UTL IM-12 Si(86), Ge(13)

Contributed by Jiri Čejka

Verified by R. Ryoo, A. Puškarić, J. Bronic, M. Derewinski
Type Material: $(SDA)_{4.6}[Si_{65}Ge_{11}O_{152}]$: w H_2O
(SDA = 6,10-dimethyl-5-azoniaspiro [4,5]decane hydroxide)

Method: J.-L. Paillaud, B. Harbuzaru, J. Patarin, N. Bats [1]

Batch Composition: 0.8 SiO_2 : 0.4 GeO_2 : 0.5 SDAOH/Br : 30 H_2O

Source Materials
deionized water
sodium hydroxide (98 %, NaOH)
1,4-dibromobutane (99 %)
2,6-dimethylpiperidine (98 %)
chloroform (99 %)
sodium sulfate anhydrous (99 %, Na_2SO_4)
diethyl ether (99 %)
Dowex® SBR LCNG, hydroxide form (Supelco)
germanium oxide (99.99 % GeO_2)
silica (Degussa Aerosil 200, or Cab-O-Sil M5)

Batch Preparation (for 4 g dry product)
(1) [43.5 g water + 1.76 g sodium hydroxide + 9.47 g 1,4-dibromobutane], stir in a flask
(2) [(1) + 5.0 g 2,6-dimethylpiperidine], add 2,6-dimethylpiperidine to (1) drop by drop over a period of 30 min under reflux; reflux for 12 h under vigorous stirring,[a] cool in ice bath
(3) [10.9 g water + 10.9 g sodium hydroxide], stir until dissolved, cool in ice bath
(4) [(2) + (3)], stir, recover solid by filtration
(5) [solid (4) + 200 ml chloroform], stir until dissolved
(6) [(5) + 30 g sodium sulfate anhydrous], stir, left for 30 min, remove solid by filtration, evaporate about 100 ml of chloroform using rotavap
(7) [(5) + 300 ml diethyl ether], mix, recover solid by filtration, wash with diethyl ether, dry at ambient temperature for 12 h
(8) [solid (6)[b] + 45 g water + 12 g Dowex®], stir for 2 h, remove Dowex® by filtration
(9) [solution (7) + 3.49 g germanium oxide], stir until dissolved[c]
(10) [(8) + 4.00 g Cabosil], stir for 30 minutes[d]

Crystallization
Vessel: Teflon-lined stainless steel autoclave
Temperature: 170 °C
Time: 6 days
Agitation: 60 rpm

Product Recovery
(1) Dilute reaction mixture with water

(2) Filter and wash with water
(3) Dry at ambient temperature or at 90°C
(4) Yield: 3.5 g

Product Characterization

XRD: UTL; competing phase: STF (when Si / Ge > 5)
Elemental analysis: 6.5 SiO_2 : GeO_2[e]
Crystal size and habit: thin platelet-like crystals

Reference

[1] J.-L. Paillaud, B. Harbuzaru, J. Patarin, N. Bats, Science 304 (2004) 990
[2] O. V. Shvets, A. Zukal, N. Kasian, N. Žilkova, J. Čejka, Chem. Eur. J. 14 (2008) 10134
[3] M. V. Shamzhy, O. V. Shvets, M. V. Opanasenko, P. S. Yaremov, L. G. Sarkisyan, P. Chlubná, A. Zukal, V. R. Marthala, M. Hartmann, J. Čejka, J. Chem. Mater. 22 (2012) 15793

Notes

a. The satisfactory mixing of two phases at > 1000 rpm.
b. 95 % yield of SDA
c. Clear solution
d. pH of final gel is 8.0
e. According to Ref. [2]