Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

$Na_3AEZn_2B_3O_9$ (AE=Mg, Ca): Two New Short-Wave Ultraviolet Beryllium-Free $Sr_2Be_2B_2O_7$-type Zincoborates Designed by Chemical Cosubstitution

Zhi Fang[a], Chun-Li Hu[a], Wen-Tong Chen*[b] and Jiang-Gao Mao*[a]

[a] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China, E-mail: mjg@fjirsm.ac.cn.

[b] Institute of Applied Chemistry, School of Chemistry and Chemical Engineering, Ji'an Key Laboratory of Photoelectric Crystal Materials and Device, Jiangxi Province Key Laboratory of Coordination Chemistry, Humic Acid Utilization Engineering Research Center of Jiangxi Province, Jinggangshan University, Ji'an, Jiangxi 343009, China, E-mail: wtchen_2000@aliyun.com.

CONTENTS

Table S1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **I** and **II**.

Atoms in I	***x***	***y***	***z***	U_{iso}*/U_{eq}	**Occ. (<1)**
Na1	0.3836 (10)	0.6164 (10)	0.250000	0.018 (3)	0.3333
Na2	1.000000	1.000000	0.33680 (19)	0.0229 (9)	
Ca1	1.000000	1.000000	0.500000	0.0093 (5)	
Zn1	0.666667	0.333333	0.39770 (5)	0.0110 (4)	
B1	0.333333	0.666667	0.4235 (5)	0.0106 (17)	
B2	0.607 (6)	0.303 (3)	0.250000	0.009 (7)	0.3333
O1	0.6168 (8)	0.6791 (9)	0.4243 (2)	0.0184 (8)	
O2	0.598 (6)	0.208 (3)	0.3065 (6)	0.038 (4)	0.3333
O3	0.682 (8)	1.004 (8)	0.2506 (13)	0.039 (7)	0.1667
Atoms in II	**x**	**y**	**z**	**Uiso*/Ueq**	**Occ. (<1)**
Na1	0.3848 (17)	0.6152 (17)	0.250000	0.060 (6)	0.3333
Na2	1.000000	1.000000	0.34133 (16)	0.0283 (9)	
Mg1	1.000000	1.000000	0.500000	0.0029 (6)	
Zn1	0.666667	0.333333	0.40767 (4)	0.0125 (4)	
B1	0.333333	0.666667	0.4332 (5)	0.0145 (17)	
B2	0.587 (5)	0.294 (2)	0.250000	0.022 (6)	0.3333
O1	0.6323 (7)	0.7016 (7)	0.43321 (15)	0.0143 (7)	
O2	0.609 (6)	0.219 (2)	0.3089 (5)	0.032 (3)	0.3333
O3	0.657 (5)	0.978 (5)	0.2515 (9)	0.025 (5)	0.1667

Table S2. Atomic displacement parameters (Å^2) for **I** and **II**.

Atoms in I	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Na1	0.021 (4)	0.021 (4)	0.003 (3)	0.004 (3)	0.001 (3)	0.001 (3)
Na2	0.0253 (14)	0.0253 (14)	0.0182 (18)	0.0126 (7)	0.000	0.000
Ca1	0.0099 (7)	0.0099 (7)	0.0081 (10)	0.0050 (4)	0.000	0.000
Zn1	0.0108 (4)	0.0108 (4)	0.0114 (6)	0.0054 (2)	0.000	0.000
B1	0.009 (2)	0.009 (2)	0.014 (4)	0.0045 (12)	0.000	0.000
B2	0.006 (11)	0.011 (9)	0.009 (6)	0.003 (5)	0.000	0.000 (9)
O1	0.0077 (18)	0.0112 (16)	0.037 (2)	0.0051 (15)	−0.0043 (15)	−0.0046 (16)
O2	0.056 (15)	0.035 (8)	0.013 (5)	0.016 (12)	0.001 (7)	−0.001 (5)
O3	0.051 (11)	0.051 (11)	0.018 (9)	0.028 (8)	0.004 (8)	0.001 (8)
Atoms in II	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Na1	0.048 (6)	0.048 (6)	0.026 (4)	-0.019 (6)	0.004 (5)	0.004 (5)
Na2	0.0323 (13)	0.0323 (13)	0.0204 (17)	0.0162 (6)	0.000	0.000
Mg1	0.0016 (8)	0.0016 (8)	0.0054 (14)	0.0008 (4)	0.000	0.000
Zn1	0.0124 (4)	0.0124 (4)	0.0126 (6)	0.0062 (2)	0.000	0.000
B1	0.015 (3)	0.015 (3)	0.013 (4)	0.0075 (13)	0.000	0.000
B2	0.031 (11)	0.020 (7)	0.018 (7)	0.015 (5)	0.000	0.000 (8)
O1	0.0092 (14)	0.0098 (14)	0.0242 (15)	0.0048 (12)	0.0007 (11)	-0.0008 (12)
O2	0.044 (11)	0.034 (7)	0.013 (4)	0.017 (11)	-0.016 (6)	-0.004 (4)
O3	0.023 (8)	0.049 (10)	0.006 (6)	0.020 (7)	-0.001 (6)	-0.003 (7)

Table S3. Selected geometric parameters for **I**.

Atoms 1,2	d 1,2 [Å]	Atoms 1,2	d 1,2 [Å]
Na1—O2^{i}	2.212 (15)	Ca1—O1^{xi}	2.343 (4)
Na1—O2^{ii}	2.212 (15)	Ca1—O1^{vi}	2.343 (4)
Na1—O3^{iii}	2.09 (4)	Ca1—O1^{xii}	2.343 (4)
Na1—O3^{iv}	2.09 (4)	Ca1—O1^{xiii}	2.343 (4)
Na2—O1	2.508 (5)	Zn1—O1^{xiv}	1.924 (4)
Na2—O1^{v}	2.508 (5)	Zn1—O1^{ii}	1.924 (4)
Na2—O1^{vi}	2.508 (5)	Zn1—O1	1.924 (4)
Na2—O2^{ii}	2.67 (3)	Zn1—O2^{xiv}	1.937 (12)
Na2—O2^{iii}	2.67 (3)	Zn1—O2	1.937 (12)
Na2—O2^{vii}	2.67 (3)	Zn1—O2^{ii}	1.937 (12)
Na2—O3^{viii}	2.38 (3)	B1—O1	1.373 (3)
Na2—O3^{vi}	2.37 (3)	B1—O1^{xv}	1.373 (4)
Na2—O3^{v}	2.37 (3)	B1—O1^{iii}	1.373 (3)
Na2—O3^{ix}	2.38 (3)	B2—O2^{xiv}	1.40 (2)
Na2—O3^{x}	2.38 (3)	B2—O2^{xvi}	1.40 (2)
Na2—O3	2.37 (3)	B2—O3^{xv}	1.45 (4)
Atoms 1,2,3	**Angle 1,2,3 [º]**	**Atoms 1,2,3**	**Angle 1,2,3 [º]**
O2^{ii}—Na1—O2^{i}	62.9 (7)	O1^{xi}—Ca1—O1^{v}	180.0
O3^{iii}—Na1—O2^{ii}	142.1 (10)	O1—Ca1—O1^{xi}	98.76 (15)
O3—Na1—O2^{ii}	99.8 (13)	O1—Ca1—O1^{vi}	81.24 (15)
O3^{iv}—Na1—O2^{ii}	141.7 (10)	O1^{xii}—Ca1—O1^{xi}	81.24 (15)
O3^{xvi}—Na1—O2^{ii}	101.8 (13)	O1—Ca1—O1^{xiii}	98.76 (15)
O3^{iv}—Na1—O2^{i}	142.1 (10)	O1^{xii}—Ca1—O1^{v}	98.76 (15)
O3^{xvi}—Na1—O2^{i}	99.8 (13)	O1^{xiv}—Zn1—O1	112.38 (11)
O3^{iii}—Na1—O2^{i}	141.7 (10)	O1^{ii}—Zn1—O1^{xiv}	112.38 (11)
O3—Na1—O2^{i}	101.8 (13)	O1^{ii}—Zn1—O1	112.38 (11)
O3^{ix}—Na1—O3	61 (2)	O1—Zn1—O2^{xiv}	108.5 (9)
O3^{xv}—Na1—O3^{iv}	161 (2)	O1^{xiv}—Zn1—O2	91.1 (5)
O3^{xvi}—Na1—O3^{iv}	100.0 (5)	O1^{ii}—Zn1—O2^{xiv}	91.1 (5)
O3^{ix}—Na1—O3^{iii}	161 (2)	O1—Zn1—O2^{ii}	91.1 (5)
O3^{ix}—Na1—O3^{xv}	83 (3)	O1—Zn1—O2	118.4 (7)
O3^{xv}—Na1—O3	144.0 (8)	O1^{ii}—Zn1—O2^{ii}	118.4 (7)
O3^{ix}—Na1—O3^{xvi}	144.0 (8)	O1^{xiv}—Zn1—O2^{ii}	108.5 (9)
O3^{xvi}—Na1—O3	155 (2)	O1^{ii}—Zn1—O2	108.5 (9)
O3—Na1—O3^{iii}	100.0 (5)	O1^{xiv}—Zn1—O2^{xiv}	118.4 (7)
O3^{ix}—Na1—O3^{iv}	116.0 (5)	O1^{iii}—B1—O1	119.99 (2)
O3^{xv}—Na1—O3^{iii}	116.0 (5)	O1^{xv}—B1—O1	119.99 (2)

O3^{xv}—Na1—O3^{xvi}	61 (2)	O1^{iii}—B1—O1^{xv}	119.99 (2)
O1^{vi}—Na2—O1^{v}	74.93 (17)	O2^{xiv}—B2—O2^{xvi}	111 (2)
O1^{vi}—Na2—O1	74.93 (17)	O2—B2—O3^{ix}	111.7 (12)
O1^{v}—Na2—O1	74.93 (17)	O2^{xiv}—B2—O3^{xv}	118.9 (15)
O1^{v}—Na2—O2^{iii}	138.5 (4)	O2^{xiv}—B2—O3^{xvii}	118.3 (15)
O1—Na2—O2^{iii}	100.4 (3)	O2^{xvi}—B2—O3^{xv}	118.3 (15)
O1^{vi}—Na2—O2^{ii}	138.5 (4)	O2^{i}—B2—O3^{xviii}	111.7 (12)
O1—Na2—O2^{vii}	138.5 (4)	O2^{ii}—B2—O3^{xviii}	111.7 (12)
O1^{vi}—Na2—O2^{vii}	100.4 (3)	O2^{xvi}—B2—O3^{xvii}	118.9 (15)
O1^{v}—Na2—O2^{ii}	100.4 (3)	Ca1—O1—Na2	86.64 (13)
O1^{vi}—Na2—O2^{iii}	64.2 (3)	Zn1—O1—Na2	88.26 (15)
O1—Na2—O2^{ii}	64.2 (3)	Zn1—O1—Ca1	111.61 (16)
O1^{v}—Na2—O2^{vii}	64.2 (4)	B1—O1—Na2	116.9 (4)
O2^{vii}—Na2—O2^{iii}	114.8 (2)	B1—O1—Ca1	120.0 (4)
O2^{ii}—Na2—O2^{vii}	114.8 (2)	B1—O1—Zn1	122.6 (3)
O2^{ii}—Na2—O2^{iii}	114.8 (2)	Na1^{xiv}—O2—Na1^{xix}	10.4 (3)
O3^{vi}—Na2—O1^{vi}	103.9 (8)	Na1^{xiv}—O2—Na2^{xviii}	80.0 (7)
O3^{vi}—Na2—O1^{v}	110.8 (8)	Na1^{xiv}—O2—Na2^{xx}	81.3 (7)
O3^{ix}—Na2—O1	94.2 (8)	Na2^{xx}—O2—Na1^{xix}	71.5 (5)
O3^{v}—Na2—O1^{v}	103.9 (8)	Na2^{xviii}—O2—Na1^{xix}	84.9 (6)
O3^{vi}—Na2—O1	173.8 (8)	Na2^{xx}—O2—Na2^{xviii}	132.7 (5)
O3^{viii}—Na2—O1^{vi}	134.2 (8)	Zn1—O2—Na1^{xiv}	137.5 (7)
O3^{ix}—Na2—O1^{vi}	145.9 (8)	Zn1—O2—Na1^{xix}	130.4 (6)
O3^{v}—Na2—O1	110.8 (8)	Zn1—O2—Na2^{xviii}	81.9 (8)
O3^{ix}—Na2—O1^{v}	134.2 (8)	Zn1—O2—Na2^{xx}	83.4 (8)
O3—Na2—O1^{v}	173.8 (8)	B2^{xiv}—O2—Na1^{xix}	86.6 (8)
O3^{viii}—Na2—O1^{v}	94.2 (7)	B2^{ii}—O2—Na1^{xix}	100.2 (10)
O3^{viii}—Na2—O1	145.9 (8)	B2^{ii}—O2—Na1^{xiv}	93.1 (10)
O3^{v}—Na2—O1^{vi}	173.8 (8)	B2—O2—Na1^{xiv}	78.4 (8)
O3^{x}—Na2—O1^{vi}	94.2 (7)	B2^{xiv}—O2—Na1^{xiv}	78.2 (8)
O3^{x}—Na2—O1	134.2 (8)	B2—O2—Na1^{xix}	84.1 (10)
O3—Na2—O1^{vi}	110.8 (8)	B2^{ii}—O2—Na2^{xviii}	110.6 (15)
O3—Na2—O1	103.9 (8)	B2^{ii}—O2—Na2^{xx}	113.5 (15)
O3^{x}—Na2—O1^{v}	145.9 (9)	B2^{xiv}—O2—Na2^{xx}	120.5 (18)
O3—Na2—O2^{ii}	73.8 (9)	B2^{xiv}—O2—Na2^{xviii}	97.4 (19)
O3^{v}—Na2—O2^{vii}	73.8 (9)	B2—O2—Na2^{xviii}	117.4 (18)
O3^{ix}—Na2—O2^{vii}	108.5 (9)	B2—O2—Na2^{xx}	101 (2)
O3—Na2—O2^{vii}	115.9 (8)	B2^{xiv}—O2—Zn1	142.4 (12)
O3^{x}—Na2—O2^{vii}	86.9 (9)	B2^{ii}—O2—Zn1	129.2 (12)
O3^{viii}—Na2—O2^{iii}	108.5 (8)	B2—O2—Zn1	143.6 (12)
O3^{vi}—Na2—O2^{ii}	115.9 (8)	B2—O2—B2^{xiv}	21 (2)
O3^{viii}—Na2—O2^{ii}	86.9 (9)	B2—O2—B2^{ii}	18.1 (17)
O3^{v}—Na2—O2^{iii}	115.9 (8)	B2^{xiv}—O2—B2^{ii}	18.2 (17)
O3^{x}—Na2—O2^{ii}	108.5 (9)	Na1^{iii}—O3—Na1	24.0 (8)

O3^{ix}—Na2—O2^{iii}	86.9 (9)	Na1—O3—Na1^{xv}	20.0 (5)
O3^{v}—Na2—O3^{x}	83.5 (12)	Na1^{iii}—O3—Na1^{xv}	4.0 (5)
O3^{vi}—Na2—O3	70.8 (11)	Na1^{iii}—O3—Na2	116.3 (17)
O3^{viii}—Na2—O3^{x}	70.2 (12)	Na1^{xv}—O3—Na2	113.8 (13)
O3^{v}—Na2—O3^{vi}	70.8 (11)	Na1—O3—Na2	101.4 (14)
O3^{v}—Na2—O3	70.8 (11)	Na1^{iii}—O3—B2^{iii}	111 (2)
O3^{vi}—Na2—O3^{ix}	83.5 (12)	Na1^{iii}—O3—B2^{vi}	111 (2)
O3—Na2—O3^{viii}	83.5 (12)	Na1—O3—B2^{vi}	134.5 (19)
O1—Ca1—O1^{v}	81.24 (15)	Na1^{iii}—O3—B2^{xxi}	98 (2)
O1^{xii}—Ca1—O1^{xiii}	81.24 (15)	B2^{iii}—O3—Na1^{xv}	115.2 (19)
O1^{v}—Ca1—O1^{xiii}	98.76 (15)	B2^{vi}—O3—Na1^{xv}	114.6 (16)
O1^{xii}—Ca1—O1^{vi}	98.76 (15)	B2^{xxi}—O3—Na1	122 (2)
O1^{xi}—Ca1—O1^{xiii}	81.24 (15)	B2^{xxi}—O3—Na1^{xv}	101.7 (17)
O1—Ca1—O1^{xii}	180.00 (15)	B2^{iii}—O3—Na1	135 (2)
O1^{xi}—Ca1—O1^{vi}	98.76 (15)	B2^{xxi}—O3—Na2	116.7 (16)
O1^{v}—Ca1—O1^{vi}	81.24 (15)	B2^{iii}—O3—Na2	108.7 (17)
O1^{xiii}—Ca1—O1^{vi}	180.0	B2^{vi}—O3—Na2	109.0 (14)

(i) *x*, *x*-*y*, -*z*+1/2; (ii) -*x*+*y*+1, -*x*+1, *z*; (iii) -*y*+1, *x*-*y*+1, *z*; (iv) -*x*+*y*, *y*, -*z*+1/2; (v) -*y*+2, *x*-*y*+1, *z*; (vi) -*x*+*y*+1, -*x*+2, *z*; (vii) *x*+1, *y*+1, *z*; (viii) -*x*+*y*+1, *y*, -*z*+1/2; (ix) *x*, *x*-*y*+1, -*z*+1/2; (x) -*y*+2, -*x*+2, -*z*+1/2; (xi) *y*, -*x*+*y*+1, -*z*+1; (xii) -*x*+2, -*y*+2, -*z*+1; (xiii) *x*-*y*+1, *x*, -*z*+1; (xiv) -*y*+1, *x*-*y*, *z*; (xv) -*x*+*y*, -*x*+1, *z*; (xvi) -*y*+1, -*x*+1, -*z*+1/2; (xvii) -*x*+*y*, *y*-1, -*z*+1/2; (xviii) *x*, *y*-1, *z*; (xix) -*x*+*y*, -*x*, *z*; (xx) *x*-1, *y*-1, *z*; (xxi) *x*, *y*+1, *z*.

Table S4. Selected geometric parameters for **II**.

Atoms 1,2	d 1,2 [Å]	Atoms 1,2	d 1,2 [Å]
Na1—O2^{i}	2.218 (15)	Mg1—O1^{xii}	2.102 (3)
Na1—O2^{ii}	2.218 (15)	Mg1—O1^{iii}	2.102 (3)
Na2—O1	2.437 (4)	Mg1—O1^{iv}	2.102 (3)
Na2—O1^{iii}	2.437 (4)	Zn1—O1^{xiii}	1.947 (3)
Na2—O1^{iv}	2.437 (4)	Zn1—O1^{i}	1.947 (3)
Na2—O2^{i}	2.68 (3)	Zn1—O1	1.947 (3)
Na2—O2^{v}	2.68 (3)	Zn1—O2	1.990 (9)
Na2—O2^{vi}	2.68 (3)	Zn1—O2^{i}	1.990 (9)
Na2—O3^{vii}	2.431 (18)	Zn1—O2^{xiii}	1.990 (9)
Na2—O3^{iii}	2.386 (18)	B1—O1	1.378 (3)
Na2—O3	2.386 (18)	B1—O1^{xiv}	1.378 (3)
Na2—O3^{viii}	2.431 (18)	B1—O1^{vi}	1.378 (3)
Na2—O3^{ix}	2.431 (18)	B2—O2^{xiii}	1.411 (15)
Na2—O3^{iv}	2.386 (18)	B2—O2^{xv}	1.411 (15)
Mg1—O1^{x}	2.102 (3)	B2—O3^{xvi}	1.435 (18)
Mg1—O1	2.102 (3)	B2—O3^{xiv}	1.435 (18)
Mg1—O1^{xi}	2.102 (3)		
Atoms 1,2,3	**Angle 1,2,3 [°]**	**Atoms 1,2,3**	**Angle 1,2,3 [°]**
O2^{ii}—Na1—O2^{i}	62.6 (6)	O1^{iv}—Mg1—O1^{iii}	85.48 (12)
O3^{xiv}—Na1—O2^{i}	50.5 (12)	O1^{x}—Mg1—O1^{iii}	180.0
O3^{xvii}—Na1—O2^{ii}	141.7 (7)	O1^{xi}—Mg1—O1	180.00 (16)
O3—Na1—O2^{ii}	102.4 (11)	O1^{xii}—Mg1—O1^{iv}	180.0
O3^{vi}—Na1—O2^{ii}	143.2 (7)	O1—Mg1—O1^{xii}	94.52 (12)
O3^{xiv}—Na1—O2^{ii}	52.3 (12)	O1^{xi}—Mg1—O1^{iii}	94.52 (12)
O3^{xv}—Na1—O2^{ii}	101.1 (10)	O1^{xii}—Mg1—O1^{iii}	94.52 (12)
O3^{vi}—Na1—O2^{i}	141.7 (7)	O1^{xi}—Mg1—O1^{x}	85.48 (12)
O3^{xv}—Na1—O2^{i}	102.4 (10)	O1—Mg1—O1^{iv}	85.48 (12)
O3^{xvii}—Na1—O2^{i}	143.2 (7)	O1^{xiii}—Zn1—O1	113.66 (7)
O3—Na1—O2^{i}	101.1 (10)	O1^{i}—Zn1—O1^{xiii}	113.66 (7)
O3^{viii}—Na1—O3	60.7 (14)	O1^{i}—Zn1—O1	113.66 (7)
O3—Na1—O3^{vi}	98.2 (7)	O1—Zn1—O2^{i}	92.2 (4)
O3^{xiv}—Na1—O3^{vi}	114.9 (5)	O1^{i}—Zn1—O2^{i}	116.2 (6)
O3^{viii}—Na1—O3^{xvii}	114.9 (5)	O1^{xiii}—Zn1—O2^{i}	105.5 (8)
O3^{viii}—Na1—O3^{xiv}	86 (2)	O1—Zn1—O2	116.2 (6)
O3^{xv}—Na1—O3^{xvii}	98.2 (7)	O1^{i}—Zn1—O2^{xiii}	92.2 (4)
O3^{xiv}—Na1—O3	146.8 (11)	O1—Zn1—O2^{xiii}	105.5 (8)
O3^{viii}—Na1—O3^{xv}	146.8 (11)	O1^{i}—Zn1—O2	105.5 (8)
O3^{xv}—Na1—O3	152.5 (16)	O1^{xiii}—Zn1—O2	92.2 (4)
O3—Na1—O3^{xvii}	54.3 (11)	O1^{xiii}—Zn1—O2^{xiii}	116.2 (6)
O3^{viii}—Na1—O3^{vi}	158.9 (16)	O1^{vi}—B1—O1	120.000 (4)
O3^{xiv}—Na1—O3^{xvii}	158.9 (16)	O1^{vi}—B1—O1^{xiv}	120.000 (4)

O1^{iv}—Na2—O1^{iii}	71.65 (14)	O1^{xiv}—B1—O1	120.000 (3)
O1^{iv}—Na2—O1	71.65 (14)	O2^{xv}—B2—O3^{xvi}	115.9 (11)
O1^{iii}—Na2—O1	71.65 (14)	O2^{xiii}—B2—O3^{xvi}	118.0 (12)
O1^{iii}—Na2—O2^{vi}	138.5 (3)	O2^{xiii}—B2—O3^{xiv}	115.9 (11)
O1—Na2—O2^{vi}	99.4 (2)	O2^{xv}—B2—O3^{xiv}	118.0 (12)
O1^{iv}—Na2—O2^{i}	138.5 (3)	Mg1—O1—Na2	85.88 (11)
O1—Na2—O2^{v}	138.5 (3)	Zn1—O1—Na2	89.09 (12)
O1^{iv}—Na2—O2^{v}	99.4 (2)	Zn1—O1—Mg1	111.11 (15)
O1^{iii}—Na2—O2^{i}	99.4 (2)	B1—O1—Na2	119.3 (4)
O1^{iv}—Na2—O2^{vi}	67.1 (3)	B1—O1—Mg1	124.5 (3)
O1—Na2—O2^{i}	67.1 (3)	B1—O1—Zn1	117.3 (2)
O1^{iii}—Na2—O2^{v}	67.1 (3)	Na1^{xiii}—O2—Na1^{xviii}	10.3 (4)
O2^{v}—Na2—O2^{vi}	114.58 (17)	Na1^{xiii}—O2—Na2^{xix}	80.1 (6)
O2^{i}—Na2—O2^{v}	114.58 (17)	Na1^{xiii}—O2—Na2^{xx}	80.1 (6)
O2^{i}—Na2—O2^{vi}	114.58 (17)	Na2^{xx}—O2—Na1^{xviii}	70.4 (5)
O3^{iii}—Na2—O1^{iv}	170.8 (5)	Na2^{xix}—O2—Na1^{xviii}	84.6 (5)
O3^{iii}—Na2—O1^{iii}	103.1 (5)	Na2^{xx}—O2—Na2^{xix}	130.6 (4)
O3^{viii}—Na2—O1	96.0 (4)	Zn1—O2—Na1^{xviii}	128.0 (5)
O3—Na2—O1^{iii}	170.8 (5)	Zn1—O2—Na1^{xiii}	135.3 (5)
O3^{iii}—Na2—O1	114.4 (4)	Zn1—O2—Na2^{xx}	81.7 (7)
O3^{vii}—Na2—O1^{iv}	136.6 (5)	Zn1—O2—Na2^{xix}	81.6 (7)
O3^{viii}—Na2—O1^{iv}	145.1 (5)	B2—O2—Na1^{xviii}	79.4 (7)
O3—Na2—O1	103.1 (5)	B2^{xiii}—O2—Na1^{xiii}	74.4 (6)
O3^{viii}—Na2—O1^{iii}	136.6 (5)	B2^{i}—O2—Na1^{xviii}	100.9 (8)
O3^{iv}—Na2—O1^{iii}	114.4 (4)	B2^{xiii}—O2—Na1^{xviii}	83.1 (5)
O3^{vii}—Na2—O1^{iii}	96.0 (4)	B2—O2—Na1^{xiii}	74.4 (6)
O3^{vii}—Na2—O1	145.1 (5)	B2^{i}—O2—Na1^{xiii}	94.0 (8)
O3—Na2—O1^{iv}	114.4 (4)	B2—O2—Na2^{xx}	95.6 (17)
O3^{ix}—Na2—O1^{iv}	96.0 (4)	B2^{i}—O2—Na2^{xix}	113.0 (14)
O3^{ix}—Na2—O1	136.6 (5)	B2^{i}—O2—Na2^{xx}	113.2 (14)
O3^{iv}—Na2—O1^{iv}	103.1 (5)	B2^{xiii}—O2—Na2^{xix}	95.4 (17)
O3^{iv}—Na2—O1	170.8 (5)	B2^{xiii}—O2—Na2^{xx}	121.7 (15)
O3^{ix}—Na2—O1^{iii}	145.1 (5)	B2—O2—Na2^{xix}	121.5 (16)
O3^{viii}—Na2—O2^{v}	110.3 (5)	B2^{i}—O2—Zn1	130.7 (9)
O3^{iv}—Na2—O2^{i}	117.0 (5)	B2—O2—Zn1	148.1 (11)
O3^{iii}—Na2—O2^{v}	71.5 (6)	B2^{xiii}—O2—Zn1	147.9 (11)
O3^{ix}—Na2—O2^{v}	83.6 (6)	B2^{xiii}—O2—B2^{i}	24.1 (14)
O3^{ix}—Na2—O2^{i}	110.3 (5)	B2—O2—B2^{xiii}	27.2 (16)
O3^{vii}—Na2—O2^{vi}	110.3 (5)	B2—O2—B2^{i}	24.1 (14)
O3—Na2—O2^{i}	71.5 (5)	Na1^{vi}—O3—Na1	26.9 (11)
O3—Na2—O2^{v}	117.0 (5)	Na1—O3—Na1^{xiv}	21.8 (7)
O3^{iv}—Na2—O2^{vi}	71.5 (5)	Na1—O3—Na2^{ix}	102.0 (9)
O3^{vii}—Na2—O2^{i}	83.6 (6)	Na1^{xiv}—O3—Na2^{ix}	115.3 (8)
O3^{viii}—Na2—O2^{vi}	83.6 (6)	Na1^{vi}—O3—Na2	120.6 (13)

O3^{iii}—Na2—O2^{vi}	117.0 (5)	Na1—O3—Na2	103.9 (9)
O3^{iv}—Na2—O3^{viii}	84.1 (6)	Na1^{xiv}—O3—Na2	117.3 (9)
O3^{viii}—Na2—O3^{vii}	70.3 (7)	Na1^{vi}—O3—Na2^{ix}	117.6 (12)
O3^{iii}—Na2—O3^{ix}	84.1 (6)	Na1^{vi}—O3—B2^{xxi}	97.1 (14)
O3^{viii}—Na2—O3^{ix}	70.3 (7)	Na1—O3—B2^{xxi}	123.9 (13)
O3^{iii}—Na2—O3^{iv}	71.8 (7)	Na1^{vi}—O3—B2^{vi}	115.1 (14)
O3^{vii}—Na2—O3^{ix}	70.3 (7)	Na2—O3—Na2^{ix}	95.7 (6)
O3—Na2—O3^{iii}	71.8 (7)	B2^{xxi}—O3—Na1^{xiv}	102.1 (11)
O3—Na2—O3^{iv}	71.8 (7)	B2^{vi}—O3—Na1	142.0 (14)
O3—Na2—O3^{vii}	84.1 (6)	B2^{vi}—O3—Na1^{xiv}	120.2 (11)
O1^{xi}—Mg1—O1^{iv}	94.52 (12)	B2^{xxi}—O3—Na2^{ix}	112.5 (9)
O1—Mg1—O1^{x}	94.52 (12)	B2^{vi}—O3—Na2	103.3 (11)
O1^{iv}—Mg1—O1^{x}	94.52 (12)	B2^{xxi}—O3—Na2	114.5 (9)
O1—Mg1—O1^{iii}	85.48 (12)	B2^{vi}—O3—Na2^{ix}	101.2 (11)
O1^{xii}—Mg1—O1^{x}	85.48 (12)	O1^{xi}—Mg1—O1^{xii}	85.48 (12)

(i) -*x*+*y*+1, -*x*+1, *z*; (ii) *x*, *x*-*y*, -*z*+1/2; (iii) -*y*+2, *x*-*y*+1, *z*; (iv) -*x*+*y*+1, -*x*+2, *z*; (v) *x*+1, *y*+1, *z*; (vi) -*y*+1, *x*-*y*+1, *z*; (vii) -*x*+*y*+1, *y*, -*z*+1/2; (viii) *x*, *x*-*y*+1, -*z*+1/2; (ix) -*y*+2, -*x*+2, -*z*+1/2; (x) *y*, -*x*+*y*+1, -*z*+1; (xi) -*x*+2, -*y*+2, -*z*+1; (xii) *x*-*y*+1, *x*, -*z*+1; (xiii) -*y*+1, *x*-*y*, *z*; (xiv) -*x*+*y*, -*x*+1, *z*; (xv) -*y*+1, -*x*+1, -*z*+1/2; (xvi) -*x*+*y*, *y*-1, -*z*+1/2; (xvii) -*x*+*y*, *y*, -*z*+1/2; (xviii) -*x*+*y*, -*x*, *z*; (xix) *x*, *y*-1, *z*; (xx) *x*-1, *y*-1, *z*; (xxi) *x*, *y*+1, *z*.

Table S5. Calculated bond valence sums (BVS) for **I** and **II**.

Atoms in I	**BVS**
Na1	1.58
Na2	0.84
Ca1	2.17
Zn1	2.19
B1	2.98
B2	2.66
Atoms in II	**BVS**
Na1	2.03
Na2	0.92
Mg1	1.99
Zn1	2.02
B1	2.83
B2	2.65

Atomic assignments in the structural refinement of I and II.

Normal atoms in the asymmetric units of **I** and **II** were automatically determined by ShelXT, meanwhile split atoms of 'Na1', 'O2', and 'B2' were also assigned to be normal atoms by ShelXT. At that time, the abnormal structural indicators of R_1 and wR_2 as well as the abnormal atomic displacement parameters of 'Na1', 'O2' and 'B2' were first clues to the splitting of them. Hence, through the splitting of 'Na1', 'O2' and 'B2', structural indicators of **I** and **II** were rationalized to a reasonable level. Still, the abnormal coordination mode of 'B2' (two-coordinated to oxygen atoms) as well as the charge imbalance of their molecular sums ($Na_3CaZn_2B_3O_8$ and $Na_3MgZn_2B_3O_8$) indicated that there are oxygen atoms near 'B2' to be determined. Accordingly, largest diff. peaks in **I** and **II** near 'B2' were assigned to be 'O3' with partially-occupied displacements, which realized the charge balance of their molecular sums, the three-coordinated connection mode of 'B2' as well as the rationalizing of *R*1 and *wR*2.