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Interrupted silicogermanate with 10-ring channels: synthesis and structure determination by combining rotation electron diffraction and powder X-ray diffraction

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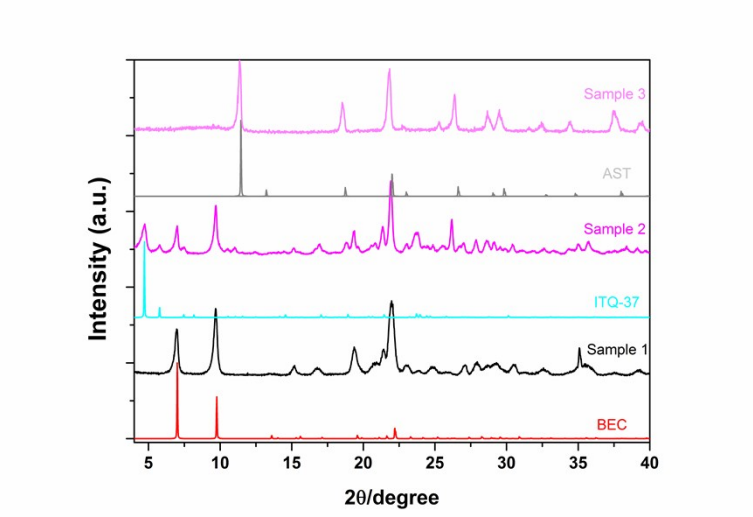

Fig. S1 PXRD patterns of the as-synthesized samples and the simulated PXRD patterns.

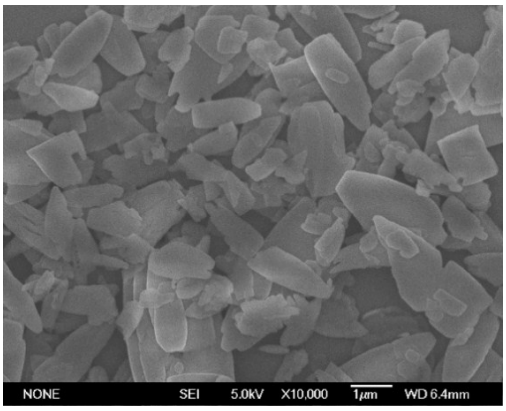

Fig. S2 The SEM image of as-synthesized JU110.

Table S1. The results of chemical and elemental analysis of the as-synthesised sample JU110 compared to the theoretical values calculated from the structure model

	In wt%					**In molar ratio**			
	Si	Ge	N	F	C	Ge/Si	C/N	N/F	(Si+Ge)/N
Observed	1.99	50.08	1.62	2.41	12.55	9.7	9.0	1.1	6.57
Calculated	2.18	52.90	1.67	2.27	12.90	9.5	9.0	1.0	6.75

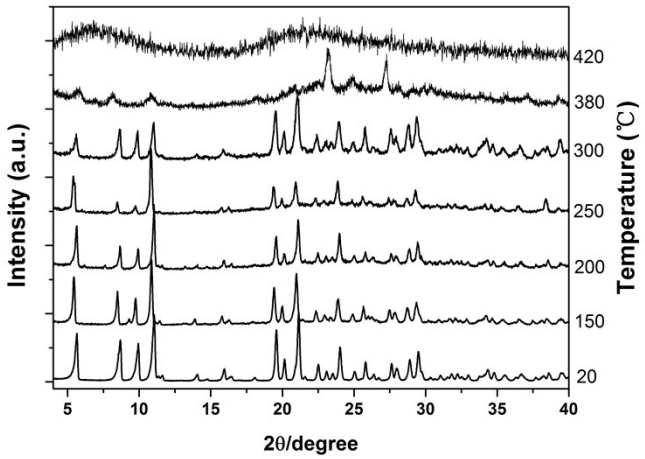

Fig. S3 The *in-situ* variable temperature PXRD patterns of Ge-JU110.

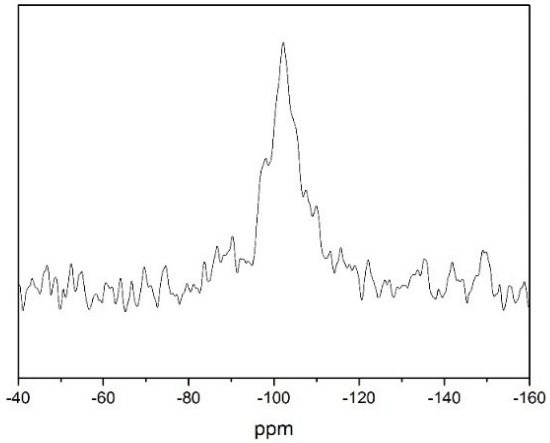

Fig. S4 The ^{29}Si MAS NMR spectrum of as-synthesized JU110

Table S2. RED data collection, crystal data and structure refinement details of JU110 (resolution cut to 1.0Å)

Tilt angle	– 63.59° to + 32.37°
Tilt step	0.2°
No. of RED frames	528
Exposure time/frame	2.0 s
a / Å	13.88
b / Å	18.56
c / Å	33.59
α / °	89.26
β / °	89.98
γ / °	89.13
Space group	*Fmmm*
Completeness	0.530
*R*int	0.335

No. of measured reflections	885
No. of independent reflections	305
h	$-13 \le h \le 13$
k	$-14 \le k \le 14$
l	$-22 \le l \le 22$
$R1$[1]	0.401
No. of parameters	53
No. of restraints	65

[1] The structure refinement was done with a structure model with Ge atoms in all the T-sites. The occupancy of Ge/Si at each site could not be refined.

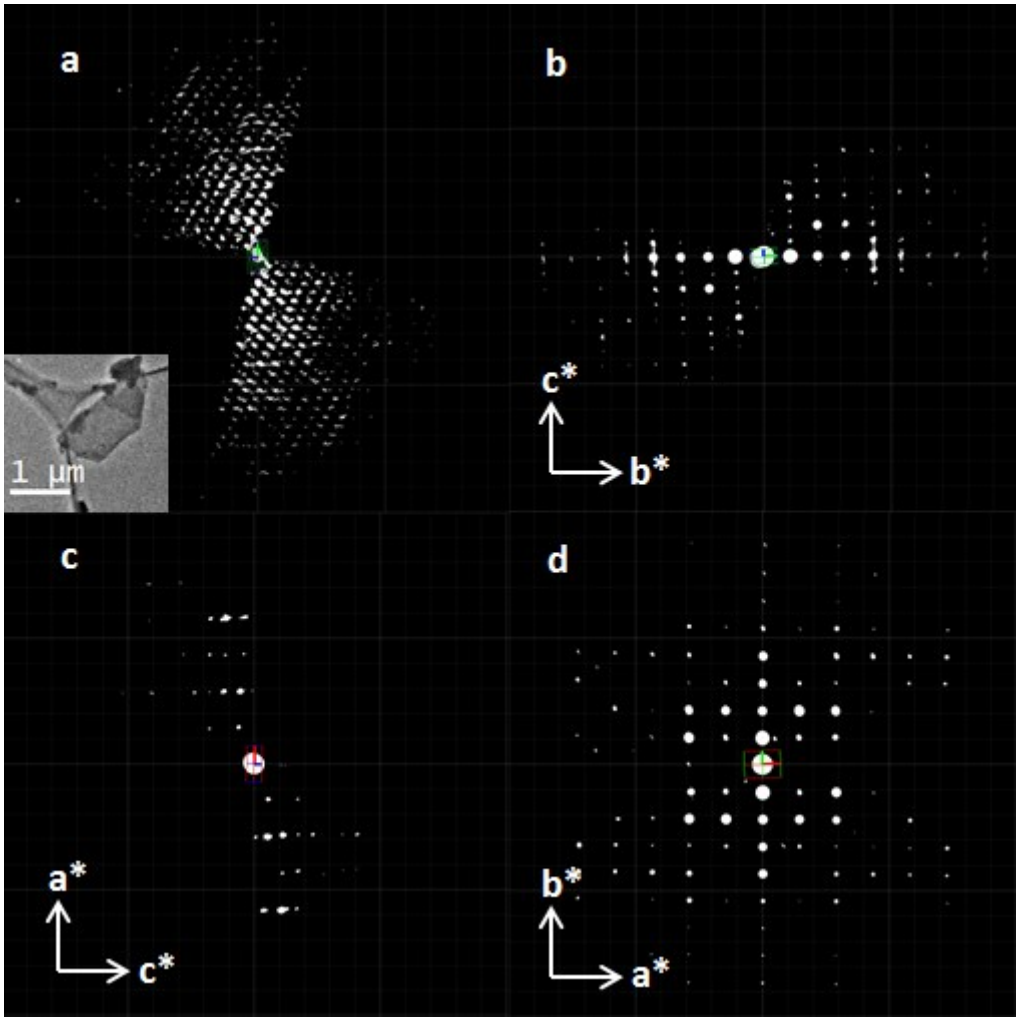

Fig. S5 (a) 3D reciprocal space reconstruction from the RED data. The target crystal from which RED data were collected is shown. The 2D slice of 0*kl* (b), *h*0*l* (c), *hk*0 (d) show mmm symmetry, confirming an orthorhombic system. The reflection conditions are deduced to be: *hkl*: *h* + *k* = 2*n*, *h* + *l* = 2*n*, *k* + *l* = 2*n*; 0*kl*: *k* = 2*n*, *l* = 2*n*; *h*0*l*: *h* = 2*n*, *l* = 2*n*; *hk*0: *h* = 2*n*, *k* = 2*n*; *h*00: *h* = 2*n*; 0*k*0: *k* = 2*n*. The possible space groups are *F*222, *Fmm*2, *Fm*2*m*, *F*2*mm*, *Fmmm*.

S1. Rietveld refinement of as-synthesised JU110 against PXRD data

High-resolution PXRD data of JU110 was collected at 100 K at experimental station 11-BM at APS, using monochromated X-rays of wavelength 0.459255 Å. The sample was sealed in a kapton capillary of 1.0 mm in diameter. The structure model of JU110 was initiated using the atomic coordinates obtained from RED data and refined by Rietveld refinement using Topas Academic version 4.1. The refinement was conducted using a Pearson VII type peak profile function, followed by refinement of background, unit cells and zero-shift. Geometric restraints were applied to all unique bond distances and angles (1.74 Å for T-O bond lengths and 109.5° for O-T-O bond angles, except the bond lengths and bond angles for Ge10). The SDA molecules were located by simulated annealing algorithm, while the F- ions and the disordered Ge7 clusters were found from the Fourier difference map. Finally, *R*-value was converged to R_p= 0.090, R_{wp}= 0.119, R_{exp}= 0.042, and GOF= 2.81.

Table S3. Crystallographic data, experimental conditions for powder X-ray data collection and results of the Rietveld refinement of JU110.

Chemical formula	$C_9H_{16}FGe_{6.11}NO_{13.75}Si_{0.64}$
Formula weight	837.98 g/mol
Crystal system	Orthorhombic
Space group	*Fm*2*m*
a/Å	13.9117(2)
b/Å	18.2980(3)
c/Å	32.7800(6)
Z	16
Temperature/K	100 K
Wavelength/Å	0.427654
2ϑ range/°	0.6-28
No. of reflections	1501
No. of structural variables	160
No. of restraints	36 for T-O and 54 for O-T-O
R_p	0.090
R_{wp}	0.119
R_{exp}	0.042
GOF	2.81

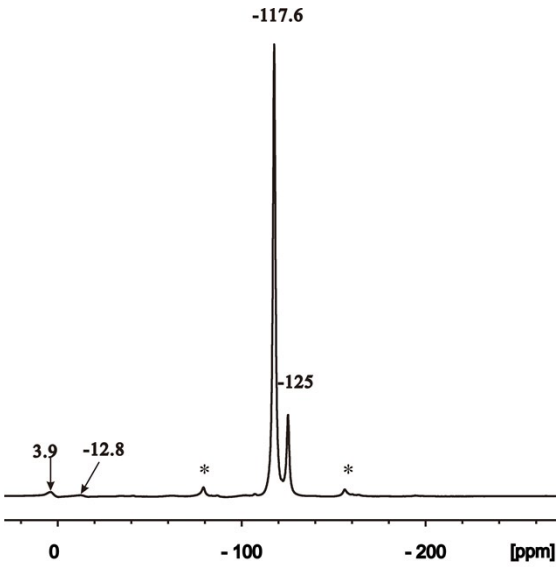

Fig. S6 The ^{19}F MAS NMR spectrum of as-synthesized JU110. The resonance at -12.8 ppm suggests fluoride inside the D4R units [Pulido *et al*, ChemPhysChem 2006, 7, 1092 – 1099]. The resonances at -117.6 ppm and -125 ppm are possibly due to germanium oxyfluoride impurities caused by hydrolysis of the materials on washing with water [Villaescusa *et al*, DaltonTrans., 2004,820 – 824].

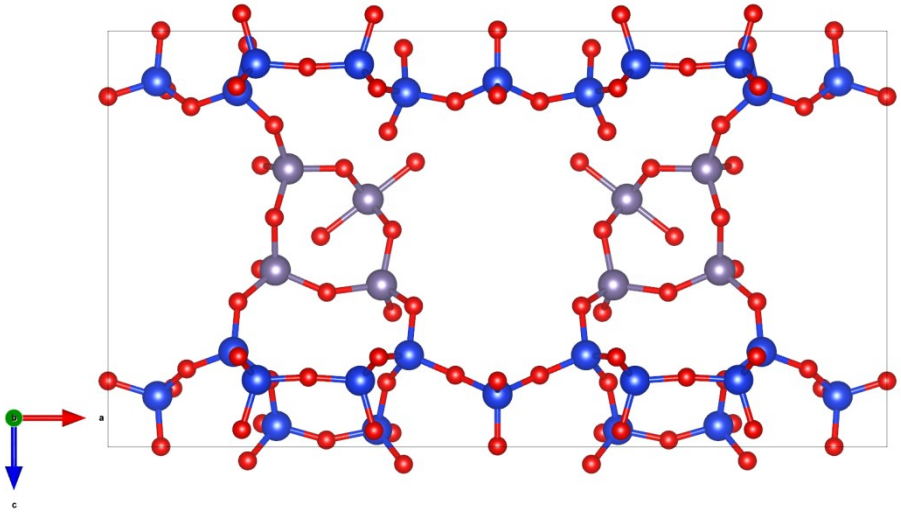

Fig. S7 [010] projection of the hypothetical structure model built by replacing the D4Rs in the **UWY** zeolite framework by Ge_7 clusters (blue: Si, gray: Ge, red: O). The hypothetical structure has space group *Pmm*2 with a = 24.22 Å, b = 11.80 Å, c =12.92 Å.

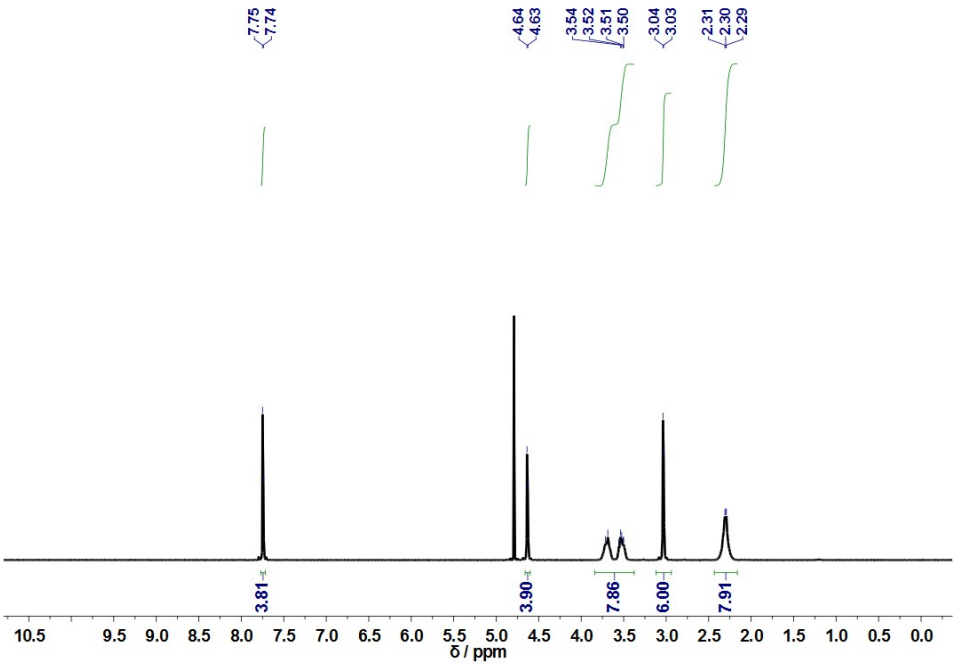

Fig.S8 The ^{1}H NMR spectra of OSDABr.