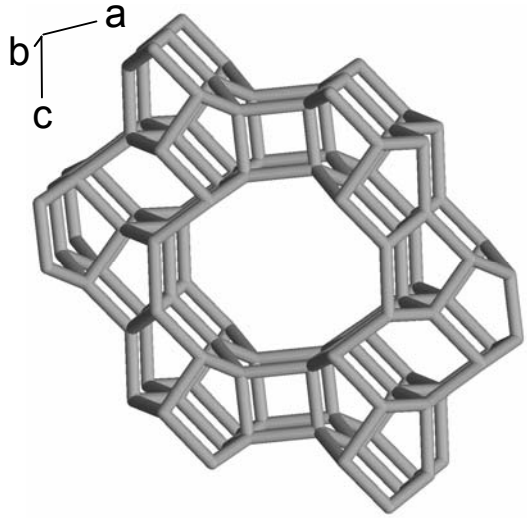
a The *bb46* units forming the **zzi** channel.



b The complete assemblage shown in a).



c Linkage of units around the *bb46* unit.



d The assemblage shown in **c**.

Fig. MTW.1.2 Building scheme of MTW-type structures. View parallel **b** rotated by 8° about **c** and **b**×**c**.

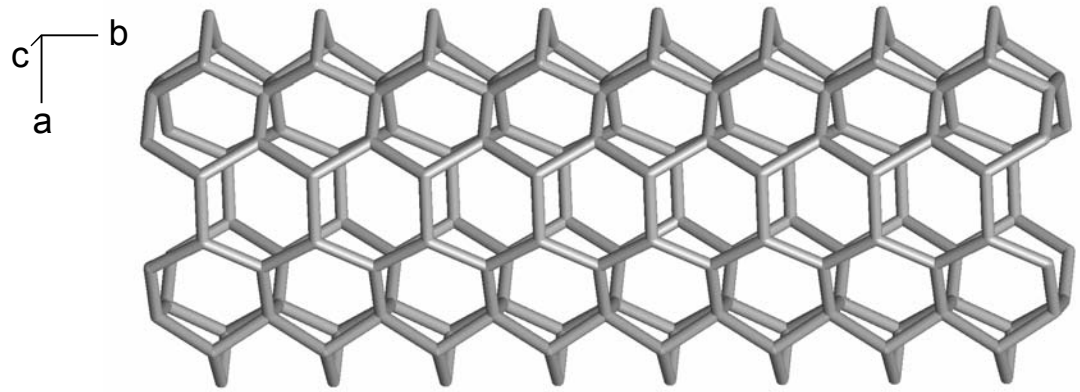


Fig. MTT.1.3 The 12-ring channel (**zzi** unit) parallel **b**. View parallel **c** rotated by 8° about **b** and **b**×**c**.

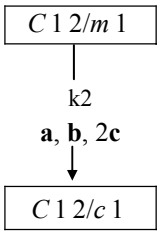


Fig. MTW.1.1. The Bärnighausen tree illustrating the symmetry relationship of the MTW types.

Table MTW.1.1 Atomic site relationships of the MTW types.

MTW-I *C* 1 2/*m* 1	MTW-II *C* 1 2/*c* 1	MTW-I *C* 1 2/*m* 1	MTW-II *C* 1 2/*c* 1
T1 [4(i), *m*]	T1 [8(f), 1]	O3 [8(j), 1]	O31 [8(f), 1] O32 [8(f), 1]
T2 [4(i), *m*]	T2 [8(f), 1]	O4 [4(i), *m*]	O4 [8(f), 1]
T3 [4(i), *m*]	T3 [8(f), 1]	O5 [4(i), *m*]	O5 [8(f), 1]
T4 [4(i), *m*]	T4 [8(f), 1]	O6 [4(i), *m*]	O6 [8(f), 1]
T5 [4(i), *m*]	T5 [8(f), 1]	O7 [4(i), *m*]	O7 [8(f), 1]
T6 [4(i), *m*]	T6 [8(f), 1]	O8 [4(i), *m*]	O8 [8(f), 1]
T7 [4(i), *m*]	T7 [8(f), 1]	O9 [4(i), *m*]	O9 [8(f), 1]
O1 [8(j), 1]	O1_1 [8(f), 1] O1_2 [8(f), 1]	O10 [4(i), *m*]	O10 [8(f), 1]
O2 [8(j), 1]	O21 [8(f), 1] O22 [8(f), 1]	O11 [4(f), $\bar{1}$]	O11 [8(f), 1]

MTW.2 Compounds and crystal data

Table MTW.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]

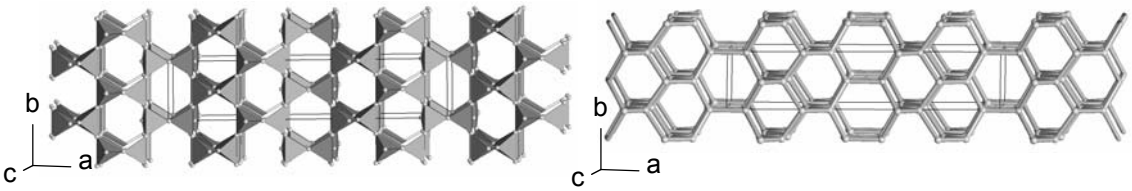
code	chemical composition	FD	SM	CE	SR	TT	T	REF
MTW-I *C* 1 2/*m* 1								
MTW1985a01	$Al_{0.1}Si_{27.9}O_{56}$	19.4	S	-	-	C	n.s.	85LaP1
MTW-II *C* 1 2/*c* 1								
MTW1990a01	$Si_{56}O_{112}$	19.4	S	-	-	C	n.s.	90Fyf1
MTW1997a01	$Al_{1.2}Si_{54.8}O_{112}$	19.3	S	-	-	C	873	97Hit1
MTW1999a01	$Si_{56}O_{112} \cdot 2C_6H_6N_2O_2$	19.4	S	-	nitroaniline	C	973	99Kin1
MTW1999b01	$Si_{56}O_{112} \cdot 1.97H_2O$	19.4	S	-	H_2O	C	973	99Der1
MTW1999b02	$Si_{56}O_{112} \cdot 1.4C_6H_{14}$	19.4	S	-	hexane	C	973	99Der1
MTW1999b03	$Si_{56}O_{112} \cdot 2.4C_6H_{14}$	19.3	S	-	hexane	C	973	99Der1
MTW1999b04	$Si_{56}O_{112} \cdot 2.6C_6H_{14}$	19.3	S	-	hexane	C	973	99Der1
MTW1999b05	$Si_{56}O_{112} \cdot 4.3C_6H_6$	19.3	S	-	hexane	C	973	99Der1
MTW2002a01	$Si_{56}O_{112} \cdot 2C_6H_6N_2O_2$	19.4	S	-	nitroaniline	C	973	2002Kin1

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

code	*a* [Å]	*b* [Å]	*c* [Å]	ß [°]	*V* [Å^3]	*T* [K]	reference
MTW-I *C* 1 2/*m* 1							
MTW1985a01	24.88(4)	5.02(2)	12.15(3)	107.7(1)	1446	n.s.	85LaP1
MTW-II *C* 1 2/*c* 1							
MTW1990a01	24.8633(3)	5.01238(7)	24.3275(7)	107.7215(6)	2888	n.s.	90Fyf1
MTW1997a01	24.9511	5.0197	24.3288	107.678	2903	n.s.	97Hit1
MTW1999a01	24.893(2)	5.0064(3)	24.250(1)	107(1)	2890	n.s.	99Kin1
MTW1999b01	24.8787(2)	5.0145(3)	24.3152(2)	107.7(2)	2890	n.s.	99Der1
MTW1999b02	24.8687(2)	5.0129(3)	24.3116(1)	107.7(2)	2887	n.s.	99Der1
MTW1999b03	24.8605(1)	5.0085(2)	24.323(1)	107.1(9)	2895	n.s.	99Der1
MTW1999b04	24.9163(2)	5.0182(3)	24.4048(1)	107.9(2)	2904	n.s.	99Der1
MTW1999b05	24.9460(3)	5.0230(3)	24.2963(2)	107.5(5)	2904	n.s.	99Der1
MTW2002a01	24.893(2)	5.0064(3)	24.250(1)	107(1)	2890	n.s.	2002Kin1

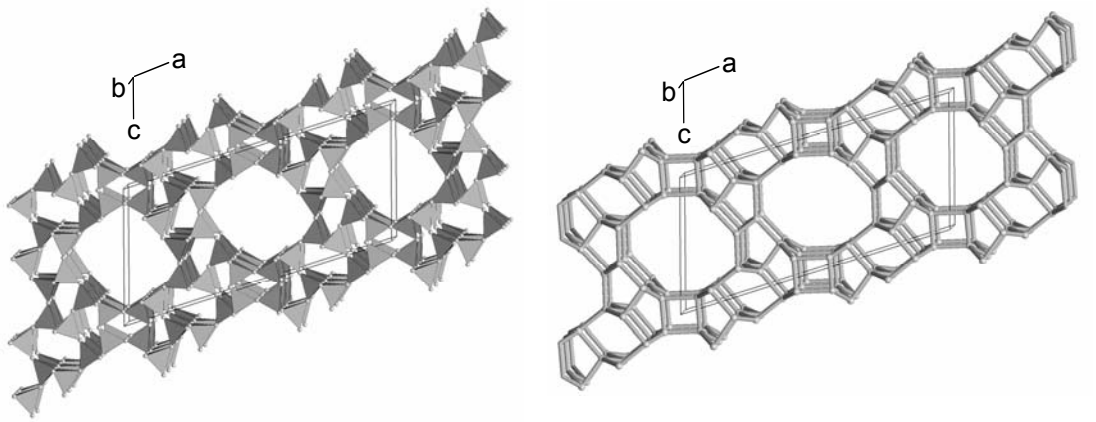
MTW.3 Framework structures

MTW.3.1 MTW-I compound (*C* 1 2/*m* 1, IT #12)



a Polyhedral representation. View parallel **c** rotated by 2° about **b** and **b**×**c**.

b Ball and stick model corresponding to a).



c Polyhedral representation. View parallel **b** rotated by 4° about **c** and **b**×**c**.

d Ball and stick model corresponding to c).

Fig. MTW.3.1.1 Projections of the MTW-I crystal structure of ZSM-12, $Al_{0.1}Si_{27.9}O_{56}$ (MTW1985a01, 85LaP1).

Table MTW.3.1.1 Atomic coordinates and site definitions for MTW-I, ZSM-12, $Al_{0.1}Si_{27.9}O_{56}$ (MTW1985a01, 85LaP1).

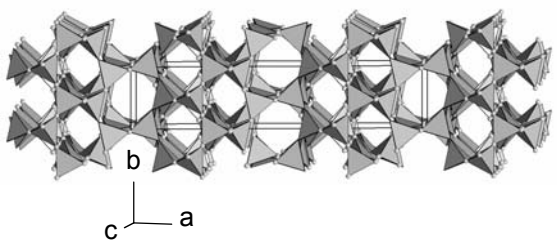
atom	*x*	*y*	*z*	site symmetry	Wyckoff position	no. of atoms in unit cell
(Si,Al)1	0.0714	0	0.1611	*m*	4(i)	3.988 / 0.012
(Si,Al)2	0.0613	0	0.9116	*m*	4(i)	3.988 / 0.012
(Si,Al)3	0.3694	0	0.7085	*m*	4(i)	3.988 / 0.012
(Si,Al)4	0.3797	0	0.1186	*m*	4(i)	3.988 / 0.012
(Si,Al)5	0.2942	0	0.8683	*m*	4(i)	3.988 / 0.012
(Si,Al)6	0.2788[1])	0	0.2127	*m*	4(i)	3.988 / 0.012
(Si,Al)7	0.2826	0	0.4751	*m*	4(i)	3.988 / 0.012
O1	0.0913	0.2495	0.2439	1	8(j)	8
O2	0.0782	0.2503	0.8487[2])	1	8(j)	8
O3	0.2465	0.2494	0.1403	1	8(j)	8
O4	0.0947	0	0.0494	*m*	4(i)	4
O5	0.0044	0	0.1077	*m*	4(i)	4
O6	0.3164	0	0.7575	*m*	4(i)	4
O7	0.3453	0	0.5684	*m*	4(i)	4
O8	0.3420	0	0.2038	*m*	4(i)	4
O9	0.3446	0	-0.0140[3])	*m*	4(i)	4
O10	0.2831	0	0.3454	*m*	4(i)	4
O11	¼	¼	½	$\bar{1}$	4(f)	4

[1]) corrected from 0.3778 [2]) corrected from 0.1513 [3]) corrected from 0.0140

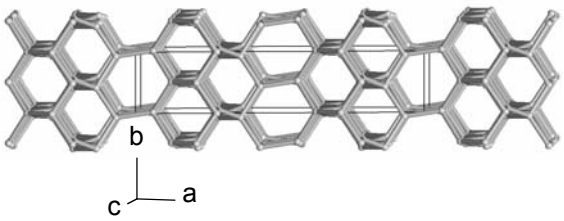
Table MWT.3.1.2 Selected interatomic distances and angles for MTW-I, ZSM-12, $Al_{0.1}$ $Si_{27.9}O_{56}$ (MTW1985a01, 85LaP1).

	T - O [Å]	T - O - T [°]		T - O [Å]	T - O - T [°]
(Si,Al)1 - O1	1.59	153	(Si,Al)2 - O5	1.58	165
(Si,Al)1 - O1	1.59	153	(Si,Al)2 - O2	1.59	138
(Si,Al)1 - O5	1.59	165	(Si,Al)2 - O2	1.59	138
(Si,Al)1 - O4	1.63	131	(Si,Al)2 - O4	1.63	131
mean	1.60	151	Mean	1.60	143
(Si,Al)3 - O1	1.59	153	(Si,Al)4 - O9	1.58	163
(Si,Al)3 - O1	1.59	153	(Si,Al)4 - O8	1.59	145
(Si,Al)3 - O6	1.60	148	(Si,Al)4 - O2	1.59	138
(Si,Al)3 - O7	1.62	135	(Si,Al)4 - O2	1.63	138
mean	1.60	147	mean	1.60	146
(Si,Al)5 - O9	1.59	163	(Si,Al)6 - O10	1.58	176
(Si,Al)5 - O3	1.60	149	(Si,Al)6 - O3	1.60	149
(Si,Al)5 - O3	1.60	149	(Si,Al)6 - O3	1.60	149
(Si,Al)5 - O6	1.60	148	(Si,Al)6 - O8	1.61	145
mean	1.60	152	mean	1.60	155
(Si,Al)7 - O11	1.57	180			
(Si,Al)7 - O11	1.57	180			
(Si,Al)7 - O10	1.58	176			
(Si,Al)7 - O7	1.63	135			
mean	1.59	168			

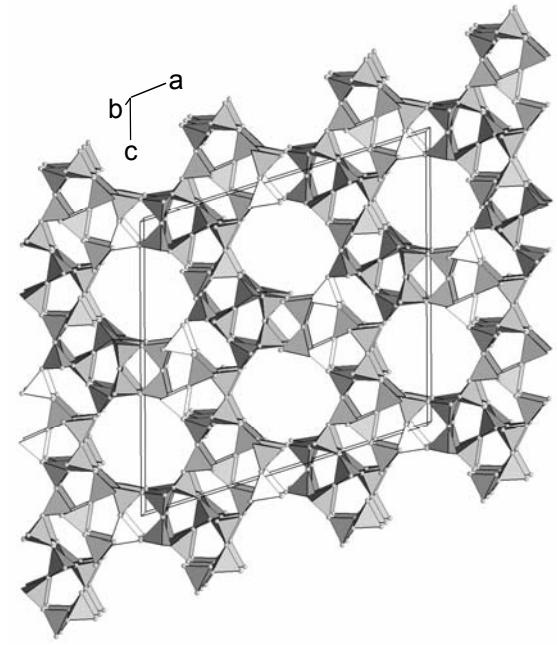
MTW.3.2 MTW-II compound (*C*1 2/*c* 1, IT #15)



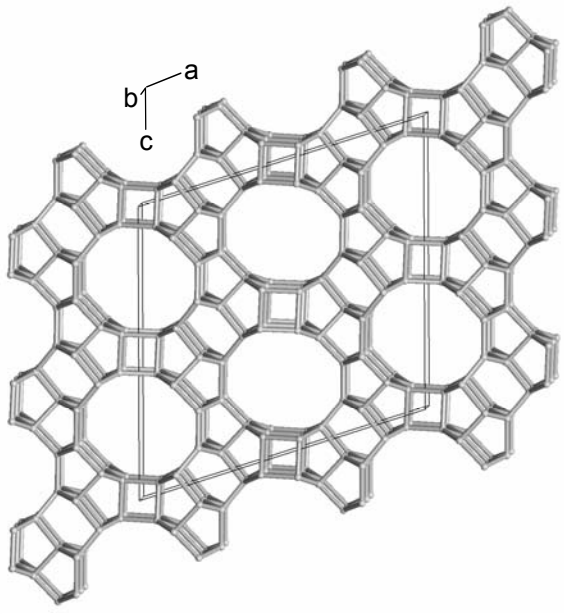
a Polyhedral representation. View parallel **c** rotated by 1° about **b** and **b**×**c**.



b Ball and stick model corresponding to a).



c Polyhedral representation. View parallel **b** rotated by 4° about **c** and **b**×**c**.



d Ball and stick model corresponding to c).

Fig. MTW.3.2.1 Projections of the MTW-II crystal structure of ZSM-12, $Si_{56}O_{112} \cdot 1.97H_2O$ (MTW1999b01, 99Der1).

Table MTW.3.2.1 Atomic coordinates and site definitions for MTW-II, ZSM-12, $Si_{56}O_{112} \cdot 1.97H_2O$ (MTW1999b01, 99Der1).

atom	*x*	*y*	*z*	*B* [Å^2]	site symmetry	Wyckoff position	no. of atoms in unit cell
Si1	0.0616(2)	0.032(1)	0.0873(2)	1.67(6)	1	8(f)	8
Si2	0.0679(2)	0.939(1)	0.4590(2)	1.67(6)	1	8(f)	8
Si3	0.3728(2)	0.028(1)	0.3616(2)	1.67(6)	1	8(f)	8
Si4	0.3642(2)	0.931(1)	0.0521(2)	1.67(6)	1	8(f)	8
Si5	0.2825(2)	0.078(1)	0.4273(2)	1.67(6)	1	8(f)	8
Si6	0.2874(2)	0.073(1)	0.1193(2)	1.67(6)	1	8(f)	8
Si7	0.2855(2)	0.020(1)	0.2458(3)	1.67(6)	1	8(f)	8
O1_1	0.0768(4)	0.323(2)	0.1153(4)	1.97(8)	1	8(f)	8
O1_2	0.1004(4)	0.176(2)	0.6325(4)	1.97(8)	1	8(f)	8
O21	0.1103(3)	0.131(1)	0.4385(4)	1.97(8)	1	8(f)	8
O22	0.0871(3)	0.364(1)	0.9501(4)	1.97(8)	1	8(f)	8
O31	0.2689(3)	0.369(1)	0.0951(4)	1.97(8)	1	8(f)	8
O32	0.2377(3)	0.117(1)	0.5867(4)	1.97(8)	1	8(f)	8
O4	0.0747(3)	0.012(2)	0.0263(3)	1.97(8)	1	8(f)	8
O5	-0.0030(3)	-0.035(2)	0.0803(3)	1.97(8)	1	8(f)	8
O6	0.3271(4)	-0.002(2)	0.3951(4)	1.97(8)	1	8(f)	8
O7	0.3456(3)	-0.018(2)	0.2922(3)	1.97(8)	1	8(f)	8
O8	0.3454(3)	-0.013(2)	0.1098(3)	1.97(8)	1	8(f)	8
O9	0.3088(3)	-0.044(2)	-0.0031(3)	1.97(8)	1	8(f)	8
O10	0.2978(4)	0.080(2)	0.1868(3)	1.97(8)	1	8(f)	8
O11	0.2497(4)	0.248(2)	0.2634(4)	1.97(8)	1	8(f)	8
Ow20	0.047(1)	-0.01(1)	0.267(1)	2.4(8)	1	8(f)	1.97(3)

Table MTW.3.2.2 Selected interatomic distances and angles for MTW-II, ZSM-12, $Si_{56}O_{112} \cdot 1.97H_2O$ (MTW1999b01, 99Der1).

	T - O [Å]	T - O - T [°]		T - O [Å]	T - O - T [°]
Si1 - O5	1.600(9)	150.8(4)	Si2 - O4	1.612(6)	159.1(6)
Si1 - O1_1	1.606(11)	142.9(7)	Si2 - O5	1.612(8)	150.8(4)
Si1 - O1_2	1.607(10)	143.4(6)	Si2 - O21	1.615(8)	140.7(5)
Si1 - O4	1.616(6)	159.1(6)	Si2 - O22	1.627(7)	149.2(5)
mean	1.607	149.1	mean	1.616	150.0
Si3 - O1_1	1.586(11)	142.9(7)	Si4 - O22	1.602(8)	149.2(5)
Si3 - O6	1.594(9)	160.0(8)	Si4 - O9	1.610(8)	146.2(5)
Si3 - O1_2	1.616(11)	143.4(6)	Si4 - O21	1.622(7)	140.7(5)
Si3 - O7	1.632(7)	136.3(5)	Si4 - O8	1.632(6)	133.0(5)
Mean	1.607	145.7	Mean	1.617	142.3
Si5 - O6	1.592(9)	160.0(8)	Si6 - O32	1.571(8)	145.9(5)
Si5 - O32	1.614(7)	145.9(5)	Si6 - O10	1.582(6)	156.9(7)
Si5 - O31	1.615(8)	146.1(5)	Si6 - O8	1.589(8)	133.0(5)
Si5 - O9	1.627(7)	146.2(5)	Si6 - O31	1.611(7)	146.1(5)
Mean	1.612	149.6	mean	1.588	145.5
Si7 - O10	1.584(8)	156.9(7)			
Si7 - O11	1.586(11)	154.9(6)			
Si7 - O7	1.587(8)	136.3(5)			
Si7 - O11	1.599(11)	156.9(7)			
mean	1.589	151.3			

MTW.4 Chemical composition

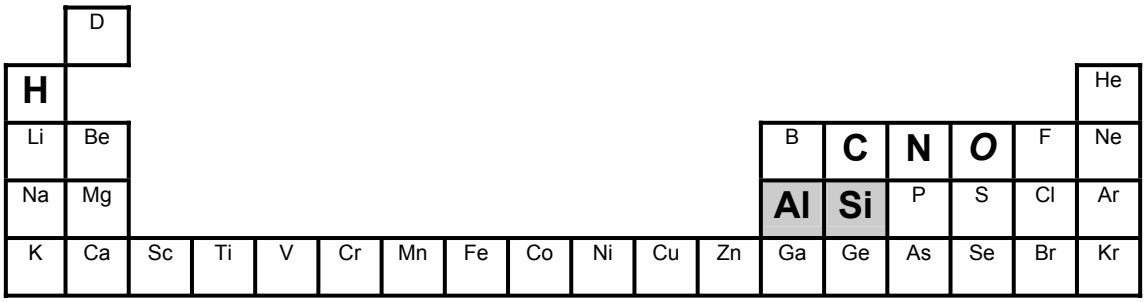


Fig. MTW.4.1 Chemical elements (highlighted) occurring in MTW-type compounds. Framework cations are in grey fields.

MTW.5 Flexibility and apertures

The value of the mean T-O-T angles of MTW1999b01 is close to 148°, with individual angles ranging from 133° to 160° (Table MTW.3.2.2). This range of values T-O-T for the MTW-type is half as large as observed for LTA-type compounds where it varies from 125° to 179° (see the LTA chapter and [92Bau1]). The full range of values displayed by numerous zeolite frameworks of different types is 115° to 180° as observed in a sample of 2436 T-O-T values [95Bau1]. The mean angleT-O-T in MTW-type compounds is slightly larger than the maximum of the distribution of T-O-T angles in silicoaluminate zeolites (about 143° [95Bau1]).

The unit cell volumes of MTW-type compounds (Table MTW.2.2) vary by only 0.6% between the samples studied so far. This is a tiny deviation, not only when compared with collapsible frameworks such as the natrolites [92Bau2], but also when compared with a rather stable framework, such as the noncollapsible framework of the LTA-type [92Bau2]. There the unit cell constants vary by about 4%. For a meaningful comparison we must contrast this with the ratio of the third root of the unit cell volumes of the MTW-type compounds, which is about 0.2%. It seems that the framework of MTW-type is relatively inflexible and does not react strongly to the filling of its pores by different molecules at different amounts of loading by water and organic molecules (Table MTW.2.1).

The 12-ring opening in the framework of MTW has free diameters ranging from 5.5 Å to 6 Å. This means that it is rather buckled compared with the opening in the FAU-type framework, which is almost 7.5 Å wide.

MTW.6 Other information

ZSM-12 catalysts are mentioned in numerous patents as useful for various chemical reactions. In the context of their catalytic properties several compounds of MTW topology have been prepared which contain various heteroatoms in their frameworks and substitute partly for Si: examples are Ga [92Zhi1], Ti [95Tue1] or V [94Mou1].

MTW.7 References

74Ros1 Rosinski, E.J., Rubin, M.K.: U.S. Patent 3,832,449 (1974).

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