crystals

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Supplementary Materials

Structural Refinement and Density Functional Theory Study of Synthetic Ge-Akaganéite (β-FeOOH)

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Received: 14 February 2020; Accepted: 23 March 2020; Published: date

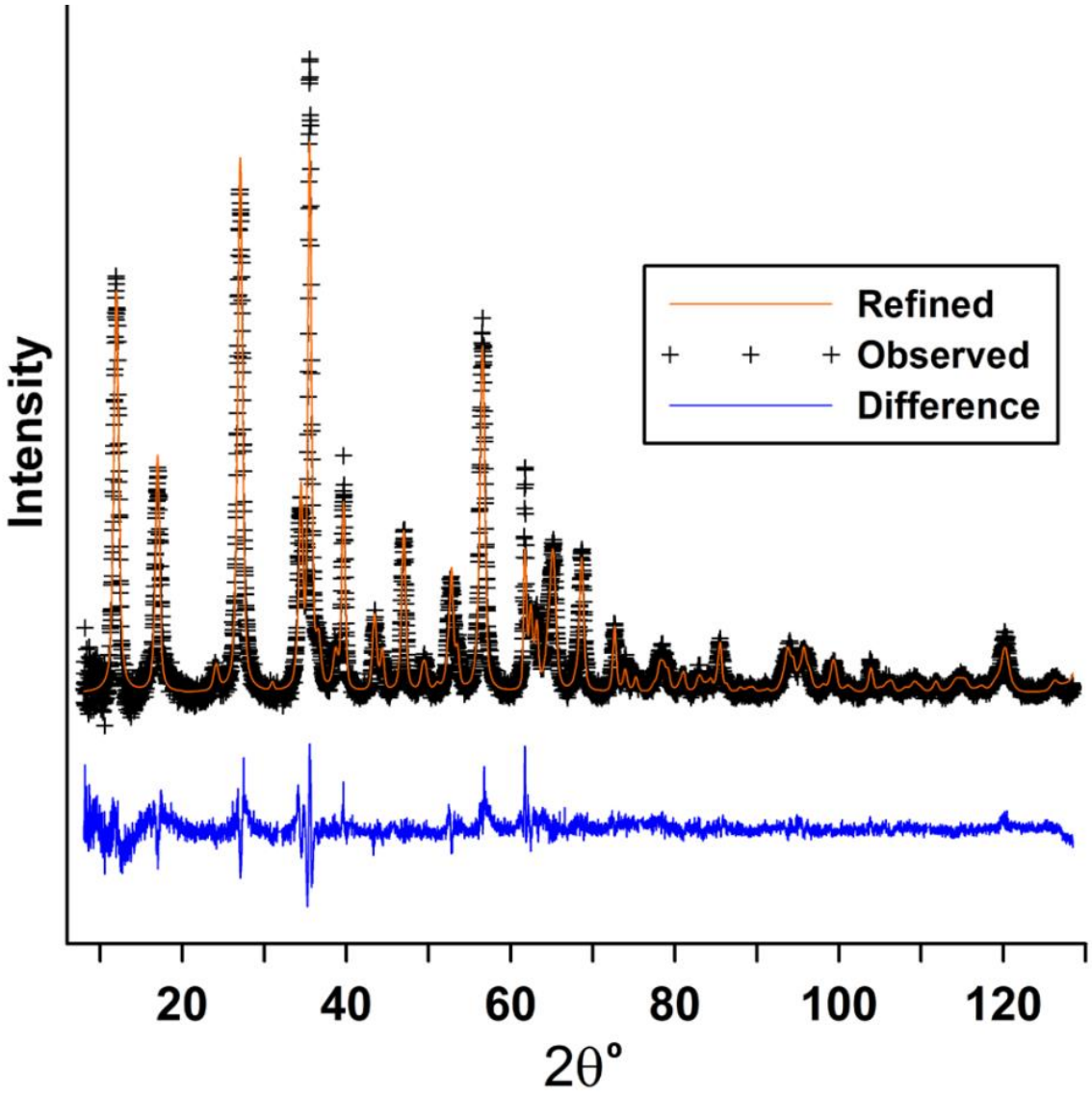

Figure S1. Profile-fitting between the observed and refined structure of Ge-akaganéite.

Table S1. Experimental details.

Crystal Data	
Chemical formula	$Cl_{0.20}Fe_{1.80}\{Ge(OH)_4\}_{0.05}Ge_{0.20}O_4$ *
M_r	194.19
Crystal system, space group	Monoclinic, *I*2/*m*
Temperature (K)	298
a, *b*, *c* (Å)	10.4441 (8), 3.01781 (15), 10.5016 (13)
β (°)	90.339 (11)
V (Å^3)	330.99 (5)
Z	4
Radiation type	Synchrotron, λ = 1.549 Å
Specimen shape	Flat sheet
Data Collection	
Diffractometer	Si-strip 1D
Specimen mounting	Flat_plate_holder
Data collection mode	Reflection
Scan method	Step
2θ values (°)	$2\theta_{min}$ = 8.01 $2\theta_{max}$ = 128.59 $2\theta_{step}$ = 0.02
Refinement	
R factors and goodness of fit	R_p = 0.051, R_{wp} = 0.068, R_{exp} = 0.040, $R(F^2)$ = 0.11396, χ^2 = 2.890
No. of parameters	27

Computer programs: *GSAS* (Larson & Von Dreele, 2004).

* $Ge(OH)_4$ was assumed to be Gd during Rietveld refinement considering the number of electrons and symmetry.

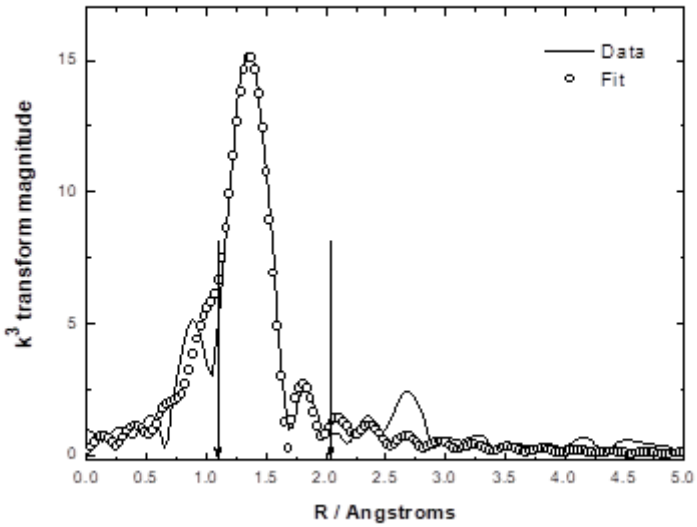

Figure S2. Magnitudes of the Fourier transform of the k3-weighted Ge K-edge EXAFS spectrum of Ge-akaganéite. The phase shifts were not corrected. The arrows indicate the r-range over which the fit was performed. EXAFS spectra were collected in the transmission mode using the powdered samples at room temperature. Ionization chambers were used as detectors for measuring the incident and transmitted X-ray beam intensities. The EXAFS data were analysed following the standard method of the UWXAFS software package.

Table S2. Curve-fitting results for Ge K-edge EXAFS spectra of Ge-akaganéite**.** The number in the parentheses is the uncertainty in last digit of the paramenters.

Shell	CN	R (Å)	σ^2 (× 10^{-4} Å ^{2})	R-Factor
Ge–O	5.1 (5)	1.759 (7)	39 (7)	0.0147

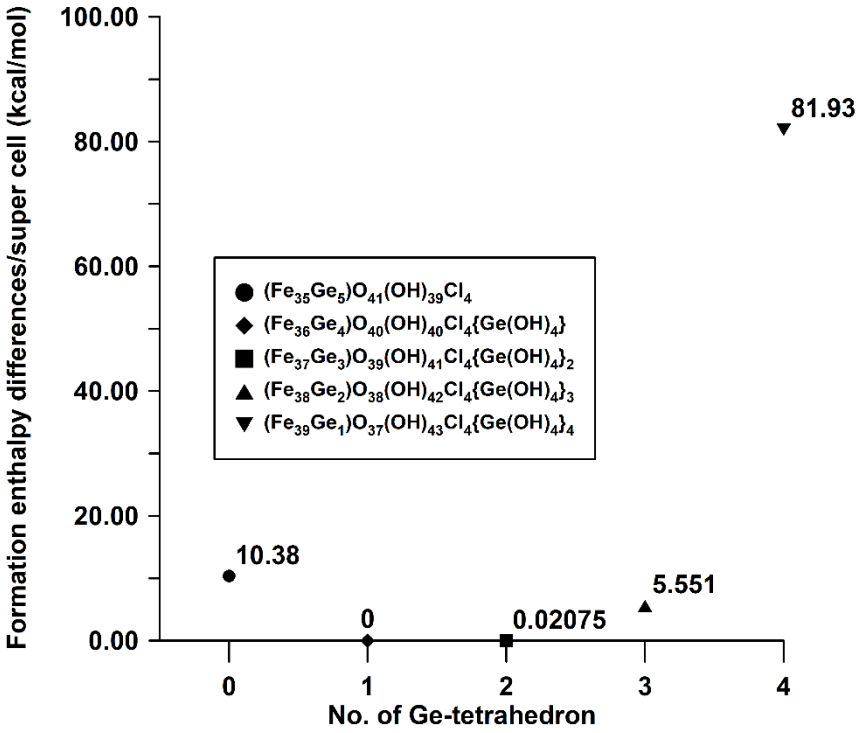

Figure S3. Plots of the formation enthalpy differences for 5 hypothetical models with different *N* values. Model enthalpy differences are 10.38, 0, 0.02075, 5.551 and 81.93 kcal/mol, respectively, with respect to model Ⅱ.

Table S3. Enthalpy of elements in the newly proposed Ge-akaganéite after DFT-D calculation.

	Energy (eV)
H	12.4760
O	432.6196
Cl	442.4557
Fe	3337.0615
Ge	2533.3904
Total energy of $Ge(OH)_4$	4363.3552
Σ enthalpy of elements in $Ge(OH)_4$ (Ge + OH × 4)	4313.7728
$Ge(OH)_4$	49.5824 †
† Formation enthalpy of Ge-tetrahedron by Equation (2).	

Table S4. akaganéite bond lengths (Å) of tunnel structure after DFT-D calculation for the proposed model.

Bond	Bond Length(Å)	Bond	Bond Length(Å)
Ge–O(T1)	1.639	-	-
Ge–O(T2)	1.660	-	-
Ge–O(T3)	1.678	-	-
Ge–O(T4)	1.946	-	-
O(T1)–H(4)	1.056	O(T3)–H(44)	1.207
O(T1)–H(13)	1.533	O(T3)–H(1)	1.283

O(T1)–H(43)	1.731	O(T3)–H(35)	1.332
O(T2)–H(3)	1.033	O(T4)–H(2)	0.975
O(T2)–H(20)	1.403	O(T4)–H(18)	1.372
O(T2)–H(34)	1.622	O(T4)–H(12)	1.408
Cl(1)…H(16)	1.800	Cl(3)…H(40)	2.075
Cl(1)…H(19)	2.044	Cl(3)…H(28)	2.106
Cl(1)…H(9)	1.940	Cl(3)…H(37)	2.183
Cl(1)…H(14)	2.437	Cl(3)…H(21)	2.210
Cl(1)…H(43)	2.340	Cl(3)…H(24)	2.361
Cl(1)…H(20)	2.622	Cl(3)…H(31)	2.370
Cl(1)…H(34)	2.475	Cl(3)…H(23)	2.463
Cl(1)…H(13)	2.917	Cl(3)…H(32)	2.470
Cl(2)…H(10)	2.047	Cl(4)…H(42)	2.121
Cl(2)…H(15)	2.072	Cl(4)…H(39)	2.117
Cl(2)…H(6)	2.268	Cl(4)…H(36)	2.154
Cl(2)…H(17)	2.248	Cl(4)…H(38)	2.207
Cl(2)…H(11)	2.424	Cl(4)…H(26)	2.379
Cl(2)…H(8)	2.269	Cl(4)…H(29)	2.389
Cl(2)…H(5)	2.567	Cl(4)…H(33)	2.440
Cl(2)…H(7)	2.414	Cl(4)…H(22)	2.436

Note: The tunnel tetrahedron corner oxygens are separately labelled to T1–T4. The hydrogens are numbered as same as program to easy to find each atom in data.

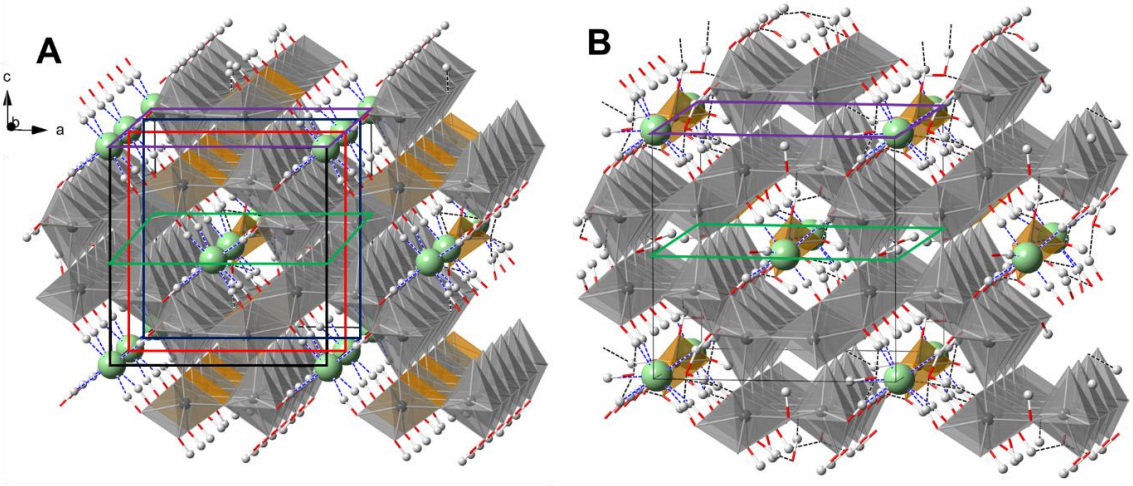

Figure S4. (**A**) The optimized crystal structure of the newly proposed Ge-akaganéite model (model Ⅱ) after DFT-D calculation (same as Figure 6A). (**B**) The optimized structure of Ge-akaganéite with N = 4 (model Ⅴ). Black line represents the unit cell of model structure. Bold black, red, and blue line represent the view of [010] at b = 0, 0.5, and 0.7, respectively. Bold purple and green line represent the view of [001] at c = 0 and 0.5, respectively.

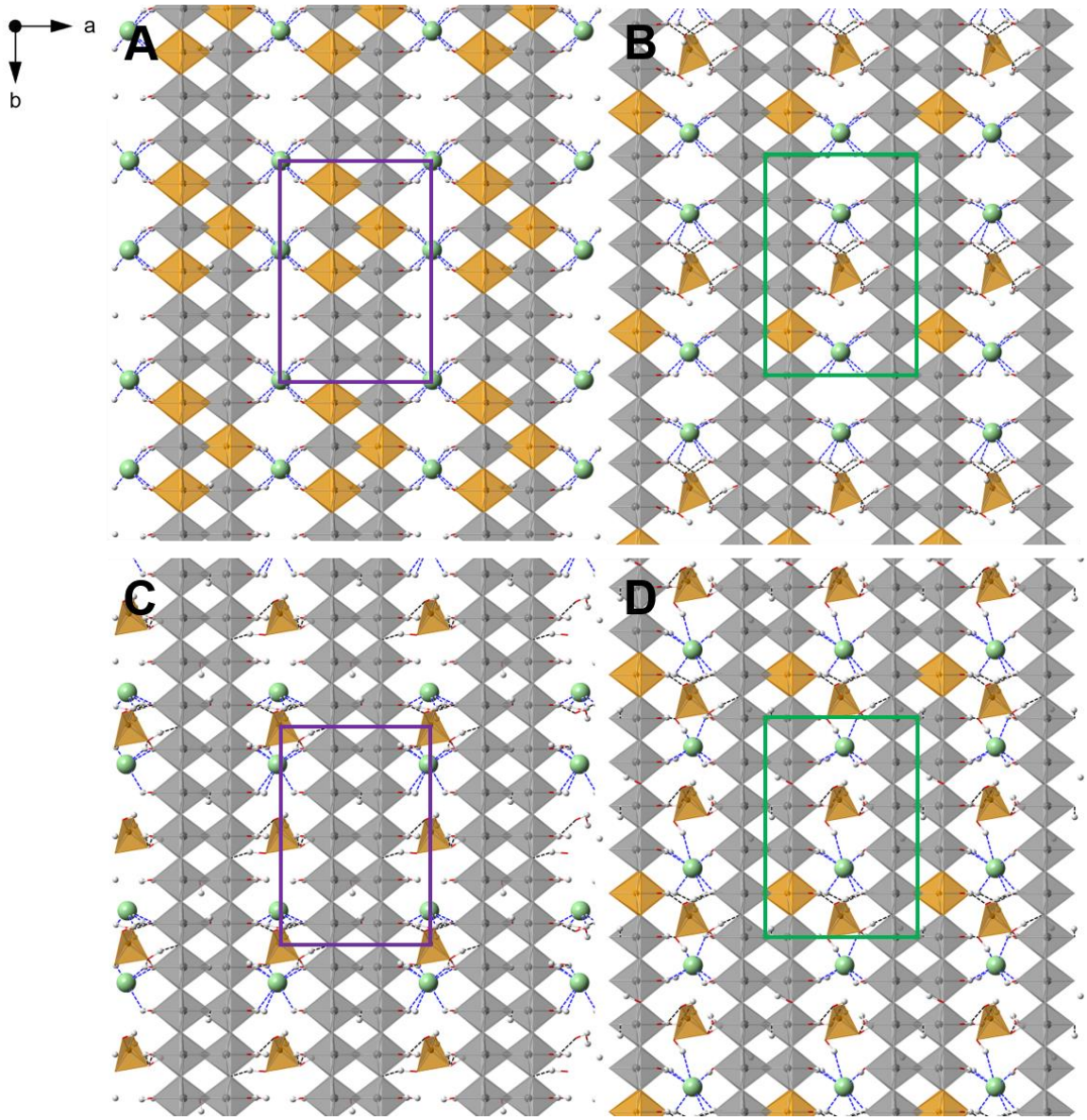

Figure S5. A view of the newly proposed Ge-akaganéite model (model Ⅱ) after DFT calculation along c-axis at c = 0 (**A**) and 0.5 (**B**). The Ge-akaganéite model with *N* = 4 (model Ⅴ) along c-axis at c = 0 (**C**) and 0.5 (**D**). Visualized range is set as 0.6 of model axial range from the view point and the viewpoint are selected at filled tunnel site. There are more Cl atoms should be located near Ge-tetrahedrons in model Ⅴ than Ⅱ, indicating the structural instability of model Ⅴ.

Table S5. Frictional coordinates of atoms in the proposed Ge-akaganéite model. The model unit cell is expanded to 1 × 5 × 1 supercell and the coordinations of the framework elements are fixed.

Atom	Number	Frictional Coordinates of Atoms		
		u	v	w
H	1	0.730211	0.523882	0.465683
H	2	0.4984	0.671402	0.483746
H	3	0.540529	0.479272	0.707117
H	4	0.46215	0.4808	0.28934
H	5	0.346798	0.994908	0.389423
H	6	0.410358	0.994822	0.633223
H	7	0.656014	0.992724	0.608126
H	8	0.655101	0.81036	0.609336
H	9	0.653369	0.207354	0.60913

H	10	0.397717	0.817985	0.626213
H	11	0.34759	0.808988	0.388115
H	12	0.342066	0.618679	0.391628
H	13	0.345521	0.391886	0.389237
H	14	0.346983	0.204138	0.389863
H	15	0.600056	0.817326	0.371323
H	16	0.598121	0.212532	0.373652
H	17	0.596834	0.99029	0.371097
H	18	0.38624	0.622902	0.619735
H	19	0.41039	0.204129	0.631882
H	20	0.421334	0.393636	0.644525
H	21	0.095799	0.309908	0.870444
H	22	0.152343	0.092636	0.111634
H	23	0.153721	0.306106	0.10997
H	24	0.152486	0.49065	0.111742
H	25	0.155574	0.701807	0.10863
H	26	0.152524	0.909166	0.111677
H	27	0.907125	0.700902	0.131635
H	28	0.903639	0.486169	0.129966
H	29	0.844344	0.909345	0.891297
H	30	0.839731	0.701366	0.89564
H	31	0.845808	0.490629	0.890031
H	32	0.846597	0.306043	0.889653
H	33	0.845095	0.091915	0.890783
H	34	0.656332	0.385354	0.61112
H	35	0.630475	0.618034	0.385869
H	36	0.903023	0.913168	0.129574
H	37	0.899216	0.313943	0.12657
H	38	0.902646	0.087855	0.129036
H	39	0.103182	0.083687	0.87459
H	40	0.102998	0.482891	0.874303
H	41	0.090579	0.709529	0.865338
H	42	0.090562	0.909234	0.867472
H	43	0.594889	0.378224	0.364355
H	44	0.660018	0.603578	0.599552
O	1	0.6527	0	0.2985
O	2	0.6741	0	0.0492
O	3	0.2798	0	0.3236
O	4	0.0369	0	0.3366
O	5	0.1527	0.1	0.7985
O	6	0.1741	0.1	0.5492
O	7	0.7798	0.1	0.8236
O	8	0.5369	0.1	0.8366
O	9	0.3473	0	0.7015
O	10	0.3259	0	0.9508
O	11	0.7202	0	0.6764
O	12	0.9631	0	0.6634
O	13	0.8473	0.1	0.2015
O	14	0.8259	0.1	0.4508
O	15	0.2202	0.1	0.1764
O	16	0.4631	0.1	0.1634
O	17	0.6527	0.2	0.2985

O	18	0.6741	0.2	0.0492
O	19	0.2798	0.2	0.3236
O	20	0.0369	0.2	0.3366
O	21	0.1527	0.3	0.7985
O	22	0.1741	0.3	0.5492
O	23	0.7798	0.3	0.8236
O	24	0.5369	0.3	0.8366
O	25	0.3473	0.2	0.7015
O	26	0.3259	0.2	0.9508
O	27	0.7202	0.2	0.6764
O	28	0.9631	0.2	0.6634
O	29	0.8473	0.3	0.2015
O	30	0.8259	0.3	0.4508
O	31	0.2202	0.3	0.1764
O	32	0.4631	0.3	0.1634
O	33	0.6527	0.4	0.2985
O	34	0.6741	0.4	0.0492
O	35	0.2798	0.4	0.3236
O	36	0.0369	0.4	0.3366
O	37	0.1527	0.5	0.7985
O	38	0.1741	0.5	0.5492
O	39	0.7798	0.5	0.8236
O	40	0.5369	0.5	0.8366
O	41	0.3473	0.4	0.7015
O	42	0.3259	0.4	0.9508
O	43	0.7202	0.4	0.6764
O	44	0.9631	0.4	0.6634
O	45	0.8473	0.5	0.2015
O	46	0.8259	0.5	0.4508
O	47	0.2202	0.5	0.1764
O	48	0.4631	0.5	0.1634
O	49	0.6527	0.6	0.2985
O	50	0.6741	0.6	0.0492
O	51	0.2798	0.6	0.3236
O	52	0.0369	0.6	0.3366
O	53	0.1527	0.7	0.7985
O	54	0.1741	0.7	0.5492
O	55	0.7798	0.7	0.8236
O	56	0.5369	0.7	0.8366
O	57	0.3473	0.6	0.7015
O	58	0.3259	0.6	0.9508
O	59	0.7202	0.6	0.6764
O	60	0.9631	0.6	0.6634
O	61	0.8473	0.7	0.2015
O	62	0.8259	0.7	0.4508
O	63	0.2202	0.7	0.1764
O	64	0.4631	0.7	0.1634
O	65	0.6527	0.8	0.2985
O	66	0.6741	0.8	0.0492
O	67	0.2798	0.8	0.3236
O	68	0.0369	0.8	0.3366
O	69	0.1527	0.9	0.7985

O	70	0.1741	0.9	0.5492
O	71	0.7798	0.9	0.8236
O	72	0.5369	0.9	0.8366
O	73	0.3473	0.8	0.7015
O	74	0.3259	0.8	0.9508
O	75	0.7202	0.8	0.6764
O	76	0.9631	0.8	0.6634
O	77	0.8473	0.9	0.2015
O	78	0.8259	0.9	0.4508
O	79	0.2202	0.9	0.1764
O	80	0.4631	0.9	0.1634
O	81 (T3)	0.635631	0.573789	0.495526
O	82 (T4)	0.425129	0.632303	0.495887
O	83 (T2)	0.529167	0.446573	0.621351
O	84 (T1)	0.465975	0.449479	0.379166
Cl	1	0.52645	0.2688	0.506435
Cl	2	0.506182	0.893424	0.505926
Cl	3	0.000568	0.404298	−0.000102
Cl	4	0.002277	−0.002497	−0.002672
Fe	1	0.8581	0	0.3416
Fe	2	0.347	0	0.1457
Fe	3	0.847	0.1	0.6457
Fe	4	0.1419	0	0.6584
Fe	5	0.653	0	0.8543
Fe	6	0.6419	0.1	0.1584
Fe	7	0.153	0.1	0.3543
Fe	8	0.8581	0.2	0.3416
Fe	9	0.347	0.2	0.1457
Fe	10	0.3581	0.3	0.8416
Fe	11	0.847	0.3	0.6457
Fe	12	0.1419	0.2	0.6584
Fe	13	0.653	0.2	0.8543
Fe	14	0.153	0.3	0.3543
Fe	15	0.8581	0.4	0.3416
Fe	16	0.347	0.4	0.1457
Fe	17	0.847	0.5	0.6457
Fe	18	0.1419	0.4	0.6584
Fe	19	0.653	0.4	0.8543
Fe	20	0.6419	0.5	0.1584
Fe	21	0.153	0.5	0.3543
Fe	22	0.8581	0.6	0.3416
Fe	23	0.347	0.6	0.1457
Fe	24	0.3581	0.7	0.8416
Fe	25	0.847	0.7	0.6457
Fe	26	0.1419	0.6	0.6584
Fe	27	0.653	0.6	0.8543
Fe	28	0.6419	0.7	0.1584
Fe	29	0.153	0.7	0.3543
Fe	30	0.8581	0.8	0.3416
Fe	31	0.347	0.8	0.1457
Fe	32	0.3581	0.9	0.8416
Fe	33	0.847	0.9	0.6457

Fe	34	0.653	0.8	0.8543
Fe	35	0.6419	0.9	0.1584
Fe	36	0.153	0.9	0.3543
Ge	1	0.3581	0.1	0.8416
Ge	2	0.6419	0.3	0.1584
Ge	3	0.3581	0.5	0.8416
Ge	4 (T)	0.5	0.51424	0.5
Ge	5	0.1419	0.8	0.6584

Note: The tunnel tetrahedron corner oxygens are separately labelled to (T1) – (T4). The tunnel Ge is labelled to (T).

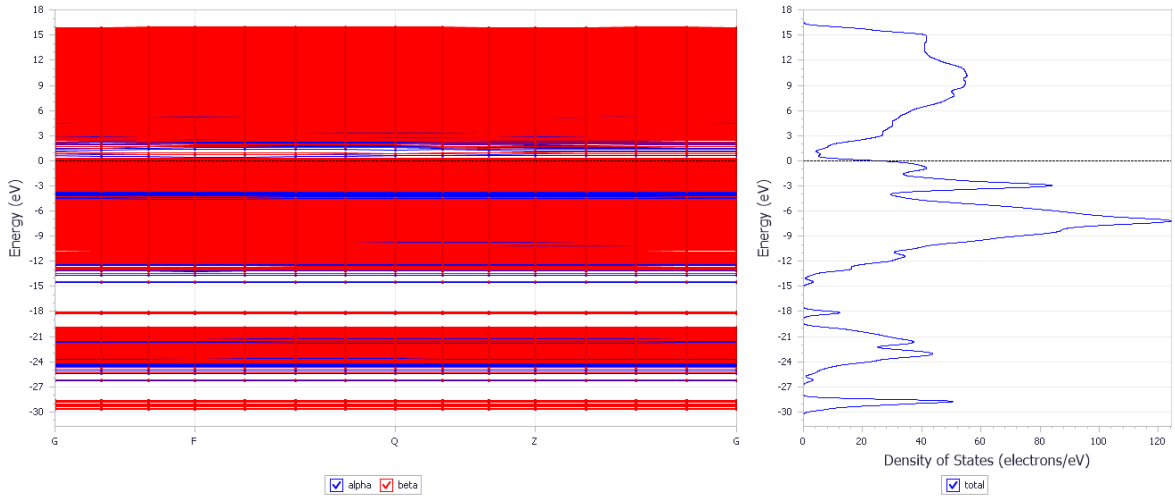

Figure S6. Band structure(**left**) and total DOS (**right**) of Ge-akaganéite model.