Supporting Information

Hierarchized bandgap and enhanced optical responses from (d-p)π conjugated interaction in trivalent d^0 transition metal nitrates

Bing-Hua Lei, [a,b‡] *Qingrong Kong,* [a,c,‡] *Zhihua Yang,* [a*] *Yun Yang,* [a] *Ying Wang,* [a] *Shilie Pan* [a*]

[a]*Key Laboratory of Functional Materials and Devices for Special Environments, Xinjiang Technical Institute of Physics & Chemistry, Chinese Academy of Sciences; Xinjiang Key Laboratory of Electronic Information Materials and Devices, 40-1 South Beijing Road, Urumqi 830011, China.*

[b]*University of Chinese Academy of Sciences, Beijing 100049, China*

[c]*College of Chemistry and Chemical Engineering, Xinjiang Normal University, Urumqi 830054,China*

**To whom correspondence should be addressed.*

E-mail: zhyang@ms.xjb.ac.cn (Zhihua Yang), slpan@ms.xjb.ac.cn (Shilie Pan);

[‡] *Equal Contributors*

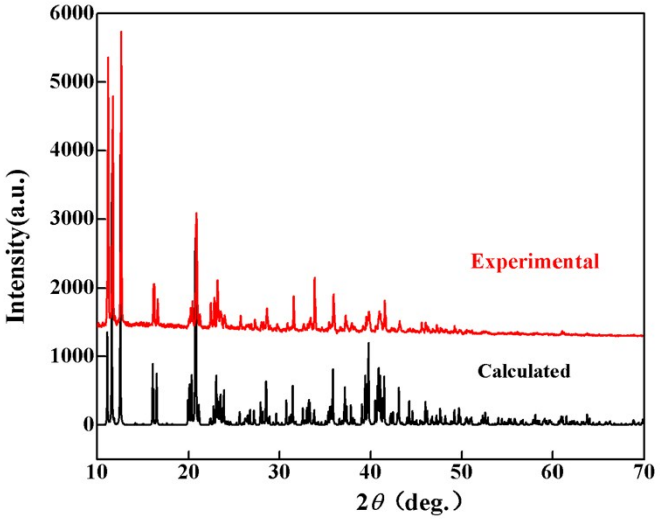


Figure S1. Experimental and calculated XRD patterns of NLN.

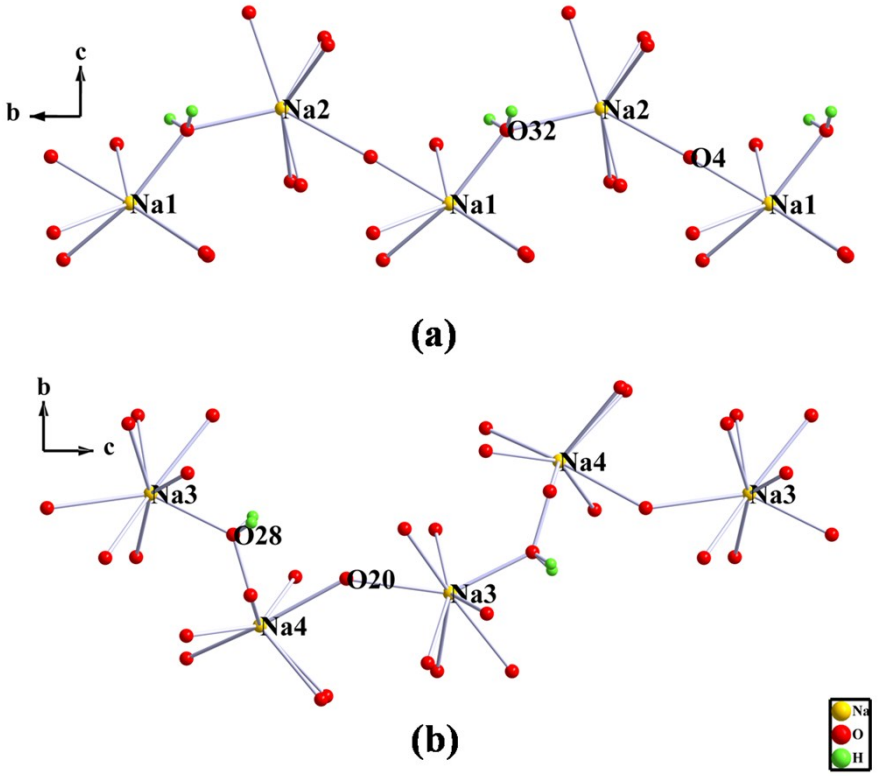


Figure S2. (a)The NaO_7 polyhedra connect further with each other via sharing two oxygen atoms alternatively forming 1D $[NaO_6]_\infty$ chain in NLN. (b)The NaO_8 octahedra connect further with each other via sharing two oxygen atoms alternatively forming 1D $[NaO_7]_\infty$ chain in NLN.

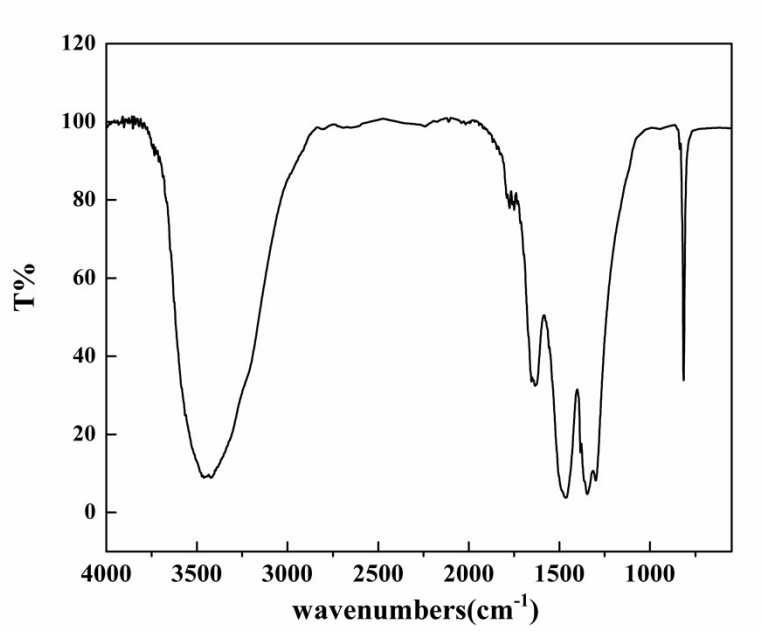
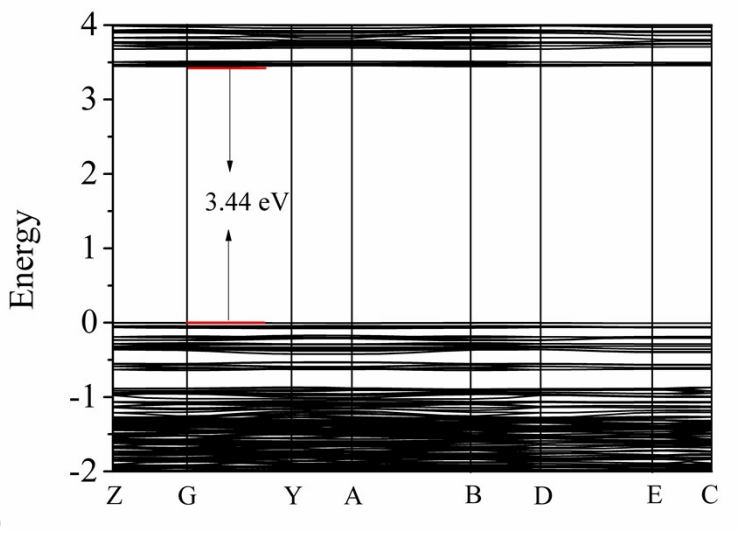
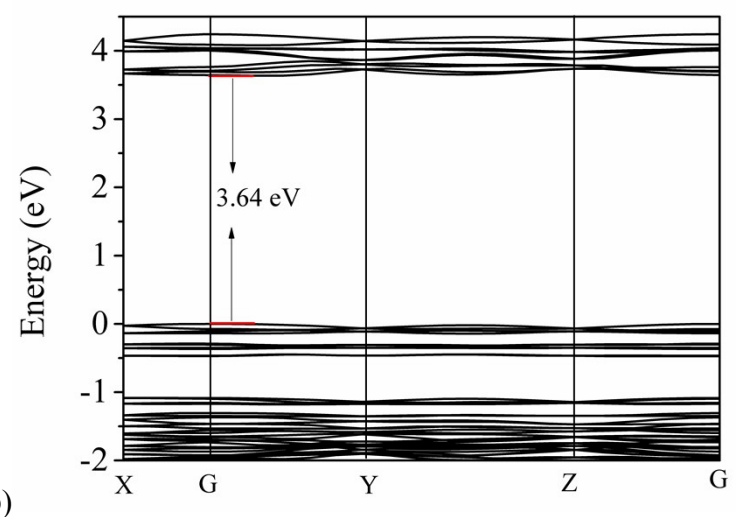


Figure S3. Infrared spectrum of NLN.



(a)



(b)

Figure S4.The bandgap of NLN(a) and KLN(b).

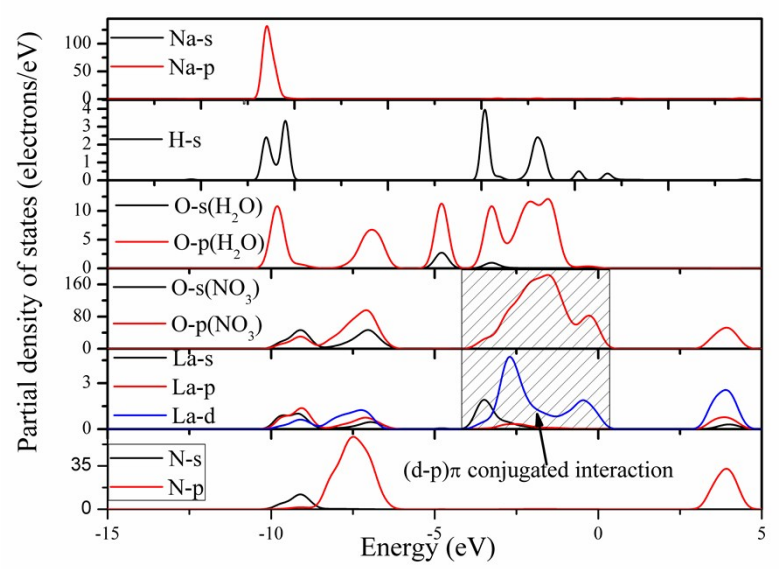
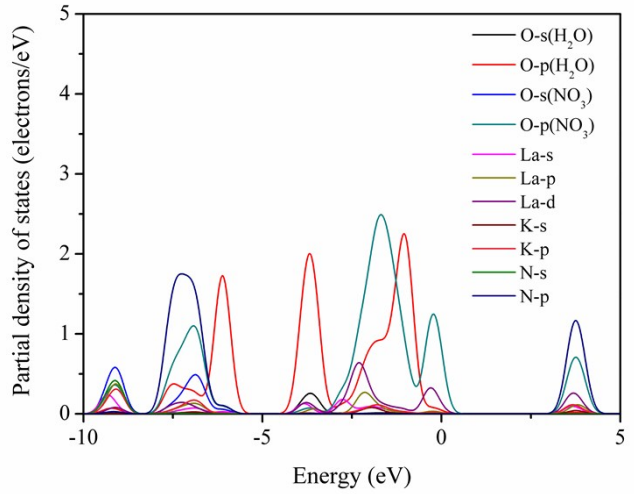
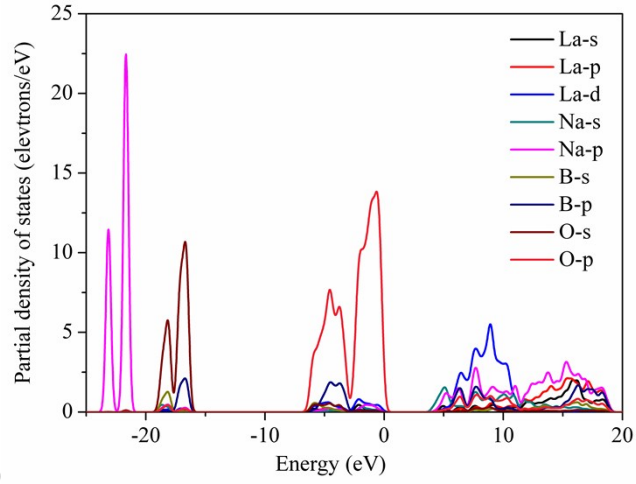


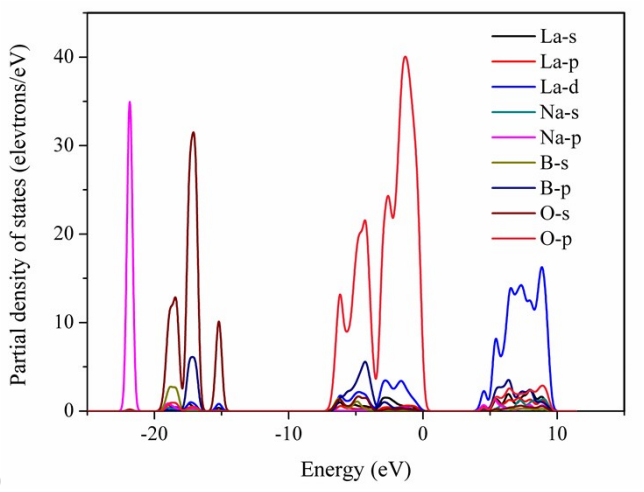
Figure S5. The PDOS of $Na_4La_2(NO_3)_{10}\cdot 2H_2O$.



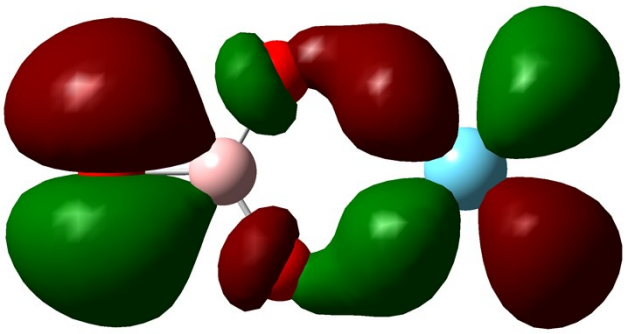
(a)



(b)

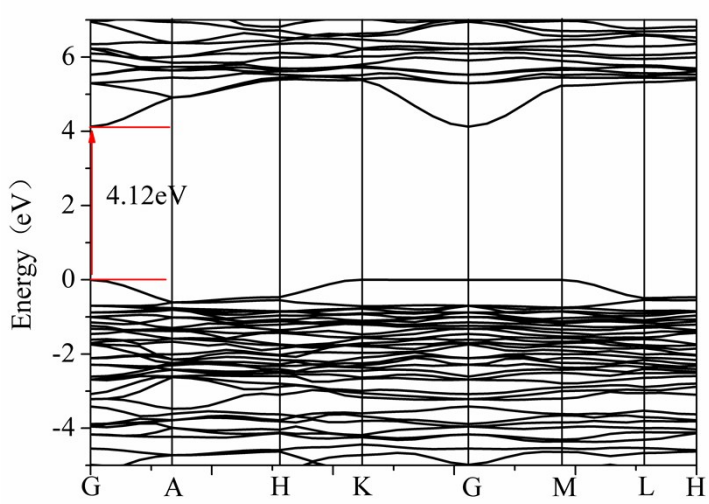


(c)

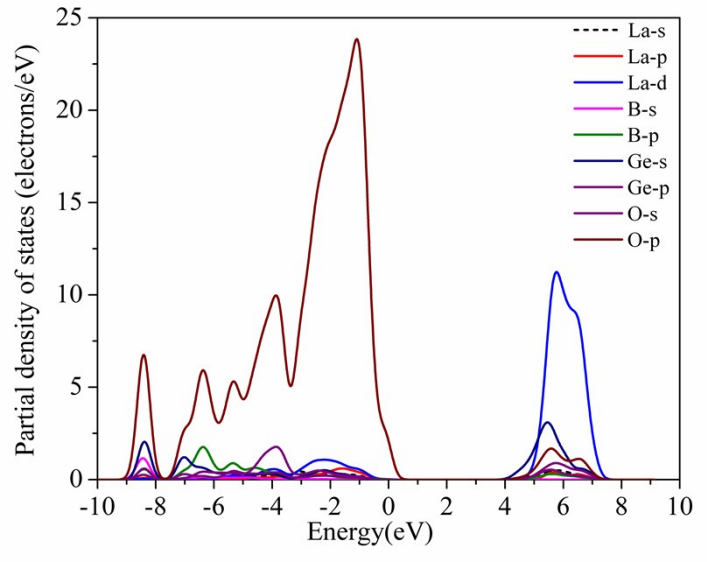


(d)

Figure S6. The PDOS of KLN (a), $La_2Na_3B_3O_9$ (b), $La_9Na_3B_8O_{27}$ (c) and the frontier orbital of La-BO_3 in $La_9Na_3B_8O_{27}$.

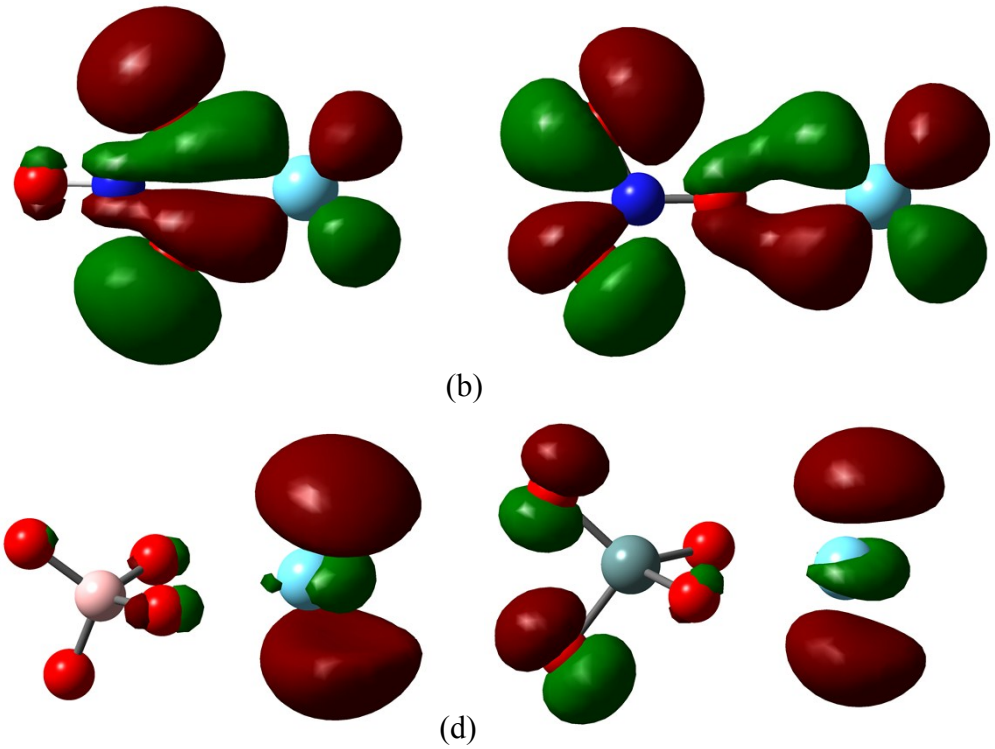


(a)



(b)

Figure S7. The band structure (a) and PDOS (b) of $LaBGeO_5$



(a) (b)

(c) (d)

Figure S8. The frontier orbital of bidenticity (a) and monodenticity (b) structural of La-NO_3 in KLN and La-BO_4 (c), La-GeO_4 in $LaBGeO_5$

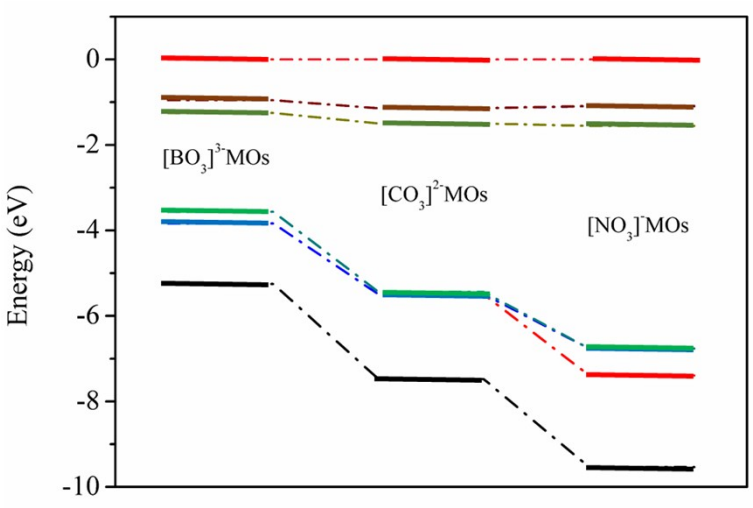
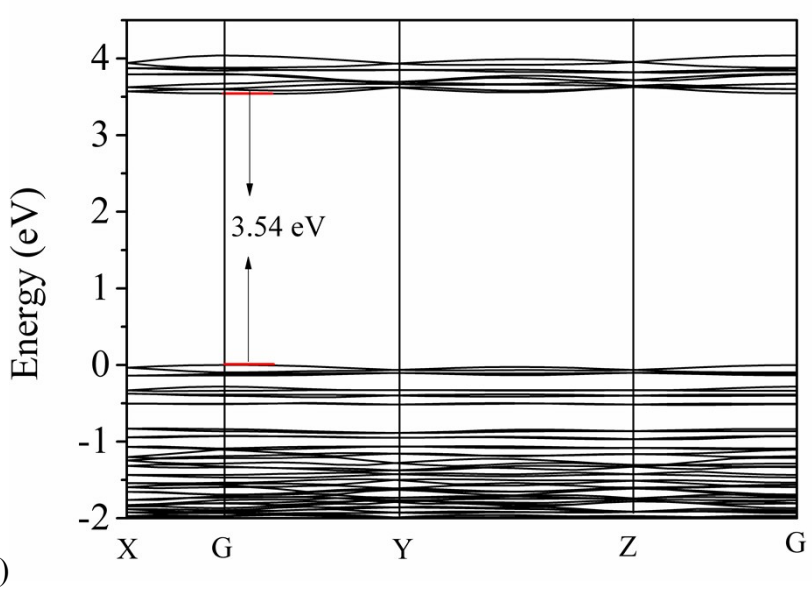
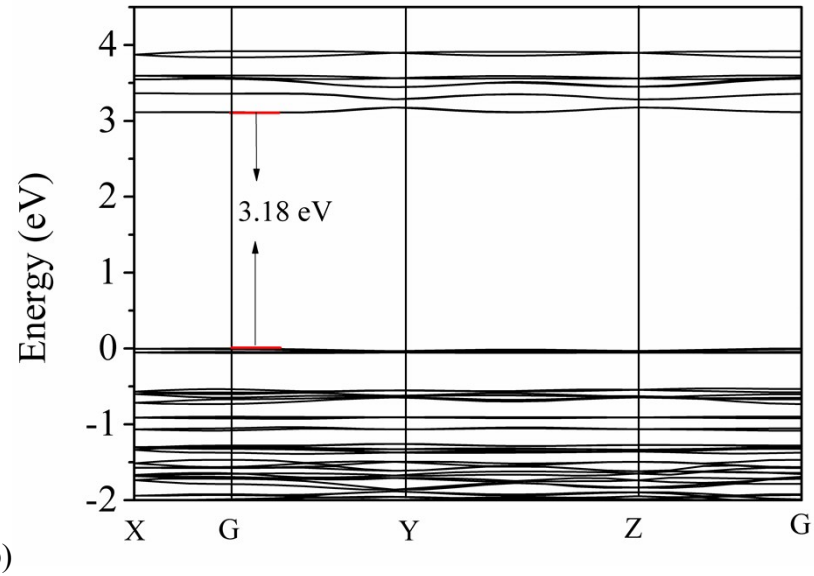


Figure S9. The molecule orbitals of BO_3, CO_3 and NO_3.



(a)



(b)

Figure S10. The bandgaps of KYN and KSN obtained by substitute lanthanum with yttrium or scandium in KLN.

Table S1. Selected bond lengths (Å) and angles [deg] for NLN.

La(1)-O(9)	2.609(6)	Na(1)-O(7)	2.412(7)
La(1)-O(2)#2	2.639(6)	Na(1)-O(4)	2.419(8)
La(1)-O(7)	2.621(7)	Na(1)-O(11)#5	2.488(8)
La(1)-O(1)#3	2.688(7)	Na(1)-O(12)#5	2.598(8)
La(1)-O(11)	2.721(7)	Na(1)-O(3)	2.683(8)
La(1)-O(10)	2.693(6)	Na(1)-O(5)	2.739(8)
La(2)-O(19)	2.599(7)	Na(1)-O(8)	2.885(8)
La(2)-O(17)	2.610(7)	Na(2)-O(32)#7	2.416(10)
La(2)-O(13)	2.571(7)	Na(2)-O(9)#8	2.439(7)
La(2)-O(6)	2.630(6)	Na(2)-O(6)	2.447(7)
La(2)-O(15)	2.638(6)	Na(2)-O(4)	2.540(8)
La(2)-O(18)	2.669(7)	Na(2)-O(8)#8	2.561(8)
La(2)-O(22)	2.687(6)	Na(2)-O(31)	2.581(7)
La(2)-O(5)	2.689(7)	Na(2)-O(1)#2	2.637(7)
La(2)-O(21)	2.745(6)	Na(3)-O(28)	2.343(8)
La(2)-O(10)	2.755(6)	Na(3)-O(19)	2.446(7)
La(2)-O(12)	2.774(7)	Na(3)-O(26)	2.456(8)
La(3)-O(25)	2.596(6)	Na(3)-O(17)#7	2.512(7)
La(3)-O(24)	2.641(6)	Na(3)-O(29)	2.531(8)
La(3)-O(29)#5	2.642(7)	Na(3)-O(30)	2.590(8)
La(3)-O(26)#4	2.673(7)	Na(3)-O(20)	2.701(8)
La(3)-O(22)	2.712(6)	Na(3)-O(16)#7	2.833(8)
La(3)-O(23)	2.730(6)	Na(4)-O(28)	2.419(9)
N(1)-O(3)	1.226(9)	Na(4)-O(24)	2.501(7)
N(1)-O(1)	1.259(9)	Na(4)-O(15)	2.535(7)
N(1)-O(2)	1.282(9)	Na(4)-O(20)#9	2.595(8)
N(2)-O(4)	1.225(9)	Na(4)-O(23)#3	2.653(8)
N(2)-O(6)	1.257(10)	Na(4)-O(21)#3	2.716(8)
N(2)-O(5)	1.260(9)	Na(4)-O(14)	2.805(8)
N(3)-O(8)	1.219(9)	Na(4)-O(27)#10	2.858(8)
N(3)-O(9)	1.268(9)	O(28)-H(1)	0.84(2)
N(3)-O(7)	1.274(9)	O(28)-H(2)	0.83(2)
N(4)-O(12)	1.240(9)	O(32)-H(4)	0.83(2)
N(4)-O(10)	1.243(10)	O(32)-H(3)	0.84(2)
N(4)-O(11)	1.264(9)	O(31)-La(2)#8	2.630(6)
N(5)-O(14)	1.213(9)	N(8)-O(22)	1.284(8)
N(5)-O(13)	1.264(9)	N(8)-O(21)	1.227(8)

N(5)-O(15)	1.271(9)	N(8)-O(23)	1.252(8)
N(6)-O(16)	1.228(10)	N(9)-O(30)#5	1.214(9)
N(6)-O(17)	1.270(9)	N(9)-O(29)#5	1.260(9)
N(6)-O(31)#3	1.275(10)	N(9)-O(24)	1.266(10)
N(7)-O(19)	1.279(8)	N(10)-O(27)	1.227(10)
N(7)-O(20)	1.206(10)	N(10)-O(25)	1.261(9)
N(7)-O(18)	1.264(9)	N(10)-O(26)	1.268(9)
O(2)#2-La(1)-O(10)	103.72(19)	Na(2)#5-O(32)-H(4)	116(8)
O(9)-La(1)-O(9)#1	103.9(3)	O(2)#3-La(1)-O(10)	66.89(18)
O(9)-La(1)-O(7)	48.92(18)	O(1)#3-La(1)-O(10)	110.21(18)
O(9)#1-La(1)-O(7)	67.8(2)	O(1)#2-La(1)-O(10)	69.09(18)
O(9)-La(1)-O(7)#1	67.8(2)	O(9)-La(1)-O(10)#1	128.07(18)
O(9)#1-La(1)-O(7)#1	48.92(18)	O(9)#1-La(1)-O(10)#1	65.57(19)
O(7)-La(1)-O(7)#1	65.9(3)	O(7)-La(1)-O(10)#1	129.33(19)
O(9)-La(1)-O(2)#2	160.38(19)	O(7)#1-La(1)-O(10)#1	69.1(2)
O(9)#1-La(1)-O(2)#2	68.9(2)	O(2)#2-La(1)-O(10)#1	66.89(18)
O(7)-La(1)-O(2)#2	112.68(19)	O(2)#3-La(1)-O(10)#1	103.72(19)
O(7)#1-La(1)-O(2)#2	113.97(19)	O(1)#3-La(1)-O(10)#1	69.09(18)
O(9)-La(1)-O(2)#3	68.9(2)	O(1)#2-La(1)-O(10)#1	110.22(18)
O(9)#1-La(1)-O(2)#3	160.39(19)	O(10)-La(1)-O(10)#1	161.0(3)
O(7)-La(1)-O(2)#3	113.97(19)	O(9)-La(1)-O(11)#1	129.93(19)
O(7)#1-La(1)-O(2)#3	112.68(19)	O(9)#1-La(1)-O(11)#1	109.53(19)
O(2)#2-La(1)-O(2)#3	123.7(3)	O(7)-La(1)-O(11)#1	175.31(19)
O(9)-La(1)-O(1)#3	69.9(2)	O(7)#1-La(1)-O(11)#1	109.5(2)
O(9)#1-La(1)-O(1)#3	112.7(2)	O(2)#2-La(1)-O(11)#1	69.0(2)
O(7)-La(1)-O(1)#3	113.69(19)	O(2)#3-La(1)-O(11)#1	67.1(2)
O(7)#1-La(1)-O(1)#3	69.89(19)	O(1)#3-La(1)-O(11)#1	63.32(19)
O(2)#2-La(1)-O(1)#3	129.6(2)	O(1)#2-La(1)-O(11)#1	113.2(2)
O(2)#3-La(1)-O(1)#3	47.9(2)	O(10)-La(1)-O(11)#1	115.1(2)
O(9)-La(1)-O(1)#2	112.7(2)	O(10)#1-La(1)-O(11)#1	46.75(19)
O(9)#1-La(1)-O(1)#2	69.9(2)	O(9)-La(1)-O(11)	109.53(19)
O(7)-La(1)-O(1)#2	69.89(19)	O(9)#1-La(1)-O(11)	129.94(19)
O(7)#1-La(1)-O(1)#2	113.69(19)	O(7)-La(1)-O(11)	109.5(2)
O(2)#2-La(1)-O(1)#2	47.9(2)	O(7)#1-La(1)-O(11)	175.31(19)
O(2)#3-La(1)-O(1)#2	129.6(2)	O(2)#2-La(1)-O(11)	67.1(2)
O(1)#3-La(1)-O(1)#2	176.0(3)	O(2)#3-La(1)-O(11)	69.0(2)
O(9)-La(1)-O(10)	65.57(19)	O(1)#3-La(1)-O(11)	113.2(2)
O(9)#1-La(1)-O(10)	128.07(18)	O(1)#2-La(1)-O(11)	63.32(19)
O(7)-La(1)-O(10)	69.1(2)	O(10)-La(1)-O(11)	46.75(19)
O(7)#1-La(1)-O(10)	129.33(19)	O(10)#1-La(1)-O(11)	115.1(2)
O(31)#3-La(2)-O(6)	111.3(2)	O(11)#1-La(1)-O(11)	75.2(3)
O(13)-La(2)-O(15)	48.8(2)	O(13)-La(2)-O(19)	69.1(2)
O(19)-La(2)-O(15)	66.4(2)	O(13)-La(2)-O(17)	103.6(2)

O(17)-La(2)-O(15)	68.3(2)	O(19)-La(2)-O(17)	123.0(2)
O(31)#3-La(2)-O(15)	66.8(2)	O(13)-La(2)-O(31)#3	67.6(2)
O(6)-La(2)-O(15)	177.32(19)	O(19)-La(2)-O(31)#3	130.1(2)
O(13)-La(2)-O(18)	110.4(2)	O(17)-La(2)-O(31)#3	48.97(18)
O(19)-La(2)-O(18)	48.04(19)	O(13)-La(2)-O(6)	129.0(2)
O(17)-La(2)-O(18)	132.1(2)	O(19)-La(2)-O(6)	114.8(2)
O(31)#3-La(2)-O(18)	178.0(2)	O(17)-La(2)-O(6)	112.1(2)
O(6)-La(2)-O(18)	70.1(2)	O(15)-La(2)-O(10)	111.77(19)
O(15)-La(2)-O(18)	111.7(2)	O(18)-La(2)-O(10)	107.97(19)
O(13)-La(2)-O(22)	117.21(18)	O(22)-La(2)-O(10)	173.64(18)
O(19)-La(2)-O(22)	66.6(2)	O(5)-La(2)-O(10)	69.1(2)
O(17)-La(2)-O(22)	68.73(19)	O(21)-La(2)-O(10)	129.98(18)
O(31)#3-La(2)-O(22)	114.28(19)	O(13)-La(2)-O(12)	68.4(2)
O(6)-La(2)-O(22)	109.26(18)	O(19)-La(2)-O(12)	70.2(2)
O(15)-La(2)-O(22)	73.39(18)	O(17)-La(2)-O(12)	162.22(18)
O(18)-La(2)-O(22)	66.08(19)	O(31)#3-La(2)-O(12)	113.94(19)
O(13)-La(2)-O(5)	124.2(2)	O(6)-La(2)-O(12)	66.54(19)
O(19)-La(2)-O(5)	161.90(19)	O(15)-La(2)-O(12)	112.3(2)
O(17)-La(2)-O(5)	68.7(2)	O(18)-La(2)-O(12)	65.16(19)
O(31)#3-La(2)-O(5)	67.9(2)	O(22)-La(2)-O(12)	128.97(19)
O(6)-La(2)-O(5)	47.91(19)	O(5)-La(2)-O(12)	101.9(2)
O(15)-La(2)-O(5)	131.1(2)	O(21)-La(2)-O(12)	124.75(19)
O(18)-La(2)-O(5)	114.0(2)	O(10)-La(2)-O(12)	46.23(18)
O(22)-La(2)-O(5)	110.70(19)	O(25)-La(3)-O(25)#4	105.5(3)
O(13)-La(2)-O(21)	163.09(19)	O(25)-La(3)-O(24)	67.2(2)
O(19)-La(2)-O(21)	103.7(2)	O(25)#4-La(3)-O(24)	122.0(2)
O(17)-La(2)-O(21)	66.71(19)	O(25)-La(3)-O(24)#4	122.0(2)
O(31)#3-La(2)-O(21)	110.4(2)	O(25)#4-La(3)-O(24)#4	67.2(2)
O(6)-La(2)-O(21)	67.8(2)	O(24)-La(3)-O(24)#4	166.4(3)
O(15)-La(2)-O(21)	114.4(2)	O(25)-La(3)-O(29)#5	110.6(2)
O(18)-La(2)-O(21)	71.3(2)	O(25)#4-La(3)-O(29)#5	126.83(19)
O(22)-La(2)-O(21)	47.10(18)	O(24)-La(3)-O(29)#5	48.12(19)
O(5)-La(2)-O(21)	66.7(2)	O(24)#4-La(3)-O(29)#5	118.8(2)
O(13)-La(2)-O(10)	66.33(19)	O(25)-La(3)-O(29)#6	126.83(19)
O(19)-La(2)-O(10)	111.5(2)	O(25)#4-La(3)-O(29)#6	110.6(2)
O(17)-La(2)-O(10)	116.26(19)	O(24)-La(3)-O(29)#6	118.8(2)
O(31)#3-La(2)-O(10)	71.75(19)	O(24)#4-La(3)-O(29)#6	48.12(19)
O(6)-La(2)-O(10)	65.63(18)	O(29)#5-La(3)-O(29)#6	76.6(3)
O(26)#4-La(3)-O(26)	63.6(3)	O(25)-La(3)-O(26)#4	68.6(2)
O(25)-La(3)-O(22)#4	65.31(18)	O(25)#4-La(3)-O(26)#4	48.33(19)
O(25)#4-La(3)-O(22)#4	119.70(18)	O(24)-La(3)-O(26)#4	127.4(2)
O(24)-La(3)-O(22)#4	108.83(19)	O(24)#4-La(3)-O(26)#4	66.0(2)
O(24)#4-La(3)-O(22)#4	70.25(18)	O(29)#5-La(3)-O(26)#4	172.56(19)

O(29)#5-La(3)-O(22)#4	110.47(19)	O(29)#6-La(3)-O(26)#4	110.0(2)
O(29)#6-La(3)-O(22)#4	63.22(19)	O(25)-La(3)-O(26)	48.33(19)
O(26)#4-La(3)-O(22)#4	76.18(19)	O(25)#4-La(3)-O(26)	68.6(2)
O(26)-La(3)-O(22)#4	110.37(19)	O(24)-La(3)-O(26)	66.0(2)
O(25)-La(3)-O(22)	119.70(18)	O(24)#4-La(3)-O(26)	127.4(2)
O(25)#4-La(3)-O(22)	65.31(18)	O(29)#5-La(3)-O(26)	110.0(2)
O(24)-La(3)-O(22)	70.25(19)	O(29)#6-La(3)-O(26)	172.56(19)
O(24)#4-La(3)-O(22)	108.82(19)	O(25)#4-La(3)-O(23)	70.3(2)
O(29)#5-La(3)-O(22)	63.22(19)	O(24)-La(3)-O(23)	103.7(2)
O(29)#6-La(3)-O(22)	110.47(19)	O(24)#4-La(3)-O(23)	68.8(2)
O(26)#4-La(3)-O(22)	110.37(19)	O(29)#5-La(3)-O(23)	65.58(19)
O(26)-La(3)-O(22)	76.18(19)	O(29)#6-La(3)-O(23)	65.66(19)
O(22)#4-La(3)-O(22)	172.6(3)	O(26)#4-La(3)-O(23)	113.41(19)
O(25)-La(3)-O(23)	166.73(18)	O(26)-La(3)-O(23)	119.77(19)
O(29)#5-La(3)-O(23)#4	65.66(19)	O(22)#4-La(3)-O(23)	127.88(18)
O(29)#6-La(3)-O(23)#4	65.57(19)	O(22)-La(3)-O(23)	47.03(17)
O(26)#4-La(3)-O(23)#4	119.77(19)	O(25)-La(3)-O(23)#4	70.3(2)
O(26)-La(3)-O(23)#4	113.41(19)	O(25)#4-La(3)-O(23)#4	166.73(18)
O(22)#4-La(3)-O(23)#4	47.03(17)	O(24)-La(3)-O(23)#4	68.8(2)
O(22)-La(3)-O(23)#4	127.88(18)	O(24)#4-La(3)-O(23)#4	103.7(2)
O(23)-La(3)-O(23)#4	116.5(3)	O(32)#7-Na(2)-O(9)#8	125.4(3)
O(7)-Na(1)-O(4)	82.7(3)	O(32)#7-Na(2)-O(6)	91.0(3)
O(7)-Na(1)-O(11)#5	94.6(3)	O(9)#8-Na(2)-O(6)	143.3(3)
O(4)-Na(1)-O(11)#5	177.1(3)	O(32)#7-Na(2)-O(4)	138.2(3)
O(7)-Na(1)-O(12)#5	116.1(3)	O(9)#8-Na(2)-O(4)	92.6(3)
O(4)-Na(1)-O(12)#5	129.8(3)	O(6)-Na(2)-O(4)	51.5(2)
O(11)#5-Na(1)-O(12)#5	50.5(2)	O(32)#7-Na(2)-O(8)#8	83.7(3)
O(7)-Na(1)-O(3)	82.6(2)	O(9)#8-Na(2)-O(8)#8	51.3(2)
O(4)-Na(1)-O(3)	85.2(3)	O(6)-Na(2)-O(8)#8	152.6(3)
O(11)#5-Na(1)-O(3)	95.6(3)	O(4)-Na(2)-O(8)#8	138.1(3)
O(12)#5-Na(1)-O(3)	140.0(3)	O(32)#7-Na(2)-O(31)	124.5(3)
O(7)-Na(1)-O(5)	70.5(2)	O(9)#8-Na(2)-O(31)	73.5(2)
O(4)-Na(1)-O(5)	48.9(2)	O(6)-Na(2)-O(31)	90.3(3)
O(11)#5-Na(1)-O(5)	129.1(3)	O(4)-Na(2)-O(31)	79.0(2)
O(12)#5-Na(1)-O(5)	91.8(3)	O(8)#8-Na(2)-O(31)	71.2(2)
O(3)-Na(1)-O(5)	128.1(3)	O(32)#7-Na(2)-O(1)#2	86.1(3)
O(7)-Na(1)-O(8)	47.5(2)	O(9)#8-Na(2)-O(1)#2	94.1(2)
O(4)-Na(1)-O(8)	112.5(3)	O(6)-Na(2)-O(1)#2	83.0(2)
O(11)#5-Na(1)-O(8)	64.6(2)	O(4)-Na(2)-O(1)#2	73.1(2)
O(12)#5-Na(1)-O(8)	68.6(2)	O(8)#8-Na(2)-O(1)#2	123.2(3)
O(3)-Na(1)-O(8)	120.3(2)	O(31)-Na(2)-O(1)#2	148.9(3)
O(5)-Na(1)-O(8)	70.5(2)	O(32)#7-Na(2)-N(3)#8	105.8(3)
O(7)-Na(1)-N(4)#5	109.4(3)	O(9)#8-Na(2)-N(3)#8	26.2(2)

O(4)-Na(1)-N(4)#5	154.9(3)	O(6)-Na(2)-N(3)#8	157.9(3)
O(11)#5-Na(1)-N(4)#5	25.58(19)	O(4)-Na(2)-N(3)#8	115.5(3)
O(12)#5-Na(1)-N(4)#5	25.19(18)	O(8)#8-Na(2)-N(3)#8	25.3(2)
O(3)-Na(1)-N(4)#5	117.4(3)	O(31)-Na(2)-N(3)#8	68.4(2)
O(5)-Na(1)-N(4)#5	113.2(3)	O(1)#2-Na(2)-N(3)#8	111.9(2)
O(8)-Na(1)-N(4)#5	66.9(2)	O(32)#7-Na(2)-O(16)#8	80.6(2)
O(7)-Na(1)-H(4)	140.5(7)	O(9)#8-Na(2)-O(16)#8	111.8(2)
O(4)-Na(1)-H(4)	87(2)	O(6)-Na(2)-O(16)#8	75.0(2)
O(11)#5-Na(1)-H(4)	96(2)	O(4)-Na(2)-O(16)#8	102.7(2)
O(12)#5-Na(1)-H(4)	99.7(12)	O(8)#8-Na(2)-O(16)#8	77.5(2)
O(3)-Na(1)-H(4)	58.5(8)	O(31)-Na(2)-O(16)#8	46.5(2)
O(5)-Na(1)-H(4)	127(2)	O(1)#2-Na(2)-O(16)#8	154.1(2)
O(8)-Na(1)-H(4)	160(2)	N(3)#8-Na(2)-O(16)#8	93.2(2)
N(4)#5-Na(1)-H(4)	96(2)	O(32)#7-Na(2)-O(3)#2	72.8(2)
O(28)-Na(3)-O(20)	144.1(3)	O(9)#8-Na(2)-O(3)#2	69.8(2)
O(19)-Na(3)-O(20)	49.3(2)	O(6)-Na(2)-O(3)#2	125.3(2)
O(26)-Na(3)-O(20)	84.0(2)	O(4)-Na(2)-O(3)#2	111.3(2)
O(17)#7-Na(3)-O(20)	76.0(2)	O(8)#8-Na(2)-O(3)#2	78.8(2)
O(29)-Na(3)-O(20)	95.1(2)	O(31)-Na(2)-O(3)#2	142.1(2)
O(30)-Na(3)-O(20)	137.1(3)	O(1)#2-Na(2)-O(3)#2	44.97(19)
O(28)-Na(3)-O(16)#7	77.0(2)	N(3)#8-Na(2)-O(3)#2	74.6(2)
O(19)-Na(3)-O(16)#7	75.4(2)	O(16)#8-Na(2)-O(3)#2	146.0(3)
O(26)-Na(3)-O(16)#7	148.7(3)	O(28)-Na(3)-O(19)	96.7(3)
O(17)#7-Na(3)-O(16)#7	47.6(2)	O(28)-Na(3)-O(26)	81.4(2)
O(29)-Na(3)-O(16)#7	117.2(3)	O(19)-Na(3)-O(26)	85.0(3)
O(30)-Na(3)-O(16)#7	80.5(2)	O(28)-Na(3)-O(17)#7	120.6(3)
O(20)-Na(3)-O(16)#7	100.6(2)	O(19)-Na(3)-O(17)#7	89.1(3)
O(28)-Na(3)-N(9)#7	99.6(3)	O(26)-Na(3)-O(17)#7	157.8(2)
O(19)-Na(3)-N(9)#7	160.2(3)	O(28)-Na(3)-O(29)	118.2(3)
O(26)-Na(3)-N(9)#7	108.4(3)	O(19)-Na(3)-O(29)	144.4(2)
O(17)#7-Na(3)-N(9)#7	73.0(2)	O(26)-Na(3)-O(29)	92.9(3)
O(29)-Na(3)-N(9)#7	25.58(18)	O(17)#7-Na(3)-O(29)	79.5(3)
O(30)-Na(3)-N(9)#7	24.65(19)	O(28)-Na(3)-O(30)	78.4(3)
O(20)-Na(3)-N(9)#7	116.1(3)	O(19)-Na(3)-O(30)	155.8(3)
O(16)#7-Na(3)-N(9)#7	97.4(3)	O(26)-Na(3)-O(30)	117.1(3)
O(28)-Na(3)-N(6)#7	98.4(3)	O(17)#7-Na(3)-O(30)	73.8(2)
O(19)-Na(3)-N(6)#7	82.6(2)	O(29)-Na(3)-O(30)	50.0(2)
O(26)-Na(3)-N(6)#7	167.5(3)	O(21)-N(8)-Na(4)#8	62.9(5)
O(17)#7-Na(3)-N(6)#7	23.9(2)	O(23)-N(8)-Na(4)#8	60.1(4)
O(29)-Na(3)-N(6)#7	98.1(3)	O(22)-N(8)-Na(4)#8	173.3(5)
O(30)-Na(3)-N(6)#7	74.9(2)	O(30)#5-N(9)-O(29)#5	122.2(9)
O(20)-Na(3)-N(6)#7	89.2(2)	O(30)#5-N(9)-O(24)	120.7(8)
O(16)#7-Na(3)-N(6)#7	23.69(19)	O(29)#5-N(9)-O(24)	117.1(8)

N(9)#7-Na(3)-N(6)#7	84.0(2)	O(30)#5-N(9)-Na(3)#5	62.8(5)
O(28)-Na(4)-O(24)	98.4(3)	O(29)#5-N(9)-Na(3)#5	60.2(5)
O(28)-Na(4)-O(15)	81.5(2)	O(24)-N(9)-Na(3)#5	169.6(6)
O(24)-Na(4)-O(15)	78.4(2)	O(27)-N(10)-O(25)	122.6(8)
O(28)-Na(4)-O(20)#9	77.4(3)	O(27)-N(10)-O(26)	120.2(9)
O(24)-Na(4)-O(20)#9	159.9(3)	O(25)-N(10)-O(26)	117.1(8)
O(15)-Na(4)-O(20)#9	119.7(3)	O(15)-Na(4)-O(14)	47.6(2)
O(28)-Na(4)-O(23)#3	148.2(3)	O(20)#9-Na(4)-O(14)	72.1(2)
O(15)-Na(4)-O(23)#3	130.2(3)	O(23)#3-Na(4)-O(14)	126.4(2)
O(20)#9-Na(4)-O(23)#3	82.6(2)	O(21)#3-Na(4)-O(14)	79.6(2)
O(28)-Na(4)-O(21)#3	143.0(3)	O(28)-Na(4)-O(27)#10	73.9(3)
O(24)-Na(4)-O(21)#3	116.6(3)	O(24)-Na(4)-O(27)#10	84.0(2)
O(15)-Na(4)-O(21)#3	93.4(3)	O(15)-Na(4)-O(27)#10	147.2(3)
O(20)#9-Na(4)-O(21)#3	73.6(2)	O(20)#9-Na(4)-O(27)#10	75.9(2)
O(23)#3-Na(4)-O(21)#3	47.8(2)	O(23)#3-Na(4)-O(27)#10	77.4(2)
O(28)-Na(4)-O(14)	69.9(3)	O(21)#3-Na(4)-O(27)#10	119.3(2)
O(24)-Na(4)-O(14)	125.4(2)	O(14)-Na(4)-O(27)#10	135.7(3)
O(27)#10-Na(4)-O(30)#5	114.2(2)	O(28)-Na(4)-O(30)#5	138.8(2)
O(28)-Na(4)-N(8)#3	152.7(2)	O(24)-Na(4)-O(30)#5	46.5(2)
O(24)-Na(4)-N(8)#3	106.8(3)	O(15)-Na(4)-O(30)#5	71.9(2)
O(15)-Na(4)-N(8)#3	113.5(3)	O(20)#9-Na(4)-O(30)#5	143.3(3)
O(20)#9-Na(4)-N(8)#3	75.4(2)	O(23)#3-Na(4)-O(30)#5	66.8(2)
O(23)#3-Na(4)-N(8)#3	24.15(18)	O(21)#3-Na(4)-O(30)#5	71.0(2)
O(21)#3-Na(4)-N(8)#3	23.71(17)	O(14)-Na(4)-O(30)#5	109.8(2)
O(14)-Na(4)-N(8)#3	102.5(2)	O(16)-N(6)-O(31)#3	121.8(8)
O(27)#10-Na(4)-N(8)#3	98.0(2)	O(17)-N(6)-O(31)#3	117.2(8)
O(30)#5-Na(4)-N(8)#3	68.4(2)	O(16)-N(6)-Na(3)#5	67.9(5)
O(3)-N(1)-O(1)	122.1(8)	O(17)-N(6)-Na(3)#5	53.3(5)
O(3)-N(1)-O(2)	121.1(8)	O(31)#3-N(6)-Na(3)#5	168.7(6)
O(1)-N(1)-O(2)	116.8(7)	O(20)-N(7)-O(18)	124.3(8)
O(4)-N(2)-O(6)	121.8(8)	O(20)-N(7)-O(19)	120.7(8)
O(4)-N(2)-O(5)	120.0(9)	O(18)-N(7)-O(19)	115.0(8)
O(6)-N(2)-O(5)	118.2(8)	O(21)-N(8)-O(23)	122.6(8)
O(8)-N(3)-O(9)	121.3(8)	O(21)-N(8)-O(22)	119.7(7)
O(8)-N(3)-O(7)	121.8(8)	O(23)-N(8)-O(22)	117.8(7)
O(9)-N(3)-O(7)	116.8(8)	O(10)-N(4)-Na(1)#7	169.1(6)
O(8)-N(3)-Na(2)#3	63.7(5)	O(11)-N(4)-Na(1)#7	58.2(5)
O(9)-N(3)-Na(2)#3	58.2(4)	O(14)-N(5)-O(13)	122.0(8)
O(7)-N(3)-Na(2)#3	171.7(6)	O(14)-N(5)-O(15)	121.6(8)
O(12)-N(4)-O(10)	121.9(8)	O(13)-N(5)-O(15)	116.3(7)
O(12)-N(4)-O(11)	120.2(8)	O(16)-N(6)-O(17)	121.1(9)
O(10)-N(4)-O(11)	117.9(8)	H(1)-O(28)-H(2)	84(8)
O(12)-N(4)-Na(1)#7	63.1(5)	H(4)-O(32)-H(3)	124(10)

Note. Symmetry transformations used to generate equivalent atoms:		
#1 -x+2,y,-z+1/2	#2 -x+2,-y,-z+1	#3 x,-y,z-1/2
#4 -x+1,y,-z+1/2	#5 x,y-1,z	#6 -x+1,y-1,-z+1/2
#7 x,y+1,z	#8 x,-y,z+1/2	#9 x,-y+1,z-1/2
#10 -x+1,-y+1,-z	#11 x,-y+1,z+1/2	

Table S2. Atomic coordinates, equivalent isotropic displacement parameters (Å^2) and bond valence sum (BVS) for $Na_4La_2(NO_3)_{10}.2H_2O$. *U*(*eq*) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	*x*	*y*	*z*	*U*(*eq*)	BVS
La(1)	10000	1476(1)	2500	20(1)	3.218
La(2)	7490(1)	1668(1)	2551(1)	19(1)	3.203
La(3)	5000	1703(1)	2500	19(1)	3.189
Na(1)	8911(2)	-3366(5)	3801(3)	52(1)	0.882
Na(2)	8721(2)	1876(5)	5352(2)	35(1)	1.038
Na(3)	6270(2)	6593(5)	1565(2)	34(1)	1.074
Na(4)	6200(2)	2365(6)	-261(2)	38(1)	0.906
N(1)	9978(4)	-2533(11)	5540(5)	28(2)	4.841
N(2)	8210(3)	-206(12)	4009(5)	27(2)	4.946
N(3)	9212(3)	-1619(10)	2099(5)	24(2)	4.869
N(4)	8775(4)	3497(11)	2831(5)	26(2)	4.992
N(5)	7449(4)	2875(11)	656(5)	30(2)	4.927
N(6)	7497(4)	-1493(12)	1419(5)	32(2)	4.814
N(7)	6814(3)	4909(11)	3120(5)	25(2)	4.929
N(8)	6250(4)	433(10)	3375(4)	21(2)	4.859
N(9)	5715(3)	-197(11)	1076(5)	28(2)	4.961
N(10)	4967(4)	4783(11)	1292(5)	31(2)	4.886
O(1)	10403(3)	-1592(9)	5836(4)	32(2)	1.945
O(2)	9572(3)	-3042(9)	6089(4)	29(2)	1.788
O(3)	9953(3)	-2956(10)	4766(4)	39(2)	1.997
O(4)	8539(3)	-900(9)	4563(4)	31(2)	2.075
O(5)	8053(3)	-982(9)	3319(4)	30(2)	1.915
O(6)	8032(3)	1290(9)	4097(4)	27(2)	2.071
O(7)	9397(3)	-1291(9)	2878(4)	26(2)	2.028
O(8)	8931(3)	-2910(9)	1921(4)	37(2)	1.902
O(9)	9340(3)	-547(8)	1511(4)	24(2)	2.044
O(10)	8765(3)	2034(8)	2542(4)	25(2)	2.12
O(11)	9299(3)	4187(8)	2948(4)	27(2)	1.963
O(12)	8291(3)	4279(8)	2994(4)	26(2)	1.998
O(13)	7897(3)	3176(9)	1179(4)	33(2)	1.911
O(14)	7452(3)	3334(11)	-104(4)	49(2)	1.558

O(15)	6999(3)	2038(9)	967(4)	32(2)	1.972
O(16)	7484(3)	-2748(10)	948(4)	41(2)	1.793
O(17)	7054(3)	-1166(9)	1936(3)	25(2)	2.007
O(18)	7032(3)	3895(9)	3685(4)	31(2)	1.832
O(19)	6930(3)	4535(9)	2322(4)	31(2)	2.008
O(20)	6507(3)	6132(9)	3295(4)	33(2)	2.048
O(21)	6745(3)	0(9)	3716(4)	30(2)	2.038
O(22)	6250(3)	1483(8)	2734(4)	25(2)	1.974
O(23)	5735(3)	-103(9)	3631(4)	28(2)	1.95
O(24)	5542(3)	1310(9)	965(4)	32(2)	2.004
O(25)	4546(3)	3680(9)	1296(4)	28(2)	1.91
O(26)	5428(3)	4560(9)	1807(4)	33(2)	1.988
O(27)	4927(3)	6073(10)	852(4)	39(2)	1.798
O_w(28)	6271(3)	5280(10)	186(4)	31(2)	0.421[a]
O(29)	5559(3)	9093(9)	1779(4)	26(2)	2.017
O(30)	6028(3)	9098(10)	528(4)	35(2)	1.798
O(31)	7944(3)	441(9)	6393(4)	28(2)	1.942
O_w(32)	8720(3)	-5158(10)	5006(5)	37(2)	0.411[a]
H(1)	6040(30)	5860(110)	-140(50)	37	1.132
H(2)	6550(30)	5660(120)	-120(50)	37	1.087
H(3)	9030(30)	-4620(120)	5180(60)	45	1.114
H(4)	8400(30)	-5310(130)	5310(50)	45	1.145

a. The H-O bonds have not been included in the bond valence calculations.

Table S3. The birefringence@1064 nm of KLN calculated by different exchange-correlation functional and pseudopotential.

Functional	Pseudopotential	birefringence@1064nm
GGA	NCP	0.115
GGA	USP	0.119
LDA	NCP	0.134
LDA	USP	0.125

Table S4. The calculated birefringence@1064 nm and SHG tensors of KYN and KSN.

Crystal	SHG coefficients	birefringence@1064nm
KYN	d_{31}=2.02 d_{32}=-2.04 d_{33}=-0.11	0.128
KSN	d_{31}= 1.76 d_{32}=-2.49 d_{33}=0.28	0.136