

New Journal of Chemistry

Supporting information for manuscript:

Synthesis of IWW-type germanosilicate zeolite using 5-azonia-spiro[4,4]nonane as structure directing agent

Ruting Yuan ^a, Nathalie Claes ^b, Elke Verheyen ^a, Alain Tuel ^c, Sara Bals ^b, Eric Breynaert ^a, Johan A. Martens ^a, Christine E. A. Kirschhock ^{a*}

^a. Centre for Surface Chemistry and Catalysis, KU Leuven, Kasteelpark Arenberg 23, 3001 Heverlee, Belgium. christine.kirschhock@biw.kuleuven.be

^b. EMAT, University of Antwerp, Groenenborgerlaan 171 B-2020 Antwerp, Belgium.

^c. IRCELYON - UMR 5256 CNRS-Université de Lyon 1, 2, Av. A. Einstein 69626 Villeurbanne Cedex (France)

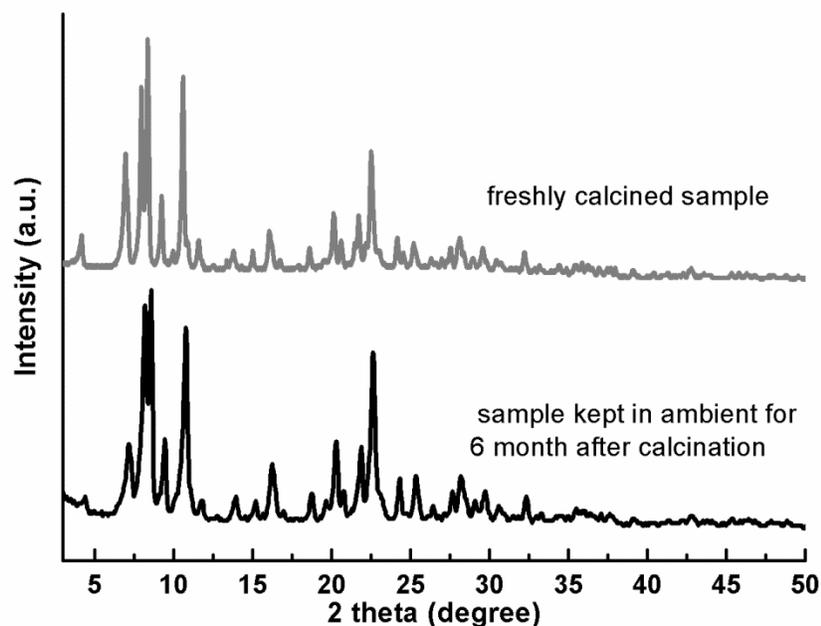


Figure S1. XRD pattern for calcined IWW-type zeolite prepared using azonia-spiro[4,4]nonane hydroxide as SDA and kept at ambient for 6 months.

Table S1. R-values and cell parameters of the refined IWW and NON. Rietveld refinement on IWW occurred in space group Pbam, resulted in an orthorhombic unit cell. Goodness of fit values (GOF) for IWW refinement is 1.29. Rietveld refinement on NON occurred in the space group Fmmm, resulted in an orthorhombic unit cell. Goodness of fit values (GOF) for NON refinement is 1.41.

Samples	R-values (%)		Cell parameters
	Rp	Rwp	
IWW synthesized by using 5-azonia-spiro[4,4]nonane	8.5	9.8	$a=42.03 \text{ \AA}$
	6.4		$b=12.96 \text{ \AA}$
			$c=12.67 \text{ \AA}$
NON synthesized using 5-azoniaspiro[4,5] decane hydroxide in absence of GeO ₂	6.1	9.1	$a=22.11 \text{ \AA}$
	5.6		$b=15.02 \text{ \AA}$
			$c= 13.62 \text{ \AA}$

Table S2. Atomic coordinates of calcined IWW using synchrotron radiation ($\lambda = 0.50493 \text{ \AA}$). The number between brackets gives the esd.

T atom name	x coordinate	y coordinate	z coordinate	Uiso	Site Multiplicity
Ge1	0.38351(25)	0.9049(7)	0.1232(5)	0.0447(9)	8
Ge2	0.42067(20)	0.7063(7)	0.1267(5)	0.0555(7)	8
Ge3	0.35514(23)	0.5785(8)	0.1262(6)	0.0704(8)	8
Ge4	0.31725(21)	0.7781(9)	0.1245(6)	0.0649(11)	8
Si1	0.38351(25)	0.9049(7)	0.1232(5)	0.0447(9)	8
Si2	0.42067(20)	0.7063(7)	0.1267(5)	0.0555(7)	8
Si3	0.35514(23)	0.5785(8)	0.1262(6)	0.0704(8)	8
Si4	0.31725(21)	0.7781(9)	0.1245(6)	0.0649(11)	8
Si5	0.37956(32)	0.9057(8)	0.5	0.0187(23)	4
Si6	0.42134(28)	0.6916(9)	0.5	0.0187(23)	4
Si7	0.35846(31)	0.5655(9)	0.5	0.0187(23)	4
Si8	0.31672(30)	0.7792(10)	0.5	0.0187(23)	4
Si9	0.35227(21)	0.4112(7)	0.3002(7)	0.0187(23)	8
Si10	0.37995(24)	0.0595(7)	0.3036(6)	0.0187(23)	8
Si11	0.27791(23)	0.8602(8)	0.3056(7)	0.0187(23)	8
Si12	0.46111(19)	0.6179(7)	0.3012(6)	0.0187(23)	8
Si13	0.28973(23)	0.2970(8)	0.3717(6)	0.0187(23)	8
Si14	0.30867(23)	0.0789(8)	0.3707(5)	0.0187(23)	8
Si15	0.40764(25)	0.2678(8)	0.3763(6)	0.0187(23)	8
Si16	0.46629(21)	0.4062(8)	0.3758(6)	0.0187(23)	8
O1	0.4070(4)	0.8159(8)	0.1794(5)	0.001(4)	8
O2	0.3948(5)	0.9134(9)	0	0.001(4)	4
O3	0.34625(26)	0.8629(12)	0.1295(18)	0.001(4)	8
O4	0.3861(4)	0.0130(7)	0.1850(5)	0.001(4)	8
O5	0.4265(4)	0.7291(13)	0	0.001(4)	4
O6	0.39209(26)	0.6187(11)	0.1397(18)	0.001(4)	8
O7	0.45249(24)	0.6675(9)	0.1851(5)	0.001(4)	8
O8	0.3474(6)	0.5644(12)	0	0.001(4)	4
O9	0.3307(4)	0.6674(10)	0.1750(8)	0.001(4)	8
O10	0.34993(31)	0.4689(7)	0.1862(5)	0.001(4)	8
O11	0.3081(4)	0.7560(17)	0	0.001(4)	4
O12	0.28597(26)	0.8161(10)	0.1877(5)	0.001(4)	8
O13	0.4010(4)	0.7999(10)	0.5	0.001(4)	4
O14	0.34146(30)	0.8766(11)	0.5	0.001(4)	4
O15	0.3876(4)	0.9729(8)	0.39384(27)	0.001(4)	8

O16	0.39644(32)	0.5942(11)	0.5	0.001(4)	4
O17	0.44381(26)	0.6865(8)	0.39422(28)	0.001(4)	8
O18	0.3371(5)	0.6711(11)	0.5	0.001(4)	4
O19	0.34999(30)	0.4977(9)	0.39438(28)	0.001(4)	8
O20	0.29408(28)	0.7836(11)	0.39438(28)	0.001(4)	8
O21	0.32319(21)	0.3291(9)	0.3135(10)	0.001(4)	8
O22	0.38650(22)	0.3509(10)	0.3096(11)	0.001(4)	8
O23	0.34330(20)	0.1012(10)	0.3162(14)	0.001(4)	8
O24	0.40486(28)	0.1551(7)	0.3205(12)	0.001(4)	8
O25	0.23941(20)	0.8649(8)	0.3225(11)	0.001(4)	8
O26	0.29323(28)	0.9749(8)	0.3190(14)	0.001(4)	8
O27	0.4483(4)	0.4981(6)	0.3091(9)	0.001(4)	8
O28	0.49942(14)	0.6186(15)	0.3198(10)	0.001(4)	8
O29	0.2924(5)	0.3185(18)	0.5	0.001(4)	4
O30	0.28383(22)	0.1741(7)	0.3498(15)	0.001(4)	8
O31	0.3130(7)	0.0631(13)	0.5	0.001(4)	4
O32	0.3951(5)	0.2622(19)	0.5	0.001(4)	4
O33	0.44512(25)	0.3016(9)	0.3743(16)	0.001(4)	8
O34	0.4718(6)	0.4427(15)	0.5	0.001(4)	4

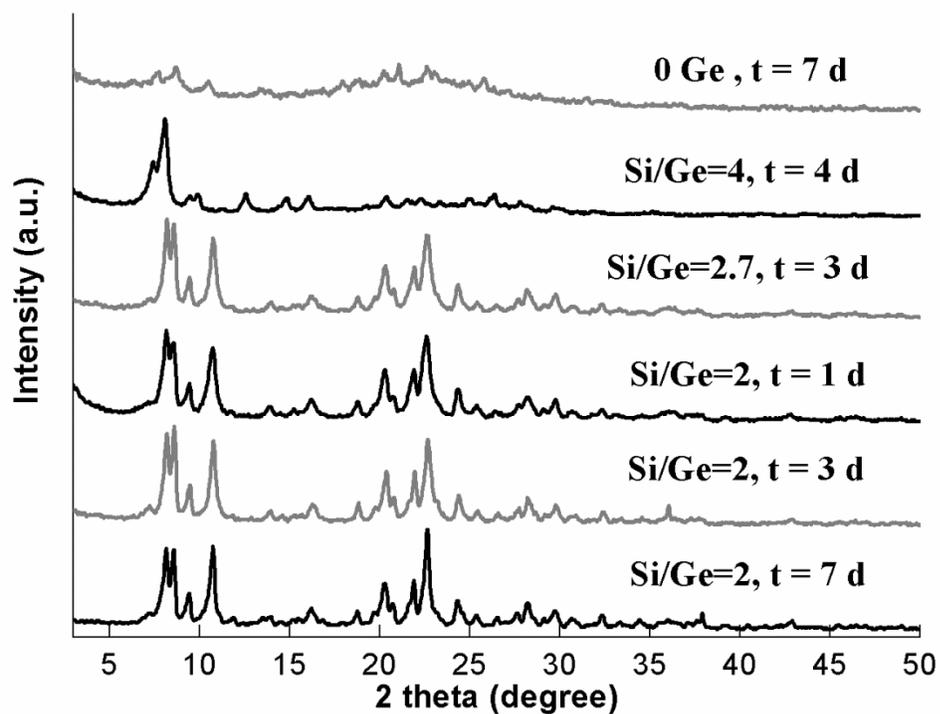


Figure S2 : XRD patterns for optimization experiments on synthesis parameters utilizing azoniaspiro[4,4]nonane as SDA. The Si/Ge ratio in the synthesis gel and hydrothermal synthesis time is given for each experiment.

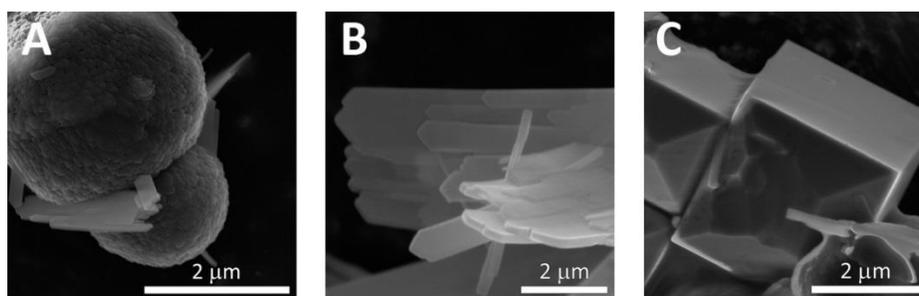


Figure S3. SEM (A-C) images of the samples containing three phases obtained in presence of 5 azoniaspiro[4,5]decane. From left to right the phases are NON as spheres, IWW as thin films, $\text{Na}_4\text{Ge}_9\text{O}_{20}$ as bricks.

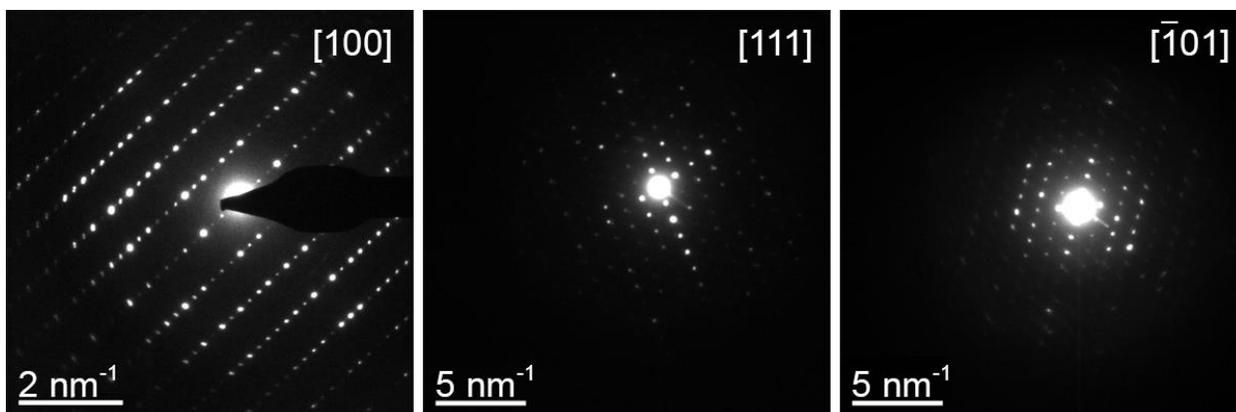


Figure S4. Indexing diffraction patterns on the IWW (sheets) prepared using azonia-spiro[4,5]decane as SDA. An orthorhombic unit cell in the space group $Pbam$ with cell parameters : $a = 12.4 \text{ \AA}$, $b = 13.4 \text{ \AA}$ and $c = 41.5 \text{ \AA}$.

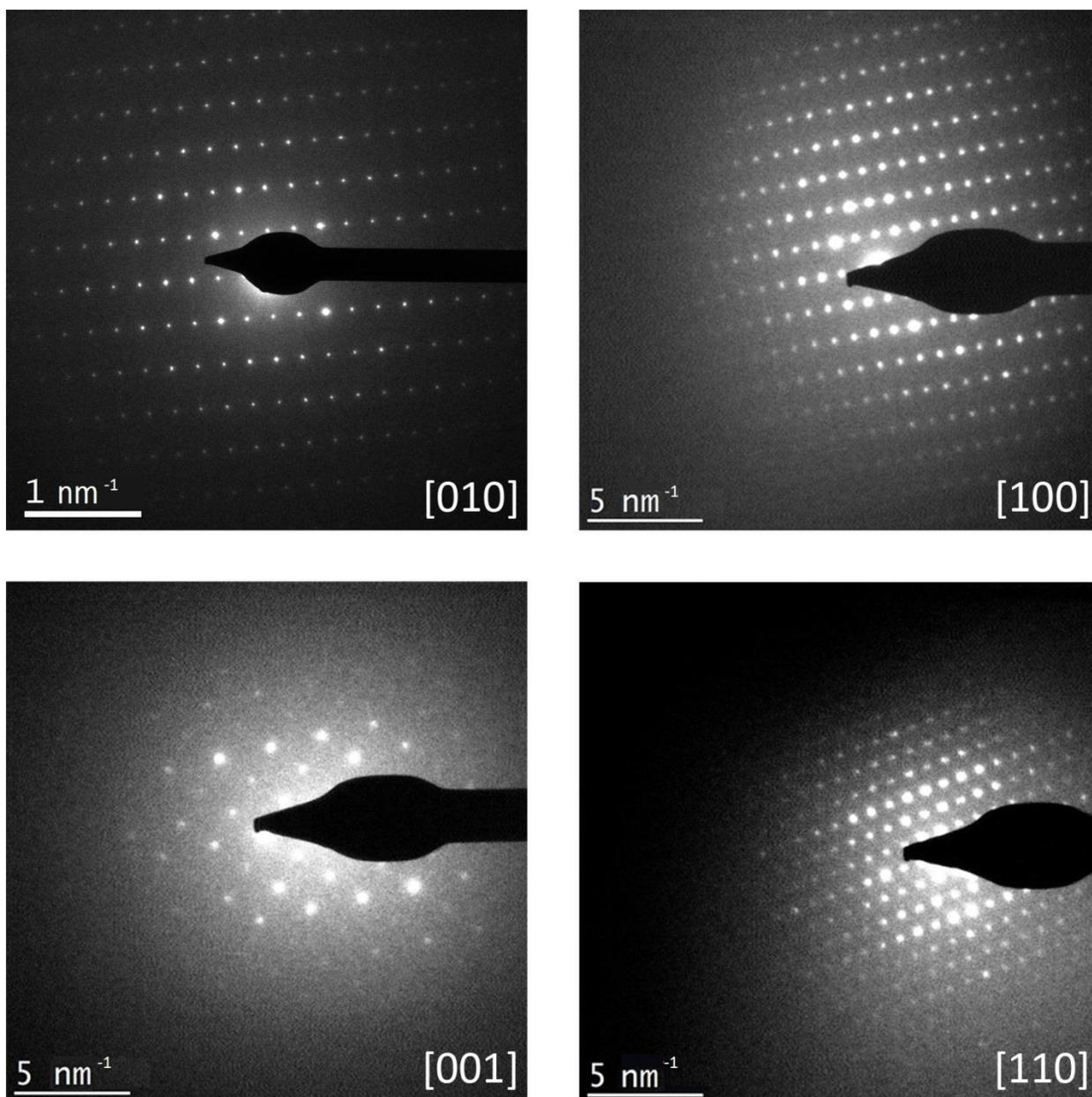


Figure S5. Indexed diffraction patterns of NON phase (spheres) synthesized with 5-azoniaspiro[4,5]decane in the presence of GeO₂. An orthorhombic unit cell in the space group Fmmm with Cell parameters: $a = 13.7 \text{ \AA}$, $b = 15.5 \text{ \AA}$ and $c = 22.8 \text{ \AA}$.

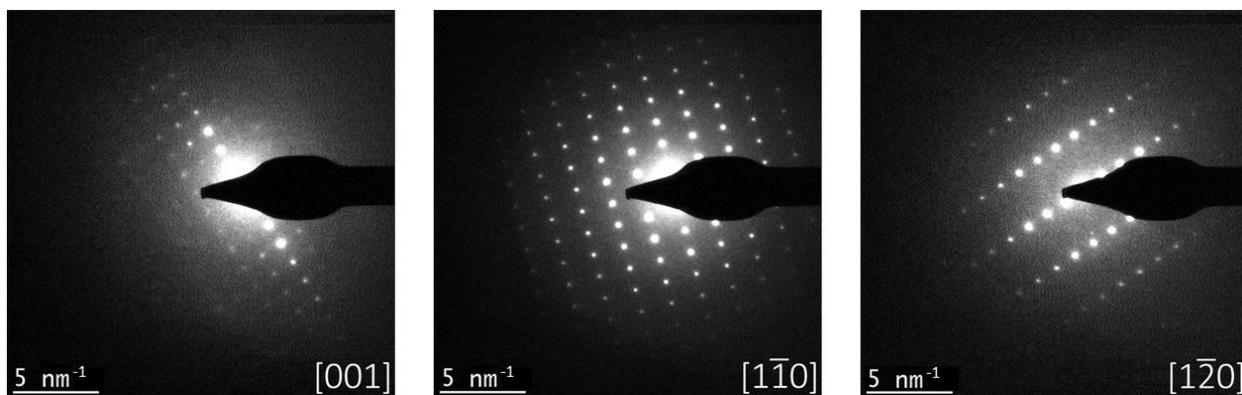


Figure S6. Indexed diffraction patterns of $\text{Na}_4\text{Ge}_9\text{O}_{20}$ phase (pyramids) synthesized with 5-azoniaspiro[4,5]decane in the presence of GeO_2 . Tetragonal unit cell ($a = b = 14.98 \text{ \AA}$, $c = 7.38 \text{ \AA}$) in the space group $I41/a$.

Table S3. Atomic coordinates of calcined NON using synchrotron radiation ($\lambda = 0.50493 \text{ \AA}$). The number between brackets gives the esd.

T atom name	x coordinate	y coordinate	z coordinate	Uiso	Site Multiplicity
O1	0.34583(29)	0.09189(23)	0.2422(5)	0.025	32
O2	0.44022(15)	0.1151(5)	0.3433(5)	0.025	32
O3	0.4001(4)	0.25	0.25	0.025	16
O4	0.33830(28)	0.1896(5)	0.40197(25)	0.025	32
O5	0.25	0.25	0	0.025	8
O6	0.2662(4)	0.41678(20)	0	0.025	16
O7	0.5	0.1723(4)	0.5	0.025	8
O8	0.5	0	0.5527(11)	0.025	8
O9	0.3235(4)	0.5	0.40464(24)	0.025	16
O10	0.25	0.5	0.25	0.025	8
Si1	0.37621(27)	0.1639(4)	0.3080(5)	0.025	32
Si2	0.30004(31)	0.3252(4)	0	0.025	16
Si3	0.5	0.1032(4)	0.5933(6)	0.025	16
Si4	0.31775(25)	0.5	0.2876(5)	0.025	16
Si5	0.2802(5)	0.5	0.5	0.025	8