Electronic Supplementary Information

Distribution of trivalent metal cations in alumino-/gallogermanate zeolites with JST topology

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Distribution of Be^{2+} cations in Zeolite OSO

OSO is the first zeolite built exclusively of 3-rings (Fig. S1), the type material of which is OSB-1 ($|K_6(H_2O)_9|[Be_3Si_6O_{18}]$).[1] The framework of OSO contains three crystallographically distinct T atom sites for Be^{2+} and Si, and their multiplicities are all the same. Two T1 and one T3 atoms form a 3-ring, and two T2 and one T3 form the other 3-ring. A pair of 3-rings form a spiro-5 building unit,[2] and each spiro-5 unit contains one T1 ($2 \times 1/2$), one T2 ($2 \times 1/2$), and one T3 atoms. Three spiro-5 units are connected with each other by sharing the vertex T1 and T2 atoms to form the complete unit cell of OSO. According to Pauling's third rule, $Be^{2+}-O-Be^{2+}$ linkages in a tetrahedrally connected zeolite framework are energetically unfavourable. If every spiro-5 unit contains one Be^{2+} cation, there are four different distributions of one Be^{2+} cation in one spiro-5 unit. If the Be^{2+} cation only occupies T1 (Fig. S1b) or T2 site (Fig. S1c), the $Be^{2+}-O-Be^{2+}$ linkage will be formed. Only when the Be^{2+} cation occupies T3 site (Fig. S1d) or half of the Be^{2+} cation occupies T1 and the other half occupies T2 site (Fig. S1e), the $Be^{2+}-O-Be^{2+}$ linkage could be avoided. If one spiro-5 unit contains more than one Be^{2+} cation, $Be^{2+}-O-Be^{2+}$ linkage would be unavoidable. Because each spiro-5 unit contains three T sites and three spiro-5 unit form the complete unit cell of OSO, the maximum Be^{2+}/Si ratio in OSO is 1/2. This result is in good agreement with the reported Be/Si ratio in OSB-1. Like in JST, the maximum content of Be^{2+} cations in zeolite OSO is determined by its unique structural feature.
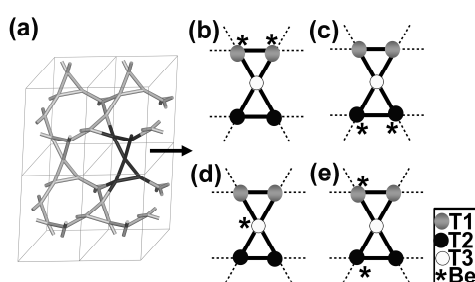

Fig. S1 (a) The framework of zeolite OSO and (b)–(e) four different distributions of one Be^{2+} cation in one spiro-5 unit. All oxygen atoms are omitted for clarity.

References:

1 A. K. Cheetham, H. Fjellvåg, T. E. Gier, K. O. Kongshaug, K. P. Lillerud and G. D. *Stucky, Stud. Surf. Sci. Catal.*, 2001, **135**, 158.

2 C. Baerlocher, L. B. McCusker, D. H. Olson, Atlas of Zeolite Framework Types, 6th ed., Elsevier, Amsterdam, 2007; see also: http://www.iza-structure.org/databases/.

Table S1. Atomic coordinates ($\times 10^4$), site occupancies, and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for compound **1**[a]

atoms	x	y	z	Occ.	U(eq)
Ge(1)	8412(1)	664(1)	774(1)	0.6789(18)	16(1)
Al(1)	8412(1)	664(1)	774(1)	0.3211(18)	16(1)
Ge(2)	8616(1)	2568(1)	888(1)	0.6545(18)	14(1)
Al(2)	8616(1)	2568(1)	888(1)	0.3455(18)	14(1)
O(1)	8193(2)	1629(1)	1169(2)	1	25(1)
O(2)	9253(2)	2880(2)	1680(2)	1	25(1)
O(3)	9216(2)	242(2)	1326(2)	1	25(1)
O(4)	7568(2)	21(2)	855(2)	1	26(1)
Ni(1)	1664(1)	1664(1)	1664(1)	1	22(1)
N(1)	1823(2)	405(2)	1525(2)	1	35(1)
N(2)	1626(4)	2967(3)	1618(3)	1	60(1)
C(1)	1392(5)	2679(4)	207(4)	1	80(2)
C(2)	1549(6)	3202(4)	812(5)	1	97(2)

[a] U(eq) is defined as one third of the trace of the orthogonalized $\mathbf{U}ij$ tensor.

Table S2. Atomic coordinates ($\times 10^4$), site occupancies, and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for compound **2**[a]

atoms	x	y	z	Occ.	U(eq)
Ge(1)	4359(1)	9214(1)	3415(1)	0.671(2)	14(1)
Al(1)	4359(1)	9214(1)	3415(1)	0.329(2)	14(1)
Ge(2)	2456(1)	9084(1)	3599(1)	0.662(2)	13(1)
Al(2)	2456(1)	9084(1)	3599(1)	0.338(2)	13(1)
Co(1)	1672(1)	1672(1)	1672(1)	1	24(1)
O(1)	3399(2)	8813(2)	3182(2)	1	23(1)
O(2)	4772(2)	8667(2)	4226(2)	1	24(1)
O(3)	5012(2)	9135(2)	2582(2)	1	25(1)
O(4)	1713(2)	9226(2)	2857(2)	1	23(1)
N(1)	1511(3)	1850(3)	390(2)	1	37(1)
N(2)	1656(5)	2997(3)	1595(3)	1	75(2)
C(1)	1387(6)	2697(4)	200(4)	1	82(3)
C(2)	1518(8)	3211(5)	813(6)	1	99(3)

[a] U(eq) is defined as one third of the trace of the orthogonalized $\mathbf{U}ij$ tensor.

Table S3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for compound **3**[a]

atoms	x	y	z	U(eq)
Ga(1)	8410(1)	663(1)	772(1)	18(1)
Ge(1)	8410(1)	663(1)	772(1)	18(1)
Ga(2)	8614(1)	2566(1)	888(1)	17(1)
Ge(2)	8614(1)	2566(1)	888(1)	17(1)
Co(1)	1671(1)	1671(1)	1671(1)	25(1)
O(1)	7560(2)	21(2)	848(2)	33(1)
O(2)	8674(2)	779(2)	-255(2)	29(1)
O(3)	8174(2)	1633(2)	1167(2)	29(1)
O(4)	9262(2)	2872(2)	1683(2)	32(1)
C(1)	208(4)	1374(7)	2684(4)	87(3)
C(2)	825(5)	1586(7)	3196(5)	100(3)
N(1)	1846(3)	399(3)	1520(3)	39(1)
N(2)	1588(3)	1663(5)	2995(3)	81(2)

[a] U(eq) is defined as one third of the trace of the orthogonalized $\mathbf{U}ij$ tensor.

Table S4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for compound **4**[a]

atoms	x	y	z	U(eq)
Ga(1)	8411(1)	656(1)	776(1)	17(1)
Ge(1)	8411(1)	656(1)	776(1)	17(1)
Ga(2)	8607(1)	2558(1)	898(1)	16(1)
Ge(2)	8607(1)	2558(1)	898(1)	16(1)
Zn(1)	11672(1)	1672(1)	1672(1)	29(1
O(1)	7565(3)	8(3)	848(3)	33(1)
O(2)	8672(3)	775(3)	-247(3)	28(1)
O(3)	8167(3)	1618(3)	1173(3)	29(1)
O(4)	7866(3)	3301(3)	750(3)	30(1)
N(1)	13003(5)	1599(5)	1702(7)	85(3)
N(2)	11858(4)	394(4)	1509(4)	47(2)
C(1)	13210(7)	840(7)	1558(10)	105(3)
C(2)	12683(6)	205(6)	1351(8)	80(3)

[a] U(eq) is defined as one third of the trace of the orthogonalized $\mathbf{U}ij$ tensor.

Table S5. Selected bond lengths (Å) and angles (deg) for compound **1**[a]

Ge(1)-O(3) #1	1.737(2)	Ge(2)-O(1)	1.754(2)
Ge(1)-O(3)	1.747(2)	O(2)-Al(2)#3	1.745(2)
Ge(1)-O(4)	1.748(2)	O(2)-Ge(2)#3	1.745(2)
Ge(1)-O(1)	1.753(2)	O(3)-Al(1)#4	1.737(2)
Ge(2)-O(4)#1	1.744(2)	O(3)-Ge(1)#4	1.737(2)
Ge(2)-O(2)#2	1.745(2)	O(4)-Al(2)#4	1.744(2)
Ge(2)-O(2)	1.749(2)	O(4)-Ge(2)#4	1.744(2)
Ge(1)-O(1)-Ge(2)	128.21(15)	Al(1)#4-O(3)-Ge(1)	126.66(14)
Al(2)#3-O(2)-Ge(2)	130.66(15)	Ge(1)#4-O(3)-Ge(1)	126.66(14)
Ge(2)#3-O(2)-Ge(2)	130.66(15)		

[a] Symmetry transformations used to generate equivalent atoms: (#1) –z + 1, –x + 1, –y; (#2) y + 1/2, –z + 1/2, –x + 1; (#3) –z + 1, x – 1/2, –y + 1/2; (#4) –y + 1, –z, –x + 1.

Table S6. Selected bond lengths (Å) and angles (deg) for compound **2**[a]

Ge(1)-O(2)#1	1.736(3)	Ge(2)-O(1)	1.757(3)
Ge(1)-O(2)	1.749(3)	O(2)-Al(1)#3	1.736(3)
Ge(1)-O(3)	1.749(3)	O(2)-Ge(1)#3	1.736(3)
Ge(1)-O(1)	1.756(3)	O(3)-Al(2)#3	1.744(3)
Ge(2)-O(3)#1	1.744(3)	O(3)-Ge(2)#3	1.744(3)
Ge(2)-O(4)	1.746(3)	O(4)-Al(2)#4	1.748(3)
Ge(2)-O(4)#2	1.748(3)	O(4)-Ge(2)#4	1.748(3)
Ge(1)-O(1)-Ge(2)	128.01(18)	Al(2)#3-O(3)-Ge(1)	131.05(17)
Al(1)#3-O(2)-Ge(1)	126.45(17)	Ge(2)#3-O(3)-Ge(1)	131.05(17)
Ge(1)#3-O(2)-Ge(1)	126.45(17)	Ge(2)-O(4)-Al(2)#4	130.77(18)
Ge(2)-O(4)-Ge(2)#4	130.77(18)		

[a] Symmetry transformations used to generate equivalent atoms: (#1) z, –x + 3/2, y – 1/2; (#2) –z + 1/2, –x + 1, y – 1/2; (#3) –y + 3/2, z + 1/2, x; (#4) –y + 1, z + 1/2, –x + 1/2.

Table S7. Selected bond lengths (Å) and angles (deg) for compound **3**[a]

Ga(1)-O(2)#1	1.765(3)	Ga(2)-O(4)	1.776(3)
Ga(1)-O(2)	1.769(3)	O(1)-Ge(2)#1	1.765(3)
Ga(1)-O(1)	1.771(3)	O(1)-Ga(2)#1	1.765(3)
Ga(1)-O(3)	1.781(3)	O(2)-Ge(1)#2	1.765(3)
Ga(2)-O(1)#2	1.765(3)	O(2)-Ga(1)#2	1.765(3)
Ga(2)-O(4)#3	1.768(3)	O(4)-Ge(2)#4	1.768(3)
Ga(2)-O(3)	1.772(3)	O(4)-Ga(2)#4	1.768(3)
Ge(2)#1-O(1)-Ga(1)	130.13(18)	Ga(2)-O(3)-Ga(1)	127.04(18)
Ga(2)#1-O(1)-Ga(1)	130.13(18)	Ge(2)#4-O(4)-Ga(2)	129.58(18)
Ge(1)#2-O(2)-Ga(1)	125.55(17)	Ga(2)#4-O(4)-Ga(2)	129.58(18)
Ga(1)#2-O(2)-Ga(1)	125.55(17)		

[a] Symmetry transformations used to generate equivalent atoms: (#1) –y + 1, –z, –x + 1; (#2) –z + 1, –x + 1, –y; (#3) y + 1/2, –z + 1/2, –x + 1; (#4) –z + 1, x – 1/2, –y + 1/2.

Table S8. Selected bond lengths (Å) and angles (deg) for compound **4**[a]

Ga(1)-O(2)	1.759(4)	Ga(2)-O(3)	1.778(4)
Ga(1)-O(2)#1	1.766(4)	O(1)-Ge(2)#1	1.764(4)
Ga(1)-O(1)	1.768(4)	O(1)-Ga(2)#1	1.764(4)
Ga(1)-O(3)	1.771(4)	O(2)-Ge(1)#2	1.766(4)
Ga(2)-O(4)	1.755(4)	O(2)-Ga(1)#2	1.766(4)
Ga(2)-O(1)#2	1.764(4)	O(4)-Ge(2)#4	1.776(4)
Ga(2)-O(4)#3	1.776(4)	O(4)-Ga(2)#4	1.776(4)
Ge(2)#1-O(1)-Ga(1)	130.0(2)	Ga(1)-O(3)-Ga(2)	126.8(3)
Ga(2)#1-O(1)-Ga(1)	130.0(2)	Ga(2)-O(4)-Ge(2)#4	129.8(3)
Ga(1)-O(2)-Ge(1)#2	125.6(2)	Ga(2)-O(4)-Ga(2)#4	129.8(3)
Ga(1)-O(2)-Ga(1)#2	125.6(2)		

[a] Symmetry transformations used to generate equivalent atoms: (#1) –y + 1, –z,   –x + 1; (#2) –z + 1, –x + 1, –y; (#3) –z + 1, x – 1/2, –y + 1/2; (#4) y + 1/2, –z + 1/2, –x + 1.

Table S9. The hydrogen bonds for compound **1**

D-H...A	d(D...A)	<(DHA)
N(1)-H(1)...O(2)	2.934	154.63
N(1)-H(1)...O(3)	2.991	144.95
N(2)-H(2)...O(1)	2.955	112.54

Table S10. The hydrogen bonds for compound **2**

D-H...A	d(D...A)	<(DHA)
N(1)-H(1)...O(4)	2.940	154.55
N(1)-H(2)...O(2)	2.979	146.15
N(2)-H(1)...O(1)	2.942	120.15

Table S11. The hydrogen bonds for compound **3**

D-H...A	d(D...A)	<(DHA)
N(1)-H(1)...O(4)	2.944	157.11
N(1)-H(1)...O(2)	2.995	145.38
N(2)-H(2)...O(3)	2.977	115.12

Table S12. The hydrogen bonds for compound **4**

D-H...A	d(D...A)	<(DHA)
N(1)-H(1)...O(4)	2.944	157.11
N(1)-H(1)...O(2)	2.995	145.38
N(2)-H(2)...O(3)	2.977	115.12