MTT

MTT.1 Zeolite framework type and topology

The designation of the FTC refers to the type material ZS**M**-**T**wenty-**T**hree (ZSM-23, Zeolite Socony Mobil with sequence number twenty-three), first synthesized by [78Pla1]. The crystal structure was solved by [85Roh1] in space group *P m m n* but it was shown by [93Mar1] that ZSM-23 is monoclinic crystallizing in space group $P2_1$. The framework structure (Fig. MTT.1.1) consists of *bb33* ($6^2 6^2 6^2 10^2$) units forming the 10-ring channels (**kcm** units, Fig. MTT.1.3) parallel **a**, crosslinked by *hes* (6^4) and *pes* ($5^2 6^2$) units as shown in Fig. MTT. 1.2. Alternatively, it can be described as a recurrently twinned form of the TON-type structures of zeolite Theta-1 [88Tho1] and ZSM-22 [93Mar1].

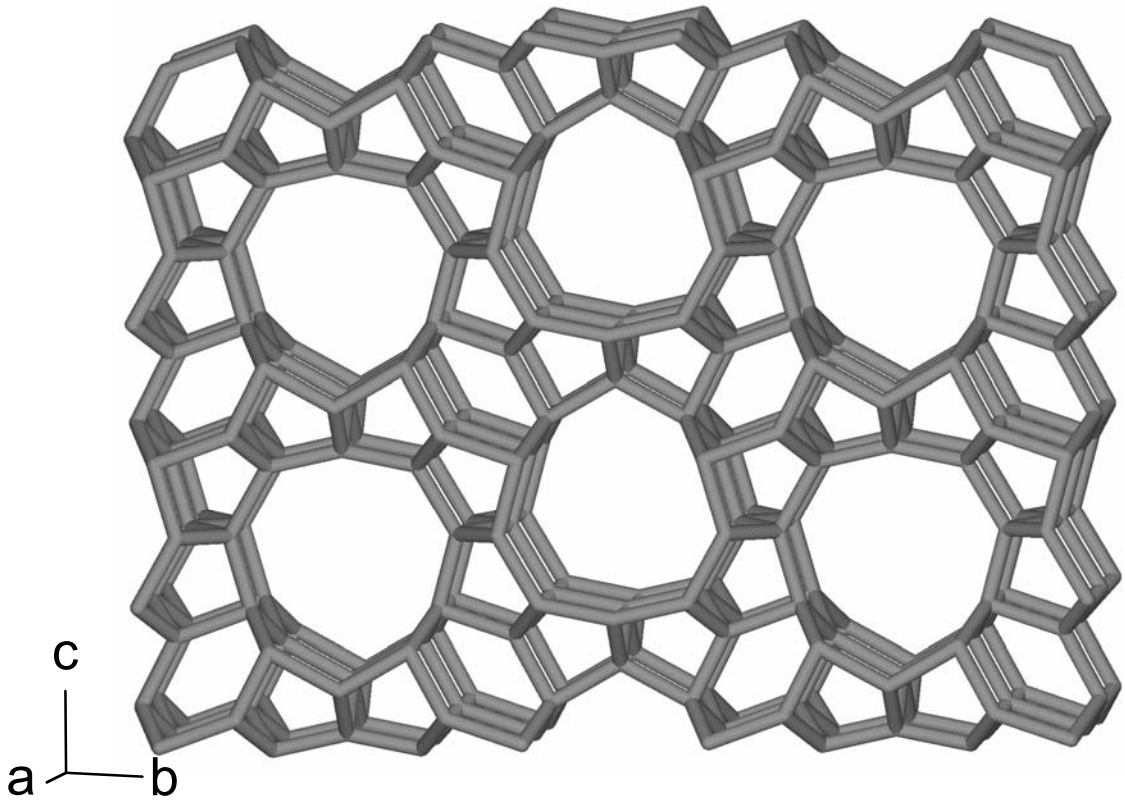
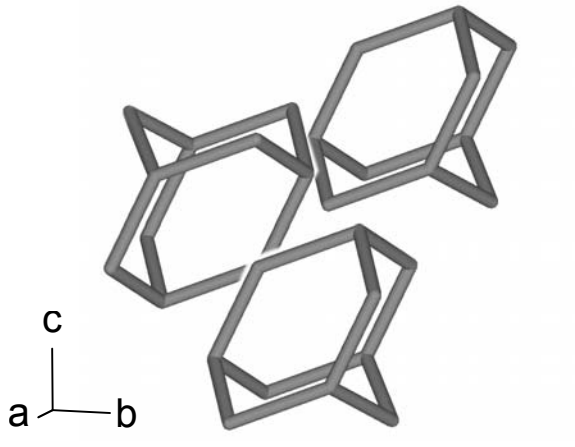
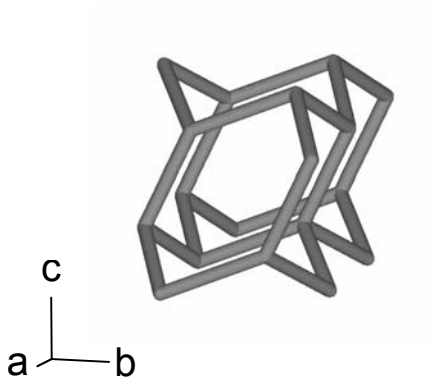


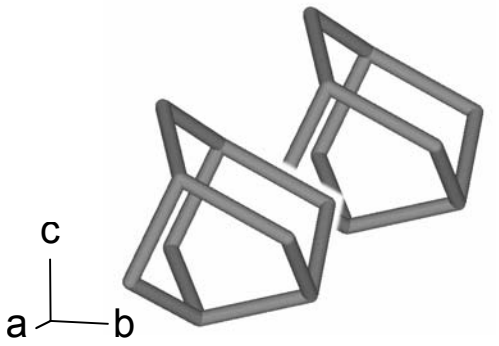
Fig. MTT.1.1. The framework structure of MTT-type compounds in the highest possible topological symmetry *P m m n* (MTT1985a01, 85Roh1). View parallel **a** rotated by 5° about **b** and 6° about **c**.



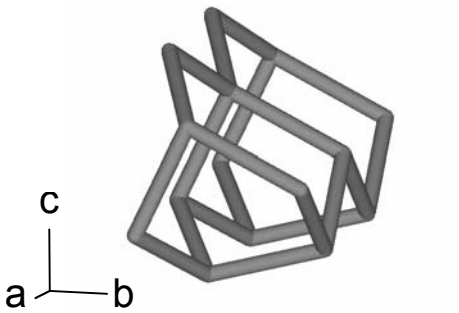
a The *hes* units forming a **ton** chain.



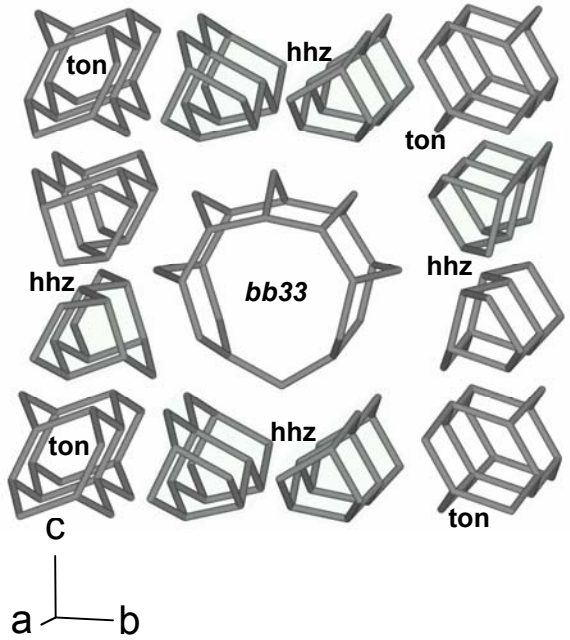
b The **ton** chain parallel **a**.



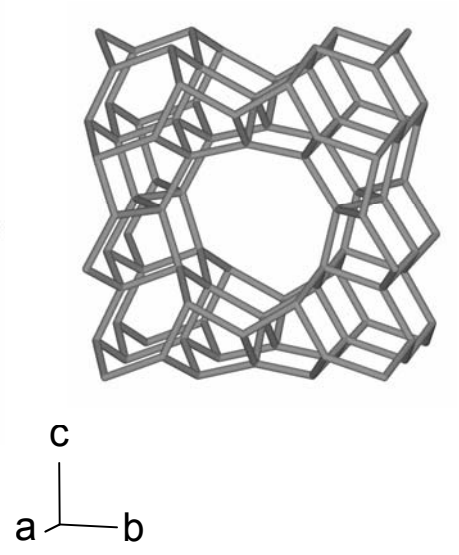
c The *pes* units forming a **hhz** chain.



d The **hhz** chain parallel **a**.



e Linkage of units around the *bb33* unit.



f The assemblage shown in **e**.

Fig. MTT.1.2 Building scheme of MTT-type structures. View parallel **a** rotated by 10° about **b** and 12° about **c**.

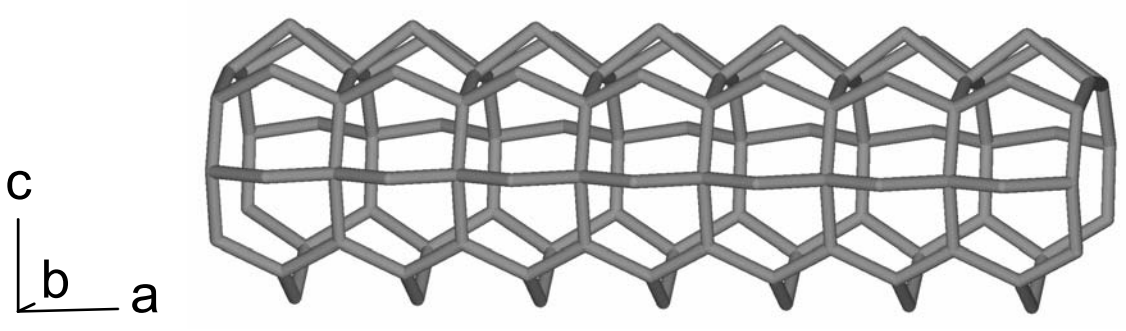


Fig. MTT.1.3 The 10-ring channel (**kcm** unit) parallel **a**. View parallel –**b** rotated by 10° about **a** and **c**.

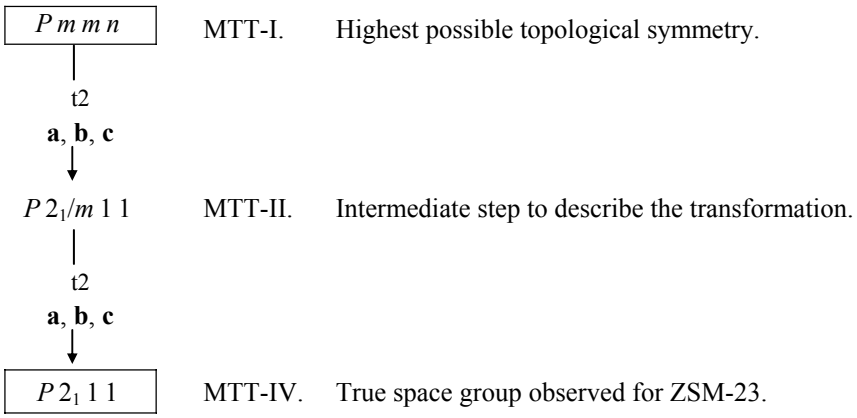


Fig. MTT.1.4 The Bärnighausen tree illustrating the symmetry relationship of the MTT types.

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

MTT-I *P m m n*		MTT-II *P* 2_1/*m* 1 1		MTT-IV *P* 2_1 1 1
T1 [4(e), *m* . .]	→	T11 [2(e), *m*]	→	T11 [2(a), 1]
		T12 [2(e), *m*]	→	T12 [2(a), 1]
T2 [4(e), *m* . .]	→	T21 [2(e), *m*]	→	T21 [2(a), 1]
		T22 [2(e), *m*]	→	T22 [2(a), 1]
T3 [4(e), *m* . .]	→	T31 [2(e), *m*]	→	T31 [2(a), 1]
		T32 [2(e), *m*]	→	T32 [2(a), 1]
T4 [4(e), *m* . .]	→	T41 [2(e), *m*]	→	T41 [2(a), 1]
		T42 [2(e), *m*]	→	T42 [2(a), 1]
T5 [4(e), *m* . .]	→	T51 [2(e), *m*]	→	T51 [2(a), 1]
		T52 [2(e), *m*]	→	T52 [2(a), 1]
T6 [2(b), *m m* 2]	→	T6 [2(e), *m*]	→	T6 [2(a), 1]
T7 [2(a), *m m* 2]	→	T7 [2(e), *m*]	→	T7 [2(a), 1]

Table MTT.1.1 (continued)

MTT-I, *P m m n*	MTT-II, *P* $2_1/m$ 1 1	MTT-IV, *P* 2_1 1 1
O1 [8(g), 1]	O11 [4(f), 1]	O11a [2(a), 1]
		O11b [2(a), 1]
	O12 [4(f), 1]	O12a [2(a), 1]
		O12b [2(a), 1]
O2 [8(g), 1]	O21 [4(f), 1]	O21a [2(a), 1]
		O21b [2(a), 1]
	O22 [4(f), 1]	O22a [2(a), 1]
		O22b [2(a), 1]
O3 [4(f), . *m* .]	O3 [4(f), 1]	O31 [2(a), 1]
		O32 [2(a), 1]
O4 [4(e), *m* . .]	O41 [2(e), *m*]	O41 [2(a), 1]
	O42 [2(e), *m*]	O42 [2(a), 1]
O5 [4(e), *m* . .]	O51 [2(e), *m*]	O51 [2(a), 1]
	O52 [2(e), *m*]	O52 [2(a), 1]
O6 [4(e), *m* . .]	O61 [2(e), *m*]	O61 [2(a), 1]
	O62 [2(e), *m*]	O62 [2(a), 1]
O7 [4(e), *m* . .]	O71 [2(e), *m*]	O71 [2(a), 1]
	O72 [2(e), *m*]	O72 [2(a), 1]
O8 [4(e), *m* . .]	O81 [2(e), *m*]	O81 [2(a), 1]
	O82 [2(e), *m*]	O82 [2(a), 1]
O9 [4(e), *m* . .]	O91 [2(e), *m*]	O91 [2(a), 1]
	O92 [2(e), *m*]	O92 [2(a), 1]
O10 [4(c), $\bar{1}$]	O101 [2(c), $\bar{1}$]	O101 [2(a), 1]
	O102 [2(a), $\bar{1}$]	O102 [2(a), 1]

MTT.2 Compounds and crystal data

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

code	*a* [Å]	*b* [Å]	*c* [Å]	*V* [Å^3]	*T* [K]	reference
MTT-I *P m m n*						
MTT1985a01	5.01(2)	21.52(4)	11.13(3)	1200	n.s.	85Roh1
MTT-IV *P* 2_1 1 1						
MTT1993a01	5.025(1)	21.519(1)	11.129(1)	1203	-	93Mar1
MTT1993a02	5.025(1)	21.519(1)	11.129(1)	1203	n.s.	93Mar1

Table MTT.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]

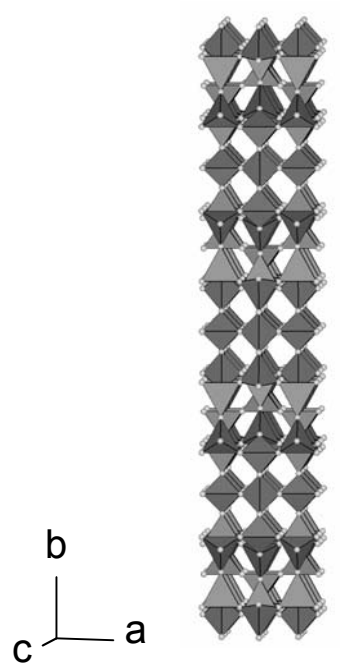
code	chemical composition	FD	SM	CE	SR	TT	T	REF
MTT-I ***P m m n***								
MTT1985a01	$Al_{0.14}Si_{23.86}O_{48}$	20.0	S	-	-	C	n.s.	85Roh1
MTT-IV ***P*** $\mathbf{2_1}$ **1 1**								
MTT1993a01	$Si_{24}O_{48}$	19.9	T	-	-	-	-	93Mar1
MTT1993a02	$Si_{24}O_{48} \cdot 1.72NH_4F$	19.9	S	-	NH_4F	C	1023	93Mar1

MTT.3 Framework structures

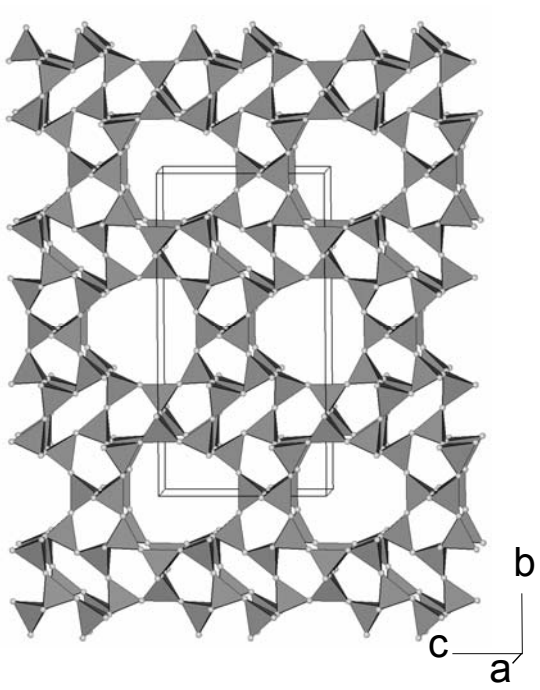
MTT.3.1 MTT-I compound (*P m m n*, IT #59)

Table MTT.3.1.2 Selected interatomic distances and angles for MTT-I, ZSM-23, $Si_{24}O_{48}$ (MTT1985a01, 85Roh1).

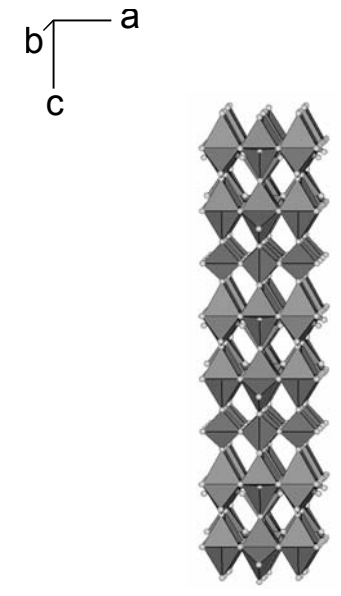
	T - O [Å]	T - O - T [°]		T - O [Å]	T - O - T [°]
(Si,Al)1- O10	1.55	180	(Si,Al)2 - O6	1.58	173
(Si,Al)1 - O10	1.55	180	(Si,Al)2 - O1	1.59	144
(Si,Al)1 - O5	1.57	168	(Si,Al)2 - O1	1.59	144
(Si,Al)1 - O4	1.60	145	(Si,Al)2 - O4	1.60	145
mean	1.57	168	mean	1.59	152
(Si,Al)3 - O5	1.57	168	(Si,Al)4 - O6	1.58	173
(Si,Al)3 - O2	1.57	161	(Si,Al)4 - O2	1.59	161
(Si,Al)3 - O2	1.57	161	(Si,Al)4 - O2	1.59	161
(Si,Al)3 - O7	1.62	135	(Si,Al)4 - O9	1.62	137
mean	1.58	156	mean	1.59	149
(Si,Al)5 - O8	1.58	172	(Si,Al)6 - O3	1.58	180
(Si,Al)5 - O1	1.58	144	(Si,Al)6 - O3	1.58	180
(Si,Al)5 - O1	1.58	144	(Si,Al)6 - O8	1.58	172
(Si,Al)5 - O9	1.61	137	(Si,Al)6 - O8	1.58	172
Mean	1.59	149	mean	1.58	176
(Si,Al)7 - O3	1.57	180			
(Si,Al)7 - O3	1.57	180			
(Si,Al)7 - O7	1.60	135			
(Si,Al)7 - O7	1.60	135			
mean	1.59	158			



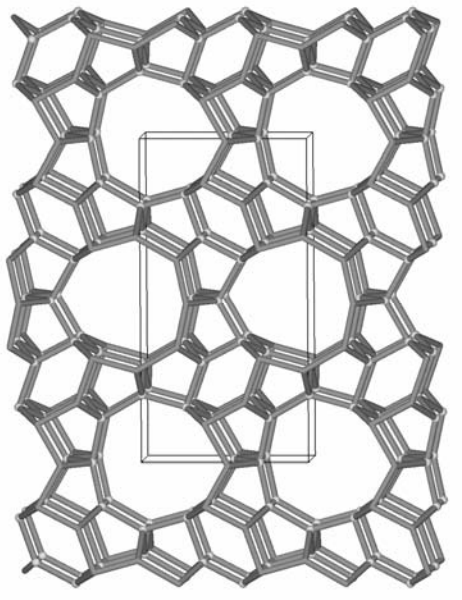
a View parallel **c** rotated by 1° about **a** and **b**.



b View parallel **a** rotated by 5° about **b** and **c**.



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



d Ball and stick model corresponding to b).

Fig. MTT.3.1.1 Projections of the MTT-I crystal structure of ZSM-23, $Si_{24}O_{48}$ (MTT1985a01, 85Roh1).

Table MTT.3.1.1 Atomic coordinates and site definitions for MTT-I, ZSM-23, $Si_{24}O_{48}$ (MTT1985a01, 85Roh1).

atom	*x*	*y*	*z*	site symmetry	Wyckoff position	no. of atoms in unit cell
(Si,Al)1	0	0.2076	0.9940	*m* . .	4(e)	3.976 / 0.024
(Si,Al)2	0	0.1700	0.7304	*m* . .	4(e)	3.976 / 0.024
(Si,Al)3	0	0.1353	0.2379	*m* . .	4(e)	3.976 / 0.024
(Si,Al)4	½	0.1921	0.3638	*m* . .	4(e)	3.976 / 0.024
(Si,Al)5	½	0.1273	0.6030	*m* . .	4(e)	3.976 / 0.024
(Si,Al)6	½	0	0.4642	*m m* 2	2(b)	1.988 / 0.012
(Si,Al)7	0	0	0.2936	*m m* 2	2(a)	1.988 / 0.012
O1	0.2498	0.1296	0.6899	1	8(g)	8
O2	0.2507	0.1540	0.3151	1	8(g)	8
O3	0.2502	0	0.3783	. *m* .	4(f)	4
O4	0	0.1671	0.8739	*m* . .	4(e)	4
O5	0	0.1647	0.1085	*m* . .	4(e)	4
O6	0	0.2375	0.6757	*m* . .	4(e)	4
O7	0	0.0611	0.2125	*m* . .	4(e)	4
O8	0	0.5612	0.4582	*m* . .	4(e)	4
O9	0	0.6838	0.4915	*m* . .	4(e)	4
O10	¼	¼	0	$\bar{1}$	4(c)	4

MTT.3.2 MTT-IV compound ($P2_1$, IT #4)

Table MTT.3.2.1 Atomic coordinates and site definitions for MTT-IV, ZSM-23, $Si_{24}O_{48}$ (MTT1993a02, 93Mar1).

Atom	*x*	*y*	*z*	*B* [Å^2]	site symmetry	Wyckoff position	no. of atoms in unit cell
Si11	-0.02(1)	0.2078(9)	0.991(2)	1.1(2)	1	2(a)	2
Si12	0.40(1)	0.7078(9)	0.010(2)	1.1(2)	1	2(a)	2
Si21	-0.082(8)	0.175(1)	0.726(2)	1.1(2)	1	2(a)	2
Si22	0.488(9)	0.673(1)	0.274(2)	1.1(2)	1	2(a)	2
Si31	-0.112(8)	0.134(1)	0.228(2)	1.1(2)	1	2(a)	2
Si32	0.423(7)	0.632(1)	0.768(2)	1.1(2)	1	2(a)	2
Si41	0.390(8)	0.184(1)	0.346(2)	1.1(2)	1	2(a)	2
Si42	-0.076(7)	0.687(1)	0.645(2)	1.1(2)	1	2(a)	2
Si51	0.417(8)	0.128(1)	0.600(2)	1.1(2)	1	2(a)	2
Si52	-0.013(8)	0.630(1)	0.397(2)	1.1(2)	1	2(a)	2
Si6	0.503(4)	-0.001(1)	0.476(2)	1.1(2)	1	2(a)	2
Si7	0	0.001(1)	0.312(2)	1.1(2)	1	2(a)	2
O11a	0.122(9)	0.131(2)	0.655(4)	1.0(4)	1	2(a)	2
O11b	0.621(9)	0.151(2)	0.701(3)	1.0(4)	1	2(a)	2
O12a	0.78(1)	0.647(2)	0.292(3)	1.0(4)	1	2(a)	2
O12b	0.286(9)	0.630(2)	0.348(4)	1.0(4)	1	2(a)	2
O21a	0.085(9)	0.169(2)	0.317(4)	1.0(4)	1	2(a)	2
O21b	0.584(8)	0.142(2)	0.269(4)	1.0(4)	1	2(a)	2
O22a	0.630(8)	0.664(2)	0.678(4)	1.0(4)	1	2(a)	2
O22b	0.132(8)	0.644(2)	0.715(4)	1.0(4)	1	2(a)	2
O31	0.292(4)	0.004(3)	0.368(3)	1.0(4)	1	2(a)	2

Table MTT.3.2.1 (continued)

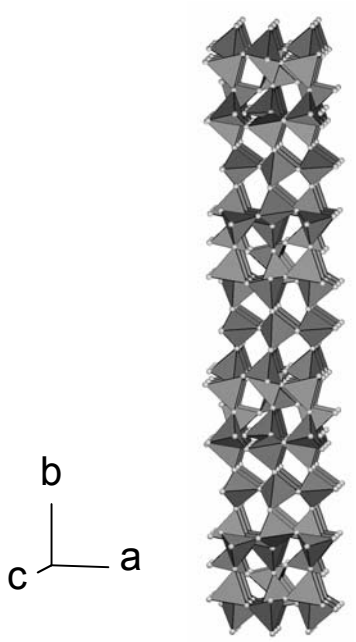
Atom	*x*	*y*	*z*	*B* [Å^2]	site symmetry	Wyckoff position	no. of atoms in unit cell
O32	0.797(5)	-0.004(3)	0.422(2)	1.0(4)	1	2(a)	2
O41	-0.02(1)	0.172(2)	0.866(2)	1.0(4)	1	2(a)	2
O42	0.43(1)	0.671(2)	0.134(2)	1.0(4)	1	2(a)	2
O51	-0.09(1)	0.158(2)	0.093(3)	1.0(4)	1	2(a)	2
O52	0.45(1)	0.661(2)	0.900(3)	1.0(4)	1	2(a)	2
O61	-0.04(1)	0.245(1)	0.683(4)	1.0(4)	1	2(a)	2
O62	0.47(1)	0.742(1)	0.321(4)	1.0(4)	1	2(a)	2
O71	-0.05(1)	0.061(1)	0.231(4)	1.0(4)	1	2(a)	2
O72	0.47(1)	0.558(1)	0.774(3)	1.0(4)	1	2(a)	2
O81	-0.07(1)	0.561(1)	0.447(4)	1.0(4)	1	2(a)	2
O82	0.49(1)	0.058(1)	0.564(4)	1.0(4)	1	2(a)	2
O91	-0.04(1)	0.679(2)	0.503(2)	1.0(4)	1	2(a)	2
O92	0.44(1)	0.173(2)	0.486(2)	1.0(4)	1	2(a)	2
O101	0.27(1)	0.237(2)	0.012(5)	1.0(4)	1	2(a)	2
O102	0.61(1)	0.764(2)	0.001(5)	1.0(4)	1	2(a)	2
F1	0.55(3)	-0.035(5)	0.938(8)	32(8)	1	2(a)	1.7(1)
N1	0.06(4)	0.011(9)	0.89(1)	32(8)	1	2(a)	1.7(1)

Table MTT.3.2.2 Selected interatomic distances and angles for MTT-IV, ZSM-23, $Si_{24}O_{48}$ (MTT1993a02, 93Mar1).

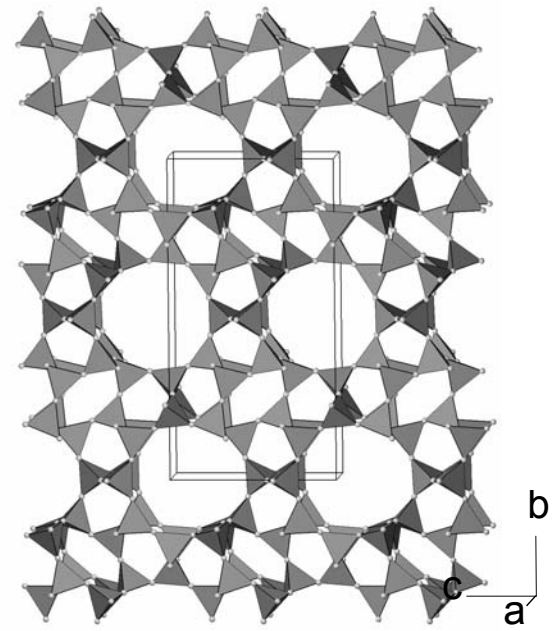
	T - O [Å]	T - O - T [°]		T - O [Å]	T - O - T [°]
Si1 1 - O101	1.59(6)	153(3)	Si1 2 - O102	1.58(7)	154(4)
Si1 1 - O41	1.59(4)	147(3)	Si1 2 - O42	1.60(4)	148(3)
Si1 1 - O51	1.60(4)	154(3)	Si1 2 - O52	1.61(4)	159(3)
Si1 1 - O101	1.60(7)	153(3)	Si1 2 - O102	1.61(6)	154(4)
mean	1.60	152	mean	1.60	154
Si2 1 - O41	1.59(3)	153(3)	Si2 2 - O62	1.58(3)	173(4)
Si2 1 - O61	1.59(3)	147(3)	Si2 2 - O12a	1.58(7)	141(3)
Si2 1 - O11b	1.60(6)	154(3)	Si2 2 - O42	1.59(3)	148(3)
Si2 1 - O11a	1.61(5)	153(3)	Si2 2 - O12b	1.60(6)	140(3)
mean	1.60	152	mean	1.59	151
Si3 1 - O51	1.59(4)	154(3)	Si3 2 - O22b	1.60(5)	151(3)
Si3 1 - O21a	1.59(5)	145(3)	Si3 2 - O22a	1.60(5)	151(3)
Si3 1 - O71	1.60(3)	147(3)	Si3 2 - O52	1.60(4)	159(3)
Si3 1 - O21b	1.60(6)	143(3)	Si3 2 - O72	1.61(3)	141(2)
mean	1.60	147	mean	1.60	151
Si4 1 - O21b	1.58(5)	143(3)	Si4 2 - O62	1.59(3)	173(4)
Si4 1 - O92	1.60(3)	148(3)	Si4 2 - O22b	1.60(5)	151(3)
Si4 1 - O21a	1.60(6)	145(3)	Si4 2 - O91	1.60(3)	145(3)
Si4 1 - O61	1.60(3)	159(4)	Si4 2 - O22a	1.60(5)	151(3)
mean	1.60	149	mean	1.60	155
Si5 1 - O92	1.60(4)	148(3)	Si5 2 - O91	1.59(4)	145(3)
Si5 1 - O11b	1.60(5)	145(3)	Si5 2 - O12b	1.60(6)	140(3)
Si5 1 - O82	1.60(4)	155(3)	Si5 2 - O12a	1.61(5)	141(3)
Si5 1 - O11a	1.61(6)	143(3)	Si5 2 - O81	1.61(4)	153(4)
mean	1.60	148	mean	1.60	145

Table MTT.3.2.2 (continued)

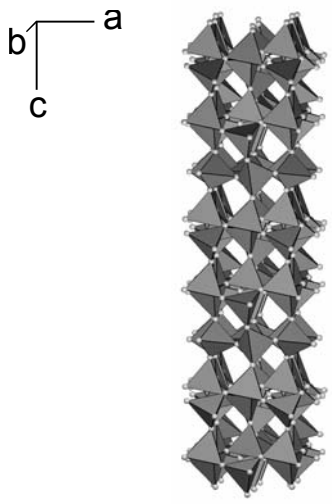
	T - O [Å]	T - O - T [°]		T - O [Å]	T - O - T [°]
Si6 - O81	1.59(4)	153(4)	Si7 - O71	1.59(4)	147(3)
Si6 - O32	1.60(3)	151(2)	Si7 - O31	1.60(2)	154(3)
Si6 - O31	1.61(4)	154(3)	Si7 - O32	1.60(3)	151(2)
Si6 - O82	1.61(4)	155(3)	Si7 - O72	1.60(3)	141(2)
mean	1.60	153	mean	1.60	148



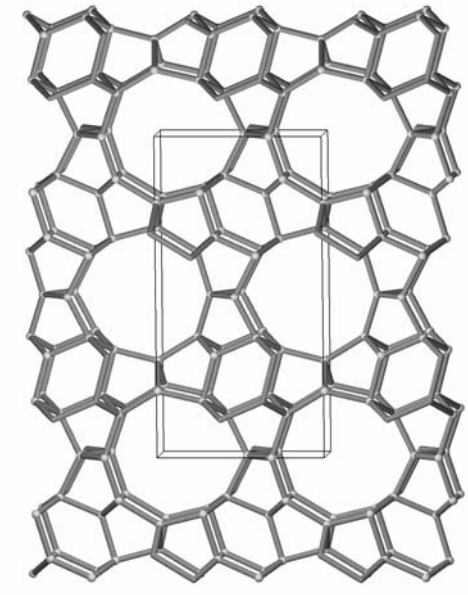
a View parallel **c** rotated by 1° about **a** and **b**.



b View parallel **a** rotated by 5° about **b** and **c**.



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



d Ball and stick model corresponding to b).

Fig. MTT.3.2.1 Projections of the MTT-IV crystal structure of ZSM-23, $Si_{24}O_{48} \cdot 1.72NH_4F$ (MTT1993a02, 93Mar1).

MTT.4 Chemical composition

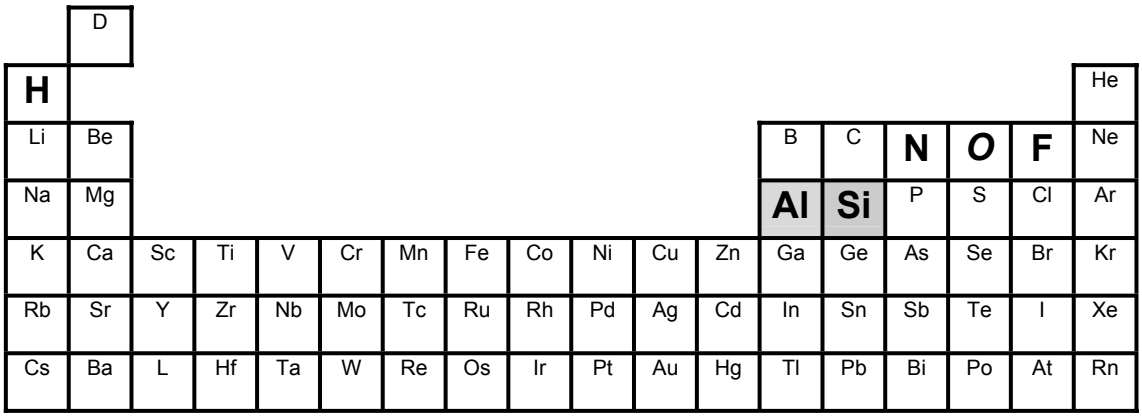


Fig. MTT.4.1 Chemical elements (highlighted) occurring in MTT-type compounds. Framework cations are in grey fields.

MTT.5 Flexibility and apertures

The value of the mean T-O-T angles for MTT1993a01 (MTT-IV) is about 150°, with individual angles ranging from 140° to 173°. This mean angle is larger than the maximum of the distribution of T-O-T angles in silicoaluminate zeolites (about 143° [95Bau1]). There is insufficient information about the MTT-type framework to deduce anything about its flexibility.

The 10-ring of the MTT-type framework (MTT-IV) is buckled and clearly smaller than in MFI- and MEL-type silicates. The diameters range from 4.5 Å to 5 Å.

MTT.6 Other information

ZSM-23-type highly siliceous zeolites have been claimed as catalysts for a wide variety of processes. About 500 patents mention ZSM-23 compounds as useful. As examples the efficient catalytic cracking of C4 alkane over ZSM-23 may be listed here [2005Ji1] or the skeletal isomerization of octadecane [2005Huy1].

MTT.7 References

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