Electronic Supplementary Information

Melilite-Type Blue Chromophore Based on Mn^{3+} in Trigonal-Bypyramidal Coordination Induced by Interstitial Oxygen

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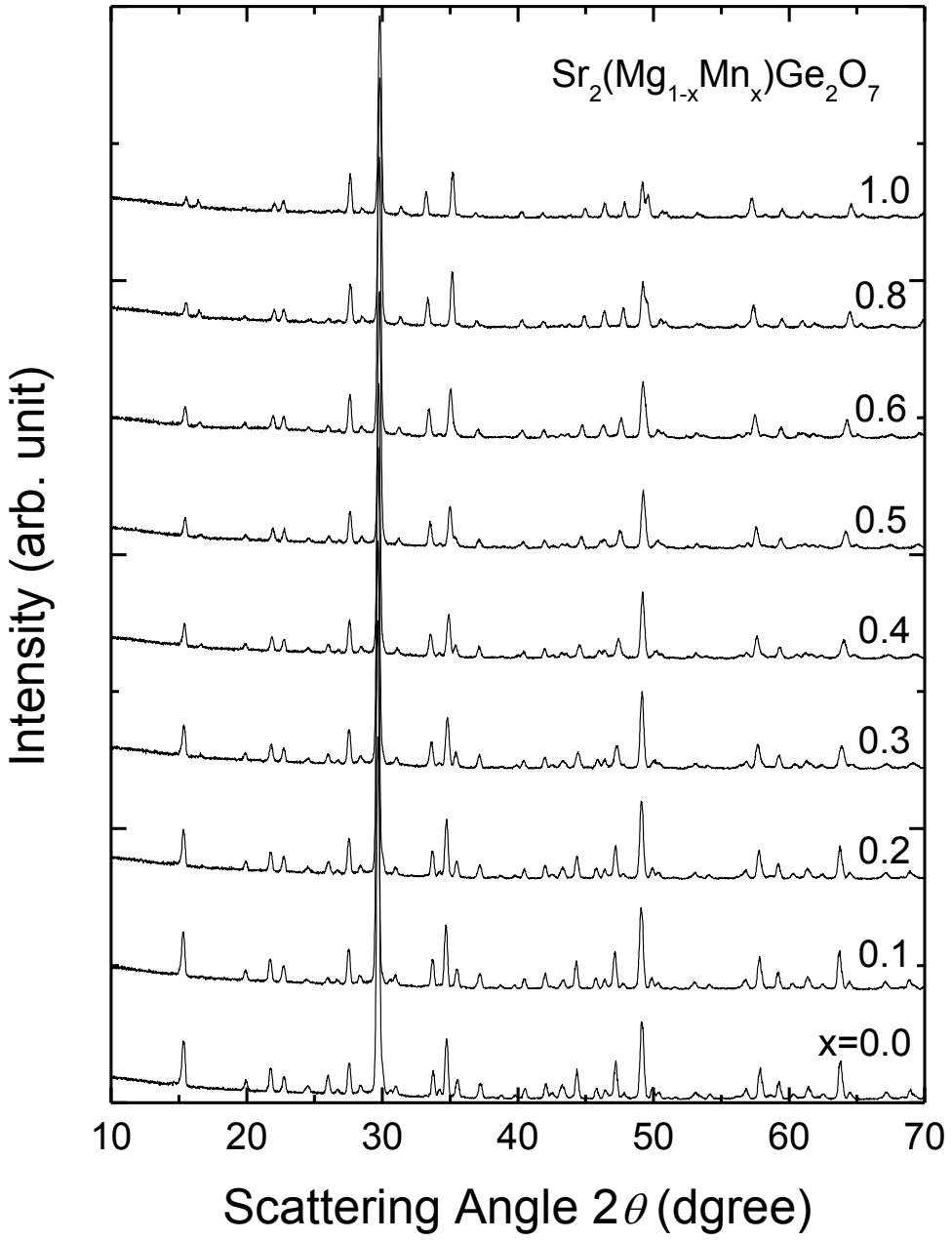

Figure S1. X-ray diffraction patterns of $Sr_2(Mg_{1-x}Mn_x)Ge_2O_7$ (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0) powders.

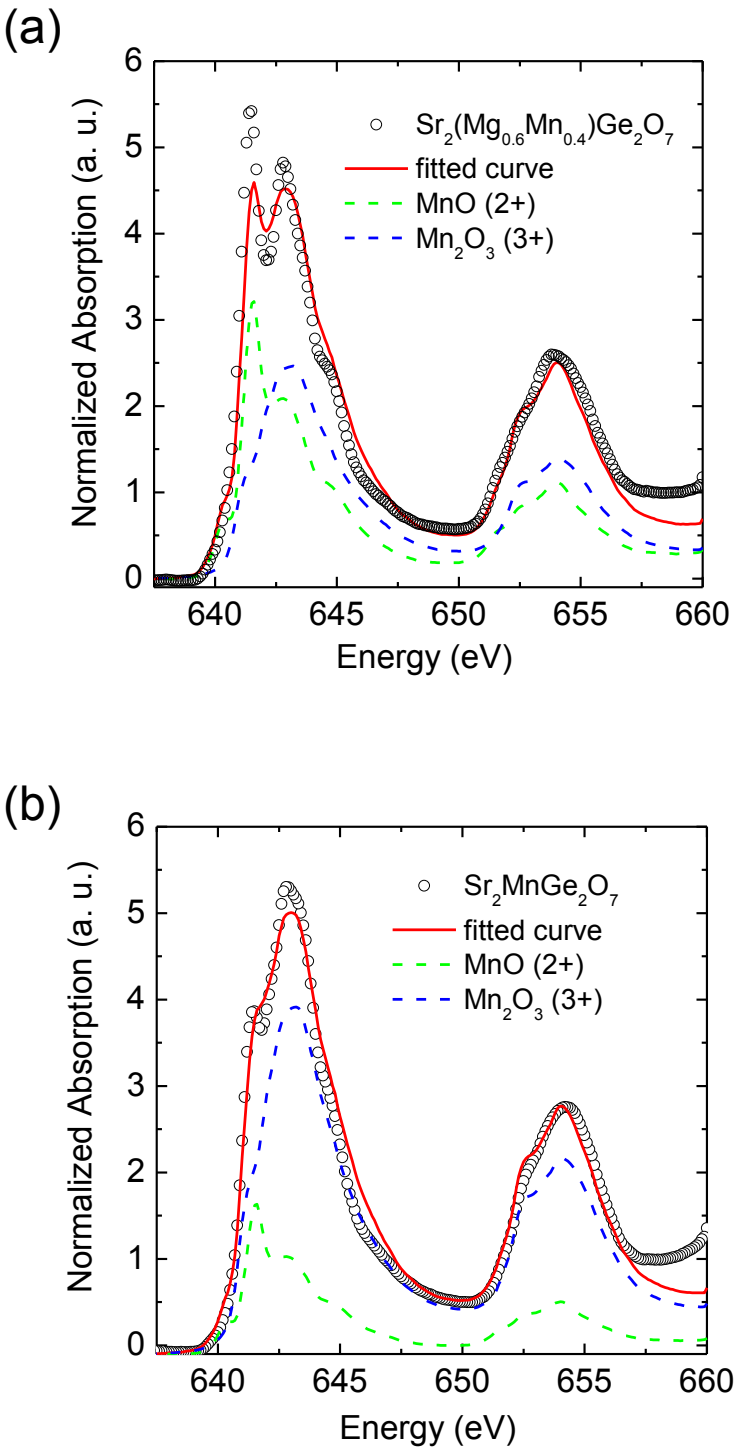

Figure S2. Fitted curves for Mn *L*-edge XANES spectra from (a) $Sr_2(Mg_{0.6}Mn_{0.4})Ge_2O_7$ and (b) $Sr_2MnGe_2O_7$ by the linear combination of *L*-edge spectra from MnO(2+) and Mn_2O_3(3+).

Table S1. Structural parameters of $Sr_2MnGe_2O_7$ without an oxygen interstitial ion determined by Rietveld refinement of the synchrotron powder XRD profile.

atom	site	*x*	*y*	*Z*	*occu.*	U_{iso} (Å^2)
Sr	4e	0.3304(1)	0.1696(1)	0.5043(3)	1	0.0130(4)
Mn	2*a*	0.0000	0.0000	0.0000	1	0.0340(12)
Ge	4*e*	0.1409(1)	0.3591(1)	0.9709(3)	1	0.0198(6)
O1	2*c*	0.5000	0.0000	0.1640(19)	1	0.0446 (55)
O2	4*e*	0.1425(5)	0.3575(5)	0.2687(12)	1	0.1247(78)
O3	8*f*	0.0874(6)	0.1810(6)	0.8252(11)	1	0.0807(49)

Space Group: $P\bar{4}2_1m$ (No. 113), $Z = 2$, $a = 8.06534(9)$ Å, $c = 5.39435(6)$ Å, $V = 350.9007(65)$ Å^3, $R_{wp} = 10.06$, $R_p = 7.75$, $S = 1.15$.

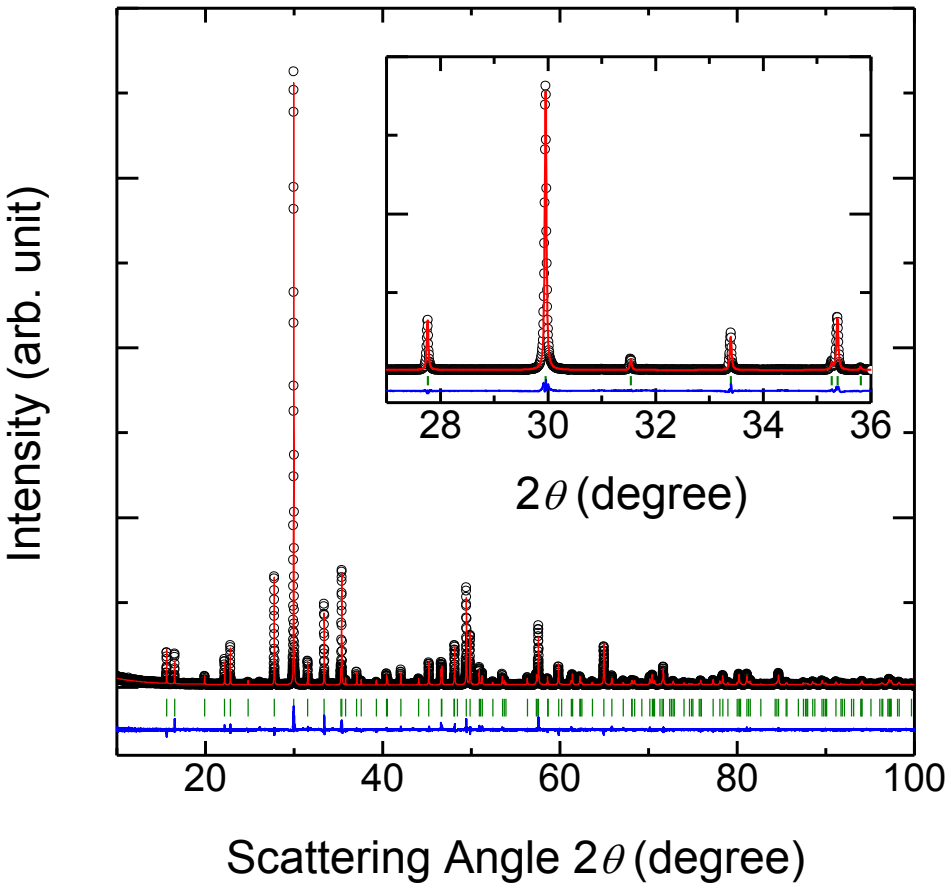

Figure S3. Rietveld refinement of the synchrotron powder XRD profile of $Sr_2MnGe_2O_{7.5}$ including a O4 oxygen interstitial atom. Measured data, fitted results, expected reflection positions, and the difference between measured and fitted results are expressed as black open circles, red solid lines, green vertical lines, and blue solid lines, respectively.

Table S2. Structural parameters of $Sr_2MnGe_2O_{7.5}$ including O4 oxygen interstitial atom determined by Rietveld refinement of the synchrotron powder XRD profile.

atom	site	*x*	*y*	*z*	*occu.*	U_{iso} (Å^2)
Sr	4e	0.3306(1)	0.1694(1)	0.5036(2)	1	0.0137(3)
Mn	2*a*	0.0000	0.0000	0.0000	1	0.0333(12)
Ge	4*e*	0.1408(1)	0.3591(1)	0.9705(2)	1	0.0202(6)
O1	2*c*	0.5000	0.0000	0.1688(16)	1	0.0402(48)
O2	4*e*	0.1411(6)	0.3590(6)	0.2717(11)	1	0.0773(49)
O3	8*f*	0.0861(7)	0.1829(6)	0.8204(11)	1	0.0961(63)
O4	8*f*	0.3432(2)	0.4208(1)	0.2117(2)	0.125	0.0561(38)

Space Group: $P\bar{4}2_1m$ (No. 113), $Z = 2$, $a = 8.06534(2)$ Å, $c = 5.39435(2)$ Å, $V = 350.9005(16)$ Å^3, $R_{wp} = 9.31$, $R_p = 7.18$, $S = 1.07$.

Table S3. Atomic positions in a $Sr_2MnGe_2O_{7.5}$ unit cell determined by *ab initio* calculation.

atom	*x*	*y*	*z*
Sr1	0.334998448	0.179327866	0.491748914
Sr2	0.166334487	0.675876998	0.471685109
Sr3	0.827272384	0.337022583	0.493280939
Sr4	0.670192186	0.845011032	0.492278896
Mn1	0.972105811	0.995240167	0.971683485
Mn2	0.485414278	0.481059082	0.970981668
Ge1	0.127393232	0.358709580	0.972556771
Ge2	0.849123023	0.637130710	0.972938296
Ge3	0.651360714	0.160547711	0.028459541
Ge4	0.355814326	0.865312665	0.010924083
O1	0.500672516	0.009616753	0.154194326
O2	0.926896565	0.436589792	0.890084169
O3	0.141438593	0.372855416	0.293595846
O4	0.863157938	0.651097690	0.294034466
O5	0.370527920	0.880188847	0.689448528
O6	0.780600357	0.061194948	0.783918126
O7	0.120469391	0.167831598	0.818257511
O8	0.970214968	0.781418325	0.801908637
O9	0.166501104	0.923635360	0.166876327
O10	0.827199651	0.091984681	0.233087234
O11	0.413298672	0.675546973	0.166039807
O12	0.582492162	0.336671618	0.232496211
O13	0.271849987	0.479179732	0.800768226
O14	0.658331822	0.630248130	0.818519849
O15	0.551539464	0.289401741	0.783633035

a = 8.08990 Å, c = 5.38990 Å, V = 352.750 Å^3

Table S4. Selected bond distances in a $Sr_2MnGe_2O_{7.5}$ unit cell determined by *ab initio* calculation

cation	anion	distances (Å)	cation	anion	distances (Å)
Sr1	O3	2.4584	Mn1	O6	1.9259
	O7	2.4734		O8	1.9570
	O15	2.5173		O9	1.9788
	O1	2.6441		O10	1.9930
	O5	2.6598		O7	2.0184
	O12	2.7534			
	O13	2.9865	Mn2	O15	1.9261
	O9	3.0336		O13	1.9562
				O11	1.9802
Sr2	O13	2.5312		O12	1.9920
	O8	2.5326		O14	2.0221
	O11	2.5896			
	O9	2.5916	Ge1	O3	1.7379
	O5	2.6150		O7	1.7548
	O3	2.6403		O13	1.7813
	O4	2.6405		O2	1.7959
Sr3	O2	2.4233	Ge2	O4	1.7380
	O10	2.4283		O14	1.7545
	O12	2.4284		O8	1.7810
	O15	2.7519		O2	1.7965
	O6	2.7524			
	O4	2.7738	Ge3	O1	1.8537
	O3	2.7753		O6	1.8645
	O7	3.2508		O15	1.8655
	O14	3.2509		O10	1.8836
	O2	3.4451		O12	1.8841
Sr4	O4	2.4576	Ge4	O5	1.7409
	O14	2.4738		O11	1.8089
	O6	2.5154		O9	1.8096
	O1	2.6410		O1	1.8255
	O5	2.6622			
	O10	2.7490			
	O8	2.9901			
	O11	3.0480			

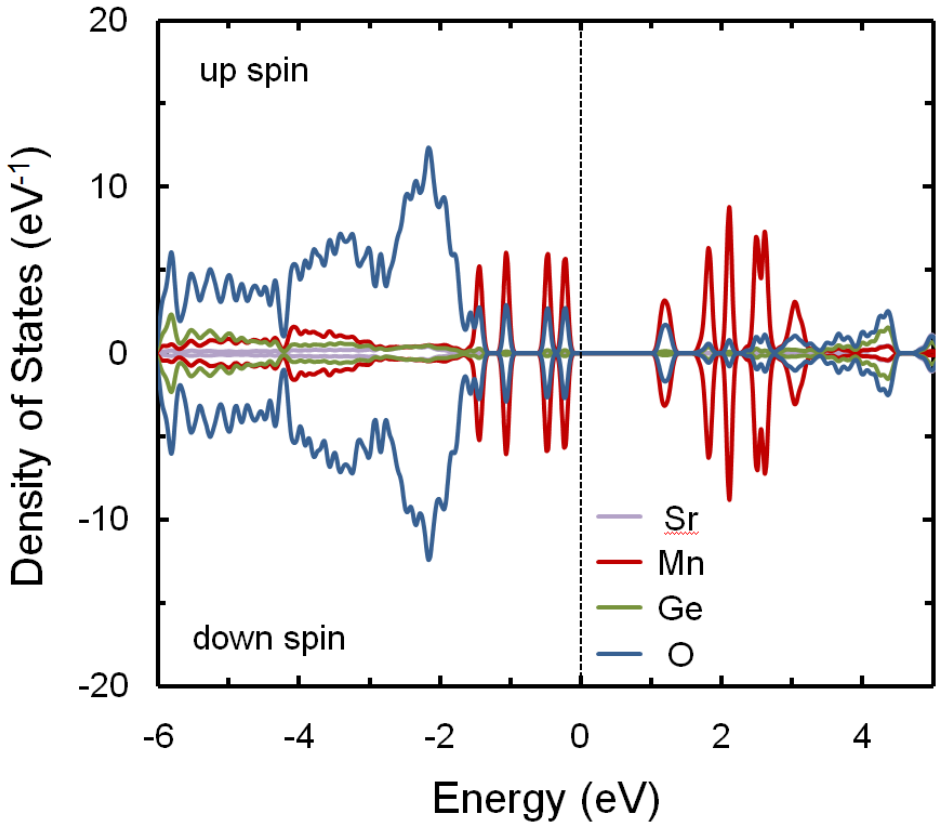

Figure S4. Calculated partial density of states for Sr, Mn, Ge, O in $Sr_2MnGe_2O_{7.5}$. The Fermi level is set to zero.

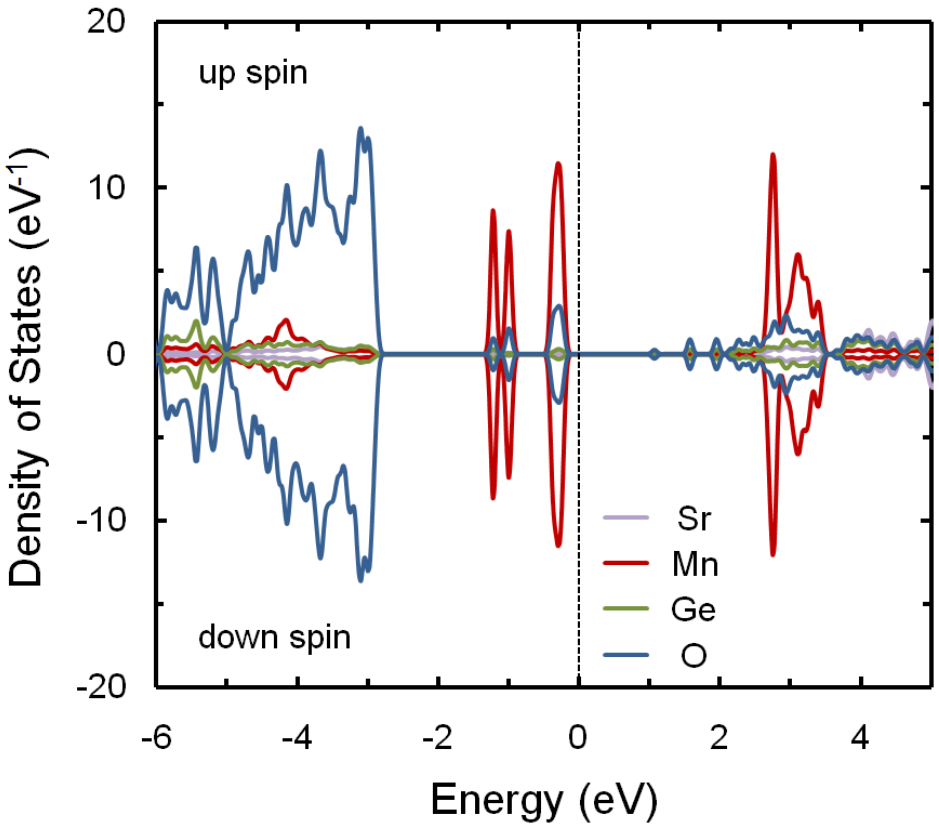

Figure S5. Calculated partial density of states for Sr, Mn, Ge, O in $Sr_2MnGe_2O_7$. The Fermi level is set to zero.

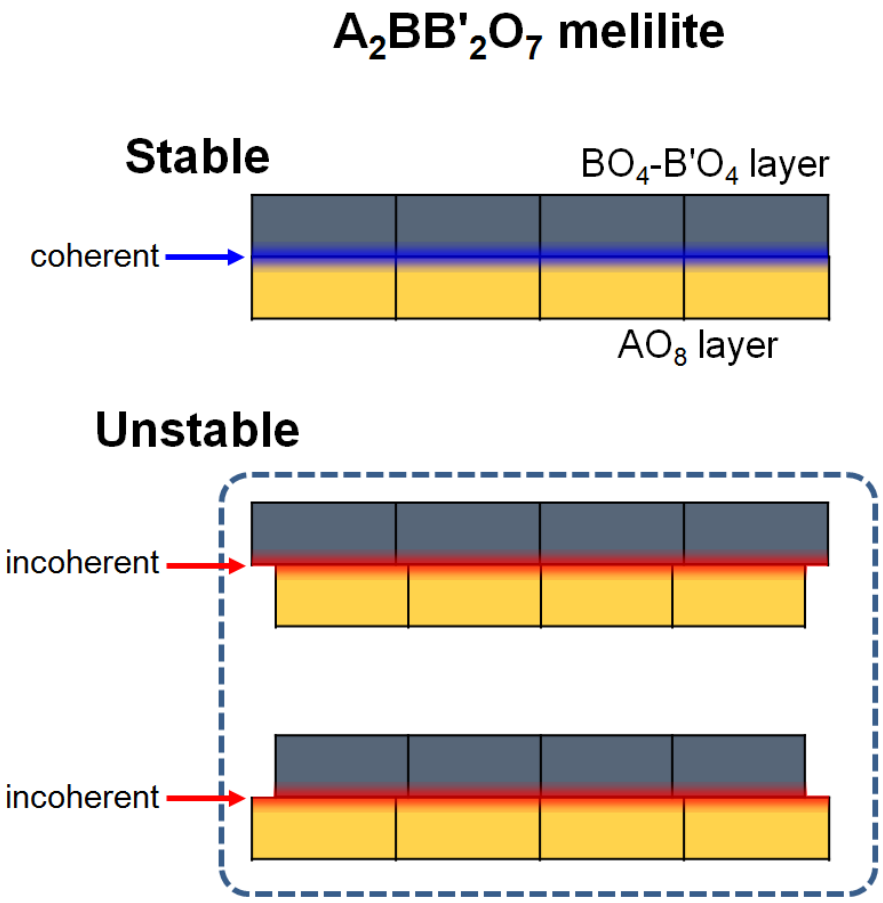

Figure S6. Schematic expression for the stability of the melilite structure determined by the coherency between BO_4–$B'O_4$ and AO_8 layers in $A_2BB'_2O_7$.