Electronic Supporting Information

Synthesis and Characterization of Hydrated Alkali Metal Calcium Nitrates

$ACa(NO_3)_3{\cdot}2H_2O$ (A = NH_4, Rb, Cs) as Short Ultraviolet Birefringent Materials

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Table S1. Crystallographic data and structure refinement for $ACa(NO_3)_3 \cdot 2H_2O$ (A = NH_4, Rb, Cs).

Molecular formula	$(NH_4)Ca(NO_3)_3(H_2O)_2$	$RbCa(NO_3)_3(H_2O)_2$	$CsCa(NO_3)_3(H_2O)_2$
Formula weight	280.18	347.61	395.05
Temp./K	124.00	124.00	296.15
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	6.4805(6)	6.4588(4)	6.4566(14)
b (Å)	7.4530(7)	7.4518(4)	7.6617(16)
c (Å)	10.4970(10)	10.5548(7)	10.810(2)
α (Å)	99.129(4)	99.093(2)	98.414(6)
β (Å)	91.341(4)	91.188(3)	92.822(7)
γ (Å)	91.711(4)	92.350(3)	92.713(7)
Volume ($Å^3$)	500.15(8)	501.00(5)	527.55(19)
Z	2	2	2
Calculated density ($g \cdot cm^{-3}$)	1.860	2.304	2.487
Absorption coefficient (μ/mm^{-1})	0.692	5.512	4.052
F (000)	288.0	340.0	376.0
Radiation	MoK_α (λ = 0.71073)	MoK_α (λ = 0.71073)	MoK_α (λ = 0.71073)
2θ range for data collection (°)	3.932 to 54.972	3.91 to 55.084	3.814 to 54.898
Completeness (%)	99.0	98.0	99.3
Index ranges	$-8 \le h \le 8$, $-9 \le k \le 9$, $-13 \le l \le 13$	$-8 \le h \le 8$, $-9 \le k \le 9$, $-13 \le l \le 13$	$-8 \le h \le 8$, $-9 \le k \le 9$, $-13 \le l \le 13$
Reflections collected	13413	14228	10045
Independent reflections	2288 [R_{int}= 0.0462, R_σ = 0.0330]	2278 [R_{int} = 0.0496, R_σ = 0.0376]	2383 [R_{int} = 0.0390, R_σ = 0.0355]
Data / restraints / parameters	2288/0/171	2280/4/148	2383/0/148
Goodness-of-fit on F^2	1.091	1.058	1.100
Final R indices [I > 2sigma(I)][a]	R_1 = 0.0292, wR_2 = 0.0768	R_1 = 0.0274, wR_2 = 0.0692	R_1 = 0.0232, wR_2 = 0.0567
R indices (all data)[a]	R_1 = 0.0311, wR_2 = 0.0786	R_1 = 0.0290, wR_2 = 0.0703	R_1 = 0.0244, wR_2 = 0.0573
Largest diff. peak/hole / e $Å^{-3}$	0.76/-0.52	0.55/-0.32	0.80/-0.38

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w F_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$.

Table S2. Selected bond lengths (Å) and angles (°) for $(NH_4)Ca(NO_3)_3(H_2O)_2$.

Ca(1)-O(2)	2.5372(12)	N(1)-O(2)	1.2662(17)
Ca(1)-O(3)	2.5076(12)	N(1)-O(3)	1.2645(17)
Ca(1)-O(4)	2.3697(12)	N(1)-O(1)	1.2064(18)
Ca(1)-O(9)	2.4699(13)	N(2)-O(6)	1.2345(18)
Ca(1)-O(7)#1	2.4552(13)	N(2)-O(7)	1.2427(18)
Ca(1)-O(10)	2.7178(15)	N(2)-O(8)	1.230(2)
Ca(1)-O(5)	2.3497(13)	N(3)-O(9)	1.2542(18)
Ca(1)-O(6)	2.4000(12)	N(3)-O(10)	1.2415(18)
Ca(1)-O(8)#1	2.8906(19)	N(3)-O(11)	1.2316(18)
O(4)-H(4A)	0.8830	N(4)-H(4C)	0.81(4)
O(4)-H(4B)	0.8824	N(4)-H(4D)	0.77(4)
O(5)-H(5A)	0.83(3)	N(4)-H(4E)	0.92(4)
O(5)-H(5B)	0.82(4)	N(4)-H(4F)	0.81(4)

O(2)-Ca(1)-O(10)	143.97(4)	O(5)-Ca(1)-O(10)	118.09(5)
O(2)-Ca(1)-O(8)#1	113.33(4)	O(5)-Ca(1)-O(6)	96.63(6)
O(3)-Ca(1)-O(2)	50.33(4)	O(5)-Ca(1)-O(8)#1	80.59(6)
O(3)-Ca(1)-O(10)	153.22(4)	O(6)-Ca(1)-O(2)	77.11(4)
O(3)-Ca(1)-O(8)#1	64.95(4)	O(6)-Ca(1)-O(3)	126.46(4)
O(4)-Ca(1)-O(2)	78.46(4)	O(6)-Ca(1)-O(9)	85.61(5)
O(4)-Ca(1)-O(3)	81.93(4)	O(6)-Ca(1)-O(7)#1	131.89(5)
O(4)-Ca(1)-O(9)	129.78(5)	O(6)-Ca(1)-O(10)	69.63(5)
O(4)-Ca(1)-O(7)#1	73.23(4)	O(6)-Ca(1)-O(8)#1	168.11(5)
O(4)-Ca(1)-O(10)	81.36(4)	H(4A)-O(4)-H(4B)	103.8
O(4)-Ca(1)-O(6)	77.88(5)	O(3)-N(1)-O(2)	115.92(12)
O(4)-Ca(1)-O(8)#1	109.07(4)	O(1)-N(1)-O(2)	121.80(14)
O(9)-Ca(1)-O(2)	142.92(4)	O(1)-N(1)-O(3)	122.28(14)
O(9)-Ca(1)-O(3)	141.80(4)	H(5A)-O(5)-H(5B)	105(3)
O(9)-Ca(1)-O(10)	48.49(4)	O(10)-N(3)-O(9)	118.28(14)
O(9)-Ca(1)-O(8)#1	82.55(5)	O(11)-N(3)-O(9)	119.59(14)
O(7)#1-Ca(1)-O(2)	131.23(5)	O(11)-N(3)-O(10)	122.13(14)
O(7)#1-Ca(1)-O(3)	86.55(4)	O(6)-N(2)-O(7)	117.87(15)
O(7)#1-Ca(1)-O(9)	84.35(5)	O(8)-N(2)-O(7)	117.68(15)
O(7)#1-Ca(1)-O(10)	68.64(5)	O(8)-N(2)-O(6)	124.44(17)
O(7)#1-Ca(1)-O(8)#1	45.73(4)	H(4C)-N(4)-H(4D)	110(4)
O(10)-Ca(1)-O(8)#1	101.34(4)	H(4C)-N(4)-H(4E)	116(3)
O(5)-Ca(1)-O(2)	78.48(5)	H(4C)-N(4)-H(4F)	105(4)
O(5)-Ca(1)-O(3)	83.65(5)	H(4D)-N(4)-H(4E)	107(3)
O(5)-Ca(1)-O(4)	156.94(6)	H(4D)-N(4)-H(4F)	109(4)
O(5)-Ca(1)-O(9)	71.16(5)	H(4E)-N(4)-H(4F)	109(3)
O(5)-Ca(1)-O(7)#1	123.74(6)		

Symmetrical transformations used to generate equivalent atoms:

#1 x + 1 , y , z

Table S3. Bond lengths (Å) and angles (°) for $RbCa(NO_3)_3(H_2O)_2$.

Rb(1)-O(10)#2	3.0179(16)	Ca(1)-O(6)	2.3920(16)
Rb(1)-O(9)#1	3.0209(16)	Ca(1)-O(8)#5	2.832(2)
Rb(1)-O(3)#3	3.0986(17)	Ca(1)-O(5)	2.3512(17)
Rb(1)-O(7)#4	3.0471(18)	O(4)-H(4A)	0.8780
Rb(1)-O(2)#4	3.2381(19)	O(4)-H(4B)	0.8784
Rb(1)-O(11)	2.920(2)	O(5)-H(5A)	0.830(10)
Rb(1)-N(2)#4	3.4548(17)	O(5)-H(5B)	0.832(10)
Rb(1)-O(6)#4	3.1412(18)	N(1)-O(1)	1.231(2)
Rb(1)-O(1)#3	2.969(2)	N(1)-O(2)	1.243(2)
Rb(1)-O(8)#2	3.0629(19)	N(1)-O(3)	1.251(2)
Ca(1)-O(10)	2.5280(15)	N(2)-O(6)	1.234(2)
Ca(1)-O(9)	2.5026(15)	N(2)-O(7)	1.240(2)
Ca(1)-O(3)	2.4686(16)	N(2)-O(8)	1.237(2)
Ca(1)-O(4)	2.3627(16)	N(3)-O(9)	1.260(2)
Ca(1)-O(7)#5	2.4528(16)	N(3)-O(10)	1.264(2)
Ca(1)-O(2)	2.7294(19)	N(3)-O(11)	1.215(2)

O(10)#2-Rb(1)-O(9)#1	91.43(4)	O(3)-Ca(1)-O(9)	142.22(6)
O(10)#2-Rb(1)-O(3)#3	109.42(4)	O(3)-Ca(1)-O(2)	48.38(5)
O(10)#2-Rb(1)-O(7)#4	139.89(5)	O(3)-Ca(1)-O(8)#5	81.78(6)
O(10)#2-Rb(1)-O(2)#4	70.60(4)	O(4)-Ca(1)-O(10)	78.08(6)
O(10)#2-Rb(1)-O(6)#4	113.77(4)	O(4)-Ca(1)-O(9)	82.47(6)
O(10)#2-Rb(1)-O(8)#2	66.40(5)	O(4)-Ca(1)-O(3)	128.92(6)
O(9)#1-Rb(1)-O(3)#3	105.99(4)	O(4)-Ca(1)-O(7)#5	73.01(6)
O(9)#1-Rb(1)-O(7)#4	96.43(4)	O(4)-Ca(1)-O(2)	80.64(6)
O(9)#1-Rb(1)-O(2)#4	161.48(4)	O(4)-Ca(1)-O(6)	78.84(7)
O(9)#1-Rb(1)-O(6)#4	134.54(4)	O(4)-Ca(1)-N(3)	78.21(6)
O(9)#1-Rb(1)-O(8)#2	57.32(5)	O(4)-Ca(1)-O(8)#5	110.01(6)
O(3)#3-Rb(1)-O(2)#4	84.89(5)	O(7)#5-Ca(1)-O(10)	131.79(6)
O(3)#3-Rb(1)-O(6)#4	100.46(5)	O(7)#5-Ca(1)-O(9)	87.63(6)
O(7)#4-Rb(1)-O(3)#3	106.01(5)	O(7)#5-Ca(1)-O(3)	83.72(6)
O(7)#4-Rb(1)-O(2)#4	94.80(5)	O(7)#5-Ca(1)-O(2)	68.56(6)
O(7)#4-Rb(1)-O(6)#4	40.14(4)	O(7)#5-Ca(1)-O(8)#5	46.59(6)
O(7)#4-Rb(1)-O(8)#2	147.20(5)	O(2)-Ca(1)-O(8)#5	101.71(6)
O(11)-Rb(1)-O(10)#2	77.73(5)	O(6)-Ca(1)-O(10)	76.16(5)
O(11)-Rb(1)-O(9)#1	71.39(5)	O(6)-Ca(1)-O(9)	126.08(6)
O(11)-Rb(1)-O(3)#3	172.63(5)	O(6)-Ca(1)-O(3)	85.06(7)
O(11)-Rb(1)-O(7)#4	67.89(6)	O(6)-Ca(1)-O(7)#5	132.29(6)
O(11)-Rb(1)-O(2)#4	99.53(6)	O(6)-Ca(1)-O(2)	69.45(6)
O(11)-Rb(1)-O(6)#4	77.66(6)	O(6)-Ca(1)-O(8)#5	166.83(7)
O(11)-Rb(1)-O(1)#3	134.62(5)	O(5)-Ca(1)-O(10)	79.34(6)
O(11)-Rb(1)-O(8)#2	114.32(6)	O(5)-Ca(1)-O(9)	84.23(6)
O(6)#4-Rb(1)-O(2)#4	54.67(5)	O(5)-Ca(1)-O(3)	71.12(6)
O(1)#3-Rb(1)-O(10)#2	132.86(6)	O(5)-Ca(1)-O(4)	157.38(7)
O(1)#3-Rb(1)-O(9)#1	127.32(6)	O(5)-Ca(1)-O(7)#5	124.63(7)
O(1)#3-Rb(1)-O(3)#3	41.41(4)	O(5)-Ca(1)-O(2)	117.55(6)
O(1)#3-Rb(1)-O(7)#4	68.99(5)	O(5)-Ca(1)-O(6)	94.53(8)
O(1)#3-Rb(1)-O(2)#4	70.65(6)	O(5)-Ca(1)-O(8)#5	80.75(7)
O(1)#3-Rb(1)-O(6)#4	60.28(5)	O(6)-N(2)-O(7)	118.42(19)
O(1)#3-Rb(1)-O(8)#2	109.42(5)	O(6)-N(2)-O(8)	124.0(2)
O(8)#2-Rb(1)-O(3)#3	68.29(5)	O(8)-N(2)-O(7)	117.60(18)
O(8)#2-Rb(1)-O(2)#4	116.04(6)	O(9)-N(3)-O(10)	116.65(16)
O(8)#2-Rb(1)-O(6)#4	167.04(6)	O(11)-N(3)-O(10)	121.37(19)
O(10)-Ca(1)-O(2)	142.35(5)	O(11)-N(3)-O(9)	121.98(19)
O(10)-Ca(1)-O(8)#5	114.63(5)	O(2)-N(1)-O(3)	118.53(18)
O(9)-Ca(1)-O(10)	50.53(5)	O(1)-N(1)-O(3)	119.93(19)
O(9)-Ca(1)-O(2)	153.97(6)	O(1)-N(1)-O(2)	121.54(18)
O(9)-Ca(1)-O(8)#5	65.98(5)	H(5A)-O(5)-H(5B)	106(2)

O(3)-Ca(1)-O(10)	143.45(6)		

Symmetrical transformations used to generate equivalent atoms:

#1 -x + 2, -y + 2, -z + 1 #2 -x + 1, -y + 2, -z + 1 #3 x , y + 1, z + 1 #4 -x + 1, -y + 1 ,-z + 1 #5 x + 1, y , z

Table S4. Bond lengths (Å) and angles (°) for $CsCa(NO_3)_3(H_2O)_2$.

Cs(1)-O(2)#1	3.1632(19)	Ca(1)-O(4)	2.3809(18)
Cs(1)-O(3)#2	3.196(2)	Ca(1)-O(11)#6	2.759(3)
Cs(1)-O(6)#3	3.345(2)	Ca(1)-O(9)	2.3893(19)
Cs(1)-O(6)#4	3.656(2)	O(4)-H(4A)	0.8708
Cs(1)-O(8)#5	3.228(2)	O(4)-H(4B)	0.8711
Cs(1)-O(10)#3	3.206(2)	O(5)-H(5A)	0.9150
Cs(1)-O(11)#2	3.257(2)	O(5)-H(5B)	0.9151
Cs(1)-O(9)#3	3.281(2)	N(1)-O(1)	1.214(3)
Cs(1)-O(1)	3.118(2)	N(1)-O(2)	1.254(3)
Cs(1)-O(7)#5	3.159(3)	N(1)-O(3)	1.265(3)
Ca(1)-O(2)	2.4985(19)	N(2)-O(6)	1.243(3)
Ca(1)-O(3)	2.5309(19)	N(2)-O(7)	1.233(3)
Ca(1)-O(5)	2.3655(19)	N(2)-O(8)	1.254(3)
Ca(1)-O(6)	2.683(2)	N(3)-O(9)	1.227(3)
Ca(1)-O(8)	2.479(2)	N(3)-O(10)	1.237(3)
Ca(1)-O(10)#6	2.467(2)	N(3)-O(11)	1.241(3)

O(2)#1-Cs(1)-O(3)#2	85.88(5)	O(2)-Ca(1)-O(11)#6	70.16(6)
O(2)#1-Cs(1)-O(6)#3	157.95(5)	O(3)-Ca(1)-O(6)	140.43(7)
O(2)#1-Cs(1)-O(6)#4	66.28(5)	O(3)-Ca(1)-O(11)#6	117.89(7)
O(2)#1-Cs(1)-O(8)#5	107.77(5)	O(5)-Ca(1)-O(2)	83.65(8)
O(2)#1-Cs(1)-O(10)#3	100.99(5)	O(5)-Ca(1)-O(3)	77.35(7)
O(2)#1-Cs(1)-O(11)#2	56.28(5)	O(5)-Ca(1)-O(6)	76.42(7)
O(2)#1-Cs(1)-O(9)#3	138.73(5)	O(5)-Ca(1)-O(8)	125.20(8)
O(3)#2-Cs(1)-O(6)#4	152.10(5)	O(5)-Ca(1)-O(10)#6	73.69(7)
O(3)#2-Cs(1)-O(6)#3	72.92(5)	O(5)-Ca(1)-O(4)	157.44(8)
O(3)#2-Cs(1)-O(8)#5	106.11(5)	O(5)-Ca(1)-O(11)#6	116.13(7)
O(3)#2-Cs(1)-O(10)#3	139.69(6)	O(5)-Ca(1)-O(9)	82.54(9)
O(3)#2-Cs(1)-O(11)#2	64.77(6)	O(6)-Ca(1)-O(11)#6	100.17(7)
O(3)#2-Cs(1)-O(9)#3	119.82(5)	O(8)-Ca(1)-O(2)	144.49(7)
O(6)#3-Cs(1)-O(6)#4	134.45(6)	O(8)-Ca(1)-O(3)	145.87(7)
O(8)#5-Cs(1)-O(6)#4	85.18(5)	O(8)-Ca(1)-O(6)	48.81(6)
O(8)#5-Cs(1)-O(6)#3	84.46(5)	O(8)-Ca(1)-O(11)#6	77.77(7)
O(8)#5-Cs(1)-O(11)#2	66.02(5)	O(10)#6-Ca(1)-O(2)	84.01(7)
O(8)#5-Cs(1)-O(9)#3	95.95(6)	O(10)#6-Ca(1)-O(3)	128.12(7)
O(10)#3-Cs(1)-O(6)#4	50.99(5)	O(10)#6-Ca(1)-O(6)	70.61(7)
O(10)#3-Cs(1)-O(6)#3	91.72(5)	O(10)#6-Ca(1)-O(8)	85.32(8)
O(10)#3-Cs(1)-O(8)#5	109.24(6)	O(10)#6-Ca(1)-O(11)#6	47.26(7)
O(10)#3-Cs(1)-O(11)#2	149.56(6)	O(4)-Ca(1)-O(2)	84.43(7)
O(10)#3-Cs(1)-O(9)#3	38.26(5)	O(4)-Ca(1)-O(3)	80.28(8)
O(11)#2-Cs(1)-O(6)#3	116.73(6)	O(4)-Ca(1)-O(6)	120.84(7)
O(11)#2-Cs(1)-O(6)#4	98.82(5)	O(4)-Ca(1)-O(8)	73.82(7)
O(11)#2-Cs(1)-O(9)#3	161.47(7)	O(4)-Ca(1)-O(10)#6	123.90(8)
O(9)#3-Cs(1)-O(6)#4	83.16(5)	O(4)-Ca(1)-O(11)#6	77.26(8)
O(9)#3-Cs(1)-O(6)#3	54.13(5)	O(4)-Ca(1)-O(9)	88.90(9)
O(1)-Cs(1)-O(2)#1	73.83(7)	O(9)-Ca(1)-O(2)	125.42(7)
O(1)-Cs(1)-O(3)#2	80.63(6)	O(9)-Ca(1)-O(3)	74.97(7)
O(1)-Cs(1)-O(6)#3	96.28(7)	O(9)-Ca(1)-O(6)	72.69(7)
O(1)-Cs(1)-O(6)#4	89.44(7)	O(9)-Ca(1)-O(8)	82.60(8)
O(1)-Cs(1)-O(8)#5	173.08(6)	O(9)-Ca(1)-O(10)#6	139.88(8)
O(1)-Cs(1)-O(10)#3	63.89(7)	O(9)-Ca(1)-O(11)#6	158.46(9)
O(1)-Cs(1)-O(11)#2	119.27(7)	H(5A)-O(5)-H(5B)	104.5

O(1)-Cs(1)-O(9)#3	79.05(7)	H(4A)-O(4)-H(4B)	103.3
O(1)-Cs(1)-O(7)#5	134.43(6)	O(2)-N(1)-O(3)	116.7(2)
O(7)#5-Cs(1)-O(2)#1	130.17(7)	O(1)-N(1)-O(2)	122.4(2)
O(7)#5-Cs(1)-O(3)#2	131.17(7)	O(1)-N(1)-O(3)	120.9(2)
O(7)#5-Cs(1)-O(6)#3	70.75(7)	N(3)-O(9)-Ca(1)	144.05(17)
O(7)#5-Cs(1)-O(6)#4	73.26(7)	O(10)-N(3)-O(11)	116.9(2)
O(7)#5-Cs(1)-O(8)#5	39.48(5)	O(9)-N(3)-O(10)	119.3(2)
O(7)#5-Cs(1)-O(10)#3	72.81(6)	O(9)-N(3)-O(11)	123.7(2)
O(7)#5-Cs(1)-O(11)#2	105.10(6)	O(6)-N(2)-O(8)	118.0(2)
O(7)#5-Cs(1)-O(9)#3	57.62(6)	O(7)-N(2)-O(6)	121.6(2)
O(2)-Ca(1)-O(3)	50.49(6)	O(7)-N(2)-O(8)	120.4(2)
O(2)-Ca(1)-O(6)	151.17(7)		

Symmetrical transformations used to generate equivalent atoms:

#1 -x +2 , -y +2, -z + 1 #2 -x + 1 ,-y +2, -z + 1 #3 -x + 1, -y + 1, -z +1 #4 -x + 2, -y + 1, -z + 1

#5 x , y + 1, z + 1 #6 x + 1, y, z

Table S5. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$), and bond valence sum (BVS) calculations for $(NH_4)Ca(NO_3)_3(H_2O)_2$.

Atom	x	y	z	U(eq)	BVS
Ca(1)	7596(1)	4262(1)	2502(1)	25(1)	2.19
N(1)	7492(2)	7924(2)	4057(1)	31(1)	4.98
N(2)	2309(2)	3725(2)	2481(1)	33(1)	5.10
N(3)	7489(2)	658(2)	752(1)	34(1)	5.01
N(4)	2593(3)	9095(2)	2502(2)	43(1)	- *
O(1)	7468(3)	9379(2)	4748(2)	58(1)	1.84
O(2)	5845(2)	7028(2)	3667(1)	38(1)	1.78
O(3)	9155(2)	7201(2)	3675(1)	38(1)	1.80
O(4)	7453(2)	3579(2)	4628(1)	41(1)	0.34 #
O(5)	7071(3)	5956(2)	822(1)	60(1)	0.36 #
O(6)	4080(2)	3192(2)	2589(2)	56(1)	2.02
O(7)	888(2)	2905(2)	2948(2)	49(1)	1.93
O(8)	1848(3)	4992(2)	1920(2)	64(1)	1.81
O(9)	7663(2)	2196(2)	417(1)	44(1)	1.88
O(10)	7328(2)	576(2)	1918(1)	48(1)	1.80
O(11)	7467(3)	-715(2)	-75(1)	61(1)	1.72
U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. * is N in NH_4 # is O in H_2O					

Table S6. Atomic coordinates (×10^4), equivalent isotropic displacement parameters (Å^2 × 10^3), and BVS calculations for $RbCa(NO_3)_3(H_2O)_2$.

Atom	x	y	z	U(eq)	BVS
Rb(1)	7322(1)	10866(1)	7494(1)	41(1)	1.08
Ca(1)	7629(1)	4282(1)	2497(1)	24(1)	2.21
N(1)	7495(3)	685(2)	742(2)	33(1)	5.02
N(2)	2298(3)	3733(2)	2454(2)	31(1)	5.10
N(3)	7494(3)	7891(2)	4072(2)	31(1)	4.97
O(1)	7465(4)	-684(2)	-82(2)	58(1)	1.88
O(2)	7291(3)	580(2)	1897(2)	47(1)	1.87
O(3)	7709(3)	2227(2)	423(2)	43(1)	1.98
O(4)	7450(2)	3539(2)	4589(2)	43(1)	0.34 #
O(5)	7084(4)	5975(2)	829(2)	55(1)	0.35 #
O(6)	4085(2)	3224(2)	2526(2)	54(1)	2.12
O(7)	895(2)	2898(2)	2935(2)	48(1)	2.07
O(8)	1807(4)	5012(2)	1908(2)	57(1)	1.91
O(9)	9170(2)	7221(2)	3685(2)	38(1)	1.96
O(10)	5846(2)	6980(2)	3685(2)	38(1)	1.92
O(11)	7452(3)	9348(3)	4773(2)	59(1)	1.97

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. # is O in H_2O

Table S7. Atomic coordinates (×10^4), equivalent isotropic displacement parameters (Å^2 × 10^3), and BVS calculations for $CsCa(NO_3)_3(H_2O)_2$.

Atom	x	y	z	U(eq)	BVS
Cs(1)	7395(1)	10825(1)	7506(1)	42(1)	1.09
Ca(1)	7617(1)	4227(1)	2484(1)	26(1)	2.22
N(1)	7440(3)	7673(3)	4060(2)	37(1)	4.99
N(2)	7535(4)	718(3)	846(2)	40(1)	4.99
N(3)	2251(3)	3800(3)	2354(2)	35(1)	5.11
O(1)	7368(5)	9102(3)	4707(2)	71(1)	1.95
O(2)	9118(3)	7059(3)	3713(2)	44(1)	1.99
O(3)	5797(3)	6737(3)	3689(2)	48(1)	1.91
O(4)	7012(4)	5970(3)	864(2)	54(1)	0.33 #
O(5)	7391(3)	3342(3)	4482(2)	52(1)	0.34 #
O(6)	7387(4)	686(3)	1986(2)	53(1)	1.92
O(7)	7487(6)	-653(3)	86(2)	76(1)	1.85
O(8)	7705(4)	2196(2)	482(2)	50(1)	1.98
O(9)	4019(3)	3287(3)	2285(3)	64(1)	2.16
O(10)	1022(3)	3105(3)	3004(2)	56(1)	2.07
O(11)	1569(4)	4938(3)	1759(2)	59(1)	1.90

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. # is O in H_2O

Table S8. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $(NH_4)Ca(NO_3)_3(H_2O)_2$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca(1)	25(1)	26(1)	25(1)	6(1)	1(1)	2(1)
N(1)	34(1)	31(1)	28(1)	4(1)	2(1)	2(1)
N(2)	31(1)	29(1)	36(1)	-2(1)	2(1)	2(1)
N(3)	42(1)	26(1)	33(1)	4(1)	-1(1)	0(1)
N(4)	56(1)	36(1)	37(1)	10(1)	3(1)	2(1)
O(1)	70(1)	40(1)	56(1)	-15(1)	3(1)	4(1)
O(2)	27(1)	40(1)	46(1)	3(1)	3(1)	2(1)
O(3)	27(1)	40(1)	44(1)	2(1)	3(1)	1(1)
O(4)	33(1)	60(1)	36(1)	21(1)	4(1)	4(1)
O(5)	117(1)	30(1)	35(1)	13(1)	-4(1)	3(1)
O(6)	22(1)	52(1)	89(1)	-6(1)	4(1)	1(1)
O(7)	28(1)	50(1)	71(1)	14(1)	10(1)	2(1)
O(8)	106(1)	40(1)	51(1)	13(1)	15(1)	20(1)
O(9)	67(1)	24(1)	41(1)	6(1)	2(1)	1(1)
O(10)	61(1)	51(1)	34(1)	12(1)	2(1)	-1(1)
O(11)	109(1)	26(1)	45(1)	-4(1)	2(1)	-1(1)
The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$						

Table S9. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $RbCa(NO_3)_3(H_2O)_2$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rb(1)	57(1)	32(1)	37(1)	10(1)	5(1)	1(1)
Ca(1)	24(1)	25(1)	26(1)	5(1)	2(1)	2(1)
N(1)	38(1)	26(1)	34(1)	4(1)	-1(1)	2(1)
N(2)	28(1)	28(1)	36(1)	-2(1)	2(1)	2(1)
N(3)	36(1)	30(1)	27(1)	4(1)	2(1)	4(1)
O(1)	106(2)	23(1)	44(1)	-2(1)	0(1)	0(1)
O(2)	60(1)	51(1)	33(1)	12(1)	3(1)	-2(1)
O(3)	67(1)	22(1)	40(1)	6(1)	3(1)	2(1)
O(4)	31(1)	62(1)	40(1)	26(1)	5(1)	7(1)
O(5)	105(2)	28(1)	34(1)	12(1)	-2(1)	2(1)
O(6)	22(1)	43(1)	92(2)	-4(1)	4(1)	0(1)
O(7)	27(1)	52(1)	68(1)	18(1)	9(1)	3(1)
O(8)	84(1)	36(1)	52(1)	11(1)	11(1)	15(1)
O(9)	28(1)	40(1)	43(1)	1(1)	3(1)	0(1)
O(10)	27(1)	40(1)	46(1)	2(1)	3(1)	2(1)
O(11)	74(1)	41(1)	56(1)	-16(1)	3(1)	6(1)
The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$						

Table S10. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $CsCa(NO_3)_3(H_2O)_2$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cs(1)	55(1)	32(1)	40(1)	11(1)	7(1)	2(1)
Ca(1)	24(1)	29(1)	28(1)	7(1)	3(1)	4(1)
N(1)	47(1)	36(1)	28(1)	4(1)	6(1)	8(1)
N(2)	50(1)	31(1)	37(1)	5(1)	1(1)	1(1)
N(3)	27(1)	29(1)	47(1)	-3(1)	3(1)	1(1)
O(1)	102(2)	49(1)	57(1)	-14(1)	12(1)	13(1)
O(2)	35(1)	49(1)	46(1)	2(1)	5(1)	-1(1)
O(3)	33(1)	52(1)	57(1)	2(1)	7(1)	8(1)
O(4)	90(2)	33(1)	38(1)	15(1)	-3(1)	-1(1)
O(5)	40(1)	82(2)	44(1)	33(1)	11(1)	16(1)
O(6)	68(1)	55(1)	38(1)	13(1)	7(1)	4(1)
O(7)	150(3)	27(1)	50(1)	3(1)	7(1)	-1(1)
O(8)	80(1)	26(1)	44(1)	6(1)	8(1)	2(1)
O(9)	25(1)	45(1)	118(2)	-10(1)	12(1)	-1(1)
O(10)	40(1)	61(1)	76(2)	29(1)	18(1)	13(1)
O(11)	79(2)	42(1)	61(1)	16(1)	17(1)	15(1)
The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$						

Table S11. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for $(NH_4)Ca(NO_3)_3(H_2O)_2$.

Atom	x	y	z	U(eq)
H(4A)	8483	2884	4776	62
H(4B)	6341	2895	4703	62
H(4C)	3650(60)	8670(50)	2740(40)	113(13)
H(4D)	2480(50)	8880(50)	1760(40)	105(12)
H(4E)	1390(60)	8700(50)	2840(40)	116(13)
H(4F)	2740(60)	10180(60)	2720(40)	129(15)
H(5A)	7310(50)	7040(50)	740(30)	90(10)
H(5B)	7120(50)	5380(50)	90(30)	98(11)

Table S12. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for $RbCa(NO_3)_3(H_2O)_2$.

Atom	x	y	z	U(eq)
H(4A)	8471	2846	4727	64
H(4B)	6329	2852	4646	64
H(5A)	7270(60)	7072(17)	790(30)	87(12)
H(5B)	7130(80)	5430(50)	82(18)	118(18)

Table S13. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for $CsCa(NO_3)_3(H_2O)_2$.

Atom	x	y	z	U(eq)
H(4A)	7639	5546	200	80
H(4B)	7598	7028	1070	80
H(5A)	6248	3317	4949	79
H(5B)	8426	2947	4962	79

Table S14. Hydrogen bonds for $(NH_4)Ca(NO_3)_3(H_2O)_2$ (Å and °).

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(4)-H(4A)...O(3)#3	0.88	2.22	2.9266(16)	137.3
O(4)-H(4A)...O(7)#1	0.88	2.50	2.8787(17)	106.4
O(4)-H(4A)...O(1)#4	0.88	2.67	3.153(2)	115.5
O(4)-H(4B)...O(2)#5	0.88	2.24	2.8904(16)	130.1
O(4)-H(4B)...O(6)	0.88	2.67	2.9979(19)	103.1
N(4)-H(4C)...O(2)	0.81(4)	2.21(4)	2.997(2)	163(4)
N(4)-H(4D)...O(9)#6	0.77(4)	2.30(4)	3.062(2)	171(4)
N(4)-H(4D)...O(11)#6	0.77(4)	2.40(4)	2.987(2)	134(4)
N(4)-H(4E)...O(3)#2	0.92(4)	2.10(4)	2.994(2)	164(3)
N(4)-H(4E)...O(8)	0.92(4)	2.81(4)	3.044(2)	96(3)
N(4)-H(4F)...O(7)#7	0.81(4)	2.37(4)	3.048(2)	142(4)
N(4)-H(4F)...O(6)#7	0.81(4)	2.41(5)	3.161(2)	155(4)
N(4)-H(4F)...O(1)#8	0.81(4)	2.63(4)	2.931(2)	104(3)
O(5)-H(5A)...O(11)#7	0.83(3)	2.00(3)	2.7970(19)	159(3)
O(5)-H(5B)...O(9)	0.82(4)	2.49(4)	2.8061(19)	104(3)
O(5)-H(5B)...O(8)#6	0.82(4)	2.20(4)	2.959(2)	153(3)

Symmetrical transformations used to generate equivalent atoms:

#1 x+1,y,z #2 x-1,y,z #3 -x+2,-y+1,-z+1 #4 x,y-1,z

#5 -x+1,-y+1,-z+1 #6 -x+1,-y+1,-z #7 x,y+1,z #8 -x+1,-y+2,-z+1

Table S15. Hydrogen bonds for $RbCa(NO_3)_3(H_2O)_2$ (Å and °).

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(4)-H(4A)...O(9)#8	0.88	2.25	2.944(2)	136.0
O(4)-H(4A)...O(7)#5	0.88	2.48	2.866(2)	106.9
O(4)-H(4A)...O(11)#9	0.88	2.67	3.160(3)	116.4
O(4)-H(4B)...O(10)#4	0.88	2.27	2.884(2)	127.2
O(4)-H(4B)...O(6)	0.88	2.70	3.019(2)	103.0

Symmetrical transformations used to generate equivalent atoms:

#4 -x+1,-y+1,-z+1 #5 x+1,y,z #8 -x+2,-y+1,-z+1 #9 x,y-1,z

Table S16. Hydrogen bonds for $CsCa(NO_3)_3(H_2O)_2$ (Å and °).

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(4)-H(4A)...O(8)	0.87	2.63	2.920(3)	100.6
O(4)-H(4A)...O(11)#9	0.87	2.19	3.018(3)	159.6
O(4)-H(4B)...O(7)#10	0.87	2.20	2.843(3)	130.1
O(5)-H(5A)...O(3)#3	0.92	2.03	2.928(3)	166.9
O(5)-H(5B)...O(2)#4	0.92	2.08	2.965(3)	160.9

Symmetrical transformations used to generate equivalent atoms:

#3 -x+1,-y+1,-z+1 #4 -x+2,-y+1,-z+1 #8 x-1,y,z #9 -x+1,-y+1,-z #10 x,y+1,z

Table 17. The birefringence of $ACa(NO_3)_3 \cdot 2H_2O$ (A = NH_4, Rb, Cs) at the wavelength of 546 nm with polarizing microscope.

Compound	Optical path difference R (nm)	Thickness (μm)	Birefringence (Δn)
$(NH_4)Ca(NO_3)_3(H_2O)_2$	1555.21	18.90	0.082
$RbCa(NO_3)_3(H_2O)_2$	1309.46	15.26	0.086
$CsCa(NO_3)_3(H_2O)_2$	2504.9	29.7	0.084

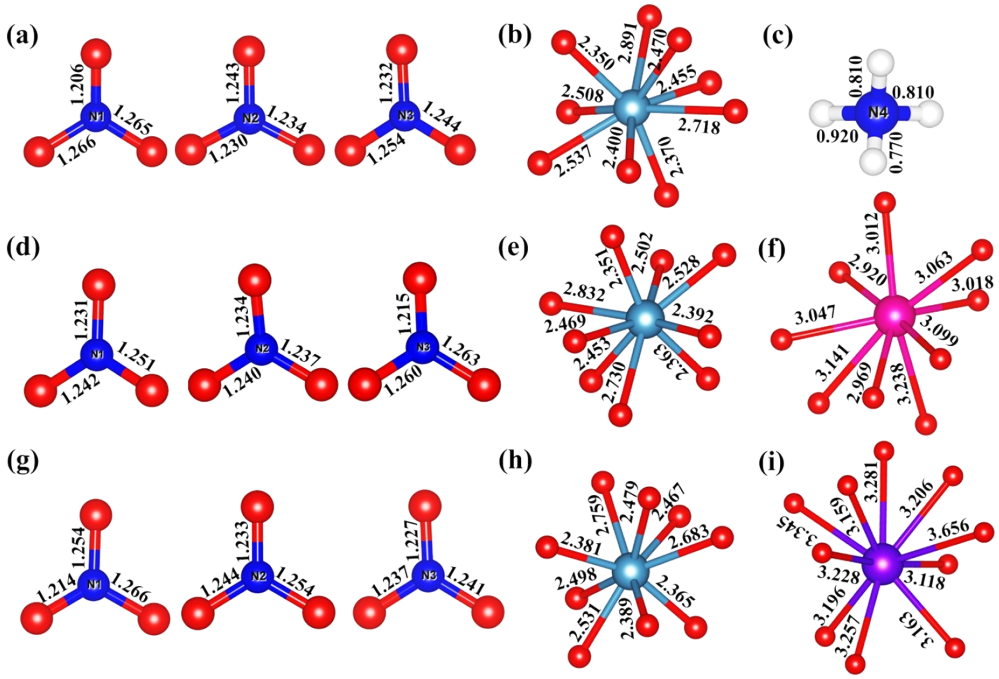

Fig. S1. The coordination modes of N^{5+} (1–3) (a,d,g), Ca^{2+} (1) (b,e,h), and N^{3+}(4) (c)/ Rb^{+} (f)/ Cs^{+} (i) in $(NH_4)Ca(NO_3)_3(H_2O)_2$, $RbCa(NO_3)_3(H_2O)_2$, and $CsCa(NO_3)_3(H_2O)_2$, respectively.

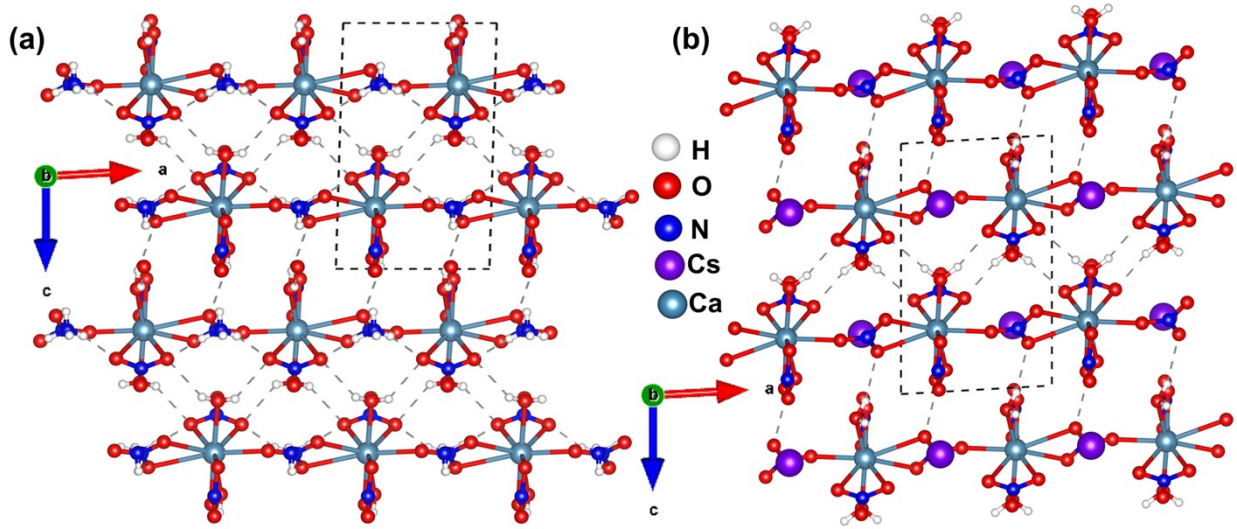

Fig. S2. Ball-and-stick models of $(NH_4)Ca(NO_3)_3(H_2O)_2$ (a) and $CsCa(NO_3)_3(H_2O)_2$ (b).

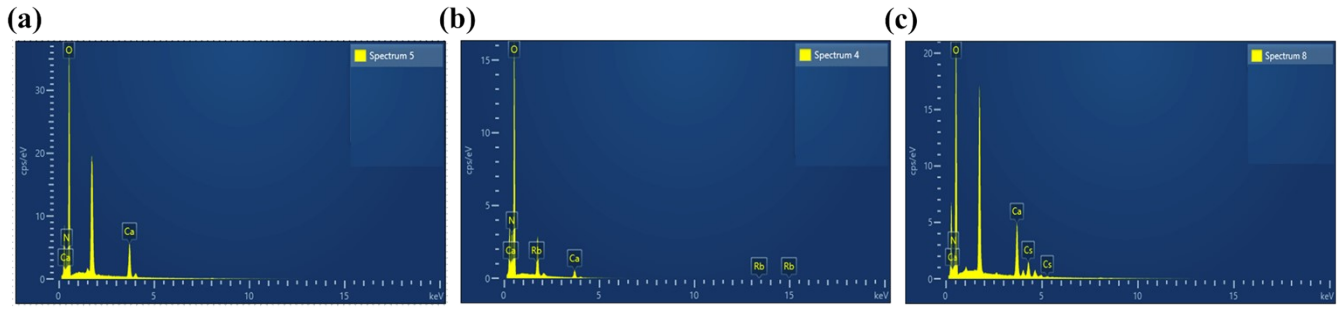

Fig. S3. EDS for $(NH_4)Ca(NO_3)_3(H_2O)_2$ (a), $RbCa(NO_3)_3(H_2O)_2$ (b), and $CsCa(NO_3)_3(H_2O)_2$ (c).

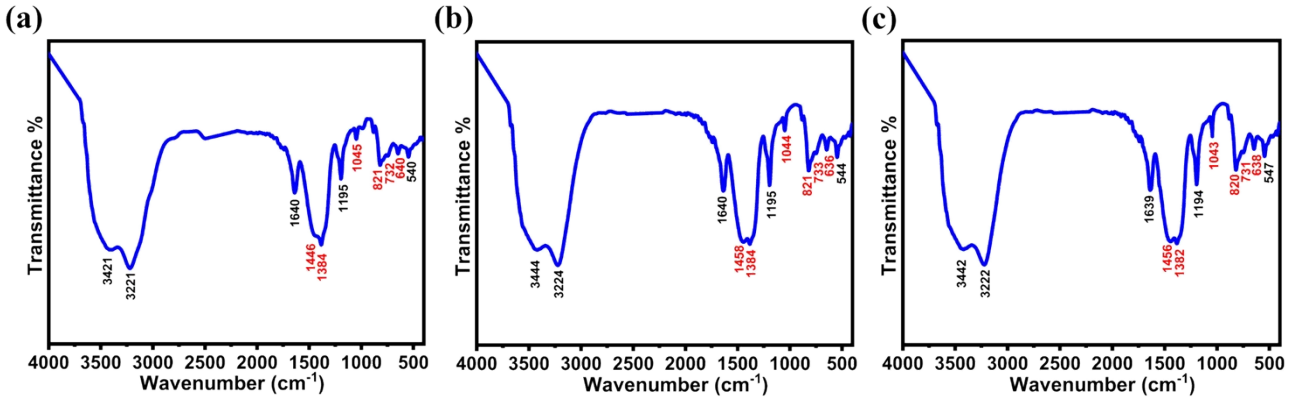

Fig. S4. IR spectra of $(NH_4)Ca(NO_3)_3(H_2O)_2$ (a), $RbCa(NO_3)_3(H_2O)_2$ (b), and $CsCa(NO_3)_3(H_2O)_2$ (c).

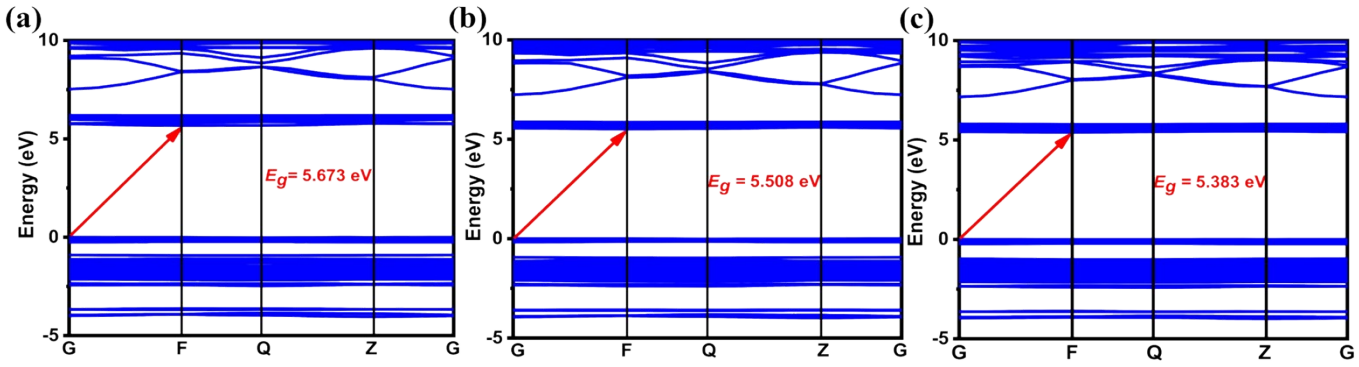

Fig. S5. Calculated band structures by the HSE06 method of $(NH_4)Ca(NO_3)_3(H_2O)_2$ (a), $RbCa(NO_3)_3(H_2O)_2$ (b), and $CsCa(NO_3)_3(H_2O)_2$ (c).

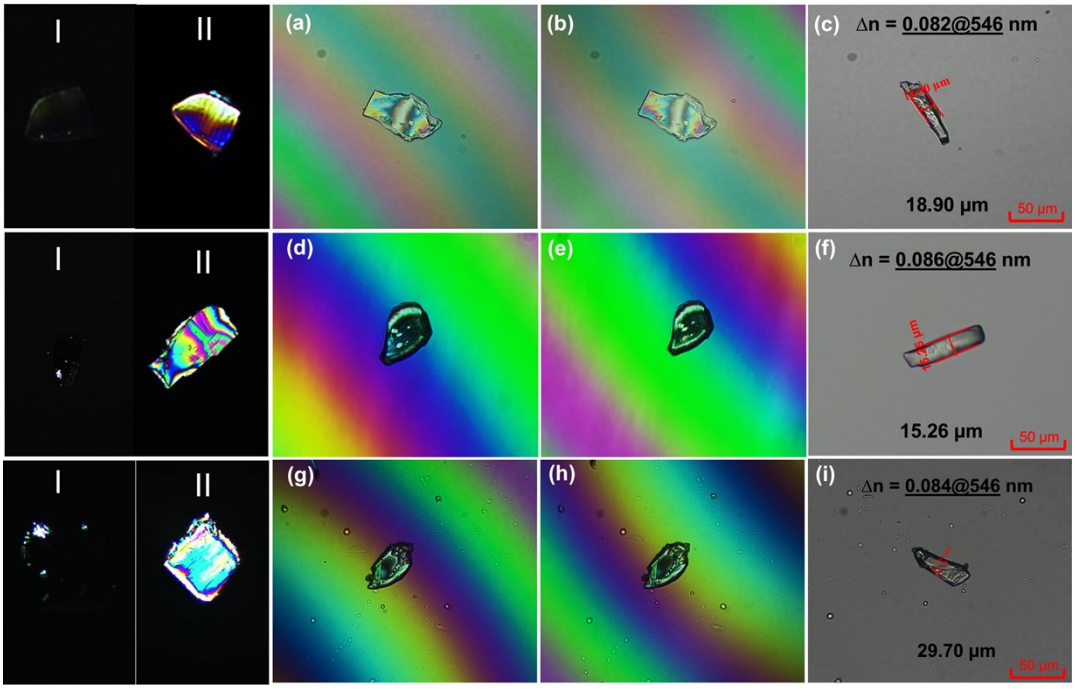

Fig. S6. Birefringence measurements of $ACa(NO_3)_3{\cdot}2H_2O$ (A = NH_4, Rb, Cs) using a polarizing microscope. Panels (a,b), (d,e) and (g,h) display the views of the crystals at extinction during negative and positive rotations of the compensator for $(NH_4)Ca(NO_3)_3(H_2O)_2$, $RbCa(NO_3)_3(H_2O)_2$ and $CsCa(NO_3)_3(H_2O)_2$, respectively; panels (c), (f) and (i) show the thickness of the crystals used for measurement. I and II are the extinction and brightness of crystals, respectively.

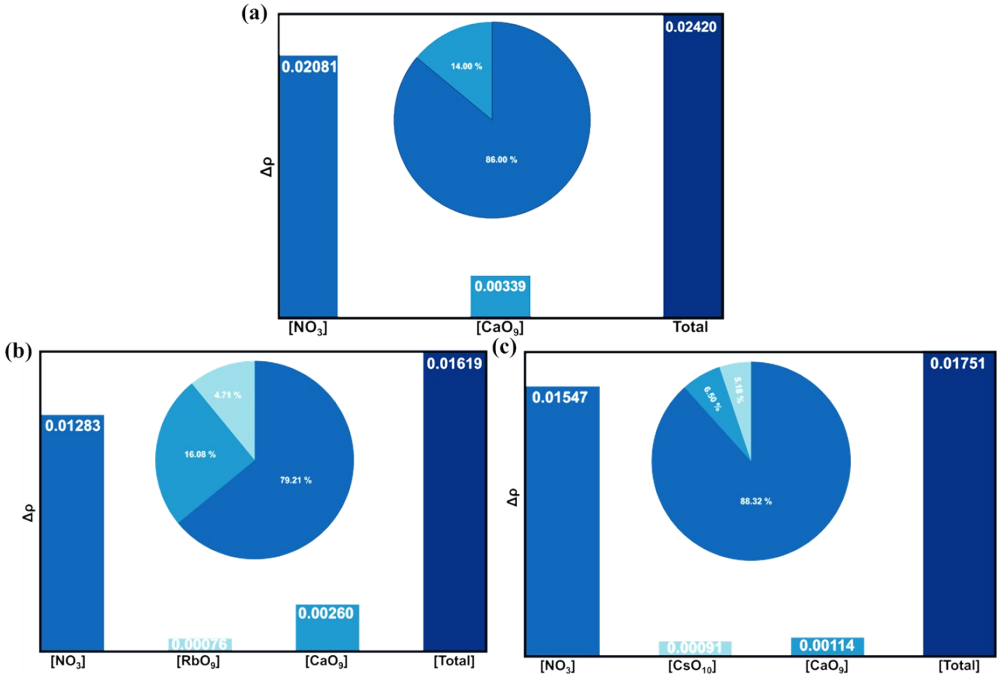

Fig. S7. Bonding electron density difference (Δρ) of constituent units calculated by adopting the REDA method for $(NH_4)Ca(NO_3)_3(H_2O)_2$ (a), $RbCa(NO_3)_3(H_2O)_2$ (b), and $CsCa(NO_3)_3(H_2O)_2$ (c).

Table S18. Summary of some alkali/alkaline-earth metal nitrate compounds reported in the literature.

Compound	Exp. Band gap (eV)	Cutoff edge (nm)	Exp. Birefringence	Reference
$(NH_4)_3ZnNO_3Cl_4$	5.10	243	0.045@546 nm	1
$(NH_4)_3ZnNO_3I_4$	4.03	308	0.073@546 nm	1
$Rb_3ZnNO_3I_4$	4.34	286	0.033@546 nm	1
$Rb_3ZnNO_3Cl_4$	-	222	0.035@546 nm	2
$Rb_5Na(NO_3)_4Cl_2$	-	238	0.083@546 nm	2
$Ba_2(OH)_3(NO_3)$	6.22	≤ 200	0.080@589.3 nm	3
$(NH_4)Ca(NO_3)_3{\cdot}2H_2O$	4.90	220	0.082@546 nm	This work
$RbCa(NO_3)_3{\cdot}2H_2O$	4.90	222	0.086@546 nm	This work
$CsCa(NO_3)_3{\cdot}2H_2O$	4.76	235	0.084@546 nm	This work
$Na_3K_6(CO_3)_3(NO_3)_3.6H_2O$	5.23	237	0.094@546 nm	4
$Cs_2Ca(NO_3)_2Cl_2$	5.64	220	0.104@546 nm	5

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