Electronic Supplementary Material (ESI) for Dalton Transactions

A Silicogermanate with 20-ring Channels Directed by a Simple Quaternary Ammonium Cation

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Synthesis and characterization of the structure directing agent. N, N-diisopropylethylamine (0.1 mol, 17.4 mL) was dissolved in absolute ethanol (~ 30ml). Methyl iodide (0.13 mol, 6.6 mL) was added dropwise into the above solution under stirring. Then the mixture was stirred for 6 hours. Diisopropylethylmethylammonium iodide was obtained. The solid product was filtered, and washed with acetone. Anal. Calc. for $C_9H_{22}NI$ (fw 271.17): C 39.86, H 8.18, N 5.16. Found: C 39.51, H 8.37, N 5.24. The ^{13}C and ^{1}H NMR spectra of the SDA diisopropylethylmethylammonium iodide were recorded at Bruker ARX-400 in a D_2O solution using TMS as the standard. The hydroxide form of the SDA is obtained by ion exchange of an aqueous solution of the iodide salt with Ag_2O. The concentration of the SDA solution is determined by titration with a 0.1 $mol \cdot L^{-1}$ HCl solution.

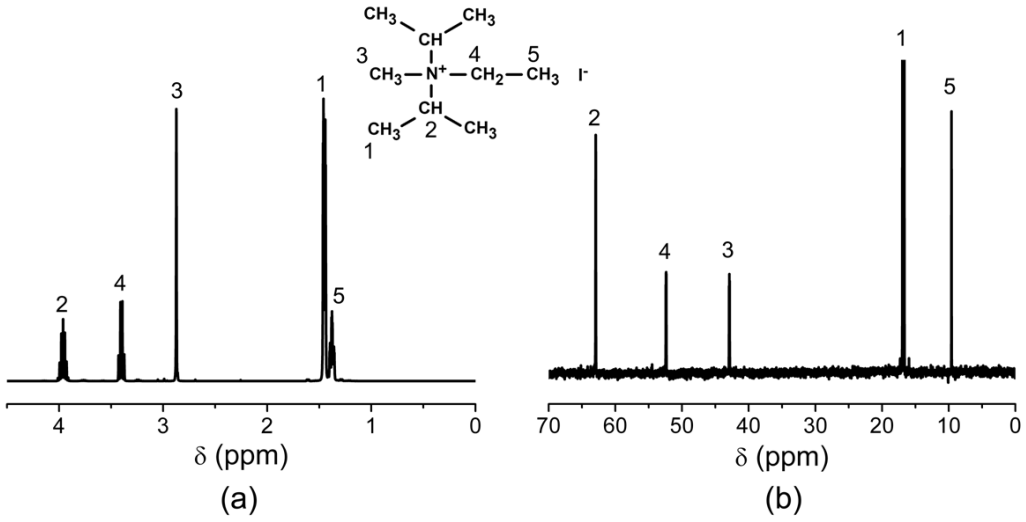

Fig. S1 NMR spectra of diisopropylethylmethylammonium iodide: (a) ^{1}H, and (b) ^{13}C.

Synthesis of PKU-12. The starting materials are all commercially available and were used as purchased without further purification. A typical synthesis procedure is as follows: GeO_2 and fumed silica were dissolved in a solution of diisopropylethylmethylammonium hydroxide. Then a solution of HF was added into the mixture. The mixture was stirred thoroughly. The water content was controlled by evaporation at 70 °C in an oven. The final composition of the gel was 0.35 SiO_2: 0.65 GeO_2: 0.5 SDA: 0.5 HF: 4.5-6.0 H_2O. The mixture was transferred into a Teflon-lined stainless steel autoclave and kept at 110 °C with a 30 rpm rotating speed for 15-30 days. The solid product was washed with distilled water and ethanol, and dried at 70 °C.

Characterization. The purity of the products was examined by powder X-ray diffraction on a Rigaku D/Max-2000 diffractometer with a CuK_α radiation. The powder X-ray diffraction data used for structure refinement was collected on a PANalytical X'Pert Pro. The elemental analysis for carbon, nitrogen and hydrogen was carried out with an Elementar Vario EL III microanalyzer. The elemental ratio (Si/Ge) was measured by using ICP method on an ESCALAB2000 analyzer, and also confirmed by energy dispersive spectroscopy (EDS) micro-analysis on a JSM-7000F SEM with an Oxford Inca Energy EDS system. Micro-infrared spectroscopy was performed on a Nicolet Magna-IR 750 FTIR spectrophotometer in the region of 4000-650 cm^{-1}. Solid state NMR experiments were performed on a Bruker Advance II 400M WB Spectrometer. The ^{13}C and ^{1}H NMR spectra of the SDA salts diisopropylethylmethylammonium iodide were recorded at Bruker ARX-400 in a D_2O solution using TMS as the standard. The morphology of PKU-12 was examined using a JSM-7000F scanning electron microscope (SEM) with an accelerating voltage of 1kV. The thermal analysis was done on TGA Q50 V20.6 with a heating rate of 10 °C/min from 25 to 900 °C in air. The pore size and void volume of the calcined PKU-12 were probed by physisorption of nitrogen gas. Nitrogen adsorption at 78 K was performed using the Micromeritics ASAP 2020. The sample was first degassed at 350 °C for 10 h prior to nitrogen adsorption. The low-pressure dose mode was used when the relative pressure was lower than 0.001. The equilibration time per dose was 40s ($p/p_0 \leq 0.001$) or 10s ($p/p_0 > 0.001$). The free space of the sample tube was measured after the completion of the isotherm. This was done to prevent the trapping of helium in small pore zeolites, which can lead to significant errors in the measurement of the isotherm. The calculation of the pore size from the adsorption isotherm was performed by using Horvath-Kawazoe method.

Rietveld refinement. The Rietveld refinement was performed using the program TOPAS 3.0 with soft restraints for the T–O bond distances considering the Si/Ge occupancies. All T positions were refined with mixed occupancies of Si and Ge and a fixed overall Si/Ge ratio of 0.45/0.55, obtained from the elemental analysis. Although the organic structure directing agents were intact in the final product, as confirmed by the elemental analysis and solid state NMR spectroscopy, they could not be located due to their partial occupancies and larger thermal displacement. Instead, 10 unique carbon and 4 oxygen atoms were added at random positions inside the pores and refined subsequently. The residuals of the refinement were R_p=0.0467, R_{wp}=0.0619 and R_{exp}=0.0321. The CIF file of PKU-12 can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; email: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-423401.

Table S1. Molar ratio of reactants in initial gels, reaction time and product for the synthesis of PKU-12

SiO_2	GeO_2	SDA	HF	H_2O	Time/day	Product
0.20	0.80	0.50	0.50	2.5	28	PKU-12 + D4R-C[a]
0.20	0.80	0.50	0.50	5.0	28	PKU-12 + D4R-C[a]
0.35	0.65	0.50	0.50	5.0	3	PKU-12 + D4R-C[a]
0.35	0.65	0.50	0.50	5.0	7	PKU-12 + D4R-C[a]
0.35	0.65	0.50	0.50	5.0	15	PKU-12 + D4R-C[a]
0.35	0.65	0.50	0.50	5.0	20	PKU-12
0.35	0.65	0.50	0.50	7.0	28	PKU-12 + ITQ-21
0.50	0.50	0.50	0.50	5.0	28	PKU-12 + ITQ-21

[a] D4R-C represents the compound that can be considered as a super-molecular assembly of D4R clusters.

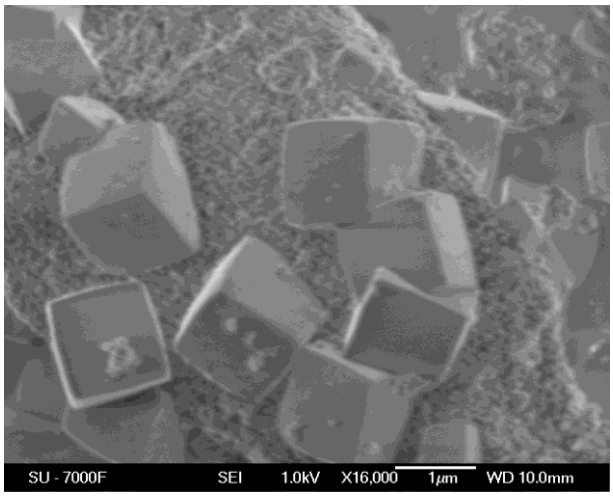

Fig. S2 SEM image of PKU-12.

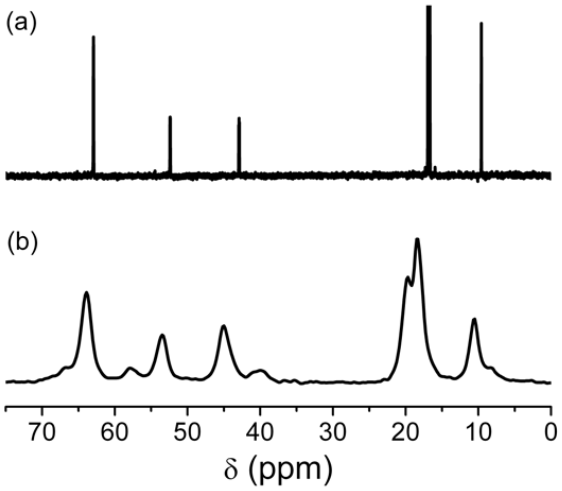

Fig. S3 ^{13}C NMR spectra of SDA (a) as quaternary salt in D_2O solution and (b) in the structure of PKU-12.

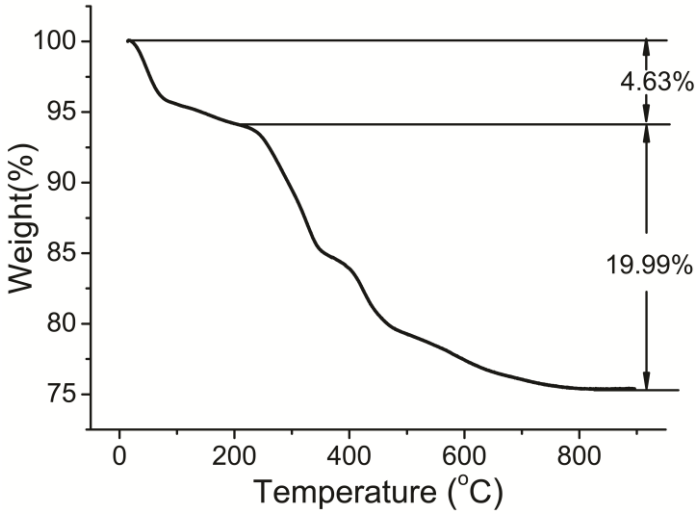

Fig. S4 TG curve of PKU-12.

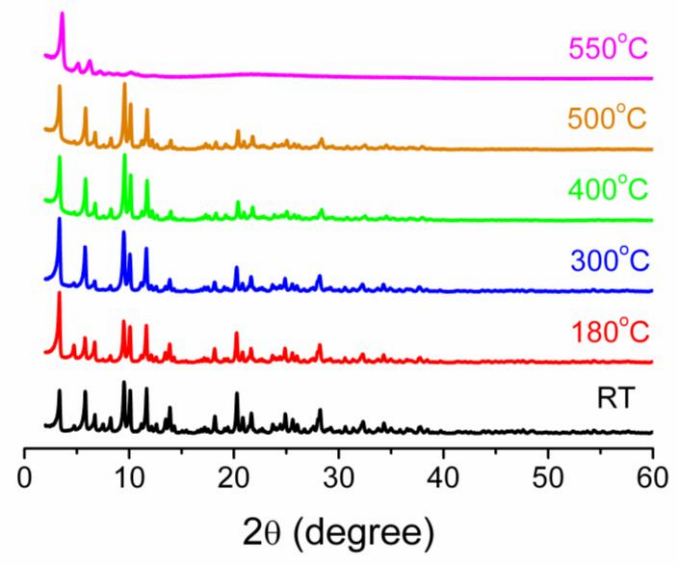

Fig. S5 XRD patterns of PKU-12 calcined at different temperature.

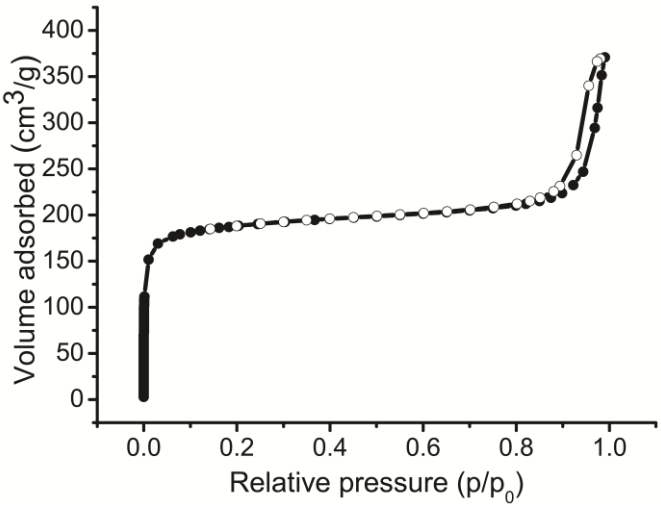

Fig. S6 N_2 sorption-desorption isotherm of PKU-12.

Table S2. EDS results of PKU-12 on different crystals.

	Si (Atomic%)	Ge (Atomic%)
1	47.17	52.83
2	47.28	52.72
3	47.80	52.20
4	45.51	54.49
5	46.35	53.65
6	46.93	53.07
7	46.94	53.06
8	48.15	51.85
9	44.82	55.18
10	46.70	53.30

Table S3. Crystallographic data, experimental conditions for X-ray data collection and results of the Rietveld analysis of PKU-12.

Chemical formula of framework	$Si_{3.61}Ge_{4.39}O_{19.60}C_{10}F$
Formula weight	872.78
Crystal system	Cubic
Space group	*Pm*-3*m*
a/Å	26.2373(2)
Cell volume/Å^3	18061.7(4)
Z	24
Temperature/K	298(2)
Wavelength/Å	1.540596
2θ range/°	2 - 90.9971
Number of points	6778
Number of reflections	1573
Number of structural variables	114
R_p	0.0467
R_{wp}	0.0619
R_{exp}	0.0321
GOF	1.925

Table S4. Atomic coordinates, thermal parameters and occupancies of PKU-12.

Atom	*x*	*y*	*z*	B_{eq}(Å^2)	Occupancy
Si1	0.18550(21)	0.73020(23)	0.44077(23)	0.830(91)	0.384(20)
Ge1	0.18550(21)	0.73020(23)	0.44077(23)	0.830(91)	0.616(20)
Si2	0.26972(25)	0.64802(23)	0.56142(25)	0.830(91)	0.468(19)
Ge2	0.26972(25)	0.64802(23)	0.56142(25)	0.830(91)	0.532(19)
Si3	0.08385(26)	0.70701(23)	0.62326(26)	0.830(91)	0.543(19)
Ge3	0.08385(26)	0.70701(23)	0.62326(26)	0.830(91)	0.457(19)
Si4	0	0.64715(31)	0.43811(37)	0.830(91)	0.428(23)
Ge4	0	0.64715(31)	0.43811(37)	0.830(91)	0.572(23)
Si5	0	0.68363(32)	0.76894(34)	0.830(91)	0.390(21)
Ge5	0	0.68363(32)	0.76894(34)	0.830(91)	0.610(21)
O1	0.1639(11)	0.7318(10)	0.5	1.07(25)	1
O2	0.22221(84)	0.77779(84)	0.4250(12)	1.07(25)	1
O3	0.21399(80)	0.67423(80)	0.42569(76)	1.07(25)	1
O4	0.13555(84)	0.73677(75)	0.40066(82)	1.07(25)	1
O5	0.31810(82)	0.68190(82)	0.5856(10)	1.07(25)	1
O6	0.2719(11)	0.59004(76)	0.59004(76)	1.07(25)	1
O7	0.2776(12)	0.6372(13)	0.5	1.07(25)	1

O8	0.1040(12)	0.66539(82)	0.66539(82)	1.07(25)	1
O9	0.05201(82)	0.75438(83)	0.65076(73)	1.07(25)	1
O10	0.05239(84)	0.68080(78)	0.57573(80)	1.07(25)	1
O11	0	0.5909(11)	0.4091(11)	1.07(25)	1
O12	0	0.6328(16)	0.5	1.07(25)	1
O13	0	0.7416(12)	0.7416(12)	1.07(25)	1
O14	0	0.6937(10)	0.8343(11)	1.07(25)	1
F1	0.73075(12)	0.73075(12)	0.5	12.0(16)	0.918(36)
F2	0.33473(12)	0.33473(12)	0	12.0(16)	0.492(35)
F3	0.4342(15)	0.4342(15)	0.4342(15)	12.0(16)	0.885(75)
C1	0.1845(16)	0.9567(15)	0.0433(15)	12.7(12)	1
C2	0.5657(18)	0.8844(30)	0.5657(18)	12.7(12)	1
C3	0.2241(22)	0.8662(31)	0.2241(22)	12.7(12)	1
C4	0.0469(36)	0.8745(29)	0.5555(40)	12.7(12)	0.5
C5	0.5	0.8715(27)	0.4178(30)	12.7(12)	1
C6	0.8672(14)	0.3598(24)	0.1328(14)	12.7(12)	1
C7	0.0831(33)	0.1054(32)	0.5121(47)	12.7(12)	0.5
C8	0.5400(27)	0.9827(49)	0.8331(25)	12.7(12)	0.5
C9	0.8492(18)	0.4784(17)	0.4784(17)	12.7(12)	1
C10	0.6544(26)	0.0360(33)	0.9354(25)	12.7(12)	0.5
O1w	0.7473(22)	0.8227(23)	0.2070(27)	25.0(27)	0.588(24)
O2w	0.5217(23)	0.5217(23)	0.6331(21)	25.0(27)	0.705(32)
O3w	0.2978(20)	0.7453(23)	0.7453(23)	25.0(27)	0.762(38)
O4w	0.5214(64)	0.5	0.2620(36)	25.0(27)	0.459(31)

Table S5. Selected bond distances and angles of PKU-12 (T = Si or Ge).

atom-atom	bond distances(Å)	atom-atom-atom	angles(°)	atom-atom-atom	angles(°)
T1_O1	1.655(11)	O1_T1_O2	114.9(15)	O10^{b}_T4_O12	109.27(80)
T1_O2	1.631(10)	O1_T1_O3	113.1(12)	O11_T4_O12	104.2(13)
T1_O3	1.694(22)	O1_T1_O4	108.4(12)	O9^{c}_T5_O9^{d}	110.7(15)
T1_O4	1.690(22)	O2_T1_O3	110.1(12)	O9^{c}_T5_O13	111.8(10)
T2_O3^{a}	1.651(22)	O2_T1_O4	102.8(13)	O9^{c}_T5_O14	107.85(88)
T2_O5	1.675(14)	O3_T1_O4	106.58(85)	O9^{d}_T5_O13	111.8(10)
T2_O6	1.697(11)	O3^{a}_T2_O5	111.9(13)	O9^{d}_T5_O14	107.85(88)
T2_O7	1.6491(95)	O3^{a}_T2_O6	108.25(87)	O13_T5_O14	106.5(17)
T3_O4^{a}	1.686(23)	O3^{a}_T2_O7	112.5(14)	T1_O1_T1^{a}	139.8(19)
T3_O8	1.642(13)	O5_T2_O6	106.37(99)	T1_O2_T1^{e}	147.16(42)
T3_O9	1.662(22)	O5_T2_O7	111.5(15)	T1_O3_T2^{a}	134.7(10)
T3_O10	1.646(22)	O6_T2_O7	105.9(15)	T1_O4_T3^{a}	143.9(13)
T4_10^{a}	1.674(23)	O4^{a}_T3_O8	107.4(12)	T2_O5_T2^{e}	131.3(16)
T4_10^{b}	1.674(23)	O4^{a}_T3_O9	102.68(99)	T2_O6_T2^{d}	142.35(43)

T4_11	1.661(12)	O4[a]_T3_O10	108.4(11)	T2_O7_T2[a]	155.48(44)
T4_12	1.667(13)	O8_T3_O9	111.5(13)	T3_O8_T3[d]	142.40(48)
T5_O9[c]	1.659(21)	O8_T3_O10	113.2(13)	T3_O9_T5[d]	144.21(37)
T5_O9[d]	1.659(21)	O9_T3_O10	112.9(11)	T3_O10_T4[a]	142.81(24)
T5_13	1.682(15)	O10[a]_T4_O10[b]	110.4(15)	T4_O11_T4[f]	144.52(65)
T5_14	1.735(30)	O10[a]_T4_O11	111.69(72)	T4_O12_T4[b]	153.97(57)
		O10[a]_T4_O12	109.27(80)	T5_O13_T5[c]	140.48(60)
		O10[b]_T4_O11	111.69(72)		

Symmetry code: a) x, y, 1-z; b) -x, y, 1-z; c) -x, z, y; d) x, z, y; e) 1-y, 1-x, z; f) –x, 1-z, 1-y.

Table S6. Crystallographic data, experimental conditions for X-ray data collection and results of the Rietveld analysis of calcined PKU-12.

Chemical formula of framework	$Si_{3.61}Ge_{4.39}O_{15.50}$ (OH)
Formula weight	872.78
Crystal system	Cubic
Space group	*Pm*-3*m*
a/Å	26.1847(1)
Cell volume/Å^3	17953 (2)
Z	24
Temperature/K	623(2)
Wavelength/Å	1.5418
2θ range/°	5 - 79.9971 (the first peak was excluded due to its inaccurate intensity)
R_p	0.048
R_{wp}	0.0674
R_{exp}	0.0208
GOF	3.24

Table S7. Atomic coordinates, thermal parameters and occupancies of calcined PKU-12.

Atom	*x*	*y*	*z*	B_{eq}(Å^2)*	Occupancy**
Si1	0.18256(49)	0.72606(50)	0.43887(45)	3.00(14)	0.384
Ge1	0.18256(49)	0.72606(50)	0.43887(45)	3.00(14)	0.616
Si2	0.26561(48)	0.64108(46)	0.55966(50)	3.00(14)	0.468
Ge2	0.26561(48)	0.64108(46)	0.55966(50)	3.00(14)	0.532
Si3	0.07862(54)	0.70462(43)	0.62103(57)	3.00(14)	0.543
Ge3	0.07862(54)	0.70462(43)	0.62103(57)	3.00(14)	0.457
Si4	0	0.64284(57)	0.44397(72)	3.00(14)	0.428
Ge4	0	0.64284(57)	0.44397(72)	3.00(14)	0.572
Si5	0	0.68459(69)	0.76740(81)	3.00(14)	0.390
Ge5	0	0.68459(69)	0.76740(81)	3.00(14)	0.610

O1	0.1633(21)	0.7124(19)	0.5	4.00(54)	1
O2	0.2216(16)	0.7784(16)	0.4381(20)	4.00(54)	1
O3	0.2106(13)	0.6681(13)	0.4236(13)	4.00(54)	1
O4	0.1291(14)	0.7334(13)	0.4063(15)	4.00(54)	1
O5	0.3156(16)	0.6844(16)	0.5595(19)	4.00(54)	1
O6	0.2799(20)	0.5914(15)	0.5914(15)	4.00(54)	1
O7	0.2542(21)	0.6165(20)	0.5	4.00(54)	1
O8	0.0973(21)	0.6526(14)	0.6526(14)	4.00(54)	1
O9	0.0513(13)	0.7476(15)	0.6530(13)	4.00(54)	1
O10	0.0515(11)	0.6799(11)	0.5695(14)	4.00(54)	1
O11	0	0.5929(20)	0.4071(20)	4.00(54)	1
O12	0	0.6190(28)	0.5	4.00(54)	1
O13	0	0.7453(22)	0.7453(22)	4.00(54)	1
O14	0	0.6936(20)	0.8322(21)	6.8(25)	1

note:* the large thermal factors may due to the higher temperature (350^{o}C) for data collection.
**the occupancy factors are taken from the structure parameters of as-synthesized PKU-12 for the consistency of the composition.

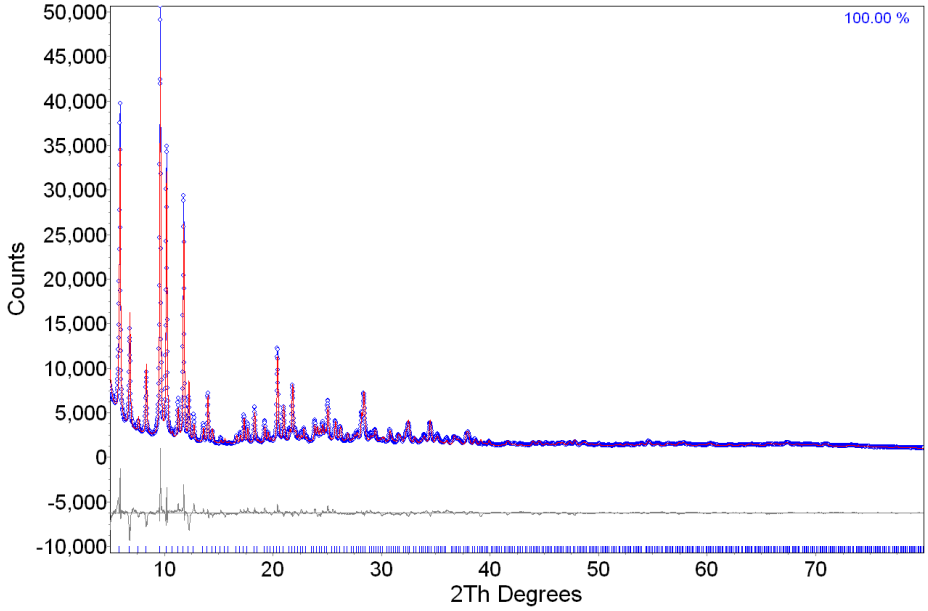

Fig S7: X-ray Rietveld refinement plot of calcined PKU-12. The blue circles are for the observed data. The red solid line is for the calculated data. The grey solid curve is for the difference. The vertical bars are for the positions of Bragg peaks.