Supporting information

Synthesis and crystal structure of $Fe_6Ca_2(SeO_3)_9Cl_4$ - a porous oxohalide

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Experimental

High purity powder of $Fe_6Ca_2(SeO_3)_9Cl_4$ **1** for adsorption- and TG measurements were prepared from a mixture of 0.120g Fe_2O_3, 0.250g SeO_2 and 0.028g CaO (molar ratio 3:9:2) that were first dissolved in 2 ml hydrochloric acid and then allowed to evaporate slowly at room temperature. The mixture was subsequently sealed in a steel autoclave and treated at 200 °C for four days. Yellow powder of **1** was obtained by washing with ethanol and drying at room temperature.

Single-crystal X-ray data were collected at 20 °C on an Oxford Diffraction Xcalibur3 diffractometer using graphite-monochromatized Mo K_α radiation, $\lambda = 0.71073$ Å. Data reduction and absorption correction were made using the software provided by the diffractometer manufacturer. The crystal structure were solved by direct methods using the program SHELXS-97 and refined by full matrix least squares on F^2 using the program SHELXL-97 [S1]. All atoms were refined with anisotropic displacement parameters. Details of the final refinement are showed in Table S1. The structural drawings are made with the program DIAMOND [S2]. The electron density map was calculated by program Jana 2006 [S3] and plotted by use of the program VESTA [S4]. Bond valence sum calculations (BVS) were made using the following R_0 values: 1.811 for Se-O bonds, 1.759 for Fe-O bonds, 1.967 for Ca-O bonds [S5] and 2.09 for Fe-Cl bonds [S6].

Thermogravimetrical analysis was carried out using a Perkin Elmer TGA7 in nitrogen atmosphere. A sample weight of ~7 mg was heated from 20 °C to 950 °C with a heating rate of 10 °C/min.

Sorption experiments with H_2O vapour (20°C), CO_2 (0 °C) and N_2 (-195.7 °C), respectively, were carried out gravimetrically using a Micromeritics ASAP2020HD instrument. All samples were degased under vacuum at 150 °C for 12 hours before start of measurement.

Crystal structure refinement data

Table S1

Crystal Data and Structure Refinement Parameters for $Fe_6Ca_2(SeO_3)_9Cl_4$.

Empirical formula	$Fe_6Se_9Ca_2O_{27}Cl_4$
Formula weight	1699.70
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Hexagonal
Space group	P 63/m
a (Å)	12.118(2)
c (Å)	12.703(4)
Volume (Å ^{3})	1615.6(6)
Z	2
$\text{Density}_{\text{calc,}}$ (g cm^{-3})	3.494
F(000)	1572
Crystal color	Yellow
Crystal habit	Needle
Crystal size (mm)	0.23 x 0.03 x 0.02
Theta range for data collection (°)	4.20 to 27.32
Index ranges	$-13 \leq h \leq 15$ $-15 \leq k \leq 11$ $-16 \leq l \leq 12$
Reflections collected	1209
Independent reflections	850[R(int) = 0.0826]
Data / restraints / parameters	1209 / 0 / 81
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	0.936
Final R indices [I > 2sigma(I)] [a]	$R_1 = 0.0393$ $wR_2 = 0.0774$
R indices (all data)	$R_1 = 0.0750$ $wR_2 = 0.0855$

[a] $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table S2

Atomic coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for $Fe_6Se_9Ca_2O_{27}Cl_4$.

Atom	*x*	*y*	*z*	*U*(eq)
Se(1)	0.41350(9)	0.44350(9)	$^{1}/_{4}$	0.0167(3)
Se(2)	0.83018(6)	0.63714(7)	0.00917(6)	0.0180(2)
Fe(1)	0.69309(15)	0.58443(19)	$^{1}/_{4}$	0.0343(5)
Fe(2)	$^{1}/_{2}$	$^{1}/_{2}$	0	0.0159(3)
Ca(1)	$^{1}/_{3}$	$^{2}/_{3}$	0.1145(2)	0.0191(6)
Cl(1)	0.7090(3)	0.7843(3)	$^{1}/_{4}$	0.0411(8)
Cl(2)	$^{2}/_{3}$	$^{1}/_{3}$	$^{1}/_{4}$	0.0580(17)
O(1)	0.5022(5)	0.6674(4)	0.0212(4)	0.0205(12)
O(2)	0.8110(5)	0.6201(5)	0.1403(4)	0.0286(13)
O(3)	0.3740(6)	0.5562(6)	$^{1}/_{4}$	0.0197(16)
O(4)	0.5343(4)	0.4997(4)	0.1550(4)	0.0193(11)
O(5)	0.3182(4)	0.4073(5)	0.0383(4)	0.0218(12)

Note. *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S3

Selected Bond Lengths (Å) and Angles (º) for $Fe_6Se_9Ca_2O_{27}Cl_4$.

Se1—O3	1.658(9)	Fe2—O1^{iii}	2.033(6)
Se1—O4^{i}	1.751(5)	Fe2—O1	2.033(6)
Se1—O4	1.751(5)	Ca1—O1^{iv}	2.361(4)
Se2—O2	1.680(5)	Ca1—O1	2.361(6)
Se2—O1^{ii}	1.708(6)	Ca1—O1^{v}	2.360(4)
Se2—O5^{iii}	1.708(5)	Ca1—O3^{iv}	2.378(2)
Se2—Ca1^{iii}	3.557(1)	Ca1—O3^{v}	2.378(2)
Fe1—O2^{i}	1.885(6)	Ca1—O3	2.379(6)
Fe1—O2	1.885(6)	Ca1—Ca1^{i}	3.443(4)
Fe1—O4^{i}	2.059(5)	Ca1—Se2^{vi}	3.556(1)
Fe1—O4	2.059(5)	Ca1—Se2^{iii}	3.557(1)
Fe1—Cl1	2.332(5)	Ca1—Se2^{vii}	3.557(1)
Fe2—O5^{iii}	1.969(4)	O1—Se2^{vii}	1.708(4)
Fe2—O5	1.969(4)	O3—Ca1^{i}	2.379(6)
Fe2—O4	2.013(5)	O5—Se2^{iii}	1.708(5)
Fe2—O4^{iii}	2.013(5)		

O3—Se1—O4^{i}	102.07(16)	O1—Ca1—O3	86.67(12)
O3—Se1—O4	102.07(16)	O1^{v}—Ca1—O3	160.10(4)
O4^{i}—Se1—O4	87.13(23)	O3^{iv}—Ca1—O3	73.41(1)
O2—Se2—O1^{ii}	100.08(25)	O3^{v}—Ca1—O3	73.4()
O2—Se2—O5^{iii}	104.60(27)	O1^{ii}—Se2—O5^{iii}	98.72(22)
O2^{i}—Fe1—O2	95.35(24)	O2^{i}—Fe1—O4^{i}	95.36(24)
O2—Fe1—O4^{i}	163.78(22)	O2^{i}—Fe1—O4	163.78(22)
O2—Fe1—O4	95.36(24)	O4^{i}—Fe1—O4	71.78(20)
O2^{i}—Fe1—Cl1	95.87(17)	O2—Fe1—Cl1	95.87(17)
O4^{i}—Fe1—Cl1	95.12(12)	O4—Fe1—Cl1	95.12(12)
O5^{iii}—Fe2—O5	179.99(23)	O5^{iii}—Fe2—O4	93.99(21)
O5—Fe2—O4	86.01(21)	O5^{iii}—Fe2—O4^{iii}	86.01(21)
O5—Fe2—O4^{iii}	93.99(21)	O4—Fe2—O4^{iii}	179.99(20)
O5^{iii}—Fe2—O1^{iii}	89.38(22)	O5—Fe2—O1^{iii}	90.62(22)
O4—Fe2—O1^{iii}	91.57(19)	O4^{iii}—Fe2—O1^{iii}	88.43(19)
O5^{iii}—Fe2—O1	90.62(22)	O5—Fe2—O1	89.38(22)
O4—Fe2—O1	88.43(19)	O4^{iii}—Fe2—O1	91.57(19)
O1^{iii}—Fe2—O1	179.99(18)	O1^{iv}—Ca1—O1	96.99(14)
Se2^{vii}—O1—Fe2	119.11(22)	O1^{iv}—Ca1—O1^{v}	97.02(12)
Se2^{vii}—O1—Ca1	121.06(28)	O1—Ca1—O1^{v}	97.01(16)
Fe2—O1—Ca1	118.94(25)	O1^{iv}—Ca1—O3^{iv}	86.7(1)
Se2—O2—Fe1	143.47(32)	Se2^{iii}—O5—Fe2	142.53(34)
O1—Ca1—O3^{iv}	160.06(14)	Se1—O3—Ca1	133.65(2)
O1^{v}—Ca1—O3^{iv}	101.99(7)	Se1—O3—Ca1^{i}	133.65(2)
O1^{iv}—Ca1—O3^{v}	160.11(12)	Ca1—O3—Ca1^{i}	92.69(1)
O1—Ca1—O3^{v}	101.95(11)	Se1—O4—Fe2	122.80(27)

O1^{v}—Ca1—O3^{v}	86.71(4)	Se1—O4—Fe1	100.44(23)
O3^{iv}—Ca1—O3^{v}	73.42(1)	Fe2—O4—Fe1	135.64(27)
O1^{iv}—Ca1—O3	101.95(10)		

Bond valence sum calculations

Table S4

Results from Bond Valence Sum (BVS) calculations of $Fe_6Se_9Ca_2O_{27}Cl_4$.

Atoms	Bonding distance	Bond valence	Atoms	Bonding distance	Bond valence
Se1—O3	1.658(9)	1.51	Fe1—O2^{i}	1.885(6)	0.71
Se1—O4^{i}	1.751(5)	1.18	Fe1—O2	1.885(6)	0.71
Se1—O4	1.751(5)	1.18	Fe1—O4^{i}	2.059(5)	0.44
		3.87	Fe1—O4	2.059(5)	0.44
			Fe1—Cl1	2.332(5)	0.52
Se2—O2	1.680(5)	1.42	Fe1—Cl2	2.897(2)	0.11
Se2—O1^{ii}	1.708(6)	1.32			**2.93**
Se2—O5^{iii}	1.708(5)	1.32			
		4.06			
Ca1—O1^{iv}	2.361(4)	0.34	Fe2—O5^{iii}	1.969(4)	0.57
Ca1—O1	2.361(6)	0.34	Fe2—O5	1.969(4)	0.57
Ca1—O1^{v}	2.360(4)	0.34	Fe2—O4	2.013(5)	0.50
Ca1—O3^{iv}	2.378(2)	0.33	Fe2—O4^{iii}	2.013(5)	0.50
Ca1—O3^{v}	2.378(2)	0.33	Fe2—O1^{iii}	2.033(6)	0.48
Ca1—O3	2.379(6)	0.33	Fe2—O1	2.033(6)	0.48
		2.01			**3.10**

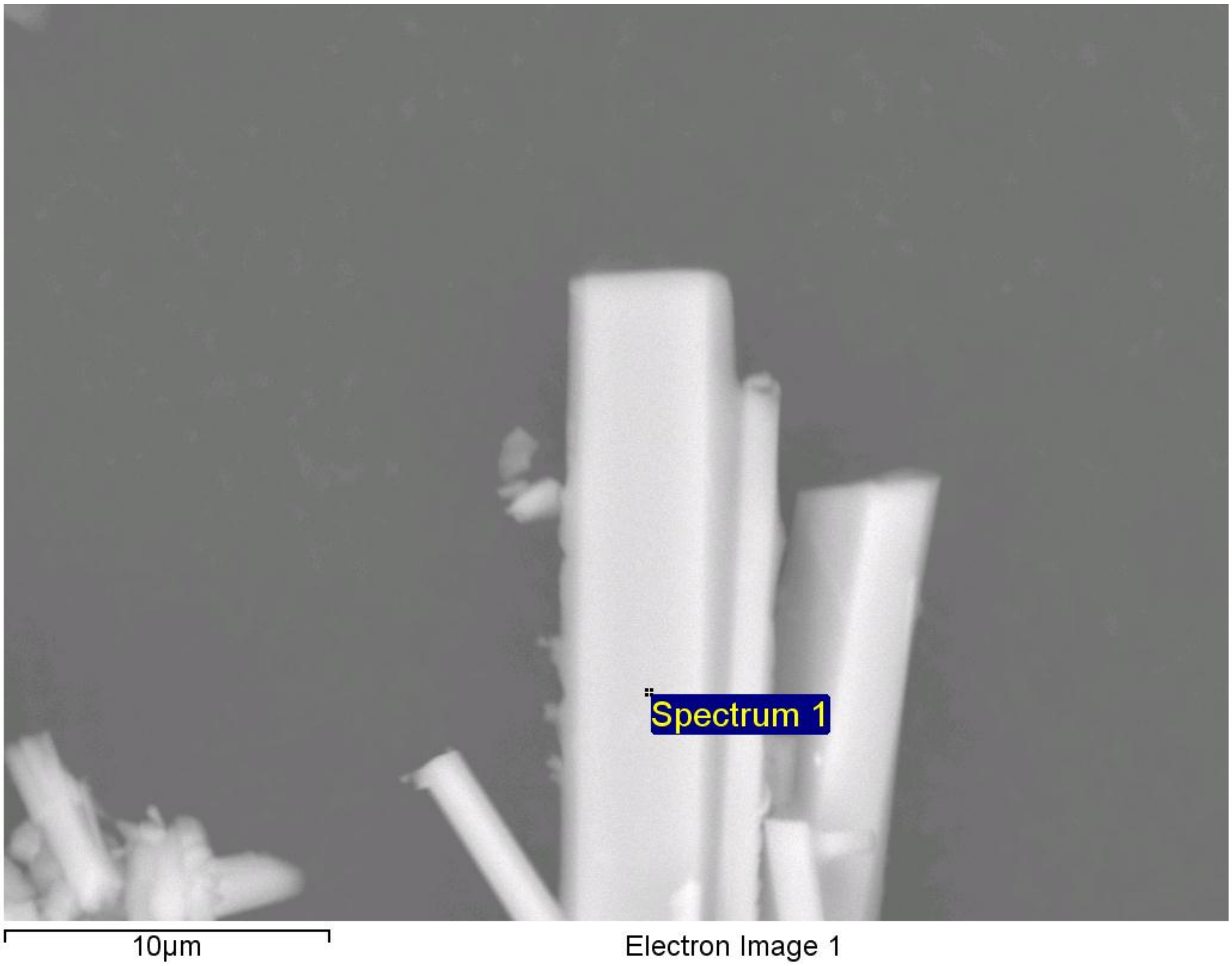
Atoms	Bond valence
Cl1	**0.52**
Cl2	**0.34**
O1	**2.14**
O2	**2.13**
O3	**2.17**
O4	**2.12**
O5	**1.89**

Note. Symmetry transformations used to generate equivalent atoms:
(i) x, y, 0.5-z; (ii) 1+x-y, x, -z; (iii) 1-x, 1-y, -z; (iv) -x+y, 1-x, z;
(v) 1-y, 1+x-y, z; (vi) x-y, x, -z; (vii) y, 1-x+y, -z.

EDS analysis

The chemical composition of the $Fe_6Se_9Ca_2O_{27}Cl_4$ and $Fe_6Se_9Ca_2O_{27}Br_4$ synthesis product was confirmed by using energy-dispersive spectrometry (EDS) in a scanning electron microscope (SEM, JEOL-7000F).

(A) $Fe_6Se_9Ca_2O_{27}Cl_4$

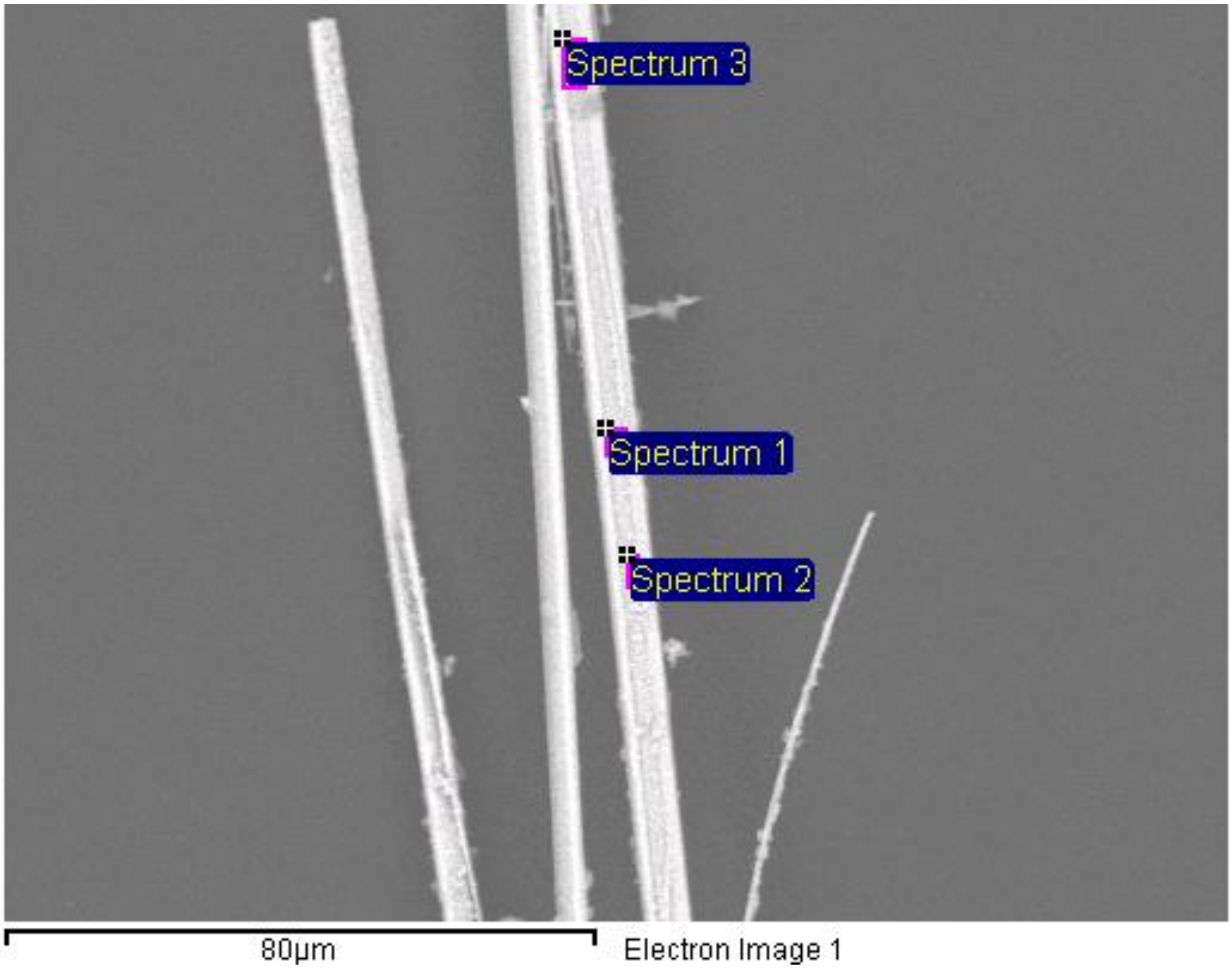


Processing option: All elements analysed (Normalised)

Spectrum	In stats.	O	Cl	Ca	Fe	Se
Spectrum 1	Yes	54.25	8.45	4.67	15.21	17.42
Mean		54.25	8.45	4.67	15.21	17.42
Std. deviation		0.00	0.00	0.00	0.00	0.00
Max.		54.25	8.45	4.67	15.21	17.42
Min.		54.25	8.45	4.67	15.21	17.42

All results in atomic%

(B) $Fe_6Se_9Ca_2O_{27}Br_4$

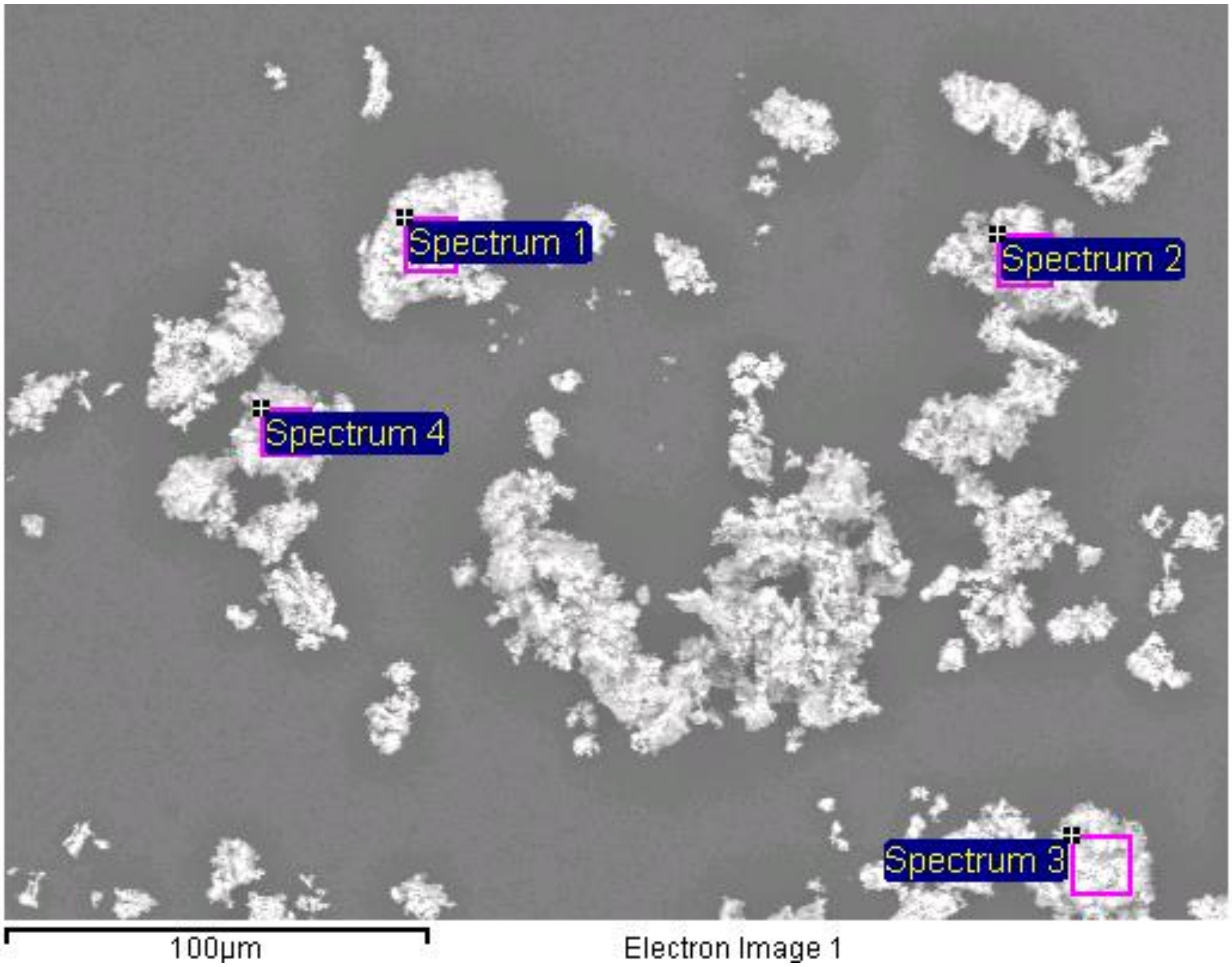


Processing option: All elements analysed (Normalised)

Spectrum	In stats.	O	Ca	Fe	Se	Br
Spectrum 1	Yes	65.03	4.11	8.53	11.83	10.49
Spectrum 2	Yes	71.24	2.84	6.93	10.40	8.59
Spectrum 3	Yes	63.57	3.86	9.60	14.03	8.94
Mean		66.61	3.60	8.35	12.09	9.34
Std. deviation		4.07	0.67	1.34	1.83	1.01
Max.		71.24	4.11	9.60	14.03	10.49
Min.		63.57	2.84	6.93	10.40	8.59

EDS analysis on the residual powder after TG measurements.

(C) Residual powder from TG measurement which was interrupted at 700 °C

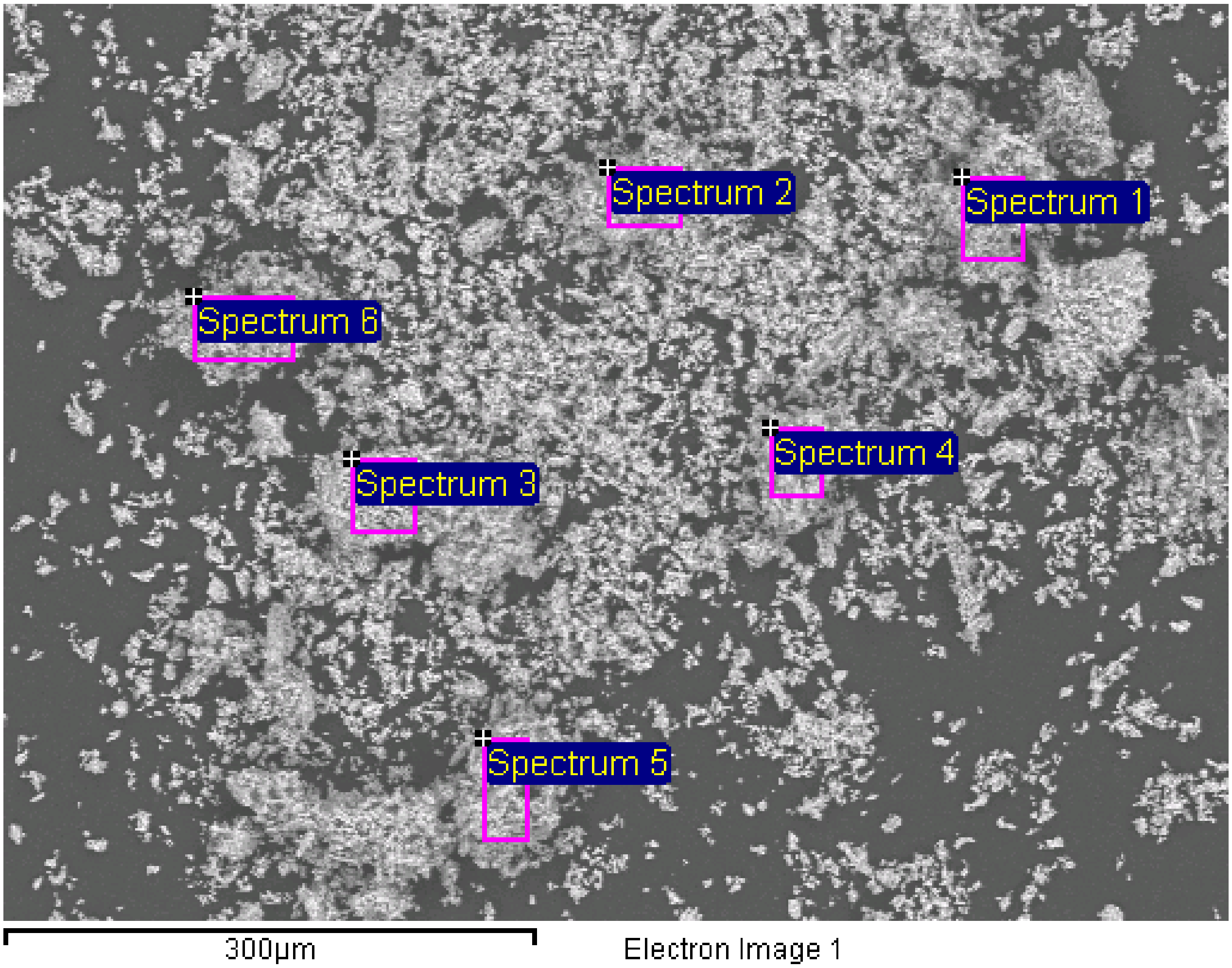


Processing option: All elements analysed (Normalised)

Spectrum	In stats.	O	Cl	Ca	Fe	Se
Spectrum 1	Yes	66.30	6.40	13.57	5.20	8.52
Spectrum 2	Yes	67.62	3.56	7.33	17.24	4.25
Spectrum 3	Yes	64.31	4.68	7.56	18.92	4.53
Spectrum 4	Yes	69.49	4.97	12.03	6.07	7.45
Mean		66.93	4.90	10.12	11.86	6.19
Std. deviation		2.18	1.17	3.16	7.23	2.12
Max.		69.49	6.40	13.57	18.92	8.52
Min.		64.31	3.56	7.33	5.20	4.25

All results in atomic%

(D) Residual powder from TG measurement terminated at 950 °C



Processing option: All elements analysed (Normalised)

Spectrum	In stats.	O	Cl	Ca	Fe	Se
Spectrum 1	Yes	66.97	0.03	11.74	21.25	0.01
Spectrum 2	Yes	64.77	0.02	11.88	23.29	0.03
Spectrum 3	Yes	60.49	0.26	12.58	26.71	-0.05
Spectrum 4	Yes	63.18	0.09	13.29	23.41	0.02
Spectrum 5	Yes	63.76	0.12	12.26	23.75	0.12
Spectrum 6	Yes	61.80	0.07	13.24	24.97	-0.08
Mean		63.50	0.10	12.50	23.90	0.01
Std. deviation		2.27	0.09	0.66	1.83	0.07
Max.		66.97	0.26	13.29	26.71	0.12
Min.		60.49	0.02	11.74	21.25	-0.08

All results in atomic%

Sorption data

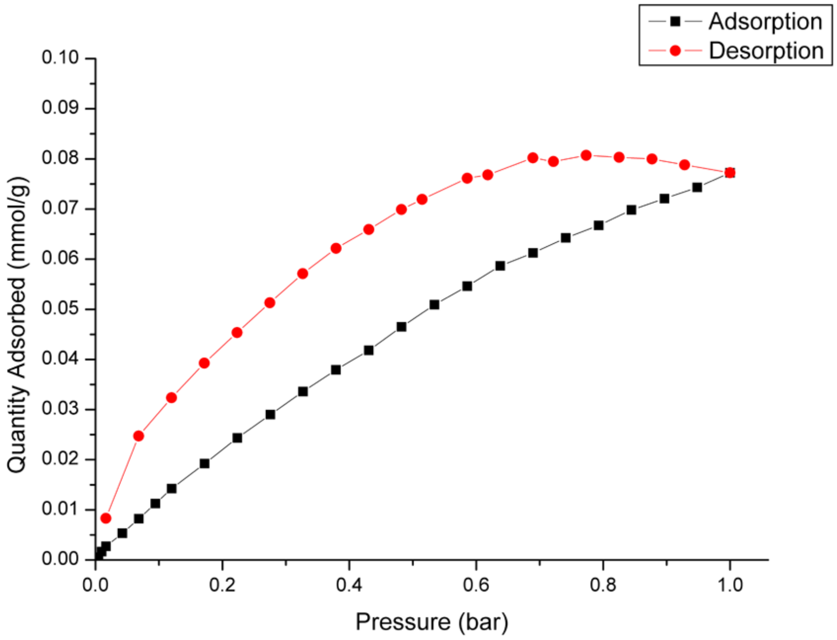


Figure S1 Carbon dioxide isotherm recorded at 273 K.

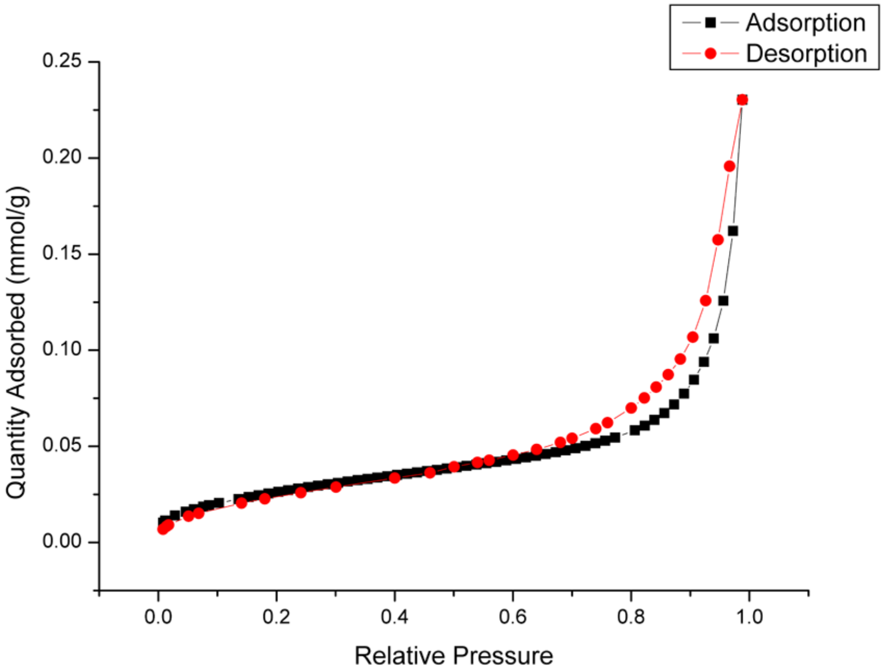


Figure S2 Nitrogen isotherm recorded at 77 K.

Powder X-Ray diffraction patterns

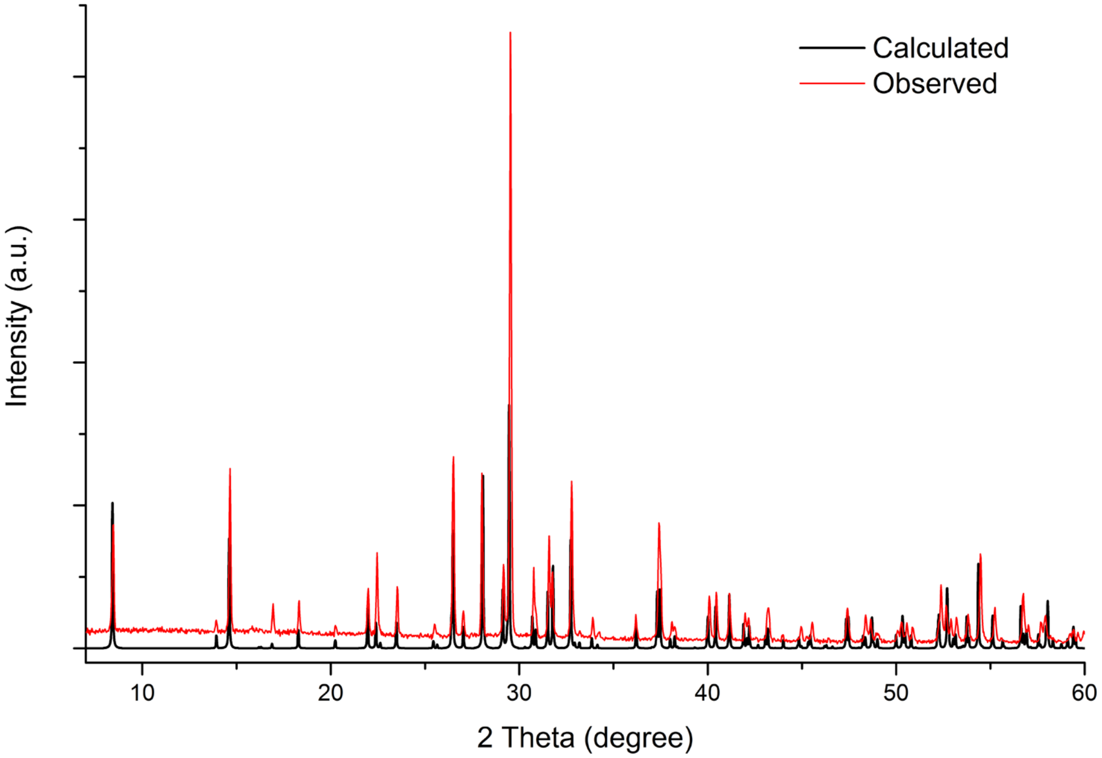


Figure S3 Simulated and experimental powder x-ray diffraction patterns (PXRD) on $Fe_6Ca_2(SeO_3)_9Cl_4$. The diffraction peaks on the experimental and simulated patterns correspond well in position indicating the purity of the as-prepared samples. The intensity difference is caused by preferred orientation in the observed diffractogram since the crystals are needle like.

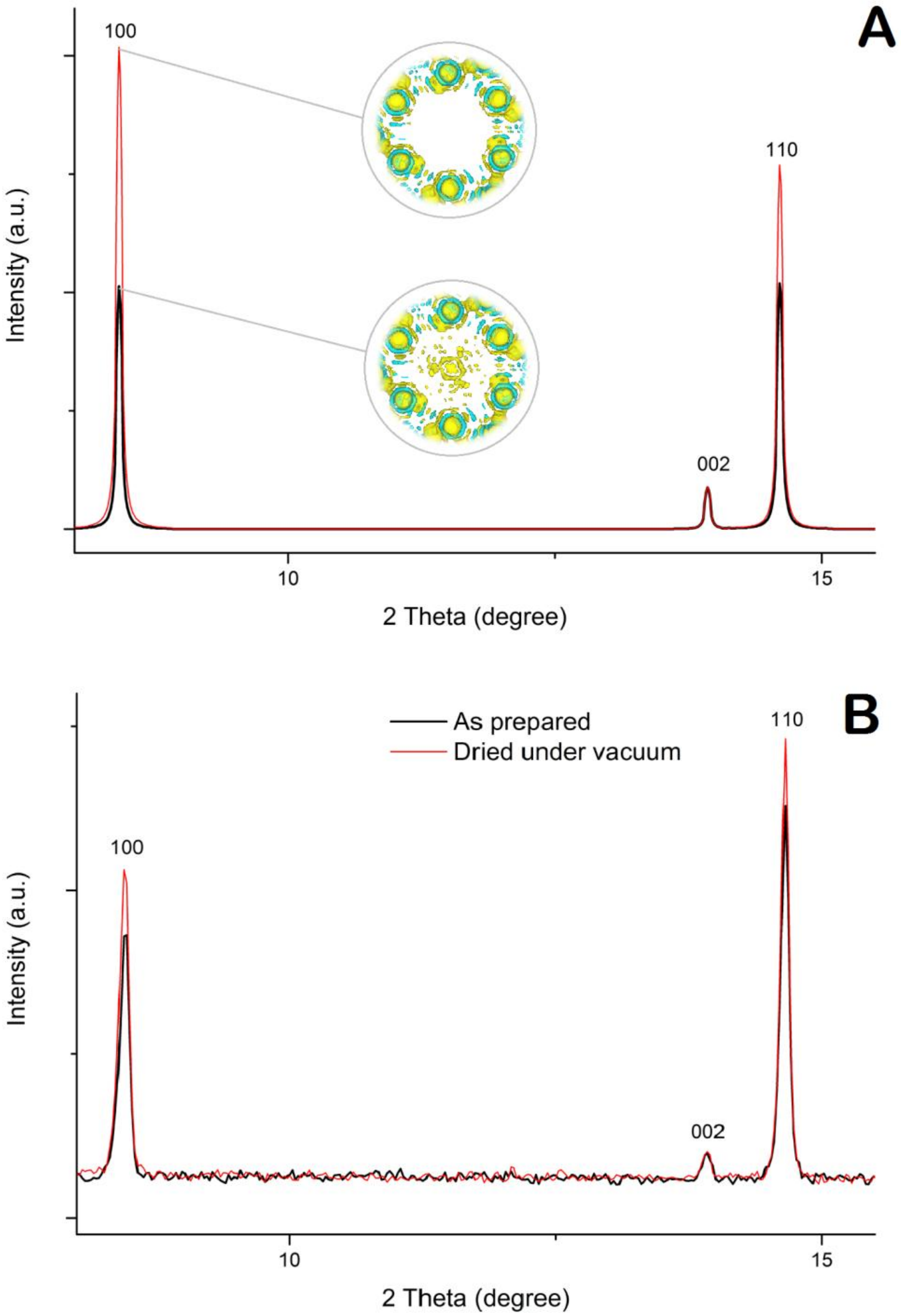


Figure S4 **(A)** PXRD patterns of $Fe_6Ca_2(SeO_3)_9Cl_4$ simulated by including and excluding the residual electron density in the channels. **(B)** PXRD collected from as-prepared and dry sample, respectively. The intensity enhancement after drying sample under vacuum suggests that part of the residual electron density which represents water molecules has been removed.

References

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