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Supporting information for article:

Structure modulations in NLO materials $\text{Cs}_2T\text{B}_4\text{O}_9$ ($T = \text{Ge, Si}$)

Zhengyang Zhou, Xiang Xu, Rao Fei, Jianggao Mao and Junliang Sun

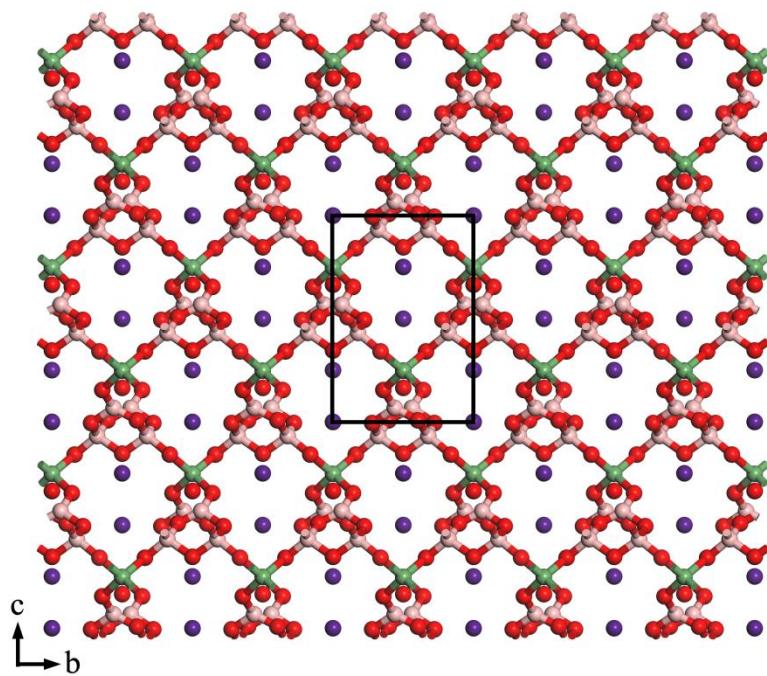


Figure S1 Average structure of $\text{Cs}_2\text{GeB}_4\text{O}_9$ projected along the **a** axis.

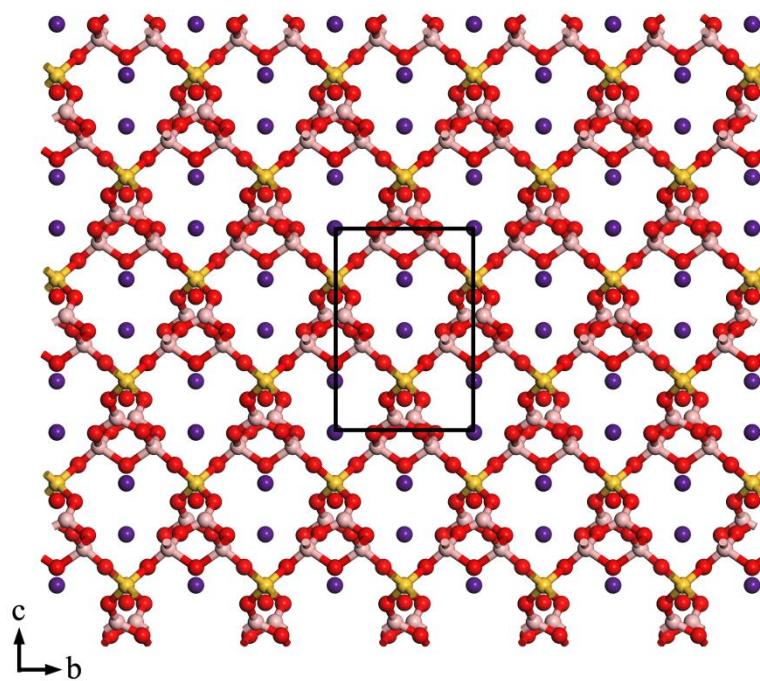


Figure S2 Average structure of $\text{Cs}_2\text{SiB}_4\text{O}_9$ projected along the **a** axis.

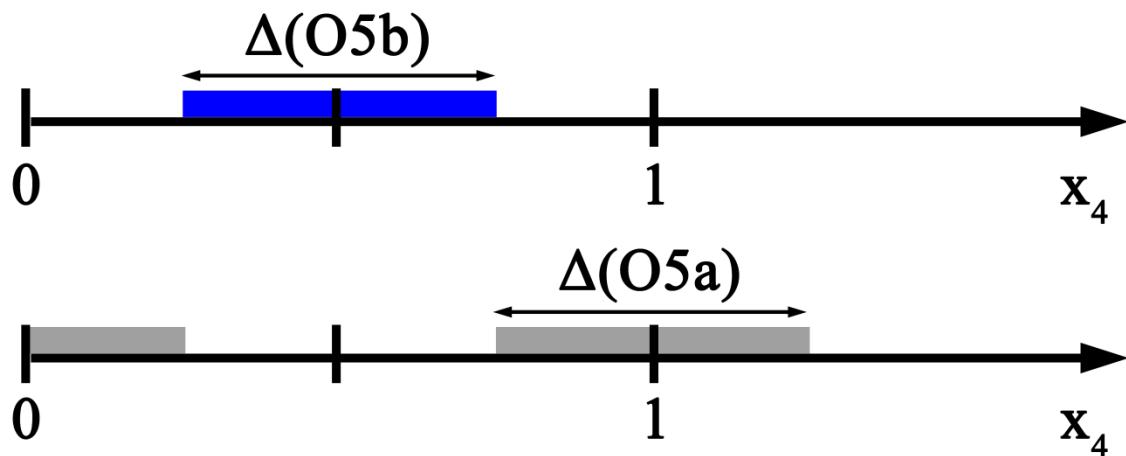


Figure S3 Schematic view of the crenel domains in superspace for $\text{Cs}_2\text{TB}_4\text{O}_9$ ($T = \text{Ge, Si}$). The occupancy of crenel domains is 1. The O5a (gray) is centered around $x_4^0 = 0$ with $\Delta = 0.5$. The O5b (blue) is centered around $x_4^0 = 0.5$ with $\Delta = 0.5$.

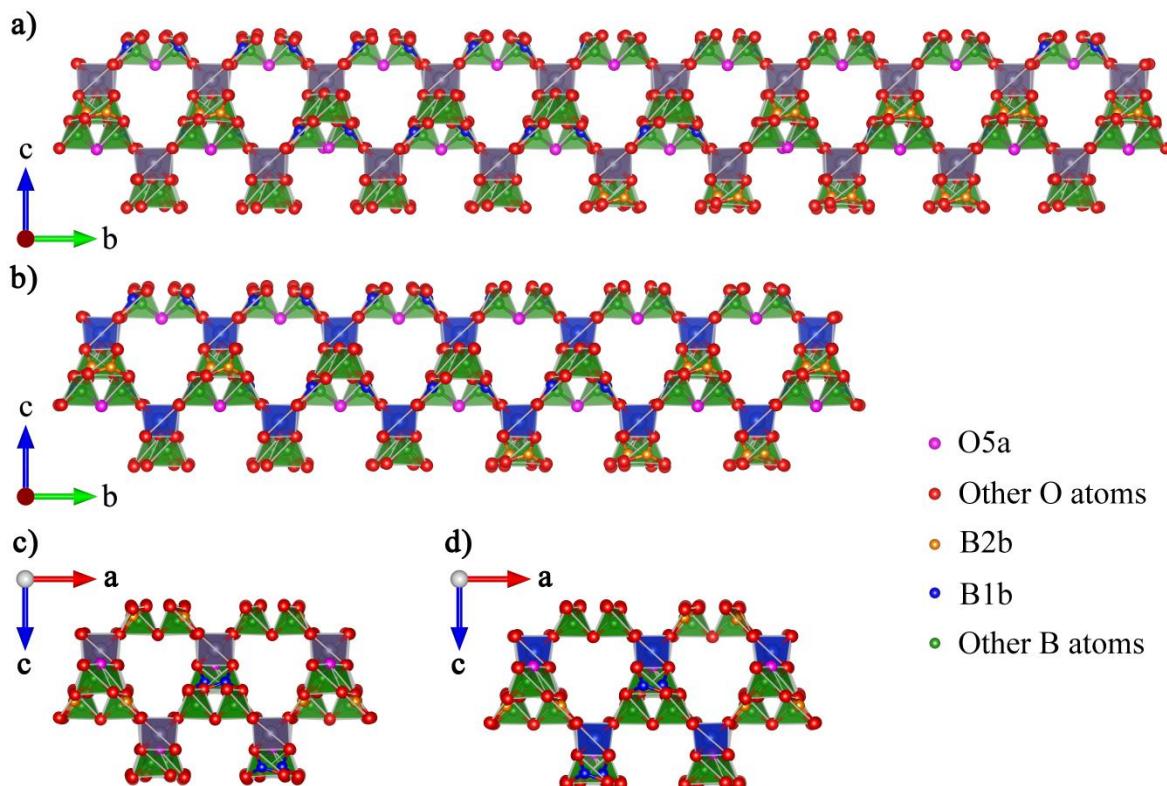


Figure S4 The $2a \times 9b \times 1c$ commensurate approximant of $\text{Cs}_2\text{GeB}_4\text{O}_9$ projected along the **a** axis (a) and along the **b** axis (c). The $2a \times 6b \times 1c$ commensurate approximant of $\text{Cs}_2\text{SiB}_4\text{O}_9$ projected along the **a** axis (b) and along the **b** axis (d). In order to observe the B-T-O anionic network clearly, the Cs1 and the Cs2, which locate in the 1D channels directed along the **a** and **b** axes, were omitted.

Table S1 Refinement results in different $\text{Cs}_2\text{GeB}_4\text{O}_9$ models.

	Refined parameters	R_{obs} (overall)	R_{obs} (main)	R_{obs} (1 st order)	R_{obs} (2 nd order)
Model 1	95	5.58	4.10	6.00	19.66
Model 2	147	5.03	3.84	5.56	14.68
Model 3	146	5.04	3.84	5.58	14.67
Model 4	177	5.03	4.05	5.45	13.24

Table S2 Atomic Parameters for $\text{Cs}_2\text{GeB}_4\text{O}_9$.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso/equ}}$	Occ.
Cs1	0	0	0.00120(10)		
cos1	0	0	0.02157(10)		
sin1	0.00636(14)	-0.03334(12)	0	0.00767(17)	1
cos2	0	0	0.00108(10)		
sin2	0.00066(16)	0.00123(12)	0		
Cs2	-0.5	0	0.24904(7)		
cos1	0	0	-0.00416(11)		
sin1	0.01377(13)	-0.00300(15)	0	0.0083(2)	1
cos2	0	0	0.00031(10)		
sin2	0.00036(15)	0.00230(12)	0		
Ge1	0	-0.5	0.25095(17)		
cos1	0	0	0.00445(17)		
sin1	-0.0187(2)	-0.0084(2)	0	0.0041(4)	1
cos2	0	0	0.00055(16)		
sin2	0.0013(2)	-0.00156(19)	0		
O1	-0.8417(8)	-0.6483(7)	0.1559(5)		
cos1	-0.0038(9)	0.0054(8)	0.0003(6)		
sin1	-0.0182(9)	-0.0125(8)	-0.0018(6)	0.0068(11)	1
cos2	0.0033(11)	-0.0005(9)	0.0012(7)		
sin2	0.0017(11)	-0.0002(9)	-0.0004(7)		

O2	-0.3523(8)	-0.8399(7)	0.8419(5)		
cos1	-0.0082(9)	0.0042(8)	-0.0002(6)		
sin1	-0.0022(9)	-0.0187(8)	-0.0016(6)	0.0070(11)	1
cos2	-0.0012(11)	0.0008(8)	0.0012(7)		
sin2	0.0007(11)	-0.0005(8)	0.0014(7)		
O3	-0.6055(6)	-0.7311(5)	0.9930(8)		
cos1	-0.0048(8)	-0.0031(7)	0.0100(6)		
sin1	-0.0059(8)	-0.0116(7)	0.0014(6)	0.0062(9)	1
cos2	-0.0011(11)	-0.0009(8)	0.0003(6)		
sin2	-0.0018(10)	0.0005(8)	0.0000(6)		
O4	-0.7269(6)	-0.3979(5)	0.0047(8)		
cos1	0.0099(9)	0.0075(7)	0.0104(6)		
sin1	0.0017(9)	-0.0091(7)	0.0113(6)	0.0058(9)	1
cos2	0.0002(11)	-0.0007(8)	0.0010(6)		
sin2	0.0001(11)	0.0003(8)	-0.0006(6)		
O5a	0	0	0.3372(12)		
Legendre1	-0.010(4)	-0.015(3)	0		
Legendre2	0	0	0.006(4)	0.0029(14)	$x_4^0 = 0, \Delta = 0.5$
Legendre3	-0.006(11)	-0.008(8)	0		
Legendre4	0	0	0.005(15)		
O5b	0	0	0.6619(13)		
Legendre1	0.004(3)	0.019(3)	0		
Legendre2	0	0	0.002(4)	0.0029(14)	$x_4^0 = 0.5, \Delta = 0.5$
Legendre3	-0.002(9)	-0.003(9)	0		
Legendre4	0	0	0.011(12)		
B1a	0.0579(18)	-0.1663(16)	0.4192(13)	0.004(2)	
Legendre1	-0.008(3)	-0.013(2)	0.000(2)		

Legendre2	0.008(4)	-0.003(4)	-0.002(3)	$x_4^0 = -$
Legendre3	0.004(6)	-0.001(5)	0.000(5)	0.0478(9), Δ
Legendre4	-0.001(9)	-0.002(7)	0.006(7)	= 0.5
B1b	0.0886(19)	-0.2241(19)	0.4423(14)	
Legendre1	0.004(3)	0.014(3)	0.002(2)	$x_4^0 =$
Legendre2	0.000(5)	0.003(9)	0.005(6)	0.007(3) 0.4305(10), Δ
Legendre3	0.000(7)	0.002(10)	-0.004(7)	= 0.5
Legendre4	-0.004(15)	0.01(4)	0.00(2)	
B2a	-0.1661(17)	-0.0615(16)	0.5797(12)	
Legendre1	0.004(3)	0.015(2)	0.0000(18)	$x_4^0 =$
Legendre2	-0.006(4)	-0.003(3)	0.005(3)	0.003(2) 0.5728(9), Δ
Legendre3	0.001(6)	-0.004(5)	0.001(4)	= 0.5
Legendre4	0.007(8)	0.000(6)	0.003(5)	
B2b	-0.227(2)	-0.0876(17)	0.5555(14)	
Legendre1	-0.010(4)	-0.015(3)	-0.001(3)	
Legendre2	0.004(8)	0.004(5)	-0.004(5)	$x_4^0 =$ 0.0989(10), Δ
Legendre3	0.007(11)	0.002(6)	0.004(8)	= 0.5
Legendre4	0.01(3)	0.007(10)	0.004(19)	

Table S3 The Ge-O bond lengths in the $\text{Cs}_2\text{GeB}_4\text{O}_9$.

Bond	average/ Å	maximum/ Å	minimum/ Å
Ge1-O1	1.753(14)	1.765(14)	1.745(14)
Ge1-O2	1.736(14)	1.754(14)	1.713(14)

Table S4 Results of different $\text{Cs}_2\text{SiB}_4\text{O}_9$ models.

Dimension	Superspace group	R_{obs} (overall)	R_{obs} (main)	R_{obs} (1 st order)	R_{obs} (2 nd order)
(3+2)D	$I2(\alpha_1\beta_10, \alpha_2\beta_20)0$	9.21	3.81	14.27/16.60	34.19/31.06
(3+1)D twin (Model 4)	$I2(\alpha\beta)0$	3.62	2.14	5.44	16.57

Table S5 Atomic Parameters for Cs₂SiB₄O₉.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso/equ}	Occ.
Cs1	0	0	0.00139(7)		
cos1	0	0	0.02111(9)		
sin1	0.00585(12)	-0.02809(15)	0	0.01290(14)	1
cos2	0	0	0.00164(7)		
sin2	-0.00191(12)	-0.00068(10)	0		
Cs2	-0.5	0	0.24894(8)		
cos1	0	0	-0.00697(8)		
sin1	0.00754(10)	0.00272(12)	0	0.0196(3)	1
cos2	0	0	0.00006(7)		
sin2	0.00225(14)	0.00075(11)	0		
Si1	0	-0.5	0.2467(5)		
cos1	0	0	0.0032(3)		
sin1	-0.0166(4)	-0.0077(5)	0	0.0043(8)	1
cos2	0	0	0.0014(3)		
sin2	0.0008(5)	-0.0032(4)	0		
O1	-0.8470(8)	-0.6289(8)	0.1598(6)		
cos1	-0.0048(6)	0.0030(6)	-0.0008(4)		
sin1	-0.0170(6)	-0.0105(6)	-0.0025(4)	0.0091(12)	1
cos2	0.0022(8)	-0.0001(7)	0.0014(5)		
sin2	-0.0002(8)	-0.0005(7)	-0.0002(5)		
O2	-0.3705(8)	-0.8463(7)	0.8405(6)		
cos1	-0.0081(6)	0.0040(5)	-0.0008(3)		
sin1	-0.0013(6)	-0.0122(6)	-0.0022(3)	0.0063(11)	1
cos2	-0.0025(9)	0.0000(7)	0.0001(5)		
sin2	0.0005(9)	-0.0008(7)	0.0006(5)		

O3	-0.6143(8)	-0.7262(7)	0.9957(6)		
cos1	-0.0039(6)	-0.0020(5)	0.0097(4)		
sin1	-0.0065(6)	-0.0062(5)	-0.0002(3)	0.0106(10)	1
cos2	0.0009(8)	-0.0012(7)	-0.0003(5)		
sin2	-0.0020(8)	-0.0016(7)	-0.0001(5)		
O4	-0.7229(7)	-0.3871(7)	0.0051(6)		
cos1	0.0089(6)	0.0040(5)	0.0081(3)		
sin1	0.0003(6)	-0.0050(5)	0.0112(4)	0.0099(10)	1
cos2	0.0008(9)	-0.0001(6)	0.0015(5)		
sin2	0.0028(9)	-0.0004(6)	0.0000(5)		
O5a	0	0	0.3347(10)		
Legendre1	-0.008(2)	-0.008(3)	0		
Legendre2	0	0	0.000(4)	0.0065(8)	$x_4^0 = 0, \Delta = 0.5$
Legendre3	0.010(10)	0.000(8)	0		
Legendre4	0	0	0.000(17)		
O5b	0	0	0.6640(10)		
Legendre1	0.004(2)	0.013(3)	0		
Legendre2	0	0	0.000(3)	0.0065(8)	$x_4^0 = 0.5, \Delta = 0.5$
Legendre3	0.000(7)	0.003(7)	0		
Legendre4	0	0	-0.002(15)		
B1a	0.0527(14)	-0.1691(14)	0.4188(10)		
Legendre1	-0.010(2)	-0.0088(19)	-0.0022(15)		
Legendre2	0.007(4)	-0.001(3)	0.001(3)	0.0075(19)	$x_4^0 = -0.0478(9), \Delta = 0.5$
Legendre3	0.004(5)	0.000(5)	0.000(4)		
Legendre4	-0.002(9)	0.003(7)	0.003(7)		
B1b	0.0789(15)	-0.2286(16)	0.4439(10)		
Legendre1	0.006(2)	0.007(2)	0.0018(16)	0.010(2)	

Legendre2	-0.003(3)	-0.006(7)	0.007(4)	$x_4^0 =$
Legendre3	-0.001(5)	-0.002(8)	0.003(5)	0.4305(10), Δ
Legendre4	-0.002(10)	0.01(3)	-0.005(16)	$= 0.5$
B2a	-0.1696(15)	-0.0558(14)	0.5840(10)	
Legendre1	0.002(2)	0.009(2)	0.0008(14)	$x_4^0 =$
Legendre2	-0.005(3)	0.002(3)	0.005(2)	0.009(2) 0.5728(9), Δ
Legendre3	0.002(5)	-0.001(4)	0.000(3)	$= 0.5$
Legendre4	0.000(9)	-0.004(6)	0.000(5)	
B2b	-0.2264(14)	-0.0773(13)	0.5584(9)	
Legendre1	-0.009(2)	-0.0089(12)	-0.0014(14)	$x_4^0 =$
Legendre2	0.006(5)	0.006(2)	-0.001(3)	0.0066(18) 0.0989(10), Δ
Legendre3	-0.007(7)	-0.001(3)	-0.005(5)	$= 0.5$
Legendre4	0.001(19)	0.001(5)	0.002(12)	

Table S6 The Si-O bond lengths in the Cs₂GeB₄O₉.

Bond	average/ Å	maximum/ Å	minimum/ Å
Si1-O1	1.602(11)	1.618(11)	1.575(11)
Si1-O2	1.645(11)	1.684(11)	1.602(11)