Electronic Supporting Information

Layered Perovskite-like Nitrates $A_2Ca(NO_3)_2Cl_2$ (A = Rb, Cs) as Ultraviolet Birefringent Optical Materials

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Table S1. Bond lengths (Å) and angles (°) for $Rb_2Ca(NO_3)_2Cl_2$.

Rb1-Cl1	3.3290(4)	Ca1-O1	2.5988(15)
Rb1-Cl1#3	3.3291(4)	Ca1-O1#13	2.5989(15)
Rb1-Cl1#4	3.8315(5)	Ca1-O1#14	2.5989(15)
Rb1-Cl1#5	3.8315(5)	Cl1-Rb1#15	3.8316(5)
Rb1-O1#6	3.1715(8)	Cl1-Rb1#4	3.8316(5)
Rb1-O1#1	3.1715(8)	Cl1-Rb1#16	3.3291(4)
Rb1-O1#2	3.1715(8)	Cl1-Ca1#8	2.74104(13)
Rb1-O1#7	3.1715(8)	Cl1-Ca1#10	2.74104(14)
Rb1-O2	3.0553(9)	O1-Rb1#1	3.1715(8)
Rb1-O2#3	3.0552(9)	O1-Rb1#2	3.1715(8)
Ca1-Cl1#10	2.74102(14)	O1-N1	1.2577(18)
Ca1-Cl1#9	2.74102(14)	O2-Rb1#16	3.0552(9)
Ca1-Cl1#11	2.74102(14)	O2-N1	1.223(3)
Ca1-Cl1#8	2.74102(13)	N1-O1#14	1.2576(18)
Ca1-O1#12	2.5989(15)		

Cl1#3-Rb1-Cl1#4	65.855(6)	O1-Ca1-O1#12	146.08(4)
Cl1-Rb1-Cl1#3	109.19(2)	O1#12-Ca1-O1#14	146.08(4)
Cl1#3-Rb1-Cl1#5	65.855(5)	O1-Ca1-O1#13	146.08(4)
Cl1#5-Rb1-Cl1#4	90.175(16)	O2#3-Rb1-O1#2	62.17(2)
Cl1-Rb1-Cl1#5	65.855(5)	O2-Rb1-O1#1	116.89(3)
Cl1-Rb1-Cl1#4	65.855(5)	O2-Rb1-O1#7	62.17(2)
O1#1-Rb1-Cl1	115.53(2)	O2-Rb1-O1#6	62.17(2)
O1#1-Rb1-Cl1#4	128.11(3)	O2#3-Rb1-O1#6	116.89(3)
O1#2-Rb1-Cl1#5	128.11(3)	O2#3-Rb1-O1#1	62.17(2)
O1#6-Rb1-Cl1#4	128.11(3)	O2#3-Rb1-O2	125.27(6)
O1#6-Rb1-Cl1#5	53.51(2)	Cl1#11-Ca1-Cl1#10	91.149(4)
O1#1-Rb1-Cl1#5	53.51(2)	Cl1#8-Ca1-Cl1#10	163.72(3)
O1#7-Rb1-Cl1#4	53.51(2)	Cl1#9-Ca1-Cl1#10	91.149(4)
O1#7-Rb1-Cl1	65.63(3)	Cl1#9-Ca1-Cl1#11	163.72(3)
O1#6-Rb1-Cl1	65.63(3)	Cl1#8-Ca1-Cl1#11	91.149(4)
O1#6-Rb1-Cl1#3	115.53(2)	Cl1#9-Ca1-Cl1#8	91.149(4)
O1#7-Rb1-Cl1#5	128.11(3)	O1-Ca1-Cl1#11	122.51(3)
O1#2-Rb1-Cl1#3	65.63(3)	O1#14-Ca1-Cl1#8	82.588(13)
O1#2-Rb1-Cl1	115.53(2)	O1#14-Ca1-Cl1#9	122.51(3)
O1#7-Rb1-Cl1#3	115.53(2)	O1#12-Ca1-Cl1#11	82.588(13)
O1#1-Rb1-Cl1#3	65.63(3)	O1-Ca1-Cl1#9	73.78(4)
O1#2-Rb1-Cl1#4	53.51(2)	O1#14-Ca1-Cl1#11	73.78(4)
O1#6-Rb1-O1#2	178.18(5)	O1-Ca1-Cl1#8	82.588(13)
O1#7-Rb1-O1#1	178.18(5)	O1#13-Ca1-Cl1#11	82.588(13)
O1#2-Rb1-O1#1	117.64(5)	O1#13-Ca1-Cl1#8	73.78(4)
O1#2-Rb1-O1#7	62.33(5)	O1-Ca1-Cl1#10	82.588(13)
O1#6-Rb1-O1#1	62.33(5)	O1#12-Ca1-Cl1#9	82.588(13)
O1#6-Rb1-O1#7	117.64(5)	O1#12-Ca1-Cl1#10	73.78(4)
O2-Rb1-Cl1#4	108.94(2)	O1#13-Ca1-Cl1#9	82.588(13)
O2#3-Rb1-Cl1#4	108.94(2)	O1#14-Ca1-Cl1#10	82.588(13)
O2#3-Rb1-Cl1	171.96(3)	O1#12-Ca1-Cl1#8	122.51(3)
O2#3-Rb1-Cl1#5	108.94(2)	O1#13-Ca1-Cl1#10	122.51(3)
O2-Rb1-Cl1	62.77(3)	O1#12-Ca1-O1#13	48.73(6)
O2#3-Rb1-Cl1#3	62.77(3)	O1-Ca1-O1#14	48.73(6)
O2-Rb1-Cl1#3	171.96(3)	O1#14-Ca1-O1#13	146.08(4)
O2-Rb1-Cl1#5	108.94(2)	O1#14-N1-O1	117.0(2)
O2#3-Rb1-O1#7	116.89(3)	O2-N1-O1#14	121.51(10)
O2-Rb1-O1#2	116.89(3)	O2-N1-O1	121.51(10)

Symmetrical transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1	#2 -x+1,-y+2,-z+1	#3 x+1,y,z	#4 y-1/4,-x+5/4,-z+3/4
#5 y-1/4,-x+1/4,-z+3/4	#6 x,y-1/2,-z+1	#7 x,y+1/2,-z+1	#8 -x,-y+1,-z+1
#9 -y+5/4,x+3/4,z+1/4	#10 -x,-y+2,-z+1	#11 -y+1/4,x+3/4,z+1/4	#12 -y+3/4,x+3/4,-z+5/4
#13 y-3/4,-x+3/4,-z+5/4	#14 -x+0,-y+3/2,z+0	#15 y-5/4,-x+5/4,-z+3/4	#16 x-1,y,z

Table S2. Bond lengths (Å) and angles (°) for $Cs_2Ca(NO_3)_2Cl_2$.

Cs1-Cl1#1	3.8818(13)	Ca1-O1#14	2.582(4)
Cs1-Cl1#2	3.4418(11)	Ca1-O1#13	2.582(4)
Cs1-Cl1#3	3.8818(12)	Ca1-O1	2.582(4)
Cs1-Cl1#4	3.4418(10)	Ca1-O1#15	2.582(4)
Cs1-O1#5	3.807(4)	Cl1-Cs1#16	3.8818(12)
Cs1-O1#6	3.265(2)	Cl1-Cs1#2	3.4417(10)
Cs1-O1#7	3.265(2)	Cl1-Cs1#17	3.8818(12)
Cs1-O1#2	3.265(2)	Cl1-Cs1#4	3.4417(10)
Cs1-O1#8	3.265(2)	Cl1-Ca1#18	2.8009(3)
Cs1-O1	3.807(4)	O1-Cs1#2	3.265(2)
Cs1-O2	3.164(3)	O1-Cs1#7	3.265(2)
Cs1-O2#9	3.164(3)	O1-N1	1.257(5)
Ca1-Cl1	2.8009(3)	O2-Cs1#19	3.164(3)
Ca1-Cl1#11	2.8009(3)	O2-N1	1.228(7)
Ca1-Cl1#12	2.8009(3)	N1-O1#15	1.257(5)
Ca1-Cl1#13	2.8009(3)		

Cl1#4-Cs1-Cl1#2	107.75(5)	O1#7-Cs1-Cl1#4	114.84(6)
Cl1#3-Cs1-Cl1#1	91.48(4)	O1#2-Cs1-Cl1#3	52.13(6)
Cl1#4-Cs1-Cl1#3	65.706(9)	O1-Cs1-Cl1#3	128.56(3)
Cl1#2-Cs1-Cl1#1	65.706(9)	O1#6-Cs1-Cl1#2	114.84(6)
Cl1#4-Cs1-Cl1#1	65.706(9)	O1#7-Cs1-Cl1#1	52.13(6)
Cl1#2-Cs1-Cl1#3	65.706(9)	O1#2-Cs1-Cl1#2	64.74(7)
Cl1#4-Cs1-O1#5	152.84(6)	O1#6-Cs1-Cl1#1	52.13(6)
Cl1#4-Cs1-O1	99.41(6)	O1#8-Cs1-Cl1#4	64.74(7)
Cl1#2-Cs1-O1	152.84(6)	O1-Cs1-Cl1#1	128.56(3)
Cl1#2-Cs1-O1#5	99.41(6)	O1#6-Cs1-Cl1#3	127.30(7)
O1#8-Cs1-Cl1#3	52.13(6)	O1#8-Cs1-Cl1#2	114.84(6)
O1#2-Cs1-Cl1#4	114.84(6)	O1#7-Cs1-Cl1#2	64.74(7)
O1#5-Cs1-Cl1#1	128.56(3)	O1#6-Cs1-Cl1#4	64.74(7)
O1#8-Cs1-Cl1#1	127.30(7)	O1#5-Cs1-Cl1#3	128.56(3)
O1#7-Cs1-Cl1#3	127.30(7)	O1#8-Cs1-O1#7	179.36(13)
O1#2-Cs1-Cl1#1	127.30(7)	O1#8-Cs1-O1#2	63.23(12)
O1#8-Cs1-O1#5	103.93(7)	O2#9-Cs1-O2	122.97(17)
O1#5-Cs1-O1	53.43(11)	Cl1#13-Ca1-Cl1#11	90.844(8)
O1#6-Cs1-O1#2	179.36(13)	Cl1#11-Ca1-Cl1	166.05(7)
O1#6-Cs1-O1#5	103.93(7)	Cl1#12-Ca1-Cl1	90.845(8)
O1#7-Cs1-O1#2	116.77(12)	Cl1#13-Ca1-Cl1	90.845(8)
O1#8-Cs1-O1#6	116.77(12)	Cl1#12-Ca1-Cl1#13	166.05(7)
O1#7-Cs1-O1	103.93(7)	Cl1#12-Ca1-Cl1#11	90.844(8)
O1#7-Cs1-O1#5	76.66(8)	O1#15-Ca1-Cl1#13	72.52(9)
O1#6-Cs1-O1	76.67(8)	O1-Ca1-Cl1#12	72.52(9)
O1#7-Cs1-O1#6	63.23(12)	O1-Ca1-Cl1#13	121.42(9)
O1#2-Cs1-O1	103.93(7)	O1#14-Ca1-Cl1#13	83.66(3)
O1#2-Cs1-O1#5	76.66(8)	O1-Ca1-Cl1	83.65(3)
O1#8-Cs1-O1	76.67(8)	O1#14-Ca1-Cl1#11	72.52(9)
O2#9-Cs1-Cl1#3	109.46(5)	O1#13-Ca1-Cl1	72.53(9)

O2#9-Cs1-Cl1#2	64.64(9)	O1#13-Ca1-Cl1#13	83.66(3)
O2-Cs1-Cl1#4	64.64(9)	O1#15-Ca1-Cl1#12	121.42(9)
O2-Cs1-Cl1#1	109.46(5)	O1#14-Ca1-Cl1	121.42(9)
O2#9-Cs1-Cl1#4	172.39(9)	O1#13-Ca1-Cl1#12	83.66(3)
O2-Cs1-Cl1#2	172.39(9)	O1-Ca1-Cl1#11	83.66(3)
O2-Cs1-Cl1#3	109.46(5)	O1#15-Ca1-Cl1#11	83.66(3)
O2#9-Cs1-Cl1#1	109.46(5)	O1#14-Ca1-Cl1#12	83.66(3)
O2#9-Cs1-O1	88.20(10)	O1#15-Ca1-Cl1	83.65(3)
O2#9-Cs1-O1#5	34.77(10)	O1#13-Ca1-Cl1#11	121.42(9)
O2-Cs1-O1#8	62.75(6)	O1-Ca1-O1#13	145.97(11)
O2-Cs1-O1#2	117.60(7)	O1#15-Ca1-O1#13	145.97(12)
O2#9-Cs1-O1#6	117.60(7)	O1#14-Ca1-O1#13	48.90(17)
O2-Cs1-O1#7	117.60(7)	O1#14-Ca1-O1#15	145.97(11)
O2#9-Cs1-O1#7	62.75(6)	O1-Ca1-O1#15	48.90(17)
O2-Cs1-O1#6	62.75(6)	O1-Ca1-O1#14	145.97(12)
O2-Cs1-O1	34.77(10)	O1#15-N1-O1	116.4(6)
O2#9-Cs1-O1#8	117.60(7)	O2-N1-O1#15	121.8(3)
O2#9-Cs1-O1#2	62.75(6)	O2-N1-O1	121.8(3)
O2-Cs1-O1#5	88.20(10)		

Symmetrical transformations used to generate equivalent atoms:

#1 -y+3/4,x+5/4,z-1/4	#2 -x+1,-y+1,-z+1	#3 -y+3/4,x+1/4,z-1/4	#4 -x,-y+1,-z+1
#5 -x+1,-y+3/2,z+0	#6 x,y+1/2,-z+1	#7 -x+1,-y+2,-z+1	#8 x,y-1/2,-z+1
#9 x+1,y,z	#10 -y+5/4,x+3/4,z+1/4	#11 x,y+1,z	#12 y+1/4,-x+3/4,-z+5/4
#13 y-3/4,-x+3/4,-z+5/4	#14 -y+3/4,x+3/4,-z+5/4	#15 -x+0,-y+3/2,z+0	#16 -y+1/4,x-1/4,z+1/4
#17 -y+5/4,x-1/4,z+1/4	#18 x,y-1,z	#19 x-1,y,z	

Table S3. Atomic coordinates (×10^4), equivalent isotropic displacement parameters (Å^2 × 10^3), and bond valence sum (BVS) calculations for $Rb_2Ca(NO_3)_2Cl_2$.

Atom	x	y	z	U(eq)	BVS
Rb1	5000	7500	4476.9(2)	37.08(16)	0.982
Ca1	0	7500	6250	16.41(18)	2.192
Cl1	0	7500	3871.8(2)	28.6(2)	1.137
O1	1976(3)	7500	5507.3(4)	32.2(4)	1.954
O2	0	7500	4917.4(6)	31.0(5)	1.994
N1	0	7500	5301.1(6)	19.1(5)	4.960

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S4. Atomic coordinates (×10^4), equivalent isotropic displacement parameters (Å^2 × 10^3), and bond valence sum (BVS) calculations for $Cs_2Ca(NO_3)_2Cl_2$.

Atom	x	y	z	U(eq)	BVS
Cs1	5000	7500	4479.4(2)	30.8(2)	1.166
Ca1	0	7500	6250	17.1(4)	2.007
Cl1	0	2500	6145.3(5)	24.8(4)	1.073
O1	1922(7)	7500	5526.3(12)	32.6(9)	2.020
O2	0	7500	4944.4(16)	33.8(13)	2.006
N1	0	7500	5322.3(17)	18.5(11)	4.950

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S5. Anisotropic displacement parameters ($Å^2$ x 10^3) for $Rb_2Ca(NO_3)_2Cl_2$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rb1	25(1)	39(1)	48(1)	0	0	0
Ca1	14(1)	14(1)	21(1)	0	0	0
Cl1	45(1)	14(1)	27(1)	0	0	0
O1	27(1)	31(1)	39(1)	0	-9(1)	0
O2	52(1)	24(1)	17(1)	0	0	0
N1	23(1)	13(1)	21(1)	0	0	0

Table S6. Anisotropic displacement parameters ($Å^2$ x 10^3) for $Cs_2Ca(NO_3)_2Cl_2$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cs1	22(1)	30(1)	39(1)	0	0	0
Ca1	16(1)	16(1)	20(1)	0	0	0
Cl1	31(1)	15(1)	28(1)	0	0	0
O1	31(2)	30(2)	37(2)	0	-10(2)	0
O2	45(4)	38(3)	19(3)	0	0	0
N1	18(3)	13(3)	25(3)	0	0	0

Table S7. The birefringence of $Rb_2Ca(NO_3)_2Cl_2$ and $Cs_2Ca(NO_3)_2Cl_2$ at the wavelength of 546 nm with polarizing microscope.

Compound	**Optical path difference R (nm)**	**Thickness (μm)**	**Birefringence (Δn)**
$Rb_2Ca(NO_3)_2Cl_2$	1243.599	12.607	0.099
$Cs_2Ca(NO_3)_2Cl_2$	775.479	07.473	0.104

Table S8. Summary of some recently reported UV/visible halide, nitrate-halide-based, and hybrid perovskites.

Compound	**Exp. Band gap (eV)**	**Exp. Birefringence**	**Reference**
$Cs_2Pb_4Br_{10}$	3.41	0.392@550 nm	1
$MLAPbBr_4$ (MLA = melamine)	3.13	0.322@550 nm	2
$Cs_2Pb(NO_3)_2Br_2$	3.01	0.147@546 nm	3
$Cs_2Pb(NO_3)_2Cl_2$	3.50	-	4
$Cs_3Sb_2Cl_9$	2.98	0.120@550 nm	5
$Rb_2Ca(NO_3)_2Cl_2$	5.51	0.104@546 nm	This work
$Cs_2Ca(NO_3)_2Cl_2$	5.64	0.099@546 nm	This work
$KRb_2(NO_3)_2Cl$	-	0.084@1064 (cal.)	6
$KCaCl_3$	5.36	-	7
$CsPbBr_3/Cs_4PbBr_6$	2.19/4.14	0.008/0.037@550 nm (cal.)	1, 8

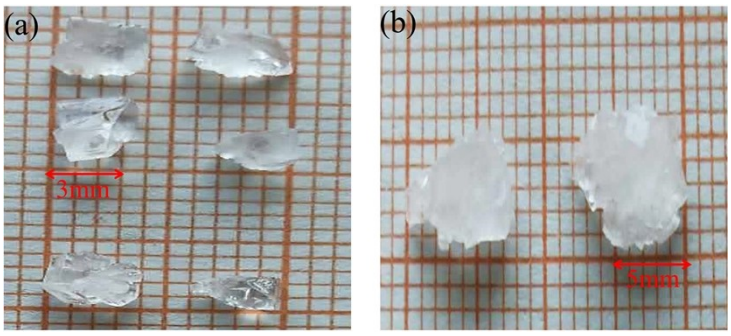


Figure S1. Photographs of $Rb_2Ca(NO_3)_2Cl_2$ (a) and $Cs_2Ca(NO_3)_2Cl_2$ (b) of millimeters-sized crystals.

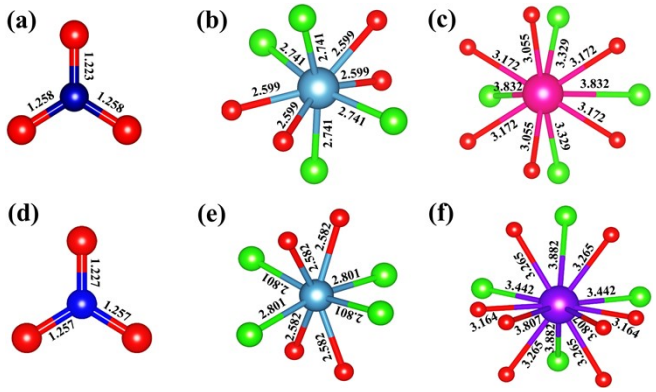


Figure S2. The coordination modes of N^{5+} (a,d), Ca^{2+} (b,e), and Rb^{+} (c)/ Cs^{+} (f) in $Rb_2Ca(NO_3)_2Cl_2$ and $Cs_2Ca(NO_3)_2Cl_2$, respectively.

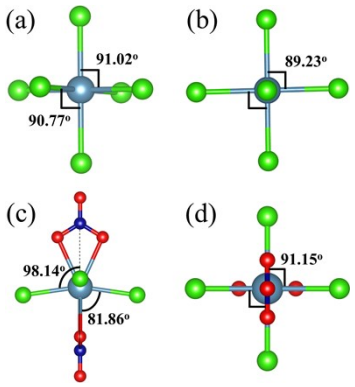


Figure S3. The angle between the Ca atom and the ligands in $RbCaCl_3$ (a) (b), and in $Rb_2Ca(NO_3)_2Cl_2$ (c) (d).

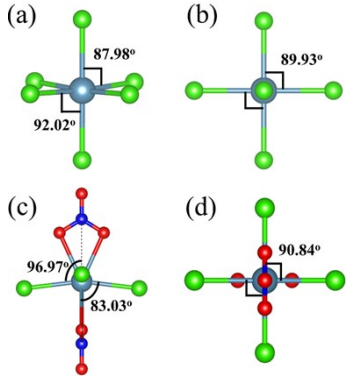


Figure S4. The angle between the Ca atom and the ligands in $Cs_3Ca_2Cl_7$ (a) (b), and in $Cs_2Ca(NO_3)_2Cl_2$ (c) (d).

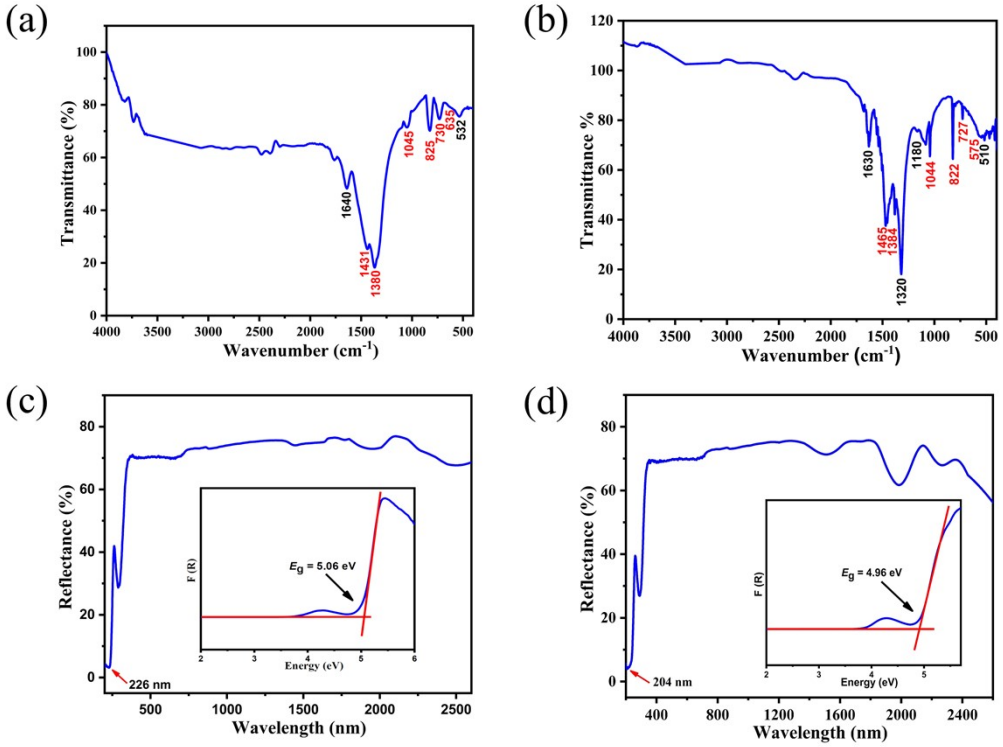
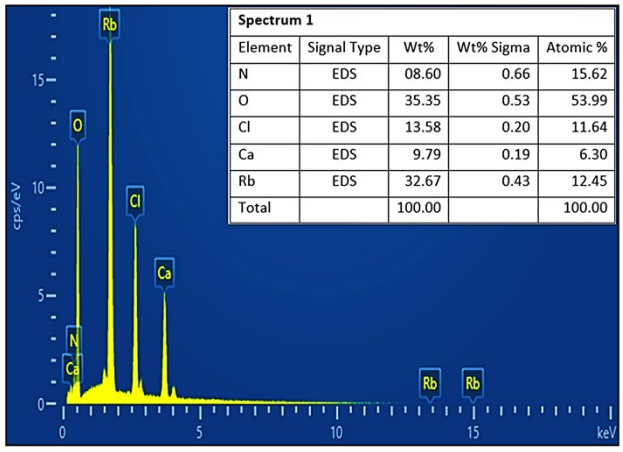


Figure S5. The IR spectra of $Rb_2Ca(NO_3)_2Cl_2$ (a) and $Cs_2Ca(NO_3)_2Cl_2$ (b). UV−vis-NIR diffuse reflectance spectra of $Rb_2Ca(NO_3)_2Cl_2$ (c) and $Cs_2Ca(NO_3)_2Cl_2$ (d). Inset is the experimental band gap calculated by Kubelka-Munk function.

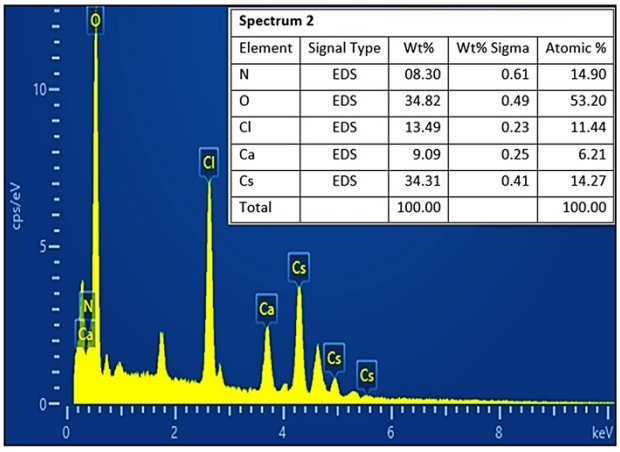
(a)



Spectrum 1

Element	Signal Type	Wt%	Wt% Sigma	Atomic %
N	EDS	08.60	0.66	15.62
O	EDS	35.35	0.53	53.99
Cl	EDS	13.58	0.20	11.64
Ca	EDS	9.79	0.19	6.30
Rb	EDS	32.67	0.43	12.45
Total		100.00		100.00

(b)



Spectrum 2

Element	Signal Type	Wt%	Wt% Sigma	Atomic %
N	EDS	08.30	0.61	14.90
O	EDS	34.82	0.49	53.20
Cl	EDS	13.49	0.23	11.44
Ca	EDS	9.09	0.25	6.21
Cs	EDS	34.31	0.41	14.27
Total		100.00		100.00

Figure S6. EDS for $Rb_2Ca(NO_3)_2Cl_2$ (a), and $Cs_2Ca(NO_3)_2Cl_2$ (b).

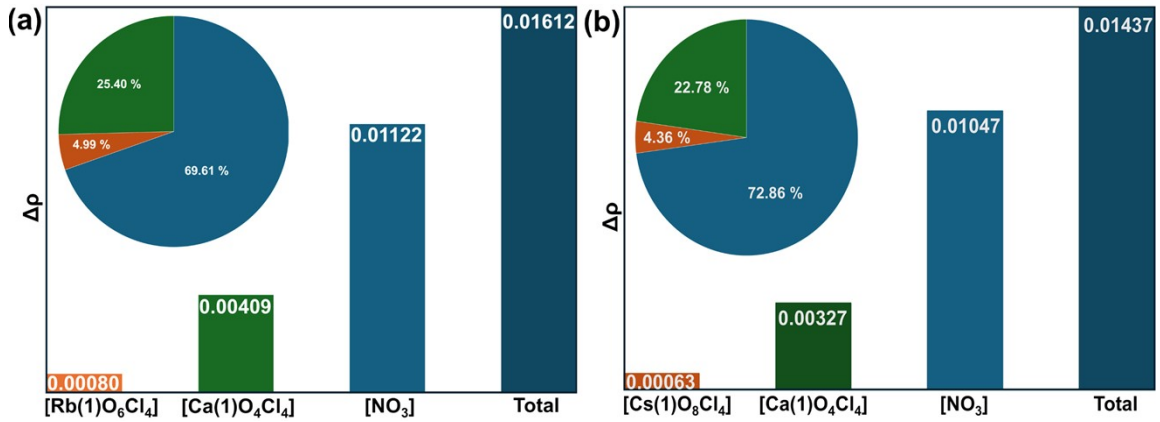


Figure S7. The response electron distribution anisotropy analysis (REDA) for $Rb_2Ca(NO_3)_2Cl_2$ (a), and $Cs_2Ca(NO_3)_2Cl_2$ (b).

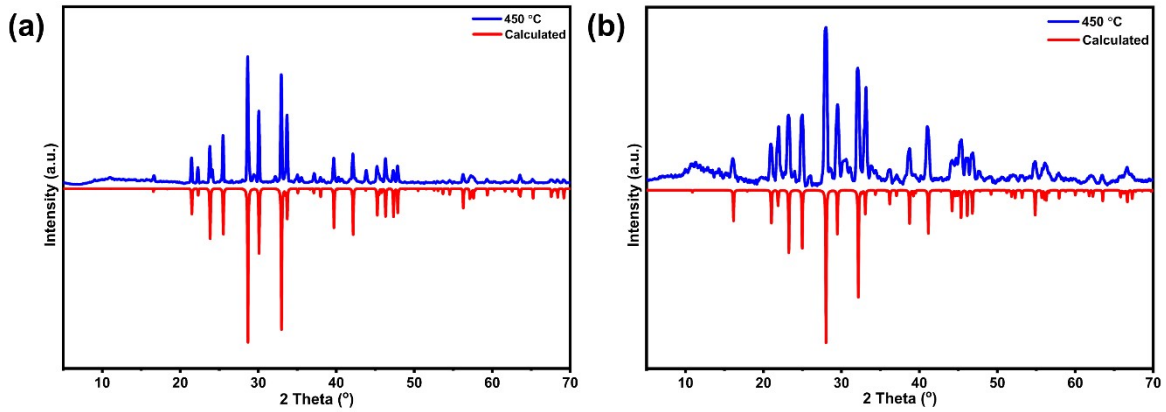


Figure S8. PXRD patterns at 450 °C for $Rb_2Ca(NO_3)_2Cl_2$ (a), and $Cs_2Ca(NO_3)_2Cl_2$ (b).

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