# MTW [Ga] ZSM-12 Si(93), Ga(7)

**Contributed by** Susan Lambert

**Verified by** K. Reddy and M. Mertens

**Type Material** $Na_2[Ga_2Si_{26}O_{56}] : 4\ H_2O$

**Method** S. L Lambert [1]

**Batch Composition** $4.5\ Na_2O : Ga_2O_3 : 52.4\ SiO_2 : 13.7$ TEMA Br : $867\ H_2O$ (TEMA = triethylmethylammonium)

**Source Materials**

deionized water
sodium hydroxide (Mallinkrodt dry pellets,> 98.5% NaOH)
gallium oxide (Alfa, 99.99%)
triethylmethylammonium bromide (TEMA Br) (Fluka, purum)
silica sol (Dupont Ludox AS-40, 40% $Si0_2$) [a]

**Batch Preparation** (for 13 g dry product)

(1) [21.72 g NaOH + 37.04 g water + 11.37 g $Ga_2O_3$], heat in a closed pressure vessel (Teflon-lined Parr acid digestion bomb) at 110°C for 23 hours
(2) [4.65 g of solution (1) + 29.22 g water + 10.78 g TEMA Br], stir until dissolved
(3) [(2) + (31.47 g silica sol + 11.63 g $H_2O$)], add diluted silica sol to (2) with stirring using an eye dropper over course of 15 min. Batch pH 13-14 [b]

**Crystallization**

Vessel: two Teflon-lined Parr acid digestion bombs (125 mL)
Time: 20 days [c]
Temperature: 150°C
Agitation: none

**Product Recovery**

(1) Supernatant liquid pH 12.5
(2) Filter and wash with 600 mL distilled water
(3) Dry at 100°C
(4) Yield: 13.64 g white solids (12.25 g volatile free), 91% recovery on $SiO_2$ or 87% on $Ga_2O_3$

**Product Characterization**

XRD: MTW framework by comparison to ZSM- 12 crystallinity reference, best is [Al] MTN.
Minor impurity: cristobalite; no other phases present
Elemental Analyses (volatile-free): 93.4% $SiO_2$, 5.35% $Ga_2O_3$, 0.62% $Na_2O$, 0.14%$Al_2O_3$.
Loss on ignition at 900°C: 10.17% [d]

Molar Composition: 0.35 $Na_2O$ : 0.05 $A1_2O_3$ : $Ga_2O_3$: 54.4 $SiO_2$ : 22 $H_2O$ [e]

**Reference**

[1] S. L Lambert in Proceedings of the 9th international Zeolite Conference, R. von Ballmoos, J. B. Higgins, M. M. J. Treacy (eds.), Butterworth-Heinemann, London, 1993, P. 223

**Notes**

a. Dupontâs Ludox HS-40 is an acceptable substitute.

b. pH values were measured with ColorpHast pH indicator paper (range 5-10 or 7.5-14, from E. M. Science, Gibbstown, NJ, USA)

c. Crystallinity vs. (Al) ZSM-12 reference: 70% after 16 days, 88% after 18 days, 90% after 20 days. The crystallization proceeds more rapidly as the amount of gallium in the synthesis batch is reduced.

d. Template burnout occurs at 460˚C in air.

e. By $^{29}Si$ MAS NMR, Si/(Ga + Al) = 14; excess $SiO_2$ by elemental analysis is attributed to amorphous silica. $^{7l}Ga$ static NMR one symmetrical Ga line at 158.5 ppm
(ref. $Ga(N0_3)_3$).